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Modeling bromide effects on yields and speciation of dihaloacetonitriles formed in chlorinated drinking water

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ABSTRACT

This study examined effects of bromide on yields and speciation of dihaloacetonitrile (DHAN) species that included dichloro-, bromochloro- and dibromoacetonitriles generated in chlorinated water. Experimental data obtained using two water sources, varying concentrations and characters of Natural Organic Matter (NOM), bromide concentrations, reaction times, chlorine doses, temperatures and pHs were interpreted using a semi-phenomenological model that assumed the presence of three kinetically distinct sites in NOM (denoted as sites S_1, S_2 and S_3) and the occurrence of sequential incorporation of bromine and chlorine into them. One site was found to react very fast with the chlorine and bromine but its contribution in the DHAN generation was very low. The site with the highest contribution to the yield of DHAN (>70%) has the lowest reaction rates. The model introduced dimensionless coefficients (denoted as φ_1^{DHAN}, φ_2^{DHAN} and φ_3^{DHAN}) applicable to the initial DHAN generation sites and their monochlorinated and monobrominated products, respectively. These parameters were used to quantify the kinetic preference to bromine incorporation over that of chlorine. Values of these coefficients optimized for DHAN formation were indicative of the strongly preferential incorporation of bromine into the engaged NOM sites. The same set of φ_i^{DHAN} coefficients could be used to model the speciation of DHAN released from their kinetically different precursors. The dimensionless speciation coefficients φ_i^{DHAN} were determined to be site specific and dependent on the NOM content and character as well as pH. The presented model of DHAN formation and speciation can help quantify in more detail the generation of DHAN and provide more insight necessary for further assessment of their potential health effects.

1. Introduction

Disinfection of drinking water by chlorine has dramatically reduced the transmission of potentially fatal waterborne diseases. While from its very inception chlorination was – and remains – one of the most efficient public health measures ever undertaken, it has deficiencies such as its limited efficiency in deactivating *Giardia lamblia* and *Cryptosporidium* and also the generation of harmful disinfection by-products (DBPs). DBPs are generated in the reactions between chlorine

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and natural organic matter (NOM) present in all source surface waters and/or effluent organic matter occurring in wastewater-impacted water sources (Sedlak and von Gunten, 2011; Krasner et al., 2009).

The concentration and reactivity of NOM play a major role in DBP formation (Reckhow et al., 1990; Leenheer and Croue, 2003). Other water quality parameters (e.g., pH, temperature, concentrations of ammonia, bromide and iodide) also impact concentrations and speciation of DBPs (Cowman and Singer, 1996; Hua et al., 2006; Obolensky and Singer, 2008). Bromide is of particular interest and importance for DBP control since it greatly increases yields of brominated DBPs (Chang et al., 2001; Hong et al., 2007) which are more toxic than their chlorinated analogues (Richardson et al., 2007; Zhang et al., 2012).

Among the identified DBPs, THMs and HAAs occur at the highest concentrations (up several hundred μg/L) in chlorinated water. The next tier of DBPs includes haloacetonitriles (HANs) (Richardson et al., 2007; Bond et al., 2011) whose concentrations may exceed 10 μg/L. Examination of HAN formation in drinking waters shows that concentrations of dihaloacetonitriles (DHAN) such as dichloro-, bromochloro- and dibromoacetonitrile (DCAN, BCAN and DBAN, respectively) tend to be much higher than those of trihaloacetonitriles and monohaloacetonitriles, and that the contributions of DCAN, BCAN and DBAN and other N-DBPs are sensitive to bromide concentrations (Chen and Westerhoff, 2010; Hu et al., 2010; Chang et al., 2011; Chu et al., 2011; Yang et al., 2011). The generation of DHAN species and other N-DBPs has been shown to involve predominantly amine nitrogen associated with practically all NOM fractions, with contributions of hydrophilic NOM fractions of primarily autochthonous origin in N-DBP yields being more prominent than those of humic fractions (Dotson et al., 2009; Chu et al., 2010; Fang et al., 2010; Yang et al., 2010, 2011; Shah and Mitch, 2012). Despite the association of N-DBPs with a limited set of NOM functionalities, concentrations of DHAN in chlorinated water tend to be correlated with those of HAAs and THMs (Goslan et al., 2009; Chu et al., 2011; Chen and Westerhoff, 2010; Bond et al., 2011).

