STUDY OF THE MOLECULAR WEIGHT DISTRIBUTION OF PRECURSORS TO VOLATILE AND NON-VOLATILE BY-PRODUCTS FORMED DURING DRINKING WATER DISINFECTION

By

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Dedicated to my parents

Jie Teng and Yu Meng

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CHAPTER I

INTRODUCTION

Since Trihalomethanes (THMs) were first discovered in drinking water as the result of the disinfection process with chlorine in 1974, widespread research on water disinfection by-products has been being underway. One of the trihalomethanes, chloroform, has been proven to be a carcinogen in laboratory mice and rats(1,2). Increasing concern over the ubiquity and probable toxicity of these compounds prompted the U.S. Environmental Protection Agency (USEPA)(3) to set a maximum contaminant level (MCL) of 0.1 mg/l for Total Trihalomethanes in a finished drinking water supply. It has been established that there were two classifications of disinfection by-products, volatile and nonvolatile halogenated organic compounds(4). Trihalomethanes are defined as volatile organic halides which included chloroform ($CHCl_3$); bromoform ($CHBr_3$); bromodichloromethane ($CHBrCl_2$) and dibromochloromethane ($CHBr_2Cl$). The mechanisms of THMs production has been investigated by numerous researchers. The overall mechanism of THM formation can be summarized in the following reaction:

$$Cl_2 + \begin{array}{c}\text{naturally occurring}\\ \text{organic material}\end{array} \text{--------->} \text{THMs}$$

The organic content of natural surface waters is generally comprised of approximately 50% aquatic humic substances(5) which are composed of humic acid and fulvic acid. When chlorine disinfectant is added to water for disinfection purposes, the aquatic humic substances react with chlorine to produce organohalides. The humic compounds are referred to as precursor compounds during that process.

A great amount of research has been done on THMs. That research has indicated that several factors, such as source-related properties of aquatic organic matter, type of disinfectant, dosage of disinfectant, reaction time and conditions (like pH), and treatment procedure selected, influence the amount of THMs production. The studies focusing on the source-related properties of the aquatic organic matter have investigated molecular weight distribution(6-9), functional groups, carboxylic acidity(8-11) and the humic substance content the of a sample(12,13). For water utilities, reaction time is determined by the distribution system and therefore is unadjustable, so methods for limiting organic halide production have concentrated on precursor removal and disinfectant selections. Many methods have been developed to minimize THMs production. The THM control methods can be divided into three main classes (1) THMs precursor removal, the common approaches used here are alum coagulation and water preozonation; (2) use of other disinfectants, such as ozone, chloramine, chlorine dioxide, ultraviolet light or a combination of two of those; and (3) removal of THMs produced, by activated carbon adsorption, etc. One of the types of studies of the source-related properties focused on the influences of different molecular weight fractions of organics in the water source. Take Veenstra and Schnoor's work(14,15) as an example. They found that an average of 87 % of the THMs were formed from organics with molecular weights of 3,000 or less. Besides the research on MW fractions, the effects of another source-related property, like hydrophobic and hydrophilic organic content of water, on THMs production have been investigated. Both types of organics do not have the same potential for THMs yield. Kuo and Amy's work(16) represented that the hydrophobic fraction accounted for more of the THM formation potential than that of the hydrophilic part.

More extensive investigations on the type of disinfection by-products have led researchers to find other organohalides at concentration levels comparable to the THMs. These new by-products were identified as nonvolatile organic products. Two major and recently characterized nonvolatile haloforms are dichloroacetic acid (DCAA) ($Cl_2CHCOOH$) and trichloroacetic acid (TCAA) (Cl_3CCOOH). More and more investigations have proven that there are higher formation potentials of nonvolatile compounds than those of volatile organics connected with the drinking water disinfection process. Dominguez et al.(17) found that the individual concentration of TCAA and DCAA (30-160 µg/l) in tap water samples were comparable to and sometimes exceeded the concentration of chloroform (10-100 µg/l). The research by Reckhow et al.(4) yielded similar results in that the formation amount of nonvolatile organic compounds were about three times that of the volatile ones using the free chlorination process. Johnson et al.(18) noted that the chlorination of diverse naturally occurring organics produced from 1.5 to 11 times as much nonvolatile organohalide compound as chloroform. An important sidelight to the discovery of large concentrations of nonvolatile organic compounds being formed during the disinfection process is that TCAA has been suspected as being a possible carcinogenic agent through a mechanism related to peroxisome proliferation.(19) Therefore, it is important to study the nonvolatile organics. Unfortunately, there is not enough work on the study of nonvolatile organic compound concerning their formation mechanisms, characteristics, measurement methods and removal methods, like that for THMs. But all of the recent findings have raised questions regarding the potential detrimental effects of nonvolatile haloforms formed during the water disinfection procedure.

It was based on these recent research findings that this study was designed. For comparative purposes, both volatile and nonvolatile halide organic compounds from Kaw Reservoir water sample were considered. The specific objectives of this research project were:

(1) Study of source-related properties of volatile and nonvolatile organic compound. What is the precursor material, hydrophilic organic and hydrophobic organic, to produce THMs, TCAA and DCAA? What are the effects of the different molecular weight fractions of the hydrophilic and hydrophobic organic compounds on THMs, TCAA and DCAA production?

(2) Study of disinfection procedure and different disinfectants. In this research, two disinfectants, free chlorine and combined chlorine (chloramine) were used. Also, the preozonation process was added to each disinfection process.

CHAPTER II

LITERATURE REVIEW

The review of the literature was divided into the following three categories:

1. General Investigation of the Organohalide Precursor and Disinfection Processes;
2. Volatile Organohalide Formation Potential:
    (1) Effect of Apparent Molecular Weight of Precursor
    (2) Precursor Investigation
    (3) Alternative Disinfectants
3. Nonvolatile Organohalide Compound Formation Potential.

Extensive studies on the volatile haloforms, have been conducted for many years. Many papers have documented the THMs´ formation mechanisms, precursor characteristics and removal approaches etc. However, for nonvolatile halide organics, relatively little work has been done. For comparison purposes with this study, it was necessary to review the related studies of other researchers.

General Investigation of the Organohalide Precursor and Disinfection Processes

Previous work(20) has proven that humic substances, which constituted about 50 % of aquatic organic matter, are the precursors of halide organics. Humic substances are composed of humic acid and fulvic acid, which are amorphous, brown or black, hydrophilic, acidic, polydisperse substances with molecular weights ranging from several hundreds to tens of thousands(21). Their structure varies with location and different conditions present at each water source, and consist mainly of aromatic polyhydroxy, polymethoxy, polycarboxylic acids with smaller amounts of sugars and nitrogen bases. Johnson and Jensen(18) analyzed the mechanisms of formation of disinfection by-products by different disinfectants from their own and other people´s experiments. They concluded there were two by-product formation mechanisms, oxidation and substitution. They rationalized that oxidation processes were responsible for the removal of the precursors to THMs and TOX (total organic halide). Substitution reactions were the source of chlorine incorporation into the organic matter to form THMs and TOX. Different disinfectants had varying oxidation abilities to contribute to the formation of different by-products. Johnson and Jensen(18) ran several tests using free chlorine and combined chlorine (chloramine) with phenol, amino acid and proteins. The results showed the free chlorine oxidized the organic material, whereas chloramines substituted to form chloro-organics. This experiment showed that the oxidation ability of chlorine was higher than that of chloramine. In fact one portion of the chlorine participated in the oxidation reaction to cleave the humic substance molecule while another portion acted as a substituting agent in the formation of halide organic compounds, such as THMs. From the analysis of the reaction mechanism, the authors believed that oxidation and cleavage would produce ultimately purgeable total organic halide (PTOX), otherwise, substitution would be the reason for nonpurgeable total organic halide (NPTOX) formation.

It had already been established that disinfection conditions (like disinfectant dosage, contact time and disinfection pH etc.) are other controlling factors in haloform compound formation. In their paper, Johnson and Jensen(18) stated the theory that at low chlorine doses, substitution products dominated. At higher chlorine doses, oxidation and cleavage products became more significant, so that lower chlorine-to-carbon ratios favorite to NPTOX formation.

Johnson and Jensen(18) also considered the effects of pH. Their experiment showed that THMs were reduced with decreasing pH. By moving to a lower pH, the TOX production was greatly increased. Thus, at low pH´s, chlorine substitution became very important. Miller and Uden(22) did a similar pH investigation, especially focusing on TCAA and DCAA. They found that the concentration of TCAA was reduced from about 1140 µg/l to 170 µg/l by raising the pH from 4 to 10. At the same time, the concentration change of DCAA was very small. Therefore, from these surveys it should be recognized that a pH at which lower THM levels are reached might not be the ideal operating condition for controlling nonvolatile organic formation.

Numerous investigator(23)(4)(24) have shown that both chloroform and NPTOX increase with chlorine contact time. Reckhow(4) found that the reaction rate varied with time. Both chloroform and TOX increased rapidly in the first few hours and then slowed to a generally steady rate of increase. The amount of chloroform became a greater fraction of the TOX with contact time, increasing from 9 percent after 30 min to 27 percent after 300 hours.

Volatile Organohalide Formation Potential

Effect of Apparent Molecular Weight of Precursor

Many researchers´ investigations have revealed that the THMFP was not equal for the different MW ranges of precursors.

Collins et al.(25) determined apparent molecular weight (AMW) distributions of their samples by using ultrafiltration. They fractionated their four water samples into six AMW groups, < 500, < 1,000, < 5,000, < 10,000, < 30,000 and > 30,000, and then tested the fractions for THM reactivity or yield (expressed in terms of μg THM/mg C) (Table 1). They found that THM reactivity generally increased as a function of molecular weight although there

TABLE 1

TRIHALOMETHANE REACTIVITIES/YIELD OF VARIOUS WATER SOURCES

	THM Yield(μg/mg C) of AMW Fractions				
Water Source	<500	<1,000	<5,000	<10,000	<30,000
Cobble Mountain Reservoir	55.4	61.3	72.0	81.0	78.6
Grasse River	56.5	68.2	75.5	93.0	92.8
Floridan Aquifer	54.1	55.2	59.4	62.1	62.4
Colorado River	55.7	58.3	56.7	56.6	55.6

were several departures from this trend. In one of their sample, Colorado River water, no significant differences were found in the THM reactivity between the various molecular weight fractions.

Schnoor et al.(14) used gel permeation chromatography (GPC) to separate naturally occurring organic matter in the Iowa River and found that 75 % of the THMs formed were derived from organics having a molecular weight of < 3,000 moreover, 20 % of the THMs were derived from compounds of < 1,000 molecular weight. In a related study, Veenstra and Schnoor(14) found that the greatest THM yield per unit of organic carbon occurred in conjunction with molecules with an apparent molecular weight of < 1,000. Oliver and Visser(26), using ultrafiltration (UF) to delineate eight MW fraction, found the highest chloroform yield to occur in conjunction with fulvic and humic acids in the 20,000-30,000 MW range for their water sample.

Sinsabaugh et al.(27) results are listed in the Table 2. Their work showed that the specific yields from DOC under 1 KD (kilodalton) and over 30 KD were 40-60 % lower than yields from organics between 1 KD and 30 KD.

At the same time, Sinsabaugh et al.(27) discussed the THM and TOX Formation Rate expressed as the ratio of 1-day/7-day THMFP. They stated that the rate of THM formation was dependent on precursor size. Molecules smaller than 0.5 KD generated only 26 % of their 7-day THMFP in one day. The proportion increased with the molecular weight of the

TABLE 2

THE RELATIONSHIP OF TOC, THMFP AND TOXFP AS THE FUNCTION OF MOLECULAR WEIGHT

MW Range	Occoquan Reservoir					Harwood's Mill Reservoir				
(KD)	TOC mg/l	THMFP µg/l	THM Yield µg/ mg c	TOXFP µg/l	TOX Yield mg/ mg c	TOC µg/l	THMFP µg/l	THM Yield µg/ mg c	TOXFP µg/l	TOX Yield µg/ mg c
>30	1.62	285	176	760	469	0.62	25	40	67	108
10-30	2.46	315	128	1030	419	0.30	20	67	66	220
5-10	1.89	265	140	660	349	0.90	75	83	86	96
1-5	0.96	140	146	440	458	1.25	120	96	315	252
0.5-1	0.81	30	37	200	247	0.52	105	202	265	510
<0.5	0.89	35	39	150	169	1.26	105	83	235	187

precursors, but stabilized at approximately 52 % for molecules larger than 5 KD. TOX generation was more rapid than THM generation. THM and TOX formation rates were slower for MW smaller than 1 KD. They thought the trend implied that at least some of the smaller precursors had different properties than the larger ones.

Sinsabaugh et al.(27) found another phenomenon in that the specific yields for bulk Occoquan water were 40 % higher than those of bulk Harwood's Mill water. They believed the difference was due to the higher concentration of fulvic acids in Occoquan water (the concentration of fulvic acids was 50 % higher in the Occoquan sample than in the Harwood's Mill sample). They concluded that the fast-reacting, high-yield precursors were fulvic acids.

Amy and co-workers(28) used ultrafiltration to fractionate water from several source. The workers then test each MW range for THMFP. From the data shown in Table 3, it is evident that there is a positive correlation between THM yield and AMW similar to that mentioned by Sinsabaugh.

Precursor Investigation

It has been established that humic substance are the major precursor for the formation of halide organic compounds (4). The different organic substances in water sources have various haloform formation potentials. Collins and co-workers (29) used XAD-8 adsorption chromatography to

TABLE 3

THE RELATIONSHIP OF TOC, THMFP AND THM YIELD AS THE FUNCTION OF MOLECULAR WEIGHT

Molecular Weight Cutoff	NVTOC mg/l	THMFP µg/l	THM Yield µg THM/mg C
Initial	4.93	314	63.7
<30,000	4.10	252	61.5
<10,000	2.44	125	51.2
<5,000	2.03	79	38.9
<1,000	1.67	68	40.7
<500	1.13	39	34.5

separate the water samples into hydrophobic (HB) and hydrophilic (HI) fractions and then tested each fraction for THMFP. Their results (Table 4) show that the THM reactivity of the hydrophobic fraction was significantly higher than the corresponding hydrophilic one. They confirmed that the humic substance, operationally defined as hydrophobic, was the primary contributor of THM precursors in natural water.

Kuo and Amy(16) did a similar experiment. They separated two water samples, Grasse River and Edisto River, into hydrophobic and hydrophilic fractions and then, chlorinated each one and held the sample for 168 hours at 20 °C and pH 7. Their results are shown in the Table 5. They concluded that the hydrophobic fractions accounted for most of the THMFP in each source.

Alternative Disinfectants

After realizing that free chlorine disinfection formed THMs, many investigators have tried to use other disinfectants to replace free chlorine in order to reduce THM formation. Ozone is by far the most powerful oxidant of the alternatives tried and it prevented production of THMs when used as the sole disinfectant. Unfortunately, due to its instability in water, ozone does not provide a stable concentration of disinfectant residual. Another very important consideration, pointed out by Anderson(30), was the possible production of non-THM organic by-products from the ozonation of humic substances. Therefore, the combined

TABLE 4

HYDROPHOBIC AND HYDROPHILIC THMFP CHARACTERIZATION

	HB Fraction			HI Fraction		
	NVTOC mg/l	THMFP µg/l	THMFP/ NVTOC	NVTOC mg/l	THMFP µg/l	THMFP/ NVTOC
Grasse River	4.39	501	114	3.32	215	65
Floridan aquifer	4.82	363	75	3.45	156	45
Cobble Mtn Reservoir	1.24	118	95	1.3	76	58
Colorado River	1.05	73	69	1.97	94	48
Fulvic acid	3.53	235	72	1.3	61	47

TABLE 5

THE RELATIONSHIP OF TOC, THMFP AND THM YIELD AS THE FUNCTION OF HYDROPHILIC AND HYDROPHOBIC FRACTION

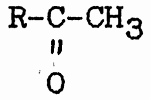
Fraction	NPOC (mg/l)	THMFP (umol/l)	THMFP/NPOC (umol/mmol)
		Grasse River	
Total	4.96	3.59	8.7
HB	3.14	2.94	11.2
HI	1.81	0.65	4.3
		Edisto River	
Total	4.35	2.97	8.2
HB	2.62	2.65	12.2
HI	1.74	0.32	2.2

use of ozone, as a precursor removal method, along with some other disinfectant became the norm for water treatment plants using ozone. A careful review of the literature revealed that most of the time a THMFP decrease following ozonation could be obtained.

