

# **Report as of FY2007 for 2007ME98B: "The influence of chloride and natural organic matter gradients on disinfection by-product formation in Maine"**

## **Publications**

Project 2007ME98B has resulted in no reported publications as of FY2007.

## **Report Follows**

# **The influence of chloride and natural organic matter gradients on disinfection by-product formation in Maine**

## **Introduction**

Disinfection by-products (DBPs) form in surface waters that are chlorinated during the production of drinking water. DBPs are halogenated compounds such as tri-halomethanes (THMs) and haloacetic acids (HAAs). Health risks associated with ingesting DBPs prompted the U.S. Environmental Protection Agency (EPA) to set maximum contaminant levels (MCLs) of 80 ppb for THM and 60 ppb for HAA (U.S. EPA, 2001; Safe Drinking Water Act 40CFR 141 and revisions).

A previous study of raw- and finished-water samples from 30 public water systems throughout the state of Maine (Peckenham et al., 2006) showed a gradient in total DBP concentrations increasing from the coast to inland (Fig. 1). A similar gradient in total organic carbon (TOC) concentrations was observed across the state (Fig. 2) that suggest a spatial control on the formation of DBPs in water sources. The cross-correlation between TOC and DBP concentrations, however, was found to be very weak (Fig. 4).

One of the difficulties with the preliminary study was the reliance of DBP data from utility reports that were collected at different times from the other chemical data. A second, and much smaller, sampling round obtained DBP concentrations from finished water samples, adding a complicating factor of highly variable treatment methods. Because of the wide range of treatment variables, it was difficult to make strong statements about the relationships between DBP concentrations and other chemical parameters. The measurement of DBP formation potential, an analysis of DBP concentrations of raw water subjected to identical chlorination treatment, would rectify this problem.

## **Background**

TOC and the character of natural organic matter (NOM) are known factors in the formation of DBPs (Amy et al., 1987; Kitis et al., 2001; Leenheer et al., 2001; Charrois et al., 2004; Xie, 2004; Kim and Yu, 2005). In general, the higher the TOC content of the source water the greater the potential to form DBPs (Canale et al., 1997; Charrois et al., 2004).  $SUVA_{254}$  is used as a surrogate parameter for aromaticity of NOM, which is related to a high proportion of humic content (Traina et al., 1990). Specific ultra-violet absorbance at 254 nm ( $SUVA_{254}$ ) correlates positively with DBP formation potential (Kitis et al., 2001; Leenheer et al., 2001), and is used to predict DBP concentrations within a water system (Chow, 2006). The ratio of absorbance at 465 nm to 665 nm is also an indicator of the degree of humification and aromaticity of NOM (Stevenson and White, 1995; Chin et al., 1994). Korshin et al. (1997) have demonstrated that absorbance at 272 nm correlates with the formation of total organic halides (TOX) following chlorination.  $SUVA_{280}$  was found to be an accurate predictor of the production of DBPs from chlorine reactivity with NOM (Kitis et al., 2001). It is therefore expected that DBP concentrations

will be greater in waters with higher TOC concentrations and with a higher proportion of humic content of the TOC.

According to the Peckenham et al. (2006) results, there was a greater prevalence of trihalomethanes (THM) over haloacetic acids (HAA) with increasing distance from the ocean in the preliminary data (Fig. 3). TOC concentrations increased (Fig. 2) and background chloride concentrations decreased (Cl-b) (Fig. 2) with distance from the ocean. Correlations between DBPs and both TOC and chloride concentrations were weak (Fig. 3), possibly due to different collection times of the DBP data from the TOC and chloride data. A smaller dataset, where DBP concentrations were measured in the same samples as the TOC and Cl-b concentrations, showed that DBP concentrations increased with increasing TOC and decreasing Cl-b concentrations. The decrease in Cl-b concentrations with distance from the ocean could be related to a salt effect caused by deposition of marine aerosols, but it is not clear what causes the TOC gradient.

It is well known that catchments are the major contributors of NOM to surface waters, hence the controls on the amount and character of NOM is controlled by processes within the catchments (Cronan et al., 1999). For example, watershed characteristics and properties such as lake volume, ratio of lake area to watershed area, percentage of wetland, are related to NOM concentrations. Wetlands are significant contributors of dissolved organic carbon (DOC) to streams (Hinton et al., 1998; Garvey and Tobiason, 2003) although the proportion of wetlands explained more of the variability of DOC in rivers than in lakes (Gergel et al., 1999). Houle et al. (1995) found that both the export of DOC to lakes and in-lake removal of DOC were important factors in the concentration of DOC in lakes. A study by Kling et al. (2000) indicated that while streams consume DOC downstream, lakes show an increase in DOC at outlet compared to inlets, indicating a production of DOC. Seasonality is likely to be another factor affecting DOC dynamics.

The color of water (a good proxy for humic content in natural water) in lakes in northern United State and Canada is related positively to drainage ratio and negatively to watershed slope, mean lake depth, and lake area (Rasmussen et al., 1989; Schiff et al., 1997). Lake volume was found to correlate negatively with TOC and positively with the ratio of phenolic to aromatic relative fluorescence peak intensities and is therefore a significant factor in explaining the character of DOC (Vogt et al., 2002)

Certain characteristics of NOM are important in the formation of DBPs. For example, the formation potential of trihalomethanes (THMFP) is highly influenced by the hydrophobic fraction of NOM, whereas the formation potential of haloacetic acids (HAAFP) is more influenced by the hydrophilic fraction (Stepczuk et al., 1998; Kim and Yu, 2005). The character of the NOM is also a factor in the effectiveness of water treatment on NOM removal and in the formation of DBPs during treatment (Kim and Yu, 2005). Because the type of treatment will affect different fractions of NOM, knowledge of NOM characteristics will be useful information for treatment plant operators in choosing appropriate treatment methods. For example, conventional water treatment removes the hydrophobic fraction more than the hydrophilic fraction (Kim and Yu, 2005).

## Methodology

Fifteen surface waters were sampled in the summer of 2007 and analyzed for major anions, cations, dissolved organic carbon (DOC), total organic carbon (TOC), pH, temperature, ultraviolet (UV) absorbance, and THM formation potential (THMFP). UV absorbance was measured at wavelengths 254 and 436 nm and divided by DOC concentrations to obtain specific UV absorbance (SUVA), resulting in  $SUVA_{254}$  and  $SUVA_{436}$ , respectively. Four aliquots of each sample were measured using a spectrophotometer, then averaged for the final SUVA values.

The pH and specific conductance were analyzed with Hach probes in accordance with standard methods. Acid neutralizing capacity was analyzed using an ARAS and TIM900 titrator system. Cations were analyzed using an Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Anions were analyzed using an ion chromatography. UV absorbance was measured using a UV-VIS spectrophotometer at 254 nm. TOC and DOC were analyzed automated persulfate digestion followed by infra-red detection of carbon dioxide.