In general, nitrogenous DBPs tend to be more cytotoxic and genotoxic than carbonaceous DBPs (Muellner et al., 2007; Richardson et al., 2007). Mutagenic and carcinogenic effects of HANs have been observed in *in vivo* and *in vitro* tests and, as observed for THMs and HAAs, brominated HANs have been observed to cause more prominent adverse effects than the homologous chlorinated HANs (Muller-Pillet et al., 2000; Zhang et al., 2012).

Given the wide occurrence of HANs, their relatively high concentrations and health effects potentially associated with them, mechanisms governing HAN formation and speciation in the presence of varying bromide levels need to be elucidated in more detail. Considerable effort has been invested in elucidating bromide effects on THM and HAA formation (Ichihashi et al., 1999; Nokes et al., 1999; Westerhoff et al., 2004; Obolensky and Singer, 2005; Fabbricino and Korshin, 2009; Francis et al., 2010; Hua and Reckhow, 2012). Recently, effects of bromide on the formation of newly identified individual DBPs have also been reported (Pan and Zhang, 2013). However, no mechanistic model of bromide effects on HAN speciation has yet been developed.

Prior research has demonstrated that the influence of bromide on the speciation of THM, HAA and other selected DBP groups can be interpreted and modeled with high precision based on two major *a priori* assumptions (Cowman and Singer, 1996; Nokes et al., 1999; Gallard and von Gunten, 2002; Fabbricino and Korshin, 2009; Pan and Zhang, 2013). These studies employed the notion that relative yields of products of NOM bromination over those of chlorination are ultimately defined by the ratios of the intrinsic rates of reactions between any reactive site in NOM and, on the other hand, bromine and chlorine species. The second assumption postulates that mono-, di- and trihalogenated DBPs are released from their precursors formed via the sequential incorporation of halogen atoms into the NOM reactive sites. Interpretation of these assumptions results in relatively complex yet unambiguous mathematical speciation formulas defining relative contributions of THM and HAA compounds with the number of bromine atoms in them ranging from zero to three (Cowman and Singer, 1996; Nokes et al., 1999).

These formulas will be presented and discussed in more details in the sections that follow. Suffice it to mention here that while they define *relative* contributions of brominated THMs and HAAs into their total yields, they do not *per se* describe the effects of bromide on the kinetics and yields of brominated THMs and HAAs. Numerous prior studies that utilize both statistical and mechanistic approaches demonstrate that the kinetics of DBP formation is affected by a variety of physico-chemical water chemistry parameters and NOM concentration and reactivity (Sohn et al., 2004; Sadiq and Rodriguez, 2004; Obolensky Chowdhury et al., 2009). These studies also show that mechanistic modeling of THM and HAA formation is possible only assuming the existence of at least two kinetically distinct reactive sites in any NOM (McClellan et al., 2000; Gallard and von Gunten, 2002; Korshin et al., 2007; Fabbricino and Korshin, 2009) that have widely different apparent rates of reaction with chlorine and bromine.

While these facts have been firmly established for HAAs and THMs, their existence has not been sufficiently well ascertained for DHAN species. In this study, the principles outlined above were applied to examine and unambiguously quantitate the formation of DHAN. Specific objectives of this study were to interpret the formation of DCAN, BCAN and DBAN based on the kinetic analysis of DHAN data, to develop and apply a model which assumes the presence of kinetically distinct sites in NOM in order to better understand the mechanism of formation and speciation of DHAN and ultimately other groups of DBPs.

2. Materials and methods

Chlorination experiments were carried using Lake Washington (LW) water (Seattle, USA) and raw and treated Lake Ancipa water (Sicily, Italy). Samples of Ancipa raw water (Ancipa Inlet) and treated water (Ancipa Outlet) were collected at the Ancipa Water Treatment Plant (WTP). In order to use waters with different NOM content and reactivity, Ancipa Inlet and Outlet waters were fractionated and the effluents from the XAD-8/XAD-4 columns were used for chlorination along with the unfractionated samples. Other details on the fractionation