Science of the Total Environment 625 (2018) 252–261

Contents lists available at ScienceDirect

Science of the Total Environment

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

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

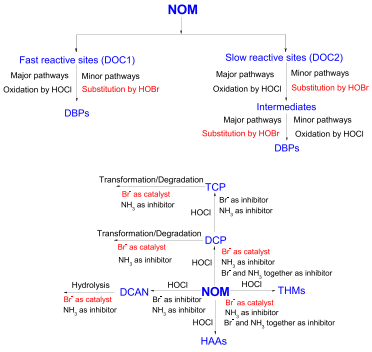
Ruiping Liu [a,b,1], Chuan Tian [a,c,1], Chengzhi Hu [a,b,*], Zenglu Qi [a,b], Huijuan Liu [a,d], Jiuhui Qu [a,b]

[a] Key Laboratory of Aquatic Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] University of Chinese Academy of Sciences, Beijing 100039, China
[c] China Academy of Urban Planning & Design, Beijing 100044, China
[d] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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 DOC_1 and slow-reactive DOC_2 by buffering effect

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 October 2017
Received in revised form 20 December 2017
Accepted 21 December 2017
Available online 28 December 2017

Editor: J Jay Gan

Keywords:
Bromide ion
Chlorination
Chloramination
Disinfection by-products
Bromide incorporation factors

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 (Cl_2) or chloramine (NH_2Cl), 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 NH_2Cl, 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 $T_{Cl_2 \rightarrow Br^-}$ is, the more significant the formation of THMs and HAAs observed. Bromide incorporation factors (BIF) increase upon the introduction of Br^-, and lower $T_{Cl_2 \rightarrow Br^-}$ 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 $T_{NH_2Cl \rightarrow Br^-}$ 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 (DOC_1) and the slowly reactive sites (DOC_2) 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

* Corresponding author at: Key Laboratory of Aquatic Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100044, China.
E-mail address: czhu@rcees.ac.cn (C. Hu).
[1] These authors contributed equally to this work (joint first authors).

https://doi.org/10.1016/j.scitotenv.2017.12.253

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

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 chlo-bromo-ammonia species, such as NH_2Br, NHClBr and $NHBr_2$ (Alsulaili, 2009). The primary reactions involved are described in Eqs. (1)–(4):

$$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O \quad (1)$$

$$HOBr + NH_3 \leftrightarrow NH_2Br + H_2O \quad (2)$$

$$HOBr + NH_2Cl \leftrightarrow NHBrCl + H_2O \quad (3)$$

$$NH_2Br + NH_2Br \rightarrow NHBr_2 + H_2O \quad (4)$$

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 ($T_{Cl_2 \rightarrow Br^-}$) and chloramine ($T_{NH_2Cl \rightarrow Br^-}$) on DBP formation during chlorination and chloramination. The objectives of this study are to: 1) evaluate the effects of $T_{Cl_2 \rightarrow Br^-}/T_{NH_2Cl \rightarrow Br^-}$ 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 THM_4 ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$) 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., monochloro acetic 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

DBPs in the process of disinfection. A 50-ml sample was used for the determination of free chlorine and total chlorine, and then samples for analysis of the other compounds were quenched with sodium sulfite, except for halogenated acetonitriles (HANs); a 20-ml sample was quenched with ascorbic acid for HAN determination. All experiments were duplicated. Relatively high HOCl and NH_2Cl doses were used in these experiments to ensure that the disinfectant was always in excess.

2.3. DBP formation experiment and analysis

Four THMs, four HANs, TCP and CH were determined by liquid/liquid extraction with hexane according to EPA method 551.1 (Munch and Hautman, 1995). Nine HAAs were analyzed by liquid/liquid extraction with MTBE followed by derivatization with acidic methanol and analysis by GC/ECD according to USEPA Method 552.3 (Domino et al., 2003). The detection limit of the abovementioned DBPs and the quality control method also refer to the EPA method.

2.4. HA characterization

The DOC concentration in HA solution was measured by a TOC-V_{CPH} total organic carbon analyzer (Shimadzu, Japan) after filtering the solution through a 0.45-μm membrane. pH was measured by using an Orion 3 Star pH Benchtop meter (Thermo Scientific, USA). Ultraviolet spectra were measured by a U-3010 UV–vis spectrophotometer (Hitachi Co., Japan) equipped with 10 mm quartz cuvettes. The DOC concentration of the HA solution was 6.3 mg/L, with specific ultraviolet absorbance (SUVA) value of 11.8 L/m mg.

Fluorescence spectra were recorded on a F-4500 fluorescence spectrophotometer (Hitachi, Japan). Experimental details followed the procedure in a previous study (Yang et al., 2008a). Excitation-Emission Matrix (EEM) figures were divided into five regions based upon the method established by a previous study (Chen et al., 2003).

3. Results and discussion

3.1. Effect of bromide on the formation and transformation of different DBPs

3.1.1. Formation and species transformation of THMs

Fig. 1 illustrates the effects of bromide at different $T_{Cl_2 \rightarrow Br^-}$ on the formation of THMs in chlorination and chloramination. Compared to the case without Br^- present, coexisting Br^-, i.e., $Br^-_{0\text{-min}}$, may decrease the formation of THMs during chlorination by 53.8%, from 0.93 μM to 0.43 μM, in the initial 5 min (Fig. 1a). Upon dosing with chlorine, Br^- may rapidly transform to HOBr with lower oxidizing ability compared to HOCl. HOBr can hardly oxidize high-molecular organics into lower ones (Westerhoff et al., 2004a), and in the initial stage the THM formation was inhibited accordingly. With prolonged reaction time to 72 h, Br^- promoted the formation of THMs by 14.9%, 11.1%, 16.2%, and 16.9% at $T_{Cl_2 \rightarrow Br^-}$ of 0 min, 5 min, 30 min, and 24 h, respectively. The positive effect of Br^- on THM formation was most significant when $T_{Cl_2 \rightarrow Br^-}$ was as high as 24 h. This may be attributed to the different reaction mechanisms for HOCl and HOBr and their synergistic effects towards THM formation. HOCl, with higher oxidizing ability, tends to transform organics into different intermediates via complicated stages (Eq. (5)) (Chiwang Li et al., 2000), and the subsequently-formed HOBr may further react with them to promote the formation of THMs by electrophilic substitution (Ichihashi et al., 1999). The later Br^- was introduced, the higher the concentrations of halogenated intermediates HOBr could react with, so that less HOBr was required to achieve the formation of THMs.

$$NOM_0 \xrightarrow{Cl_2} NOM_1 \xrightarrow{Cl_2} NOM_2 \xrightarrow{Cl_2} \cdots \xrightarrow{Cl_2} NOM_n \quad (5)$$

The bromide incorporation factor (BIF) is indicative of the incorporation of Br^- into organics and may be calculated by Eq. (6) (Tian et al., 2013a). It was observed that BIF_{THMs} rapidly underwent a sharp increase to near maximum values upon the introduction of Br^- at any $T_{Cl_2 \rightarrow Br^-}$, 0 min, 5 min, 30 min, or 24 h.

$$BIF_{THMs} = \frac{0 \times [CHCl_3] + 1 \times [CHCl_2Br] + 2 \times [CHClBr_2] + 3 \times [CHBr_3]}{[CHCl_3] + [CHCl_2Br] + [CHClBr_2] + [CHBr_3]} \quad (6)$$

