



Effects of bromide on the formation and transformation of disinfection by-products during chlorination and chloramination

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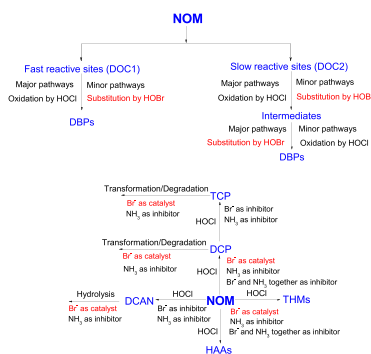
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HIGHLIGHTS

- Effect of Br⁻ on different stages of DBPs formation in chlorination and chloramination is investigated
- The latter Br⁻ introduced, more significant formation of THMs and HAAs during chlorination
- Br⁻ inhibits DCAN and TCP formation by catalytic degradation in both processes
- Br⁻ promotes oxidation of reactive DOC₁ and slow-reactive DOC₂ by buffering effect

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of bromide ion (Br⁻) complicates the formation of disinfection by-products (DBPs) during chlorination and chloramination greatly. To better illustrate the role of Br⁻, Br⁻ was introduced at different time intervals, i.e., 0 min, 5 min, 30 min, and 24 h, after dosing with chlorine (Cl₂) or chloramine (NH₂Cl), and the formation of trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles, and haloacetones was investigated during these two disinfection scenarios. Ammonia rapidly reacts with chlorine and forms low-reactivity NH₂Cl, and this effect inhibits the formation of these DBPs greatly. Br⁻ promotes the formation of THMs, HAAs, and dichloroacetone (DCP) during chlorination, and the later bromide is introduced, i.e., the higher T_{Cl₂ → Br⁻} is, the more significant the formation of THMs and HAAs observed. Bromide incorporation factors (BIF) increase upon the introduction of Br⁻, and lower T_{Cl₂ → Br⁻} is related to higher BIF values. Additionally, Br⁻ inhibits the formation of dichloroacetonitrile (DCAN) and trichloroacetone (TCP), owing to its catalytic degradation effect towards them. In the chloramination process, Br⁻ shows similar effects towards the formation of THMs and HAAs, except that higher T_{NH₂Cl → Br⁻} inhibits their formation. Br⁻ greatly inhibits the formation of DCP, TCP, and DCAN, and the formed haloacetones rapidly degrade upon the introduction of Br⁻. The results of UV and EEM spectral analysis indicate that the reducing Br⁻ may improve rather than inhibit the oxidation of both the reactive components (DOC₁) and the slowly reactive sites (DOC₂) within HA, possibly owing to its buffering effect towards chlorine. In chlorination of source water with Br⁻ present, Br⁻ promotes the formation of most DBPs and enhances the

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incorporation of Br atoms therein, and in this case, DBP formation may be remarkably decreased by dosing with ammonia to transform chlorination to chloramination.

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1. Introduction

Chlorination of raw waters in water treatment plants leads to the formation of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs), which have potential toxicological effects (Harvey, 2011). It has been reported that chlorinated DBPs may primarily form by the reaction between chlorine and organic matters such as humic acids (HA) (Meier et al., 1985). Bromide ion (Br^-) is widely present in natural water and may complicate the formation of DBPs. Hypochlorous acid (HOCl) can rapidly oxidize naturally occurring Br^- to hypobromous acid (HOBr), which shows stronger halogenating activity than HOCl does (Westerhoff et al., 2004a). HOBr promotes the formation of brominated DBPs (Br-DBPs), some of which may pose more significant health risks than their chlorinated analogs (Myllykangas et al., 2003).

An alternative disinfectant, monochloramine, is widely used to control the formation of DBPs during chlorination. On the other hand, ammonia is also ubiquitous in natural water, due to soil erosion or anthropogenic sources such as nutrient-rich agricultural runoff (De et al., 2002). When ammonia is present in the source water, several competitive reactions occur and lead to the coexistence of chloro-bromo-ammonia species, such as NH_2Br , NHClBr and NHBr_2 (Alsulaili, 2009). The primary reactions involved are described in Eqs. (1)–(4):



These species have been found to react with HA and result in the formation of various DBPs [i.e. chlorinated DBPs (Cl-DBPs), brominated DBPs (Br-DBPs) and nitrogenous DBPs (N-DBPs)] (Alsulaili, 2009). The distribution of different DBP species depends on the relative ratio between HA, HOCl, Br^- , and ammonia, and is also dependent on the reagent addition order (Tian et al., 2013a).

