N-nitrosamine formation during chlorination/chloramination of bromide-containing water

Z. Chen, L. Yang, X. Zhai, S. Zhao, A. Li and J. Shen

ABSTRACT

This study investigated the impact of bromide on the formation of *N*-nitrosamines during chlorination and chloramination, and tried to identify the reactive intermediates responsible for variations in the yield of *N*-nitrosamines. As an intermediate of the reaction between bromide and HOCl, bromine chloride (BrCl) may improve the yield of *N*-nitrosodimethylamine (NDMA) formation. But increasing the amount of bromide added would result in BrCl being converted into HOBr, which is a weaker oxidant than HOCl. This would result in less nitrite being formed, leading to a decreased yield of NDMA via the nitrosation pathway. When NH_4^+, was present with the bromide during chlorination, both the rate of formation and yield of *N*-nitrosamines were improved markedly by highly reactive bromamines. Interestingly, bromide had an inhibitory effect on NDMA formation during the chloramination process when tertiary alkylamines, such as 3-(Dimethylaminomethyl) indole (DMAI) and trimethylamine (TMA), were used as precursors. This phenomenon provides indirect evidence for the hypothesis that the pathway of NDMA formation using tertiary amines with DMA groups is different from that of NDMA formation using secondary alkylamines.

Key words | bromide, chloramination, chlorination, disinfection by-product (DBP), *N*-nitrosamines

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INTRODUCTION

N-nitrosamines are highly mutagenic compounds that are suspected of carcinogenic activity in the human body (Loeppky & Micheljda 1994). The US Environmental Protection Agency (USEPA) has chlasssified *N*-nitrosodimethylamine (NDMA, $(CH_3)_2NNO$), a typical *N*-nitrosamine, as a probable human carcinogen and has estimated that it has a 10^{-6} cancer risk in drinking water when present at 0.7 ng/L (US EPA 1997). As a new type of disinfection by-product (DBP), NDMA formed during chlorine disinfection has caused significant concern among drinking-water and wastewater recycling utilities recently (Najm & Trussel 2001; Mitch *et al.* 2003; Wilczak *et al.* 2003). Currently, the most effective and commonly applied method for treating aqueous *N*-nitrosamines is photolysis by ultraviolet (UV) radiation (Liang *et al.* 2003; Lee *et al.* 2005; Xu *et al.* 2009*a*) or combination degradation by UV/O_3 (Xu *et al.* 2009*b*), but this method is not cost-effective. It is important, therefore, to study the mechanisms and influencing factors of NDMA formation in water treatment processes, and to develop a useful method for minimising the yield of NDMA.

Three pathways have been proposed for NDMA formation during the chlorine disinfection process. All of these pathways involve secondary alkylamines, specifically dimethylamine (DMA, $(CH_3)_2NH$), as precursors (Choi & Valentine 2002*a*; Choi *et al.* 2002; Mitch & Sedlak 2002; Choi & Valentine 2003; Schreiber & Mitch 2005; Schreiber & Mitch 2006). Since the rate of NDMA formation by nitrosation is very low at neutral pH, nitrosation cannot be the major pathway occurring during actual water treatment processes. Choi & Valentine (2003) reported that the formation of NDMA by the nitrosation of DMA is

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enhanced in the presence of free chlorine, following the reaction shown in Equations (1)–(3).

$$HOCl + NO_2^- \rightarrow NO_2Cl + OH^- \quad (1)$$

$$NO_2Cl + NO_2^- \rightarrow N_2O_4 + Cl^- \quad (2)$$

$$(CH_3)_2NH + N_2O_4 \rightarrow (CH_3)_2NNO \quad (3)$$

In the presence of NH_4^-, both the rate of formation and yield of NDMA may increase significantly because of the formation of chloroamines (Choi & Valentine 2002*a*; Choi *et al.* 2002; Mitch & Sedlak 2002; Schreiber & Mitch 2005; Schreiber & Mitch 2006). Choi *et al.* (2002) as well as Mitch & Sedlak (2002) proposed a mechanism that included a reactive intermediate known as unsymmetrical dimethylhydrazine (UDMH). UDMH can be further oxidized to yield many different by-products, including NDMA. Schreiber & Mitch (2005, 2006) re-examined the pathway of nitrosamine formation, and they emphasized the role of dichloroamine and dissolved oxygen in NDMA formation. Until now, the most effective precursor of NDMA formation has remained unknown. Research has shown that some tertiary amines, mostly from pesticides and industrial wastewater, increase the yield of NDMA (Schreiber & Mitch 2008).

