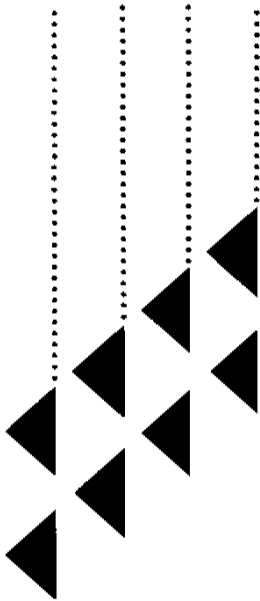




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# **A One-Year Survey of Halogenated Disinfection By-Products in the Distribution System of Treatment Plants Using Three Different Disinfection Processes**



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# Summary

This study examined disinfection by-product (DBP) concentrations in drinking water as a function of treatment practice, season and location in the distribution system for each of three water treatment plants that applied different treatment processes (chlorine-chloramine, chlorine-chlorine, ozone-chlorine). On a monthly basis, over a 13 month period, DBP concentrations were measured in raw water samples and in treated water samples collected at four locations in the distribution system for each treatment plant. The major DBPs observed were chloroform (TCM), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). The concentrations of other DBPs (chloral hydrate, haloacetonitriles, halo-propanones, chloropicrin) were usually an order of magnitude lower. The overall picture that emerged was that no single sampling event captured the complete image of the behaviour of DBPs in the distribution system. DBP concentrations were observed to fluctuate as a function of water treatment practice (and variations therein), age of the water and temperature of the water. DBP concentrations were usually higher in the summer than in the winter for all treatment processes. With chlorine-chloramine treatment DBP concentrations did not, in general, increase significantly with distance (time) in the distribution system. With chlorine-chlorine treatment THM concentrations increased with distance (time) in the distribution system and maximum values were found at the sampling point furthest from the treatment plant. The behaviour of the other DBPs was more complex. Their concentrations showed an increase in the first part of the distribution system but depending on the season and age of the water the DBP concentrations could either increase or decrease at greater distances (time) in the distribution system. Of particular importance from a regulatory viewpoint was that no single site or time of year could be selected to provide simultaneous maximum values for the three major DBPs (TCM, DCAA and TCAA). The development of a sound sampling strategy to assess consumer exposure to DBPs will require more in depth studies to provide a greater understanding of the DBP behaviour within distribution systems.

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# 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 recognised 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 the 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 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 Quality (Federal-Provincial Subcommittee, 1996). No Canadian guidelines exist for other disinfection by-products although a guideline is under development for the haloacetic acids. Summary information on these Canadian and WHO guidelines are given in Appendix 1.

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. Therefore, 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 35 US water treatment facilities (Krasner *et al.*, 1989) and for 35 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). In a 1993 survey of DBPs in drinking water from 53 Canadian treatment facilities, trihalomethanes (THMs) and haloacetic acids (HAAs) were the major DBPs detected and they were found in all chlorinated drinking water supplies examined (Williams *et al.*, 1995a). HANs, halopropanones (HPs), CH and CPK were often detected in treated water samples but at lower concentrations. The DBP levels were observed to vary with season (summer and

winter), water treatment practices (chlorination, chloramination and ozonation), and distance of the sampling point from the treatment plant.

There have been many studies related to THMs in drinking water and a number of these studies have investigated the temporal and spatial variation in THM concentrations. The general conclusions of these studies have been that THM levels tended to be higher in the summer than in the winter and that THM levels increased within the distribution system (Arguello *et al.*, 1979; Brett and Calverley, 1979; Smith *et al.*, 1980; Otson *et al.*, 1981; Singer *et al.*, 1979). More recent studies (Krasner *et al.*, 1989; Nieminski *et al.*, 1993; Singer *et al.*, 1995) have extended these investigations to other DBPs and have shown that levels of DCAA and TCAA were of the same magnitude as the THMs. Some evidence has been presented that the HAAs have different spatial and temporal variation compared with the THMs. The present study was designed to examine in greater detail the effect of water treatment, season and location of sample collection on the levels of a range of DBPs. On a monthly basis for 13 months, DBP concentrations were determined in water samples collected at five locations for each of three water treatment plants that apply different treatment processes. Some interim results have been reported previously (Benoit *et al.*, 1995; LeBel *et al.*, 1995a). The final results of this survey are presented in this report.

