

Relationship between trihalomethanes and haloacetic acids with total organic halogen during chlorination

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Abstract The effects of bromide ion, pH and reaction time on the formation of four trihalomethanes, nine haloacetic acids and total organic halogens in chlorinated drinking water have been investigated. In this extensive study, the relationship of total trihalomethanes and total haloacetic acids with total organic halogen have been evaluated. The study determined the concentration range of nine haloacetic acids and four trihalomethanes as a percentage of total organic halogen. The results showed that the percentage of total organic halogen made up of total trihalomethanes plus total haloacetic acids significantly increases with increasing bromide ion concentrations and pH. These observations suggest that both a higher bromide concentration and pH cause the formation of mainly brominated trihalomethanes with the reduction of haloacetic acids which could be identified and quantified by current USEPA methods.

Keywords Chlorination by-products; HAAs; THMs; TOX

Introduction

Although humic materials are probably innocuous by themselves at the level at which they occur in surface waters, those naturally occurring compounds can serve as precursors to possible carcinogens when fresh water supplies are subjected to chlorination for disinfection purposes (Miller and Uden, 1983). The chlorinations by-products are generally suspected of causing adverse health effects. Some of these by-products, e.g. trichloromethane (TCM), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), are animal carcinogens (Parnell *et al.*, 1986; Deangelo and McMillan, 1998). The United States Environmental Protection Agency (USEPA) is considering some of the by-products (TCAA, DCAA) for regulation under the Safe Drinking Water Act (Orme *et al.*, 1987). Raw-water bromide concentration is a significant factor in the formation of chlorination of by-products in chlorinated drinking water. In one study, 28 of 196 chlorinated organic by-products were only formed in the presence of bromide (Stevens *et al.*, 1989). Bromide ion influences the by-product mixture by forming Br-containing species when chlorine oxidizes bromide to HOBr, which behaves in a manner analogous to HOCl.

More than 780 compounds are formed by reaction of chlorine with humic acid solution, most of them are halogenated (Stevens *et al.*, 1989).

The parameter TOX represents the concentration of total organic halogens in a water sample. It is a collective parameter that is being used increasingly as a surrogate in drinking water. The analysis of organic halides as a group parameter is valuable as a unique indicator of these potentially harmful substances (Stevens *et al.*, 1985; Dressman and Stevens, 1983). Ratios of TOX to trihalomethane (THM) of 3–10 have been measured for various waters depending on treatment conditions. TOX formations from chlorination of a variety of aquatic humic and fulvic extracts from several different sources was relatively uniform, with approximately 220 µg TOX produced per mg of total organic carbon (TOC) by chlorination at pH 7, at a Cl₂/C ratio of about 4 or 5 to 1 (mg/mg basis), and a 72 hour contact time (Bull and Robinson, 1984).

Although many other organic halides have been identified in chlorinated humic and

fulvic solutions and in treated drinking water, their concentrations in most cases have not been quantified (Christman *et al.*, 1983). In all such studies, no more than approximately 50% of the TOX content has been accounted for, despite evidence that several of these halogenated by-products of water chlorination may be harmful to humans. Haloacetonitrile (HANs) contribution to TOX is negligible compared to THMs and HAAs. Accordingly, because the concentration of TOX as readily measurable (*Standard Methods for the Examination of Water and Wastewater*, 1985) this surrogate parameter has become the focus of increased attention. Although TOX itself is currently not regulated in chlorinated drinking water, good practice suggests that TOX formation should be controlled as well as THM formation. It should be noted that TOX formation tends to parallel THM formation for several utilities (Singer and Chang, 1989).

In this study, two main groups of chlorination by-products (THM, HAA) resulting from the chlorination of water containing humic acid (HA) solutions have been identified and quantified. The relationship between HAA and THM with TOX have been evaluated at four levels of bromide concentrations, three reaction times, and three pH values.

Experimental procedure

Ultrapure water containing commercial humic acid (Fluka), buffer and different concentrations of bromide ion were chlorinated to prepare a known drinking water model. Experimental procedure have been detailed elsewhere (Pourmoghaddas *et al.*, 1993) except with the following changes. Humic acid concentration is measured as non volatile total organic carbon (NVTOC). High chlorine dose (25 mg/l as Cl_2 , $\text{Cl}_2/\text{NVTOC} = 8.6$ (non volatile total organic carbon) were used. Residual chlorine was measured using the iodometric method (*Standard Methods for the Examination of Water and Wastewater*, 1985). Table 1 shows the proposed chlorination by-products.