In addition to these organic precursors, some inorganic substances, such as hydroxylamines (Yang *et al.* 2009), NO_2^- and NH_4^+, also play important roles in NDMA formation. Our investigations into factors influencing NDMA formation suggest that there is a link between bromide and NDMA formation. Bromide is present naturally in untreated water in coastal cities due to saltwater intrusion or anthropogenic processes. Once present in the water, bromide cannot be removed readily using conventional techniques. Bromide ions in water can result in the formation of several different kinds of bromide-containing DBPs during the disinfection process, as well as an increased total yield of chlorinated DBPs.

Valentine *et al.* (2005) discussed the effect of high concentrations of bromide (0.1–2.0 mM) on NDMA formation. The dosage of bromide discussed was much higher than the normal bromide concentration occurring in natural water (on the order of 1 milligram or less) (Amy *et al.* 1994). They proposed that two operationally defined pathways could be expected to enhance NDMA formation: (i) oxidation of bromide by monochloramine (slow and long lived) and (ii) oxidation of bromide by HOCl, followed by a rapid reaction with NH_4^+ (fast and short-lived).

In this investigation, we focussed on the influence of low concentrations of bromide on the formation of *N*-nitrosamines from secondary and tertiary alkylamines during chlorination/chloramination. The aims of this paper are to further discuss the mechanism of NDMA formation during chlorine disinfection in the presence of bromide, and to assess the importance of inorganic intermediates in the formation of NDMA.

MATERIALS AND METHODS

Chemicals

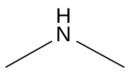
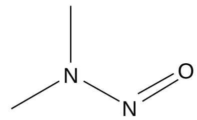
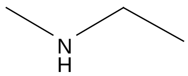
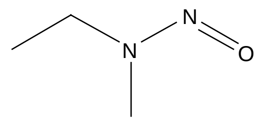
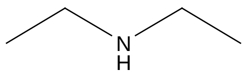
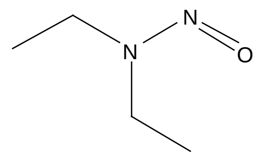
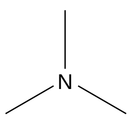
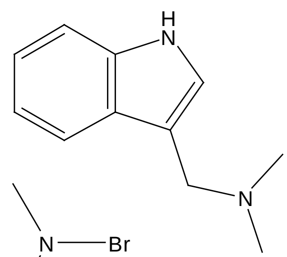
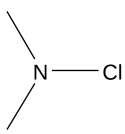
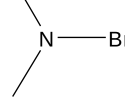
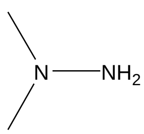
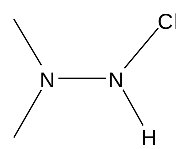
All experiments were conducted using distilled water. *N*-nitrosodimethylamine (NDMA, 200 μg/mL in methanol), *N*-nitrosomethylethylamine (1.0 mg/mL in methanol, NMEA) and *N*-nitrosodiethylamine (NDEA, ≥99.0%) were obtained from Superlco, AccuStandard and Sigma-Aldrich, respectively. Dimethylamine hydrochloride (99%, Acros Organics), methylethylamine (94%, MEA, Acros Organics), diethylamine (DEA, ≥99%, Acros Organics), sodium nitrite (≥97%, Bodi, China), sodium bromide (≥99%, Shuangchuan, China), trimethylamine hydrochloride (98%, Acros Organics), 3-(Dimethylaminomethyl) indole (DMAI, 99%, Acros Organics) and all other reagents were used without further purification. The structures of the important organic compounds mentioned in this study are listed in Table 1.

All glassware used was soaked in a solution of H_2SO_4–$K_2Cr_2O_7$ overnight, and then washed in tap water, followed by three rinses in distilled water.

Disinfection process

In this study, hypochlorous acid (HOCl) and monochloramine (NH_2Cl) were all prepared daily, and the concentrations were determined using the colorometric

Table 1 | Structures of the organic compounds mentioned in this study

Name	Structure	Name	Structure
Dimethylamine (DMA)		*N*-nitrosodimethylamine (NDMA)	
Methylethylamine (MEA)		*N*-nitrosomethylethylamine (NMEA)	
Diethylamine (DEA)		*N*-nitrosodiethylamine (NDEA)	
Trimethylamine (TMA)		3-(Dimethylaminomethyl) indole (DMAI)	
Chlorinated dimethylamine (CDMA)		Brominated dimethylamine (BDMA)	
Unsymmetrical dimethylhydrazine (UDMH)		Chlorinated UDMH (UDMH-Cl)	

N, *N*-diethyl-*p*-phenylenediamine (DPD) method (APHA AWWA WEF 1998). Unless otherwise specified, all experiments were conducted in sealed 500 mL bottles. DMA and varied concentrations of other reagents were mixed thoroughly in 500 mL water. Disinfectant was then added immediately. The pH was adjusted to 7.0 using 0.5 M phosphate buffer. The solutions were reacted for 36 h in the dark at 25°C before NDMA analysis. The reactions were quenched using Na_2SO_3 as terminator.