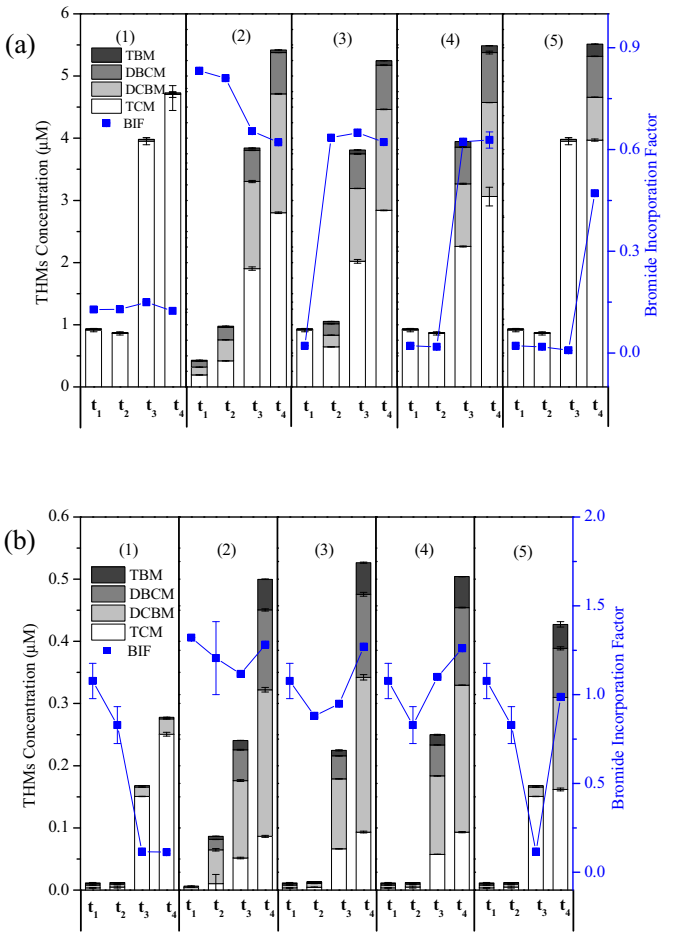


Fig. 1. Effect of Br^- on the formation of THMs during (a) chlorination and (b) chloramination. (1) $Br^- = 0$ mg/L; (2) $T_{Cl_2/NH_2Cl \rightarrow Br^-} = 0$ min; (3) $T_{Cl_2/NH_2Cl \rightarrow Br^-} = 5$ min; (4) $T_{Cl_2/NH_2Cl \rightarrow Br^-} = 30$ min (5) $T_{Cl_2/NH_2Cl \rightarrow Br^-} = 24$ h. Reaction time: $t_1 = 5$ min, $t_2 = 30$ min, $t_3 = 24$ h, $t_4 = 72$ h.

Interestingly, in the presence of $Br^-_{0\text{-min}}$, BIF was as high as 0.83 after 5-min contact time, and then decreased continuously to 0.81, 0.65, and 0.62 after 30 min, 24 h, and 72 h, respectively. HOBr exhibits strong substitution activity, and the rate of substitution by HOBr is 17 times higher than by HOCl (Ichihashi et al., 1999). Upon being formed, the molar ratios of HOBr to HOCl ($R_{HOBr:HOCl}$) were relatively high, and HOBr may be rapidly incorporated into organics to increase BIF_{THMs}. As reaction time went on, HOBr was consumed and the extent of Br incorporation was lower compared to atomic chorine, and lowered BIF_{THMs} were observed accordingly. The postponed introduction of Br^- with elevated $T_{Cl_2 \rightarrow Br^-}$ may show effects on BIF_{THMs}; however, this effect was relatively low after 72-h contact time.

Br^- at different $T_{NH_2Cl \rightarrow Br^-}$ also showed effects on the formation and transformation of THMs during chloramination (Fig. 1b). Similar to results observed in chlorination, $Br^-_{0\text{-min}}$ also significantly inhibited THM formation by 45.5%, from 0.011 μM to 0.006 μM, in the initial 5-min. Over the long timescale of 72 h, Br^- significantly

promoted the formation of THMs by 89.1%, 99.1%, 90.7%, and 61.6% at $T_{NH_2Cl \rightarrow Br^-}$ of 0 min, 5 min, 30 min, and 24 h, respectively. The positive effects of Br^- on THM formation by chloramination were much more significant than those during chlorination. In chloramine solution, there is an equilibrium reaction between NH_2Cl and HOCl (Eq. (7)) (Alsulaili, 2009). The introduced Br^- consumes HOCl to form HOBr and shifts the reaction equilibrium to the formation of HOCl. The continuous formation of HOBr and its incorporation into organics promoted THM formation greatly.

$$NH_2Cl + H_2O \leftrightarrow HOCl + NH_3 \quad (7)$$

Furthermore, Br^- also consumes NH_2Cl to form NH_2Br, NHClBr and $NHBr_2$, and it was reported that the bromo-species have more reactivity towards organic matter than NH_2Cl (Alsulaili, 2009).

Additionally, the effects of Br^- were observed to be dependent on $T_{NH_2Cl \rightarrow Br^-}$, and the extension of $T_{NH_2Cl \rightarrow Br^-}$ to 24 h inhibited THM formation as compared to $T_{NH_2Cl \rightarrow Br^-}$ of 0 min, 5 min, and 30 min. NH_2Cl, although with lower oxidizing ability than HOCl, still exhibits relatively high halogenation ability to form macromolecular by-products, i.e., THM precursor intermediates, with the fast reactive sites (DOC_1), based on a model proposed by a previous study (Tian et al., 2013b). The introduction of Br^- in the early stage, at $T_{NH_2Cl \rightarrow Br^-}$ of 0 to 30 min, may transform HOCl to HOBr with strong substitution ability as early as possible and facilitate THM formation. On the other hand, NH_2Cl and HOBr are generally viewed as substitution oxidants with regard to THM formation (Sun et al., 2009), and the substituting rather than oxidizing effect was predominant for these two oxidants. At the high $T_{NH_2Cl \rightarrow Br^-}$ of 24 h, the reactive sites available for substitution have been largely consumed by NH_2Cl, and the positive effect of HOBr on THM formation was inhibited accordingly. The consumption of reactive sites by chloramine was supported by the decreased BIF of 23.4% at $T_{NH_2Cl \rightarrow Br^-}$ of 24 h.

Moreover, it can be inferred that much lower amounts of chloro-THMs than bromo-THMs were produced during chloramination, and the BIF_{THMs} values after 72-h reaction time were as high as 1.28, 1.27, 1.26, and 0.98 at different $T_{NH_2Cl \rightarrow Br^-}$, and were much higher than those observed in chlorination. Bromide may also be transformed to HOBr and NH_2Br by chloramines, owing to substitution reactions. The incorporation of HOBr and NH_2Br into organics was less affected by ammonia as compared to the oxidation reactions by chlorine (Tian et al., 2013a). It was noted that a trace amount of Br^- may be introduced into the experimental system unintentionally. This effect contributed to the relatively high BIF_{THMs} value of 1.08 in the initial 5-min during chloramination, although the THM concentration was as low as 0.011 μM.

3.1.2. Formation and species transformation of HAAs

The effects of Br^- on the formation and species distribution of HAAs during chlorination are shown in Fig. 2a. During the rapid 5-min reaction, coexisting Br^- ($Br^-_{0\text{-min}}$) may remarkably decrease the HAA formation by 45.6%, i.e., from 1.49 μM to 0.81 μM, during chlorination. With the prolonged contact time of 72 h, Br^- promoted the HAA formation by 0.8%, 0.4%, 17.2%, and 7.4% at $T_{Cl_2 \rightarrow Br^-}$ of 0 min, 5 min, 30 min, and 24 h compared to that without Br^- introduction. Comparatively, the positive effect of Br^- on HAA formation was lower than that on THM formation, which is in accordance with a previous study (Hua et al., 2006). Upon being introduced, Br^- was rapidly transformed by chlorine to HOBr, with stronger substituting activity, and was then incorporated into NOM and its intermediates to form DBPs. Bromine was reported to be more reactive than chlorine in substitution reactions with regard to DBP formation (Westerhoff et al., 2004a). These results indicated that the substitution reactions played a more important role in the formation of THMs than that of HAAs.