# Sample Collection and Analytical Procedures

Each month from December 1993 to December 1994, during a single day for each plant, replicate water samples were collected at three water treatment plants (Ottawa, Hull and Buckingham). Samples obtained were raw water (R), treatment plant water (T; after final disinfection but before distribution) and treated water from well-flushed taps at three locations along a distribution system main line, representing near-plant (D1; *ca* 3 km), mid-system (D2; *ca* 10 km) and end-of-line (D3; *ca* 18 km) sampling locations. Samples were also collected (R, T and D3) for the analyses of total organic carbon (TOC), total organic halides (TOX) and pH. Water samples were collected once in December 1994 for the determination of bromide ion, Kjeldahl nitrogen, colour, turbidity, hardness and alkalinity.

The analytical methods used for DBP analyses, which have been reported previously (Williams *et al.*, 1995a; Benoit *et al.*, 1995; LeBel *et al.*, 1995b), are given in detail in Appendix 2 and described briefly below. Water samples for the analysis of HAAs were collected in amber vials containing sodium thio-sulfate; those for the analysis of other DBPs were collected in amber bottles containing ammonium chloride and to ensure DBP stability were adjusted to pH 4.5 at the time of collection. Samples were capped with teflon-lined seals, returned to the laboratory in a cooler and stored in a cold room until analyzed (usually within 1-2 days). The water samples which had been adjusted to pH 4.5 in the field were extracted with methyl t-butyl ether (MTBE), containing dibromomethane and 1,2-dibromopropane as internal standards, and analyzed for THMs, HANs, HPs, CH and CPK using a Varian Vista 6000 gas chromatograph equipped with an electron capture detector (GC-ECD), an on-column injector and a J&W DB-5 capillary column. The HAAs 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, TOC was determined using a SKALAR SK12 total organic analyzer and TOX was determined using a Mitsubishi TOX-10 analyzer.

For quality control purposes, all samples were collected at least in duplicate, control samples were included for all groups of target analytes and additional fortified samples were analyzed at scheduled intervals. The identification of DBPs analyzed by GC-ECD was confirmed by GC-MS or by GC-ECD analysis using a second GC column (DB-17). The DBPs analysed in this survey are listed in Table 1 together with their minimum quantifiable limit. Tribromoacetic acid was not analysed due to its instability in water and HAAs containing both chlorine and bromine were not analysed due to a lack of reference standards.

**Table 1. DBPs Analysed in 1994 Monthly Survey**

Compound	MQL*
Chloroform (CHCl <sub>3</sub> ) [TCM]	0.2 µg/L
Bromodichloromethane (CHBrCl <sub>2</sub> ) [BDCM]	0.1 µg/L
Chlorodibromomethane (CHBr <sub>2</sub> Cl) [CDBM]	0.1 µg/L
Bromoform (CHBr <sub>3</sub> ) [TBM]	0.1 µg/L
Monochloroacetic acid (CH <sub>2</sub> ClCOOH) [MCAA]	0.01 µg/L
Dichloroacetic acid (CHCl <sub>2</sub> COOH) [DCAA]	0.01 µg/L
Trichloroacetic acid (CCl <sub>3</sub> COOH) [TCAA]	0.01 µg/L
Monobromoacetic acid (CH <sub>2</sub> BrCOOH) [MBAA]	0.01 µg/L
Dibromoacetic acid (CHBr <sub>2</sub> COOH) [DBAA]	0.01 µg/L
Dichloroacetonitrile (CHCl <sub>2</sub> CN) [DCAN]	0.1 µg/L
Trichloroacetonitrile (CCl <sub>3</sub> CN) [TCAN]	0.1 µg/L
Bromochloroacetonitrile (CHBrClCN) [BCAN]	0.1 µg/L
Dibromoacetonitrile (CHBr <sub>2</sub> CN) [DBAN]	0.1 µg/L
1,1-Dichloro-2-propanone (CHCl <sub>2</sub> COCH <sub>3</sub> ) [DCP]	0.1 µg/L
1,1,1-Trichloro-2-propanone (CCl <sub>3</sub> COCH <sub>3</sub> ) [TCP]	0.1 µg/L
Chloral hydrate (CCl <sub>3</sub> CH(OH) <sub>2</sub> ) [CH]	0.1 µg/L
Chloropicrin (CCl <sub>3</sub> NO <sub>2</sub> ) [CPK]	0.1 µg/L
Bromide ion	0.002 mg/L
Total organic carbon [TOC]	0.1 mg/L
Total organic halide [TOX]	5.0 µg/L

\*MQL = minimum quantifiable limit



## Results and Discussion

Three potable water treatment plants that utilize one of the three main treatment processes (chlorine-chloramine, chlorine-chlorine, ozone-chlorine) used in Canada were selected for this study. Table 2 shows general information and the type of treatment processes used at each facility: Ottawa – prechlorination, flocculation, sedimentation, multimedia filtration, pH correction (lime), fluoridation and chloramination; Hull – mechanical screening, flocculation, sedimentation, chlorination, sand filtration, pH correction (lime), post chlorination; Buckingham – mechanical screening, flocculation, sedimentation, chlorination (summer months), sand filtration, ozonation, pH correction (lime) and post chlorination. The three plants serve a different size of population and consequently have different production outputs.

