Use of multiple regression models to evaluate the formation of halonitromethane via chlorination/chloramination of water from Tai Lake and the Qiantang River, China

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HIGHLIGHTS

- The established models could well describe the HNMs formation.
- DON did not play significant role in HNMs formation in chloramination.
- NO_2^- did not raise the HNMs yields significantly in chlorination of NOM with low SUVA.
- Factors affecting the bromine incorporation factors (BIF) for HNMs were evaluated.

ARTICLE INFO

ABSTRACT

The deterioration of water quality, especially organic pollution in Tai Lake and the Qiantang River, have recently received attention in China. The objectives of this study were to evaluate the formation of halonitromethanes (HNMs) using multiple regression models for chlorination and chloramination and to identify the key factors that influence the formation of HNMs in Tai Lake and the Qiantang River. The results showed that the total formation of HNMs (T-HNMs) during chlorination and chloramination could be described using the following models: (1) $\text{T-HNM}_{Cl_2} = (10)^{5.267}(DON)^{6.645}(Br^-)^{0.737}(DOC)^{-5.537}(Cl_2)^{0.333}(t)^{0.165}$ ($R^2 = 0.974$, $p < 0.01$, $n = 33$), and (2) $\text{T-HNM}_{NH2Cl} = (10)^{-2.481}(Cl_2)^{0.451}(NO_2^-)^{0.382}(Br^-)^{0.630}(t)^{0.640}(Temp)^{0.581}$ ($R^2 = 0.961$, $p < 0.05$, $n = 33$), respectively. The key factors that influenced the T-HNM yields during chlorination were dissolved organic nitrogen (DON), bromide and dissolved organic carbon (DOC). The nitrite and bromide concentrations and the reaction time mainly affected the T-HNM yields during chloramination. Additional analysis indicated that the bromine incorporation factors (BIFs) for tri-halogenated HNMs generally decreased as the chlorine/chloramine dose, temperature and reaction time decreased and increased as the bromide concentration increased.

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1. Introduction

Disinfection byproducts (DBPs) have become an important hidden danger in drinking water safety due to their potential carcinogenicity and reproductive toxicity (WHO, 2000). To date, over 600 DBP species have been identified in tap water, yet only a small fraction of them are regulated, including trihalomethanes (THMs) and haloacetic acids (HAAs) (Richardson et al., 2007). Among the unregulated DBPs, halonitromethanes (HNMs) have received special attention due to their high toxicity and frequent occurrence in finished water (Plewa et al., 2004; Krasner et al., 2006).

Overall, nine species of HNMs exist: chloro-(CNM), dichloro-(DCNM), trichloro-(TCNM), bromo-(BNM), dibromo-(DBNM), tribromo-(TBNM), bromochloro-(BCNM), bromodichloro-(BDCNM) and dibromochloronitromethane (DBCNM). Toxicological studies have shown that HNMs are among the most cyto- and genotoxic of the identified DBPs (Plewa et al., 2004, 2008). Although the levels of HNMs in drinking water (ND-10 μg/L) were lower than the levels of THMs (4–164 μg/L) and HAAs (5–130 μg/L), the health risks posed by HNMs are comparable or even greater than those of the two regulated DBPs (Krasner et al., 2006; Plewa et al., 2008; Hong et al., 2013). Currently, additional research efforts are being directed towards improving our understanding of the formation of HNMs.

HNMs can be formed from chlorination and chloramination processes, especially for water subjected to pre-ozonation (Hu et al., 2010a,b). Similar to THMs and HAAs, the formation of HNM varies with the quality of the source water and the disinfectant conditions. Generally, water with high organic nitrogen concentrations or low SUVA$_{254}$ (specific ultraviolet absorbance at 254 nm) values will result in the high formation of HNMs (Song et al., 2010; Hu et al., 2010a). In addition, high doses of disinfectants such as chlorine and chloramine, long reaction times and high bromide concentrations will increase the HNM yields (Hu et al., 2010b; Hong et al., 2013). In the chlorination process, the formation of HNMs may increase as the pH of the water increases. However, during the chloramination process, the opposite trend may occur (Hong et al., 2013). Despite this knowledge, few studies have been conducted to identify the key factors that influence the formation of HNMs.

HNM monitoring in drinking water involves costly HNM standards and expensive instruments and is generally time consuming (Hu et al., 2010a,b; Huang et al., 2013). Theoretically, the regression models of the HNMs may be used for evaluating the formation of HNMs. This method is also effective for identifying the key factors that influence the formation of HNMs (Hong et al., 2007). However, the available references regarding the use of regression models on DBPs have mainly focused on THMs and HAAs (Sadiq and Rodriguez, 2004; Hong et al., 2007; Chen and Westerhoff, 2010), with few articles on haloacetonitriles (HANs) or nitrosodimethylamine (NDMA) (Chen and Westerhoff, 2010). Furthermore, to our knowledge, no studies have been reported for HNMs. In addition, the formation of DBPs may vary with location due to different source water qualities and diverse water treatment conditions (Hong et al., 2007). Therefore, it is important to develop HNM regression models for specific districts to guide decision making and minimize the formation of HNMs during water treatment.