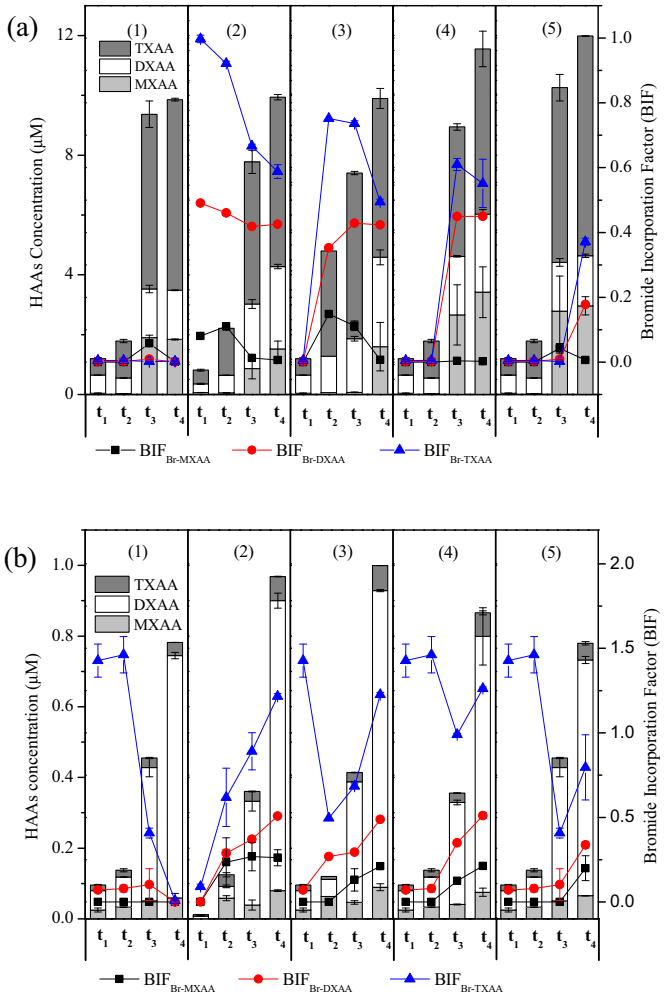


Fig. 2. Effect of Br^- on the formation of HAAs during (a) chlorination and (b) chloramination. (1) $Br^- = 0$ mg/L; (2) $T_{Cl_2/NH_2Cl \rightarrow Br^-} = 0$ min; (3) $T_{Cl_2/NH_2Cl \rightarrow Br^-} = 5$ min; (4) $T_{Cl_2/NH_2Cl \rightarrow Br^-} = 30$ min (5) $T_{Cl_2/NH_2Cl \rightarrow Br^-} = 24$ h. Reaction time: $t_1 = 5$ min, $t_2 = 30$ min, $t_3 = 24$ h, $t_4 = 72$ h.

To provide insight into the effects of Br^- on HAA formation, the bromide incorporation factors of monohalogenated HAAs (MXAA), dihalogenated HAAs (DXAA), and trihalogenated HAAs (TXAA), i.e., $BIF_{Br\text{-}MXAA}$, $BIF_{Br\text{-}DXAA}$, and $BIF_{Br\text{-}TXAA}$, were calculated by Eq. 8–10, and results are shown in Fig. 2a. In the absence of Br^-, the brominated HAAs were detected, possibly due to trace amounts of Br^- in HA and NaClO stock solutions or Br^- that was unintentionally introduced during experiments; and the BIF values showed little variation with prolonged contact time, up to 72 h. The introduction of Br^- significantly increased the BIF values of $BIF_{Br\text{-}MXAA}$, $BIF_{Br\text{-}DXAA}$, and $BIF_{Br\text{-}TXAA}$, with the order of $BIF_{Br\text{-}MXAA} < BIF_{Br\text{-}DXAA} < BIF_{Br\text{-}TXAA}$ for a disinfection scenario. It has been reported that each of the MXAA species are formed through similar chemical pathways and likewise for the DXAA and TXAA, and the presence of Br^- may promote the formation of higher halogenated species (Cowman and Singer, 1996). The later Br^- was introduced, the lower the values of these three BIF observed. This was attributed to the consumption of active sites within NOM by chlorine, and the incorporation of subsequently-introduced Br^- was inhibited thereafter. Additionally, upon the introduction of Br^-, these BIF values rapidly achieved near maximum values and then showed a decreasing trend with prolonged contact time. This result may be attributed to the fact that bromine reacts with NOM faster than chlorine (Hua and Reckhow, 2012), and the bromine-containing species may

be formed rapidly. In case of Br^- exhaustion, the proportion of chlorine-containing species may become dominant, with BIF decreasing accordingly.

$$BIF_{Br-MXAA} = \frac{[MBAA]}{[MCAA] + [MBAA]} \quad (8)$$

$$BIF_{Br-DXAA} = \frac{2 \times [DBAA] + [BCAA]}{[DBAA] + [BCAA] + [DCAA]} \quad (9)$$

$$BIF_{Br-TXAA} = \frac{3 \times [TBAA] + 2 \times [CDBAA] + [BDCAA]}{[TBAA] + [CDBAA] + [BDCAA] + [TCAA]} \quad (10)$$

Br^- showed different effects on HAA formation during chloramination (Fig. 2b). In the initial 5-min stage, the coexisting Br^- inhibited HAA formation by 87.5%, i.e., from 0.096 μM to 0.012 μM, as compared to that without the addition of Br^-. After 72-h contact time, Br^- showed positive effects, and the formation of HAAs was increased by 23.8%, 27.8%, and 10.7% at $T_{NH_2Cl \rightarrow Br^-}$ of 0 min, 5 min, and 30 min, whereas at the high $T_{NH_2Cl \rightarrow Br^-}$ of 24 h, HAA formation was slightly inhibited by −0.31%, with the HAA concentration determined to be 0.78 μM. Br^- also showed effects on the formation of HAAs and their species distribution. When Br^- coexisted with HA, i.e., $T_{NH_2Cl \rightarrow Br^-} =$ 0 h, the values of $BIF_{Br\text{-}MXAA}$, $BIF_{Br\text{-}DXAA}$, and $BIF_{Br\text{-}TXAA}$ increased with prolonged contact time, and were determined to be 0.26, 0.51, and 1.22 after 72-h contact time. When Br^- was introduced later than chloramine, the $BIF_{Br\text{-}MXAA}$ and $BIF_{Br\text{-}DXAA}$ increased, whereas $BIF_{Br\text{-}TXAA}$ significantly decreased upon the introduction of Br^-, and this was related to the more rapid formation of Br-MXAA and Br-DXAA compared with their chloral species. With prolonged contact time, the formation of Br-TXAA increased, and elevated $BIF_{Br\text{-}TXAA}$ values were observed accordingly.

