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Disinfection by-products formation and precursors transformation during chlorination and chloramination of highly-polluted source water: Significance of ammonia

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ABSTRACT

Many studies have demonstrated the different trends of disinfection by-products (DBPs) formation between chlorination and chloramination. However, the reactions between precursors and disinfectants are widely assumed to be “black box” and the reasons for abovementioned difference are not well illustrated. This study focused on source water with high levels of natural organic matter (NOM) and bromide, and compared the transformation of NOM specific characteristics and the ratios of specific DBPs as an equivalent of chlorine to total organic halogen (TOX) among three disinfection scenarios of chlorination, chloramination and chlorine–chloramine sequential treatment (Cl_2–NH_2Cl process). A three-reaction-phrases model was proposed thereafter to illustrate the major reactions involved in, i.e., stage-I: rapid consumption of fast reactive sites (DOC_1), which transformed to slow reactive sites (DOC_2) and measured DBPs, i.e., trihalomethanes, haloacetic acids, etc; stage-II: oxidation and/or halogenation of DOC_2 into unknown TOX (UTOX) intermediates; stage-III: oxidation of UTOX intermediates into measured DBPs. The effect of ammonia was also quantified. Ammonia is observed to inhibit the formation of measured DBPs by 68–92%, 94–99%, and 92–95% of that in chlorination in Stage-I, II, and III, respectively, and the formation of UTOX is reduced by 2–80%, 60–94%, and 82–93% accordingly. These effects lead to the steady accumulation of DBPs intermediates such as UTOX, and to the elevated UTOX/TOX during chloramination and Cl_2–NH_2Cl process thereafter. The results illustrate the mechanism of ammonia participating in DBPs formation, and are valuable to fill in the gap between the transformation of precursors and the formation of different DBPs.

1. Introduction

The formation of disinfection by-products (DBPs) arises global concerns on the safety of chlorination (Rook, 1974), and other alternative disinfectants such as monochloramine are proposed (Seidel et al., 2005) to control the formation of chlorinated DBPs and their carcinogenicity, teratogenicity and mutagenicity (Harvey, 2011). However, chloramination has

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been reported to generate higher levels of nitrogenous DBPs (N-DBPs) than chlorination (Shah and Mitch, 2012). In addition, the species distribution of the formed DBPs, which contributes to the total organic halogen (TOX), also differs greatly between chlorination and chloramination (Goslan et al., 2009). Chloramination forms larger proportion of unknown TOX (UTOX) (Hua and Reckhow, 2007b; Kristiana et al., 2009) than chlorination does. Furthermore, during chloramination the formation of dihalogenated haloacetic acids (HAAs) is significant whereas that of trihalomethanes (THMs) and other HAAs species is in extraordinarily low levels (Goslan et al., 2009; Hua and Reckhow, 2007b; Lu et al., 2009).

On the other hand, chlorine–chloramine sequential treatment (Cl_2–NH_2Cl process) is often used to balance the goals of bacteria inactivation and DBPs formation control (Chen et al., 2007). In this process, the subsequently formed NH_2Cl reacts to the intermediates rather than the origins of the DBPs precursors and the formation of DBPs shows critical difference from either chlorination or chloramination. In our previous study, Cl_2–NH_2Cl process was observed to form higher levels of N-DBPs than chlorination and chloramination, and the bromide incorporation factors of HAAs and THMs were also the highest (Tian et al., 2013). Although many previous studies have reported the DBPs difference between chlorination and chloramination, the reason for the DBPs diversity between chlorination and chloramination is far to be well illustrated.