**Table 2. General information for the three water treatment facilities**

	Ottawa	Hull	Buckingham
Treatment type	Chlorine-Chloramine	Chlorine-Chlorine	Ozone-Chlorine*
Water source	Ottawa River	Ottawa River	La Lièvre River
Production	ca 160 ML/day	ca 84 ML/day	ca 19 ML/day
Population served	300,000 +	100,000 +	15,000 +

\* Chlorine-Ozone-Chlorine in the summer.

Table 3 shows general water quality and auxiliary parameters for raw and treated water samples taken at the plant for each facility. TOC, pH and TOX (treated water only) were determined monthly. All three plants are located within 35 km of each other and draw their raw water from rivers. The Ottawa and Hull plants which draw water from the same source (Ottawa River) exhibited very similar pH and TOC raw water values. The Buckingham plant which draws water from a different river (La Lièvre) exhibited slightly different pH and

TOC raw water values. However, the differences were small and to a first approximation it could be concluded that the quality of the raw water at the three plants was similar. The bromide ion concentrations at all three plants were low ( $\leq 0.005$  mg/L) and, consequently, brominated DBPs were not expected to be observed at significant levels. The treated water TOX values for Ottawa and Hull were also similar to one another with the TOX values for Buckingham being slightly lower.

Figure 1 shows the raw water temperatures for the three plants from December 1993 to December 1994. The Ottawa and Hull plants, located *ca* 6 km apart on the same river, have essentially the same raw water temperature profile. The Buckingham plant has a raw water temperature profile which is very similar to the other two plants.

DBPs were either non-detectable or found at extremely low levels in the raw water samples for each plant. The yearly mean for each sampling point (T, D1, D2, D3), the overall mean (All) and the minimum (Min) and maximum (Max) values for the target analytes, which were selected based on the known occurrence of halogenated DBPs in drinking water treated with chlorine disinfectants, are presented in Tables 4, 5 and 6. Detailed monthly results for each treatment plant, for all parameters analyzed, are reported in Appendix 3. At each plant the chlorinated species were more abundant than the brominated species which in many instances were below the detection limit of the analytical method. After disinfection the dominant species found for each treatment process were TCM, DCAA and TCAA. Low levels of CH were found for Ottawa and Hull but significantly higher levels of CH were found in water samples from Buckingham which used ozone-chlorine treatment. Concentrations of the other target analytes were usually an order of magnitude less than the TCM, DCAA and TCAA levels. Monthly data provide a greater insight into short term variations; however, seasonal (quarterly) averages capture prominent variations in analyte concentration and provide a simpler and clearer display of the results. This is illustrated in Figures 2e and 2f where the data for TCM at Buckingham is presented in monthly format and as seasonal averages (January-March, April-June, July-September, October-December) of the monthly data. The trend for TCM levels to be lower in

the cold water months and higher in the warm water months was evident in both the monthly and seasonal formats. In addition, the trend for TCM levels to increase with increasing distance from the treatment plant was also evident in both formats but was easier to visualize in the seasonal format. However, the slight increase in TCM in February that was evident in the monthly format (Figure 2e) cannot be observed in the seasonal format (Figure 2f). The increase in DBP levels in February was attributed to the substitution of chlorine instead of ozone because of a malfunction of the ozone generator (personal communication). The data are presented in both formats in Figures 2 to 10 in order to provide maximum information.

**THMs.** TCM was the main THM detected and represented >90% of the TTHM concentration in each of the three systems (Tables 4, 5 and 6). Figure 2 illustrates the seasonal and monthly TCM variation for the three treatment processes which all show a typical pattern of lower TCM concentrations in the cold water months (raw water temperatures < 5°C from December to April) and higher TCM concentrations during the warm water months (raw water temperatures 15-23°C from June to September). For chlorine-chloramine treatment (Ottawa; Table 4 and Figures 2a and 2b) TCM concentrations were relatively constant within the distribution system and increased only slightly after leaving the treatment plant. For chlorine-chlorine treatment (Hull; Table 5 and Figures 2c and 2d), the most common treatment type in the 1993 national DBP survey (Williams *et al.*, 1995a), the spatial variation was considerably more pronounced. TCM concentrations increased significantly within the distribution system with maximum TCM levels at the end-of-line (D3) sample location at levels which were often 2 to 3 times those obtained at the treatment plant (T). For ozone-chlorine treatment (Buckingham; Table 6 and Figures 2e and 2f) TCM levels during the cold water months were generally lower than those observed for the two other treatment plants. However, at Buckingham the treatment process (ozone-chlorine) was modified by the introduction of a prechlorination

