A National Survey of Chlorinated Disinfection By-Products in Canadian Drinking Water

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Summary

The study was designed to determine the concentrations of halogenated disinfection by-products in Canadian drinking water supplies where chlorine was used at some stage in the treatment process. The effects of applied disinfectants (chlorine, chloramine and ozone), seasonal variation (winter and summer) and spatial variation (treatment plant and distribution system) were examined. Trihalomethanes and haloacetic acids were the major disinfection by-products found in all facilities for all treatment processes and haloacetic acid levels often equalled or exceeded trihalomethane concentrations. Haloacetonitriles, halopropanones, chloral hydrate and chloropicrin were usually detected in treated water samples but at lower concentrations. Mean and median trihalomethane levels were higher in the summer than the winter for all three treatment processes and increased in the distribution system except for chlorine-chloramine treatment. Mean and median trichloroacetic acid levels for chlorine-chlorine disinfection increased in the distribution system but winter and summer levels were similar. Mean and median trichloroacetic acid levels for chlorine-chloramine and ozone-chlor(am)ine treatment and mean and median dichloroacetic acid levels for all processes were slightly higher in summer compared to winter but levels were not higher in the distribution system. Additional research is required to delineate more clearly the spatial and temporal variations in disinfection by-product levels in drinking water at specific facilities. To obtain an accurate estimation of human exposure to disinfection by-products from drinking water, it would appear that samples should be collected at the consumer tap and not at the treatment plant. Further studies are in progress to define the most appropriate sampling strategy.

Acknowledgement

Introduction

The treatment of water supplies by disinfection has proven highly effective in destroying or inactivating human pathogenic microorganisms, particularly those responsible for typhoid fever and cholera (Ellis 1991). However, the lack of adequate disinfection can still lead to cholera epidemics (Glass *et al.*, 1992). Consequently, in Canada, it is recognized that disinfection of all surface waters used for human consumption is crucial and that the health risks from pathogenic microorganisms far exceed those potential health risks associated with chemical disinfection by-products (DBPs) produced during potable water treatment. The challenge is, therefore, to minimize the potential risks from DBPs without compromising disinfection efficiency.

Chlorine is effective as both a primary and residual disinfectant and is also relatively easy to use. However, chlorine also reacts with biogenic organic matter, such as humic and fulvic acids, present in all natural surface water supplies. The resultant chlorinated organic contaminants have been widely reported in drinking water supplies but since the chemistry involved is extremely complex, it is not yet feasible to predict the concentrations of the various DBPs that will be formed in any given water sample. Following the first reports by Rook (1974) and Bellar *et al.* (1974), initial concerns focused on the health effects and levels of trihalomethanes (THMs) in drinking water. More recent surveys have also included haloacetic acids (HAAs), haloacetonitriles (HANs), chloropicrin (CPK), chloral hydrate (CH) and other DBPs. The World Health Organization has published drinking water guidelines (WHO 1993) for chloroform (TCM, 0.2 mg/L), bromodichloromethane (BDCM, 0.06 mg/L), dibromochloromethane (DBCM, 0.1 mg/L) and bromoform (TBM, 0.1 mg/L) and provisional guideline values for dichloroacetic acid (DCAA, 0.05 mg/L), trichloroacetic acid (TCAA, 0.1 mg/L), chloral hydrate (CH, 0.01 mg/L), dichloroacetonitrile (DCAN, 0.09 mg/L), dibromoacetonitrile (DBAN, 0.1 mg/L) and trichloroacetonitrile (TCAN, 0.001 mg/L). In addition to the guidelines for individual THMs, the World Health Organization suggests (WHO, 1993) that a guideline for the total THM (TTHM) be derived from the sum of the ratios (ratio not to exceed 1) of the measured values to the guideline values for each individual THM. It should be emphasized that WHO guidelines do not have any formal recognition in Canada, and they do not include consideration of achievability, which is a feature of Canadian guidelines. The current USEPA maximum contaminant level for TTHMs was set at 0.1 mg/L but a Disinfectants-Disinfection By-products Rule, expected to be promulgated by the USEPA in 1996 (USEPA 1991, AWWA 1994, Pontius 1995), will set new maximum contaminant levels for TTHMs (0.08 mg/L) and the sum of five haloacetic acids (HAA5, 0.06 mg/L). An interim maximum acceptable concentration (IMAC) for TTHMs (0.1 mg/L) has recently been assigned in the Guidelines for Canadian Drinking Water (Health Canada in press). No Canadian guidelines exist for other disinfection by-products although a guideline is under development for the haloacetic acids.

The formation of DBPs has been reported to be a function of precursor concentration, chlorine dose, chlorination pH, temperature, contact time and bromide ion concentration. Stevens *et al.* (1989) have discussed the formation and control of DBPs and have confirmed that the most important chemical variable in chlorination DBP formation was pH. THM formation was increased at high pH and decreased at low pH. TCAA formation was minimized at high pH and maximized at low pH whereas DCAA formation was essentially independent of the reaction pH. This implies that some measures used to decrease THM production might favour the formation of other DBPs. The occurrence of THMs, HANs, HAAs, CPK and other DBPs in drinking water has been reported for thirty-five US water treatment facilities (Krasner *et al.*, 1989) and for thirty-five Utah water treatment facilities (Nieminski *et al.*, 1993). The 1976 national survey of Canadian drinking water focused on THMs (Williams and Otson, 1978; Williams *et al.*, 1980).

The current survey on the levels of DBPs in Canadian drinking water was intended to provide data which could be used in the preparation of future Canadian Drinking Water Guidelines. A total of 17 different chlorinated DBPs were determined as well as bromide ion, total organic carbon and total organic halides.

Sample Collection and Analytical Procedures

The 53 sites investigated (Table 1) were selected in consultation with provincial officials and represented most of the large population centres in nine provinces; Prince Edward Island was not included in the survey because of the limited use of chlorine in that province. The 53 sites were selected to represent the major populated geographical areas of the country and were distributed according to population as follows: <10,000 – 2 sites, 10,000 to 100,000 – 17 sites and > 100,000 – 34 sites. A questionnaire (Appendix 1) on water treatment processes and operating practices was prepared to record the plant operating conditions at the time of sampling and to record the location of each sampling point. The treatment plants drew raw water from the main types of Canadian sources: lakes, rivers and wells. Three main disinfection treatment processes were in use in the water treatment plants included in this survey. These were chlorine-chlorine, chlorine-chloramine and ozone-chlor(am)ine.

Samples were collected in 1993 during the winter season (February-March) and the summer season (August-September) when DBP levels were expected to be lowest and highest respectively. In order to minimize variations in sampling technique, the number of persons involved in sampling was kept to a minimum. Four technologists were involved in winter sample collection and one technologist was responsible for the summer sample collection. Replicate samples were collected of raw water, treatment plant water (after final disinfection but before distribution) and treated water from a well-flushed tap at a point in the distribution system (approximately the mid-point) some 5-10 kilometres from the treatment plant. Water samples for the analysis of HAAs were collected in amber bottles containing sodium thiosulphate; those for analysis of THMs, HANs, chloropropanones, chloral hydrate and chloropicrin were collected in amber bottles containing ammonium chloride and were adjusted to pH 4.5 at the time of collection. LeBel and Williams (1995) have shown that it is critical to adjust the water samples to pH 4.5 at the time of collection to prevent or minimize the production of additional THMs during transportation and storage. Samples also were collected in prewashed bottles for the analysis of total organic carbon, total organic halogen and bromide ion. The bottles were filled just to overflow with samples, sealed with Teflon-lined caps, returned to the laboratory in a cooler by the fastest available route and stored in a cold room until analyzed (usually within 1-4 days). Complete details of the sampling protocols are given in Appendix 2.

Table 1
Sampling Locations

Province	Location	Water Source	Disinfectant
Newfoundland	St. John's(Windsor)	Lake	CL
	St. John's(Bull Pond)	Lake	CL,O
Nova Scotia	Dartmouth	Lake	CL
	Halifax	Lake	CL
	New Glasgow	Lake	CL
	Truro	Dam	CL
New Brunswick	Fredericton	Well	CL
	Moncton	River	CL
	Oromocto	River	CL
	Saint John East	Lake	CL
Québec	Drummondville	River	CL
	Gatineau	River	CL
	Granby	River	CL
	Laval	River	CL, O
	Lévis	River	CL
	Montréal	River	CL
	Pierrefonds	River	O,CA
	Québec	River	CL,O
	Repentigny	River	CL,O
	St. Jean	River	CL,O
	Trois-Rivières	River	CL
Ontario	Barrie	Well	CL
	Brantford	River	CL,CA
	Grand Bend	Lake	CL
	Guelph	Well	CL
	Kingston	Lake	CL
	Mississauga	Lake	CL,CA
	North Bay	Lake	CL
	Ottawa(Britannia)	River	CL,CA
	Ottawa(Lemieux)	River	CL,CA
	Peterborough	River	CL
	St Catharines	Lake	CL
	Sudbury	River	CL
	Toronto	Lake	CL,CA
Manitoba	Letellier	River	CL
	Portage-La-Prairie	River	CL,O
	Selkirk	River	CL
	Winnipeg	Lake	CL
	Whitemouth	River	CL
Saskatchewan	Moose Jaw	Lake	CL
	Prince Albert	River	CL
	Saskatoon	River	CL,CA
	Swift Current	Lake	CL
Alberta	Calgary	Lake	CL
	Edmonton	River	CL,CA
	Lethbridge	River	CL,CA
	Red Deer	River	CL,CA
British Columbia	Chilliwack	River	CL
	Kamloops	Well, River	CL
	Nanaimo	Lake	CL
	Penticton	Lake	CL
	Vancouver	Lake	CL
	Victoria	Lake, River	CL,CA

