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Formation of *N*-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product

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Abstract

Studies have been conducted specifically to investigate the hypothesis that *N*-nitrosodimethylamine (NDMA) can be produced by reactions involving monochloramine. Experiments were conducted using dimethylamine (DMA) as a model precursor. NDMA was formed from the reaction between DMA and monochloramine indicating that it should be considered a potential disinfection by-product. The formation of NDMA increased with increased monochloramine concentration and showed maximum in yield when DMA was varied at fixed monochloramine concentrations. The mass spectra of the NDMA formed from DMA and ^{15}N isotope labeled monochloramine ($^{15}NH_2Cl$) showed that the source of one of the nitrogen atoms in the nitroso group in NDMA was from monochloramine. Addition of 0.05 and 0.5 mM of preformed monochloramine to a secondarily treated wastewater at pH 7.2 also resulted in the formation of 3.6 and 111 ng/L of NDMA, respectively, showing that this is indeed an environmentally relevant NDMA formation pathway. The proposed NDMA formation mechanism consists of (i) the formation of 1,1-dimethylhydrazine (UDMH) intermediate from the reaction of DMA with monochloramine followed by, (ii) the oxidation of UDMH by monochloramine to NDMA, and (iii) the reversible chlorine transfer reaction between monochloramine and DMA which is parallel to (i). We conclude that reactions involving monochloramine in addition to classical nitrosation reactions are potentially important pathways for NDMA formation.

Keywords: Disinfection by-product (DBP); *N*-nitrosodimethylamine (NDMA); Monochloramine; 1,1-dimethylhydrazine (UDMH); Chlorine transfer

1. Introduction

Nitrosamines are a class of compounds, many of which are carcinogenic, mutagenic, and teratogenic [1,2]. Particularly, *N*-Nitrosodimethylamine (NDMA) has been classified as a probable human carcinogen by the US Environmental Protection Agency [3]. Risk assessments from the US EPA identify a theoretical 10^{-6} lifetime risk level of cancer from NDMA exposures as 0.7 ng/L [3]. There is no state or federal drinking water maximum contaminant level, however the State of California has established a temporary action level of 20 ng/L for NDMA in drinking water [4].

Nitrosamines have been found in many food products as well as soils, wastewater, and drinking water [5,6]. It is generally thought that nitrosamine formation involves N-nitrosation, a reaction between nitrosatable amines and nitrite [7,8]. Therefore, NDMA is likely to be found especially where both secondary amines and nitrite occur. Environmentally oriented NDMA occurrence and formation studies have been generally empirical in nature and have focussed primarily on determining if, not how, nitrosamines may be formed in water. Most studies are predicated on the assumption that nitrite is a required reactant and have added it to water to determine an NDMA formation potential. Ayanaba and Alexander [9] demonstrated the formation of

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NDMA in the lake water at neutral pH values when dosed with nitrite and dimethylamine (DMA) and trimethylamine. Studies have also investigated the influence of other precursors or fulvic acid on nitrosamine formation with added nitrite [10,11].

Recently, NDMA was found in highly purified wastewaters intended for recycle as well as some treated drinking waters while absent in the influent streams [4]. The current investigations in California indicate that NDMA could be more commonly observed in treated waters than previously suspected, which suggests that NDMA occurrences may be related to treatment and disinfection processes.

Our studies were conducted to investigate the hypothesis that NDMA is a disinfection by-product specifically produced by the reaction of monochloramine and DMA in the absence of nitrite. Monochloramine is purposely produced as a disinfectant, which may also form in chlorinated water in the presence of ammonia. We selected DMA as a potential precursor because it is ubiquitous in surface and wastewater [12,13]. Other alkylamines or pesticides may also decompose to give rise to potential precursors of NDMA [9]. A series of experiments were conducted to identify the formation of NDMA from monochloramine and DMA. Unlike N-nitrosation that requires nitrite, we propose a new NDMA formation mechanism that involves monochloramine. A kinetic model was developed and used to validate the proposed mechanism.

2. Materials and methods

2.1. Chemicals

N-nitrosodimethylamine (NDMA, 100 μg/mL in methanol) was obtained from Chem Service. Deuterated N-nitrosodimethylamine (d_6-NDMA, 1000 μg/mL in methanol) was obtained from Protocol Analytical Supplies. ^{15}N isotope labeled ammonium sulfate ($^{15}N_2$, 98% +) was obtained from Cambridge Isotope Lab, Inc. Sodium nitrite, 1,1-dimethylamine hydrochloride, and ammonium sulfate were obtained from Aldrich. Sodium hypochlorite solution was obtained from Fisher Scientific. All other chemicals used in these experiments were analytical laboratory grade.