Natural organic matter (NOM), which is dominated by humic acid (HA) (Li et al., 2011), is viewed as one of the major DBPs precursors (Richardson et al., 2007). The characteristics of NOM are intrinsically complex and the reactions involved in chlorination, chloramination, and Cl_2–NH_2Cl process are multistep and branching (Rook, 1977). The disinfectants decay with prolonged contact times, owing to their interactions with not only the original NOM species (NOM_0) but also the NOM oxidation intermediates (NOM_1 to NOM_n) (Li et al., 2000).

$$NOM_0 \overset{Cl_2/NH_2Cl}{\rightarrow} NOM_1 \overset{Cl_2/NH_2Cl}{\rightarrow} NOM_2 \rightarrow \cdots\cdots \rightarrow NOM_n$$

In addition, bromide is widely present in the natural source water and can be oxidized in chlorination to be HOBr, which shows stronger halogenating activity than HOCl does (Sun et al., 2009). HOBr promotes the formation of brominated DBPs (Br-DBPs) with higher health risks than their chlorinated analogs (Zhang et al., 2000). In chloramination, NH_2Cl can react with Br^-/HOBr to form NH_2Br, NHClBr, and $NHBr_2$ (Bousher et al., 1989), which further complicates the reactions between NOM and disinfectants.

The complicate reaction pathways make it extremely difficult and unrealistic to figure out the exact transformation of NOM characters and to illustrate the reactions involved in three aforementioned disinfection scenarios. Therefore, many studies took the disinfectant process as "black box" from the input of "precursors + disinfectants" to the output of "cleavage by-products, i.e., THMs and HAAs" (Bougeard et al., 2010; Goslan et al., 2009). The mechanistic gap between precursors transformation and DBPs formation inhibits us the understanding of the disinfection process, and the proposing of feasible strategy to control the formation of DBPs. Therefore, the improved understanding of the significance of ammonia and the mechanism involved in chlorination and chloramination is valuable.

To overcome the abovementioned difficulty, the use of simple and feasible surrogate parameters of different techniques of ultraviolet (UV) absorbance spectroscopy, fluorescence spectroscopy, and high pressure size exclusion chromatography (HPSEC) have been proposed to characterize the transformation of NOM (Matilainen et al., 2011). These methods exhibit the advantages of small injection volume, little or no need for pre-treatment, and high speed of analyzing (Matilainen et al., 2011). There have been previous studies using these surrogate parameters to characterize the NOM and to predict of the formation of DBPs in a specified disinfection strategy (Matilainen et al., 2011; Roccaro and Vagliasindi, 2009; Yang et al., 2008). However, rare studies use these surrogate parameters to indicate the different trends of NOM transformation and DBPs formation, and to illustrate the different mechanisms involved in among abovementioned different disinfection scenarios.

This study focus on source water with high levels of NOM and bromide, and aims to: (1) compare the transformation of NOM specific characteristic and the formation of main DBPs during the three disinfection scenarios of chlorination, chloramination, and Cl_2–NH_2Cl process; (2) illustrate the relationship between the transformation of NOM specific characteristic and the formation of DBPs; (3) illustrate the effect of ammonia on the transformation of NOM specific characteristic and the formation of DBPs; (4) propose the pathways of NOM specific properties transformation and DBPs formation during three aforementioned disinfection scenarios and to quantify the significance of ammonia in DBPs formation thereafter.

2. Materials and methods

2.1. Materials and reagents

Natural surface waters were collected from LuWen drinking water treatment plant (DWTP) intake, which uses Weishan Lake as a source. The source water was with high level of NOM (NPOC = 6.2 mg/L) and bromide (0.16 mg/L). The main properties of the source water and the treatment process of Luwen DWTP were provided in Table S1. Raw water samples were collected in 25 L glass bottles container and then delivered to laboratory without pretreatment. The samples were then filtered through a 0.45-μm membrane, stored at 4 °C to minimize the changes of character. The reasons for choosing raw water as precursor are provided in Supporting information.

HA was brought from Aldrich (lot no. 1430030), and the stock solution of which was prepared by diluting 1.5 g of commercially HA into 500 mL of 0.1 mmol/L sodium hydroxide. After constant stirring for 24 h in darkness, the solution was filtered through 0.45 μm glass fiber membrane filters and then stored in the dark at 4 °C. The Aldrich HA was characterized in our previous study (Li et al., 2011).

Unless otherwise noted, all reagents used in experimental tests were of reagent grade. Chlorine stock solution used for disinfection was prepared from 10% sodium hypochlorite (NaClO) solution (m/v) and stored in aluminum foil-covered glass stopped flask. Monochloramine solution was freshly