The concentration of the proposed chlorination by-products were converted to chloride ion (Cl^-) to establish a relationship with TOX which was expressed as chloride ion. The mass concentrations of DBCM, DCBM, TBM were converted to TCM and then converted to chloride ion. For the conversion of μg of a HAA to μg of chloride ion, first mass concentration of mono, dihalogenated, and trihalogenated HAAs were converted to MCAA, DCAA and TCAA, respectively, and then converted to chloride ions. The mass concentration of four THMs or nine HAAs were added together for each bromide concentration, reaction time, pH value and visualized as total HAAs (THAAs) or total trihalomethane

Table 1 Proposed chlorination by-products

Parameter	By-product
<i>Total Organic Halogen (TOX)</i>	
<i>Haloacetic acid (HAAs)</i>	
Monochloroacetic acid (MCAA)	$\text{CH}_2\text{Cl}-\text{CO}_2\text{H}$
Dichloroacetic acid (DCAA)	$\text{CHCl}_2-\text{CO}_2\text{H}$
Trichloroacetic acid (TCAA)	$\text{CCl}_3-\text{CO}_2\text{H}$
Monobromoacetic acid (MBAA)	$\text{CH}_2\text{Br}-\text{CO}_2\text{H}$
Dibromoacetic acid (DBAA)	$\text{CHBr}_2-\text{CO}_2\text{H}$
Tribromoacetic acid (TBAA)	$\text{CBr}_3-\text{CO}_2\text{H}$
Bromochloroacetic acid (BCAA)	$\text{Br}_2\text{Cl}-\text{CO}_2\text{H}$
Dichlorobromoacetic acid (DCBAA)	$\text{CCl}_2\text{Br}-\text{CO}_2\text{H}$
<i>Trihalomethanes (THMs)</i>	
Trichloromethane (TCM)	CHCl_3
Dichlorobromomethane (DCBM)	CHCl_2Br
Dibromochloromethane (DBCM)	CHBr_2Cl
Tribromomethane (TBM)	CHBr_3

Table 2 Factors used for conversion of chlorination by-products (CBP) chloride ion

Mass concentration of CBP in $\mu\text{g/l}$	Conversion factor
TCM as Cl	$\times 106.5/119.5$
DCBM as TCM	$\times 119.5/164$
DBCM as TCM	$\times 119.5/208.5$
TBM as TCM	$\times 119.5/253$
MCAA as Cl	$\times 35.5/94.5$
DCAA as Cl	$\times 71/129$
TCAA as Cl	$\times 106.5/163.5$
MBAA as MCAA	$\times 94.5/1139$
DBAA as DCAA	$\times 129/218$
TBAA as TCAA	$\times 163.5/297$
DCBAA as TCAA	$\times 163.5/208$
DBCBA as TCAA	$\times 163.5/252.5$
BCAA as DCAA	$\times 129/173.5$

(TTHMs) in terms of chloride ion. Factors used to convert the chlorination by products (THMs and HAAs) to chloride ions are shown in Table 2.

Summary of the analytical methods

The EPA developed methods were applied for the analysis of the nine HAAs. The method involved liquid–liquid extraction with diethyl ether and esterification with diazomethane prior to GC/ECD analysis, The method is detailed elsewhere (Pourmoghaddas and Dressman, 1992). THMs were analyzed using EPA method 551. TOX concentration were determined by using EPA method 450.1.

Results and discussion

Figure 1 displays TOX results of chlorination of HA under different bromide concentration, pH values and reaction times. pH showed a significant effect on the formation of the TOX. Increasing pH causes a decrease in concentration of TOX. The low values for TOX at pH 7 and 9.4 compared to pH 5 is probably due to the relatively lower fraction of HAAs in the total TOX (see Figure 2). Note that at pH 5 and 7 more halogenated acids, including halogenated acetic acids were formed. Difference between concentration of HAAs at pH 5 and 7 do not show as much effect on TOX formation, but TOX concentration significantly