step during the warmer months (June 17 to October 20) in order to control algae growth (personal communication). The TCM levels during this period were similar to those observed with chlorine-chlorine treatment. The spatial variation is more pronounced, with maximum TCM levels occurring at the end-of-line location (D3) at levels 2 to 10 times those obtained at the treatment plant (T).

The temporal and spatial variations of bromodichloromethane are shown in Figure 3. These variations are similar to those of TCM but neither the spatial nor the temporal variations are as pronounced. The levels of chlorodibromomethane and bromoform were too low to evaluate their temporal and spatial variations.

**HAAs.** Monochloroacetic acid (MCAA), DCAA and TCAA were each found in all treated water samples analyzed in the present study, however, the MCAA levels observed were always low (1 to 3 µg/L). Monobromoacetic acid and dibromoacetic acid were not detected in any water samples in this study. For the chlorine-chlorine treatment (Hull; Table 5 and Figures 4c and 4d) the DCAA levels were similar to those obtained with the chlorine-chloramine treatment (Ottawa; Table 4 and Figures 4a and 4b). However, DCAA levels observed at the furthest sampling point (D3) in the distribution system, for the chlorine-chlorine treatment, were much lower than those at sampling points (D1, D2) closer to the treatment plant. A similar observation has been reported by other workers who attributed this effect to bacterial degradation, although whether the degradation mechanism is biological or chemical has not been resolved conclusively (Williams *et al.*, 1994b, 1995b). Nonetheless, mature water at D3 (age being determined relative to the time of disinfection at the treatment plant) exhibited lower DCAA values. This observation was the opposite found for TCM where mature water at D3 contained maximum TCM levels. For the chlorine-chloramine treatment (Ottawa; Table 4 and Figures 4a and 4b) the DCAA levels remained relatively constant in the distribution system throughout the year except during the summer at site D2. The low

**Table 3. General water quality and other auxiliary parameters of raw and treated (plant) water for the three facilities**

Parameters	n <sup>a</sup>	Ottawa		Hull		Buckingham		
		raw	treated	raw	treated	raw	treated	
pH	12	mean range	7.3 7.1-7.5	7.9 6.8-9.2	7.3 7.1-7.6	8.1 7.1-9.4	7.2 6.8-7.6	7.8 7.2-8.5
TOC (mg/L)	12	mean range	5.9 5.6-6.4	2.7 2.2-3.2	5.9 5.1-6.4	2.9 2.4-3.6	4.1 3.4-5.8	2.3 1.8-3.0
TOX (µg/L)	12	mean range		101 33-228		102 76-166		76 13-210
Bromide ion (mg/L)	1		0.005	<0.002	0.005	<0.002	<0.002	0.002
Kjeldahl Nitrogen (mg/L)	1		<0.1	0.6	<0.1	<0.1	<0.1	<0.1
Colour (TCU)	1		29.1	2.1	29.0	2.1	27.4	1.7
Turbidity (NTU)	1		3.0	0.3	3.8	0.8	3.4	0.3
Hardness (CaCO <sub>3</sub> ; mg/L)	1		29	44	27	41	20	31
Alkalinity (CaCO <sub>3</sub> ; mg/L)	1		20	20	20	20	12	12
Residual Chlorine <sup>b</sup> (mg/L)	12	range		0.8-1.1		0.8-1.2		0.6-1.6

<sup>a</sup> samples analysed, <sup>b</sup> total residual chlorine as measured by plant personnel

DCAA levels observed at D2 for Ottawa may also be attributed to mature water samples – the sampling point at this site was situated in a line that connected the main pipe to a distribution system reservoir. The age of water at this sampling point at any specific time of the day or year would depend on the direction of flow in the line. A more mature water sample would be collected when the water flow was outward from the reservoir than when the water flow was towards the reservoir. For the ozone-chlorine treatment (Buckingham; Table 6 and Figures 4e and 4f) the DCAA levels were generally lower throughout the year when compared to the two other plants except at location T where the DCAA levels were considerably higher during the summer. The reason for the high DCAA value in the summer was the additional application of chlorine, as discussed above. Of importance is the observation that DCAA maximized at or near the treatment plant around the time that the additional application of chlorine was made. The spatial distribution of DCAA in the fall at Buckingham closely resembles the spatial distribution in the fall at Hull which uses chlorine-chlorine treatment.