Amy et al.(31) studied the preozonation processes on several MW fractions of two samples, one was peat fulvic acid and the other was Biscayne Aquifer DOM. Their data showed that different organic MW ranges had different THMs reduction potentials when using the same ozonation processes. For the high MW fraction (MW > 30,000), a good decrease in the THMFP was seen. The low MW fraction always showed an enhancement of the THMFP.

Amy et al.(32) investigated the ozonation of eight different waters; six waters obtained from natural sources and two synthetic waters produced from soil-derived humic and fulvic acids. On the basis of the different water sources and applied ozone doses used, 168-hour THMFP reductions varied from as a low of 1 % to high of 68 % for their samples. Veenstra et al.(33) used the same water source as used in this work (Kaw Reservoir) to investigate the effects of preozonation treatment on THMFP. They reported their THMFP to be from 194 µg/l to 1380 µg/l for the chlorinated unozonated water and from 186 µg/l to 944 µg/l for the chlorinated ozonated sample. Overall, their studies showed the preozonation process affected a 15.3±13.9% removal of THMFP during the eleven months of monitoring. Their seasonal tests for THMFP indicated that the summer samples had higher THMFPs than the winter ones. They explained the reason for this as being more humic compounds, derived by plant decomposition, were in the water source during the summer.

The same preozonation process was studied by Reckhow et al.(34) on Black Lake fulvic acid solutions. They determined THM production in the process was a function of pH of the chlorination following preozonation. Chloroform formation potential was enhanced with elevated chlorination pHs. They analyzed the reasons for this from the reaction mechanism by taking methyl ketones as an example:



$$\mathrm{R-\underset{\underset{O}{\Vert}}{C}-CH_3}$$

They explained that the methyl protons in the species were not sufficiently acidic to undergo significant chlorine addition at neutral pH. However, at elevated pH, it became far more reactive and structures of this type must be considered as a major source of THMFP. Since ozone was particularly well suited for production of such ketones from a wide variety of organic compounds, the enhancement in THM formation at high pHs following ozonation was understandable.

Jacangelo et al.(35) surveyed the influence of ozonation on THM formation. They compared samples subjected to chlorination alone with those receiving ozonation prior to chlorination. In comparing the results of the two treatment processes, they found that chloroform was reduced from 42 to 37 µg/l using preozonation, and the other brominated THMs were increased in the preozonation scheme.

Due to the formation of disinfectant by-products under free chlorine residual conditions, an increasing amount of interest has been focused on combined chlorine (chloramine), because it possess several advantages, like low THMFP, economic feasibility, and long residual stability. However, it was recognized that the THM formation potential could not be reduced completely by the disinfection. Jacangelo et al.(35) also studied the chloramination disinfection process. They established three experimental schemes; chlorination-alone, chloramination-alone, and preozonation followed by chloramination. The TTHMs were monitored in each of these processes. Comparing chlorine and chloramine disinfections, a 96 percent reduction of THM could be achieved. In the chloramine-only scheme, the remaining TTHMs concentrations were 44 µg/l. After preozonation was added to the process, an 85 percent reduction in TTHMs was seen.

Nonvolatile Organohalide Compound Formation Potential

Recent investigations have shown that the concentration of nonvolatile haloorganics formed in the chlorine disinfection process were comparable with and sometimes higher than those of THMs. The data in Table 6, gathered from the literature, illustrates this fact. Therefore, more

TABLE 6

SIGNIFICANCE OF NPTOX COMPARED WITH THMs

Substrate	Conditions	Average NPTOX/THM	Reference
Various humics, fulvics, groundwater, secondary effluent	pH 7 TOC=3 mg/L T=100 h Cl_2 dose=2-100 mg/L	3.1-4.4	23
Various humics and fulvics	pH 7 TOC=5 mg/L T=72 h Cl_2 dose=20 mg/L	3.3-4.4	4
Black lake (N.C.), fulvic	pH 7 TOC=421 mg/L T=24 h Cl_2 dose=2488 mg/L	4.8	36
Rhine River (FRG), humic	pH 6.9 TOC=0.8-8 mg/L T= 0.5 h Cl_2 dose=15 mg/L	7.0-11.2	37
	pH 9.2	3.0-4.0	37
Chlorophyll	pH 7 TOC=4.4 mg/L T=24 h Cl_2 dose=20 mg/L	4.6	38
Soil, humic	pH 6 TOC=5.5 mg/L Cl_2 dose=10 mg/L	1.6	39
Amherst (Mass.) tap water		1.5-2.4	40

and more researchers have been giving attention to the nonvolatile by-products during the disinfection processes.

Reckhow and Singer(4) sampled several water sources and separated them into fulvic acid and humic acid. Those humic and fulvic acid fractions were then chlorinated. They discovered that chloroform, TCAA and DCAA were produced at higher concentrations from humic acid precursor than fulvic acid. The TCAA, DCAA and chloroform concentrations for Black Lake fulvic acid (TOC = 4.1 mg/l) were 286 µg/l, 110 µg/l and 290 µg/l, respectively, for a 168-hour chlorination test.

Uden and Miller(22)(40) tested two tap water samples which were collected near the two water treatment plants that supply Amherst, Mass. Their test results are shown in Table 7. From the data, the three compounds' formation potential showed a big difference with different water sources. The data showed that the chlorination of surface water not only produced chloroform at concentrations of 40-190 µg/l, but also produced similar concentrations of DCAA and TCAA. In fact, in each sample tested, the combined concentrations of the chloroacetic acids were significantly greater than the concentration of chloroform. Based on those test results they believed that DCAA was not a intermediate product of TCAA. From the contact time test, conducted using fulvic acid, they showed that nearly 90 % of the final concentrations were obtained for the three compounds within a 24-hr contact time. At the end of an 80-

TABLE 7

TCAA, DCAA AND CHLOROFORM FORMATION POTENTIAL IN SEVERAL WATER SOURCES

Sample	Concentration µg/l		
	TCAA	DCAA	Chloroform
Atkins Reservoir	not detected		trace
Atkins Tap Water (0 hr)	33.6	63.1	39.6
Atkins Tap Water (24 hr)	72.8	79.5	87.4
Pelham Reservoir	not detected		trace
Pelham Tap Water (0 hr)	161	123	139
Pelham Tap Water (24 hr)	160	133	190

hour incubation time, TCAA concentration was 1.5 times higher than chloroform and about 2.6 times higher than DCAA.

Jacangelo et al.(35) surveyed the influence of ozonation on NPOX compounds. They found that DCAA and TCAA were reduced by 9 and 41 percent, respectively, by the ozone-chlorine scheme compared to the chlorine alone scheme. In the chloramination disinfection process, HAAs (haloacetic acid) reduction achieved 80 percent although it was not as good as that for THMs. Comparing the four experimental schemes which were chlorine only, chloramine only, and preozonation addition to the two disinfections, the highest levels of TTHMs and HAAs were observed with the chlorine-only disinfection. If preozonation was added to the treatment, it was observed that there was a slight increase in the TTHMs level and a slight decrease in the sum of the HAAs. Large decreases of THMs and AHHs were observed when using chloramines as the sole disinfectant and when using a preozonation addition. In their experiments, the reduction levels of TTHMs and HAAs in both the chloramines-only and ozone-chloramines schemes were very significant in contrast to the chlorine-only and ozone-chlorine treatments. The HAAs concentrations in the two disinfection processes using chloramines (chloramine only and ozone-chloramine) were a little higher than TTHMs ones. Therefore, they recommended that the chloramination and ozone-chloramine approaches were the most efficient methods to remove TTHMs and HAAs.

Stevens and co-workers(41) did a similar test on

NPOX(non-purgeable organic halide) to compare the effect of chlorination and chloramination disinfection processes. Their results showed there was about an 81 percent reduction of NPOX for chloramination compared with using chlorination. Dore et al.(42) studied the TCAA and DCAA formation potentials by a preozonation and chlorination process. They observed that the TCAAFP was reduced by preozonation. However, when the ratio of O_3 to TOC of the sample was greater than one, the reduction of TCAAFP became very insignificant. The DCAA concentration change showed very little in their research.

CHAPTER III

MATERIALS AND METHODS

To illustrate the whole experiment procedure clearly, the process diagram is shown in Figure 1.

Sampling

The sample water originated from Kaw Reservoir, Oklahoma. The samples were taken from the raw water storage tank at the Water Treatment Plant of the City of Stillwater, Oklahoma.

Sample Pretreatment

To remove turbidity, each sample was filtered three times. First, the sample was run through a sand filter, constructed in a 4 inches diameter column which contained 7.5 inches of sand, at the rate of one gallon per minute per square feet. Second, the sample was filtered through 4.25 cm diameter glass microfiber filter paper which had a 1.5 µm pore size (Whatman, 934-AH). Third, the sample was filtered through a 0.45 µm pore size filter paper (Millipore Type HA). After filtration, the sample was stored at 4 °C in a glass bottle which was prewashed by detergent, nitric acid ($H_2O:HNO_3$ = 1:1) and then rinsed with distilled water.

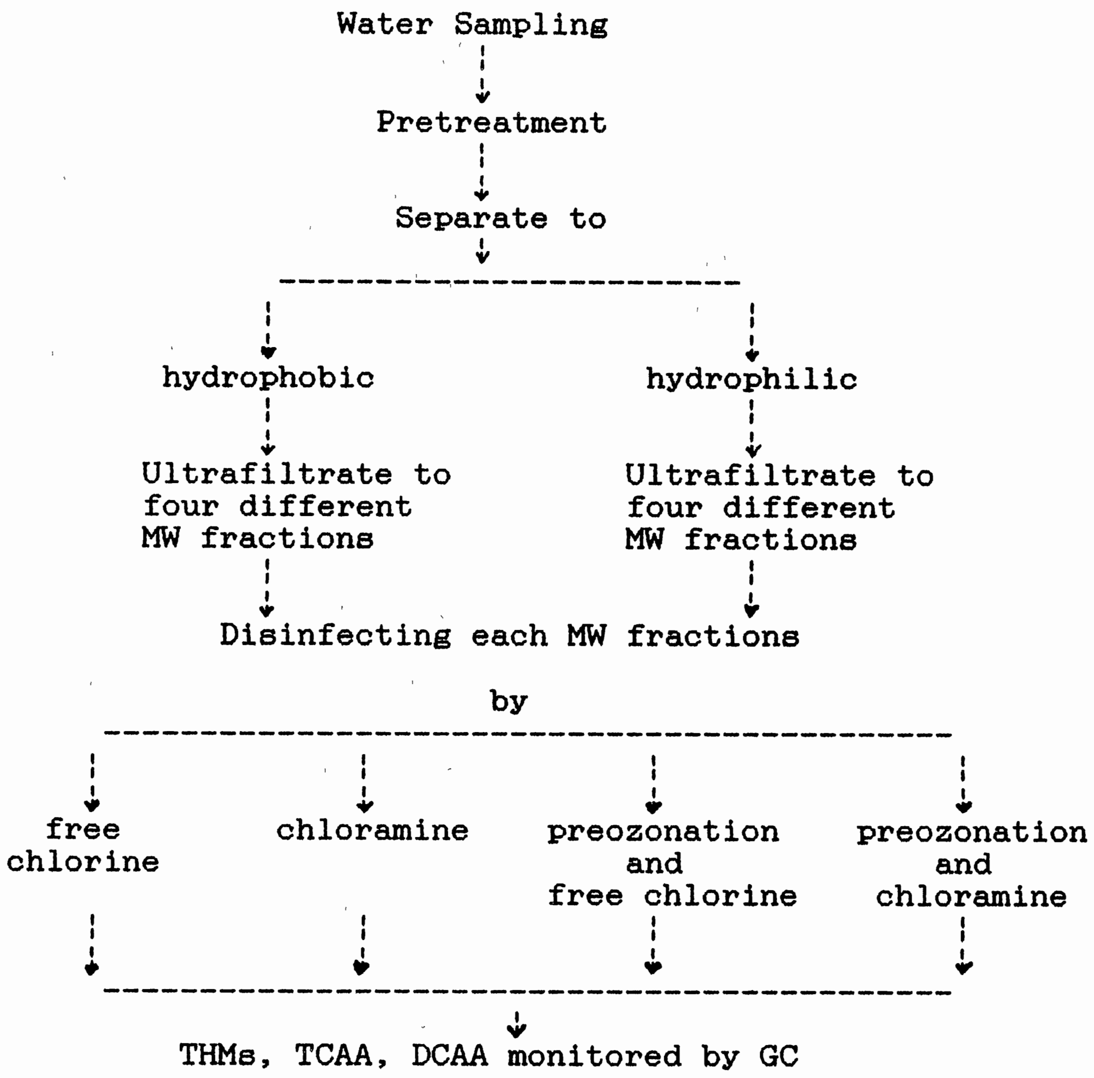


Figure 1. Research Design Flow Diagram

Separation of Hydrophilic and Hydrophobic Materials

A resin extraction method(43) was utilized to fractionate the dissolved organic matter present in the water sample into hydrophobic and hydrophilic groups. A column packed with XAD-8 resins (acrylic ester copolymer, 40-60 mesh, from Rohn-Haas) was used. The column was one inch in diameter and had a resin depth of 11 inches.

Operating conditions and procedures are outlined in subsequent paragraphs.

To avoid any organic interference, the following steps were taken to prepare the resins for use:

(a) The resin was Soxlet-extracted sequentially for 24 h with methanol, diethyl ether, acetonitrile and methanol.

(b) Distilled water was used to rinse the resin until the total organic carbon contained was lower than 1 mg/l.

(c) After placing the resin in the column, it was cleaned three times with two bed volumes of 0.1 N NaOH and 0.1 N HCl, alternating between the two solutions just prior to use.

(d) The column was left saturated with 0.1 N HCl.

After preparation of resins, the following procedures were shown below.

(a) Acidify sample to pH 2.0 with concentrated HCl.

(b) Three liters of sample (filtered raw water) were run through the XAD-8 resin at a 0.2 gpm/ft^2 (4 ml/min) loading rate. The hydrophilic substances were obtained in the effluent from the column.

(c) To obtain the hydrophobic component which is sorbed on the resin, a 0.1 N NaOH eluant was used at a flow rate of 0.05-0.1 gpm/ft^2 (1-2 ml/min) to back elute the column.

(d) As the pH started to increase from 2.0 (monitored with pH paper), the eluant was changed to distilled water. Five bed volume of distilled water were used to elute the column. The eluant contained the hydrophobic substances. Both the hydrophilic and hydrophobic fractions were neutralized to pH 7 by 5 N NaOH prior to storage.

(e) Measurement of the TOC (total organic carbon) of the raw water, hydrophilic and hydrophobic fraction was done using a Beckman Model 915 Total Organic Carbon Analyzer.

(f) The TOC of hydrophobic fraction was concentrated during the XAD-8 resin absorption process, so it was necessary to dilute the TOC of hydrophobic fraction to the same value as the TOC of the hydrophilic fraction for comparison purposes.

Ultrafiltration

The following method, as set out by Anderson et al.(44), was used to separate the hydrophilic and hydrophobic samples into the molecular weight fractions.

A 150 ml sample of the solution was placed in an Amicon stirred ultrafiltration cell. Less than 90% of this amount of the solution was filtered through the ultrafiltration membrane under a pressure of 40-60 psi of nitrogen gas. The membranes used in this work were YM2 (cutoff MW < 1,000) (Dia 62 mm, LOT AS 2797B AAE), YM10 (cutoff MW < 10,000)(Dia 62 mm, LOT AO 2912G LAE), and YM30 (cutoff MW < 30,000)(Dia 62 mm, LOT AP 2637R AAE) produced by Amicon Corporation. Since all Amicon membranes are pretreated with glycerin to prevent drying, it was necessary to rinse the membranes to remove the glycerin before use. The rinsing of the membrane was done by floating it skin (glossy) side down in a beaker of distilled water for at least one hour, changing water three times (the method was recommended by the operating instructions for diaflo ultrafilters of the Amicon Company) The stepwise procedure of the ultrafiltration scheme is shown in Figure 2.

Disinfection

Four different disinfection processes were studied in this research:

(a) Using free chlorine as the only disinfectant.

(b) Using chloramines as the only disinfectant.

(c) Using a combination of preozonation and free chlorine to disinfect the water.

(d) Using a combination of preozonation and chloramine to disinfect the water.

