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Investigating effects of bromide ions on trihalomethanes and developing model for predicting bromodichloromethane in drinking water

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ABSTRACT

Chlorination for drinking water can form brominated trihalomethanes (THMs) in the presence of bromide ions. Recent studies have reported that bromodichloromethane (BDCM) has a stronger association with stillbirths and neural tube defects than other THMs species. In this paper, the results of an experimental investigation into the factors forming THMs in the presence of bromide ions are presented. The experiments were conducted using synthetic water samples with different characteristics (e.g., pH, temperature, dissolve organic content). Different combinations of these characteristics were considered in the experimental program. The results showed that increased bromide ion concentrations led to increases in the formation of total THMs, with higher BDCM and dibromochloromethane (DBCM), and lower chloroform formation. By increasing the pH from 6 to 8.5, increased chloroform and decreased BDCM and DBCM formation were observed. Higher bromide ions to chlorine ratios increased BDCM and DBCM and decreased chloroform formation, while higher temperatures increased BDCM, DBCM and chloroform formation. In most cases, bromoform ($CHBr_3$) concentrations were found to be below the detection limit. Significant factors influencing BDCM formation were identified using a statistical analysis. A model for BDCM formation was estimated from 44 experiments and statistical adequacy was assessed using appropriate diagnostics, including residual plots and an R^2 of 0.97. The model was validated using external data from 17 water supply systems in Newfoundland, Canada. The predictive performance of the model was found to be excellent, and the resulting model could be used to predict BDCM formation in drinking water and to perform risk-cost balance analyses for best management practices.

1. Introduction

Chlorine is widely used in the municipal water supply systems in Canada and the USA due to its excellent disinfection performance and low cost (Clark et al., 1994, 1998; Reiff, 1995; USEPA, 2006; Chowdhury and Husain, 2006; Chowdhury et al., 2007; Health Canada, 2008). However, natural organic matter (NOM) in the water can react with chlorine during disinfection, forming disinfection byproducts (DBPs), such as trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), as well as other known and unknown compounds (Richardson, 2005). The possible effects

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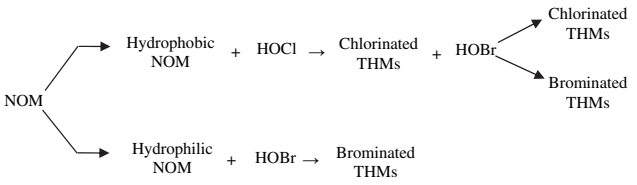

Fig. 1 – Possible formation pathways for brominated THMs in drinking water.

of THMs on animal and human health have been extensively studied from toxicological and epidemiological perspectives since their discovery in 1974 (King and Marrett, 1996; Wigle, 1998; Mills et al., 1998; Waller et al., 1998; King et al., 2000; Richardson et al., 2002; Dodds et al., 2004; Villanueva et al., 2004). More than 90% (87–98%) of the THMs in drinking water supplies across the Canadian provinces typically consist of $CHCl_3$ and BDCM, while BDCM alone contributes 2.1–14% of the THMs. The occurrences of BDCM often exceed the Canadian regulatory limit of 16 ppb (Health Canada, 2008). It has been reported that BDCM in drinking water has a much stronger association with stillbirths and low birth weights than the other THMs species (King et al., 2000). The BDCM targets human placental trophoblasts that produce a hormone which is required during pregnancy. A decrease in bioactive levels of this hormone can lead to adverse effects during pregnancy (Health Canada, 2007). Dodds and King (2001) reported an increased risk of neural tube defects from BDCM at exposure concentrations of 20 ppb or higher. Toxicological studies have characterized BDCM as a probable human carcinogen with a slope factor (upper bound lifetime probability of an individual developing cancer) of 0.062 (mg/kg/day)$^{-1}$ and a reference dose (maximum safe dose to human) of 0.02 mg/kg/day (IRIS, 2008).