Figure 5 illustrates the seasonal variation of TCAA for the three treatment systems. For chlorine-chloramine treatment (Ottawa; Table 4 and Figures 5a and 5b) the TCAA levels exhibited little variation in the distribution system and although there was some variation from month to month (Figure 5a) the mean seasonal TCAA levels were relatively consistent throughout the year. For chlorine-chlorine treatment (Hull; Table 5 and Figures 5c and 5d) both seasonal and spatial variations were observed in the TCAA levels. At Hull TCAA behaved in a similar way to DCAA and a mature water effect was observed. An important distinction however was that TCAA maximized at D2 whereas DCAA maximized at D1. This suggested that the kinetics of degradation and/or rate of formation were different for these two acids. If the rate of degradation was faster

for DCAA than for TCAA this could explain the lack of a drop for TCAA at D2 (Ottawa; Figure 5b) which had been observed for DCAA (Ottawa; Figure 4b). We suggest that the age of the water at D2 was old enough to exhibit a drop in DCAA levels but not in TCAA levels. At Buckingham (Buckingham; Table 6 and Figures 5e and 5f) the behaviour of TCAA supported this explanation. In the summer TCAA maximized at D1 and showed a steady decrease towards the end of the system whereas DCAA maximized at T (Figure 4f), i.e. DCAA maximized at locations nearer the plant than TCAA indicating more rapid formation and subsequent degradation. By contrast the behaviour of TCAA in the winter, spring and fall seasons was markedly different than in the summer. In these three seasons TCAA maximized at D3 and more closely resembled the behaviour of TCM.

**CH.** After the THMs and HAAs, CH was the most prominent DBP with levels ranging from <0.1 µg/L to 23.4 µg/L. The seasonal variation of CH for the plants showed (Figure 6) lower levels of chloral hydrate during the cold water months than during the warm water months. With chlorine-chloramine treatment (Ottawa; Table 4 and Figures 6a and 6b) the CH levels were relatively constant throughout the distribution system except for location D2 where a low level was observed during the warm water months. We attribute this to the mature water effect discussed above. With chlorine-chlorine treatment (Hull; Table 5 and Figures 6c and 6d) the spatial variation was considerably more pronounced, with levels increasing in the distribution system to a maximum at D2 (mean level at D2 about twice the mean level at T). The minimum CH levels were observed in the end-of-line samples; again this observation is evidence of the mature water effect observed for the HAAs. With ozone-chlorine treatment (Buckingham; Table 6 and Figures 6e and 6f) the CH levels were considerably higher than at the other two plants. It is noteworthy that lower CH levels

**Table 4. Yearly mean DBP values (µg/L): Ottawa chlorine-chloramine treatment**

	T	D1	D2	D3	All	Min	Max
Chloroform	29.2	32.4	37.0	35.4	33.5	8.9	65.1
Bromodichloromethane	2.4	2.4	2.4	2.2	2.4	1.1	3.9
Chlorodibromomethane	0.3	0.3	0.1	0.1	0.2	<0.1	0.8
Bromoform	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3
Total Trihalomethanes	32.0	35.1	39.4	37.7	36.0	10.3	68.6
Monochloroacetic acid	2.1	1.9	1.7	1.8	1.8	0.3	3.9
Dichloroacetic acid	15.7	15.3	14.4	17.3	15.6	1.8	25.2
Trichloroacetic acid	7.9	7.7	8.3	7.7	7.9	2.5	15.1
Monobromoacetic acid	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dibromoacetic acid	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Trichloroacetonitrile	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dichloroacetonitrile	1.6	1.7	0.9	0.7	1.2	<0.1	3.0
Bromochloroacetonitrile	0.2	0.2	0.1	0.1	0.2	<0.1	0.5
Dibromoacetonitrile	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,1-Dichloro-2-propanone	1.8	1.8	1.3	1.3	1.6	<0.1	2.8
1,1,1-Trichloro-2-propanone	2.6	2.2	0.7	0.5	1.5	<0.1	4.4
Chloral Hydrate	2.9	2.8	1.4	1.6	2.2	<0.1	6.6
Chloropicrin	0.3	0.4	0.2	0.2	0.3	<0.1	0.5