2.2. NDMA formation reactions

Experiments were conducted in batch 1 L sealed bottles at 25°C. All reaction solutions were prepared using deionized water buffered with 1 mM bicarbonate, and adjusted to approximately pH 7 by acid addition. DMA was added from 0.01 to 4.0 mM at fixed monochloramine concentration of 0.1 mM. Monochloramine was added from 0.01 to 2.0 mM at fixed DMA concentration of 0.1 mM. This study used preformed monochloramine additions to the DMA containing solutions as opposed to forming it in the presence of DMA and ammonia by addition of HOCl. This was done to simplify interpretation of the results by avoiding the need to consider initial competing reactions involving HOCl. The concentration of ammonia was also varied from 0.14 to 1.0 mM to obtain varied monochloramine Cl/N molar ratios (0.1–0.7). The mixtures were reacted in the dark for 0.5–40 h. An experiment was also conducted to evaluate the relative importance of nitrosation by reacting sodium nitrite with DMA in the absence of monochloramine. DMA was also reacted with isotopically labeled $^{15}NH_2Cl$ to identify the source of the nitrogen atoms in the nitroso group of NDMA. Lastly, NDMA formation potential in collected secondarily treated wastewater was evaluated by adding 0.05 and 0.5 mM of monochloramine.

2.3. Preparation and analysis of monochloramine

Monochloramine stock solutions were prepared in 4 mM bicarbonate buffer by adding predetermined amount of sodium hypochlorite solution into ammonium sulfate solution. The pH was adjusted to approximately 9.6 by addition of NaOH and aged in the dark for at least 1 h before use. ^{15}N isotope labeled monochloramine ($^{15}NH_2Cl$) stock solutions were prepared using ^{15}N isotope labeled ammonium sulfate. The concentration of monochloramine was measured using the N,N–diethyl–p–phenylenediamine ferrous ammonium sulfate (DPD-FAS) method [14].

2.4. NDMA analysis

NDMA was determined by isotope dilution gas chromatography/mass spectrometer (GC/MS) method [15]. Prior to extraction, all 1 L samples are dosed with the isotopically labeled d_6-NDMA as an internal standard. 1 L sample is added with 200 mg of carbonaceous adsorbent (Ambersorb 572, Aldrich) and extracted by shaking the solution for 1 h at 200 rpm. Ambersorb beads are vacuum filtered onto a glass fiber filter, and dried in air for 30 min. Beads are transferred to a 2 mL amber vial where beads are soaked with 0.5 mL of methylene chloride for 20 min before analysis. A 95 μL aliquot of methylene chloride extract is injected into GC/MS (Finnigan MAT) equipped with Large Volume Injector (Optic2). NDMA is quantified based on the mass detection of the characteristic molecular ion ($m/z = 74.048$) of NDMA and molecular ion of d_6-NDMA ($m/z = 80.086$). The MDL at the 99% confidence level was determined to be 2.4 ng/L.

3. Results and discussion

3.1. NDMA formation studies

Initial experiments compared NDMA formation by the reaction of DMA with nitrite to that from the reaction of DMA with monochloramine (Fig. 1). NDMA was not found as a contaminant in any of the individual reactant solutions. Approximately 12 μg/L of NDMA was formed after 24 h from the reaction of 0.1 mM of DMA and 0.1 mM of preformed monochloramine, while about 2 μg/L of NDMA was produced by the reaction of 0.1 mM of DMA with 0.1 mM of nitrite. In the absence of nitrite, the formation of NDMA is attributed to monochloramine with the reaction of DMA. No significant amount of NDMA was produced by the addition of HOCl to a solution of DMA, presumably because of the absence of free ammonia.

NDMA formation continued over 40 h period reaching 18 μg/L and the formation potential did not appear to be exhausted after 40 h as shown in Fig. 2. The DPD-FAS titration and UV absorbance at 244 nm indicated that monochloramine concentration decreased from 0.1 mM to approximately 0.06 mM after 40 h. Included on this figure and several that follow (Figs. 3–5), are lines showing predicted NDMA concentrations based upon the proposed reaction mechanism and kinetic modeling to be discussed in subsequent subsections.

NDMA formation was studied as a function of monochloramine concentration at a fixed DMA concentration of 0.1 mM (Fig. 3). NDMA formation increased with increasing monochloramine concentration from 0.01 to 2 mM. The formation appeared to reach an apparent plateau with addition of approximately 2 mM of monochloramine.

