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Experimental Study of the Formation of Chlorination By-Products in Potable Water of Quebec City, Canada

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The formation of by-products in drinking water after chlorination constitutes an important issue for utility managers, water epidemiologists and drinking water regulators. Chlorination disinfection by-products (CDBPs) in drinking water are considered potentially carcinogenic and have been associated recently with adverse reproductive outcomes following exposure during pregnancy (Cantor et al., 1998; Nieuwenhuijsen et al., 2000). The most important groups among CDBPs are trihalomethanes (THMs) and haloacetic acids (HAAs). Total THM (TTHMs) include chloroform, dichlorobromomethane (DCBM), dibromochloromethane (DBCM) and bromoform. HAAs include nine substances, but those most commonly found in drinking water are monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA). The sum of these five HAAs is commonly denoted as HAA5. Due to their potential adverse outcomes, legislation for CDBPs in drinking water has been established. For example, Stage I of the U.S. EPA DBP rule sets maximum levels for TTHMs and HAA5 at 80 μg/L and 60 μg/L, respectively, and stage II is under consideration (USEPA, 1994; Sharfenaker, 2001). Canada recently set out drinking water guidelines stating a maximum level for TTHM of 100 μg/L (Health Canada, 1996). Levels for HAAs will be considered in a future update of guidelines.

The potential for formation of CDBPs in water is generally determined by means of experimental assays in which raw or treated waters are chlorinated under bench-scale conditions. In recent years, most studies of experimental chlorination have focused notably on THMs (because they were the most regulated) while very few have considered HAAs (those which have, with limited data) (Amy et al, 1987; Montgomery Watson, 1993). Experimental chlorination studies are designed to theoretically compare the CDBP precursor content in different waters and, in some cases, to explain CDBP occurrence according to the levels of indicators for the precursors. Some experimental studies have been designed to investigate the formation of CDBPs according to the reaction time with variable chlorine dose. But in most cases chlorine dose in essays is much higher than those typically used in drinking water treatment. In addition, the studies published up till which have been based on experimental water chlorination have considered neither the variations in water temperature which occur throughout the year, nor the variations in water quality that occur on a seasonal basis.

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The aim of this paper is to paint a portrait of the simultaneous formation of THMs and HAAs in treated waters of two different utilities. The investigation is based on data generated through a large number of chlorination experiments, carried out through an entire year, which take into account the temporal variations in temperature and CDBP precursors (thus, with variable experimental conditions). The experimental protocol for this investigation also favors chlorination conditions close to those existing in full distribution systems (in terms of chlorine dose and chlorine contact time in water).

MATERIAL AND METHODS

The waters under study come from the two principal utilities of Quebec City (Canada). In Quebec City, there are important climate changes over the year, with winter being long and very cold and summer relatively hot. The utilities together provide drinking water to about 60% of the population of the city: about 280,000 people. The waters of the two utilities are very different in terms of the water source and the treatment to which they are subjected. The first utility (Utility I) takes the water from a river near the outlet of a lake (Lake Saint-Charles) which has high color (an annual average of about 30 TCU - true color) and relatively low turbidity (annual average of about 3 NTU). The treatment in the plant consists of pre-chlorination, coagulation-flocculation (microsand ballasted), sedimentation, ozonation, post chlorination and pH adjustment. The second utility (Utility II) takes its water from the Saint-Lawrence River (average annual colour and turbidity of 15 NTU and 15 TCU - true colour -, respectively). Raw water is subjected to pre-ozonation, coagulation-flocculation, sedimentation, filtration, post-ozonation, chlorination and pH adjustment. In both cases, selected waters for carrying out the experimental study were collected after the final ozonation and before the final chlorination. Thus, they are treated waters which have already been disinfected but which have not been subjected to the chlorine dose aimed at maintaining residuals in the distribution system.