CL – chlorine
CA – chloramine
O – ozone

The water samples which had been adjusted to pH 4.5 in the field were extracted with methyl t-butyl ether (MTBE) and analyzed for THMs, HANs, chloropropanones, chloral hydrate and chloropicrin by gas chromatography using a Varian Vista 6000 GC equipped with an electron capture detector, an on-column injector and a J&W DB-5 capillary column. The HAA water samples were pH adjusted in the laboratory, extracted with diethyl ether and the HAAs converted to their methyl esters which were analyzed by gas chromatography-mass spectrometry (selected ion monitoring) using a Finnigan MAT 90 GC/MS fitted with a DB-1701 capillary column. Bromide ion was determined by ion chromatography, total organic carbon was determined using a SKALAR SA5 segmented flow analyzer and total organic halogen was determined using a Mitsubishi TOX-10 analyzer. Instrumental parameters and full analytical details are provided in Appendix 2 and the minimum quantifiable limits for each parameter are listed in Table 2.

For quality control purposes all samples were collected at least in duplicate and control samples were included for all groups of target analytes (usually one field blank per two sites). All DBP analytical methods incorporated surrogate internal standards and quantification was based on response factors established by multi-level calibration with fortified samples analyzed under identical conditions. Additional fortified samples were analyzed at scheduled intervals. DBPs identified by GC-ECD were confirmed by GC-MS or by GC-ECD analysis on a second GC column (DB-17). Each week during the analytical period, duplicate 30 mL groundwater samples, known to be free of HAAs, were spiked with a HAA standard mixture of known concentration, stored in a refrigerator until the following week and, along with field samples, analyzed as described above.

Results and Discussion

Raw, treatment plant and distribution system water samples were collected from fifty-three drinking water treatment facilities on two occasions (winter and summer) in 1993 and were analyzed for the DBPs listed in Table 2. The analytes listed in Table 2 were selected based on the known occurrence of halogenated DBPs in drinking water treated with chlorine disinfectants and on the possibility that they may at some time be considered for inclusion in Canadian drinking water guidelines. One site was subsequently excluded from the statistical analyses when it was determined that chlorine was added at the raw water source some 160 km from the municipality and, consequently, no representative raw or treatment plant samples were obtained. Water samples (raw, plant and system waters) were collected from the three sampling locations on the same day and hence, the raw and plant waters present similar organic profiles. However, the system water sample is older and represents water that was processed within the plant at some undetermined time prior to the sampling date. Such a water sample could have a different burden of organic material and could also have been the subject of minor variations in the water treatment process. The exact age (from treatment to sampling) of a water sample taken within the distribution system is difficult to ascertain because of the wide variety of parameters that determine the time spent within the distribution system before discharge from the tap. Certainly, the age of the system water will vary between facilities because of different treatment plant sizes, capacities and water consumption.

Thirty-seven of the fifty-two treatment facilities used disinfection coupled with alum coagulation and filtration as the main treatment processes. The other fifteen facilities used only disinfection as the main process. Pre- and/or post-chlorination (chlorine-chlorine) was used at thirty-five facilities and pre-chlorination coupled with post-chloramination (chlorine-chloramine) was used at ten facilities. Ozone coupled with chlorine or chloramine (ozone-chlor(am)ine) was used at seven facilities. Some of these facilities used significant levels of pre-chlorination during the summer to control algal growth and to prevent filter media fouling. The raw water sources were rivers (28), lakes (18), wells (3), a dam (1) and a mixture of these sources (2). Appendix 3 contains an individual data sheet for each municipality which lists the raw water source and the

general process used for water treatment. The data sheets also report the levels for the DBPs listed in Table 2 for raw, treated and distribution water samples collected in winter and summer.

Table 2
DBPs analyzed in 1993 National Survey

Compound	MQL*	
Chloroform (CHCl$_3$) [TCM]	0.2	µg/L
Bromodichloromethane (CHBrCl$_2$)[BDCM]	0.1	µg/L
Chlorodibromomethane (CHBr$_2$Cl)[CDBM]	0.1	µg/L
Bromoform (CHBr$_3$)[TBM]	0.1	µg/L
Monochloroacetic acid (CH$_2$ClCOOH) [MCAA]	0.01	µg/L
Dichloroacetic acid (CHCl$_2$COOH) [DCAA]	0.01	µg/L
Trichloroacetic acid (CCl$_3$COOH) [TCAA]	0.01	µg/L
Monobromoacetic acid (CH$_2$BrCOOH) [MBAA]	0.01	µg/L
Dibromoacetic acid (CHBr$_2$COOH) [DBAA]	0.01	µg/L
Dichloroacetonitrile (CHCl$_2$CN) [DCAN]	0.1	µg/L
Trichloroacetonitrile (CCl$_3$CN) [TCAN]	0.1	µg/L
Bromochloroacetonitrile (CHBrClCN) [BCAN]	0.1	µg/L
Dibromoacetonitrile (CHBr$_2$CN) [DBAN]	0.1	µg/L
1,1-Dichloro-2-propanone (CHCl$_2$COCH$_3$) [DCP]	0.1	µg/L
1,1,1-Trichloro-2-propanone (CCl$_3$COCH$_3$) [TCP]	0.1	µg/L
Chloral hydrate (CCl$_3$CH(OH)$_2$) [CH]	0.1	µg/L
Chloropicrin (CCl$_3$NO$_2$) [CPK]	0.1	µg/L
Bromide ion (winter)	0.01	mg/L
Bromide ion (summer)	0.002	mg/L
Total organic carbon [TOC]	0.1	mg/L
Total organic halide [TOX]	5.0	µg/L

*MQL = minimum quantifiable limit

The individual results were sent to each of the respective municipalities and provinces who participated in the study, together with relevant excerpts from the Canadian and WHO Drinking Water Guidelines, with a description of the toxic effects attributed to each of the disinfection by-products (see Appendix 4). Although the DBP data can be compared with guideline values, it should be emphasized that the present study was not designed to evaluate compliance with guideline values. As can be seen in Appendix 4, it is recommended that, for compliance purposes, TTHM be measured at least quarterly in order to obtain an annual running average. This approach is particularly appropriate for carcinogens which usually require very long exposures before an effect is seen. It is not the approach taken with non-carcinogenic effects; hence for DCAA, TCAA and CH, shorter periods of exceedance are considered significant. However, even in these cases, short-term excursions over the guideline, if only occasional, may not be a reason for concern. As is clearly stated in the TTHM guideline (Appendix 4), the solution to any problems with high concentrations of disinfection by-products is ***not to reduce disinfection since this would pose an unacceptable health risk***. The preferred approach is to reduce the organic precursors in the raw water that react with the disinfectant to produce the by-products. Fine tuning of the treatment system may also achieve a reduction in by-products without impairing disinfection.

Mean and median levels and concentration ranges for the major DBPs of each target group in summer and winter are reported in Table 3 for the three main disinfection processes for samples collected at the treatment plant just before distribution and for samples collected at the approximate mid-point of the distribution system. The target DBPs were either non-detectable or found at extremely low levels in the raw water samples. At most facilities, the dominant species found were chlorinated DBPs and, of these, TCM, DCAA and TCAA were the major components. The concentrations of the other target DBPs were usually an order of magnitude less.

TriHaloMethanes

The percentage distributions of THMs in winter and summer for treatment plant and distribution system samples are shown in Table 4. The percentage of chloroform was higher in summer than in winter for all three treatment processes and was slightly higher for chlorine-chlorine treatment compared to the other two processes. The bromine-containing THMs were relatively higher in the winter samples and for the chlorine-chloramine and ozone-chlor(am)ine treatment processes. Chloroform was the major THM detected except at three facilities where ground water sources (low TOC) were treated with minimal chlorination and, therefore, had low TTHM levels (<15 µg/L). At these three sites, chlorodibromomethane (2 sites) and bromoform (1 site) were the major THMs detected. For chlorine-chlorine treatment, mean TTHM levels (Table 3) were higher in summer than winter (e.g. 62.5 µg/L compared to 33.4 µg/L for distribution system samples) and were higher in the distribution system than at the treatment plant (e.g. 62.5 µg/L compared to 33.5 µg/L for summer samples). For chlorine-chloramine treatment, mean TTHM levels were higher in summer than winter (e.g. 32.8 µg/L compared to 13.7 µg/L for distribution system samples) but mean and median treatment plant TTHM levels were similar to those in the distribution system in both winter and summer. Those facilities which used ozone in their treatment process had mean TTHM levels which were low in winter but in the summer had mean and median levels similar to or higher than those at facilities using chlorine-chlorine treatment. A probable reason for this was that pre-chlorination was commonly used to supplement ozone disinfection during the warm water months at some facilities. This can be clearly seen (Table 5) by the significant increase in mean TOX concentrations in the summer samples compared to the winter samples for those facilities using ozone. The frequency distributions of facilities based on TTHM concentrations are illustrated in Figure 1 for the plant and distribution system samples for the three treatment processes. While the majority of treatment facilities had relatively low TTHM levels (<50 µg/L) for all three treatment processes during both winter and summer, a small number of facilities had relatively high TTHM values (>100 µg/L), particularly in the summer (except for chlorine-chloramine disinfection). This can also be seen in Table 3 where the median TTHM values are lower than the mean TTHM values except for ozone treatment.