For THMFP analysis, surface-water samples were collected in 500-mL amber glass bottles with Teflon-lined caps. The bottles were washed with Liquinox soap, rinsed with copious organic-free water, and baked at 400°C in a muffle furnace for one hour. No preservatives were added to the sample. The samples were stored at 4°C and tested for THMFP within 24 hours using the APHA Standard Method 5710. Chlorine demand was measured in each sample in order to estimate the chlorine dose that results in a residual chlorine concentration between 3 and 5 mg/L after the sample was held in the dark for 7 days at  $25 \pm 2^\circ\text{C}$ . THM concentrations were measured for chlorinated and raw water samples and for each site with Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometry at the University of Maine. THMFP was obtained by subtracting the raw water THM concentration from the chlorinated concentration. Details of the FT-ICR method is provided in Appendix A.

## Results

There is no correlation between THMFP concentrations and either DOC or Cl-b concentrations, although it appears that high THMFP concentrations are associated with high DOC concentrations (Figure 5) and low Cl-b concentrations (Figure 6). The THMFP appear to cluster at high and low concentrations (Figures 5 and 6).

There is an inverse correlation between Cl-b and DOC concentrations (Figure 7). Separating these data into low and high THMFP (based on Figures 5 and 6) shows that the high THMFP values are associated with low Cl-b and high DOC concentrations.

As the percentage of particulate organic matter ( $(\text{TOC}-\text{DOC})/\text{TOC} \times 100$ ) increases, total THM concentrations decrease (Figure 8). This association is uncertain because it is highly leveraged by the two samples.

The source lakes with the greatest average depths have the lowest THMFP concentrations (Figure 9), but the relationship between average lake depth and THMFP concentration is not linear. Source lakes with the largest surface areas are associated with lowest THMFP concentrations (Figure 10). Watershed area for the source lakes has a similar relationship (Figure 10), but is not as simple. Watershed and lake surface areas are not linear with THMFP concentrations.

## Discussion and Conclusions

An inverse relationship between Cl-b and DOC concentrations was observed in samples from this study and the previous one (Peckenham et al., 2006). Although no explanation for this relationship was revealed in this study, it is clear that there is an inverse relationship between Cl-b and DOC in Maine surface waters. It is also clear that THM concentrations are connected to either, or both, the DOC and Cl-b concentrations. The relationship between DOC and DBPs has been noted in other studies, but the influence of Cl-b on DBP formation is enigmatic. This should be distinguished from a different process of adding aqueous chlorine to the source that forms THM (Karimi and Singer, 1991). It is possible that DOC and Cl-b concentrations are related to distance from the coast and have no direct correlation to each other. Future experimental laboratory studies on the influence of Cl-b concentrations on the formation of DBPs would help illuminate this relationship.

This study has confirmed that existence of a spatial gradient for TOC, Cl-b, and DBPs in Maine. The changes observed with respect to distance from the coast were: decreasing Cl-b, increasing TOC, and decreasing relative THM content. Additional controls on DBP formation appear to be related to lake size and watershed area. Particulate size for TOC may also be a controlling factor. Also, the sensitivity and utility of FT-ICR determination of DBPs has been documented. A key finding of this study is the apparent independence of the TOC and Cl-b contributions to DBP formation. Although not addressed in this study, other THM formation processes may be occurring in the coastal regions followed by volatilization of THM. This mechanism needs to be investigated in future research.

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## Figures

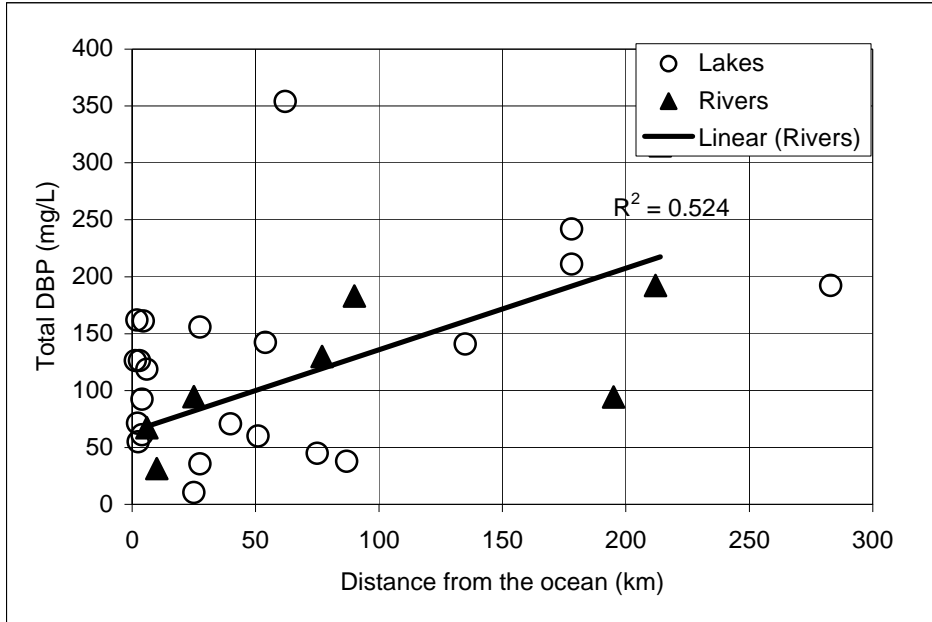


Fig. 1. Total DBP concentrations versus distance from the ocean from the preliminary dataset. The data are separated by source type.

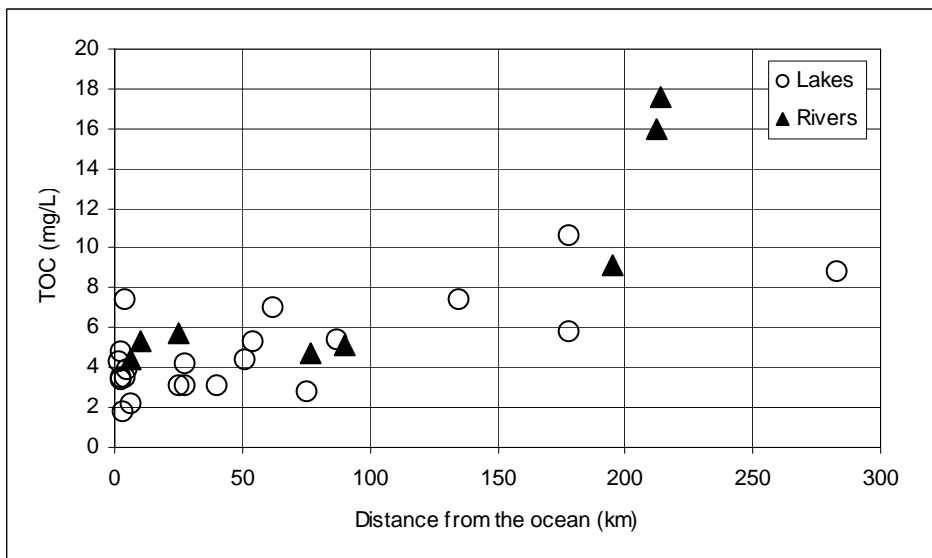


Fig. 2. TOC concentrations versus distance from the ocean from the initial study. Data are separated by source type.

