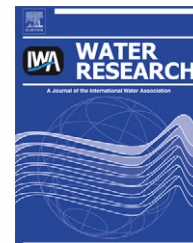




ELSEVIER

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Formation of haloacetic acids from dissolved organic matter fractions during chloramination

Ying Hong^{a,*}, Hocheol Song^b, Tanju Karanfil^{c,**}

^a Greater Cincinnati Water Works, 5651 Kellogg Ave., Cincinnati, OH 45230, USA

^b Department of Environment and Energy, Sejong University, 98 Gunja-dong, Gwnagjin-gu, Seoul 143-747, Republic of Korea

^c Department of Environmental Engineering and Earth Sciences, Clemson University, Anderson, SC 29625, USA

ARTICLE INFO

Article history:

Received 5 August 2012

Received in revised form

14 November 2012

Accepted 18 November 2012

Available online 30 November 2012

Keywords:

Haloacetic acid

DOM fractions

Chloramine

pH

Bromide

SUVA

ABSTRACT

The objective of this study was to investigate the roles of dissolved organic matter (DOM) fractions, pH and bromide concentration in the formation of haloacetic acids (HAA) during chloramination. DOM from two surface waters with a low (2.9 L/mg-m) and high (5.1 L/mg-m) specific UV absorbance (SUVA₂₅₄) values was isolated and fractionated into three fractions based on the hydrophobicity [i.e., hydrophobic (HPO), transphilic (TPH) and hydrophilic (HPI)]. DOM mass balances and DBP reactivity checks were performed to characterize the effects of isolation and fractionation steps. The fractions were chloraminated at three pHs and three bromide concentrations. The results showed that pH was the most important factor controlling HAA formation and speciation. The HAA yields significantly decreased with increase in pH from 6.3 to 9.0. The impact of bromide in the formation of brominated HAA species also became less important with increasing pH, and no brominated specie was detectable at pH 9. HPO fractions of the two source waters consistently showed higher HAA yields than TPH and HPI fractions. On the other hand, HPI fractions showed higher bromine incorporation than HPO and TPH fractions. To maintain higher and relatively stable combined chlorine residuals while reducing HAA formation, water utilities may consider keeping pH above 7.5 as one strategy. This will also lower the formation of brominated HAA species which have been shown to be more cyto- and genotoxic than their chlorinated analogs.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction and objectives

Trihalomethanes (THM) and haloacetic acids (HAA) are the two major classes of disinfection by-products (DBPs) found in waters disinfected with free chlorine. Due to their potential health risks, the United States Environmental Protection Agency (USEPA) has been imposing increasingly stringent regulations for DBPs under Disinfectants/Disinfection Byproducts Rule (D/DBPR). The Stage 2 of the D/DBPR

promulgated on January 6, 2006 requires utilities to comply with the maximum contaminant levels (MCLs) of THM and HAA5 at 80 and 60 µg/L, respectively, for the running annual average at individual locations in a distribution system (USEPA, 2006). To comply with these DBP regulations, drinking water utilities in the United States (US) have been considering various treatment and disinfection strategies. Chloramination, using preformed chloramines, suppresses THM formation almost completely, while reducing HAA concentrations to

* Corresponding author.

** Corresponding author. Tel.: +1 864 656 1005; fax: +1 864 656 0672.

E-mail addresses: hongying1@yahoo.com (Y. Hong), tkaranf@clemson.edu (T. Karanfil).

0043-1354/\$ – see front matter © 2012 Elsevier Ltd. All rights reserved.

<http://dx.doi.org/10.1016/j.watres.2012.11.025>

3–30% of the levels observed during chlorination (Long et al., 1992; Cowman and Singer, 1996; Symons et al., 1998; Zhang et al., 2000; Hong et al., 2007). Chloramination has received increased attention during the last decade in the US. A 2005 survey of 363 drinking water utilities across all 50 states showed that 68 and 29% of utilities use chlorine and chloramines as secondary disinfectant, respectively (Seidel et al., 2005). Although regulated carbonaceous DBP (C-DBP) formation is significantly suppressed during chloramination, the formation of some unregulated nitrogenous DBPs (N-DBPs) [e.g., N-Nitrosodimethylamine (NDMA) and Haloacetonitriles (HAN)] may increase. It has been shown that N-DBPs exhibit orders of magnitude higher cyto- and geno-toxicity than any of the regulated C-DBPs (Plewa and Wagner, 2008).