**Table 5. Yearly mean DBP values (µg/L): Hull chlorine-chlorine treatment**

	T	D1	D2	D3	All	Min	Max
Chloroform	21.3	33.3	43.5	55.9	38.5	10.7	92.1
Bromodichloromethane	3.1	3.9	4.6	5.1	4.2	2.3	6.7
Chlorodibromomethane	0.3	0.3	0.3	0.3	0.3	<0.1	0.5
Bromoform	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3
Total Trihalomethanes	24.8	37.5	48.4	61.4	43.0	13.3	98.0
Monochloroacetic acid	2.0	1.7	1.4	0.8	1.5	0.2	7.8
Dichloroacetic acid	16.2	17.1	13.8	3.7	12.7	2.1	26.2
Trichloroacetic acid	13.0	15.6	17.9	4.3	12.7	1.7	36.8
Monobromoacetic acid	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dibromoacetic acid	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Trichloroacetonitrile	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dichloroacetonitrile	2.0	2.7	3.2	0.9	2.2	0.4	5.2
Bromochloroacetonitrile	0.3	0.2	0.2	<0.1	0.2	<0.1	0.5
Dibromoacetonitrile	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,1-Dichloro-2-propanone	0.9	0.7	0.6	0.5	0.7	0.4	1.3
1,1,1-Trichloro-2-propanone	2.5	3.0	3.3	0.7	2.4	<0.1	5.7
Chloral Hydrate	2.5	4.0	5.7	1.5	3.4	0.6	10.5
Chloropicrin	0.3	0.3	0.4	0.1	0.3	<0.1	0.5

**Table 6. Yearly mean DBP values (µg/L): Buckingham ozone-chlorine treatment**

	T	D1	D2	D3	All	Min	Max
Chloroform	19.2	23.3	28.7	47.3	29.6	1.5	100.1
Bromodichloromethane	1.0	1.2	1.5	2.1	1.5	0.4	3.2
Chlorodibromomethane	0.1	<0.1	0.1	0.1	0.1	<0.1	0.2
Bromoform	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total Trihalomethanes	20.3	24.5	30.2	49.5	31.2	2.0	103.4
Monochloroacetic acid	1.9	1.1	1.2	1.0	1.3	0.2	3.4
Dichloroacetic acid	18.3	8.3	9.3	6.1	10.5	2.6	53.2
Trichloroacetic acid	5.9	8.1	8.3	9.8	8.0	0.2	21.9
Monobromoacetic acid	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dibromoacetic acid	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Trichloroacetonitrile	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
Dichloroacetonitrile	1.3	1.4	1.8	1.9	1.6	0.4	4.8
Bromochloroacetonitrile	0.2	0.1	0.1	<0.1	0.1	<0.1	0.4
Dibromoacetonitrile	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,1-Dichloro-2-propanone	1.3	1.1	1.1	0.7	1.1	0.4	2.2
1,1,1-Trichloro-2-propanone	2.8	3.5	3.8	3.5	3.4	0.6	6.4
Chloral Hydrate	9.5	8.5	8.9	8.7	8.9	1.0	23.4
Chloropicrin	0.7	0.5	0.7	0.8	0.7	0.1	1.5

were observed in February when the ozone was replaced with chlorine (Figure 6e) which suggests that ozone treatment enhances CH formation. During July to September when pre-chlorination was added to the treatment process, the CH levels maximized at the treatment plant and decreased with increasing distance from the plant (Figure 6f). This behaviour, which was also observed for DCAA, suggests that the reaction that produces CH was accelerated under the conditions of ozonation in combination with pre-chlorination and warm water temperatures.

**DCAN.** The seasonal and temporal variations of DCAN for the three plants are shown in Figure 7. With chlorine-chloramine treatment (Ottawa; Table 4 and Figures 7a and 7b) the DCAN levels were somewhat higher in the warm water months but were relatively constant throughout the distribution system except for locations D2 and D3 where a low level was observed during the warm water months. We attribute this to the mature water effect discussed above. With chlorine-chlorine treatment (Hull; Table 5 and Figures 7c and 7d) the seasonal variation was considerably more pronounced, with levels

increasing in the warm water months. Spatial variation was seen in the distribution system with DCAN levels reaching a maximum at D2. The minimum DCAN levels were observed in the end-of-line samples; again this observation is evidence of the mature water effect observed for the HAAs. With ozone-chlorine treatment (Buckingham; Table 6 and Figures 7e and 7f) the DCAN levels were somewhat higher in the warm water months and also increased in February when additional chlorine was used instead of ozone. Significantly higher DCAN levels were seen in October but the reason for this is unknown.

**DCP.** The seasonal and temporal variations of DCP for the three plants are shown in Figure 8. Very little seasonal variation in DCP levels was seen at any of the three treatment plants. DCP levels showed very little spatial variation within the distribution system for any of the treatment processes except for some evidence of the mature water effect at location D3 (Figures 8b and 8f).