In each utility, 18 samples of both raw and treated water were collected (in average every three weeks) from February 2001 to January 2002. Raw water was used only for the purposes of a portrait of its quality during the study period, whereas treated waters were collected in order to carry out the experimental chlorination assays. Samples were collected in one-liter bottles and stored in a cooler to be transported to the laboratory and then transferred to a refrigerator set at 4°C. One portion of the samples was used for measurement of pH and two indicators of natural organic matter (NOM), that is, total organic carbon (TOC) and ultraviolet absorbance at 254 nm (UV-254). The other portion of the sample was transferred to an incubator the day before the batch chlorination experiments were carried out. Temperature within the incubator was adjusted in order to reproduce the same temperature of water as at the moment of sampling. Also, before the experiments, pH was adjusted at 7.5 to replicate the average values in the distribution systems of the two utilities.

For waters of both utilities, bench chlorination experiments were undertaken based on the same protocol, that is, applying two different sodium hypochlorite doses (NaOCl) (1,5 and 2,5 mg/L) in 500 mL amber bottles that have been previously cleaned. In both cases, these selected chlorine doses are close to the lowest and the highest chlorine levels, respectively, applied in final chlorination at the treatment plants of the two utilities under study. Once chlorine was applied within the bottle, sub-samples were distributed in six vials representing six different contact times of chlorine in water: 15 min, 1, 2, 6, 24 and 48 hours. THMs, HAAs and free residual chlorine were measured in each vial in order to study their evolution according to time.

Water pH was measured in the raw and experimental waters using an electron pH-meter (Corning 320, Hanning Instruments). TOC and UV-254 were also measured in both raw and experimental waters. TOC was analyzed using a Shimadzu TOC analyzer (model ASI 5000) following the standard method 5310B (APHA, AWWA and WPCF, 1995) whereas UV-absorbance was measured by UV/visible spectrophotometry (Jenway, model 6405) at 254 nm with 10 mm optical path quartz cells. Free residual chlorine, THMs and HAAs were measured in the sampled treated water of Utility I (in order to evaluate the impact of pre-chlorination) and in each vial representing the various contact times following experimental chlorination. Measurements for free residual chlorine were conducted using the DPD titrimetric method (Standard method 4500-Cl-F) with a DR-700 colorimeter from Hach. Samples for THM and HAA were analysed according to EPA methods 551.1 and 552.2, respectively (USEPA, 1990; USEPA, 1995). Samples for THM and HAA analysis were extracted using pentane and methyl-tert-butyl-ether (MTBE), respectively. For HAA extraction, a surrogate standard (100 ppm 2,3-dibromopropionic acid in methyl-tert-butyl-ether, MTBE, HPLC grade) was added to each sample to monitor method performance. After sample extraction, analysis for THMs and HAAs was conducted by means of two Perkin Elmer autosystem XL gas chromatographs with electron capture detectors (GC-ECD). ZB-624 and ZB-1701 (30m x 0.32mm) Zebron columns were used for quantification of THMs and HAAs, respectively. For THM species, analytical protocols ensured detection limits of 0.5 µg/L for chloroform and of 0.3 µg/L for DCBM, DBCM, and bromoform. The method for HAAs allowed for the identification of different species. Detection limits were 1.2, 1.1, 0.6, 0.9, 1.3 and 0.9 µg/L for MCAA, DCAA, TCAA, MBAA, DBAA and BCAA, respectively.

RESULTS AND DISCUSSION

As shown in Table 1, the indicators for NOM for the experimental waters were comparable in the two utilities (except for the winter season). This is surprising, considering that Utility II applies ozonation to raw water, which is a more powerful oxidizing process than chlorination. As a consequence, it would appear that experimental waters of the two utilities would have comparable theoretical potential for the formation of CDBPs following chlorination.

According to the analytical procedures and the afore-mentioned detection limits, three different species of each CDBP group under study were found to be above the detection limits in the experimental chlorinated waters. Among THMs, chloroform, DCBM and DBCM were identified, whereas among HAAs, the

Table 1. Characteristics of experimental waters according to season (range of water quality parameters are shown) (*Winter*: Jan, Feb, Mar; *Spring*: Apr, May, Jun; *Summer*: Jul, Aug, Sep; *Fall*: Oct, Nov, Dec).

