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BROMIDE CONCENTRATION ON THE
TRIHALOMETHANE REACTION OF CHLORINE
WITH AQUATIC HUMIC MATERIAL

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ABSTRACT

Wide seasonal changes have been reported in the trihalo-methane concentrations in water supplies. It is not known to what extent these changes can be ascribed to the effect of temperature on the haloform reaction or to what extent this is due to fluctuations in precursor concentration. This study reports the temperature dependence of the chloroform production from the reaction of chlorine with aquatic humic material (the major chloroform precursor in most natural waters) over the temperature range 2°C to 30°C at pH7 and pH11. The chloroform concentration was found to increase by a factor of 2.1 at pH7 and a factor of 1.7 at pH11 for each 10°C rise in temperature. The chlorination of several natural water samples under similar excess chlorine conditions yielded virtually the same temperature coefficients for total trihalo-methane production.

Alteration of the temperature and pH of humic solutions in which the excess chlorine had been quenched with $\text{Na}_2\text{S}_2\text{O}_3$ after a suitable reaction period showed that chloroform intermediates were produced at low temperatures and low pH's which could be converted to CHCl_3 on warming or on increasing the pH of the solutions.

Qualitatively it is well known that the concentration of CHBrCl_2 , CHBr_2Cl and CHBr_3 increase with bromide concentration when natural waters are chlorinated, but little quantitative information on the formation of these compounds is available. We have studied the production of these brominated compounds from the reaction of chlorine with aquatic humic material over a wide range of bromide concentration and at several temperatures between 2°C and 30°C. It was found that much higher concentrations of brominated trihalo-methanes were formed at low temperatures than at higher temperatures.

INTRODUCTION

Large seasonal fluctuations have been reported in the trihalomethane concentrations in water supplies^{1,2,3} particularly under Canadian environmental conditions where water temperatures can change from near freezing in the winter, to the upper twenties in the summer. For example, in Ottawa, Williams¹ reported that trihalomethane concentrations changed from an average of 20µg/l in the winter to an average of 120 µg/l in the summer despite only small changes in the total organic carbon concentrations of the water. Since humic material appears to be the major trihalomethane precursor in most natural waters^{4,5,6}, studies were undertaken to measure the temperature coefficient of the reaction of chlorine with aquatic humic material. Also because bromide concentration not only plays an important role in the formation of brominated trihalomethanes but, in addition, seems to influence the total trihalomethane concentrations in water supplies,⁷ studies were undertaken on the influence of temperature on the reaction of chlorine with aquatic humic material in the presence of bromide.

EXPERIMENTAL

Aquatic fulvic acid was isolated from a local stream (Spencer Creek, TOC=7.7mg/l) by the XAD-2/methanol-ammonia extraction technique.⁸ The elemental analysis of this extracted material (44.11%C, 5.78%H, 3.16%N, 1.23%S, 1.12% ash) was typical of humic material from other natural waters.^{9,10}

The chlorination experiments were carried out in headspace free serum vials with crimp tops in thermostats controlled at $2 \pm 0.01^\circ\text{C}$, $10 \pm 0.01^\circ\text{C}$, $20 \pm 0.01^\circ\text{C}$ and $30 \pm 0.01^\circ\text{C}$. The solutions were 2.5 mg/l fulvic acid plus 25 mg/l chlorine (NaOCl) buffered to pH7 and 11 with phosphate buffers. The excess chlorine to organic carbon (10:1) was chosen to assure significant chlorine residuals at the highest reaction temperatures and the longest reaction times. Trihalomethane concentrations were determined using a pentane extraction and electron capture gas chromatographic procedure.¹¹ It should be noted that it was necessary to perform the pentane extractions in a cold room at 2°C for the 2°C and 10°C samples in order to prevent formation of trihalomethanes from thermally unstable intermediates.