Analysis

NDMA, NMEA and NDEA were detected using an LC–10A high-pressure liquid chromatograph (HPLC, Shimadzu, Japan) with ultraviolet detector using the method developed by Chen *et al.* (2007). This method is simple, quick to operate and suitable for determining trace amounts of NDMA in drinking water. A Venusil Mp–C18 column (5 μm particles, 4.6 × 150 mm, Agela Technologies Inc.) was used to separate peaks in the HPLC before the samples were injected into the ultraviolet detector. The mobile phase was methanol:water (5:95, v/v) at a flow rate of 1.0 mL min^{-1}. NDMA, NMEA and NDEA were detected by the ultraviolet detector at a wavelength of 228 nm. The practical detection limit was 0.1 μg/L.

DMA was detected using a gas chromatogram method after derivatization with benzenesulfonyl chloride (Frank *et al.* 1997). In this study, the derivatization was conducted in a 22 mL extraction vial. The volume of sample used was 10 mL, and the amounts of all other reagents were scaled down accordingly. After optimization, 25 samples could be derivatized at the same time within 1.5 h, the solvent volume used was reduced by 90%. And the expensive MS detector was replaced by FID to detect trace DMA better. The method detection limit was 0.5 μg/L, the standard deviation of the method was 0.048–0.0221 μg/L, while the linear range was 1–50.0 μg/L, and the relative standard deviation was less than 4.43%, the recovery with standard addition was 95.0%–104.6%. This improved method was simple and quick to operate and fit for determination of trace DMA and other primary/secondary aliphatic amines in the water.

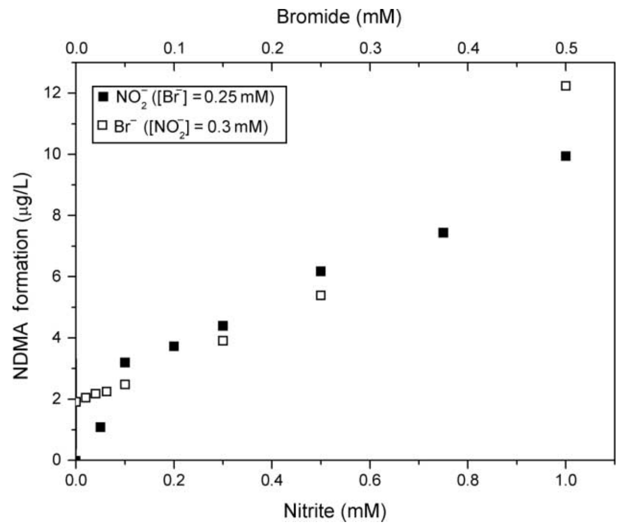


Figure 1 | NDMA formation as a function of nitriteconcentration (mM) during chlorination in the presence of 0.25 mM bromide, and as a function of bromide concentration (mM) in the presence of 0.3 mM nitrite [HOCl] = [DMA] = 0.3 mM, pH = 7.0, 20°C, duration of experiment 24 h.

RESULTS AND DISCUSSION

NDMA formation during chlorination with bromide presence

Choi & Valentine (2003) reported that the formation of NDMA by the nitrosation of DMA can be enhanced by the presence of free chlorine. Since HOBr has similar physico-chemical properties to HOCl, we proposed that the formation of NDMA via nitrosation could also be enhanced by HOBr using an analogous mechanism (Equations (4) and (5)). In this mechanism, the inorganic intermediate N_2O_4 is a reactive species which could react further with DMA to form NDMA (Equation (3)). Experiments were conducted to discuss the influence of the coexistence of bromide and nitrite on NDMA formation during chlorination. In one of them, nitrite increased from 0 to 1 mM with the fixed concentration of bromide 0.25 mM. Another experiment was performed with nitrite 0.3 mM while bromide increased from 0 to 0.5 mM. As shown in Figure 1, both bromide and nitrite improved the yield of NDMA formation when they were both present during chlorination. This observation is consistent with the research of Valentine *et al.* (2005), who indicated that nitrosation of DMA by nitrite is the fundamental pathway of NDMA formation during chlorination in the presence of bromide.