All disinfection processes were conducted at pH 7, in

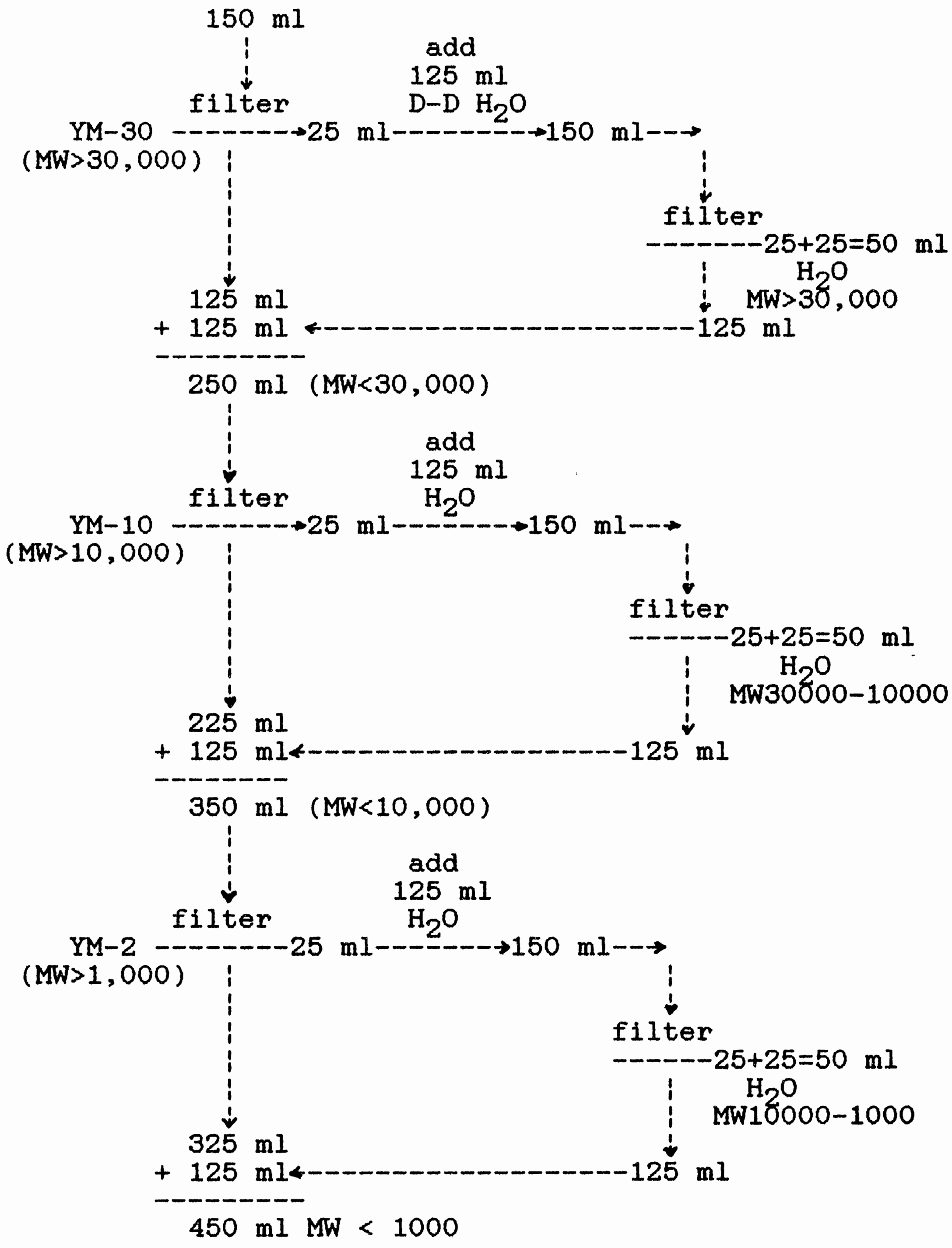


Figure 2. Ultrafiltration Operation Procedure

the presences of a phosphate buffer (0.19 molar KH_2PO_4 and 0.24 molar Na_2HPO_4) at room temperature (about 22 C) in the dark.

The THMs and TCAA, DCAA production amount was monitored at 1, 2, 12, 24, 72, 168 hours for all molecule weight fractions of both the hydrophobic and hydrophilic compounds.

The disinfectant residuals were checked at the end of every incubation period to make sure there was enough disinfectant left in each fraction at the end of the reaction and to estimate the amount of disinfectant consumed. The disinfectant residuals were measured using a DR3 Spectrophotometer at 530 nm wavelength, by the DPD colorimetric method(45). A 4-6 % sodium hypochlorite (from the Fisher Chemical) was used as the source of free chlorine. The free chlorine disinfectant dosage was set at a 5 to 1 mass ratio of free chlorine to total organic carbon (TOC).

The same dosages (mass ratio) of chloramine as those of free chlorine were used in the study. The monochloramine solutions were prepared by reacting ammonium chloride (NH_4Cl) with a previously prepared aqueous chlorine solution at a three to one molar ratio (NH_3 to OCl), at pH 10(46). The chloramine solutions pH was then adjusted to pH 7-7.5 by use of a 5 N NaOH solution. The combined chlorine residuals were measured on a DR3 Spectrophotometer with the DPD colorimetric method(47). Greater than a 98 % combined chlorine solution was obtained by this method.

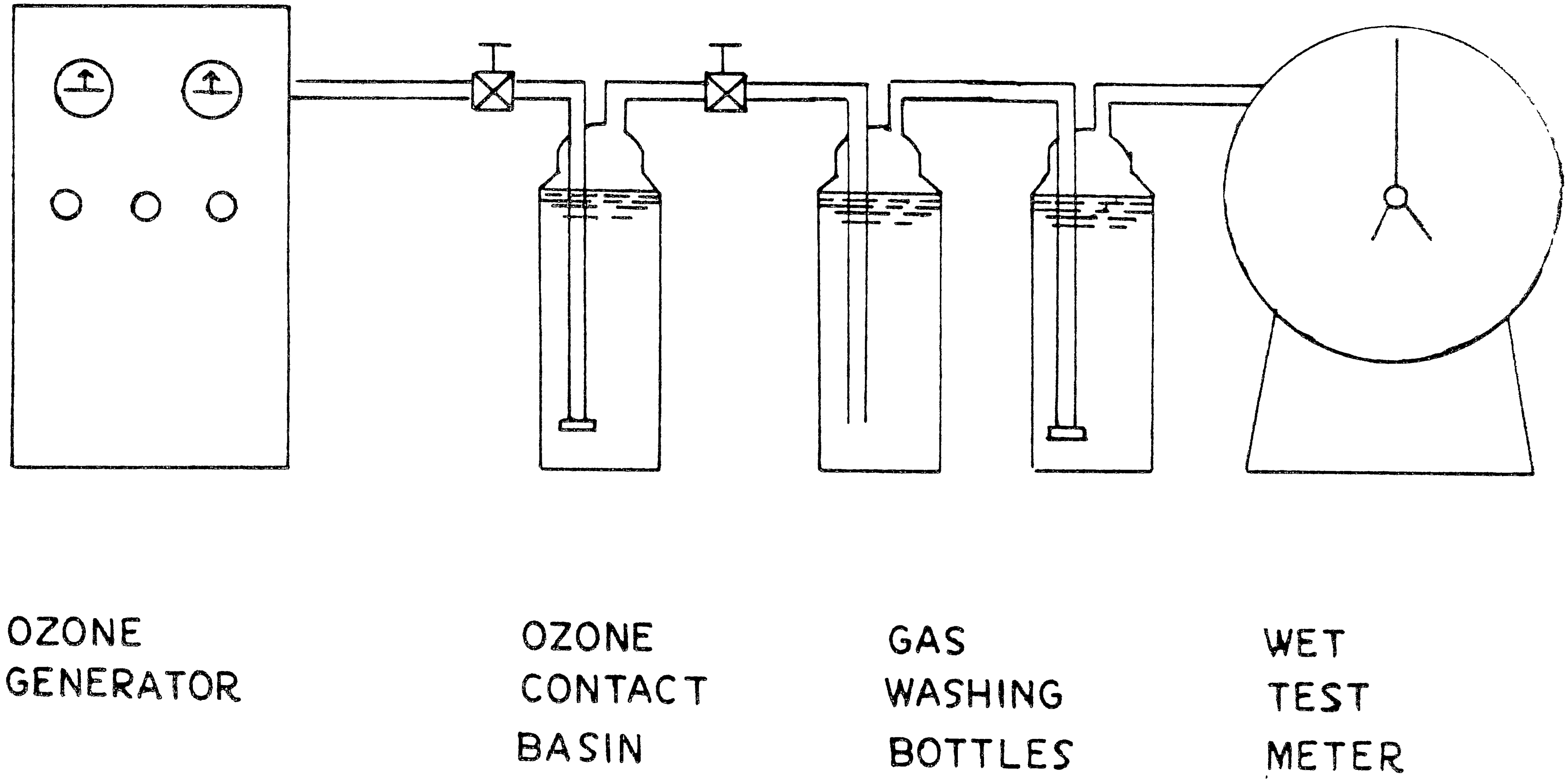


Figure 3. Schematic Diagram of Ozonation Facility Set Up

Ozonation

Ozonation was used to remove or alter the precursor before disinfection. Ozone was generated from air with a Griffin Ozone Generator (Technics Corporation). The ozone generator was connected to a series of semi-batch gas washing bottles and a wet test meter (Fig. 3). The first gas washing bottle acted as an ozone contact basin, the second and third ones contained 250 ml of a 10 g/l potassium iodide solution and were used to absorb the off gas ozone. Ozone generation conditions were maintained at 0.5 amperes of cycle current and 1 liter per minute (l/min) flow rate for a contact time ranging from 1.5 to 2.5 min. in order to obtain the desired absorbed ozone dosages of 0.5-1.5 times the TOC. Applied ozone doses were determined from the potassium iodide traps using the iodometric titration method(48).

THMs Measurement Method

THMs was analyzed by Gas Chromatography (GC) (Perkin-Elmer Sigma 2000) with a 3 % SP-1000 on 100/120 Supelcoport column by a liquid/liquid (pentane solvent) extraction method(49). The GC operation conditions used were:

Oven temperature: 100 °C
Injector temperature: 160 °C
Detector temperature: 350 °C
Carry gas flow rate: 60 ml/min

Carry gas composition: 95 % argon, 5 % methane

DCAA and TCAA Measurement

Because TCAA and DCAA are not ready detected by the GC directly, a methylating derivation process was necessary to convert the acidic form to the more volatile methyl esters that can then be detected by the GC. Since there were no derivation and extraction approaches documented in Standard Methods, the methodology used, which was a modified form of that from the work of Calabrese et al.(50), can be explained as follow:

(a) 1 mg of NaCl was added to 10 ml of the water sample which was then acidified to pH < 0.5 using concentrated hypochloric acid.

(b) Extraction of the sample, described in (a) above was achieved by adding 2 ml of diethyl ether and shaking for 1 minute.

(c) One mililiter of the ether layer was removed and added to a 10 ml reaction vessel along with 0.2 ml of hexane and 1 ml of BF_3/methanol. This mixture was allowed to methylate for 15 min, in a 60 °C water bath. During the methylation step, the samples were periodically shaken.

(d) To stop the reaction, 1 ml of water (obtained from the NANO pure II system by Barnstead) was added to the vessel and shaken. The ether layer was removed and placed in a 1 ml storage vessel.

The GC operating conditions used to detect the haloacids were as follow:

The type of column: GP 10 % SP-2330 on 100/120
Chromosorb WAW column.

Oven temperature: 105 °C

Injector temperature: 160 °C

Detector temperature: 350 °C

Carry gas flow rate: 60 ml/min

Carry gas composition: 95 % of argon and 5 % of methane

Physical Characteristic Measurement

UV absorptions of the samples were measured by Perkin-Elmer Lambda 3 UV/VIS Spectrophotometer at 254 nm wavelength. The pH of these samples was adjusted to 7 prior to the UV measurement.

The anion ion concentrations of the samples were detected by a ion chromatography (Dionex Corporation, Model 2000i/SP).

CHAPTER IV

RESULTS

For clarity of presentation, the results of each sample ultrafiltration process, disinfection schemes and volatile and nonvolatile disinfection by-products (DBP) formation potentials are presented individually. The 24 hour formation potentials of the DBP were selected for use in this chapter, except where specifically noted.

Characteristic of Raw Water

In this research, two water samples were collected. One was in winter (Feb.10, 1989), and the other one was in spring (May, 1, 1989). The physical and chemical data of the samples are listed in the Table 8. The THMs, DCAA and TCAA formation potentials under different disinfection schemes are shown in Table 9. THMs, DCAA and TCAA were measured by the GC. The detection limits of the GC were 5 µg/l for chloroform, 1 µg/l for all other THMs and 20 µg/l for the DCAA and TCAA.

Separation of Hydrophobic and Hydrophilic Fractions

To separate water into hydrophilic(HI) and hydrophobic

TABLE 8

CHARACTERISTICS OF RAW WATER

	Winter sample	Spring sample
Sampling time	Feb. 10, 1989	May. 1, 1989
Temp. °C	8	17
pH	8.3	8.4
Total Alkalinity (mg/l)	163	179
Turbidity(NTU):		
Before filt.	5.8	6.4
After filt.	0.1	0.1
Total Hardness (mg/l as $CaCO_3$)	257	280
Fluoride (mg/l)	0.59	0.62
TOC (mg/l)	3.75	8.0
UV Absorption (cm^{-1})	0.071	0.075
SO_4^{-2} (mg/l)	109	114
NO_3^- (mg/l)	2.2	2.3
Cl^- (mg/l)	155	170
Ca^{+2} (mg/l)	68	72
Mg^{+2} (mg/l)	19	18
Fe^{+3} (mg/l)	0.05	0

TABLE 9

THMs, DCAA AND TCAA FORMATION POTENTIALS OF WINTER AND SPRING RAW WATER UNDER DIFFERENT DISINFECTION OPERATIONS

Sample	Chlorine	Chloramine	Ozone and Chlorine	Ozone and Chloramine
Winter Sample				
$CHCl_3$(µg/l)	77	10	50	6.3
$CHBrCl_2$(µg/l)	32	<1	29	<1
$CHBr_2Cl$(µg/l)	27	<1	21	<1
$CHBr_3$(µg/l)	3.3	<1	3.5	<1
DCAA (µg/l)	67	60	43	44
TCAA (µg/l)	43	83	25	74
Spring Sample				
$CHCl_3$(µg/l)	88	5.7	63	4.7
$CHBrCl_2$(µg/l)	33	<1	30	<1
$CHBr_2Cl$(µg/l)	28	<1	15	<1
$CHBr_3$(µg/l)	2.7	<1	1.9	<1
DCAA (µg/l)	93	115	73	110
TCAA (µg/l)	63	104	35	110

(HB) fractions, a column packed with XAD-8 resin was used. For checking the mass loss in the process, total organic carbon was measured on the influent, raw water, and the two effluents, hydrophilic and hydrophobic, of the column. Table 10 lists the TOC and mass for the three streams through the column.

For purposes of comparison, the physical and chemical characteristics of the HI and HB water sample are listed in Tables 11, 12 and 13.

Ultrafiltration(UF)

Four apparent molecular weight (AMW) fractions were obtained by the UF process and are listed in Table 14. TOC was monitored for each molecular weight fraction and the data are shown in Table 15.

Free Chlorine Disinfection

A 5:1 mass ratio of free chlorine to TOC was used to establish the chlorine dosage for the disinfection processes(22). Free chlorine residuals were monitored at the end of the disinfection period for each AMW fraction and the results are shown in Appendix B. The THMs, DCAA and TCAA formation potentials were monitored at predetermined intervals (1, 2, 12, 24, 72, and 168 hours) during the disinfection period and this information is listed in Appendix A.

