

Trihalomethanes in drinking water: Effect of natural organic matter distribution

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Abstract

Effects of distribution of natural organic matter (NOM) on formation and distribution of trihalomethanes (THMs) in municipal water were investigated. Water samples were fractionated using serial ultrafiltration with membranes of molecular weight cut-off (MWCO) values of 500, 1 000 and 3 000 Da. The resulting 4 fractions of water with NOM of (i) < 500 Da; (ii) 500 Da – 1 kDa; (iii) 1 kDa – 3 kDa; and (iv) > 3 kDa were separated. Variable amounts of bromide ion (0, 40, 80, 120 and 200 µg/l) were added to these samples. The samples were chlorinated at pH of 6 and 8.5 and held at 20°C for various reaction periods (3, 8, 28, 48 and 96 h). The results demonstrate that the higher molecular weight NOM is strongly correlated with UV_{254} and specific ultraviolet absorbance (SUVA), while the lower molecular weight NOM is weakly correlated with UV_{254} and SUVA. Increase in bromide ion concentration increases total THM formation. Fractions of brominated THMs decrease with increasing NOM molecular size. Lower molecular weight NOM forms more brominated THMs than the corresponding higher molecular weight NOM. Increase of bromide to chlorine ratio decreases chloroform and increases brominated THMs. Increase in pH increases chloroform and decreases brominated THMs. This study demonstrates that the distribution of NOM and bromide ion can have important role on the distribution of THMs in drinking water.

Keywords: bromide ion, molecular weight distribution, natural organic matter, trihalomethane distribution

Introduction

The natural organic matter (NOM) and/or other inorganic substances in water react with chlorine and other disinfectants to produce disinfection byproducts (DBPs) in drinking water. Since their discovery in 1974, a number of DBPs, including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), halo ketones (HKs), nitrosamines and iodo-THMs have been investigated. DBPs are of potential concern as some have been noted to have associated cancer risks, as well as other acute and chronic effects on human health (Richardson et al., 2007, 2008; King et al., 2004; Health Canada, 2008; USEPA, 2006, 2009; Krasner et al., 2006). The regulated THMs consist of 4 compounds: chloroform ($CHCl_3$), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform ($CHBr_3$), some of which might be possible/probable human carcinogens (USEPA, 2009). However, in recent years, non-regulated THMs (e.g., iodo-THMs) have been reported in drinking water. Epidemiological studies have reported that brominated THMs in drinking water have a stronger association with stillbirths, low birth weights and neural tube defects than the chlorinated THMs (King et al., 2000, Dodds and King, 2001). Toxicological studies have characterised brominated THMs as more toxic than their chlorinated counterparts (USEPA, 2009). The brominated THMs, specifically, BDCM, target 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). THMs are regulated in many countries around the world (USEPA, 2006; Health Canada, 2008; WHO, 2008).

NOM is considered to be the main precursor for THM formation, with the molecular weight of NOM in source water typically varying between 500 Da and 5.5 kDa (MWH, 2005). Past studies have reported that differences in molecular weight of NOM can affect the type and distribution of THMs (Liang and Singer, 2003; Chowdhury et al., 2010). NOM particles with higher molecular weight are hydrophobic and composed of activated aromatic rings, phenolic hydroxyl groups and conjugated double bonds, while lower molecular weight NOM particles are hydrophilic and composed of aliphatic ketones and alcohols (Liang and Singer, 2003; Hellur-Grossman et al., 2001). The hydrophobic fractions of NOM exhibit higher specific ultraviolet absorbance (SUVA, defined as: $100 \times UV_{254} / DOC$); while the hydrophilic fractions of NOM exhibit lower SUVA (Liang and Singer, 2003; Hellur-Grossman et al., 2001; Chowdhury et al., 2010). The nature and molecular weight distributions of NOM largely depend on the sources and biogeochemical processes associated with carbon recycling in terrestrial and aquatic systems (Uyak and Toroz, 2007). Past studies have reported that NOM with higher molecular weight might be more reactive with chlorine, while NOM with lower molecular weight may be more reactive with bromide (Liang and Singer, 2003).

Natural water often contains bromide ions, while chlorination of bromide-containing waters can alter the reaction process and increases the fractions of brominated THMs in drinking water (Liang and Singer, 2003; Hellur-Grossman et al., 2001). An increase in brominated THMs can be attributed to the reactions of HOBr with lower molecular weight NOM and/or a shift of chlorinated THMs to brominated THMs (Uyak and Toroz, 2007; Chowdhury et al., 2010). Several factors, including bromide to chlorine ratio, pH, temperature and relative

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