$$HOBr + NO_2^- \rightarrow NO_2Br + OH^- \quad (4)$$

$$NO_2Br + NO_2^- \rightarrow N_2O_4 + Br^- \quad (5)$$

Nitrite can be formed by oxidation of DMA or other nitrogenous species by HOCl/HOBr, leading to a detectable yield of NDMA during chlorination, even without nitrite in the source water. The oxidizing strength of HOBr is less than that of HOCl, so we expected that the yield of NDMA would decrease as the concentration of bromide decreased. Experiments were conducted to discuss the variation of NDMA formation with the increasing bromide (from 1.25 μM to 31.25 μM) during chlorination without addition nitrite. But interestingly, the results shown in Figure 2 were not completely consistent with our hypothesis. When bromide ions were present at 1.25 μM, approximately 40 μg/L NDMA formed after 36 h, which was greater than the yield observed in the absence of bromide (nearly 27 μg/L). The yield of NDMA decreased with increasing dosage of bromide. When the concentration of bromide increased to 8.75 μM, the yield of NDMA approached that observed in the absence of bromide.

During the chlorination process, there was competition between DMA and bromide for the HOCl. The formation of chlorinated dimethylamine (CDMA) from DMA and

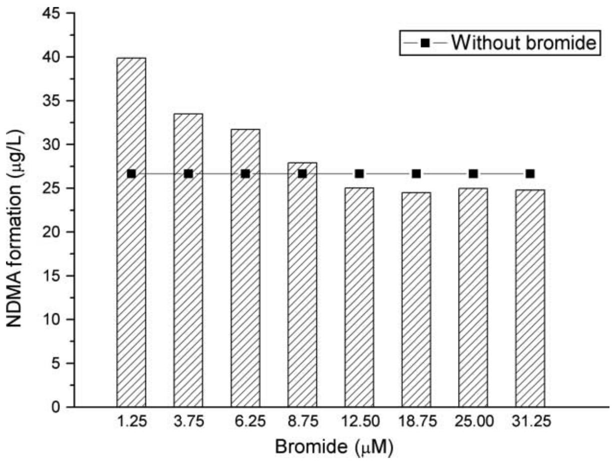


Figure 2 | NDMA formation as a function of bromide concentration during chlorination. [HOCl] = [DMA] = 0.3 mM, pH = 7.0, 25°C, 36 h.

HOCl is a rapid reaction, which has a rate constant $k_1 = 4.22 \times 10^4\,M^{-1}\,S^{-1}$ (Choi & Valentine 2002*b*), while the formation of HOBr from bromide and HOCl is a two-step reaction (Margerum & Hartz 2002). Bromine chloride (BrCl), a reactive intermediate, forms with a rate constant $k_2 = 1.55 \times 10^3\,M^{-1}\,S^{-1}$, which is an order of magnitude less than k_1. Then, BrCl rapidly hydrolyzes to form HOBr ($k_3 = 3.0 \times 10^6\,M^{-1}\,S^{-1}$). The higher yield of NDMA in the presence of lower bromide concentrations may be caused by the reaction between nitrite and BrCl. With high reactive activity, BrCl might be able to react more easily with nitrite to form NO_2Br (Equation (6)), which could continue to react with nitrite to form N_2O_4 (Equation (5)), a good nitrosating reagent.

$$BrCl + NO_2^- \rightarrow NO_2Br + Cl^- \quad (6)$$

As the dosage of bromide increased, most bromide was converted into HOBr by the hydrolysis of BrCl (the formation of HOBr has a high rate constant, which promotes the transformation of bromide). The yield of NDMA decreased with the increasing bromide dosage, as shown in Figure 2. This observation could be explained by that HOBr is a weaker oxidant than HOCl. Unfortunately, neither BrCl nor N_2O_4 could be detected under the experimental conditions because of their instability. Further work needs to be done to validate this hypothesis.

Bromate (BrO_3^-) and chlorate (ClO_3^-) were also formed as by-products during the chlorination of bromide-containing water. We conducted experiments to determine whether they would be effective precursors of NDMA formation. However, after a 36 h reaction of DMA with BrO_3^- or with ClO_3^-, no significant NDMA was detected, even with a high dosage of reactants (0.3 mM DMA,1 mM BrO_3^- or 1 mM ClO_3^-).