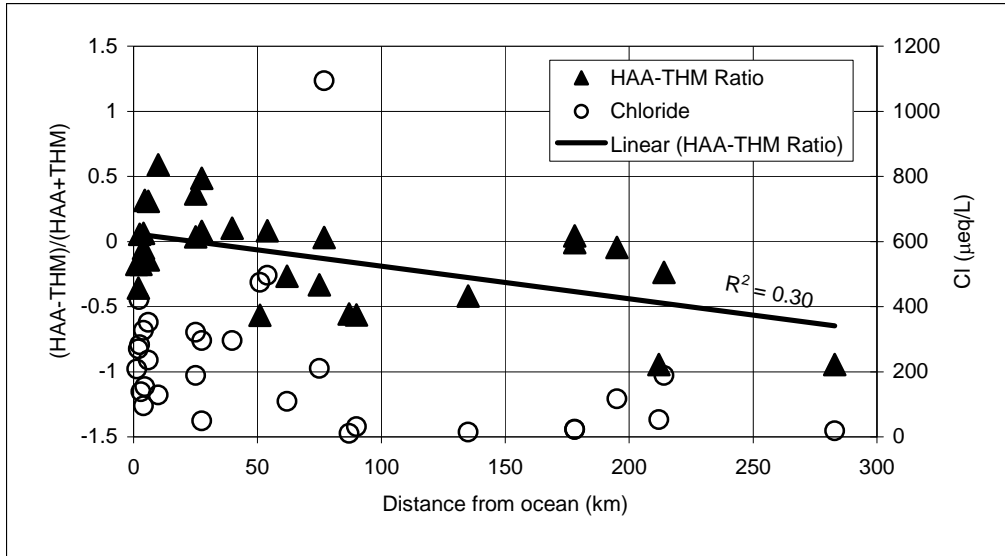


Fig. 3. HAA to THM ratio and Cl concentrations versus distance from the ocean for the data from the preliminary study.

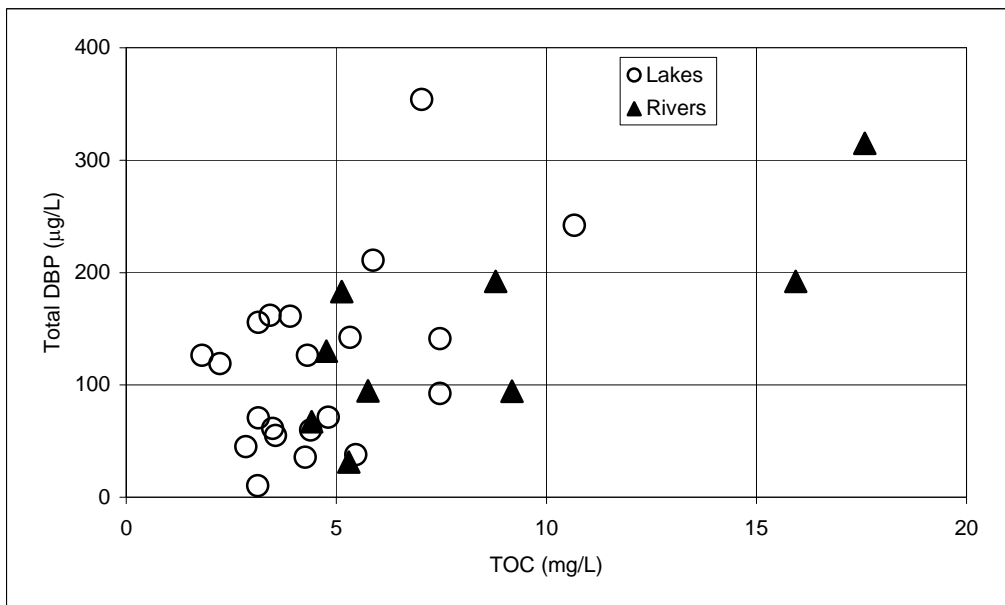


Fig. 4. Relationship between total DBP concentrations versus TOC from the preliminary dataset, separated by water source from the previous study.

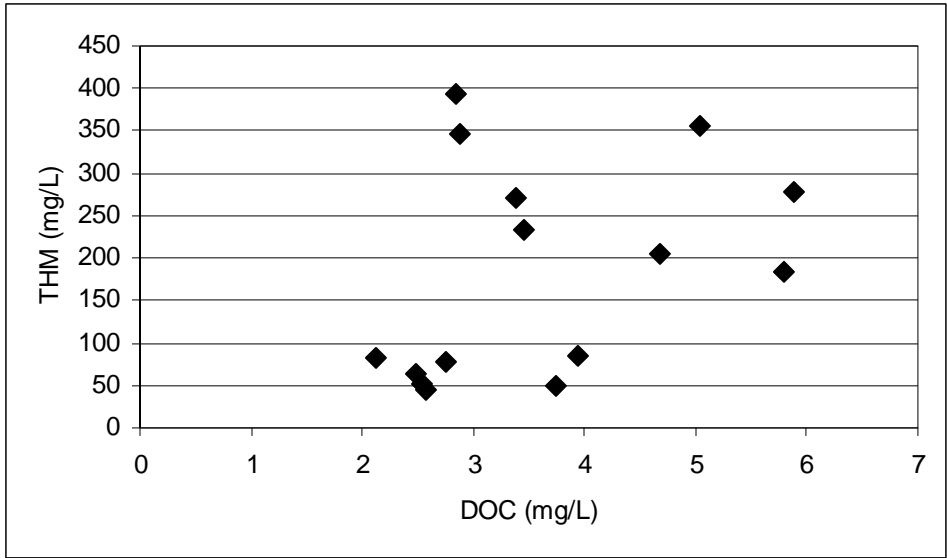


Figure 5. Relationship between THMFP and DOC concentrations for this study.

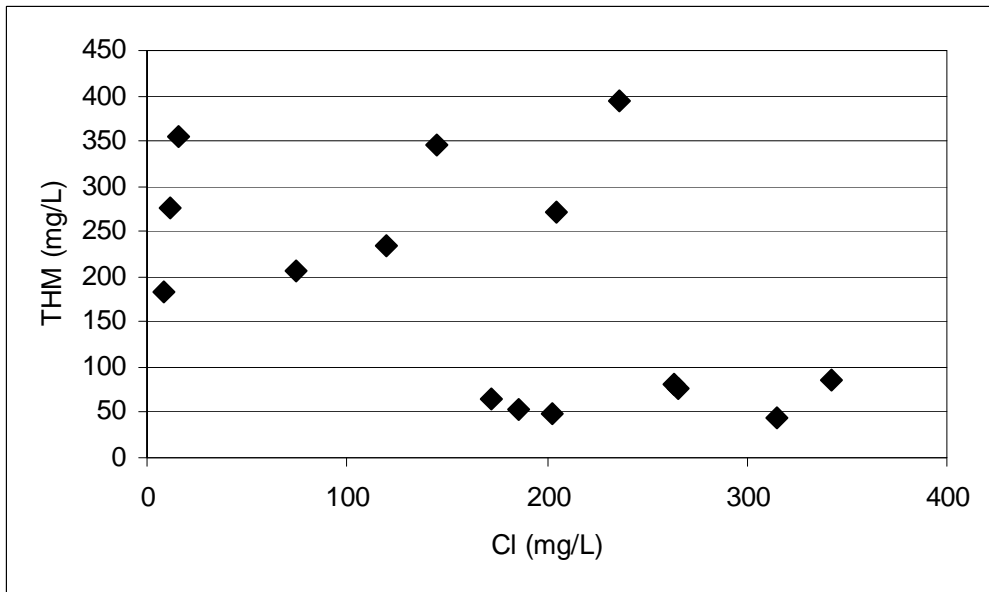


Figure 6. Relationship between THMFP and Cl-b concentrations for this study.