		Temperature (°C)	COT (mg/L)	UV-254 (cm^{-1})	pH	TTHMs (µg/L)	HAAs (µg/L)
U1	Winter	1.4-1.9	1.1-1.4	0.022-0.031	6.8-7.1	2.4-12.5	1.0-20.0
	Spring	2.4-15.9	1.7-2.5	0.019-0.027	6.4-6.9	14.4-23.1	22.7-37.0
	Summer	15.0-22.0	1.7-2.4	0.025-0.041	6.2-6.7	16.6-54.1	12.6-24.3
	Fall	3.0-12.8	1.7-2.3	0.024-0.032	6.0-6.7	3.3-19.6	14.8-27.0
U2	Winter	3.8-6.0	2.1-2.6	0.029-0.041	7.2-7.4	n.a	n.a
	Spring	9.4-16.7	2.2-2.5	0.025-0.034	7.2-7.5	n.a	n.a
	Summer	20.8-25.1	1.8-2.5	0.022-0.037	7.2-7.5	n.a	n.a
	Fall	8.1-16.1	2.3-2.5	0.028-0.031	7.1-7.2	n.a	n.a

U1: Utility I; U2: Utility 2; n.a.: non applicable

identified species were DCAA, TCAA and BCAA. However in the waters of Utility I, very low levels of brominated CDBPs were found. For this utility, chloroform constituted on average (all samples of all assays together) about 96% of TTHMs while DCAA and TCAA represented about 55% and 45% of HAAs, respectively. For Utility II, chloroform, DCBM and DBCM represented about 54%, 26% and 20% of TTHMs, respectively while DCAA, TCAA and BCAA represented about 50%, 45% and 5% of HAAs, respectively. The differences in the distribution of CDBP species between the two utilities can be explained by the content of bromide in the water sources. For both utilities, the distribution of THM species was comparable to that obtained for the distribution system in a study undertaken two years earlier (no data for HAAs available in this study) (Rodriguez and Sérodes, 2001).

The average concentrations of CDBPs, taking the results of all assays (and all contact times) together were significantly higher in Utility I than in Utility II. In Utility I, the average concentrations of TTHMs and HAAs were comparable: 32 and 36 µg/L, respectively (the initial levels in experimental waters associated with pre-chlorination being 18 and 20 µg/L, respectively). For Utility II the average concentrations of TTHMs were considerably higher than concentrations of HAAs: 15 and 5 µg/L, respectively. The differences observed between the waters of the two utilities could be explained in part by the CDBP levels already present in the experimental waters of Utility I (due to pre-chlorination). A complementary explanation is that the pre-ozonation practiced in Utility II is very efficient in removing the hydrophobic molecules that are the principal precursors of CDBPs in NOM (and particularly HAA precursors). If this were the case, the three indicators of NOM used in this study would not adequately represent the CDBP precursors contained in one or the other type of water under study.

Seasonal variations of both CDBPs formed following experimental chlorination were considerable in chlorinated waters from Utility I (Figure 1a): indeed, the levels found in waters collected in summer were approximately three times higher

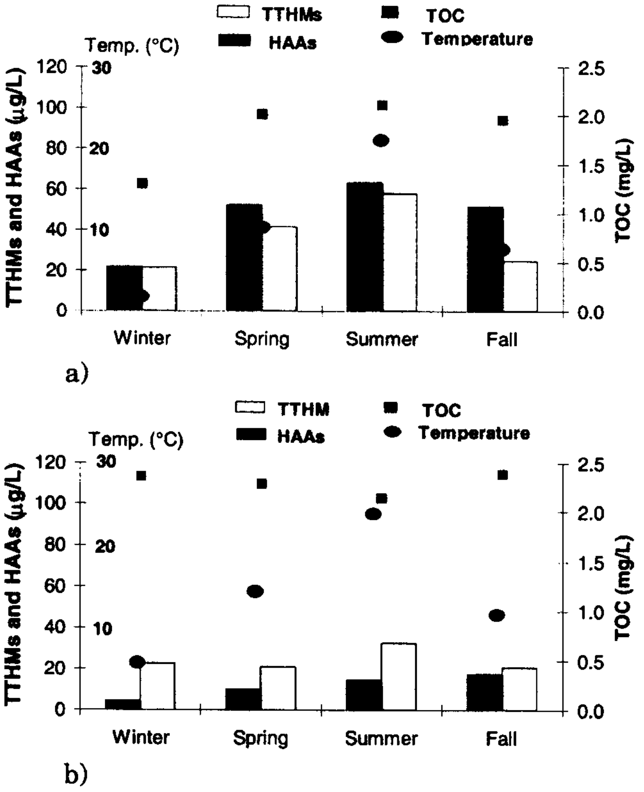

Figure 1. Seasonal variations TTHMs and HAAs generated during chlorination experiments with chlorine dose = 1,5 mg/L and contact time = 48 h (average levels are shown); a) Utility I; b) Utility II.