NDMA formation during chlorination in the presence of both bromide and ammonium ions

Effect of the order of reagent addition

Schreiber & Mitch (2005) indicated that nitrosamine formation is associated with chloramination rather than chlorination, meaning that ammonium ion (NH_4^+) is the key species for NDMA formation during chlorine disinfection. When NH_4^+ and bromide are both present, HOCl is converted into more effective inorganic precursors of NDMA, i.e. halamines. Three different regimes were tested, in which various reagents were added to the reaction mixture in different orders to simulate different chloramination disinfection processes (Table 2). The dosage of NH_4^+ was varied from 0 to 1.5 mM.

The main difference between the three orders was the species of reagents B and C. In Order 1, NH_4^+ was added before HOCl, which is equivalent to chlorination of water with DMA when both bromide and NH_4^+ are present. In Order 2, preformed monochloramine was added after NH_4^+, while NH_4^+ was added after HOCl in Order 3. The order of addition used in Order 3 would help maintain residual levels of chlorine for longer in a long pipe network.

As shown in Figure 3, the lowest yield of NDMA was in Order 3, while the maximum was in Order 1. Similar results were observed by Schreiber & Mitch (2005) where no

Table 2 | Details of the three orders of reagent additon used in the chloramination of DMA and Br^-

Order #	A	B	C
1	DMA + Br^-	NH_4^+	HOCl
2	DMA + Br^-	NH_4^+	NH_2Cl
3	DMA + Br^-	HOCl	NH_4^+

Note: The scenarios were denoted according to the following scheme: C → (B → A) indicating that B was added to a well-mixed solution containing A, and after complete mixing, C was added to solution. The addition interval between B and C was 5 min.

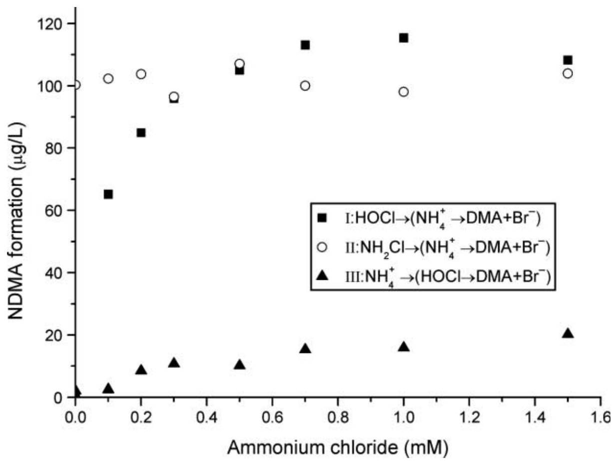


Figure 3 | NDMA formation as a function of NH_4^+ concentration during chlorination with 31.25 μM bromide. [HOCl] = [DMA] = 0.3 mM, pH = 7.0, 25°C, 36 h.

bromide was present. However, in their study, yield of NDMA increased noticeably in the presence of bromide.

With the addition of NH_4^+ to the water, competition for HOCl becomes more complicated, leading to many reactive intermediates being formed, such as bromamines. Valentine *et al.* (2005) indicated that bromamines are much more reactive than chloramines because of their nucleophilicity. They also found that there are two pathways which are expected to enhance NDMA formation: (a) oxidation of bromide by monochloramine and (b) oxidation of bromide by HOCl, followed by a rapid reaction with NH_4^+. During chlorination, the yield of NDMA formation is not expected to be much, even though the reaction of bromide and HOCl is fast, due to the rapid formation of CDMA. This could explain why the lowest yield of NDMA came from Order 3.

Therefore, pathway (a) may be the major pathway for NDMA formation in the presence of NH_4^+ and bromide. Once halamines are formed, NH_4^+ has no obvious effect on NDMA formation, according to the results of Order 2 shown in Figure 3.

Effect of bromide dosage

As shown in Figure 4(A), both NDMA and NDEA yields increased with increasing bromide concentration, which varied from 0 to 300 μM during chloramination where DMA and DEA were used as the respective precursors. This indicates that the secondary aliphatic amines could react with halamines to form the relevant *N*-nitrosamines via analogous pathways, as shown in Equations (7) and (8).

$$NH_2X + R_1R_2NH \rightarrow R_1R_2NNH_2 \xrightarrow{NH_2X} R_1R_2NNO \quad (7)$$

$$NHX_1X_2 + R_1R_2NH \rightarrow R_1R_2NNHX_1 \xrightarrow{[O]} R_1R_2NNO \quad (8)$$