TABLE 10

TOC RECOVERY FOR SEPARATION OF HYDROPHOBIC AND HYDROPHILIC OF WINTER SAMPLE

Flow	TOC (mg/l)	Water Volume (ml)	Mass (mg)
Influent	3.75	2000	7.5
HI	3.0	1992	6.0
HB	7.5	550*	4.1
TOC Recovery			135 %

* Elution volume

TABLE 11

CHARACTERISTICS OF HYDROPHILIC AND HYDROPHOBIC FRACTIONS FOR WINTER SAMPLE

	Raw Water	Hydrophilic	Hydrophobic
UV absorption (cm^{-1})	0.071	0.063	0.035
TOC (mg/l)	3.75	3	3
SO_4^{-2} (mg/l)	109	120	< 1
NO_3^- (mg/l)	2.2	13	< 0.1
Cl^- (mg/l)	155	1760	78
Ca^{+2} (mg/l)	68	102	1.16
Mg^{+2} (mg/l)	19	18	0.52
Fe^{+3} (mg/l)	0.05	0.2	0

TABLE 12

CHARACTERISTICS OF HYDROPHILIC AND HYDROPHOBIC FRACTIONS FOR SPRING SAMPLE

	Raw Water	Hydrophilic	Hydrophobic
UV absorption (cm^{-1})	0.075	0.048	0.040
TOC (mg/l)	8	5.4	5.4
SO_4^{-2} (mg/l)	114	114	2
NO_3^- (mg/l)	2.3	2.4	0.2
Cl^- (mg/l)	170	1720	50
Ca^{+2} (mg/l)	72	68	0.9
Mg^{+2} (mg/l)	18	17.5	0.34
Fe^{+3} (mg/l)	0	0.09	0

TABLE 13

BROMIDE CONCENTRATION IN WINTER SAMPLE

MW Fraction (Dalton)	Hydrophilic Fraction (mg/l)	Hydrophobic Fraction (mg/l)	Raw Water (mg/l)
> 30,000	0.1	0.13	
30,000-10,000	0.097	0.16	
10,000-1,000	0.085	0.096	
< 1,000	0.157	0.08	
			0.33

TABLE 14

AMW FRACTIONS DERIVED FROM UF SEPARATIONS

Fraction	AMW
I	> 30,000
II	30,000-10,000
III	10,000-1,000
IV	<1,000

TABLE 15

TOC CONCENTRATION AS A FUNCTION OF MW FRACTION

MW Fraction (Dalton)	TOC (mg/l) Winter Sample		Spring Sample	
	HI	HB	HI	HB
> 30,000	2.7	2.6	3.8	1.4
30,000-10,000	2.8	1.9	9.1	4.6
10,000-1,000	4.6	8.4	21.1	5.7
< 1,000	3.9	1.0	2.2	1.2

Combined Chlorine Disinfection

A 5:1 mass ratio of combined chloramine to TOC was used to establish the chloramine dosage for the disinfection processes. The combined chlorine residuals were monitored and are listed in Appendix C. The THM, DCAA and TCAA formation potentials for the various samples under the combined chlorine region are shown in Appendix A.

Preozonation

The TOC shifts in the various AMW fractions caused by ozonation were checked and are shown in Table 16.

The UV absorption was another parameter used to indicate the ozonation effect. Therefore, the UV absorption of the samples before and after ozonation were measured and presented in Table 17.

To study preozonation treatment effects, the THMs, DCAA and TCAA concentration changes percentages before and after the ozonation option, are set out in Tables 18 and 19 (positive refers to reduce and negative refers to increase in the concentrations after ozonation).

THMs Formation Potential

The THMs formation potentials as a function of the molecular weight fractions were detected under the four different disinfection schemes (chlorine-only, chloramine-only, preozonation-chlorine, and preozonation-chloramine)

TABLE 16

PREOZONATION EFFECTS ON TOC CONCENTRATION SHIFT FOR HYDROPHILIC SPRING SAMPLE

MW Fraction (Dalton)	TOC Concentration (mg/l)	
	Before preozonation	After preozonation
> 30,000	3.8	3.0
30,000-10,000	9.1	3.6
10,000-1,000	21.1	11.4
< 1,000	2.2	16.6

TABLE 17

THE RATIO OF OZONE TO TOC AND UV ABSORPTION SHIFT CAUSED BY PREOZONATION

Sample	Ratio mg O_3/ mg TOC	UV Absorption (cm^{-1}) Without Ozonation	UV Absorption (cm^{-1}) With Ozonation	Change Percentage
Winter Raw Water	0.8	0.071	0.045	37
Winter HI	0.8	0.063	0.021	67
Winter HB	0.8	0.035	0.018	49
Spring Raw Water	0.7	0.075	0.034	55
Spring HI	0.7	0.048	0.017	65
Spring HB	0.8	0.040	0.015	63

TABLE 18

PERCENTAGE CHANGE IN THMs BY OZONATION

	MW Fraction			
	> 30000	30000-10000	10000-1000	< 1000
	Free Chlorine Disinfection			
Winter HI	37	95	45	61
Winter HB	56	-125	36	-130
Spring HI	49	45	34	-67
Spring HB	13	18	85	76
	Chloramine Disinfection			
Winter HI	-380*	100	86	79
Winter HB	23	0	-65*	-1171
Spring HI	100	100	35	50
Spring HB	-500*	100	80	94

*: Actual changes in concentration were small (see Table 20)

TABLE 19

PERCENTAGE CHANGES IN DCAA AND TCAA BY OZONATION

	MW Fraction							
	> 30000		30000-10000		10000-1000		< 1000	
	DCAA	TCAA	DCAA	TCAA	DCAA	TCAA	DCAA	TCAA
	Free Chlorine Disinfection							
Winter HI	-53	-29	38	32	35	15	-177	-72
Winter HB	5	32	-81	39	13	50	-129	-17
Spring HI	25	23	51	37	19	28	-186	-213
Spring HB	-8	17	-17	27	22	48	-869	-170
	Chloramine Disinfection							
Winter HI	-12	6	61	4	58	25	-531	-118
Winter HB	-3	66	-11	-13	54	17	-909	-56
Spring HI	40	13	63	28	52	45	-713	-127
Spring HB	33	78	65	87	48	74	-86	74

and are shown in Table 20.

DCAA and TCAA Formation Potential

The DCAA and TCAA formation potentials as a function of the molecular weight fractions for the different disinfection schemes (chlorine-only, chloramine-only, preozonation-chlorine, and preozonation-chloramine) are shown in Table 21.

TABLE 20

THMs FORMATION POTENTIAL AS A FUNCTION OF MW FRACTION

MW Fraction (Dalton)	THMs Formation Potential (µg/l)			
	Chlorine	Chloramine	Ozone and Chlorine	Ozone and Chloramine
Winter HI				
>30,000	21	<1	13.2	3.8
30,000-10,000	73	1.3	3.4	<1
10,000-1,000	42	1.6	23.2	1
<1,000	110	77.1	43.2	16.4
Winter HB				
>30,000	34	1.3	15	1
30,000-10,000	28	<1	63	<1
10,000-1,000	99	2.6	63	4.3
<1,000	27	3.1	62	58
Spring HI				
>30,000	24	4.4	12.3	<1
30,000-10,000	27	3	14.9	<1
10,000-1,000	68	5.7	45	3.7
<1,000	31	14	52	7
Spring HB				
>30,000	23	<1	20	5
30,000-10,000	38	2.3	31	<1
10,000-1,000	179	16.1	26	3.3
<1,000	139	113	34	7

TABLE 21

DCAA AND TCAA FORMATION POTENTIAL AS A FUNCTION OF MW FRACTIONS

MW Fraction (Dalton)	AHH Formation Potential (μg/l)							
	Chlorine		Chloramine		Ozone and Chlorine		Ozone and Chloramine	
	DCAA	TCAA	DCAA	TCAA	DCAA	TCAA	DCAA	TCAA
Winter HI								
>30,000	15	14	33	81	23	18	37	76
30,000-10,000	16	19	33	80	10	13	13	77
10,000-1,000	26	20	67	96	17	17	28	72
<1,000	26	25	48	77	72	43	303	168
Winter HB								
>30,000	21	28	33	79	20	19	34	27
30,000-10,000	16	23	19	63	29	14	21	71
10,000-1,000	45	62	139	135	39	31	64	112
<1,000	14	24	11	82	32	28	111	128
Spring HI								
>30,000	20	22	67	112	15	17	40	97
30,000-10,000	35	30	130	136	17	19	48	98
10,000-1,000	75	58	373	303	61	42	177	168
<1,000	14	8.3	29	85	40	26	236	193
Spring HB								
>30,000	12	23	15	76	13	19	10	17
30,000-10,000	24	37	74	118	28	27	26	15
10,000-1,000	36	42	90	118	28	22	47	31
<1,000	13	23	21	76	126	62	39	20

CHAPTER V

DISCUSSION

The discussion was classified into two categories, the disinfection by-product formation potentials and disinfection schemes. For comparison purposes, the data which were collected after a 24 hours disinfection contact time have been used in the following discussions, except were specifically noted.

THMs Formation Potential

The THMs formation potentials were surveyed as a function of the hydrophilic and hydrophobic fractions and MW ranges of the water samples for different disinfection combinations. The THMFP under the comparison conditions are shown in Table 20. The free chlorination of the hydrophilic winter sample showed the highest THMFP formation in the MW < 1,000 fraction. The highest MW fraction showed the lowest THMFP. The THMFP of the hydrophobic winter sample showed a maximum in the 10,000-1,000 MW range. There were no significant differences in the THM concentration among the other three MW fractions. THMFP in hydrophilic and hydrophobic spring samples showed approximately the same trend as seen in hydrophobic winter sample. The maximum

THMs concentration was located in MW 10,000-1,000 and the minimum concentration was in MW > 30,000. Therefore, the more reactive THM precursors were contained in MW 10,000-1,000 in all the water samples except for the hydrophilic winter sample. The same type of trend was mentioned by Sinsabaugh et al.(27). In their study, the largest concentrations of THMs were contained in the MW 1,000-30,000 and a 40-60 % lower concentrations was seen in the MW over 30,000 and under 1,000.

The THMFP using the chloramination disinfection was also shown in Table 20. For all four water samples, MW < 1,000 had the highest THMFP and MW > 10,000 gave lower productions of THMs.

The review of preozonation addition was the next step. The ratios of ozone dosage to total organic carbon concentrations of the samples were controlled at 0.5-1 (listed in Table 16). Jacangelo et al.(35) used a similar range of ozone dosage (0.5-1.4 ratio of O_3 to TOC) in their investigation of the ozonation process. A TOC shift before and after the ozonation process was observed. The TOC changes in the hydrophilic spring sample has been used as an example to discuss (Table 15). This data shows that there was a distinct TOC shift from heavier MW fractions to the lighter MW fractions. This phenomena was indicated by Veenstra (33) and Amy et al.(31). The UV absorption change for each sample following ozonated is another parameter which has been often used to indicate the effect of ozonation. The UV absorption shift listed in the Table 17 shows that the decline of UV absorption after ozonation was evident for all samples. It is well known that ozone is a very strong oxidant. Therefore, the TOC shifts to lighter molecular weight by ozonation could be caused by oxidatively cleaving bigger organic molecular chain (like aromatic) to smaller ones. The UV absorption decrease was interpreted by Anderson et al.(44) as being due to the degradation of the double bond system and the oxidation of chromophoric group components such as -OH and $-NH_2$.

THMs removal percentages by preozonation addition were shown in Table 18. THMFP reductions were found in most fractions of molecular weight over 1,000 in the post-chlorine process. The high THM formations were moved from MW < 10,000-1,000 to MW < 1,000 except for the hydrophilic winter sample (Table 20). Higher THM concentrations were obtained at MW < 1,000 for all four treatment schemes. This phenomena corresponded to the TOC shift trend. The study by Amy et al.(31) showed the identical outcome. They reported an enhancement of THMFP, after ozonation, in the lowest MW faction.

In the preozonation-chloramine scheme the highest THMFPs were seen in MW < 1,000 in all four sample sources while a similar was observed for the preozonation-chlorine scheme. The results were agree with the study by Amy et al.(31). A enhancement of the THMFP in the lowest MW fraction was observed in their experiment for a preozonation-chlorine scheme. The reason may be that the ozone cleaves oxidatively the bigger molecules to smaller ones, which is shown by the TOC concentrations shifts from higher MW fractions to lower MW fraction. Dore et al.(42) expounded a ozonation mechanism. They stated that the aromatic ring could be cleaved to ketones, aldehydes, organic acids, aliphatic compounds and carbon dioxide. The molecules cleaved were more activity for chlorine ion substitutions.

The formation potentials of individual THM compounds were also studied. The brominated halogen compound formation concentrations depended on the bromide ion content of the sample as well as the disinfection conditions. Table 13 shows the bromide concentrations in the winter sample. Using the hydrophilic fraction as an example, the highest concentration of bromide was in MW < 1,000. The corresponding brominated trihalomethanes formation potentials at 168 hour incubation time are listed in Table 22. The data in that table shows that the highest productions of brominated compounds were located in the molecular range which the highest bromide concentration. The reductions of brominated halogens by preozonation were also observed in the experiment.

DCAA and TCAA Formation Potential

To verify the productions of DCAA and TCAA from acetic acid, a sample experiment was designed. A 2.5 % solution of acetic acid was prepared and buffered at pH 7. The solution

TABLE 22

THE CONCENTRATIONS OF BROMINATED TRIHALOMETHANES OF HYDROPHILIC WINTER SAMPLE AS A FUNCTION OF MW FRACTIONS

MW Fraction (Dalton)	$CHBrCl_2$ (µg/l)	$CHBr_2Cl$ (µg/l)	$CHBr_3$ (µg/l)
> 30,000	27	6	< 1
30,000-10,000	17	1	< 1
10,000-1,000	7	< 1	< 1
< 1,000	73	24	3

was chloraminated using the same chloramination conditions as mentioned in Chapter III. The 24-hour DCAA and TCAA formation concentraions were 98 µg/l and 195 µg/l, respectively. The results represented the formations of AHHs from acetic acid under chloramination conditions.

The DCAA and TCAA formation potentials are set out in Table 21.

Under conditions of free chlorination, the highest DCAAFP and TCAAFP were in the MW < 1,000 for hydrophilic winter sample, like that for the THMs. However, the differences between the of DCAAFP and TCAAFP among the four molecular weight fractions for this sample were insignificant. The MW 10,000-1,000 showed highest DCAA and TCAA formations while MW < 1,000 showed the lowest formation potentials of the two nonvolatile by-products for the hydrophobic winter sample and both of hydrophilic and hydrophobic spring samples.

When using chloramine as the disinfectant, the maximum DCAA and TCAA formation potentials were located in the MW 10,000-1,000 in all samples. This differs from the pattern shown by the THMs using the same disinfectant where the highest THMFPs occurred in the MW < 1,000 fraction.

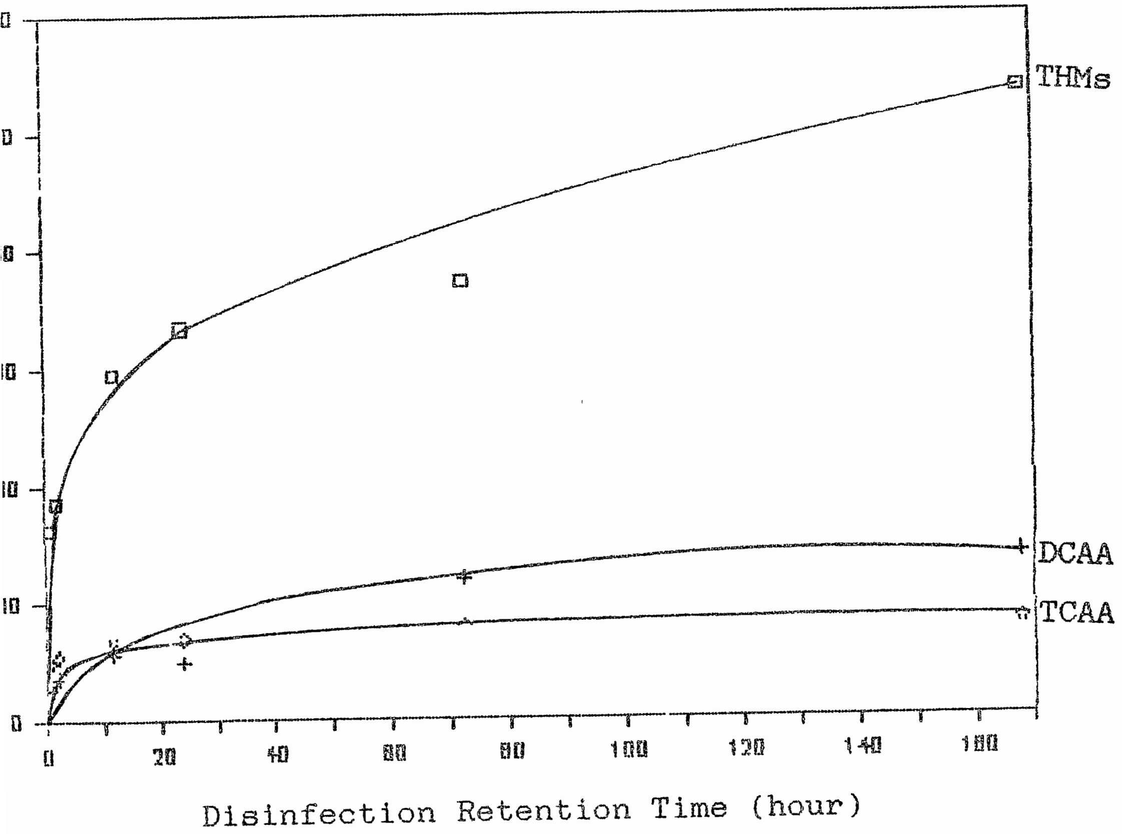
When the preozonation operation was used with the chlorine disinfection process, the change (mostly decreases) in the DCAA and TCAA formation potential (Table 19) in MW > 30,000 was not significant in all four different water samples, also a consistent decrease of concentrations in MW

30,000-1,000 was obtained except for only two DCAA points. It was clear that the two compounds formation potentials were increased in the MW < 1,000 in all the samples compared with the no preozonation treatment. In the ozonation-chloramine scheme, similar trends were obtained as in the ozonation-chlorine scheme. The increases in the TCAA and DCAA were much more significant in MW < 1,000 using the ozonation-chloramine scheme than those in the ozonation-chlorine scheme. The investigation of DCAA and TCAA production properties as a function of molecular weights of organic has not been reported. Therefore, there is no comparative reference with the study.