Tai Lake and Qiantang River are two of the most important drinking water sources in the Yangtze River delta of China. Tai Lake is located on the borders of Jiangsu and Zhejiang provinces, which cover an area of 2340 km^2 and supply potable water for the surrounding cities. The Qiantang River obtains water from Kaihua County in Zhejiang Province (i.e., the Qianjiang source), and supplies drinking water to approximately 100 million people along the river (Dong et al., 2012). However, the water quality deterioration of these two water sources is a public concern. Cyanobacteria blooms have been observed in Tai Lake for over a decade. These blooms produced algal toxins and yield large amounts of dissolved organic matter after the peak algal bloom (Ye et al., 2011). Because algae-derived organic matter is hydrophilic in nature and abundant in organic nitrogen, the water from Tai Lake may contain potent HNMs precursors (Wetzel and Likens, 2001; Nguyen et al., 2005; Hu et al., 2010a). Regarding the Qiantang River, the data that were obtained by monitoring in 2004–2010 (Dong et al., 2012) indicated that the water quality generally belonged to classes III–IV according to the GB3838-2002 standard of China (State Environmental Protection Administration of China, 2002a,b), and the water was considered unsuitable for a drinking water source. The ammonia, total phosphorus, fecal coliform and organic pollutants were the main factors responsible for the deterioration of the water quality in the Qiantang River (Dong et al., 2012). Thus, the formation of HNMs in the Qiantang River and Tai Lake are of concern. However, no related information is currently available.

Considering the above information, a series of laboratory disinfection experiments (chlorination and chloramination) were conducted using water from Tai Lake and the Qiantang River. Multiple regression models were established for evaluating the formation of HNMs, and the key factors that affected the HNMs yields were identified. In addition, due to the higher toxicity of the brominated HNMs relative to the chlorinated HNMs, the factors that influenced the bromine incorporation factors (BIF) of the HNMs were evaluated.

2. Materials and methods

2.1. Field sampling

The sampling site at Tai Lake was selected at the water intake of Gonghu Water Works (short for Gonghu). The sampling sites of the Qiantang River included the (1) Qianjiang source, upstream of the Qiantang River in Kaihua County and with little human activity; (2) water intake of the Jiuxi Water works (short for Jiuxi), which is located downstream of the Qiantang River in Hangzhou City and is subjected to a great deal of human activity.

Field sampling was conducted in November 2011. The glassware that was used for sampling was washed with detergent and tap water, presoaked in 15% sulfuric acid for 24 h, and rinsed with Milli-Q water. Water samples were collected without headspace at a depth of approximately 0.1–0.5 m below the water surface using several plain glass bottles (each having a 5-L capacity). After collection, the bottles were covered with ground glass stoppers and immediately wrapped with black plastic bags. In addition, the water samples that were analyzed for total nitrogen and ammonia analysis were collected separately and adjusted to pH < 2 with H$_2$SO$_4$. All of the water samples (Gonghu: ≈21 L; Jiuxi: ≈21 L; Qianjiang source: ≈6 L) were transported to the laboratory in coolers on the day they were collected.

2.2. Analysis of water quality parameters

The raw water samples were filtered through pre-weighed GC/F filters (pore size = 0.45 μm). The particles that were retained on the filter were dried at 105 °C until a constant weight was achieved, and the difference between the filter weights before and after filtration was calculated to determine the total suspended solids (TSS) content (APHA, 1998). Next, the filtrate was used to determine the dissolved organic carbon (DOC, using an ELEMENTAR Liqui TOCII TOC analyzer), UV$_{254}$ (UV absorbance at 254 nm, using a Shimadzu UV-1601 UV–visible spectrophotometer), TDN (total dissolved nitrogen, by the K$_2$S$_2$O$_8$ digestion method), NH$_4^+$ (using the salicylic acid–hypochlorous acid colorimetric method), NO$_2^-$ (using the n-(1-naphthyl)-ethylenediamine dihydrochloride colorimetric method), NO$_3^-$ and Br$^-$ (using Dionex ICS-2100 ion chromatography). The DON (total dissolved organic nitrogen) and SUVA$_{254}$ were calculated using the following equations: DON = TDN − NH$_4^+$ − NO$_2^-$ − NO$_3^-$ and SUVA$_{254}$ = UV$_{254}$ × 100/DOC. All of the above parameters were detected according to Standard Methods (APHA, 1998; State Environmental Protection Administration of China, 2002).

Water samples for the chlorophyll a (Chl a) measurements were stored in one-liter bottles that were wrapped with black plastic bags and preserved by adding 3–5 ml of 1% saturated magnesium carbonate. The water samples were filtered through GC/F filters (pore size = 0.45 μm). Next, the filters and the retentate were extracted with 95% ethanol and examined using a UV–visible spectrophotometer according to the following equation (Wintermans and De Mots, 1965):

$$\text{Chl a} = [13:7(A_{665} - A_{750}) - 5.76(A_{649} - A_{750})] \times E/F \times l$$

where E = extraction volume in mL; F = filtration volume in L; l = cuvette path length in cm; and Ax = absorbance at a wavelength of x nm.