To provide insight on the effects of Br^- on HAA species transformation, the ratios of HAAs with zero to three bromide atoms incorporated to the total HAAs, as expressed by $R_{0Br\text{-}HAAs}$, $R_{1Br\text{-}HAAs}$, $R_{2Br\text{-}HAAs}$, and $R_{3Br\text{-}HAAs}$, were calculated by Eqs. (11)–(14).

$$R_{0Br-HAAs} = \frac{[MCAA] + [DCAA] + [TCAA]}{[HAAs]} \quad (11)$$

$$R_{1Br-HAAs} = \frac{[MBAA] + [BDCAA] + [BCAA]}{[HAAs]} \quad (12)$$

$$R_{2Br-HAAs} = \frac{[DBAA] + [CDBAA]}{[HAAs]} \quad (13)$$

$$R_{3Br-HAAs} = \frac{[TBAA]}{[HAAs]} \quad (14)$$

Without the extra addition of Br^-, the 0br-HAAs were the dominant HAA species, with ratios of as high as 99.95%. The introduction of Br^- favored the formation of Br-HAAs, and $T_{NH_2Cl \rightarrow Br^-}$ of 0 min, 5 min, 30 min, and 24 h remarkably decreased $R_{0Br\text{-}HAAs}$ values, i.e., by 57.4%, 59.0%, 57.5%, and 72.6%. Additionally, as for the brominated HAAs (Br-HAAs), the 1Br-HAAs, i.e., MBAA, BCAA, and BDCAA, were the dominant HAA species, whereas the maximum ratio of TBAA (i.e., $R_{3Br\text{-}HAAs}$) was as low as 0.33% among these scenarios. Lower $T_{NH_2Cl \rightarrow Br^-}$ benefited the incorporation of bromide atoms into HAAs and the formation of brominated HAAs increased accordingly, and the 1Br-HAA formation was mostly affected by $T_{NH_2Cl \rightarrow Br^-}$. During chlorination, Br^- also inhibited the formation of Cl-DBPs, and the $R_{0Br\text{-}HAAs}$ decreased from 99.8% to 64.1%, 69.1%, 73.2%, and 85.4% at $T_{Cl_2 \rightarrow Br^-}$ of 0 min, 5 min, 30 min, and 24 h, respectively. Comparatively, the inhibitive effect of Br^- on Cl-DBP formation, as indicated from the decreased $R_{0Br\text{-}HAAs}$, was more significant in chloramination than that observed in chlorination. This effect contributed to the decrease of HAA formation during chloramination accordingly. With elevated $T_{NH_2Cl \rightarrow Br^-}$, the formation of all brominated HAAs in chloramination, i.e., 1Br-HAAs, 2Br-HAAs, and 3Br-HAAs, decreased after 72-h contact time. During chlorination, the formation of 2Br-HAAs and 3Br-HAAs increased, whereas that of 1Br-HAAs decreased with higher $T_{Cl_2 \rightarrow Br^-}$ values. This effect contributed to the different effects of Br^- on HAA formation in these two disinfection scenarios (Fig. 2).

3.1.3. Effect of bromide on halogenated ketone formation and degradation

The effects of Br^- and the time interval before its introduction on the formation of halogenated ketones during chlorination and cloramination are shown in Fig. 3. In the absence of Br^-, DCP rapidly achieved the maximum concentration of 7.2 nM within 5-min contact time and then began to decrease to as low as 1.1 nM after 72 h. Br^- promoted DCP formation, and the DCP concentrations increased from 7.2 nM to 10.1 nM, from 6.9 nM to 13.2 nM, and from 1.1 nM to 3.3 nM in the three different timescale stages of $T_{0min-5min}$ (reaction time from 0 min to 5 min), $T_{5min-30min}$ (reaction time from 5 min to 30 min), and $T_{24h-72h}$ (reaction time from 24 h to 72 h) respectively. That DCP concentrations decreased with prolonged contact time was indicative of the possible transformation of formed DCP to a brominated analogue and/or its degradation (Hua and Reckhow, 2008). Br^- favored the formation of DCP in the initial 30 min, and then accelerated its transformation and/or degradation thereafter. Generally, the later Br^- was introduced, the less significant the effect of Br^- on DCP formation. This may be due to the higher substitution activity of formed HOBr, which may promote the formation of halogenated DBPs, such as DCP. Additionally, it was observed as shown in Fig. 3a that Br^- inhibited the formation of TCP. The coexisting Br^- ($T_{Cl_2 \rightarrow Br^-} = 0$ min) remarkably decreased the formed TCP concentrations from 24.1 nM to 6.4 nM at contact time of 5 min, and the maximum TCP formation was postponed to the contact time of 24 h. In cases where Br^- was introduced later than chlorine, TCP concentrations degraded more rapidly upon the introduction of Br^-, possibly owing to its accelerating effects on TCP transformation and/or degradation. The abovementioned phenomenon was in accordance with a previous study (Yang et al., 2007).

The formation of DCP and TCP during chloramination was rather different from that observed in chlorination (Fig. 3b). In the absence of Br^-, the concentrations of DCP and TCP increased continuously with prolonged contact time. The formation of DCP was much higher than that of TCP, whereas in chlorination the opposite trend was observed. Additionally, Br^- showed more significant inhibition towards the formation of DCP and TCP in chloramination as compared to that in chlorination, and the formation of TCP may even be neglected. The formation of TCP may be classified as occurring in two stages, i.e., Stage-I: humic acid reacts with chlorine to form intermediate by-products, such as DCP, and Stage-II: DCP is further oxidized by chlorine to form TCP (Yang et al., 2007). The presence of ammonia may inhibit the reactions of Stage-II, while the presence of Br^- may inhibit the reactions of Stage-I and Stage-II.

3.1.4. Effect of bromide on HAN formation and degradation

Effects of Br^- on the formation and degradation of DCAN are shown in Fig. 4. It was observed that DCAN was the dominant species, and the formation of other HAN species, i.e., BCAN and DBAN, was too low to be detectable. During chlorination, the formation of DCAN was rapid, with the maximum concentration of 0.21 μM at 5 min, and then began to decrease continuously to as low as 0.03 μM at 72 h (Fig. 4). Coexisting Br^- ($T_{Cl_2 \rightarrow Br^-} = 0$ min) significantly inhibited DCAN formation, and the maximum DCAN concentration was decreased by nearly 90%. It has been reported that DCAN concentrations may decrease with increased concentration of Br^- (Yang et al., 2007). The reason may be that Br^- inhibits the formation of DCAN and/or accelerates the degradation of formed DCAN. In this study, we assumed that when Br^- was introduced later than chlorine, Br^- acted as an activator to accelerate DCAN transformation upon its introduction. DCAN tends to transform to other compounds such as dichloroacetic acid via hydrolysis (Eq. (15)) (Hayes-