It was observed that no significant differences and unified trends of DCAAFP and TCAAFP were shown in the sample hydrophilic and hydrophobic fractions.

Comparison of THMFP, DCAAFP and TCAAFP

Figures 4 and 5 represent the THMs, DCAA and TCAA concentration changes with disinfection incubation time. The proportional increases of the three compounds with time are shown. In the first 24 hour, the formation rates of the THMs, DCAA and TCAA were very significant and 40, 46 and 47 percent of 168 hour concentrations of THMs, DCAA and TCAA were achieved. This result is very similar to that obtained during Dore et al.'s(42) investigation. They reported a very fast production of chloroform, DCAA and TCAA during the first minutes of the reaction followed by much lower ones



ure 4. THMs, DCAA and TCAA Formation Potentials of the Winter Raw Water as a Function of Chlorine Disinfection Contact Time

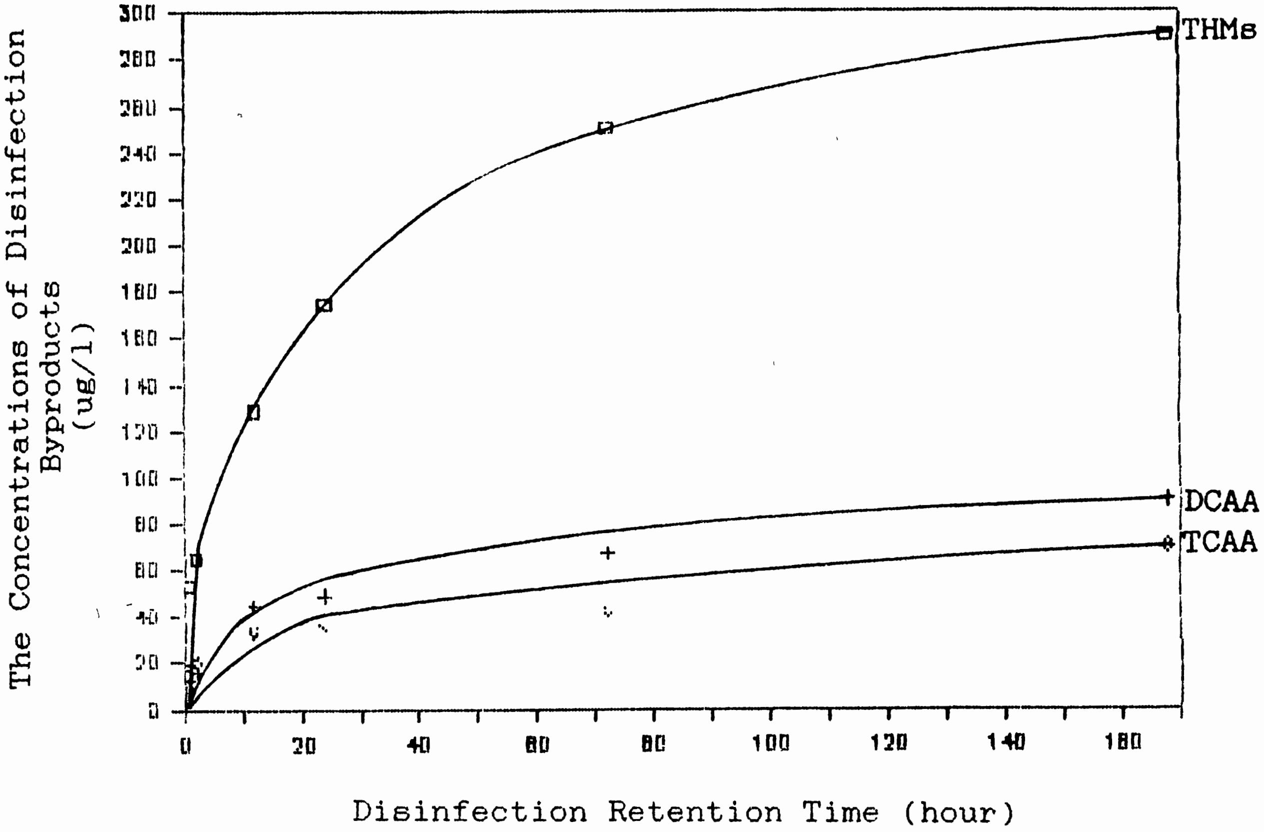


Figure 5. THMs, DCAA and TCAA Formation Potentials of the Spring Raw Water as a Function of Chlorine Disinfection Contact Time

Dore et al.(42) also showed the amount of the three compounds continued to increase even after a 100 hour reaction. In the Figure 4 and 5 increases of the three compounds after 100 hours were observed.

In this research, the THM formation concentration was higher than DCAA and TCAA during chlorination. However, the DCAA and TCAA formation amounts using chloramines were always much higher than the THMs. This result was contrary to the results obtained by Jacangelo et al.(35). Their chloramination tests showed a very high efficiency for reducing DCAAFP and TCAAFP as well as THMFP.

Comparison of Disinfection Options

A comparison of the different disinfection processes on THMFP can be illustrated by the results in Table 20. Comparing the effects of the disinfection options, chlorination would product the highest THMFP in all molecular weight fractions except for three points. Using chloramine instead of free chlorine as a disinfectant, obvious THMs declines were acquired in all the sample situations and all the different MW fractions. These results were verified by Jacangelo's work(35). The THM reduction in MW 10,000-1,000 were the most significant. When combining ozonation with chlorine disinfection, the THMFP declined in all MW > 1,000 range compared to the scheme without preozonation. Under chloramination, preozonation addition could further reduce THMFP in MW

> 1,000. The results illustrated that ozone reduced the reactivities of THMs´ precursor by oxidation, so that the THMFP was decreased. Among the four operational schemes, preozonation-chloramine represented the best option for THMFP control. This was the process selection recommended by Jacangelo(35) also.

Differing from the THMs, the DCAA and TCAA formation potentials were increased in all MW fraction by chloramination compared to free chlorine, except for the departure of one point in the hydrophobic winter sample (Table 21). The increase of TCAAFP in this disinfection process was very significant. When preozonation was added to the two disinfection process, chlorine and chloramine, changes of the DCAA and TCAA formation potentials did not show a consistent trend in the different MW fractions.

Taking the raw water samples as an example to illustrate the optimum disinfection process selection might be more useful. Figures 6 and 7 showed the differnt disinfection scheme. It can be seen that combining ozonation with chloramination was the most efficient at reducing THMFP. It was important to notice that chloramine-only scheme already achieved a 93 and 96 percent (compared to free chlorine) of TTHM removal for winter and spring samples. Therefore, the best disinfection process option was chloramine-only scheme because of economics. The results of this work relative to DCAA and TCAA removal show that chloramination was not a good option. Contrarily,

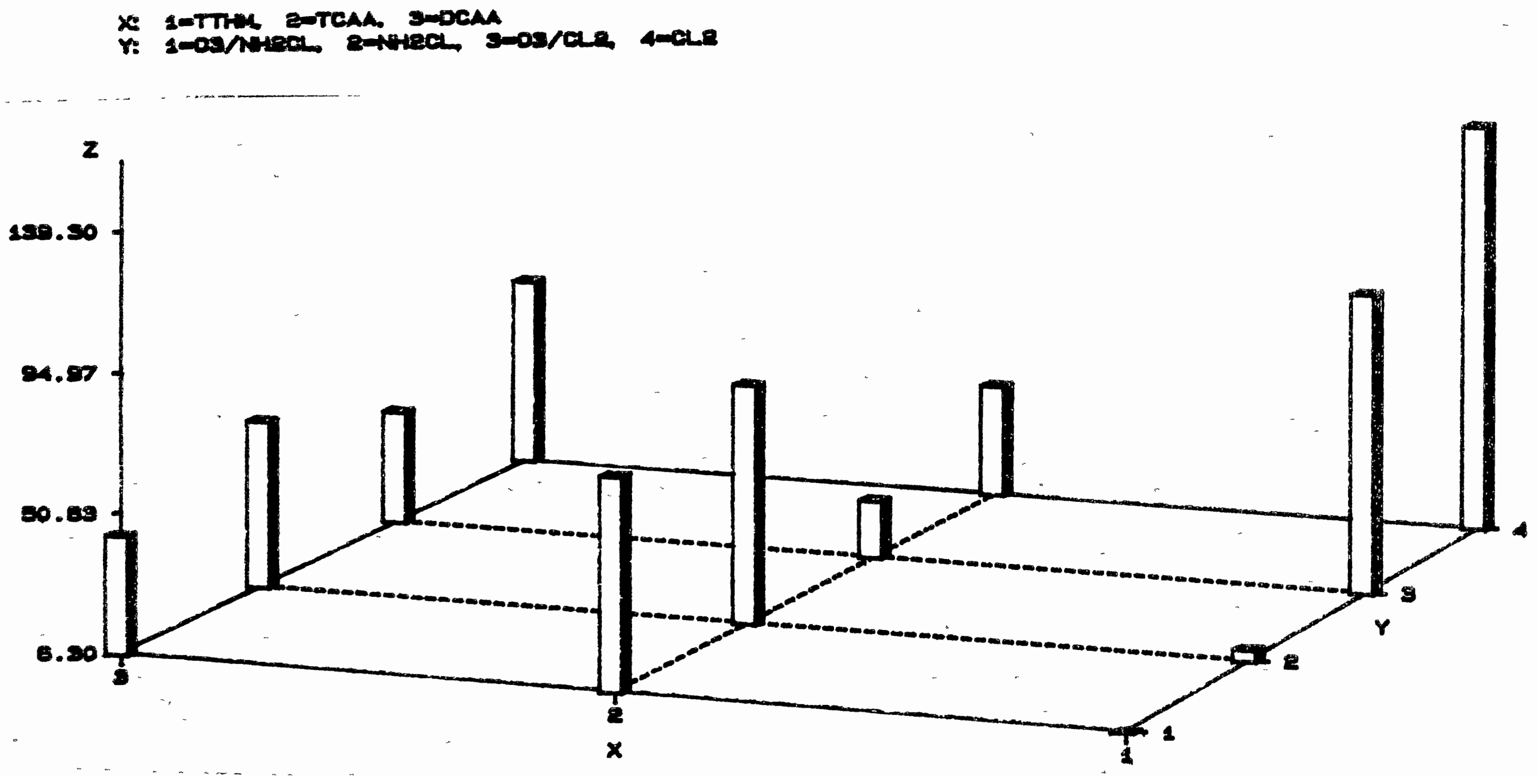


Figure 6. Effect of Various Disinfection Schemes on Disinfection By-product Formation of Winter Raw Sample

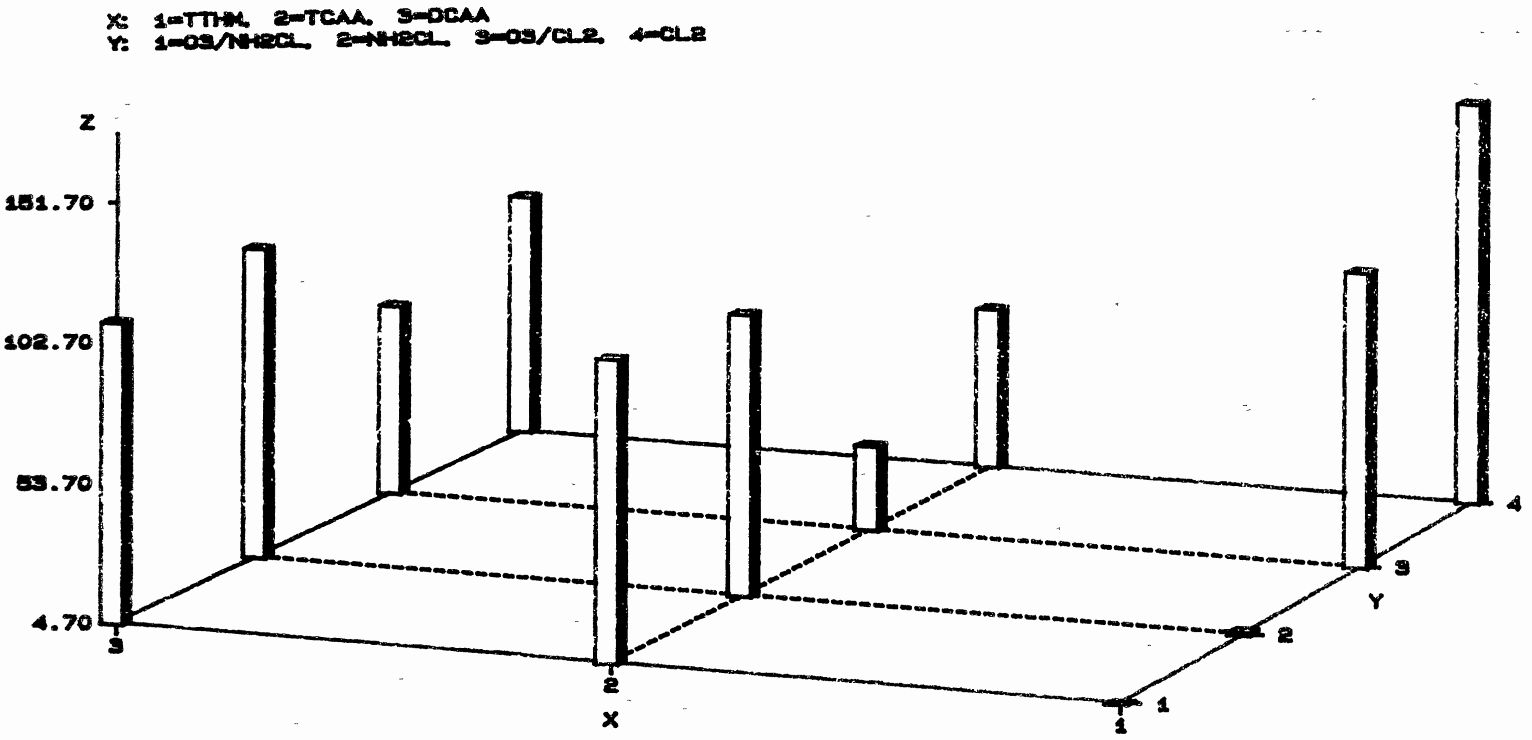


Figure 7. Effect of Various Disinfection Schemes on Disinfection By-product Formation of Spring Raw Sample

ozonation-chlorine scheme represented a better DCAA and TCAA removal approach compared with the ozonation-chloramine one, although a final concentrations for the two compounds could not achieve levels as low as that of THMs by the ozonation-chloramine scheme.

The Seasonal Investigation

The THMs, DCAA and TCAA formation potential changes from winter to spring were observed in this research. Table 9 lists the THMs, DCAA and TCAA formation potential for winter and spring raw water sample. In the chlorination mode the concentrations of THMs in the spring sample were higher than those of winter sample. The same trend was reported by Veenstra(33). Increases in DCAA and TCAA of the spring sample were observed. A 26 µg/l and 20 µg/l increases in DCAA and TCAA and 12 µg/l increase in THMs were seen from the winter to the spring samples in the chlorination mode. The total enhancement percentage of DCAA and TCAA was 29 compared to 8 for the TTHM. Using chloramination, chloroform was the only THM compound to be detected and its concentration was very low. However, the DCAA and TCAA formation potential enhancements in the spring sample were very clear. The DCAA and TCAA concentrations rose 55 µg/l and 21 µg/l, respectively. In the ozonation-chlorine process only a 7 µg/l increase in TTHMs was seen between the winter and spring samples. DCAA and TCAA productions in the spring sample were higher using both ozonation-chlorine and ozonation-chloramine scheme than the winter sample. The increase of HAAs formation was higher than that of THMs formation. The rise ratio of HAAs to THMs was 3.7 using chlorination. The increases of the compound formations were due to TOC enhancement of spring sample (Table 8). The reason for the enhancement of TOC of spring sample might be caused by increase in the amount of humic substances, which were derived from plant decomposition and bacteria degradation, in the water.