than those observed in winter. Such variations appear more closely related to the variations of water temperature than to the variations of TOC throughout the year. In this utility, average levels of THMs and HAAs for each season were comparable, except for fall. A possible explanation for this is that NOM composition in fall is probably affected by the vegetation decay occurring in October and November in the Quebec City region and that such decomposition does not affect the occurrence of the two CDBPs under study in the same manner. For waters of Utility II, seasonal variations were important for TTHMs and moderate for HAAs (Figure 1b). In all seasons except in fall, TTHM levels were significantly higher than HAA levels. The explanation for this could be similar to the mentioned in the case of Utility I.

For the waters of both utilities, the impact of chlorine dose was appreciable only for experiments with water temperature higher than 15°C (most of them during summer), as shown in Figure 2. For the remaining experimental conditions, the levels of CDBPs were comparable or just slightly higher, at chlorine dose of 2.5 mg/L in comparison with the dose of 1.5 mg/L. Indeed, at high temperatures of water, the chlorine demand by oxidizable compounds in water (including CDBP

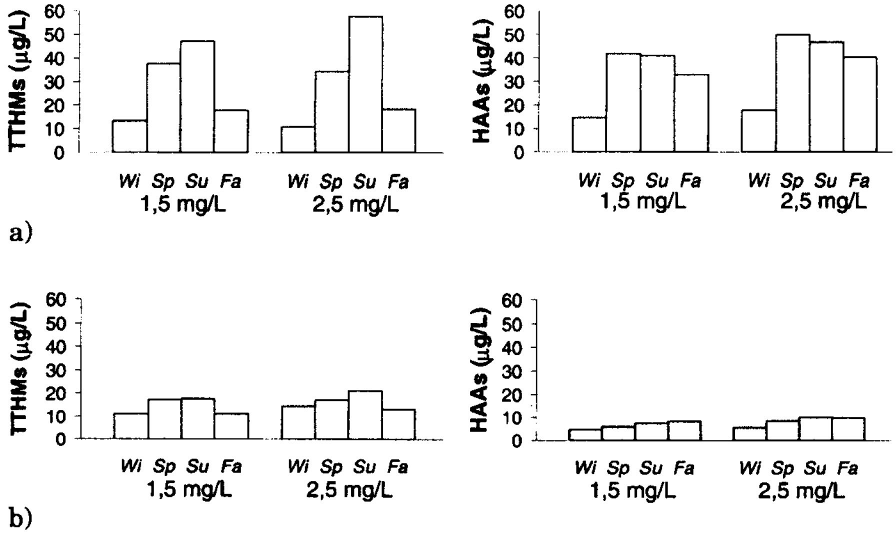

Figure 2. Average seasonal levels of TTHMs and HAAs according to the experimental chlorine dose; a) Utility I; b)Utility II (Wi: Winter; Sp: Spring; Su: Summer; Fa: Fall).

precursors) are fast, so after a long reaction time higher initial chlorine dose would produce higher CDBP levels.

The increase in CDBP concentrations in accordance with essay contact time was appreciable in chlorinated waters of both utilities (Figure 3). However the increase was significantly higher in waters of Utility II where TTHM and HAA concentrations augmented on average of about five times and about 10 times, respectively, between the beginning and the end of the reaction. In the waters of Utility II, the increase was only about 1.5 times and about 2 times for TTHMs and HAAs, respectively. The relatively limited increase in CDBPs in Utility I is probably due to the fact that the experimental waters had already been pre-suggesting that an important part of the NOM occurring in raw water susceptible to react with chlorine to form CDBPs has already reacted and been transformed within the treatment plant and just a small fraction is left to react after the application of chlorine in experiments. In Utility II, even if pre-ozonation has removed a large part of CDBP precursors, the formation of CDBPs begin once the experimental chlorination essay starts.