X, X_1, X_2 = Cl or Br

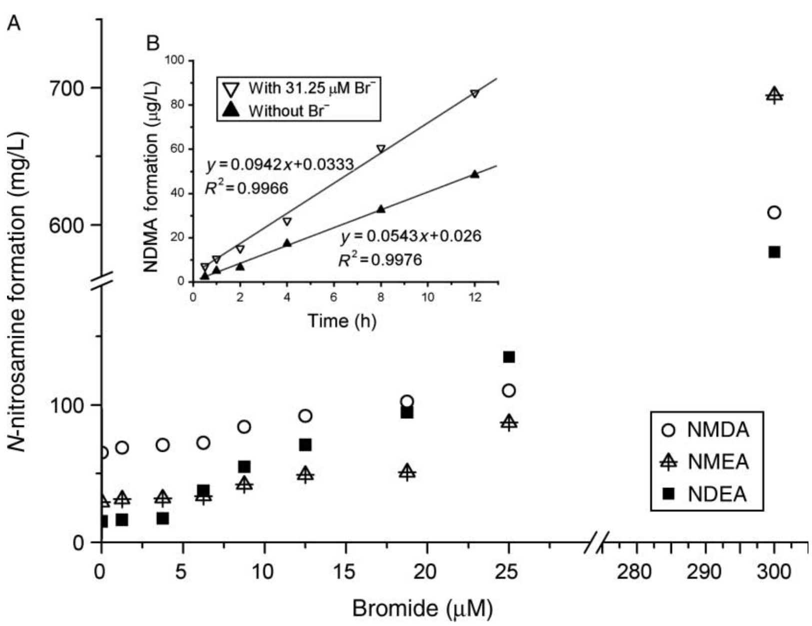


Figure 4 | (A) Nitrosamine formation as a function of bromide concentration during chloramination. [NH_2Cl] = [DMA] = [MEA] = [DEA] = 0.3 mM, pH 7.0, 25°C, 24 h; (B) NDMA formation as a function of reaction time with and without 31.25 μM Br^-, pH = 7.0, 25°C, [DMA] = 0.3 mM, [NH_2Cl] = 1 mM.

The rate of NDMA formation also increased notably after bromide was added to the water. Excellent linear correlations were observed between reaction time and NDMA formation during chloramination with and without bromide. The slopes of the regression equations are $K_1 = 0.055$ and $K_2 = 0.094$, respectively, as shown in Figure 4(B).

Schreiber & Mitch (2006) indicated that dichloroamine might play an important role in NDMA formation during chloramination, possibly even more important than monochloramine. So, it is possible that another pathway exists for bromamine formation, i.e. oxidation of bromide by dichloramine. As the tests of NDMA formation under different orders of reagent addition were conducted at pH 7, dichloramine may have been formed by the partial conversion of monochloramine. This could mean that the NDMA formation in Order 1 was contributed to by the formation of bromamines via all three pathways, indicating that pathway (b) might not be the major one.

Effect of pH

The influence of pH on NDMA formation during chloramination, both with and without bromide, was conducted at pH 4, pH 7, pH 9 and pH 12. As shown in Figure 5, the greatest NDMA formation was at neutral pH, regardless of the presence or absence of bromide. In the absence of bromide, NH_2Cl and $NHCl_2$ coexist at neutral pH, while NCl_3 (which cannot react further with DMA) is the major chloramine species at acidic pH (pH < 4), and NH_2Cl is the major species at pH > 9. So at pH 7, NDMA should form via both UDMH and UDMH–Cl (UDMH–Br) pathways. UDMH and UDMH–Cl (UDMH–Br) might be more readily formed with the participation of bromide. Since the N-Cl linkage in UDMH–Cl is so weak that it can be oxidized into NDMA by dissovled oxygen (Schreiber & Mitch 2006), more NDMA could be formed by $NHCl_2$ (UDMH–Cl pathway) than by NH_2Cl (UDMH pathway). It follows that using preformed NH_2Cl (Order 2 in Table 2) could be an effective method of controlling NDMA formation. This result is consistent with the report of Schreiber & Mitch (2005), which did not consider the effects of the presence of bromide.

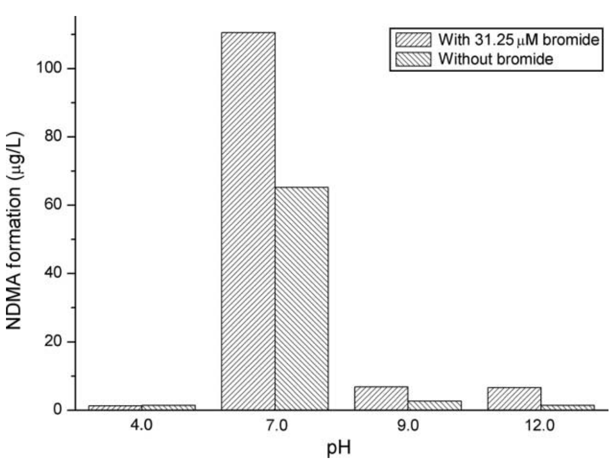


Figure 5 | NDMA formation as a function of pH value during chloramination with and without 31.25 μM bromide. $[NH_2Cl] = [DMA] = 0.3$ mM, pH = 7.0, 20°C, 24 h.