The TTHM data from the present Canadian survey are consistent with data reported for USA facilities. A 1987 survey of 727 US facilities reported median TTHM values of 44 and 30 µg/L for the summer and winter seasons for water samples collected at the treatment plant after disinfection but before distribution (McGuire and Meadow, 1988). A 1988-89 survey of 35 US facilities also reported median values for TTHM of 44 and 30 µg/L for the summer and winter seasons for water samples collected at the treatment plant (Krasner *et al*., 1989). No breakdown of data by type of disinfectant was provided. In a 1990 survey of 35 Utah facilities which used chlorine as the only disinfectant, median (mean) summer values for TTHM of 22.4 (31.3) µg/L and 55.7 (60.0) µg/L for plant effluent and distribution system samples were reported; for a sub-set of 14 facilities, median (mean) values for TTHM of 21.6 (28.8) µg/L and 15.9 (20.9) µg/L for summer and winter plant effluent samples were reported (Nieminski *et al*., 1993).

Table 3
DBPs (µg/L) in Canadian Drinking Water - 1993

Compound	Treatment	Site	Winter			Summer		
			Mean	Median	Range	Mean	Median	Range
TTHM	Chlorine –	Plant	16.8	10.9	2.0 – 67.9	33.5	17.2	1.6 – 120.8
	Chlorine	System	33.4	21.8	2.8 – 221.1	62.5	33.8	0.3 – 342.4
	Chlorine –	Plant	12.1	10.1	0.6 – 40.3	31.2	19.7	2.9 – 80.1
	Chloramine	System	13.7	10.9	1.5 – 42.1	32.8	21.7	4.3 – 85.2
	Ozone –	Plant	6.8	5.7	1.7 – 12.3	44.0	57.4	2.5 – 74.9
	Chlor(am)ine	System	9.9	11.0	2.4 – 15.4	66.7	90.9	4.9 – 107.8
DCAA	Chlorine –	Plant	13.2	9.0	0.3 – 45.4	21.1	12.5	0.6 – 163.3
	Chlorine	System	15.6	11.8	0.2 – 63.6	19.0	10.4	0.3 – 120.1
	Chlorine –	Plant	9.8	7.7	1.2 – 23.3	12.5	10.5	5.3 – 27.6
	Chloramine	System	10.0	9.9	1.2 – 22.6	11.4	10.8	4.2 – 23.8
	Ozone –	Plant	6.9	6.4	1.6 – 15.0	21.2	22.6	5.3 – 47.6
	Chlor(am)ine	System	4.6	4.8	0.4 – 9.3	14.1	10.7	0.9 – 42.6
TCAA	Chlorine –	Plant	27.8	13.0	0.1 – 139.8	34.0	11.9	0.04 – 273.2
	Chlorine	System	56.7	24.7	0.1 – 473.1	48.9	25.1	0.1 – 263.4
	Chlorine –	Plant	13.7	6.9	0.5 – 66.2	25.1	9.3	2.1 – 85.9
	Chloramine	System	13.2	7.0	0.5 – 57.9	21.4	8.7	1.9 – 71.5
	Ozone –	Plant	5.8	1.5	0.7 – 16.9	24.6	21.6	1.3 – 66.1
	Chlor(am)ine	System	4.1	2.0	0.9 – 12.8	28.3	13.3	0.7 – 77.3
CH	Chlorine –	Plant	2.2	1.4	<0.1 – 13.8	4.3	2.9	<0.1 – 14.7
	Chlorine	System	3.8	2.5	<0.1 – 22.5	6.1	4.8	<0.1 – 18.9
	Chlorine –	Plant	1.2	0.8	<0.1 – 3.2	3.9	3.3	0.3 – 15.1
	Chloramine	System	1.2	0.8	0.2 – 3.2	3.6	2.9	0.3 – 13.6
	Ozone –	Plant	1.5	1.0	0.2 – 2.9	8.1	10.4	0.7 – 14.5
	Chlor(am)ine	System	2.2	1.9	0.2 – 5.8	8.4	5.6	0.2 – 20.1
DCAN	Chlorine –	Plant	2.1	1.0	0.1 – 12.6	2.7	1.7	<0.1 – 9.0
	Chlorine	System	2.9	1.9	0.1 – 16.3	2.9	1.9	<0.1 – 9.5
	Chlorine –	Plant	1.5	1.0	<0.1 – 7.3	2.6	1.6	0.4 – 11.2
	Chloramine	System	1.7	0.9	0.2 – 7.3	2.5	1.4	0.4 – 10.7
	Ozone –	Plant	0.8	0.6	0.2 – 1.3	2.5	3.1	0.3 – 4.1
	Chlor(am)ine	System	0.8	0.7	<0.1 – 1.6	2.2	1.7	<0.1 – 5.0
DCP	Chlorine –	Plant	1.1	0.9	<0.1 – 3.7	0.9	0.8	<0.1 – 2.6
	Chlorine	System	1.0	0.9	<0.1 – 3.3	0.8	0.6	<0.1 – 2.1
	Chlorine –	Plant	0.8	0.9	<0.1 – 1.5	1.3	1.4	0.3 – 2.4
	Chloramine	System	1.0	1.2	0.3 – 1.6	1.3	1.4	0.3 – 2.1
	Ozone –	Plant	1.5	1.2	0.9 – 2.3	1.5	1.3	0.5 – 2.9
	Chlor(am)ine	System	1.3	1.2	0.8 – 2.1	1.0	0.9	0.4 – 2.3
TCP	Chlorine –	Plant	1.7	1.4	<0.1 – 7.6	2.7	2.0	<0.1 – 9.1
	Chlorine	System	2.7	2.2	<0.1 – 10.1	2.5	1.9	<0.1 – 7.8
	Chlorine –	Plant	1.0	0.9	<0.1 – 2.6	1.7	0.6	0.1 – 6.4
	Chloramine	System	0.9	0.7	<0.1 – 2.6	1.3	0.6	<0.1 – 5.3
	Ozone –	Plant	1.3	0.9	0.2 – 3.1	4.4	4.1	0.5 – 9.2
	Chlor(am)ine	System	1.6	1.3	0.3 – 3.3	2.5	1.5	0.4 – 10.4
CPK	Chlorine –	Plant	0.2	0.1	<0.1 – 1.2	0.3	0.2	<0.1 – 2.5
	Chlorine	System	0.3	0.2	<0.1 – 1.6	0.3	0.2	<0.1 – 1.2
	Chlorine –	Plant	0.2	0.2	<0.1 – 0.9	0.2	0.2	<0.1 – 0.9
	Chloramine	System	0.2	0.2	<0.1 – 0.9	0.3	0.3	<0.1 – 0.9
	Ozone –	Plant	0.2	0.1	<0.1 – 0.3	1.2	1.5	<0.1 – 2.2
	Chlor(am)ine	System	0.3	0.3	<0.1 – 0.6	1.3	1.1	<0.1 – 2.3