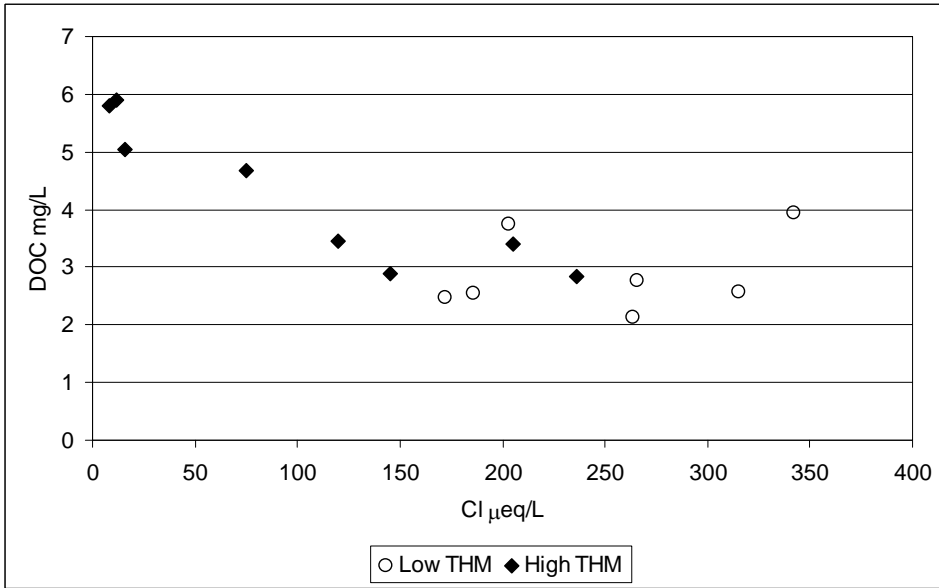


Figure 7.

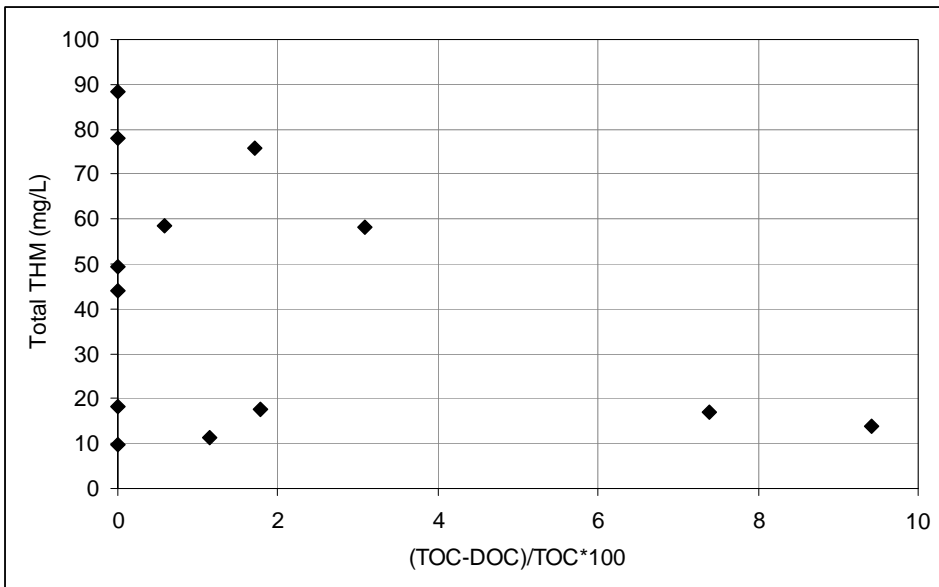


Figure 8

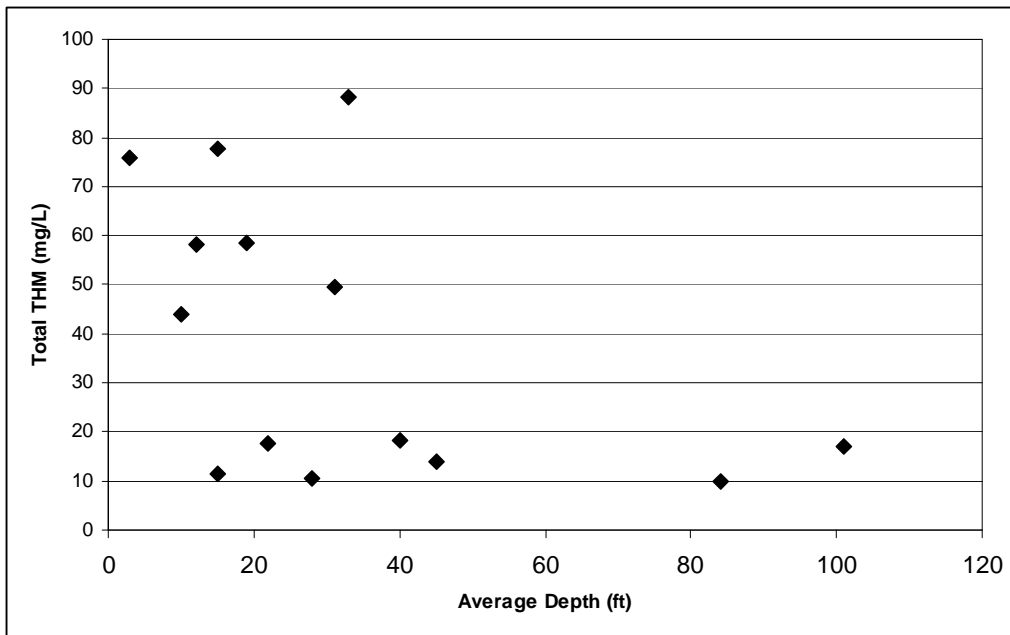


Figure 9. Total THMFP concentrations versus the average depths in the corresponding lake source.

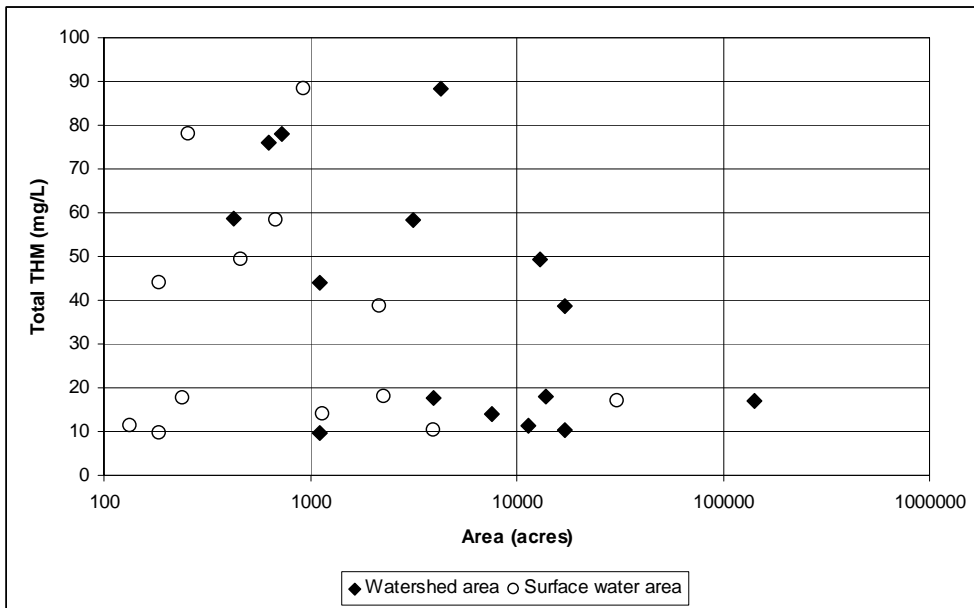


Figure 10. Total THMFP concentrations versus watershed area and lake surface area for each source.