The dissolved organic matter (DOM) in natural waters serves as major precursors in the formation of many DBPs. In order to examine the reactions between DOM and various disinfectants, different approaches have been employed. Due to its heterogeneous nature, fractionation of DOM into more homogenous components facilitates its characterization and understanding the reactivity of its different components with disinfectants. The most commonly used technique is a resin fractionation procedure developed to separate DOM components according to their hydrophobicity. This technique, initially developed by Thurman and Malcolm (1981) and Leenheer (1981), fractionates the DOM components into more structural-specific and more physicochemically-analogous subgroups. Although its different modified versions have been introduced in the past three decades, the technique mainly involves adsorption of the hydrophobic DOM components (HPO fraction) onto XAD-8 resin, and relatively hydrophilic components, known as the transphilic (TPH) fraction, from the XAD-8 effluent onto XAD-4 resin, and collection of the most hydrophilic or non-adsorbing components (HPI fraction) at the XAD-4 effluent. The transphilic term is used to describe components of an intermediate polarity between HPO and HPI fractions. If desired, each fraction can be further separated into its corresponding acid, base, and neutral sub-fractions. Several studies have reported a good correlation between specific ultraviolet absorbance ($SUVA_{254}$, see [Supplementary Information](#)) of DOM fractions and HAA formation during chlorination (Reckhow et al., 1990; Najm et al., 1994; Krasner et al., 1996; Croue et al., 2000; Kitis et al., 2002; Liang and Singer, 2003). It has been shown that HPO fractions with high $SUVA_{254}$ values had the higher HAA formation than HPI fractions with low $SUVA_{254}$ values. However, a poor correlation between dichloroacetic acid (DCAA) formation potential and $SUVA_{254}$ of the fractions was also reported for two surface waters (Croue et al., 2000). The authors suggested that organic structure (e.g., proteins) other than aromatics might be responsible for the production of DCAA during chlorination.

Although literature is rich in terms of THM and HAA formation from different DOM fractions during chlorination, only a few studies have provided information about HAA reactivity of DOM fractions during chloramination. Furthermore, DOM mass balances and DBP reactivity checks of DOM fractions with the raw waters are usually absent in many previous studies. Duirk et al. (2005), Duirk and Valentine (2006) developed a model to predict monochloramine loss and DCAA

formation by examining six dissolved organic matter sources, three natural waters and three fractions from two rivers. The model uses a DCAA formation coefficient to describe DCAA concentration over a wide range of experiment conditions. It was reported that the DCAA formation coefficients of the six DOM sources were linearly correlated with $SUVA_{280}$. Duirk's work focused mainly on the model development and limited studies have been performed with DOM fractions and their reactivity toward HAA formation. In addition, no HPI fraction was examined. Speitel et al. (2004) reported that waters after conventional treatment processes always had lower dihaloacetic acid (DXAA) reactivity than the source waters during chloramination, indicating that HAA precursors were hydrophobic in character. Hua and Reckhow (2007) fractionated three surface waters, and the chloramination result showed that HPO and TPH fractions were more reactive to form DXAA than HPI fractions in a water with high $SUVA_{254}$ (4.4 L/mg-m), while in other two low $SUVA_{254}$ waters (2.8 and 1.6 L/mg-m), the DXAA reactivity were similar for all three fractions. In contrast, Hwang et al. (2000) studied Colorado River water, a low $SUVA_{254}$ water (1.6 L/mg-m), and showed that the yields of DXAA from hydrophilic acid and neutral fraction were almost three times higher than that from hydrophobic acid during chloramination. The authors explained their observations using the model proposed by Reckhow and Singer (1985), which suggested that high content of ketoacids ($R'-CO-CH_2-COOH$) in low $SUVA_{254}$ waters favored formation of DXAA.

With increasing popularity of chloramination in the US and limited studies regarding the contribution of different DOM components to HAA formation during chloramination, the objective of this study was to systematically investigate the formation and speciation of HAA from DOM components in two surface waters, one with low $SUVA_{254}$ and one with high $SUVA_{254}$, during chloramination. The DOM components from each water source were carefully isolated using a pilot reverse osmosis (RO) system and subsequently separated into three fractions (HPO, TPH and HPI) using XAD-8 and XAD-4 resins. DOM mass balances and DBP reactivity checks were performed to characterize the effects of isolation and fractionation steps. The formation of HAA from each fraction during chloramination was examined. The roles of pH and bromide on HAA formation were studied due to their practical significance for water treatment operations. Kinetics experiments were conducted to gain some insight to the formation of HAA from different DOM fractions as a function of time. Most of the HAA formation results for chloramination in the literature are for 24 h or longer time periods. Furthermore, some of the available kinetics data are not reliable due to the type of quenching agent used in the experiments (Hong et al., 2008). However, modeling of the kinetics data was beyond the scope of the study.

2. Material and methods

2.1. RO isolation of DOM

Two DOM solutions were collected from the influents of two drinking water treatment plants in South Carolina, Greenville

Download English Version:

<https://daneshyari.com/en/article/6367375>

Download Persian Version:

<https://daneshyari.com/article/6367375>

[Daneshyari.com](https://daneshyari.com)