Figure 1. Distribution of facilities based on TTHM levels

Chlorine/Chlorine (N = 35)
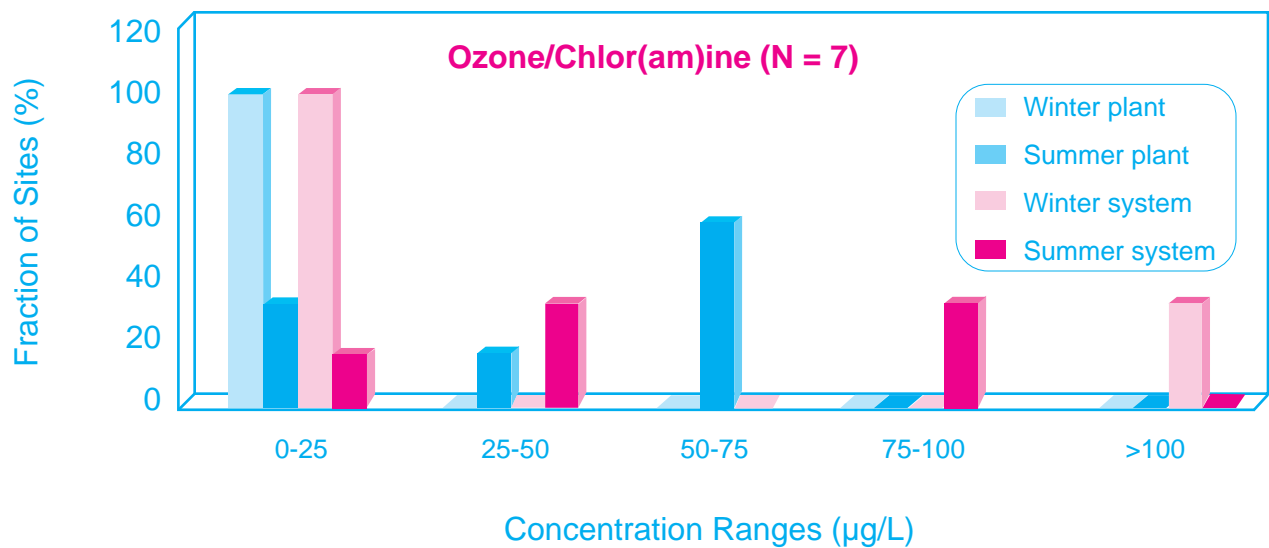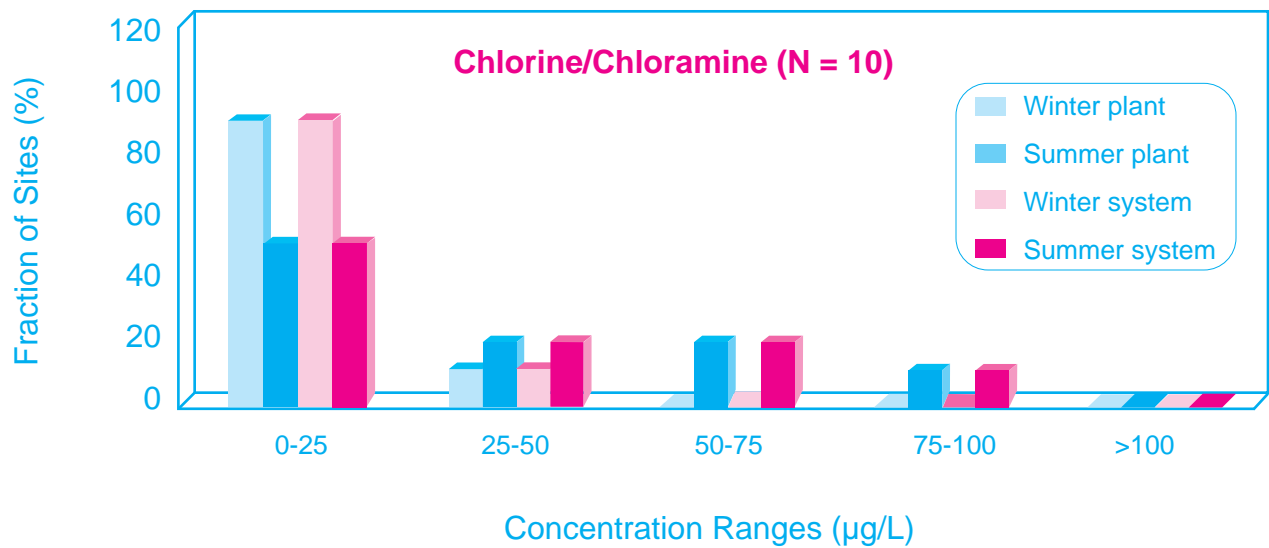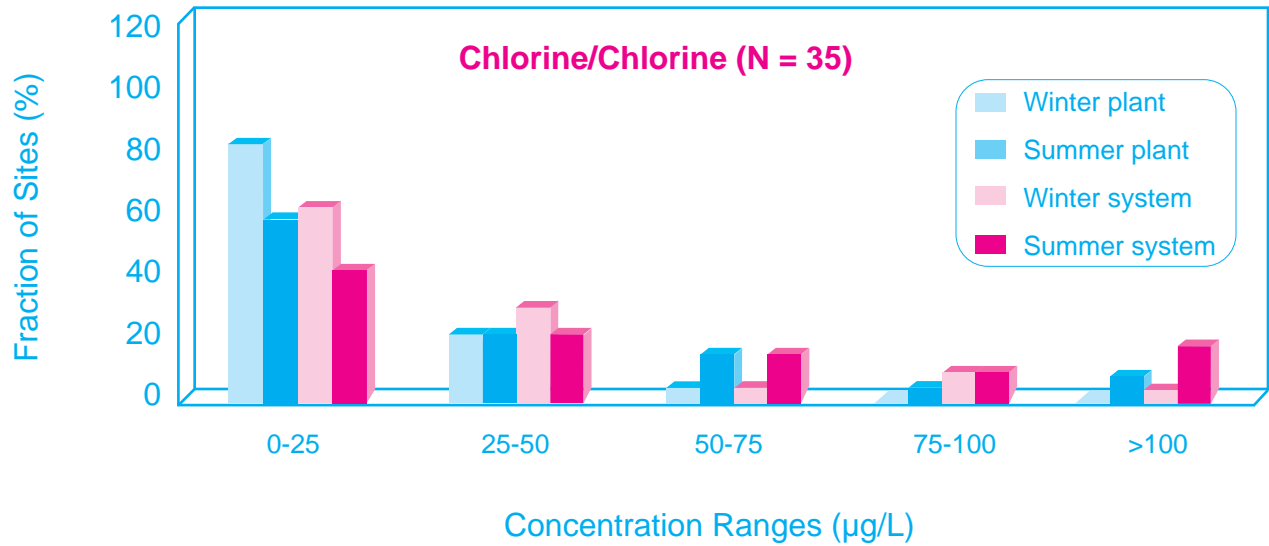
Table 4
% THM Distribution in Drinking Water

	Treatment	Site	Winter %	Summer %
TCM	Chlorine - Chlorine	Plant	82.3	88.3
		System	88.3	91.4
	Chlorine - Chloramine	Plant	77.2	86.2
		System	77.9	86.8
	Ozone - Chlor(am)ine	Plant	78.6	85.2
		System	75.5	86.7
BDCM	Chlorine - Chlorine	Plant	13.1	9.1
		System	9.4	7.1
	Chlorine - Chloramine	Plant	16.9	10.6
		System	16.5	10.3
	Ozone - Chlor(am)ine	Plant	15.5	11.0
		System	17.1	9.9
CDBM	Chlorine - Chlorine	Plant	3.8	2.3
		System	1.9	1.2
	Chlorine - Chloramine	Plant	4.7	2.4
		System	4.5	2.3
	Ozone - Chlor(am)ine	Plant	5.0	3.2
		System	5.7	3.1
TBM	Chlorine - Chlorine	Plant	0.8	0.4
		System	0.4	0.2
	Chlorine - Chloramine	Plant	1.2	0.6
		System	1.2	0.6
	Ozone - Chlor(am)ine	Plant	0.9	0.3
		System	1.6	0.3

Table 5
TOX [µg Cl⁻/L] in Drinking Water

Treatement	Site	Mean	Winter Median	Range
Chlorine – Chlorine	Plant	95.0	81.5	6-396
	System	126.1	96.5	11-572
Chlorine – Chloramine	Plant	68.6	55.0	8-279
	System	71.7	51.0	7-286
Ozone – Chlor(am)ine	Plant	69.7	90.0	15-114
	System	55.6	56.0	20- 85

| Treatement	Site	Mean	Summer Median	Range
Chlorine – Chlorine	Plant	103.5	66.0	8-473
	System	141.3	106.0	<5-609
Chlorine – Chloramine	Plant	109.0	79.0	27-283
	System	92.2	71.0	20-218
Ozone – Chlor(am)ine	Plant	130.0	156.0	23-225
	System	124.0	87.0	17-229

HaloAcetic Acids

For all treatment processes, mean DCAA levels changed very little within the distribution system for either winter or summer samples (Table 3). For both chlorine-chlorine and chlorine-chloramine treatment, mean DCAA levels were only slightly higher in summer samples compared to winter samples. Those facilities which used ozone in their treatment process had mean DCAA levels which were low in winter (e.g. 4.6 µg/L, distribution system) but in the summer (e.g. 14.1 µg/L, distribution system) were similar to those for the other treatment processes. The frequency distributions of facilities based on DCAA concentration ranges are illustrated in Figure 2 for the plant and distribution system samples from the three treatment processes. While the majority of treatment facilities had relatively low DCAA levels (<50 µg/L) during winter and summer, there were a small number of facilities using chlorine-chlorine treatment which had relatively high DCAA values (>50 µg/L) in both summer and winter.