*APPENDIX A*

**Identification of Halogenated Disinfection by Products in Drinking Water**

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## **1. Background:**

During chemical disinfection of drinking water, disinfectants (chlorine, ozone, chlorinedioxide, chloramines) react with naturally occurring inorganic, organic substances, and/or bromide/iodide that are present in the raw water and form disinfection by products ((DBPs). The trihalomethanes (THM) are most common routinely measured DBPs which include chloroform, bromodichloromethane, dibromochloro-methane, and bromoform. We studied water samples from different sites in Maine to identify the most abundant halogenated disinfection byproducts that are present in laboratory prepared water samples.

## **2. Experimental Section:**

### **2.1. Solid-phase Microextraction (SPME) Sample Preparation Procedure:**

We have used 85  $\mu\text{m}$  carboxen-polies (dimethylsiloxane) (CARPDMS) fiber for headspace SPME sampling. Twenty mL of water sample and a magnetic stirring bar were placed in a 40 mL septum sealed VOA vial. The SPME fiber was exposed to the headspace directly above the liquid to allow analyte molecules to adsorb to stationary-phase coating while stirring the sample on a magnetic stirrer plate. After 30 min (chosen to assure a “near-equilibrium” analyte adsorption and/or absorption) sampling, the fiber was simply retracted and exposed in a hot GC injection port to desorb the collected analytes for GC/FT-ICR MS analysis.

### **2.2. Instrumentation:**

All experiments were performed on an in-house designed {Szulejko, 2002 #17}, {Solouki, 2004 #18} 7-T GC/FT-ICR MS (Ion Spec Corp., Forest Lake, CA). The SRI model 8610C GC and an in-house configured cryofocuser interface with FT-ICR MS based on a Jacoby et al design {Jacoby, 1990 #27}. A 105-m (0.25-mm i.d., 1- $\mu\text{m}$  crossbonded 100% dimethyl polysiloxane stationary phase coating) MXT-1 capillary column (Restek Corp., Bellefonte, PA) was used for all solid phase micro extraction GC experiments. The vacuum chamber surrounding the ICR cell was maintained at  $\sim 87 \pm 5$   $^{\circ}\text{C}$  by a set of DC heating elements {Bennett, 2003 #26}.

### **2.3. GC Programming:**

The GC programming used for all SPME experiments was as follows: initial temperature was set at 40  $^{\circ}\text{C}$  and held for 4 minutes to park the desorbing species at the injection port, and ramped at 5  $^{\circ}\text{C}$  per minute to 180  $^{\circ}\text{C}$  and kept isothermal at 180  $^{\circ}\text{C}$  for 12 minutes. The carrier gas (He) head pressure was set at 15 psi.

#### **2.4. Sample Injection and MS data Acquisition:**

Analytes extracted by headspace SPME were injected into GC column. The GC/FT-ICR mass spectra were acquired using IonSpec Omega Software (version 8.0.294, IonSpec Corporation). All MS data were acquired under broadband (16 MHz analog-to-digital converter {ADC} rate) mode. The original time domain transient signal contained 256 k data points. Blackman window apodization was used for all of the mass spectra included in this study.

#### **2.5. Results and Discussion:**

Experiments were conducted using headspace SPME methods for sample preparation. The GC/FT-ICR MS total ion chromatogram (TIC), and the mass spectra corresponding to the peaks in the GC (from a 20-mL portion of a water sample from different sites extracted by headspace SPME with an 85  $\mu\text{m}$  Carboxen/PDMS Stableflex<sup>TM</sup> fiber) shows that two most abundant halogenated disinfection byproducts (i.e., chloroform and bromodichloromethane) are present at concentration range of (a) between 40 ppb to 100 ppb, and (b) above 100 ppb in different water samples. In order to validate our result, we carried out experiment using different reagents, methods, and sample blanks and analyzed the data. The results of the type of DBPs and the concentration value of the monitored ions present from different sites in Maine are tabulated in Table 1.

A summary of the GC/FT-ICR MS results for headspace SPME water sample from different site is tabulated in Tables 2.1-2.15. In Table 2, for each site (1-15), columns one through six contain the observed retention time(RTs), m/z values (experimental and theoretical), mass measurement error (MME) in ppm, assigned elemental compositions, and potential parent molecules corresponding to the major components present in the analyzed sample. In Table 2, all of the theoretical m/z values are calculated by exact mass calculator (Version 8.0.1., IonSpec Co, CA) and elemental compositions are assigned using the “IonSpec composition calculator” software.

**Table 1. The result of the type of DBPs and concentration of monitored ions (CHCl<sub>2</sub><sup>+</sup>) present in different sites of Maine**

Site	Final THM	Concentration (of CHCl <sub>2</sub> <sup>+</sup> ion) in ppb
Dexter	CLF, CHClBr <sup>+</sup>	60-80
KWD	CLF	40-50
NE Harbor	CLF, CHClBr <sup>+</sup> , C <sub>2</sub> HCl <sub>3</sub> <sup>+</sup>	40
Portland	CLF, CHClBr <sup>+</sup>	40-60
Auburn	CLF, CHClBr <sup>+</sup>	80
Winthrop	CLF, CHClBr <sup>+</sup>	80-100
York	CLF, CHClBr <sup>+</sup>	80-100
Jack man	CLF	Above 100
Newport	CLF, CHClBr <sup>+</sup>	Above 100
Bath	CLF	Above 100
Damariscotta	CLF, CHClBr <sup>+</sup>	Above 100
Millinocket	CLF	Above 100
Mars Hill	CLF, CHClBr <sup>+</sup>	Above 100
Bucksport (Silver Lake)	CLF, CHClBr <sup>+</sup>	Above 100
SW Harbor	CLF, CHClBr <sup>+</sup>	Above 100

CLF = Chloroform (82.94, 84.94, 86.938) , ClBrCH<sup>+</sup> = fragment ion from Bromodichloromethane

**Table 2.1. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
Jackman						
	22.72	82.9450 116.9083 129.9140	82.9449 116.9059 129.9138	1.2	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )

**Table 2.2. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
Newport						
	22.34	82.9456 116.9080 129.9167	82.9449 116.9059 129.9138	8.43	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	27.49	126.89397 113.8884 90.9197 82.9466 78.9193	126.89447 113.8901 90.91779 82.9449	-3.94	CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> ClBr <sup>+</sup> CBr <sup>+</sup> CHCl <sub>2</sub> <sup>+</sup> Br <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )