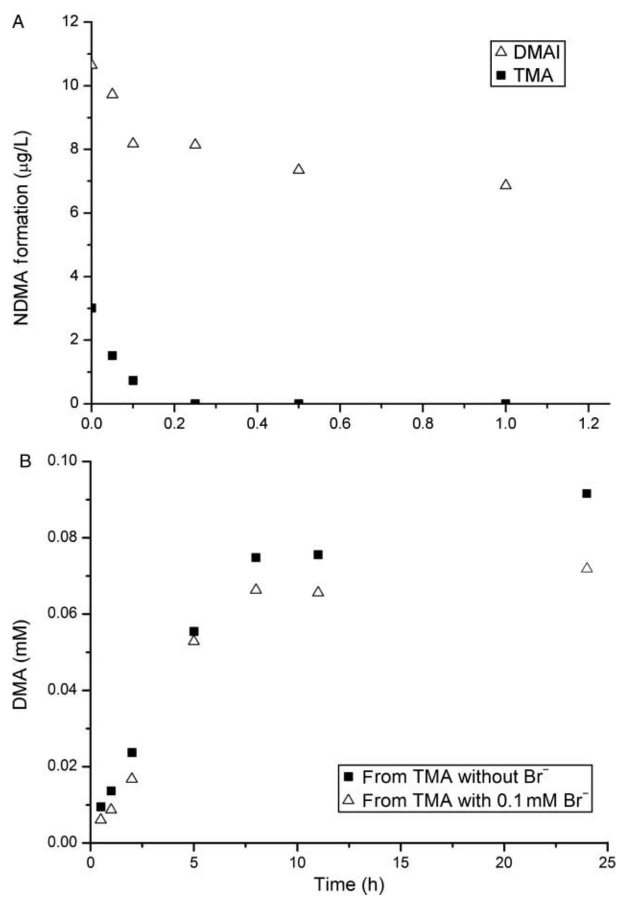


Figure 6 | (A) NDMA formation as a function of bromide concentration during chloramination when tertiary amines were used as the organic precursors. $[NH_2Cl] = [DMAI] = [TMA] = 0.3$ mM, pH = 7.0, 20°C, 24 h; (B) Formation of DMA during chloramination of TMA with and without 0.1 mM bromide. $[NH_2Cl] = [TMA] = 0.3$ mM, pH = 7.0, 20°C.

NDMA formation from tertiary alkylamines during chloramination in the presence of bromide

Tertiary alkylamines with a DMA group could also form NDMA during chlorination and chloramination (Schreiber & Mitch 2008). A series of experiments were processed to discuss the influence of bromide on NDMA formation via tertiary alkylamines during chloramination with increasing bromide (from 0 to 1 mM). As shown in Figure 6(A), the yield of NDMA formed during chloramination was inhibited by bromide, while 3-(Dimetylaminomethyl) indole (DMAI) and trimethylamine (TMA) were used as precursors. These results were contrary to those found with secondary aliphatic amines. The restraining effect of bromide on NDMA formation indirectly indicates that NDMA formation from tertiary amines during chloramination follows a different pathway from that of NDMA formation from secondary amines.

Mitch & Schreiber (2008) proposed that tertiary alkylamines degrade during chloramination to form aldehydes and secondary alkylamines, leading to several nitrogenous DBPs (including nitrosamines) being formed. So with more bromide present in the water, more chloramines might be converted into less oxidative bromamines, resulting in smaller amounts of secondary alkylamines being formed. Evidence for this hypothesis was provided by the results shown in Figure 6(B). Furthermore, the formation of brominated alkylamines, which are less reactive than DMA, also limited the formation of NDMA.

Proposed mechanisms

As shown by the experiments described above, the reactive inorganic nitrogenous intermediates formed during disinfection of bromide-containing water were important for NDMA formation. Based on the results of this and other related studies (Mitch & Sedlak 2002; Choi & Valentine 2003; Schreiber & Mitch 2006; Valentine *et al.* 2005), the possible pathways of NDMA formation during chlorine disinfection in the presence of bromide are summarized in Figure 7.

Since disinfectants such as chlorine and chloramines are strong oxidants, they can oxidize organic nitrogenous precursors into the relevant products (e.g. hydroxylamines, nitrite, nitrate). In the presence of bromide, the species of intermediates become more diversified.