At facilities with chlorine-chlorine treatment, mean TCAA levels increased from the plant to the mid-point of the distribution system (from 27.8 to 56.7 µg/L and from 34.0 to 48.9 µg/L for winter and summer samples respectively) but the mean TCAA levels in winter (56.7 µg/L) and summer (48.9 µg/L) distribution system samples were similar (Table 3). For chlorine-chloramine treatment, mean TCAA levels were higher in summer than winter (e.g. 21.4 µg/L compared to 13.2 µg/L for distribution system samples) but did not appear to increase within the distribution system in either winter or summer. Those facilities which used ozone in their treatment process had mean TCAA levels which were low in winter (e.g. 4.1 µg/L, distribution system) but in the summer (e.g. 28.3 µg/L, distribution system) were similar to those at facilities using chlorine-chloramine treatment. The frequency distributions of facilities based on TCAA concentration ranges for the plant and distribution system samples are illustrated in Figure 3 for the three treatment processes. While the majority of treatment facilities had relatively low TCAA levels (<50 µg/L) during winter and summer, a few facilities had relatively high TCAA values (>100 µg/L) in both summer and winter for chlorine-chlorine disinfection. This can also be seen in Table 3 where the median TCAA values are lower than the mean TCAA values.

The other target HAAs – monochloroacetic acid (100% occurrence, range 0.3 to 9.7 µg/L), monobromoacetic acid (31% occurrence, range <0.01 to 9.2 µg/L) and dibromoacetic acid (62% occurrence, range <0.01 to 1.9 µg/L) – were present at lower levels than the DCAA and TCAA (Table 3). Tribromoacetic acid is unstable in aqueous solution and consequently was not amenable to analysis; the mixed (Cl-Br) haloacetic acid standards were not available and, therefore, quantitative values are not presented here.

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Figure 2. Distribution of facilities based on DCAA levels
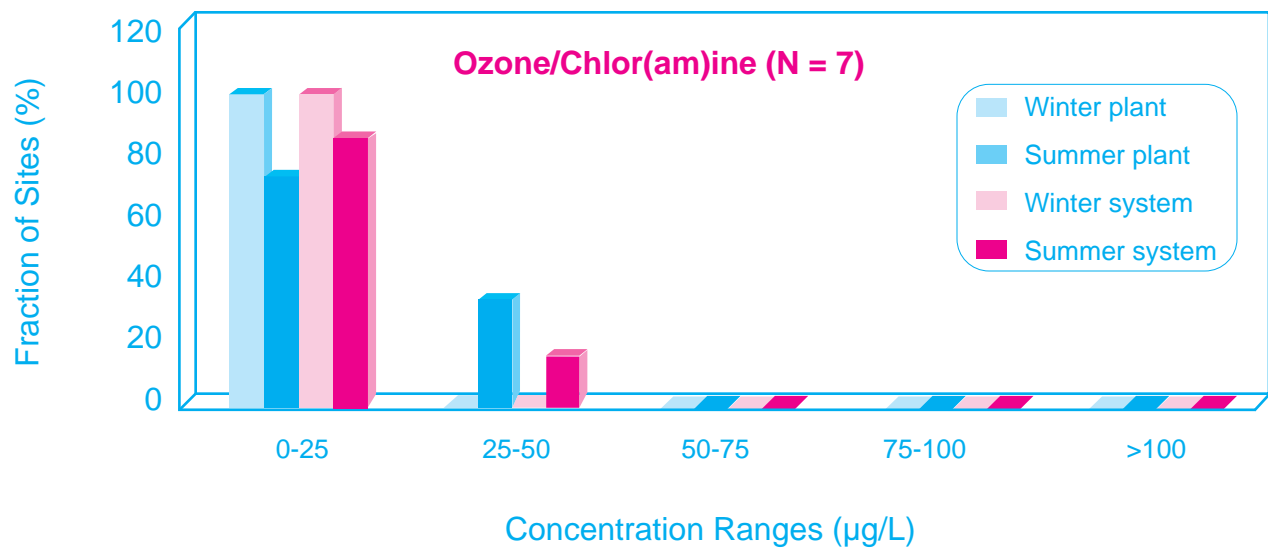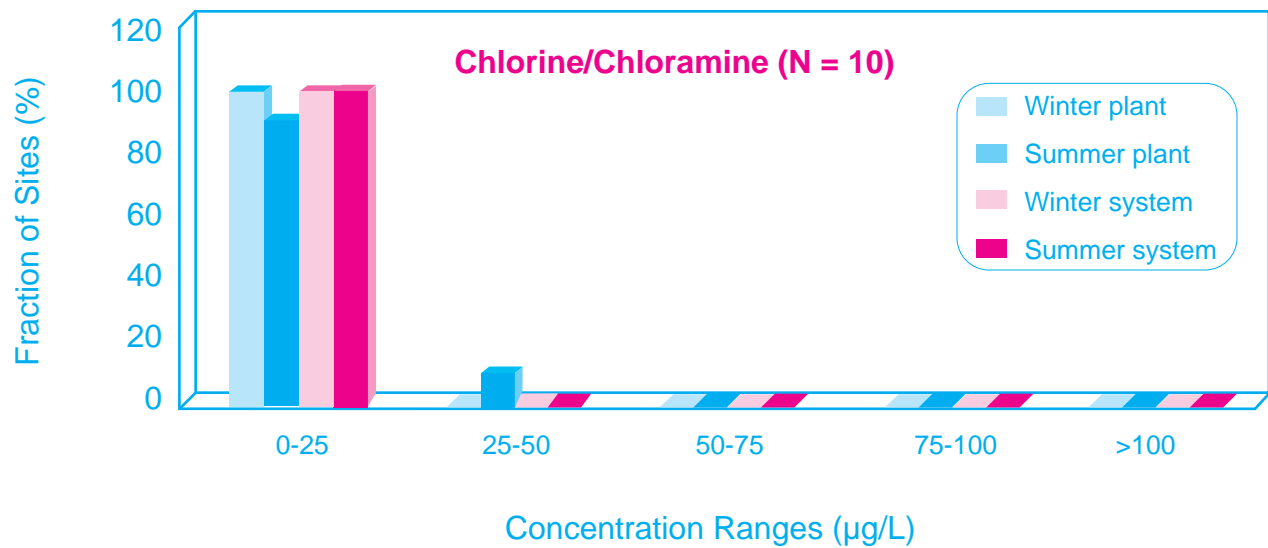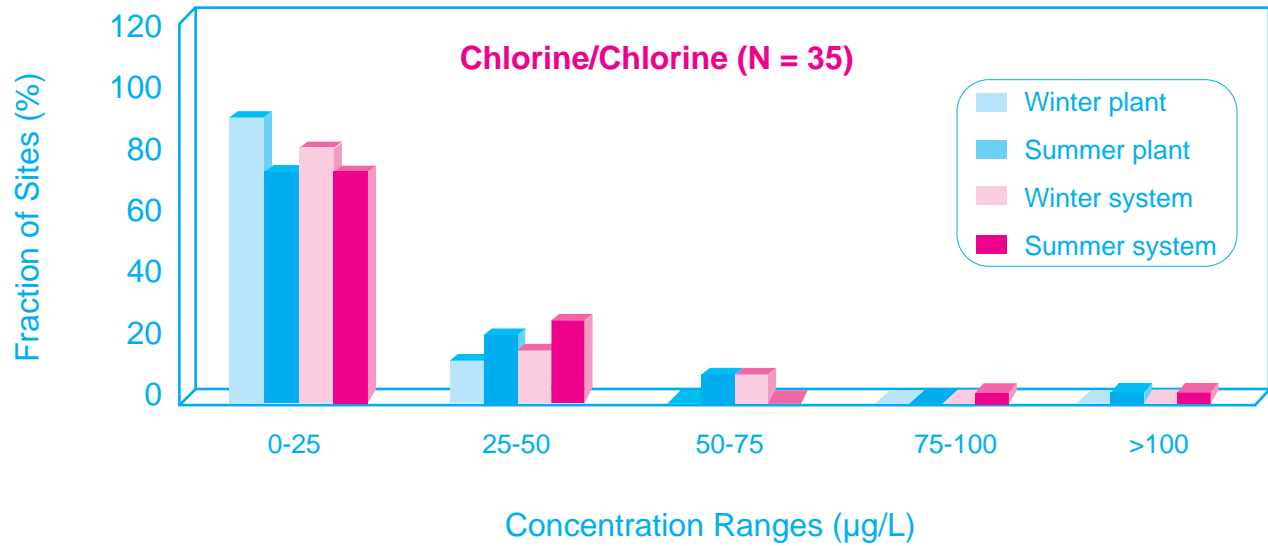
Figure 3. Distribution of facilities based on TCAA levels
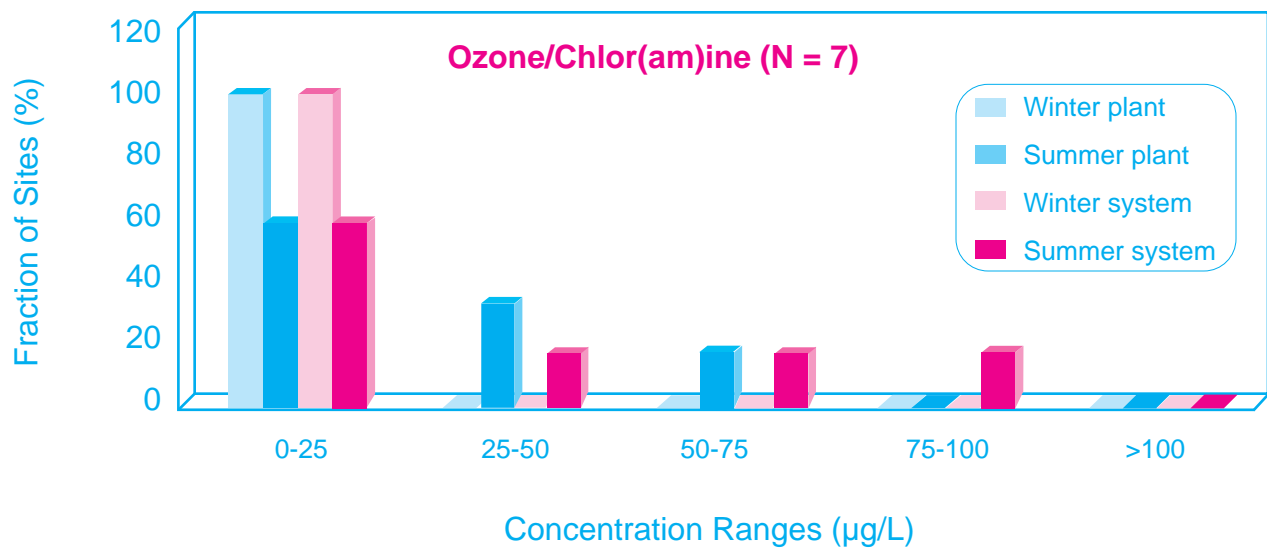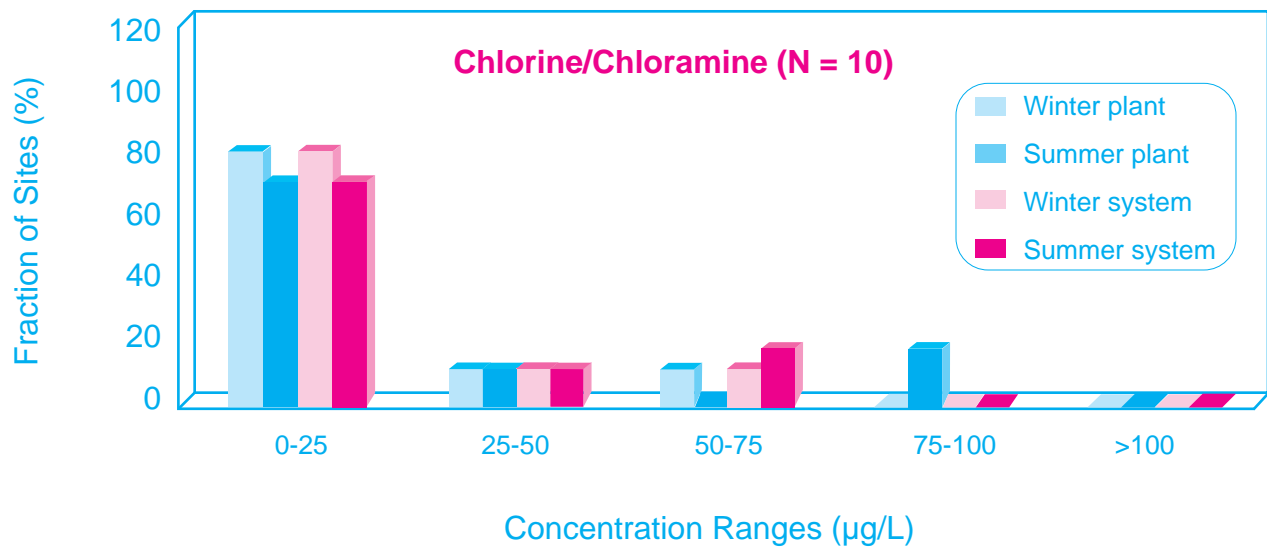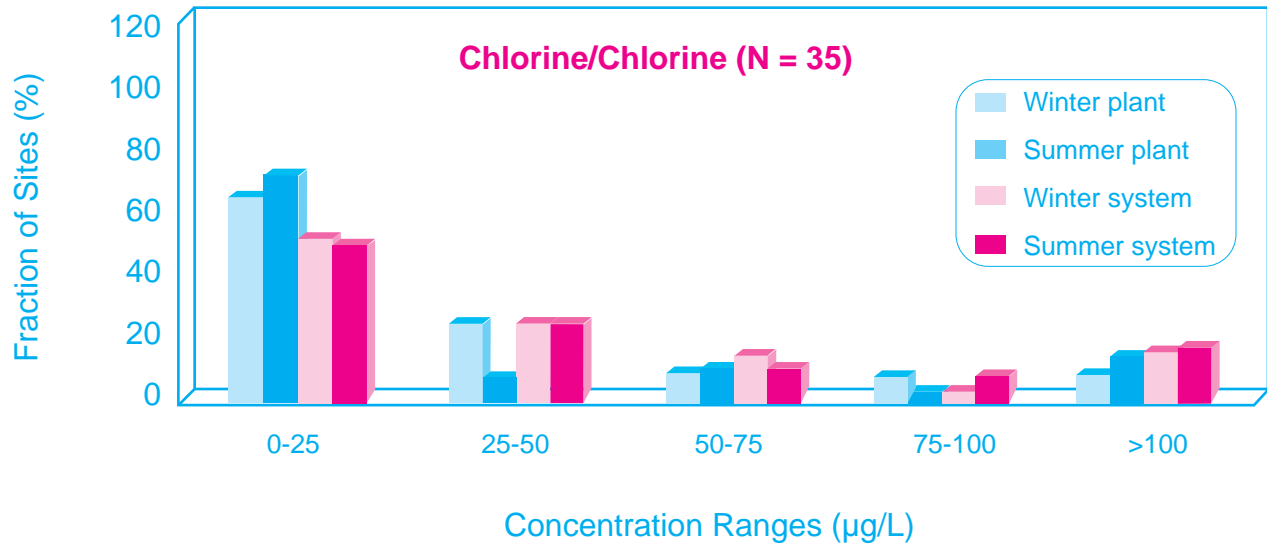
A 1988-89 survey (Krasner *et al*., 1989) of 35 US facilities gave median values for total haloacetic acids (THAA) of 20 and 13 µg/L for the summer and winter seasons for water samples collected at the treatment plant. No breakdown of data by type of disinfectant was provided. In a 1990 survey (Nieminski *et al*., 1993) of 35 Utah facilities which used chlorine as the only disinfectant, median (mean) summer values for THAA of 13.2 (17.3) µg/L and 20.9 (29.6) µg/L for plant effluent and distribution system samples were reported. For a subset of 14 Utah facilities, median (mean) values for THAA of 11.4 (12.6) µg/L and 14.4 (11.9) µg/L for summer and winter plant effluent samples were reported.