Correlations between TTHMs and HAAs were moderate and vary greatly according to seasons (Tables 2a and 2b). This confirms, on one hand, that the origins of these two groups of CDBPs in chlorinated waters are quite different and, on the other hand, that factors responsible for the preponderance of one or the other CDBP group in chlorinated waters vary strongly throughout the year. In addition these results demonstrate that, for these types of waters, TTHMs cannot be used as surrogate for HAAs and, thus, that controlling only TTHMs through existing standards is not necessarily an acceptable strategy for controlling the levels of DBPs in drinking water.

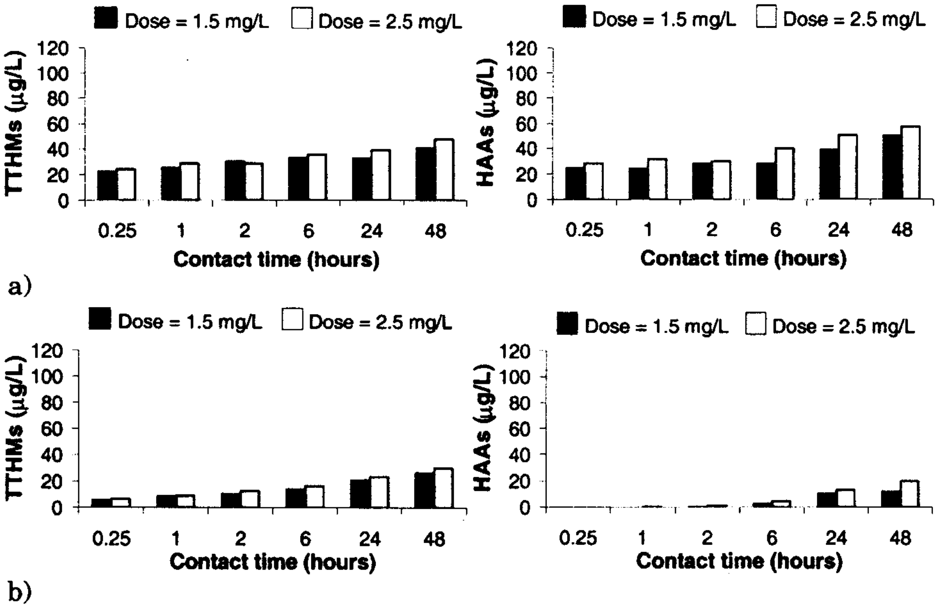

Figure 3. Evolution of TTHMs and HAAs according to the experimental contact time and chlorine dose(average of all experiments); a) Utility I; b) Utility II.

Table 2. Coefficients for correlation between TTHMs and HAAs according to season (data of all experiments together).

	Winter	Spring	Summer	Fall	All year
Utility I	0.44	0.55	0.29*	0.65	0.52
Utility II	0.30*	0.36*	0.68	0.74	0.61

*correlation non-significant ($p < 0.05$)

This latter result and the fact that TTHMs and HAAs varied considerably according to season and to contact time may have important implications on both epidemiological and regulation perspectives. In fact, until now, and mainly because of a lack of data, epidemiological studies on possible reproductive outcomes associated to DBPs in drinking water have not adequately considered either the variations of exposure through the year or the variations throughout the water distribution system. Within the perspective of establishing drinking water quality regulations, most countries have established annual averages of seasonal data for compliance with maximum acceptable levels of CDBPs. But the higher the variations of CDBP throughout the year, the less representative the CDBP average of human exposure to these compounds. This would be the case in northern temperate environments, as it is the case in the region under study, where climate variations through the year are significant.

The observations made in this investigation must, however, be validated in a full-scale study in which data for TTHMs and HAAs has been generated by means of an extensive sampling program within locations of the distribution systems (work that is currently in progress) and where real contact time in sampling points can be estimated. In addition, this would allow for the evaluation of the use of laboratory-scale data and eventual models for decision-making purposes. Additional efforts must be made to identify more refined indicators for the component of the NOM responsible for the occurrence of CDBPs.

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