**TCP.** The seasonal and temporal variations of TCP for the three plants are shown in Figure 9. With chlorine-chloramine treatment (Ottawa; Table 4 and Figures 9a and 9b) the TCP levels were somewhat higher in the warm water months but were relatively constant throughout the distribution system except for locations D2 and D3 where a low level was observed during the summer months. With chlorine-chlorine treatment (Hull; Table 5 and Figures 9c and 9d) the seasonal variation was more pronounced, with levels increasing in the warm water months. Spatial variation was seen in the distribution system with TCP levels reaching a maximum at D2. The minimum TCP levels were observed in the end-of-line samples; again this observation is evidence of the mature water effect observed for the HAAs. With ozone-chlorine treatment (Buckingham, Table 6 and Figures 9e and 9f) the TCP levels were higher in the warm water months. TCP levels also increased within the distribution system except for location D3 where TCP levels decreased during the warmer water months.

**CPK.** The seasonal and temporal variations of CPK for the three plants are shown in Figure 10. With chlorine-chloramine treatment (Ottawa; Table 4 and Figures 10a and 10b) the CPK levels were somewhat higher in the warm water months but were relatively constant throughout the distribution system, except for locations D2 and D3 where a low level was observed during the summer months. With chlorine-chlorine treatment (Hull; Table 5 and Figures 10c and 10d) there was some seasonal variation, with CPK levels increasing in the warm water months. Spatial variation was seen in the distribution system with CPK levels reaching a maximum at D2. The minimum CPK levels were observed in the end-of-line samples; again this observation is evidence of the mature water effect observed for the HAAs. With ozone-chlorine treatment (Buckingham; Table 6 and Figures 10e and 10f) the CPK levels were higher in the warm water months. CPK levels did not increase significantly within the distribution system. CPK levels were higher with the ozone-chlorine treatment than with the other two treatments.

**Other DBPs.** TCAN and DBAN were not detected in any raw or treated water samples. BCAN was detected in some treated water samples but the concentration was always very low (maximum 0.5 µg/L).

**Speciation.** The evidence presented above clearly demonstrated that each of the major DBPs behaved differently. In Figure 11, the relationship between the levels of the four main target DBP (TCM, DCAA, TCAA and CH) within the distribution system of each plant for representative cold water (April, 2°C) and warm water (September, 19°C) months is shown. For chlorine-chloramine treatment (Ottawa), the DCAA levels in April were similar to the TCM levels but the TCAA levels were about half the TCM levels (Figure 11a). The proportion of the four target DBP was significantly different in September (Figure 11b) when the DCAA and TCAA concentrations were significantly less than the TCM concentration. CH levels were considerably lower than TCM levels in either month. These observations suggested that warm water temperatures favour the formation of TCM over HAAs. For chlorine-chlorine treatment (Hull), the HAAs concentrations in April (Figure 11c) were similar to the TCM concentration at T, D1 and D2 but were considerably less at D3. In September (Figure 11d), the HAAs concentrations were similar to the TCM concentration at T but were significantly lower at D1 and D2 and almost depleted at D3. CH levels were considerably lower than TCM levels in either month. For ozone-chlorine treatment (Buckingham) in April (Figure 11e) DCAA was the most prominent DBP except at D3 where TCM was most prominent. The DCAA levels were about twice the TCM concentration at T, D1 and D2 whereas the TCAA levels were about half the TCM concentration at these locations. In contrast with chlorine-chloramine treatment (Ottawa) and chlorine-chlorine treatment (Hull) the CH concentrations were similar to the TCM concentrations at all four locations. In September (Figure 11f), TCM was the dominant DBP at all four locations; the DCAA concentration was comparable to the TCM concentration only at T but was significantly lower than TCM at D1, D2 and D3. At all locations CH concentrations were significantly lower than TCM concentrations.