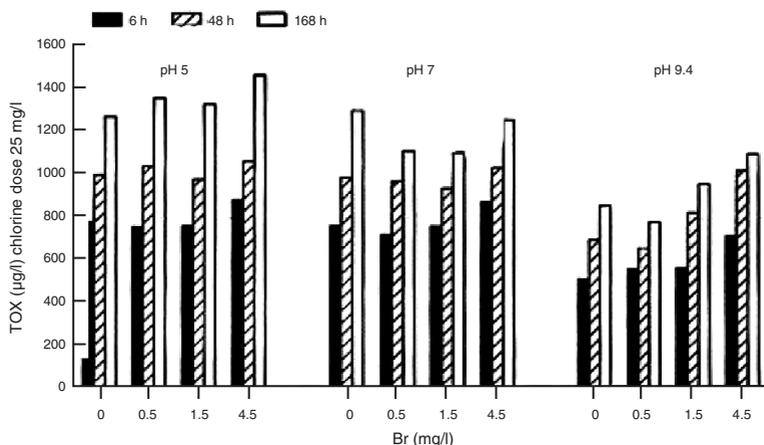


Figure 1 Effect of Br^- , pH and reaction time on formation of total organic halogen (TOX) (humic acid 2.9 mg/l as nonvolatile total organic carbon)

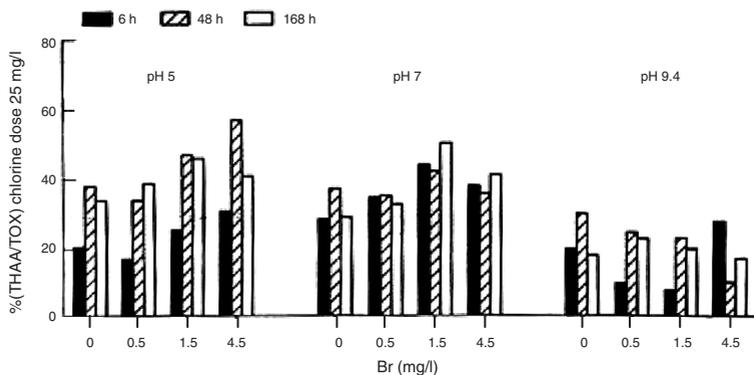


Figure 2 Total haloacetic acids (THAAs) as a percentage of total organic halogen (TOX) (humic acid 2.9 mg/l as nonvolatile total organic carbon)

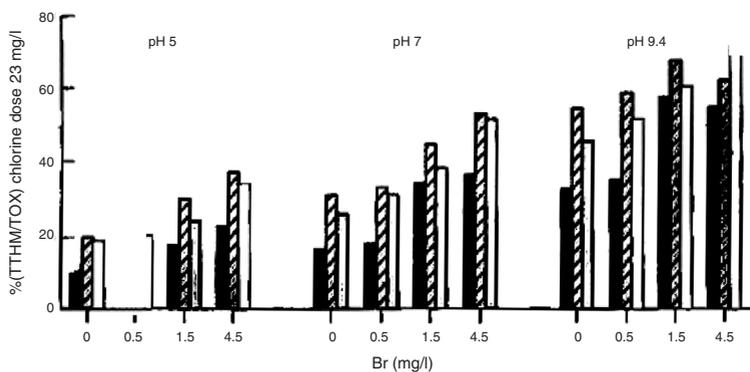


Figure 3 Total trihalomethanes (TTHMs) as a percentage of total organic halogen (TOX) (humic acid 2.9 mg/l as nonvolatile total organic carbon)

dropped at pH 9.4 under the experimental conditions. At pH 9.4, TOX significantly increased with increasing Br concentration. This phenomenon occurs because of the formation of more brominated THMs at higher bromide concentration than at lower bromide concentration (Figures 1 and 3). At pH 9.4 the TOX is more related to THMs than at the other two pH values. It can be seen by comparing Figure 2 with Figure 3 that bromide does not show as significant effect on increasing total HAAs as is the case for THMs. Reaction time had a significant effect on the formation of TOX. The concentration of TOX increases with increasing reaction time for all the experimental conditions (see Figure 1). In general, 70% of the TTHMs formed during 6 hours reaction time for the varied experimental conditions. But significant differences were not observed between 48 and 168 hours reaction time. This trend is confirmed by other research (USEPA, 1981). Figure 4 shows the relationship between THAAs and TTHMs as percentage of TOX in varying experimental conditions. In this figure, the TTHM bars project from the lower horizontal axis and THAA from the upper one as a percentage of TOX at the different experimental conditions.

Conclusion

The result of this study showed that the percentage of TOX made up of total THMs + HAAs significantly increases with increasing bromide ion concentration and pH. These observations suggest that both a higher concentration of bromide and pH causes the formation of mainly brominated THMs with the reduction of HAAs which could be identified and quantified by the current methods.