**Table 2.3. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
Dexter						
	22.53	46.9676 82.9446 129.9144	46.9683 82.9449 129.9138	-3.61	CCl <sup>+</sup> CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	27.54	126.8948 82.9455 78.9183	126.89447 82.9449	3.15	CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> CHCl <sub>2</sub> <sup>+</sup> Br <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )

**Table 2.4. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
Bath						
	22.10	82.9447 116.9059 129.9142	82.9449 116.9059 129.9138	-2.41	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )

**Table 2.5. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
Damariscotta						
	22.11	82.9447 116.9059 129.9142	82.9449 116.9059 129.9138	-2.41	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	27.25	126.89397 113.8884 90.9197 82.9466 78.9193	126.89447 113.8901 90.91779 82.9449	-3.94	CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> ClBr <sup>+</sup> CBr <sup>+</sup> CHCl <sub>2</sub> <sup>+</sup> Br <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )

**Table 2.6. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
KWD						
	22.34	82.9450 100.9575 129.9132	82.9449 100.9555 129.9138	1.2	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CH <sub>3</sub> OC <sub>2</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )

**Table 2.7. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
Millinocket						
	22.34	82.943 9 116.8829 129.8843	82.9449 116.9059 129.9138	-12	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )

**Table 2.8. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
Mars Hill						
	22.57	82.9442 116.9059 129.9129	82.9449 116.9059 129.9138	- 8.43	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	27.55	126.8994 113.8884 82.9177 78.9196	126.8944 113.8901 82.9449	0.39	CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> ClBr <sup>+</sup> CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> Br <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )

**Table 2.9. Summary of SPME GC/FT-ICR MS Results**

<b>Site</b>	<b>Retention Time (min)</b>	<b>Experimental m/z values</b>	<b>Theoretical m/z values</b>	<b>Calc. Mass Error (PPM)</b>	<b>Elemental Composition</b>	<b>Potential Parent Molecule &amp; Observed Product Ions</b>
Bucksport (Silver Lake)						
	22.75	82.9440 116.9059 100.9581 129.9131	82.9449 116.9059 100.9555 129.9138	-10	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup> CH <sub>3</sub> OCl <sub>2</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	27.49	126.8980 113.8910 82.9461 78.9193	126.89447 113.8901 82.9449		CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> ClBr <sup>+</sup> CHCl <sub>2</sub> <sup>+</sup> Br <sup>+</sup>	Bromodichloromethane BDCM ([M +H - HCl] <sup>+</sup> )

**Table 2.10. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
NE Harbor						
	22.91	46.9683 61.0282 82.9446 100.9551 129.9135	46.9683  82.9449 100.9555  129.9138	-3.6	CCl <sup>+</sup>  CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CH <sub>3</sub> OCl <sub>2</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	27.55	126.89387 82.9472 78.9199	126.89447 82.9449	-4.72	CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> Br <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )
	31.63	75.0228 91.0540 128.0621			C <sub>3</sub> H <sub>7</sub> S <sup>+</sup> C <sub>4</sub> H <sub>11</sub> S <sup>+</sup> C <sub>7</sub> H <sub>12</sub> S <sup>+</sup>	Not known

**Table 2.11. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
SW Harbor						
	22.28	82.9434 116.9059 129.9166	82.9449 116.9059 129.9138		CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	27.18	126.8988 113.8904 90.9200 82.9467 78.9194	126.89447 113.8901 90.91779 82.9449		CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> ClBr <sup>+</sup> CHCl <sub>2</sub> <sup>+</sup> Br <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )

**Table 2.12. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
Portland						
	22.09	82.9451 116.9059	82.94498 116.9059	1.44	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	27.22	126.89397 100.9563 82.9455	126.89447 82.94498	-3.94	CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> CH <sub>3</sub> OCl <sub>2</sub> <sup>+</sup> CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )

**Table 2.13. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
Auburn						
	22.09	82.9451 100.9556 116.9059	82.94498 100.9555 116.9059	1.44	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CH <sub>3</sub> OC <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	26.77	126.89397 90.9197 82.9454	126.89447 90.91779 82.9449	-3.94	CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> CBr <sup>+</sup> CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )

**Table 2.14. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
Winthrop						
	22.07	46.9686 82.9451 116.9048 129.9141	46.9683 82.94498 116.9059 129.9138	1.44	CCl <sup>+</sup> CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup> C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	27.65	126.89358 90.9187	126.89447 90.91779	-7.0	CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> CBr <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )

**Table 2.15. Summary of SPME GC/FT-ICR MS Results**

Site	Retention Time (min)	Experimental m/z values	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
York						
	22.05	82.9456 116.9072 129.9148	82.94498 116.9059 129.9138	7.4	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> CCl <sub>3</sub> <sup>+</sup> C <sub>2</sub> H <sub>35</sub> Cl <sub>3</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	27.41	126.8970 90.9187 82.9458 78.9197	126.89447 90.91779 82.94498		CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup> CBr <sup>+</sup> CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> Br <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )

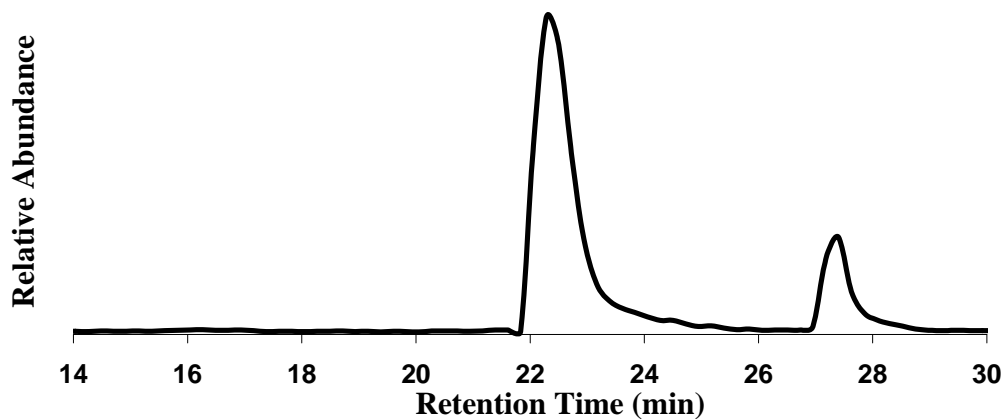
The average retention time and the average experimental m/z value obtained from n =15 run is tabulated in Table3.