RESULTS AND DISCUSSION

The Effect of Temperature on Chloroform Production

Figure 1 shows the effect of temperature on the chloroform production from the chlorination of aquatic fulvic acid at pH 7 and pH 11. It is evident that as the temperature increases, the chloroform concentration rises quite rapidly at both pH's. Since it was not possible to obtain rate constants from the data, the temperature coefficients (T.C.'s) for the reaction were found by comparing the CHCl_3 concentration at fixed times for the four temperatures. There was no significant difference between the T.C.'s for the time intervals 6, 24, 48, 72 or 96 hrs or between the three temperature intervals studied. The average T.C. was 2.1 per 10°C for pH 7 and 1.7 per 10°C for pH 11.

Assuming the T.C. changes linearly with pH between pH 7 and 11, it can be approximated for samples at intermediate pH's by the equation:

$$\text{T.C.} = 2.1 - 0.1 (\text{pH} - 7) \quad (1)$$

To find out whether this temperature coefficient equation could be used to predict the effect of temperature on the chloroform produced when natural waters were chlorinated, water samples were collected from Lake Ontario, the Grand River and Spencer Creek and chlorinated under similar excess chlorine conditions at 2°, 10°, 20°, and 30°C. The concentration of chloroform was measured after 24 hours of reaction and the T.C. for each 10°C interval was calculated and averaged. In addition, two humic material samples, one a fulvic acid extracted from Lake Ontario sediment and the other, commercially available Aldrich humic acid, were chlorinated at pH 7 and 11 and the chloroform produced at the four temperatures measured after 24 hrs reaction time. It can be seen from this data, which is presented in Table I, that there is good agreement between the measured temperature coefficients and those predicted by equation (1). These results show that changes in temperature alone can cause up to an eight-fold difference between winter and summer chloroform concentrations in water supplies where water temperatures fluctuate from near freezing in the winter to near 30°C in the summer.

Additional Chloroform Produced by Heating and pH Adjustment

An experiment was carried out in which the residual chlorine in the humic/chlorine solutions was quenched after 24 hrs., and the samples were then heated to 30°C and/or adjusted to pH 11 with NaOH

and kept under these conditions for an additional 24 hr period prior to analysis. The results, in Table II, show that heating the samples chlorinated at pH 7 or adjusting their pH upwards produced considerable additional chloroform, with the combination of heating and pH adjustment producing the most. Heating the samples chlorinated at pH 11 did not produce additional chloroform. This data indicates that CHCl_3 intermediates are produced at pH 7 which are easily hydrolyzed to CHCl_3 at 30°C and/or pH 11. The existence of thermally unstable CHCl_3 intermediates was postulated earlier^{12, 13} as an explanation for the higher CHCl_3 levels found by the direct aqueous injection technique as opposed to the purge and trap technique.¹⁴ Also Morris and Baum¹⁵ showed that upward adjustment of pH after chlorine quenching produced additional CHCl_3 with certain compounds. Although the combination of temperature and pH adjustment produced about the same amount of additional CHCl_3 for the four temperatures studied (≈ 27 ppb), the percent increase in concentration is much higher at the lower temperatures. Therefore, it would be expected that there would be a larger percentage difference between chloroform analysis performed by the direct aqueous injection technique and the purge and trap technique for natural waters chlorinated at lower temperatures.

In an earlier study¹⁶ it was shown that the same degree of organic chlorine incorporation into humic materials occurred at low pH as at high pH, but that a greater percentage of chlorinated compounds produced at low pH were non-volatile. This study shows that, even though the CHCl_3 concentration of the pH 7 samples approaches the pH 11 CHCl_3

level with heating and pH elevation, it never quite reaches that value. Thus, it appears that a smaller fraction of the chlorinated compounds produced at the lower pH, 7, are chloroform or readily hydrolyzable chloroform intermediates.

The Effect of Bromide on Trihalomethane Production at 20°C

Fig. 2 shows the effect of bromide on the individual trihalomethane concentrations from the chlorination of fulvic acid. An increase in brominated trihalomethanes with increasing Br^- concentration is expected due to the rapid reaction of Br^- with chlorine in water to produce hypobromous acid and hypobromite ion.^{17, 18} It can be seen that the CHCl_3 concentration decreases rapidly, the CHBrCl_2 and CHBr_2Cl concentrations pass through a maximum, and the CHBr_3 concentration increases with increasing Br^- . It is interesting to note that the total concentration of trihalomethanes increases markedly with increasing Br^- to 3 times the initial concentration in the absence of bromide at $\text{Br}^-/\text{chlorine}$ ratios greater than one. Therefore, the presence of Br^- in natural waters not only affects the distribution of the individual trihalomethanes but also influences their total concentration.