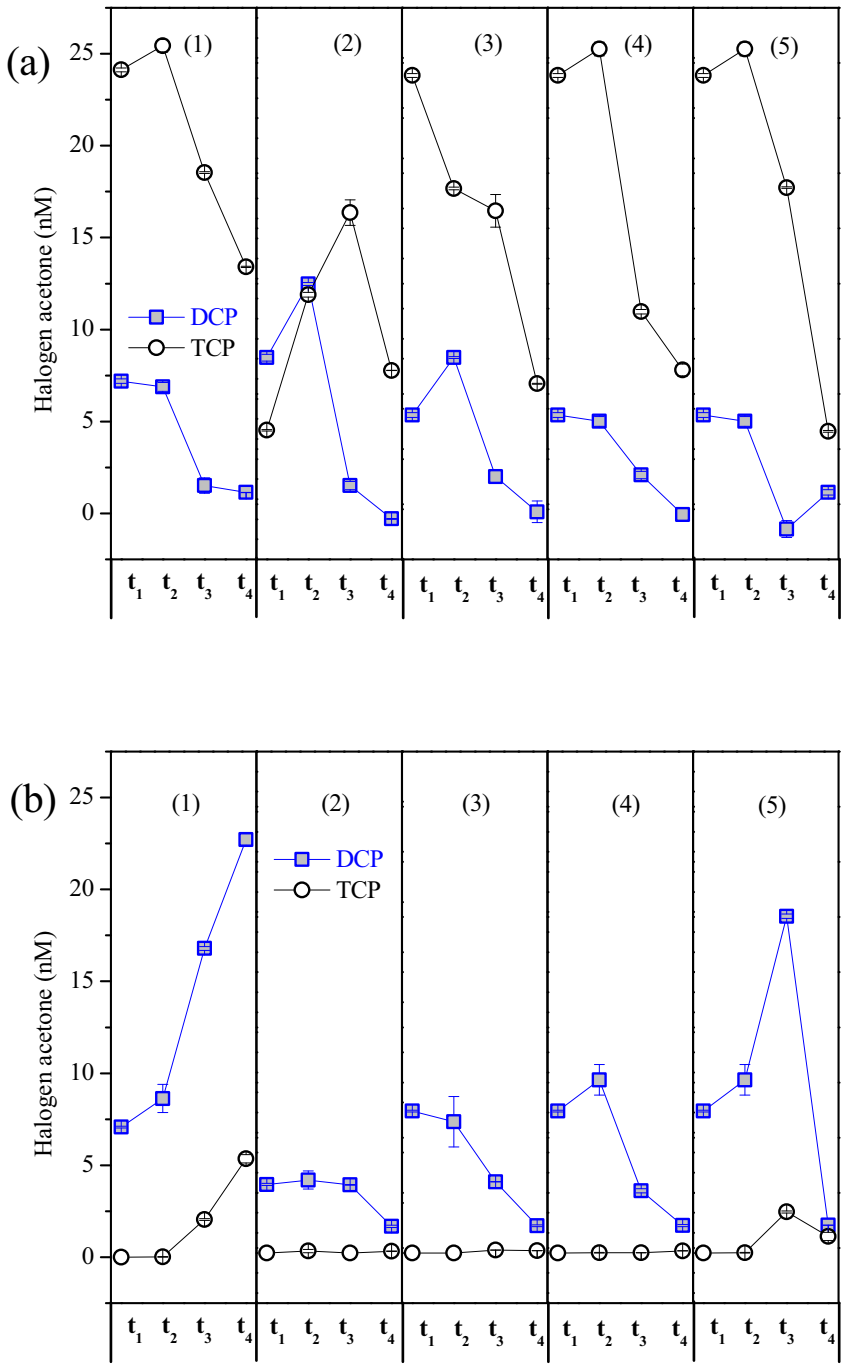


Fig. 3. Effect of Br^- on the formation of halogen acetone during (a) chlorination and (b) chloramination. (1) Br^- = 0 mg/L; (2) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 0 min; (3) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 5 min; (4) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 30 min (5) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 24 h. Reaction time: t_1 = 5 min, t_2 = 30 min, t_3 = 24 h, t_4 = 72 h.

Larson and Mitch, 2010), and Br^- is assumed to promote this reaction, although further studies are required to illustrate the dominant mechanism involved.

$$CHCl_2CN + 2H_2O \rightarrow CHCl_2COOH + NH \quad (15)$$

The trend of DCAN formation during chloramination was rather different from that observed in chlorination. Br^- significantly inhibited DCAN formation, and the DCAN concentrations after 72-h contact time were nearly 50% of those in the absence of Br^- no matter when Br^- was introduced. Additionally, Br^- postponed DCAN formation, and at $T_{NH_2Cl \rightarrow Br^-}$ of 0 min, remarkable DCAN formation occurred on the time scale of $T_{24h-72h}$.

3.2. Effect of bromide on transformation of the characteristics of HA

3.2.1. UV spectrometry

HA comprises different functional groups, some of which (e.g., aromatic groups) absorb light strongly in the wavelength range from 220 to 280 nm (Matilainen et al., 2012). UV absorbance is widely used as a surrogate parameter, for example the absorbance at 254 nm ($A_{254\ nm}$) and that at 272 nm ($A_{272\ nm}$). The reactions between the oxidizing species, e.g., chlorine, chloramine, and bromine, and HA were associated with the oxidation and halogenation of these functional groups, and a decrease in the absorbance in this wavelength range could be observed (Fig. 5). To quantitatively evaluate this effect, the differential UV absorbance (ΔUV_λ), such as that at 272 nm ($\Delta UV_{272\ nm}$),

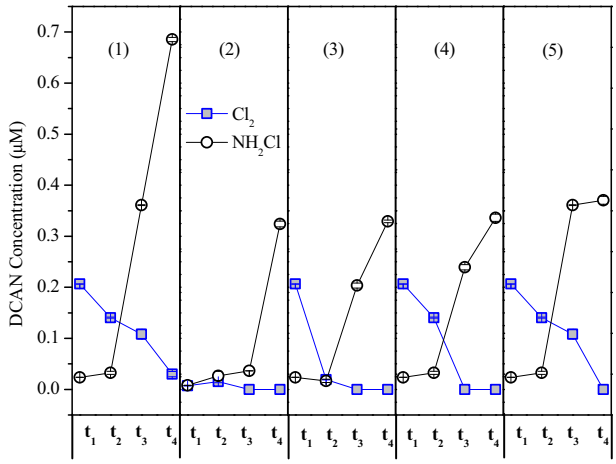


Fig. 4. Effect of Br^- on the formation of DCAN during chlorination and chloramination bromide adding time (1) Br^- = 0 mg/L; (2) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 0 min; (3) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 5 min; (4) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 30 min (5) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 24 h. Reaction time: t_1 = 5 min, t_2 = 30 min, t_3 = 24 h, t_4 = 72 h.

was calculated by Eq. (16), and this was reported to be indicative of the reactive components (Roccaro and Vagliasindi, 2009). In addition, $\Delta R_{A_{350}:A_{272}}$, as calculated by Eq. (17), was used to indicate the contribution of the slow reactivity component to the differential spectrum (Korshin et al., 2007). These two parameters of $\Delta UV_{272\ nm}$ and

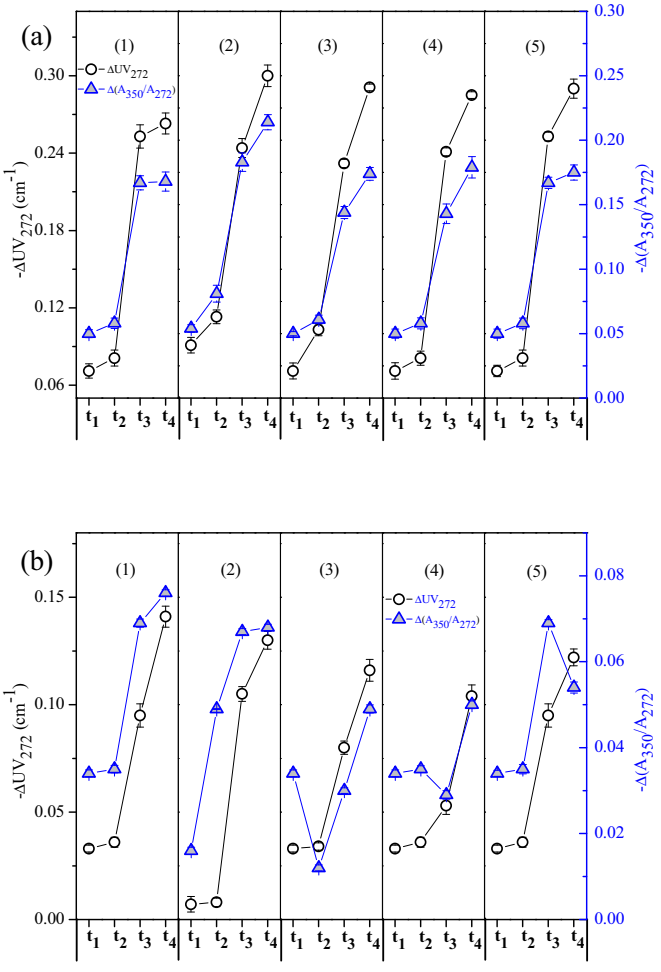


Fig. 5. ΔUV_{272} and ΔR of HA during (a) chlorination and (b) chloramination. (1) Br^- = 0 mg/L; (2) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 0 min; (3) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 5 min; (4) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 30 min (5) $T_{Cl_2/NH_2Cl \rightarrow Br^-}$ = 24 h. Reaction time: t_1 = 5 min, t_2 = 30 min, t_3 = 24 h, t_4 = 72 h.