**Table 3. Summary of SPME GC/FT-ICR MS Results (Average)**

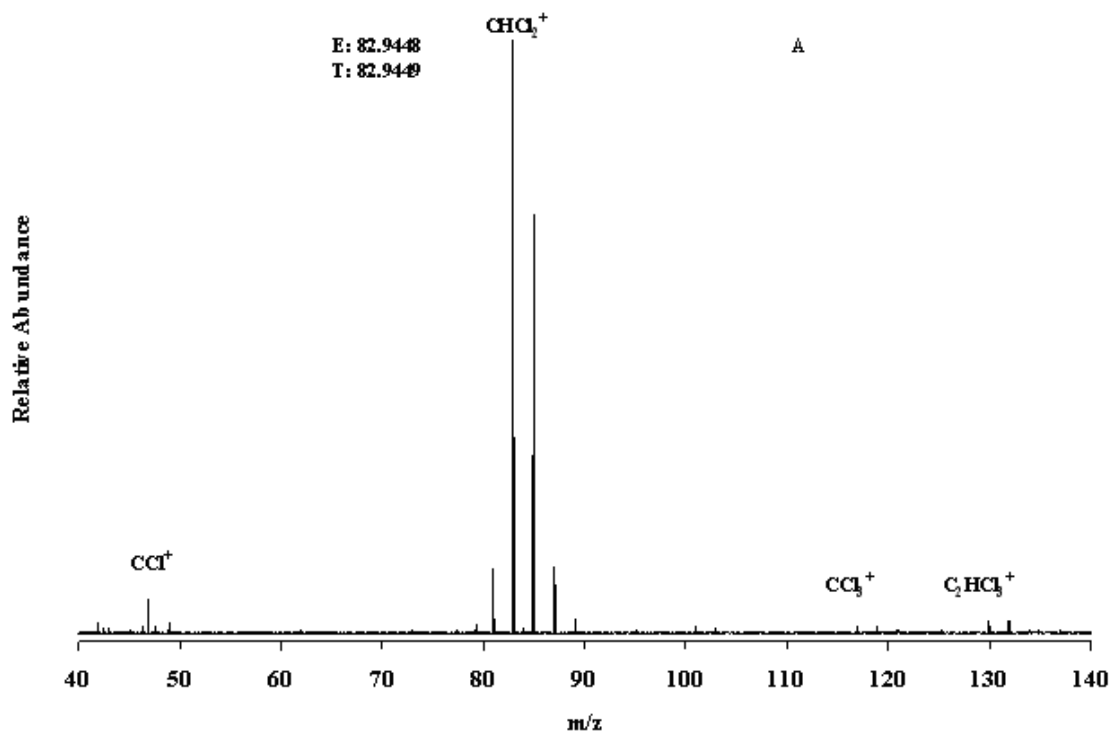
Retention Time (min) (avg (n=15))	Experimental m/z values (avg)	Theoretical m/z values	Calc. Mass Error (PPM)	Elemental Composition	Potential Parent Molecule & Observed Product Ions
22.35	82.9448 (n=15)	82.9449	-1.2	CH <sup>35</sup> Cl <sub>2</sub> <sup>+</sup>	Chloroform CLF ([M + H - HCl] <sup>+</sup> )
	116.9059	116.9059		CCl <sub>3</sub> <sup>+</sup>	CLF ([M - H] <sup>+</sup> )
	129.9132	129.9138		C <sub>2</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	CLF ([M - H + CH] <sup>+</sup> )
27.34	126.89397 (n=11)	126.89447	-3.94	CH <sup>79</sup> Br <sup>35</sup> Cl <sup>+</sup>	Bromodichloromethane BDCM ([M + H - HCl] <sup>+</sup> )
	113.8884	113.8901		CIBr <sup>+</sup>	
	90.9197	90.91779		CBr <sup>+</sup>	
	82.9448	82.9449		CHCl <sub>2</sub> <sup>+</sup>	
	78.9193			Br <sup>+</sup>	

The average experimental m/z value is used for calculating the mass measurement error in ppm. Figure 1(a) shows the section (RT= 14-30 min) of total ion chromatogram (TIC), and b(i-ii) shows the GC/FT-ICR MS corresponding to the peaks A and B in the section of total ion chromatogram (TIC) from a 20-mL portion of a water sample extracted by headspace SPME with an 85 μm Carboxen/PDMS Stableflex™ fiber

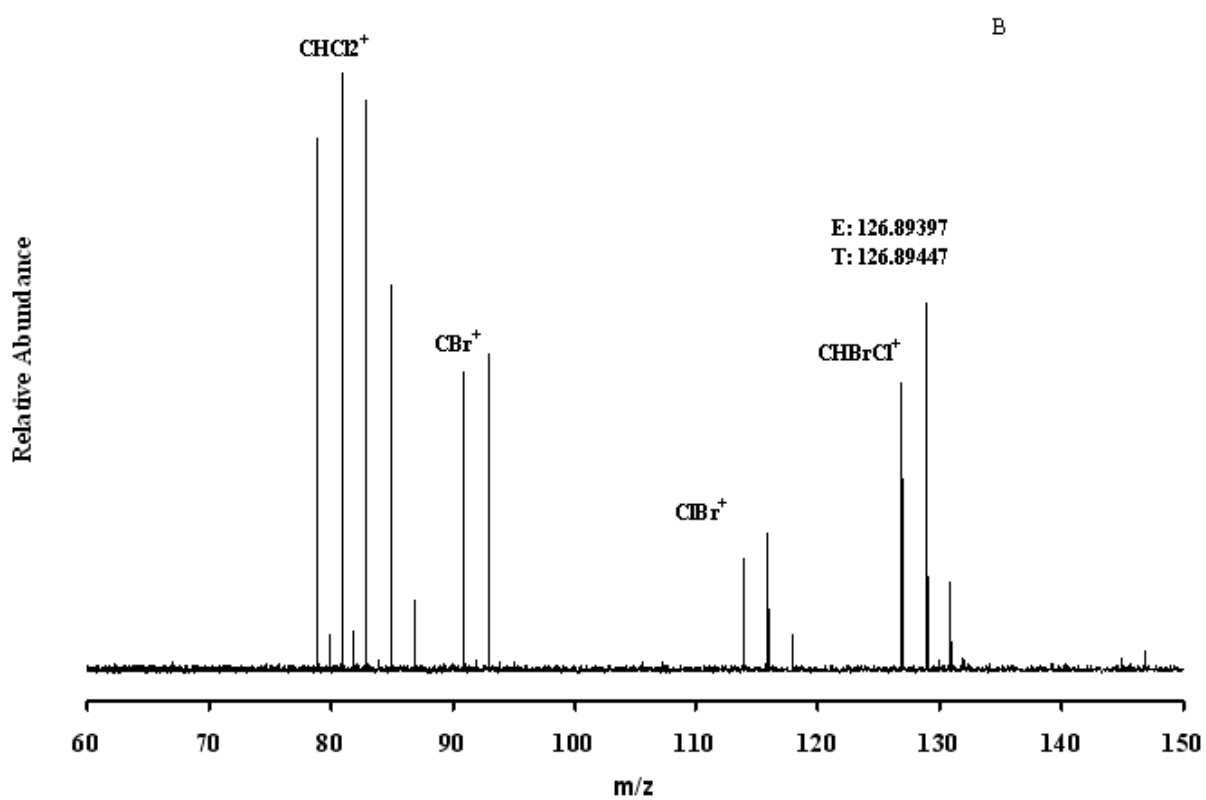
**Total Ion Chromatogram (RT = 14-30 min)**



**Figure 1(a)** : The section (RT= 14-30 min) of total ion chromatogram (TIC) from a 20-mL portion of a water sample extracted by headspace SPME with an 85  $\mu\text{m}$  Carboxen/PDMS Stableflex<sup>TM</sup> fiber.



**Figure 1b(i)** : The mass spectra corresponding to the peaks A in the section (RT= 14-30 min) of total ion chromatogram (TIC) from a 20-mL portion of a water sample extracted by headspace SPME with an 85  $\mu\text{m}$  Carboxen/PDMS Stableflex<sup>TM</sup> fiber.