CHAPTER VI

CONCLUSIONS

The study focused on the formation potential of the disinfection by-products, such as THMs, DCAA and TCAA, using different disinfectant alternatives and the effects of preozonation. The influences of precursor, like molecular weight, and hydrophilic and hydrophobic fractions on disinfection by-products formation potential were investigated. Two samples were collected, one in the winter and one in the spring, to study any seasonal changes of disinfection by-products.

The precursor study showed that MW 10,000-1,000 supplied the highest THMs, DCAA and TCAA formation potential using free chlorine, although there were excepts in the data. After ozonation was added, the highest by-product formation range shifted to the lightest molecular weight fraction. In the chloramination scheme, the MW <1,000 provided the highest THMFP. The MW 10,000-1,000 still showed the highest productions of DCAA and TCAA. In ozonation-chloramine scheme, the same trend as ozonation-chlorine one was observed.

The various disinfection options had different influences on the by-product formations. The DCAAFP and

TCAAFP were similar to those found for THMs in the chlorination process. Using chloramines as the disinfectant was very efficient for THM reduction. However, DCAA and TCAA formation potential were significantly increased in the process. The preozonation additions could reduced all three disinfection by-products formation potential in MW 30,000-1,000 in most tests. The significant enhancements of THMFP, DCAAFP and TCAAFP in MW < 1,000 was observed in the process. The data of raw water showed that preozonation was effective at reducing the three compounds formation potentials. The DCAA and TCAA removal by the process were not as effective as those for the THMs. The chloramination process was a good disinfection option for THM removal, but it was not an ideal selection for DCAA and TCAA reductions.

The seasonal survey represented that the THM, DCAA and TCAA formation potentials of spring sample were higher than those of winter sample.

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APPENDIX A

CONCENTRATION OF DISINFECTION BY-PRODUCTS

TABLE 1. Concentration of DBPs for Free Chlorine Disinfection of the HI Winter Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	8.3	1.5	1.0	<1	13.0	<1	10.8	13.0
2	13.0	3.0	1.0	<1	17.0	14.0	17.0	31.0
12	34	7	2	<1	30	23	43	53
24	57	13	4	<1	73	34	74	107
72	122	24	3	3	80	51	152	131
168	192	27	6	<1	95	60	225	155

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	8	<1	<1	<1	12	<1	8	12
2	12	1	<1	<1	13	<1	13	13
12	25	5	1	<1	13	<1	31	13
24	38	7	2	<1	19	46	47	65
72	89	11	1	<1	63	58	99	121
168	109	17	1	<1	282	62	127	344

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	9	<1	<1	<1	<10	<10	9	0
2	18	1	<1	<1	15	<10	19	15
12	21	3	<1	<1	14.8	<10	24	14.8
24	29	4	<1	<1	46	53	33	99
72	67	6	<1	<1	91	68	73	159
168	92	7	<1	<1	323	69	99	391

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	25	9	6	<1	9	<10	40	9
2	25	12	9	<1	9.1	<10	46	9.1
12	50	20	12	<1	10.2	<10	82	10.2
24	63	28	17	<1	16	47	108	63
72	115	52	19	3	55	49	189	104
168	167	73	24	3	275	43	267	318

TABLE 2. Concentration of DBPs for Free Chlorine Disinfection of the HB Winter Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	6	1	9	3.3	9	<10	19.3	9
2	7.7	1.3	10	4.2	9.5	<10	23.2	9.2
12	19.7	1.8	10	4.3	15	14	35.8	29
24	23	2	10	4.3	47	54	39.3	101
72	44	2.8	10	4.3	71	58	61.1	129
168	101	3.4	10.5	4.3	270	56	119	326

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	20	<1	12	2.5	9.6	<10	34.5	9.6
2	24	1	12.3	2.7	13.6	20	40	33.6
12	44	1.8	12.3	3.3	33.8	5.7	61.4	90.8
24	52	23	13	3.3	58.4	60	70.6	118
72	127	2.7	13.5	3.3	90	68	147	158
168	187	3.7	13.5	3.2	391	98	207	489

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	5	<1	8.2	<1	<10	<10	13.2	0
2	5	<1	6.7	<1	14.4	10	11.7	24.4
12	16	<1	6.7	<1	55.4	15	22.7	70.4
24	24	<1	7.2	<1	50	53	31.2	103
72	46.7	<1	7.2	<1	154	84	54	238
168	135	1	7.2	<1	383	83	143	466

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	10	1	9	2.6	<10	<10	22.6	0
2	13	1	8.7	2.2	<10	<10	24.9	0
12	33	2	9.2	2.7	11.2	45	46.9	56.2
24	37	27	9.5	2.7	20.8	47	51.9	67.8
72	67	3.7	15	2.7	37	51	88.4	88
168	157	5.7	10.5	3	282	49	176	331

TABLE 3. Concentration of DBPs for Free Chlorine Disinfection of the HI Spring Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	8.3	1	1	<1	<5	<5	10.3	0
2	10	1.2	1.2	<1	<5	<5	12.4	0
12	22.3	3.8	1.6	<1	8.7	6	27.7	14.7
24	38	4.4	1.8	<1	12.3	15	44.2	27.3
72	52	5.8	1.8	<1	28	15	59	43
168	70	15.5	1.9	<1	60	44	87.4	104

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	7.7	1	1.3	1.4	<5	<5	11.4	0
2	9.3	1	1.3	1.1	<5	<5	12.7	0
12	23	2.8	2.4	1.2	5	11	29.4	16
24	38	3.7	2	1.5	10	11	45.2	21
72	44	4.8	2	1.5	26	16	52.3	42
168	50	9.3	1.7	1.1	59	39	62.1	98

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	23	2.7	2.5	2.2	<5	11	30.4	11
2	26	3	2.4	2.2	<5	13	33.6	13
12	60	5.9	3	2.2	29	23	71	52
24	77	8.3	3.1	2.1	32	24	90.5	56
72	181	9	3.8	2.7	43	31	197	74
168	178	12.7	4.1	2.8	87	68	198	155

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	15	2	2.3	1.4	<5	<5	20.7	0
2	18	2.3	2.7	1.4	<5	<5	24.4	0
12	29	4.9	3.1	1.5	8.3	4	38.5	12.3
24	33	6	3.3	1.6	11	7.3	43.9	18.3
72	47	11.3	4.1	1.6	13	12	64	25
168	63	28.5	5.3	1.8	57	32	98.6	89

TABLE 4. Concentration of DBPs for Free Chlorine Disinfection of the HB Spring Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	29	10.5	13.7	5.7	25	18	58.5	43
2	34	11.5	13	5.5	25.7	19	64	44.7
12	49	14	16.5	6.4	26	25	85.9	51
24	88	14.5	17	6.4	30	25	125.9	55
72	110	16.1	17.5	5.7	30.7	30	149.3	60.7
168	136	15.7	15.8	6	49	33	173.5	82

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	26	11.3	13.6	4.5	31.7	46	55.4	77.7
2	40	12.3	13.4	5	32	48	70.7	80
12	74	14.7	14	5.1	32.7	51	107.8	83.7
24	106	14	13.7	5.5	55	55	139.2	110
72	174	12	12.7	4.9	55.3	45	203.6	100.3
168	200	12.9	12.3	5.2	113	80	230.4	193

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	32	9.7	12.5	6.5	31.7	42	60.7	73.7
2	60	10.3	12.6	6.2	33	43	89.1	76
12	97	12.2	13	6.3	53	46	128.5	99
24	168	14	14.3	6.6	58	45	202.9	103
72	194	15	12.8	5.3	73	60	227.1	133
168	225	16.1	14.3	6.3	142	90	261.7	232

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	19	8.3	10	4.5	23	13.7	41.8	36.7
2	34	11	10.7	4.7	23	15.3	60.4	38.2
12	54	11.3	14.7	5.8	24	18.3	85.8	42.3
24	87	12	14.9	6	25	21	119.9	46
72	107	11	11.8	4.8	27	25	134.6	52
168	127	13.3	14.7	5.5	42	26.7	160.5	68.7

TABLE 5. Concentration of DBPs for Chloramine Disinfection of the HI Winter Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	1.7	<1	1.2	<1	68	127	2.9	195
2	3.3	<1	1.2	<1	77	130	4.5	207
12	3.3	<1	1.4	1	73	153	5.7	226
24	4.1	<1	1.4	1	89	148	6.5	237
72	4.7	1.3	1.4	<1	84	210	7.4	294
168	4.5	1.4	1.5	1.2	122	256	8.6	378

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	12.3	<1	1.4	<1	52	108	13.7	160
2	11.3	<1	1.4	<1	65	112	12.7	177
12	16	<1	1.7	1.2	65	145	18.9	210
24	14	<1	1.6	1.1	68	140	16.7	208
72	14.8	1	1.6	1.1	78	168	18.5	246
168	14.3	1.1	1.6	1.2	161	229	18.2	390

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	4.5	<1	1.8	<1	40	74	6.3	114
2	5.8	<1	1.7	<1	43	93	7.5	136
12	5.2	1	2.2	1.4	50	87	9.8	137
24	4.7	1	1.8	1.5	47	91	9	138
72	7.3	1.2	2.1	1.3	56	96	11.9	152
168	7.3	1	2.8	1.4	54	123	12.5	177

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	8.4	<1	2	1.3	52	102	11.7	154
2	8.7	<1	1.9	1.3	60	120	119	180
12	9.7	1	2.1	1.3	58	116	14.1	174
24	9.8	1.2	2.1	1.3	65	131	14.4	196
72	11.3	1.4	2.3	1.3	58	136	16.3	194
168	11	2	2.3	1.7	78	155	17	233

TABLE 6. Concentration of DBPs for Chloramine Disinfection of the HB Winter Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	5.8	1.3	1.8	1.5	23	69	10.4	92
2	3.3	1.3	1.8	1.5	33	70	7.9	103
12	3.3	1.2	1.8	1.5	40	74	7.8	114
24	3.3	1.2	1.6	1.3	39	75	7.4	114
72	5.8	1.6	2.2	1.5	43	90	11.1	133
168	6	1.6	2.3	1.5	50	152	11.4	202

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	5.8	1	1.5	<1	52	86	8.3	138
2	6.2	1.7	2.5	1	50	90	11.4	140
12	7.5	1.5	2.2	1	58	101	12.2	159
24	7.7	1	2	1.1	55	103	11.8	158
72	9.2	1	2	1.1	61	137	13.3	198
168	12.7	1	2.2	1.1	50	147	17	197

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	5	<1	1.3	<1	35	78	6.3	113
2	6.2	<1	1.3	1	62	92	8.5	154
12	6.7	<1	1.4	1	61	97	9.1	158
24	8	<1	1.3	1.1	61	105	10.4	166
72	12.5	1.2	1.5	<1	63	143	15.2	206
168	18	1.6	1.7	<1	75	215	21.3	290

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	1.7	<1	1.5	1	58	103	4.2	161
2	1.8	<1	2	1.3	68	125	5.1	193
12	2.3	<1	1.7	1.3	68	136	5.3	204
24	2.3	<1	1.6	1.3	71	158	5.2	229
72	4.5	1	1.9	1.2	67	149	8.6	216
168	5.5	1	1.8	1.3	78	232	9.6	310

TABLE 7. Concentration of DBPs for Chloramine Disinfection of the HI Spring Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	7	<1	<1	<1	99	127	7	226
2	7	<1	<1	<1	105	127	7	232
12	8	<1	<1	<1	167	173	8	340
24	8.3	<1	1.4	<1	133	215	9.7	348
72	8.3	1.2	1.4	<1	144	210	10.9	354
168	9.3	1.6	1.8	1	193	270	13.7	463

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	12	<1	1.4	1.7	110	167	15.1	277
2	13	1	1.8	1.8	110	183	17.6	293
12	14	1.2	2.5	2.1	140	236	19.8	376
24	13	1.1	2.3	1.8	137	229	18.2	366
72	12	1.5	2.9	2.2	150	233	18.6	383
168	14	1.2	2.5	1.9	215	267	19.6	482

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	16	<1	2	1.6	72	143	19.6	215
2	15	<1	2	1.6	70	135	18.6	205
12	22	1	2.3	1.9	109	183	27.2	292
24	24	1.6	2.7	2.2	120	221	30.5	341
72	28	1.6	2.7	2.3	129	215	34.6	344
168	29	2.5	3.4	2.6	187	273	37.5	460

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	15.6	<1	2.2	1.8	63	74	19.6	137
2	15.6	<1	2.1	1.8	67	74	19.5	141
12	16.7	1.1	2.2	1.8	83	120	21.8	203
24	17.7	1.6	2.4	1.8	117	193	23.5	310
72	19.3	2	2.6	1.8	147	221	25.7	368
168	25	2.6	3.7	2.4	187	233	33.7	420

TABLE 8. Concentration of DBPs for Chloramine Disinfection of the HB Spring Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	3.2	5	8.3	3.4	273	540	19.9	813
2	4.7	5.3	9.3	3.7	290	542	23	832
12	6.9	7.7	11.7	4.7	423	597	31	1020
24	10.9	7.7	11.0	4.5	413	603	34.1	1016
72	15.2	6.7	11.7	4.2	443	606	37.8	1049
168	17.0	7.6	12.0	4.0	420	590	40.6	1010

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	13.7	4.9	6.0	3.2	330	417	27.8	747
2	18.7	5.2	6.6	3.5	307	440	34.0	747
12	21.0	5.9	6.8	5.3	355	479	39.0	834
24	22.5	6.4	7.0	4.8	363	527	40.7	890
72	20.0	8.0	10.0	5.0	370	530	43.0	900
168	25.0	8.4	9.8	3.7	440	720	46.9	1160

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	13.0	6.1	11.8	3.9	327	440	34.8	767
2	14.0	6.2	11.8	3.9	323	447	35.9	770
12	17.5	6.8	13.7	6.0	348	513	44.0	861
24	19.6	7.0	13.5	6.0	375	560	46.1	935
72	22.4	8.3	14.7	5.7	443	693	51.1	1136
168	27.0	8.4	13.0	5.8	510	970	54.2	1480

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	9.8	6.9	9.8	2.7	330	433	29.2	763
2	15.5	7.0	9.7	2.9	330	437	35.1	767
12	17.9	7.4	10.0	3.1	343	520	38.4	863
24	20.0	7.0	11.5	3.7	450	580	42.2	1030
72	21.0	9.0	13.5	4.0	365	590	47.5	955
168	21.5	7.9	11.7	4.1	370	600	45.2	970

TABLE 9. Concentration of DBPs for Ozonation-Chlorine Disinfection of the HI Winter Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	667	8.8	7.2	1.5	10	2.7	684.5	12.7
2	666	8.6	7.2	1.5	14	2.7	683.3	16.7
12	730	14	7.2	3.2	35	6.6	754.4	41.6
24	747	17.7	7.1	3	87	15	774.8	102
72	768	25	7.9	3.1	95	62	804	157
168	807	26	7.5	2.5	101	56	843	157

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	220	4.7	3.9	1.5	17	<10	230.1	17
2	373	5	3.2	2.2	20	<10	383.4	20
12	450	14	3	1.5	21	14.8	468.5	35.8
24	487	16	3.8	1.6	24	15	508.4	39
72	750	13.7	3.6	1.9	40	15.3	769.2	55.3
168	793	18	3.3	3.3	41	15.2	817.6	56.2

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	127	2.5	2.1	1.3	<10	<10	132.9	0
2	427	5.4	3.5	1.5	20	<10	437.4	20
12	407	8.4	3.7	1.9	22	<10	421	22
24	407	12	3.6	1.8	22	20.8	424.4	42.8
72	453	16	3.8	1.7	34	22.5	474.5	56.5
168	523	25	4.5	1.8	45	25	554.3	70

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	100	16	<1	<1	<10	<10	116	0
2	103	20	1.7	1.4	18	<10	126.1	18
12	167	11	3.8	1.8	21	14	183.6	35
24	177	16	4.4	1.8	23	14	199.2	37
72	200	30.7	6.6	2.0	28	15	239.3	43
168	363	45	8.4	2.1	28	15	418.5	43

TABLE 10. Concentration of DBPs for Ozonation-Chlorine Disinfection of the HB Winter Sample

MW > 30,000

Time	Cl	DiCl	DiBr	Br	DCAA	TCAA	THMs	HAAs
(hour)				(ug/l)				
1	420	2.1	1.8	1.8	<5	14	425.7	14
2	433	2.1	2.0	1.9	<5	14.7	439	14.7
12	587	2.9	3.2	2.4	10	25	595.5	35
24	727	4.5	4.5	3.3	40	43	739.3	83
72	740	5.1	4.4	3.2	62	52	752.7	114
168	747	5.9	4.3	3.2	110	64	760.4	174