Other Disinfection By-Products

Although the concentration of the other target DBPs were usually an order of magnitude lower, they were detected in most treated water samples and also exhibited spatial, seasonal and treatment types variations similar to those of the major DBPs. After the THMs and HAAs, CH (94% occurrence) was the most prominent DBP with concentrations ranging up to 22.5 µg/L for the winter samples and up to 20.1 µg/L for the summer samples. The frequency distributions of facilities based on CH concentration ranges for the plant and distribution system samples are illustrated in Figure 4 for the three treatment processes. In general, for all treatment types, the mean CH concentration (Table 3) was higher in the summer samples compared to the winter samples. Compared to TTHM the overall mean CH concentrations were 14% (plant) and 11% (distribution) of the overall mean TTHM concentration in both winter and summer samples. Based on treatment types, a significant variation was observed with ozone disinfection where the mean CH concentrations were 22% (plant) and 23% (distribution) of the mean TTHM concentration for the winter samples. For the summer samples, the mean CH concentrations were 18% (plant) and 13% (distribution) of the mean TTHM concentration, probably due to the added pre-chlorination used during the summer months.
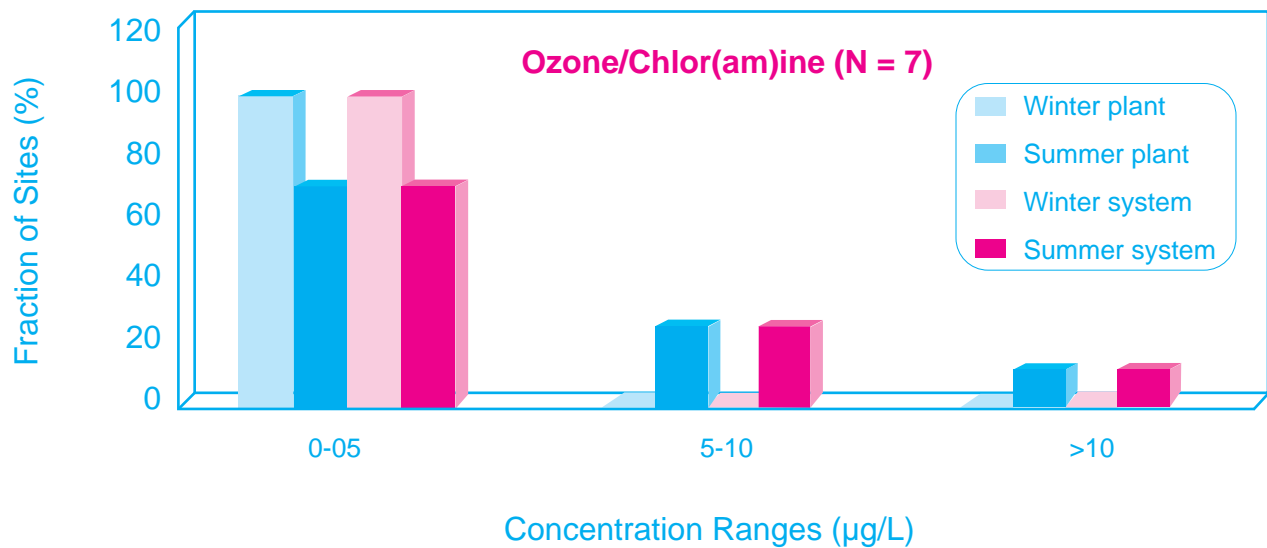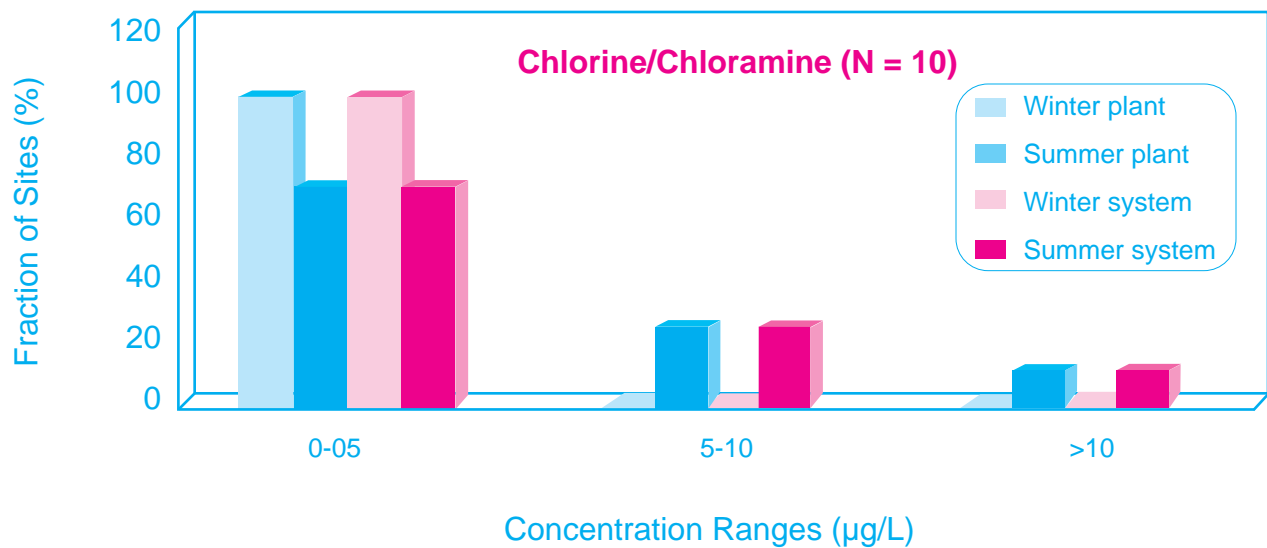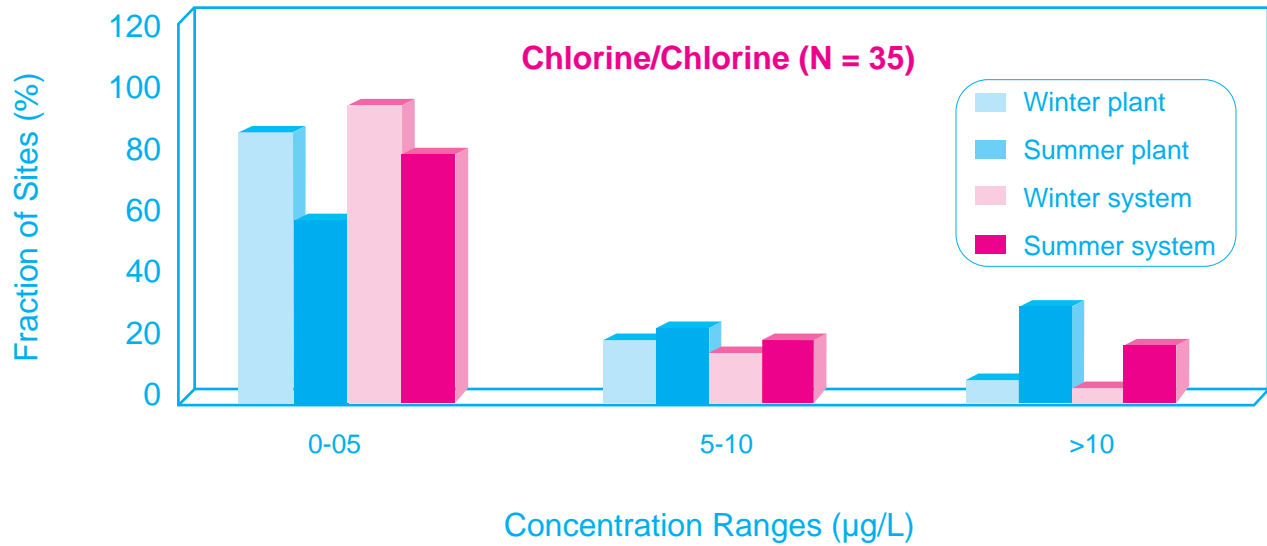
The other target DBPs had mean concentrations less than 5 µg/L and occurred with the following frequencies – DCAN 97%, TCAN 9 %, BCAN 92%, DBAN 57%, DCP 93%, TCP 91%, CPK 73%. Very little spatial variation was seen for DCAN, TCP, DCP and CPK with the chlorine-chloramine treatment. For the chlorine-chlorine treatment for both seasons DCAN concentrations increased in the distribution system whereas DCP and CPK remained relatively unchanged. TCP increased only for the winter samples and was relatively unchanged in the summer samples. For the ozone treatment, mean concentrations of DCAN, DCP and TCP in distribution water compared to treated water were similar in winter but decreased in summer; the CPK mean concentration did not exhibit marked spatial variation but was considerably higher for the summer samples than for the winter samples (e.g. 1.2 µg/L compared to 0.3 µg/L). These data for CH, HAN, DCP, TCP and CPK are consistent with those reported in other surveys (Uden and Miller 1983; Krasner *et al*., 1989; IARC 1991; Nieminski *et al*.,1993).