**Figure 1b(ii)** : The mass spectra corresponding to the peaks B in the section (RT= 14-30 min) of total ion chromatogram (TIC) from a 20-mL portion of a water sample extracted by headspace SPME with an 85  $\mu\text{m}$  Carboxen/PDMS Stableflex<sup>TM</sup> fiber.

The mass spectrum (MS) corresponding to the RT ~ 22.35 min shows the MS assigned to chloroform. The observed ions with m/z values at 46.9683, 82.9446, and 116.9067 correspond to elemental compositions of  $C^{35}Cl^+$ ,  $CH^{35}Cl_2^+$ , and  $C^{35}Cl_3^+$ , respectively. The observed ions match the expected EI fragments from chloroform (NIST web book MS data base). The observed MS pattern closely matches the theoretically calculated isotopic pattern. Electron impact GC/ FT-ICR experiments were performed to confirm the retention times of standard chloroform. Under the identical GC conditions used for the analysis of water sample, the retention time of chloroform was indeed confirmed as 22.35 min. The mass spectrum (MS) at RT ~27.34 min shows the MS assigned to bromodichloromethane ( $CHBrCl_2$ ). This tentative assignment is based on the EI mass spectral appearance. The observed ions with m/z values at 126.89397, 113.8884, 90.9197, and 82.9466, correspond to elemental compositions of  $CH^{79}Br^{35}Cl^+$ ,  $^{35}Cl^{79}Br^+$ ,  $C^{79}Br^+$ , and  $CH^{35}Cl_2^+$  respectively. The mass measurement accuracy (MMA) is better than one part-per-million (MMA < 1 ppm).

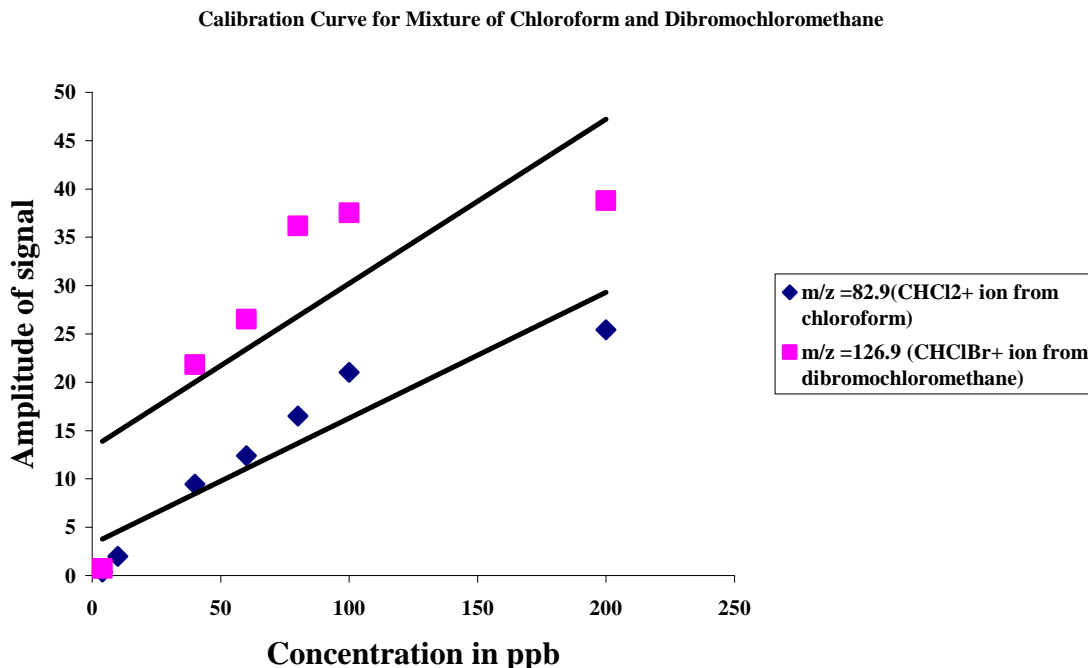
#### **Method Detection Limit of Car/PDMS Headspace SPME Analyses of standard trihalomethane (THM):**

Experiments were carried out to estimate the headspace SPME GC/FT-ICR MS detection limit for THM, which include chloroform, bromodichloromethane, dibromochloromethane, and bromoform. The known concentrations of standard THM were analyzed with headspace SPME. The amplitude of signal (an analytical response) of m/z = 82.94 (i.e.,  $CHCl_2^+$  fragment ion of chloroform), m/z = 126.89 (i.e.,  $ClBrCH^+$  fragment ion of bromodichloromethane), and m/z = 172.84 (i.e.,  $CHBr_2^+$  fragment ion of dibromochloromethane) were monitored as a function of concentration. The GC/FT-ICR MS analysis indicated that our method detection limit for standard THM was 35 ppb. No signal of m/z = 82.94, m/z = 126.89, and m/z = 172.84 were detected below 35ppb. Relative abundances of both ions (i.e.,  $CHCl_2^+$ , and  $CHClBr^+$ ) from standard THM were very weak. After closer examination, we found that standard THM solution was prepared in methanol. During SPME process, the SPME fiber was saturated with methanol and THM adsorption is less from standard solution than from water sample. The amplitude of

THM signal is very low. The higher signal at 40 ppb than the 50 ppb is associated with introduction of methanol (in excess from SPME, which results in high pressure and lower signal at 50 ppb).

### Method Detection Limit of Car/PDMS Headspace SPME Analyses of standard chloroform and dibromochloromethane:

In order to overcome the matrix problem, standard chloroform, and dibromochloromethane were ordered from Sigma Aldrich and electron impact GC/ FT-ICR experiments were performed to obtain the calibration curve. The calibration curve for standard chloroform and dibromochloromethane mixture is shown in Figure 2.



**Figure 2 :** The calibration curve for standard chloroform and dibromochloromethane mixture

The GC/FT-ICR MS analysis indicated that our method detection limit was 4 ppb. The linear concentrations range (over which detector response is proportional to concentration) is 4 ppb to 100 ppb (at filament turn at 7.5).

We monitored the  $\text{CHCl}_2^+$  fragment ion of chloroform and  $\text{CHClBr}^+$  fragment ion of bromodichloromethane in water sample. The experiments for water samples were done a few months before the experiment used for the calibration curve. Relative abundances of both ions (*i.e.*,  $\text{CHCl}_2^+$ , and  $\text{CHClBr}^+$ ) shows that the concentration of these halogenated compounds in water samples fall into two ranges: (a) between 40 ppb to 100 ppb, and (b) above 100 ppb. The concentrations range above 100 ppb of  $\text{CHCl}_2^+$  fragment ion of chloroform and  $\text{CHClBr}^+$  fragment ion of bromodichloromethane from different sites have measurable responses but do not fall in the linear range. This makes it difficult to find out the exact concentration of these halogenated compounds in the water sample. Though there are many ways to overcome this, such as sample dilution, etc., further experiments will be necessary to develop a fully quantitative method.

**Conclusion:**

Based on experimental results, it is concluded that the two most abundant halogenated disinfection byproducts (*i.e.*, chloroform and bromodichloromethane) are present in different water samples. The concentration of monitored ions ( $\text{CHCl}_2^+$ ) in different water samples vary from site to site and categorized into two ranges: (a) between 40 ppb to 100 ppb, and (b) above 100 ppb.