MW 30,000-10,000

Time	Cl	DiCl	DiBr	Br	DCAA	TCAA	THMs	HAAs
(hour)				(ug/l)				
1	453	2	2	1.8	11	23	458.8	34
2	467	2.1	2.2	2	12.7	25	473.3	37.7
12	593	2.8	2.8	2.4	17.3	38	601	55.3
24	623	3.7	3.2	2.7	47	43	632.6	90
72	700	4.8	3.5	2.9	60	48	711.2	108
168	780	5.7	3.8	3	100	74	792.5	174

MW 10,000-1,000

Time	Cl	DiCl	DiBr	Br	DCAA	TCAA	THMs	HAAs
(hour)				(ug/l)				
1	497	2.6	2.3	1.5	25.7	36	503.4	61.7
2	510	2.4	2.2	1.5	28	39	516.1	67
12	587	3.2	2.7	2.3	42	50	595.2	92
24	697	4.6	3.5	2.8	62	67	707.9	129
72	750	5.6	3.3	2.6	110	85	761.5	195
168	830	7.1	3.6	2.7	166	107	843.4	273

MW < 1,000

Time	Cl	DiCl	DiBr	Br	DCAA	TCAA	THMs	HAAs
(hour)				(ug/l)				
1	193	1.3	1.2	1.3	<5	8	196.8	8
2	210	1.5	1.2	1.5	<5	9	214.2	9
12	287	2	2.2	2	12.3	10.7	293.2	23
24	317	3	2.7	2.4	22	22	325.1	44
72	340	4.4	2.8	2.2	32	26	349.4	58
168	380	6	3	2.4	43	28	391.4	71

TABLE 11. Concentration of DBPs for Ozonation-Chlorine Disinfection of the HI Spring Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	915	11.2	15.7	7.5	21	18	949.4	39
2	910	11	16	8	21	18	945	39
12	920	13	18.5	8.2	23	19	959.7	42
24	980	17	19.7	8.8	26	27	1025.5	53
72	985	20	20.5	9	37	26	1034.5	63
168	970	27.7	22	7.7	127	47	1027.4	174

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	796	6.2	9	4	20	13	815.2	33
2	795	6.4	9.1	4.1	20.3	14	814.6	34.3
12	855	9.3	13	4.7	23	14.7	882	37.7
24	880	10.7	12.7	4.6	20	18	908	38
72	910	13.7	13	5.7	25	25	942.4	50
168	900	15	13	6	87	40	934	127

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	213	3.8	6.3	3	20	14.3	226.1	34.3
2	220	4.3	6.7	3	19	24.5	234	43.5
12	227	7.3	10.8	2.9	23	14.7	248	37.7
24	273	11	14	4.9	22	19	302.9	41
72	325	14.2	13.3	5.3	47	31	357.8	78
168	330	20	11.8	5.3	120	46	347.1	166

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	817	7	12.3	6.7	5	14.1	843	19.1
2	826	8	13	7	6	14.5	854	20.5
12	910	14.5	23	7.3	23	17.8	954.8	40.8
24	930	18.2	24	8.2	25	23	980.4	48
72	960	26.3	24.3	9.3	39	18	1019.9	57
168	955	34.7	22.5	8.6	150	46	1020.8	196

TABLE 12. Concentration of DBPs for Ozonation-Chlorine Disinfection of the HB Spring Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	660	2.3	3.1	2.7	16.7	42	668.1	58.7
2	654	2.3	3.1	2.5	21	42.3	661.9	63.3
12	653	2.4	3.3	2.5	73	52	661.2	125
24	650	2.7	3.6	2.8	90	54	659.1	144
72	655	2.5	3.6	3	99	57	664.1	156
168	680	3	3.4	3.1	106	60	689.5	166

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	770	2.4	3.8	3	17	42	779.2	59
2	773	2.5	3.8	2.8	22	45	782.1	67
12	780	2.7	3.9	3.1	37	57	789.7	94
24	750	2.5	3.4	2.7	87	60	758.6	147
72	790	2.9	3.6	2.9	120	67	799.4	187
168	907	4.3	4.6	3.6	147	89	919.5	236

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	690	1.7	3	2.6	19	45.7	697.3	64.7
2	707	1.7	3	2.5	21	45	714.2	66
12	760	2	3	2.4	50	52	767.4	102
24	735	2.2	3.1	2.6	113	81	742.9	194
72	790	2.6	3.1	2.8	150	124	798.5	274
168	1060	4.4	5.1	4.9	173	130	1074.4	303

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	530	<1	2.6	2.5	16	33	535.1	49
2	523	<1	2.5	2.3	25	32	527.8	57
12	530	1.3	2.5	2.4	33	30.7	536.2	63.7
24	557	1.6	2.6	2.6	38	37	563.8	75
72	560	1.9	2.5	2.3	56	50	566.7	106
168	587	3.2	3.4	3.1	73	53	596.7	126

TABLE 13. Concentration of DBPs for Ozonation-Chloramine Disinfection of the HI Winter Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	170	2	2.4	1.9	85	61	176.3	146
2	187	2	1.9	<1	91	63	190.9	154
12	180	2.4	2.2	1.7	104	127	186.3	231
24	181	2.6	2.3	1.7	101	124	187.6	225
72	167	2.8	2.3	1.7	107	165	173.8	272
168	193	2.9	2.4	1.7	163	280	200	443

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	253	3.6	2.7	2	75	63	261.3	138
2	287	5.3	3.5	2.1	75	63	297.9	138
12	330	2.9	2.5	1.7	83	97	337.1	180
24	330	2.9	2.3	1.7	87	108	336.9	195
72	340	3.3	2.4	1.7	86	118	347.4	204
168	340	3	2.5	1.8	96	128	347.3	224

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	127	2.2	2.1	1.3	41	47	132.6	88
2	206	3	2.5	1.4	73	49	212.9	122
12	233	3	2.6	1.8	63	81	240.4	144
24	227	3.1	2.6	1.7	71	83	234.4	154
72	293	2.8	2.4	1.6	90	108	299.8	198
168	330	3.4	2.9	1.8	91	114	338.1	205

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	113	2.6	1.9	1.2	73	59	118.7	132
2	114	2.9	2.2	1.4	80	66	120.5	146
12	113	1.8	2.1	1.6	74	66	118.5	140
24	120	2.1	2.2	1.6	87	79	125.9	166
72	120	2.1	2.2	1.6	108	110	125.9	218
168	123	2.3	2.6	1.8	112	162	129.7	274

TABLE 14. Concentration of DBPs for Ozonation-Chloramine Disinfection of the HB Winter Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	403	1	1.3	1.9	73	200	407.2	273
2	410	1.1	1.5	1.8	87	222	414.4	309
12	513	1.5	2.3	2	180	297	518.8	477
24	617	2.4	4	3	233	363	626.4	596
72	613	2.3	3.7	3.1	210	373	622.1	583
168	633	2.4	3.6	2.5	340	480	641.5	820

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	383	<1	1.2	<1	117	240	384.2	357
2	390	1	1.3	1	113	280	393.3	413
12	433	1.3	2.3	1.7	205	313	438.3	518
24	467	1.8	2.9	2.7	213	323	474.4	536
72	467	1.8	3	3	295	327	474.8	622
168	465	1.7	2.9	2.9	280	320	472.5	600

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	360	<1	1	1.2	67	227	362.2	294
2	370	<1	1.2	1.3	97	230	372.5	327
12	473	1.3	2.4	2	167	263	478.7	430
24	547	1.8	3.1	2.5	200	207	554.4	407
72	560	1.9	3.2	2.7	238	297	567.8	535
168	555	1.9	3	2.7	233	312	562.6	545

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	103	<1	1	1	133	213	105	346
2	113	<1	1.4	1.2	147	227	115.6	374
12	257	1.1	2.2	2	203	315	262.3	518
24	280	1.3	2.5	2.3	190	327	286.1	517
72	283	1.3	2.3	2.3	187	313	288.9	500
168	313	1.3	2.4	2.5	233	328	319.2	561

TABLE 15. Concentration of DBPs for Ozonation-Chloramine Disinfection of the HI Spring Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	783	6.5	9.6	7	143	270	806.1	413
2	787	6.7	9.8	7.5	160	283	811	443
12	833	9	10	7.7	213	347	859.7	560
24	870	9.3	11	7.8	203	333	898.1	536
72	886	8.3	12	7.5	243	423	913.8	666
168	893	8.2	11.8	7.7	263	430	920.7	693

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	540	3.3	3.8	3.3	173	267	550.4	440
2	555	3.1	4	3	160	257	565.1	417
12	560	4.3	4.5	3.6	172	260	572.4	432
24	633	4.7	4.7	3.6	220	314	646	534
72	647	4.4	5.5	3.9	223	357	660.8	580
168	640	4.5	5.5	4.6	277	367	654.6	644

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	210	2	4	3.4	200	337	219.4	537
2	210	2.1	4.6	3.2	203	343	219.9	546
12	228	2.2	5.3	3.8	213	372	239.3	585
24	220	2.2	5.4	4	210	373	231.6	583
72	230	2.3	5.4	4.2	218	387	241.9	605
168	240	3	5.7	4.5	225	380	253.2	605

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	723	2.7	3.7	5.2	180	313	734.6	493
2	740	3	4	5.8	185	320	752.8	505
12	805	3.5	5.5	6.9	215	350	820.9	565
24	877	4	6.7	5.7	213	372	893.4	585
72	887	5.5	7.7	9.5	219	390	909.7	609
168	880	6.3	9.2	9.3	330	497	904.8	827

TABLE 16. Concentration of DBPs for Ozonation-Chloramine Disinfection of the HB Spring Sample

MW > 30,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	435	<1	1.6	1.5	262	307	438.1	569
2	415	<1	1.6	1.6	250	312	418.2	562
12	420	<1	1.7	1.6	258	360	423.3	618
24	450	<1	1.8	1.8	263	375	453.6	638
72	430	<1	1.8	1.6	283	413	433.4	696
168	448	1.6	2.2	2	293	420	453.8	713

MW 30,000-10,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	640	1.6	3.4	2.6	234	343	647.6	577
2	647	1.7	3.3	2.5	247	350	654.5	597
12	690	1.9	3.2	2.5	253	365	697.6	618
24	705	1.8	3.3	2.6	273	400	712.7	673
72	720	2.2	3.4	2.7	260	427	728.3	687
168	820	2.8	4	3.3	310	437	830.1	747

MW 10,000-1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	725	1.3	2.7	1.3	247	365	730.3	612
2	730	1.3	2.5	1.3	250	367	735.1	617
12	720	1.4	2.5	2.3	253	377	726.2	630
24	723	1.4	2.4	2.4	257	389	729.2	646
72	760	1.3	2.6	2.2	280	417	766.1	697
168	797	2.3	3.6	2.3	313	433	805.2	746

MW < 1,000

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	350	<1	1.3	1.2	213	293	352.5	506
2	355	<1	1.5	1.3	217	300	357.8	517
12	373	<1	2.1	1.8	247	343	376.9	590
24	380	<1	2.2	2.2	237	353	384.4	590
72	440	<1	2	1.8	253	387	443.8	640
168	490	1.8	3.1	2.8	277	380	497.7	657

TABLE 17. Concentration of DBPs of Winter Raw Water

Chlorine Disinfection:

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	36	41	42	43	25	49	162	74
2	41	49	49	47	35	54	186	89
12	84	88	75	49	55	67	296	122
24	77	95	80	61	48	68	334	116
72	157	91	90	34	119	79	372	198
168	286	79	107	63	138	80	535	218

Chloramine Disinfection:

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	2.8	<1	<1	<1	46	83	2.8	129
2	3.3	<1	<1	<1	42	82	3.3	124
12	3.3	<1	<1	<1	48	123	3.3	171
24	3.3	<1	<1	<1	50	115	3.3	165
72	5	1.7	1.4	<1	48	131	8.1	179
168	6.6	2.5	2.1	2.7	167	184	13.9	351

Ozonation-chlorine Disinfection:

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	6.7	4	5	1.5	33	<10	17.2	33
2	11	5.8	7.1	1.9	39	<10	25.8	39
12	24	22	19	4.5	48	<10	69.5	48
24	45	30.5	23.3	4.9	58	<10	103.7	58
72	113	70	32.5	6.3	66	<10	221.8	66
168	138	99	36.5	6.4	88	22	279.9	110

Ozonation-chloramine Disinfection:

Time (hour)	Cl	DiCl	DiBr	Br (ug/l)	DCAA	TCAA	THMs	HAAs
1	<1	<1	<1	<1	34	30	0	64
2	<1	<1	<1	<1	35	31	0	66
12	<1	<1	<1	<1	35	42	0	77
24	1.7	<1	1.1	<1	38	45	2.8	83
72	2.3	1.8	1.6	<1	59	60	5.7	119
168	4.8	4.3	3.6	2.7	63	67	15.4	130

TABLE 18. Concentration of DBPs of Spring Raw Water

Chlorine Disinfection:

Time	Cl	DiCl	DiBr	Br	DCAA	TCAA	THMs	HAAs
(hour)				(ug/l)				
1	25	18	9.3	0.9	12	18	53.2	30
2	32	21.8	10.2	1.2	16	20	65.2	36
12	67	43	17	1.6	45	34	128.6	79
24	107	46.5	19	2	49	37	174.5	86
72	157	67.5	24	2.1	67	43	250.6	110
168	177	84	26.2	2.5	90	70	289.7	160

Chloramine Disinfection:

Time	Cl	DiCl	DiBr	Br	DCAA	TCAA	THMs	HAAs
(hour)				(ug/l)				
1	12	0.8	1.2	<1	117	120	14	237
2	12	0.9	1.2	<1	143	157	14.1	300
12	15	1.6	1.9	<1	277	273	18.5	550
24	19	4	1.5	1	303	427	25.5	730
72	17	5.1	3.6	1.6	310	459	27.3	769
168	18	8.7	8	4.1	420	560	38.8	980

Ozonation-chlorine Disinfection:

Time	Cl	DiCl	DiBr	Br	DCAA	TCAA	THMs	HAAs
(hour)				(ug/l)				
1	806	10.8	11	3.1	23	28	830.9	51
2	820	11	11.2	3	29.7	31	845.2	60.7
12	890	33	17.7	3.1	73	40	943.8	113
24	910	50	22.7	3.7	117	45	986.4	162
72	915	67	24	3.8	172	51	1009.8	363
168	940	98	28.7	4	253	110	1070.7	363

Ozonation-chloramine Disinfection:

Time	Cl	DiCl	DiBr	Br	DCAA	TCAA	THMs	HAAs
(hour)				(ug/l)				
1	647	4	3.3	1.9	306	593	656.2	899
2	663	4.1	3.7	1.9	330	590	672.7	920
12	767	5.3	5.2	2.1	400	610	779.6	1010
24	760	8	5.3	1.7	413	640	775	1053
72	800	8.5	5.7	1.5	440	683	815.7	1123
168	813	10.8	9.3	2.6	520	733	835.7	1253

SYMBOLS IN APPENDIX A

DBPs -- Disinfection by-products

HI -- Hydrophilic fraction

HB -- Hydrophobic fraction

Time -- Disinfection contact time.

Cl -- Cholroform.

DiCl -- Bromodichloromethane.

DiBr -- Dibromochloromethane.

Br -- Bromoform.

DCAA -- Dichloroacetic acid.

TCAA -- Trichloroacetic acid.

THMs -- Sum of four haloforms.

HAAs -- Sum of two haloacetic acids.