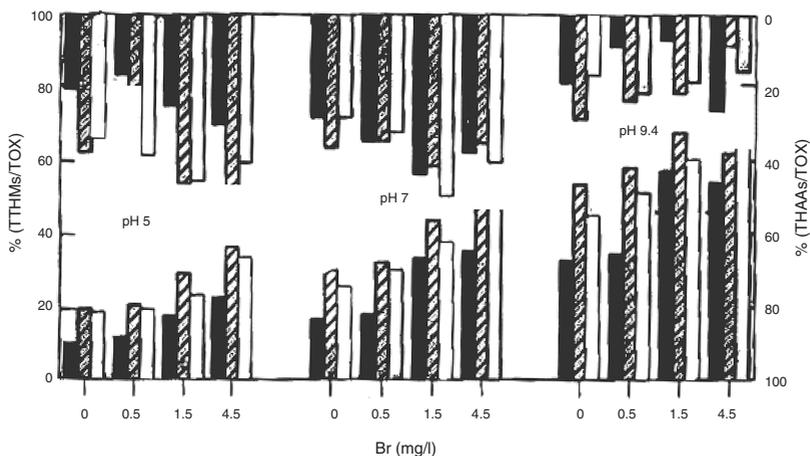


Figure 4 The relationship between total trihalomethane (TTHMs) and total haloacetic acids (THAAs) as a percentage of total organic halogen (TOX)

The study of the two main groups of chlorination by-products indicated that TTHMs were the largest class of by-product detected on a weight basis at pH 9.4. The concentration of HAAs significantly increase with decreasing pH. At pH 5 THAAs showed a higher concentration than TTHMs (see Figure 4).

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References

- Bull, R.J. and Robinson, M. (1984). Carcinogenic activity of halo-acetonitrile and haloacetic derivatives in the mouse skin and lung. In: *Water Chlorination: Chemistry, Environmental Impact and Health Effects*, Vol. 5. Ann Arbor Science.
- Chistman, D.L, Norweek, Millington, D.S., Johnson, J.D. and Stevens, A.A. (1983). Identity and yields of major halogenated products of aquatic fulvic acid chlorination. *Envir. Sci. Technol.*, **17**, 625–631.
- Deangelo, A.B. and McMillan, L.P. (1988). *The Carcinogenicity of the Chlorinated Acetic Acids*. United States Environmental Protection Agency, Health Effect Res. Lab., Cincinnati, Ohio, USA.
- Dressman, R.C. and Stevens, A.A. (1983), The analysis of organohalides in water – an evaluation update. *J. Am. Wat. Works Assoc.*, **75**, 431–434.
- Miller, J.W. and Uden, P.C. (1983). Characterization of nonvolatile aqueous chlorination products of humic substances. *Envir. Technol.*, **17**, 150–434.
- Orme, J., Mullin, C.S. and Ohanian, E.V. (1987). Health effects of disinfectants and disinfection by-products: a regularity perspective. In: *Water Chlorination: Chemistry, Environmental Impact and Health Effects*, Vol. 5. Ann Arbor Science.
- Parnell, M.J., Koller, L.D., Exon, J.H. and Arnzen, J.M. (1986). TCAA effects on rat liver peroxisomes and enzyme-altered foci. *Envir. Hlth Perspect.*, **69**, 73–79.
- Pourmoghaddas, H. and Dressman, R.C. (1992). Determination of nine haloacetic acids in finished drinking water. *Proc. Wat. Quality Technol. Conf.*, Toronto, Canada, pp. 447–464.
- Pourmoghaddas, H., Stevens, A.A., Kinman, R.N., Dressman, R.C., Moore, L.A. and Ireland, J.C. (1993). Effect of bromide ion on formation of HAAs during chlorination. *J. Am. Wat. Works Assoc.*, **85**, 82–87.
- Singer, P.C. and Chang, S.D. (1989). Correlation between trihalomethanes and total organic halides formed during water treatment. *J. Am. Works Assoc.*, **77**, 146–152.
- Standard Methods for the Examination of Water and Wastewater* (1985). 16th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

- Stevens, A.A., Dressman, R.C., Sorrel, R.K. and Brass, H.J. (1985). Organic halogen measurements: current uses and future prospects. *J. Am. Wat. Works Assoc.*, **77**, 146–152.
- Stevens, A.A., Moore, L.A., Slocum, C.J., Smith, B.L., Seeger, D.R. and Ireland, J.C. (1989). By-product of chlorination at ten operating utilities. In: *Water Chlorination: Chemistry, Environmental Impact and Health Effects*, Vol. 6, pp. 579–604. Ann Arbor Science.
- USEPA (1981). *Treatment Techniques for Controlling THMs in Drinking Water*. Municipal Environmental Res. Lab., Cincinnati, Ohio, USA.