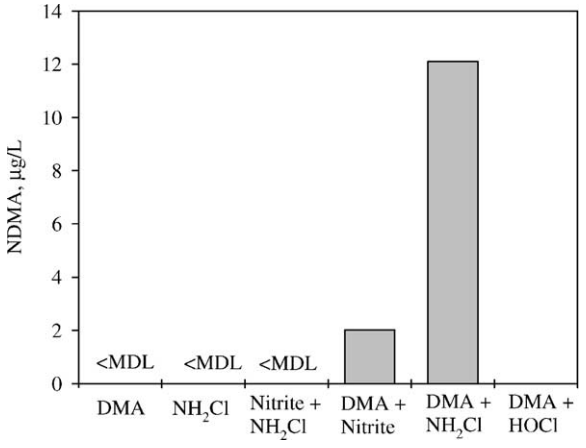

Fig. 1. NDMA formation after 24 h as a function of added component. The concentration of each compound is 0.1 mM. The pH was adjusted to 7.0±0.1 using 1 mM bicarbonate buffer. Solutions were kept in the dark at 25°C.

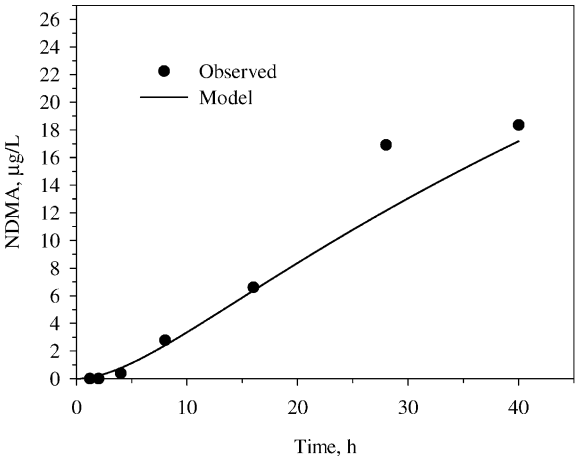

Fig. 2. NDMA formation as a function of time. 0.1 mM of DMA was reacted with 0.1 mM of monochloramine. The pH was adjusted to 7.0±0.1 using 1 mM bicarbonate buffer. Solutions were kept in the dark at 25°C. Model results are calculated NDMA concentrations based upon reactions and rate constants shown in Table 1.

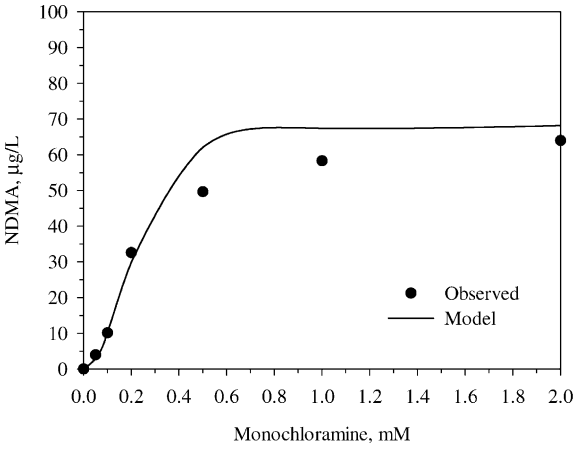

Fig. 3. NDMA formation after 24 h as a function of monochloramine concentration. DMA concentration was fixed at 0.1 mM. The pH was adjusted to 7.0±0.1 using 1 mM bicarbonate buffer. Solutions were kept in the dark at 25°C. Model results are calculated NDMA concentrations based upon reactions and rate constants shown in Table 1.

NDMA formation showed a maximum in yield when DMA was varied (0.01–4.0 mM) at fixed monochloramine concentrations of 0.1 and 0.5 mM (Figs. 4 and 5). The maximum occurred when the ratio of DMA to monochloramine was approximately 1.0 mM. The amount of NDMA produced rapidly decreased as the ratio of DMA to monochloramine was further increased beyond 1.0 mM.

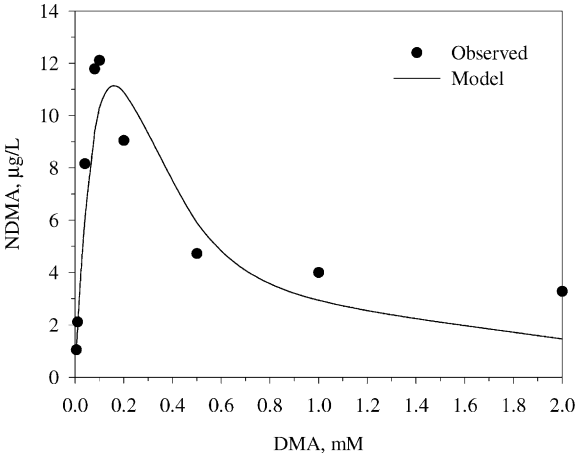

Fig. 4. NDMA formation after 24 h as a function of DMA concentration. Monochloramine concentration was fixed at 0.1 mM. The pH was adjusted to 7.0 ± 0.1 using 1 mM bicarbonate buffer. Solutions were kept in the dark at 25°C. Model results are calculated NDMA concentrations based upon reactions and rate constants shown in Table 1.