**Regulatory Compliance.** None of the three treatment plants would have any difficulty meeting the current Canadian TTHM drinking water guideline (100 µg/L, Federal-Provincial Subcommittee, 1996) or United States TTHM maximum contaminant level (100 µg/L, National Research Council, 1987). Compliance with the Canadian guideline is based on a running annual average of quarterly TTHM measurements; however, there is no definition as to when in each quarter the TTHM measurements should be made. Table 7 shows the calculated mean values assuming that the samples were collected in the first month of each quarter (M1; January, April, July, October), the second month of each quarter (M2; February, May, August, November), the third month of each quarter (M3; March, June, September, December) and the mean value for all twelve months of the year (T12). The calculated means (M1, M2 and M3) based on one value per quarter were all within 15-20% of the overall yearly mean (T12). Although it is not possible to

apply this conclusion directly to all treatment plants and processes, it does indicate that the mean of single quarterly values can give a good approximation of a mean based on more frequent monthly sampling. What was obvious from the data in Table 7 was that a more important factor relating to guideline compliance was the location in the distribution system where the samples were collected. It is clear that although samples taken near the end of the distribution system would indicate maximum consumer exposure for TTHMs, this would not always be the case for other DBPs. Mean values for DCAA,

TCAA and CH were seldom maximum in end-of-line samples and the sampling point where the maximum values occurred varied for each analyte. Therefore, the sampling strategy for each DBP needs to be evaluated individually. The concentrations of THMs do not, in general, correlate with the concentrations of other DBPs. Therefore, THMs should not be used as a surrogate for other DBPs without a full understanding of all of the factors involved.

**Table 7. Yearly mean values ( $\mu\text{g/L}$ ) based on quarterly samples**

	Ottawa				Hull				Buckingham			
	TTHM	DCAA	TCAA	CH	TTHM	DCAA	TCAA	CH	TTHM	DCAA	TCAA	CH
M1 (T)	34.0	12.8	7.3	3.2	21.7	15.4	13.5	2.6	17.6	17.0	6.4	8.6
M2 (T)	31.5	17.6	7.8	3.0	27.0	19.7	16.6	2.5	23.3	21.4	5.8	9.3
M3 (T)	30.5	16.5	8.5	2.6	25.5	13.5	9.0	2.4	20.1	16.4	5.6	10.6
T12 (T)	32.0	15.7	7.9	2.9	24.8	16.2	13.0	2.5	20.3	18.3	5.9	9.5
M1 (D1)	37.6	14.4	7.9	3.2	39.3	17.8	16.9	4.6	23.4	9.1	8.5	8.3
M2 (D1)	34.8	14.9	6.6	2.8	40.5	18.2	17.5	4.2	25.6	7.5	7.8	7.1
M3 (D1)	32.8	16.5	8.6	2.4	32.7	15.5	12.5	3.2	24.6	8.2	7.9	10.2
T12 (D1)	35.1	15.3	7.7	2.8	37.5	17.1	15.6	4.0	24.5	8.3	8.1	8.5
M1 (D2)	41.1	13.9	8.4	1.6	42.9	13.1	17.9	5.3	31.7	10.4	11.3	8.3
M2 (D2)	37.8	13.2	7.2	1.1	51.1	15.5	20.4	5.9	30.5	9.1	6.6	7.9
M3 (D2)	39.5	16.1	9.4	1.5	51.3	12.7	15.5	5.9	28.4	8.4	7.0	10.5
T12 (D2)	39.4	14.4	8.3	1.4	48.4	13.8	17.9	5.7	30.2	9.3	8.3	8.9
M1 (D3)	41.0	18.6	8.9	2.2	65.6	4.1	4.9	1.7	51.5	5.6	10.0	7.7
M2 (D3)	34.1	15.5	6.9	1.0	58.5	3.7	4.5	1.5	49.2	7.2	9.7	8.3
M3 (D3)	37.9	17.8	7.3	1.5	60.0	3.3	3.5	1.5	47.9	5.6	9.8	10.2
T12 (D3)	37.7	17.3	7.7	1.6	61.4	3.7	4.3	1.5	49.5	6.1	9.8	8.7

# Conclusions

In the present study, which examined DBP variations as a function of treatment practice, season and sampling location, the overall picture that emerged was that no single sampling event captured the complete image of the behaviour of DBPs in drinking water. DBP concentrations were observed to fluctuate as a function of water treatment practice (and variations therein), age of the water and temperature of the water. DBP concentrations were usually higher in the summer than in the winter for all treatment processes. With chloramine treatment DBP concentrations did not, in general, increase significantly with distance (time) in the distribution system. With chlorine treatment THM concentrations increased with distance (time) in the distribution system and maximum values were found at the sampling point furthest from the treatment plant. The behaviour of the other DBPs was far more complex. Their concentrations showed an initial increase with distance (time) in the distribution system, but depending on the season and age of the water the concentrations could either increase or decrease at greater distances (time) in the distribution system. Of particular importance from a regulatory viewpoint is that no single site or time of year could be selected to provide simultaneous maximum values for the three major DBPs (TCM, DCAA and TCAA). The development of a sound sampling strategy to assess consumer exposure to DBPs will require more in depth studies to provide a greater understanding of the DBP behaviour within distribution systems.

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