The reaction pathways and factors influencing THMs formation are well established in the existing literature (Stevens et al., 1976; Minear and Morrow, 1983; Clark et al., 2001; Rodrigues et al., 2007; Chowdhury et al., 2008, 2009). To address the effects of bromide ion (Br^-) concentrations in water, a number of previous studies incorporated bromide ion in THMs formation model development (Minear and Morrow, 1983; Amy et al., 1987; Golfinopoulos et al., 1998; Westerhoff et al., 2000; Elshorbagy et al., 2000; Rodriguez et al., 2003; Lekkas and Nikolaou, 2004). Bromide ions form brominated THMs following complex reaction pathways during the chlorination of drinking water (Liang and Singer, 2003). Uyak and Toroz (2007) reported that Br^- produces hypobromous acid (HOBr) in chlorinated water, which is approximately 20 times more reactive with NOM than hypochlorous acid (HOCl). Increases in bromide ion concentrations gradually shift chlorinated THMs to mixed bromochloro THMs. As such, the bromide ions to chlorine ratio in water may be an important factor, which may describe the relative distributions of brominated and chlorinated THMs (Uyak and Toroz, 2007; Hellur-Grossman et al., 2001; Nokes et al., 1999). Further complexity arises due to the partial conversion of Br^- into brominated THMs (18–28%), which also depends on water pH, temperature and relative distributions of hydrophobic and hydrophilic fractions of NOM in water (Sohn et al., 2006; Liang

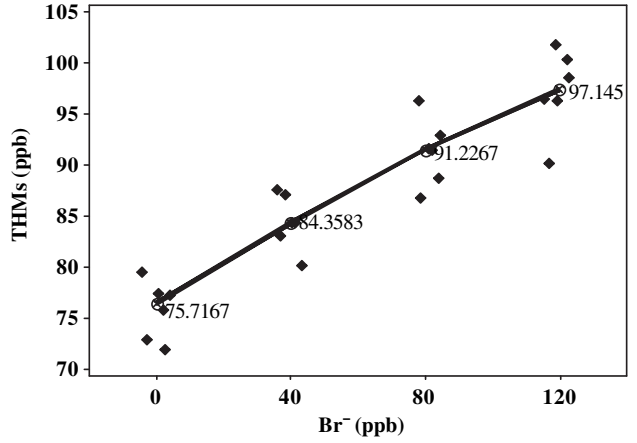

Fig. 2 – Effects of bromide ion on THMs formation (temperature = 8 °C, pH = 6, DOC = 3.0 mg/L; [SUVA = 6.34 L/mg m], chlorine dose = 4.05 mg/L, reaction time = 48 h).

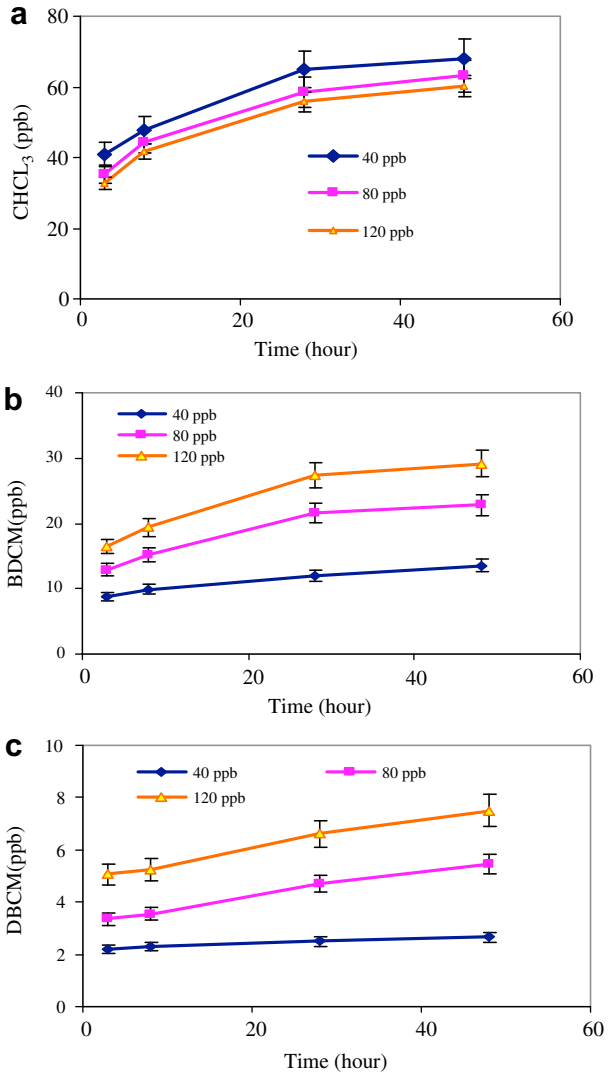

Fig. 3 – Effects of Br^- on $CHCl_3$, BDCM and DBCM (Cl_2 dose = 4.05 mg/L; pH = 6, DOC = 3.0 mg/L; [SUVA = 6.34 L/mg m], temperature = 8 °C).