$\Delta R_{A_{350}:A_{272}}$ were respectively used to indicate the two fractions, the reactive components (DOC_1) and the slow reactivity sites (DOC_2) herein.

$$\Delta UV_{272nm} = UV_{272nm,0} - UV_{272nm,t} \quad (16)$$

$$\Delta R_{A_{350}:A_{272}} = \left(\frac{A_{350}}{A_{272}}\right)_0 - \left(\frac{A_{350}}{A_{272}}\right)_t \quad (17)$$

As shown in Fig. 5a, chlorination of HA contributed to a significant increase in $\Delta UV_{272\ nm}$ and $\Delta R_{A_{350}:A_{272}}$, and this was indicative of marked degradation of both DOC_1 and DOC_2. The coexisting Br^- ($T_{NH_2Cl \rightarrow Br^-}$ of 0 min) enhanced the degradation of both these two sites within HA, and after 72-h contact time, the observed $\Delta UV_{272\ nm}$ increased from 0.26 to 0.30 cm^{-1}, whereas $\Delta R_{A_{350}:A_{272}}$ increased from 0.17 to 0.21 cm^{-1}. With the postponed introduction of Br^-, i.e., the increase of $T_{Cl_2 \rightarrow Br^-}$ from 0 min to 24 h, $\Delta UV_{272\ nm}$ decreased slightly, whereas the extent of $\Delta R_{A_{350}:A_{272}}$ decrease was more significant. The reducing Br^- may consume the active chlorine, and it was assumed to inhibit the degradation of the functional groups within HA. The observed positive effect might be first ascribed to the active bromine being more selective with regard to the oxidation of aliphatic precursors (Sun et al., 2009), which may be classified as DOC_2. Additionally, Br^- might act as a 'buffer' of oxidizing species, and the buffering effect inhibited the autonomous decay of chlorine and improve its oxidation efficacy accordingly.

The effects of Br^-, introduced at different time intervals, on the variation of $\Delta UV_{272\ nm}$ and $\Delta R_{A_{350}:A_{272}}$ during chloramination are illustrated in Fig. 5b. Br^- at $T_{NH_2Cl \rightarrow Br^-}$ of 0 min slowed down the degradation of DOC_1 and DOC_2, especially in the timescale of $T_{5-30\ min}$, and $\Delta UV_{272\ nm}$ and $\Delta R_{A_{350}:A_{272}}$ after 72-h contact time also decreased. The elevation of $T_{NH_2Cl \rightarrow Br^-}$ to 5 and 30 min further decreased the final $\Delta UV_{272\ nm}$ and $\Delta R_{A_{350}:A_{272}}$ at 72-h. Br^- inhibited the reactions between DOC_1/DOC_2 and the oxidizing species, and different effects towards these two components were observed. Upon the introduction of Br^-, the velocity of $\Delta UV_{272\ nm}$ increase was slowed down greatly. For example, in the absence of Br^-, $\Delta UV_{272\ nm}$ increased from 0 to 0.033 within 5-min contact time, and the corresponding value decreased to as low as 0.007 in the presence of coexisting Br^- ($T_{NH_2Cl \rightarrow Br^-}$-$T_{NH_2Cl \rightarrow Br^-}$ = 0 min). By contrast, Br^- significantly decreased the $\Delta R_{A_{350}:A_{272}}$ values, which were even lower than those observed prior to the addition of Br^-. We assumed that the reason may be that the formed intermediates reacted with Br^-, leading to the formation of compounds with relatively higher absorbance at 350 nm. The complicated reactions between NOM and halogenation reagents were reported to include multiple steps and branching (Gonzalez et al., 1996). This supported the more selective oxidation towards HA components observed after the introduction of Br^- into chloramines. In addition, $\Delta UV_{202\ nm}$ and $\Delta UV_{280\ nm}$ were also studied, and the results are shown in Fig. S3. It can be inferred that $\Delta UV_{202\ nm}$ is an indicator of DOC_1, and $\Delta UV_{280\ nm}$ is an indicator of DOC_2. The variation during the reaction time was in accordance with the previously described principle, that Br^- may inhibit the reaction between DOC_1/DOC_2 and chlorine in the initial reaction time.

3.2.2. EEM fluorescence

The widely-used fluorescence regional integration (FRI) method divides EEM spectra into five regions: Regions I and II (aromatic protein-like, λ_{ex} < 250 nm, λ_{em} < 380 nm), Region III (fulvic acid-like, λ_{ex} < 250 nm, λ_{em} > 380 nm), Region IV (soluble microbial by-product-like, λ_{ex} > 250 nm, λ_{em} < 380 nm), and Region V (humic acid-like, λ_{ex} > 250 nm, λ_{em} > 380 nm). EEM volume may be used as an index for DBP precursors, i.e., humic acid, and it was reported that EEM volume correlated well with the formation of DBPs during chlorination and chloramination (Johnstone and Miller, 2009; Yang et al., 2008b). To quantitatively evaluate the effect of Br^- on NOM transformation and DBP formation, the regional integration of the fluorescence spectra

beneath region III and V was conducted using Eq. (18) (Chen et al., 2003).

$$\Phi_{III+V,n} \approx MF_{III+V} \sum_{ex} \sum_{em} I(\lambda_{ex}\lambda_{em}) \Delta\lambda_{ex} \Delta\lambda_{em} \quad \text{(For discrete data)} \quad (18)$$

where $\Phi_{III+V,n}$ is the normalized EEM volume beneath region "III + V" of the EEM; MF_{III+V} is a multiplication factor for each region.

The EEM spectra measured during the aforementioned disinfection scenarios are shown in Fig. S1, and the variation trends of the integrated $\Phi_{III+V,n}$ values with prolonged contact time are illustrated in Fig. S2. To provide insight on the effect of Br^- on the $\Phi_{III+V,n}$, the ratios of $\Phi_{III+V,n}$ ($T_{NH_2Cl \to Br^-} R_{\Phi III+V,n}$) $T_{NH_2Cl \to Br^-} T_{NH_2Cl \to Br^-}$ with the introduced Br^- to that without dosing Br^- ($\Phi_{\overline{III}+V,n|Br=0\ mg/L}$) are illustrated in Fig. 6. The data above the dashed line, with the slope of 1: 1, was related to the higher values of $\Phi_{III+V,n}$ than $\Phi_{\overline{III}+V,n|Br=0\ mg/L}$, and this corresponded to the inhibitive effect of Br^- on the degradation of the fulvic acid-like and humic acid-like groups within HA.

During chlorination, the introduction of Br^- contributed to increased $R_{\Phi III+V,n}$, i.e., $\Phi_{III+V,n} > \Phi_{\overline{III}+V,n|Br=0\ mg/L}$, over the wide time scale of 5 min to 24 h, and more significant increase was associated with lower $T_{Cl_2 \to Br^-}$ (Fig. 6a). Chlorination may substantially decrease the fluorescence intensity (Shuang et al., 2009), and Br^- at 1 mg/L inhibited the degradation of fluorescence-active groups by chlorination within 24-h contact time. This may be ascribed to Br^- consuming chlorine and decreasing the amount of chlorine available for oxidation. However, after 72-h contact time, the obtained $\Phi_{III+V,n}$ values were lower than that in the absence of Br^-, i.e., $\Phi_{\overline{III}+V,n|Br=0\ mg/L}$. This positive effect might be attributed to the buffering effect of Br^- towards the degradation of slow-reactivity sites. Further studies are required to provide insight into the effect of Br^- on the degradation of fluorescent groups in different stages.