APPENDIX B

CONCENTRATION OF FREE CHLORINE RESIDUAL

TABLE 1. Disinfection of HI Winter Sample

Contact Time (hour)	MW Fraction			
	> 30000	30000-10000	10000-1000	< 1000
1	20.4	15.0	7.1	17.9
2	17.6	16.3	6.0	18.4
12	15.3	15.1	4.0	14.5
24	12.5	11.0	1.2	14.0
72	13.0	9.0	1.3	12.0
168	12.0	8.6	0.9	12.2

TABLE 2. Disinfection of HB Winter Sample

Contact Time (hour)	MW Fraction			
	> 30000	30000-10000	10000-1000	< 1000
1	7.9	15.8	16.9	10.4
2	7.5	12.4	16.5	10.0
12	7.3	10.1	16.0	9.8
24	7.1	10.3	16.4	10.0
72	4.8	10.5	10.0	10.2
168	6.0	11.3	15.0	11.0

TABLE 3. Disinfection of HI Spring Sample

Contact Time (hour)	MW Fraction			
	> 30000	30000-10000	10000-1000	< 1000
0	20.5	20.5	20.5	20.5
1	20.3	17.5	10.0	17.5
2	18.8	15.5	10.8	15.5
12	14.3	9.8	9.5	14.8
24	12.8	10.3	7.0	13.8
72	9.3	6.8	4.5	12.0
168	3.8	6.0	4.0	5.3

TABLE 4. Disinfection of HB Spring Sample

Contact Time (hour)	MW Fraction			
	> 30000	30000-10000	10000-1000	< 1000
0	20.8	20.8	20.8	20.8
1	21.0	20.0	20.7	19.0
2	19.0	19.4	18.5	17.3
12	10.0	14.5	8.0	12.5
24	9.5	8.0	5.0	13.0
72	7.0	7.5	4.3	12.7
168	6.0	7.0	4.0	11.0

TABLE 5. Preozonation and Disinfection of HI Winter Sample

Contact Time (hour)	MW Fraction			
	> 30000	30000-10000	10000-1000	< 1000
0	24.0	10.7	6.3	11.9
1	21.0	8.2	4.5	12.5
2	15.0	6.3	3.4	12.1
12	14.0	9.0	3.4	9.3
24	9.5	9.5	4.5	7.0
72	10.5	5.7	2.5	4.9
168	11.0	7.1	1.7	4.2

TABLE 6. Preozonation and Disinfection of HB Winter Sample

Contact Time (hour)	MW Fraction			
	> 30000	30000-10000	10000-1000	< 1000
0	14.7	20.0	20.3	18.8
1	12.3	10.3	10.0	11.5
2	11.7	9.8	9.4	11.8
12	12.7	10.2	9.5	11.9
24	8.7	9.7	7.0	8.0
72	9.7	10.2	6.7	9.3
168	11.5	12.3	6.5	13.0

TABLE 7. Preozonation and disinfection of HI spring sample

Contact Time (hour)	MW Fraction			
	> 30000	30000-10000	10000-1000	< 1000
0	21.5	21.5	21.5	21.5
1	16.0	13.5	11.8	13.3
2	16.0	12.4	11.0	12.9
12	12.5	10.8	9.5	12.5
24	9.8	9.9	9.5	11.8
72	10.5	9.0	10.0	10.3
168	7.5	7.8	6.8	8.7

TABLE 8. Preozonation and disinfection of HB spring sample

Contact Time (hour)	MW Fraction			
	> 30000	30000-10000	10000-1000	< 1000
0	20.7	20.7	20.7	20.7
1	35.5	20.0	19.5	19.0
2	35.0	25.0	22.7	23.0
12	37.5	40.0	46.5	46.5
24	43.5	40.0	40.0	43.0
72	45.0	32.0	50.0	43.0
168	44.0	35.0	33.5	45.0

TABLE 9. Disinfection of Winter Raw Water

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
free chlo.	10	8.9	8.0	5.8	5.4	3.3	2.6

TABLE 10. Preozonation and Disinfection of Winter Raw Water

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
free chlo.	18.4	14.3	10.7	5.1	4.7	3.4	2.7

TABLE 11. Disinfection of Spring Raw Water

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
free chlo.	45.0	40.5	40.0	35.5	34.0	32.0	30.0

TABLE 12. Preozonation and Disinfection of Spring Raw Water

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
free chlo.	41.5	36.0	35.0	32.5	32.0	9.0	8.5

APPENDIX C

CONCENTRATION OF CHLORAMINE RESIDUAL

TABLE 1. Disinfection of HI Winter Sample

MW > 30,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	26.8	25.7	22.3	22.1	16.3	9.3	2.8
B free chlo.	0.6	0.3	0.3	0.4	0.2	0.8	0.1
chloramine	26.8	26.5	25.5	34.7	14.3	6.8	2.1
free chlo.	0.6	1.0	0.5	0.3	0.2	0.2	0.2

MW 30,000-10,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	24.3	27.2	20.5	23.6	19.5	15.9	4.1
B free chlo.	0.7	0.4	0.5	0.4	0.5	0.6	0.3
chloramine	24.3	23.8	26.3	24.4	16.4	9.6	2.6
free chlo.	0.7	0.3	0.3	0.6	0.2	0.4	0.2

MW 10,000-1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	18.2	16.3	18.3	9.3	9.9	4.9	2.8
B free chlo.	0.3	0.3	0.2	0.3	0.1	0.1	0.1
chloramine	18.2	23.3	20.9	15.8	11.8	4.6	2.5
free chlo.	0.3	0.3	0.8	0.8	0.1	0.2	0.3

MW < 1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	24.3	26.2	26.5	27.6	26.5	16.9	4.4
B free chlo.	0.7	0.4	0.5	0.4	0.5	0.6	0.3
chloramine	24.3	24.8	24.8	24.7	18.7	11.0	4.0
free chlo.	0.7	0.3	0.3	0.3	0.3	0.2	0.2

B: The blank test.

TABLE 2. Disinfection of HB Winter Sample

MW > 30,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	17.4	7.9	6.2	5.8	2.8	3.2	3.2
B free chlo.	0.7	0.4	0.4	0.2	0.3	0.1	0.1
chloramine	17.4	11.4	9.9	7.5	6.0	3.3	2.3
free chlo.	0.7	0.2	0.3	0.5	0.2	0.3	0.1

MW 30,000-10,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	22.3	16.5	19.3	11.9	5.2	4.9	2.7
B free chlo.	0.2	0.2	0.1	0.1	0.1	0.1	0.1
chloramine	22.3	19.4	16.3	16.3	9.8	4.5	2.5
free chlo.	0.2	0.2	0.2	0.2	0.2	0.2	0.1

MW 10,000-1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	22.3	19.3	16.5	11.9	5.2	4.9	2.7
B free chlo.	0.2	0.2	0.1	0.1	0.1	0.1	0.1
chloramine	22.3	16.9	18.3	13.3	10.8	6.2	2.3
free chlo.	0.2	0.2	0.7	0.8	0.3	0.1	0.1

MW < 1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	21.8	25.7	22.3	22.1	16.3	9.3	2.8
B free chlo.	0.6	0.3	0.3	0.4	0.2	0.3	0.2
chloramine	21.8	25.8	25.0	34.5	20.8	12.0	3.9
free chlo.	0.6	0.3	0.6	0.5	0.2	0.2	0.3

TABLE 3. Disinfection of HI Spring Sample

MW > 30,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	17.4	16.0	15.3	13.7	12.9	10.3	3.4
B free chlo.	0.4	0.4	0.3	0.4	0.2	0.3	0.2
chloramine	17.4	16.6	16.8	16.5	16.1	13.4	3.6
free chlo.	0.2	0.3	0.3	0.3	0.3	0.4	0.3

MW 30,000-10,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	17.4	16.0	15.3	13.7	12.9	10.3	3.4
B free chlo.	0.4	0.4	0.3	0.4	0.2	0.3	0.2
chloramine	17.4	18.2	16.3	15.7	14.8	13.6	7.1
free chlo.	0.2	0.4	0.3	0.3	0.3	0.4	0.4

MW 10,000-1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	17.4	16.0	15.3	13.7	12.9	12.3	3.4
B free chlo.	0.4	0.4	0.3	0.4	0.2	0.3	0.2
chloramine	17.4	16.6	16.1	15.9	16.1	14.5	8.6
free chlo.	0.2	0.3	0.4	0.3	0.3	0.3	0.4

MW < 1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	17.4	16.0	15.3	13.7	12.9	12.3	3.4
B free chlo.	0.4	0.4	0.3	0.4	0.2	0.3	0.2
chloramine	17.4	17.3	16.8	15.8	14.8	12.6	8.5
free chlo.	0.2	0.2	0.2	0.3	0.3	0.4	0.4

TABLE 4. Disinfection of HB Spring Sample

MW > 30,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	20.5	18.8	14.3	13.2	10.2	3.2	2.8
B free chlo.	0.4	0.4	0.3	0.2	0.2	0.1	0.1
chloramine	20.5	16.6	15.7	10.8	9.3	4.4	1.7
free chlo.	0.4	0.3	0.3	0.3	0.2	0.2	0.1

MW 30,000-10,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	20.5	18.8	14.3	13.2	10.2	3.2	2.8
B free chlo.	0.4	0.4	0.3	0.2	0.2	0.1	0.1
chloramine	20.5	13.1	12.8	13.0	11.2	7.4	4.3
free chlo.	0.4	0.2	0.3	0.4	0.3	0.2	0.1

MW 10,000-1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	20.5	18.8	14.3	13.2	10.2	3.2	2.8
B free chlo.	0.4	0.4	0.3	0.2	0.2	0.1	0.1
chloramine	20.5	14.6	13.8	11.5	11.0	8.3	4.8
free chlo.	0.4	0.2	0.3	0.5	0.3	0.2	0.1

MW < 1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	20.5	18.8	14.3	13.2	10.2	3.2	2.8
B free chlo.	0.4	0.4	0.3	0.2	0.2	0.1	0.1
chloramine	20.5	14.1	13.7	12.1	11.6	9.0	6.5
free chlo.	0.4	0.2	0.3	0.4	0.4	0.2	0.1

TABLE 5. Preozonation and Disinfection of HI Winter Sample

MW > 30,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	26.6	22.5	21.8	16.1	15.3	5.4	3.1
B free chlo.	0.2	0.5	0.8	0.2	0.2	0.1	0.1
chloramine	26.6	26.9	25.6	21.4	18.4	12.4	8.5
free chlo.	0.2	0.6	0.8	0.4	0.4	0.4	0.1

MW 30,000-10,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	28.3	23.6	22.3	16.3	12.6	3.7	2.4
B free chlo.	0.5	0.5	0.3	0.3	0.1	0.1	0.1
chloramine	28.3	23.3	23.2	17.2	14.6	10.0	7.0
free chlo.	0.5	0.5	0.6	0.4	0.3	0.2	0.1

MW 10,000-1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	23.8	19.8	19.1	13.6	12.1	8.1	3.9
B free chlo.	0.3	0.2	0.2	0.2	0.2	0.1	0.1
chloramine	23.8	18.9	18.4	13.4	12.7	7.9	5.9
free chlo.	0.3	0.4	0.5	0.4	0.4	0.4	0.1

MW < 1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	22.0	22.4	22.3	20.6	16.3	11.3	6.7
B free chlo.	0.4	0.5	0.3	0.2	0.3	0.2	0.1
chloramine	22.0	22.1	24.5	19.7	15.0	10.6	7.3
free chlo.	0.5	0.9	0.3	0.4	0.6	0.3	0.2

TABLE 6. Preozonation and Disinfection of HB Winter Sample

MW > 30,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	11.3	10.2	10.5	9.3	8.4	6.0	3.2
B free chlo.	0.2	0.2	0.1	0.1	0.1	0.1	0.1
chloramine	11.3	9.8	9.2	8.8	7.8	5.5	3.6
free chlo.	0.2	0.2	0.1	0.1	0.1	0.1	0.1

MW 30,000-10,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	15.8	13.2	10.2	9.0	8.4	5.3	3.9
B free chlo.	0.3	0.3	0.2	0.2	0.3	0.1	0.1
chloramine	15.8	9.3	8.5	7.8	7.5	5.5	4.0
free chlo.	0.3	0.3	0.2	0.2	0.1	0.1	0.1

MW 10,000-1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	15.8	13.2	10.2	9.0	8.4	5.3	3.9
B free chlo.	0.3	0.3	0.2	0.2	0.3	0.1	0.1
chloramine	15.8	9.8	8.3	7.8	6.3	5.8	3.8
free chlo.	0.3	0.4	0.3	0.2	0.2	0.2	0.1

MW < 1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	13.3	11.2	10.0	8.3	7.3	6.9	5.3
B free chlo.	0.3	0.2	0.2	0.1	0.1	0.1	0.1
chloramine	13.3	9.3	8.3	7.3	7.0	6.7	4.0
free chlo.	0.4	0.3	0.2	0.2	0.1	0.1	0.1

TABLE 7. Preozonation and Disinfection of HI Spring Sample

MW > 30,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	13.5	17.3	15.8	9.8	6.7	3.2	1.0
B free chlo.	0.5	0.4	0.1	0.2	0.1	0.1	0.1
chloramine	13.5	16.0	16.3	15.3	12.7	10.6	6.7
free chlo.	0.5	0.7	0.3	0.2	0.2	0.2	0.1

MW 30,000-10,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	13.5	17.3	16.0	9.8	6.7	3.2	1.0
B free chlo.	0.5	0.2	0.1	0.2	0.1	0.1	0.1
chloramine	13.5	15.0	15.0	14.8	11.8	10.1	6.1
free chlo.	0.5	0.7	0.7	0.7	0.2	0.2	0.2

MW 10,000-1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	13.5	17.3	15.0	9.8	6.7	3.2	1.0
B free chlo.	0.5	0.2	0.1	0.2	0.1	0.1	0.1
chloramine	13.5	15.0	15.0	15.3	12.8	10.3	5.7
free chlo.	0.5	0.8	0.8	0.2	0.2	0.1	0.1

MW < 1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	13.5	17.3	15.0	9.0	6.6	3.2	1.0
B free chlo.	0.5	0.1	0.1	0.2	0.1	0.1	0.1
chloramine	13.5	14.6	15.0	14.3	13.0	11.3	7.2
free chlo.	0.5	0.8	0.8	0.2	0.2	0.2	0.1

TABLE 8. Preozonation and Disinfection of HB Spring Sample

MW > 30,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	13.2	11.9	14.8	14.4	7.4	2.0	1.0
B free chlo.	0.3	0.1	0.2	0.1	0.1	0.1	0.1
chloramine	13.2	13.0	18.0	20.5	16.0	11.0	8.1
free chlo.	0.3	0.2	0.3	0.3	0.2	0.1	0.1

MW 30,000-10,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	13.2	12.0	14.8	14.3	7.5	10.0	2.0
B free chlo.	0.3	0.1	0.1	0.1	0.1	0.1	0.1
chloramine	13.2	12.6	19.0	21.3	11.8	9.0	7.0
free chlo.	0.3	0.3	0.4	0.4	0.2	0.1	0.1

MW 10,000-1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	13.2	12.0	14.8	14.3	7.5	10.0	2.0
B free chlo.	0.3	0.1	0.1	0.1	0.1	0.1	0.1
chloramine	13.2	13.1	20.0	22.5	16.8	10.0	7.5
free chlo.	0.3	0.8	0.7	0.7	0.6	0.3	0.1

MW < 1,000

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	13.2	12.0	14.8	14.3	7.5	10.0	2.0
B free chlo.	0.3	0.1	0.1	0.1	0.1	0.1	0.1
chloramine	13.2	12.8	20.0	22.5	16.5	10.3	8.3
free chlo.	0.3	0.7	0.8	0.6	0.4	0.1	0.1

TABLE 9. Disinfection of Winter Raw Water

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	13.1	12.4	12.3	6.2	5.3	4.9	2.8
B free chlo.	0.3	0.1	0.3	0.7	0.4	0.1	0.1
chloramine	13.1	12.9	14.4	10.6	9.8	5.9	2.4
free chlo.	0.3	0.2	0.2	0.9	0.2	0.1	0.1

TABLE 10. Perozonation and Disinfection of Winter Raw Water

Residual (mg/l)	Contact time (hour)						
Contact time (hour)							
	0	1	2	12	24	72	168
B chloramine	13.9	15.2	8.4	13.5	11.3	5.6	2.8
B free chlo.	0.2	0.1	0.1	0.3	0.2	0.2	0.1
chloramine	13.9	16.9	12.4	11.5	14.8	9.4	5.5
free chlo.	0.2	0.2	0.3	0.3	0.3	0.3	0.2

TABLE 11. Disinfection of Spring Raw Water

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	39.8	35.4	33.6	32.1	29.3	27.8	18.2
B free chlo.	0.7	0.3	0.5	0.4	0.5	0.3	0.2
chloramine	39.8	34.4	35.4	33.0	31.6	25.9	16.0
free chlo.	0.3	0.6	0.4	0.3	0.2	0.4	0.5

TABLE 12. Preozonation and Disinfection of Spring Raw Water

Residual (mg/l)	Contact time (hour)						
	0	1	2	12	24	72	168
B chloramine	26.5	27.8	26.8	18.2	9.8	7.0	3.0
B free chlo.	0.1	0.1	0.3	0.3	0.1	0.1	0.1
chloramine	26.5	27.5	27.2	24.0	24.5	18.3	10.8
free chlo.	0.5	0.5	0.4	0.2	0.5	0.2	0.2

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