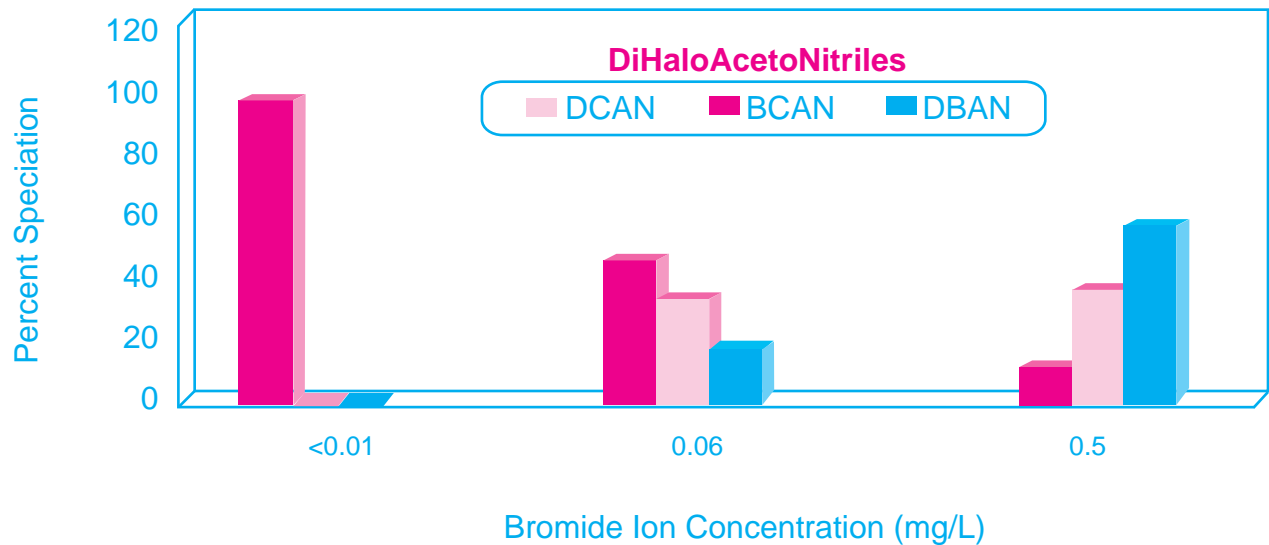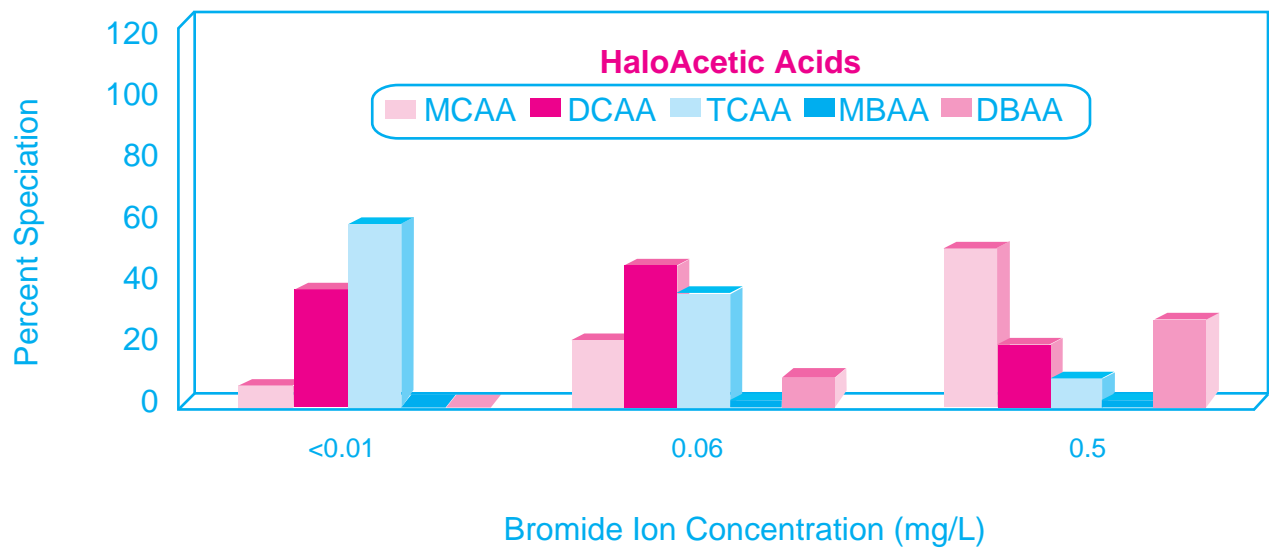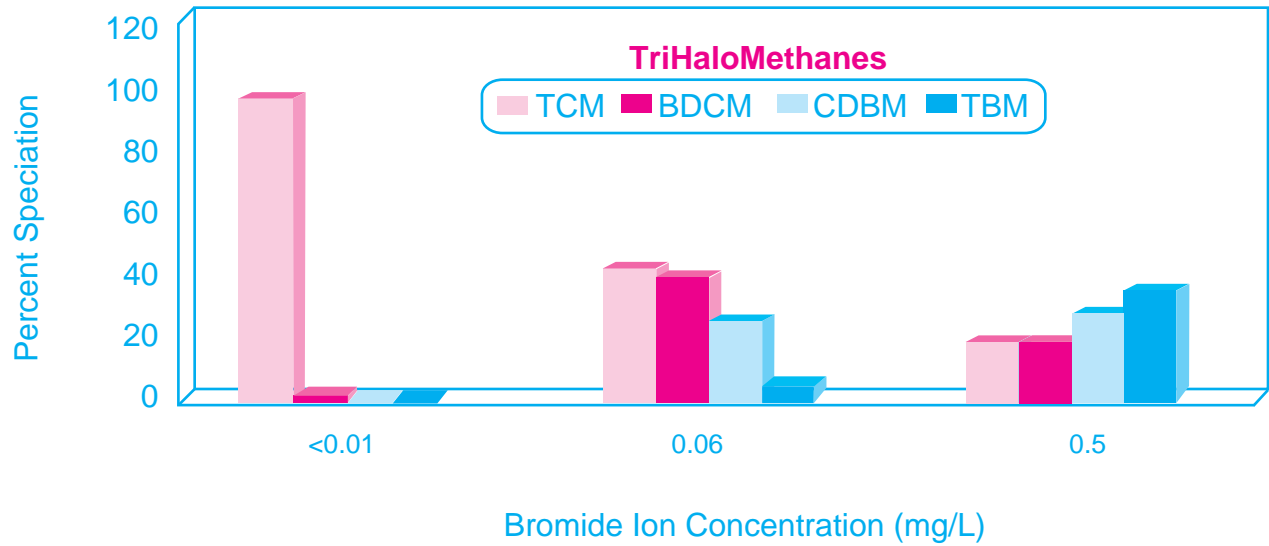## Correlation of DBPs with Other Parameters

The effect of bromide ion on DBP formation has been shown to be dependent on the bromide ion concentration, the chlorine dose and residual, the pH and the concentration and nature of the organic precursors (Pourmoghaddas *et al*., 1993; Summers *et al*., 1993; Symons *et al*., 1993). The percentage of brominated and mixed halogenated DBPs increases both as the molar ratio of bromide ion to chlorine increases and as the TOC concentration decreases. Some countries have reported that brominated DBPs are significant components of their drinking waters (Peters *et al*., 1991; Fayad 1993). In this study only four sites in winter and eight sites in summer had raw water bromide ion levels >0.01 mg/L (maximum 0.5 mg/L) and at these sites the relative percentage of brominated and mixed halogenated DBPs increased. The changes in speciation for THMs, HAAs and HANs in winter, treatment plant samples are shown in Table 6, expressed as µg/L concentrations, and in Figure 5, expressed as % speciation, for three sites with very low (Site A, <0.01 mg/L), low (Site B, 0.06 mg/L) and moderate (Site C, 0.5 mg/L) bromide ion concentrations. As the bromide ion concentration increases the relative percentage of brominated and mixed halogenated DBPs increases for all three groups. This is consistent with data reported in laboratory and field studies (Krasner *et al*., 1989; Fayad 1993; Pourmoghaddas *et al*., 1993; Summers *et al*., 1993).

A comparison of total DBP as a function of raw water source for chlorine-chlorine treated waters suggested that the DBP burden was least with groundwater, higher with lake water and highest with river water in both summer and winter periods. This trend may be a reflection of the TOC content of the various water sources, however, only weak correlations (r^2=0.2-0.4) were found between TOC and DBP burden. Correlations of individual DBP levels with TOX were weak but the correlation of total DBP (µmoles/L) with TOX (µg/L) was significantly stronger (r^2=0.71-0.87) for all chlorine-chlorine treated water samples. No significant correlations were observed between DBP levels and any other parameters. Because of the wide variety of parameters and the treatment variations at each facility, the database obtained in the present study was not large enough and was too heterogeneous to permit meaningful multivariate analysis.

Figure 4. Distribution of facilities based on CH levels

Chlorine/Chlorine (N = 35)

Legend: Winter plant, Summer plant, Winter system, Summer system

Y-axis: Fraction of Sites (%)
X-axis: Concentration Ranges (µg/L) — 0-05, 5-10, >10

Chlorine/Chloramine (N = 10)

Legend: Winter plant, Summer plant, Winter system, Summer system

Y-axis: Fraction of Sites (%)
X-axis: Concentration Ranges (µg/L) — 0-05, 5-10, >10

Ozone/Chlor(am)ine (N = 7)

Legend: Winter plant, Summer plant, Winter system, Summer system

Y-axis: Fraction of Sites (%)
X-axis: Concentration Ranges (µg/L) — 0-05, 5-10, >10

Figure 5. DBP% Speciation in presence of bromide ion

Table 6
DBP Speciation in Drinking Water

Compound	Site A	Site B	Site C
TOC (mg/L)	1.3	0.9	1.2
Br⁻ (mg/L)	<0.01	0.06	0.5
THM (µg/L)			
TCM	15.4	3.1	0.5
BDCM	0.5	3.9	0.7
CDBM	<0.1	2.9	1.5
TBM	<0.1	0.8	3.3
HAA (µg/L)			
AMCA	2.1	1.2	0.6
ADCA	20.6	3.8	0.3
ATCA	43.4	3.8	0.1
AMBA	0.1	0.1	<0.01
ADBA	<0.01	0.9	0.8
HAN (µg/L)			
TCAN	<0.1	<0.1	<0.1
DCAN	0.9	0.9	0.1
BCAN	<0.1	0.9	0.6
DBAN	<0.1	0.6	1.2

Conclusions

TTHMs and HAAs were the major DBPs found in all facilities for all treatment processes and HAA levels often equalled or exceeded TTHM concentrations. Mean and median TTHM levels were higher in the summer than the winter for all three treatment processes and increased in the distribution system except for chlorine-chloramine treatment.

Mean and median TCAA levels for chlorine-chlorine disinfection increased in the distribution system but winter and summer levels were similar. Mean and median TCAA levels for chlorine-chloramine and ozone-chlor(am)ine treatment and mean and median DCAA levels for all processes were slightly higher in summer compared to winter but levels were not higher in the distribution system. Further studies are required to delineate more clearly the spatial and temporal variations in DBP levels in drinking water at specific facilities. To obtain an accurate estimation of human exposure to DBPs from drinking water, it would appear that samples should be collected at the consumer tap and not at the treatment plant. Further studies are in progress to define the most appropriate sampling strategy.

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