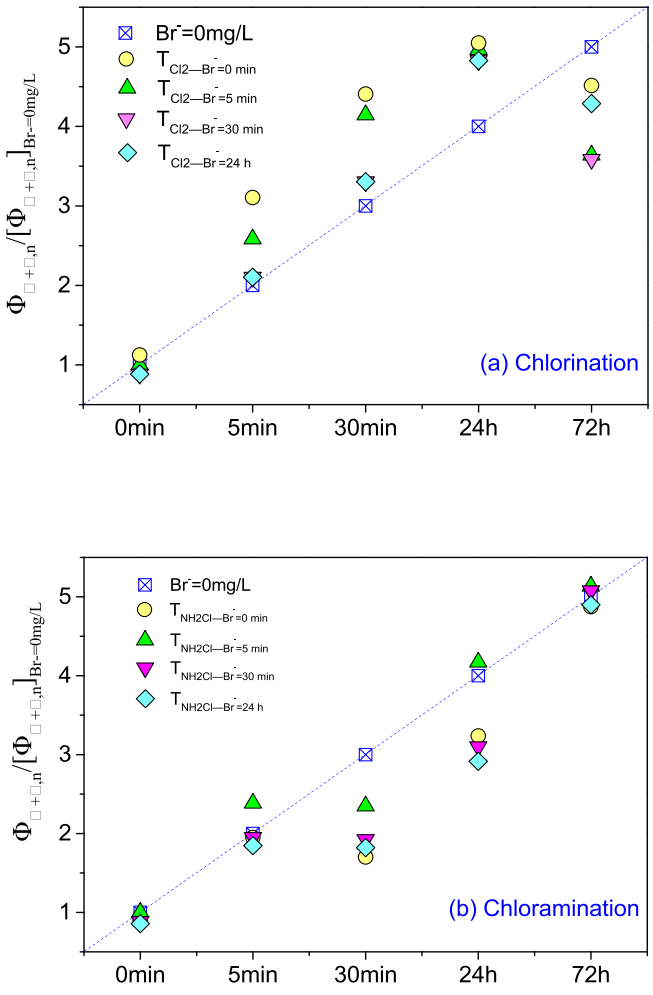


Fig. 6. The ratios of $\Phi_{III+V,n}$ ($T_{NH_2Cl \to Br^-} R_{\Phi III+V,n}$) $T_{NH_2Cl \to Br^-} T_{NH_2Cl \to Br^-}$ with the introduced Br^- at different $T_{Cl_2/NH_2Cl \to Br^-}$ to that in the absence of Br^- ($\Phi_{\overline{III}+V,n|Br=0\ mg/L}$) during (a) chlorination and (b) chloramination.

Chloramination showed a lower extent of fluorescence intensity decrease as compared to chlorination (Fig. S1), and the inhibitive effect of ammonia on the fluorescence intensity has also been reported before (Wu et al., 2010). Coexisting Br^- may further inhibit the decrease of fluorescence intensity; however, a slight difference between the $\Phi_{III+V,n}$ values and $\Phi_{\overline{III}+V,n|Br=0\ mg/L}$ was observed after 72-h contact time. Generally, Br^- showed little effect on the degradation of slow-reactivity fluorescent groups by chloramine.

3.3. Proposed mechanism

On the basis of these results, the mechanisms responsible for the effects of ammonia and Br^- on chlorine species transformation and DBP formation are illustrated in Fig. 7. Ammonia and Br^- complicated the species distribution of the oxidative species besides HClO, owing to the rapid formation of NH_2Cl and hypobromous acid (HBrO), and NH_2Cl and HBrO may be further transformed to NHClBr, NH_2Br, and $NHBr_2$ when ammonia and Br^- coexist. The species transformation of these species was related to the concentrations of HClO, ammonia, and Br^-, and the associated kinetic constants are illustrated.

Ammonia and Br^- also affected the formation of DBPs greatly. In the absence of ammonia and Br^-, the oxidation of the DOC_1 and DOC_2 sites by HClO is the major pathway, and the formation of DBPs from DOC_1 and the intermediates from DOC_2 rapidly occurred. The substitution and incorporation of elemental Cl does occur to form DBPs; however, the oxidation effect of HClO is more significant during the chlorination of NOM. Upon the addition of Br^-, HBrO is rapidly formed, and HBrO shows lower oxidation efficiency whereas stronger substitution effects with regard to the formation of DBPs as compared to HClO. The direct incorporation of elemental Br into either DOC_1 or DOC_2 was weak and was viewed as a minor pathway in this stage. With prolonged contact time, the substitution effect of activated elemental Br was dominant as the major pathway in the DBP formation. The coexisting ammonia significantly inhibited the formation of DBPs by the formation of NH_2Cl.

These pathways contributed to the different effects of ammonia and Br^- on the subsequent DBP formation. Ammonia mainly acts as an inhibitor, and decreases the formation of most DBPs such as THMs, HAAs, DCP, TCP, and DCAN, and their formation in chloramination was much lower than in chlorination. By contrast, Br^- plays two critically different roles in the formation and transformation of DBPs during chlorination. First, Br^- acts as an activator to enhance the formation of THMs, HAAs, and DCP and as an inhibitor with respect to the formation of DCAN after 72-h contact time. Additionally, Br^- accelerates the transformation/degradation of the formed DCP and TCP and catalyzes the hydrolysis of DCAN. The postponed introduction of Br^- was observed to have effects on the variation trends. The formation of THMs and HAAs was more significant at higher $T_{Cl_2 \to Br^-}$ whereas that of DCP, TCP, and DCAN was relatively less affected by $T_{Cl_2 \to Br^-}$. In the chloramination process, i.e., with the co-existence of ammonia and Br^-, Br^- remarkably inhibited the formation of these DBPs except for DCAN, owing to their combined effects on DBP formation.

4. Conclusion

During chlorination, Br^- enhances the formation of THMs and HAAs and inhibits the formation of DCAN and TCP by catalytic degradation effects. Additionally, the incorporation of more Br atoms into DBPs may adversely affect the toxicity. To control the detrimental effects of Br^-, the transformation of chlorination to chloramination is feasible. The combined effects of Br^- and ammonia may promisingly decrease the formation of regulated THMs and HAAs and accelerate the degradation