During chlorination, nitrosation is the main pathway for NDMA formation. Although nitrite is important for NDMA formation, the essential inorganic precursors are in the form of NO-X (X can be NO_2, NO_3 among others) known as nitrosating reagents (Patai 1982). The reaction of nitrosating agents with DMA are known to occur by nucleophilic substitution (SN_2). As discussed above, N_2O_4 might be formed more easily from a reaction between nitrite and reactive BrCl than from a reaction between nitrite and HOBr/HOCl. However, as the dosage of bromide increases, HOBr will become the major species. Also, BrCl can react further with OBr^-/OCl^- to form BrO_3^-/ClO_3^-, which does not contribute to NDMA formation.

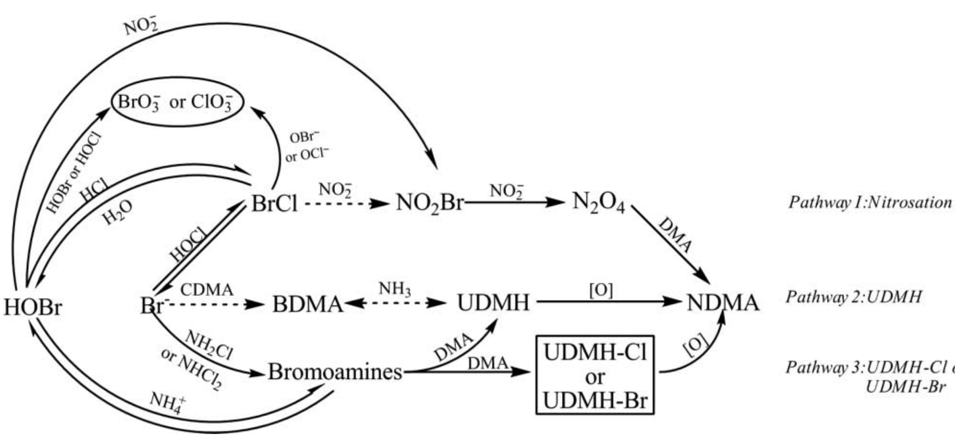


Figure 7 | Possible pathways of NDMA formation in the presence of bromide.

Even though the chlorination process in our experiment without NH_4^+ was conducted under ideal conditions, a certain amount of NH_4^+ should exist in the practical disinfection process. With the formation of chloramines and bromamines, NDMA formation can be explained by the UDMH or UDMH–Cl mechanism. Therefore, the addition Order 3 mentioned in Table 2 is unlikely to be feasible, despite it being the best of the tested regimes in controlling the formation of NDMA.

CDMA is the common product during both chlorination and chloramination of DMA-containing water, and it can react with NH_3 to form UDMH via a reversible reaction (Mitch & Sedlak 2002). Brominated dimethylamine (BDMA) might form UDMH more readily than CDMA due to the Cl being replaced by reactive Br.

Since this study focuses on the mechanisms of *N*-nitrosamine formation, the precursors concentration used and *N*-nitrosamines yield formed in this study are higher than practical water treatment process. It should be known that some of the pathways might be disrupted by the reaction between reactive intermediate and other coexisted organic compounds, leading to lower yield of *N*-nitrosamines. But this study still has directive significance to the practical water treatment because of the high cancer risk of NDMA. According to the results we discussed above, the concentrations of organic precursors, bromide and NH_4^+ are crucial to the yield of *N*-nitrosamines. NH_4^+ could be removed by common water treatment technology, while bromide is hard to be eliminated. Removal of organic precursors is the best method to prevent *N*-nitrosamine formation once and for all. Therefore, secure and effective methods for removing alkylamines need to be developed under the pressure of the necessity.

CONCLUSIONS

On the base of former studies on *N*-nitrosamine formation mechanism, the formation pathways were further discussed in this study.

1. Reactive intermediates formed during chlorination or chloramination, such as BrCl and halamines, might be responsible for variations in the yield of NDMA formation. Therefore, two new possible pathways were hypothesized: (i) nitrosation via N_2O_4 formed by the reaction of BrCl and nitrite; (ii) UDMH-Br pathway via oxidation of bromide by dichloramine.
2. The yield of NDMA during chloramination with bromide could be limited by adopting an appropriate order of reagent addition.
3. Nitrosamines can be formed via a similar formation pathway during chlorination in the presence of secondary amines and bromide.
4. The yield of NDMA from tertiary alkylamines with a DMA group during chloriamination may be limited by the presence of bromide.

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