Recently, long term experiments comparing the reaction of aquatic humic material with bromine and chlorine individually have shown that while the molar trihalomethane yield is three times higher for bromine at reaction time 24 hrs., the trihalomethane yield is only 1.5 times higher for bromine than for chlorine after 3 weeks reaction. Since the yields of the two reactions approach one another at long reaction

times, it is likely that the large difference in trihalomethane yields at shorter times is due to a faster reaction rate between the humic material and bromine compared to humic material and chlorine, and does not necessarily mean that bromine is any more reactive than chlorine toward humic material.

The Effect of Temperature on Brominated Trihalomethane Production at Low Bromide Concentrations

Table III shows the large effect of temperature on the yield of brominated trihalomethanes at several low Br^- concentrations. At the two lowest Br^- levels the mole % brominated compounds resulting from the chlorination of humic material is three times higher at the lower temperatures of 2°C and 10°C than at 30°C . It is also evident from the Table that even at relatively low Br^- concentrations of 1.5 ppm, where the Cl_2/Br^- ratio is 18:1, an inordinately large percentage (>93%) of all the compounds produced contain bromine. Both these observations are further indications that the reaction rate between bromine and humic material is much faster than that between chlorine and humic material.

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Table I: Average Temperature Coefficients (2°C - 30°C)
for Natural Water and Humic Material Samples

<u>Sample</u>	<u>pH</u>	<u>Measured T.C.</u>	<u>Predicted T.C.</u>
L. Ontario	8.4	2.0	2.0
Grand R.	8.4	1.8	2.0
Spencer Ck.	8.4	1.8	2.0
Sediment F.A.	7	2.0	2.1
Sediment F.A.	11	2.0	1.7
Aldrich H.A.	7	1.7	2.1
Aldrich H.A.	11	1.6	1.7

Table III: The Effect of Temperature on Brominated
Trihalomethane Concentrations*

<u>Bromide Concentration (mg/l)</u>	<u>Mole % Brominated Trihalomethanes</u>			
	<u>2°C</u>	<u>10°C</u>	<u>20°C</u>	<u>30°C</u>
0.025	16	15	11	6
0.10	33	32	25	10
0.40	69	68	60	55
1.50	99	95	93	94

* Solution 2.5 mg/l TOC fulvic acid, 25 mg/l chlorine,
pH = 7, Reaction Time = 24 hrs.

Table II: The Production of Additional Chloroform ($\mu\text{g}/\ell$) from Intermediates by Heating and/or pH Adjustment

Chlorination pH \rightarrow Temperature $^{\circ}\text{C}$ (C.T.) \downarrow	7		11	
	Kept at C.T.	Heated to 30°C pH Adjusted to 11, kept at C.T.	Kept at C.T.	Heated to 30°C pH Adjusted to 11, heated to 30°C
2	23	48	56	62
10	43	65	100	95
20	98	117	166	160
30	162	---	---	250

* The solution containing 2.5 mg/ ℓ water fulvic acid and 25 mg/ ℓ chlorine was allowed to react at a constant "chlorination temperature" (C.T.) and a constant pH (7 or 11) for 24 hrs. before being quenched with $\text{Na}_2\text{S}_2\text{O}_3$. The pH and/or temperature was changed (or left the name in the case of the control) for an additional 24 hr period prior to analysis.

Figure Captions

Fig. 1 The effect of temperature on the production of chloroform from the chlorination of fulvic acid at pH 7 and pH 11.

Fig. 2 The concentrations of trihalomethanes from the chlorination of fulvic acid as a function of the milligram ratio bromide/chlorine. Reaction conditions: 2.5 mg/l fulvic acid, 25 mg/l chlorine, pH 7, T 20°C, reaction time 24 hrs.