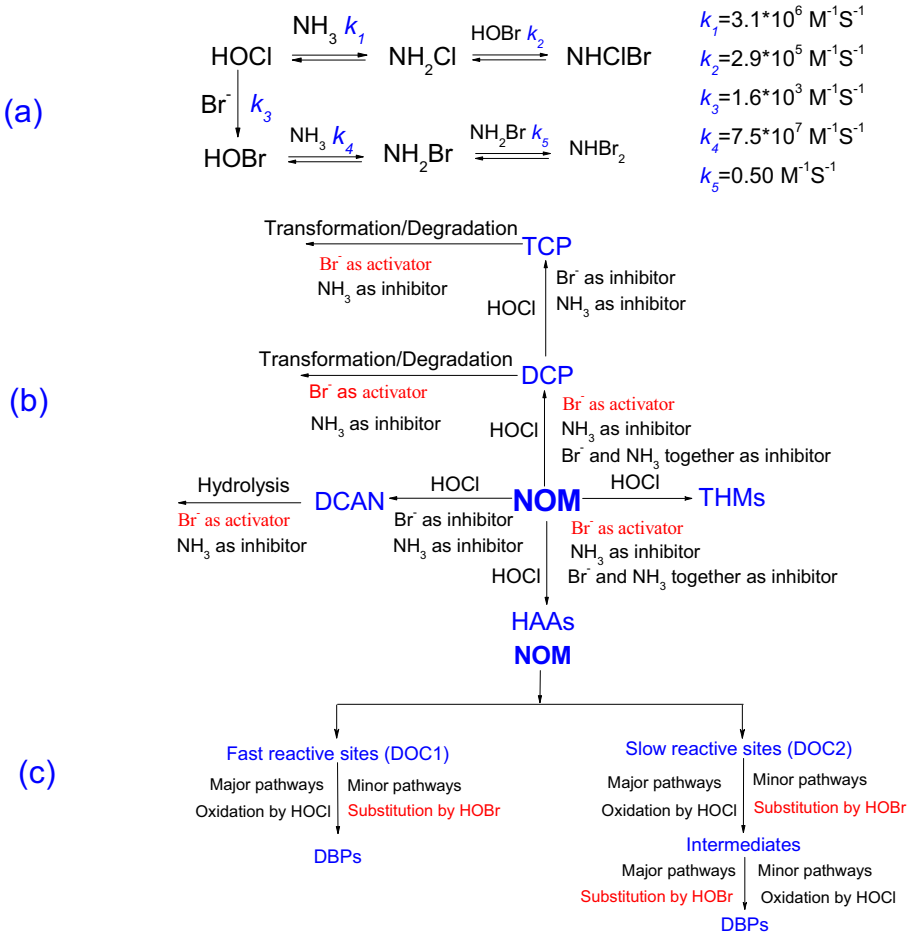


Fig. 7. Proposed effects of Br^- and ammonia on the formation of DBPs in chlorination.

of unregulated DBPs such as DCAN and TCP. This study may be valuable to understanding the mechanism of Br^--involved reactions during chlorination and chloramination, and further to control the formation of Br-DBPs.

Acknowledgements

This study was supported by the National Key R&D Program of China (2016YFC0400802), the major program (51290282) and the Excellent Young Scientists Fund (51422813) granted by the National Natural Science Foundation of China.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.12.253.

References

Alsulaili, A.D., 2009. Impact of Bromide, NOM, and Prechlorination on Haloamine Formation, Speciation, and Decay during Chloramination. University of Texas, Austin.
Chen, W., Westerhoff, P., Leenheer, J.A., Booksh, K., 2003. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. Environ. Sci. Technol. 37, 5701–5710.
Cowman, G.A., Singer, P.C., 1996. Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances. Environ. Sci. Technol. 30, 16–24.
De, S., Pettit, K.E., Bishop, C.A., Cheng, K.M., Elliott, J.E., 2002. Effects of agricultural runoff on native amphibians in the Lower Fraser River Valley, British Columbia, Canada. Environ. Toxicol. Chem. 21, 353–360.
Domino, M., Pepich, B., Munch, D., Fair, P., Xie, Y., 2003. EPA METHOD 552.3, Revision 1.0, Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Micro Extraction, Derivatization, and Gas Chromatography with Electron Capture Detection. EPA/815/B-03/002.
Eaton, AndrewD, 2005. Standard methods for the examination of water & wastewater. 21st ed. Centennial ed: American Public Health Association.
Eleanor, L.H.-L., William, A.M., 2009. Influence of the method of reagent addition on dichloroacetonitrile formation during chloramination. Environ. Sci. Technol. 44, 700–706.
Gonzalez, A.C., Olson, T.M., Rebenne, L.M., 1996. Aqueous Chlorination Kinetics and Mechanism of Substituted Dihydroxybenzenes.
Harvey, R.G., 2011. Historical overview of chemical carcinogenesis. Curr. Cancer Res. 6, 1–26.
Hayes-Larson, E.L., Mitch, W.A., 2010. Influence of the method of reagent addition on dichloroacetonitrile formation during chloramination. Environ. Sci. Technol. 44, 700.
Hua, G., Reckhow, D.A., 2008. DBP formation during chlorination and chloramination: effect of reaction time, pH, dosage, and temperature. J. Am. Water Works Assoc. 100, 82–95.
Hua, G., Reckhow, D.A., 2012. Evaluation of bromine substitution factors of DBPs during chlorination and chloramination. Water Res. 46, 4208–4216.
Hua, G., Reckhow, D.A., Kim, J., 2006. Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination. Environ. Sci. Technol. 40, 3050.
Ichihashi, K., Teranishi, K., Ichimura, A., 1999. Brominated trihalomethane formation in halogenation of humic acid in the coexistence of hypochlorite and hypobromite ions. Water Res. 33, 477–483.
Johnstone, D.W., Miller, C.M., 2009. Fluorescence excitation-emission matrix regional transformation and chlorine consumption to predict trihalomethane and haloacetic acid formation. Environ. Eng. Sci. 26, 1163–1170.
Korshin, Gregory V., Benjamin, Mark M., Chang, H., Gallard, H., 2007. Examination of NOM chlorination reactions by conventional and stop-flow differential absorbance spectroscopy. Environ. Sci. Technol. 41, 2776.
Li, Chiwang, Benjamin, M.M., Korshin, G.V., 2000. Use of UV spectroscopy to characterize the reaction between NOM and free chlorine. Environ. Sci. Technol. 34, 2570–2575.
Matilainen, A., Gjessing, E.T., Lahtinen, T., Hed, L., Bhatnagar, A., Sillanpää, M., 2012. An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. Chemosphere 83, 1431.
Meier, J.R., Ringhand, H.P., Coleman, W.E., Munch, J.W., Streicher, R.P., Kaylor, W.H., et al., 1985. Identification of mutagenic compounds formed during chlorination of humic acid. Mutat. Res. Genet. Toxicol. 157, 111–122.

Munch, D., Hautman, D., 1995. US EPA Method 551.1 Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography With Electroncapture Detection. US EPA, Cincinnati, Ohio.

Myllykangas, T., Nissinen, T.K., Mäki-Paakkanen, J., Hirvonen, A., Vartiainen, T., 2003. Bromide affecting drinking water mutagenicity. Chemosphere 53, 745–756.

Roccaro, P., Vagliasindi, F.G., 2009. Differential vs. absolute UV absorbance approaches in studying NOM reactivity in DBPs formation: comparison and applicability. Water Res. 43, 744–750.

Shuang, X., Wang, K., Zhao, Q.L., Wei, L.L., 2009. Chlorine reactivity and transformation of effluent dissolved organic fractions during chlorination. Desalination 249, 63–71.

Sun, Y.X., Wu, Q.Y., Hu, H.Y., Jie, T., 2009. Effect of bromide on the formation of disinfection by-products during wastewater chlorination. Water Res. 43, 2391.

Tian, C., Liu, R., Guo, T., Liu, H., Luo, Q., Qu, J., 2013a. Chlorination and chloramination of high-bromide natural water: DBPs species transformation. Sep. Purif. Technol. 102, 86–93.

Tian, C., Liu, R., Liu, H., Qu, J., 2013b. Disinfection by-products formation and precursors transformation during chlorination and chloramination of highly-polluted source water: significance of ammonia. Water Res. 47, 5901–5910.

Westerhoff, P., Chao, P., Mash, H., 2004a. Reactivity of natural organic matter with aqueous chlorine and bromine. Water Res. 38, 1502–1513.

Wu, Q.Y., Hu, H.Y., Zhao, X., Li, Y., 2010. Effects of chlorination on the properties of dissolved organic matter and its genotoxicity in secondary sewage effluent under two different ammonium concentrations. Chemosphere 80, 941–946.

Yang, X., Shang, C., Westerhoff, P., 2007. Factors affecting formation of haloacetonitriles, haloketones, chloropicrin and cyanogen halides during chloramination. Water Res. 41, 1193–1200.

Yang, X., Shang, C., Lee, W., Westerhoff, P., Fan, C., 2008a. Correlations between organic matter properties and DBP formation during chloramination. Water Res. 42, 2329–2339.