The effects of chlorine-ammonia ratio, chlorine-bromide ratio, chlorine-HA ratio etc. on the formation of DBPs have been extensively studied (Alsulaili, 2009; Cowman and Singer, 1996). There have also been many reports focusing on the effects of the addition order of chlorine and ammonia (Eleanor and William, 2009). The majority of the literature available involves the addition of chlorine to waters in the presence of Br^- (Westerhoff et al., 2004b). However, few studies have studied the effect of the reagent addition order of chlorine, ammonia and Br^- into NOM, and especially the postponed introduction of Br^- , on the formation and species distribution of DBPs during chlorination and chloramination. We believe that this study may help in better understanding the mechanism of Br^- -involved reaction during chlorination and chloramination, which may be valuable for controlling the formation of Br-DBPs. In actual practice the addition of Br^- does not occur; however, this experimental design does help to clarify the function of Br^- and HOBr at different reaction stages during chlorination and chloramination. In water blending systems, e.g., the unintentional discharge of chlorinated wastewater into environments such as seas and coastal rivers, the reaction between Br^- and chlorine/chloramine does occur.

This study uses humic substance from Sigma-Aldrich, and focuses on the effects of bromide introduced at different time intervals after

chlorine ($\text{T}_{\text{Cl}_2 \rightarrow \text{Br}^-}$) and chloramine ($\text{T}_{\text{NH}_2\text{Cl} \rightarrow \text{Br}^-}$) on DBP formation during chlorination and chloramination. The objectives of this study are to: 1) evaluate the effects of $\text{T}_{\text{Cl}_2 \rightarrow \text{Br}^-}/\text{T}_{\text{NH}_2\text{Cl} \rightarrow \text{Br}^-}$ on the formation and distribution of THMs and HAAs; 2) investigate the effects of bromide on the formation and degradation of N-DBPs; 3) characterize the species transformation of HA and correlate it with subsequent DBP formation; 4) examine the roles of ammonia and Br^- in DBP formation and the mechanisms involved. These efforts may benefit the development of a feasible strategy for effective control of Br-DBP and N-DBP formation.

2. Materials and methods

2.1. Chemicals and reagents

Unless otherwise noted, all the reagents used in this study were of reagent grade, and solutions were prepared with ultra-pure water. HOCl stock solution (about 8 g/L) was prepared from 10% sodium hypochlorite (NaClO) and stored in an aluminum foil-covered glass stoppered flask. Monochloramine (NH_2Cl) solution was prepared daily by reacting equal volumes of ammonium chloride (NH_4Cl) and NaClO solution in well-mixed bottles at a weight ratio of 4 to 1. The HOCl and NH_2Cl were standardized by the N, N-diethyl-p-phenylenediamine (DPD) ferrous titration method (Eaton, 2005). Sodium phosphate at 50 mmol/L was used as a buffer to maintain solutions at pH 7.0. Stock solutions of bromide ions were prepared by mixing analytical grade potassium bromide (KBr) with ultrapure water. The abovementioned reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. Hexane and methyl tert-butyl ether (MTBE) used to extract DBPs were obtained from Fisher. Standards for THM₄ (CHCl_3 , CHCl_2Br , CHClBr_2 , CHBr_3) and halogenated volatiles as a mixture of DBPs, i.e., dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), trichloroacetone (TCP), and chloroal hydrate (CH), were purchased from AccuStandard (USA). A standard for nine HAAs, i.e., monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), trichloroacetic acid (TCAA) and tribromoacetic acid (TBAA), was purchased from AccuStandard (USA).

Commercial HA was purchased from Aldrich (lot no. 1430030) and its source was from soil. HA stock solution was prepared by diluting 1.5 g HA into 500-ml 0.1 mmol/L sodium hydroxide (NaOH). The solution was filtered through 0.45- μm glass fiber membrane filters, after 24-h stirring, and then stored in the dark at 4 °C. The HA solution used in this study was further diluted to obtain DOC of about 6 mg/L.

2.2. Experimental setup

Raw water samples were all treated at bench-scale in the laboratory. The pH of the water was adjusted to 7 using sulfuric acid or sodium hydroxide, as necessary, and then buffered with 0.05 mM phosphate. The experiments were conducted at pH 7 to simulate the pH commonly used in chlorination and chloramination practice. Chlorination was conducted by adding 25 mg/L Cl_2 as HOCl; the NH_2Cl process was conducted by adding 25 mg/L total Cl_2 as NH_2Cl solution. Br^- with concentration of 1 mg/L was added to evaluate the effect of bromide on DBPs. The experimental samples were then incubated in 1.0 L chlorine demand-free, glass-stoppered glass vials with no headspace in the dark at 25 ± 0.5 °C. Reaction times were set to 30 min, 24 h and 72 h to investigate the species of

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