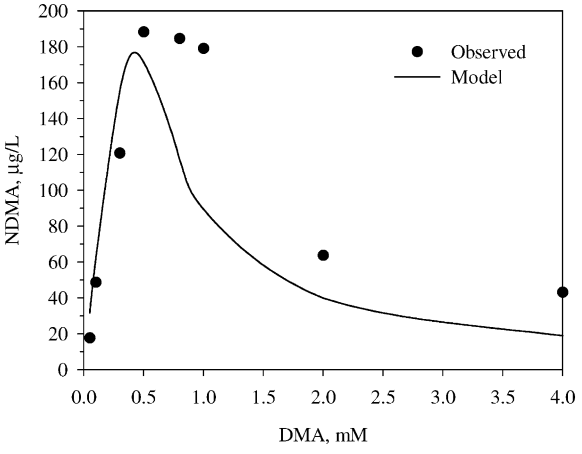

Fig. 5. NDMA formation after 24 h as a function of DMA concentration. Monochloramine concentration was fixed at 0.5 mM. The pH was adjusted to 7.0 ± 0.1 using 1 mM bicarbonate buffer. Solutions were kept in the dark at 25°C. Model results are calculated NDMA concentrations based upon reactions and rate constants shown in Table 1.

The influence of excess ammonia was investigated by varying ammonia concentration from 1.0 to 0.14 mM (Cl/N molar ratio of 0.1–0.7) (Fig. 6). Both monochloramine and DMA concentrations are fixed at 0.1 mM. This range was chosen because it is in the sub-breakpoint region and the monochloramine is relatively stable over the 24 h reaction time period. The amount of NDMA formed slightly increased with decreasing ammonia (increasing Cl/N ratio) at fixed monochloramine of 0.1 mM. The influence, however, was not as significant as that observed when varying the ratio of DMA to monochloramine. It should be noted that decomposition of monochloramine occurred over this time period (less than 30%) at pH 7. The rate of decomposition of monochloramine tends to increase with increasing Cl/N ratio [16].

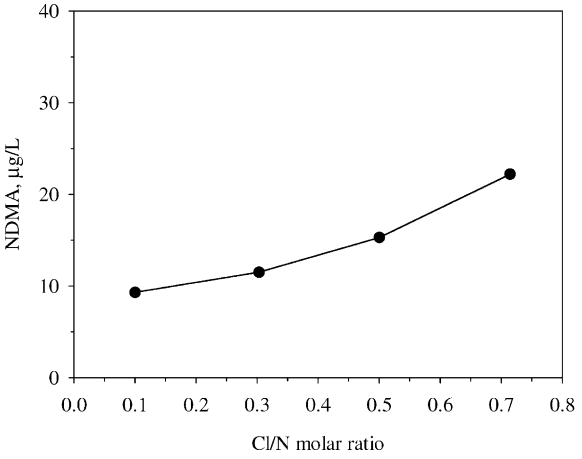

Fig. 6. NDMA formation as a function of monochloramine Cl/N molar ratio. Both concentrations of monochloramine and DMA are 0.1 mM. Solutions were kept in the dark at 25°C. The pH was adjusted to 7.0 ± 0.1 using 1 mM bicarbonate buffer. Line connects data points. No model results shown.

DMA was reacted with preformed $^{15}NH_2Cl$ and the mass spectra of NDMA peak was examined. Fig. 7b shows that the mass spectra of NDMA produced from $^{14}NH_2Cl$ and DMA was identical to that of commercially obtained NDMA (Fig. 7a) made from ^{14}N (Fig. 7a). Both spectra show a parent molecular ion peak for NDMA at m/z ratio of 74. However, the mass spectra of NDMA from the reaction of $^{15}NH_2Cl$ and DMA (Fig. 7c) results in a parent molecular ion at m/z ratio of 75. The one mass unit shift from 74 to 75 shows that one of nitrogen atoms in NDMA is ^{15}N and must be from $^{15}NH_2Cl$ because DMA was not labeled, i.e. $(CH_3)_2N\ ^{15}N{=}O$. Note that the mass peak at m/z ratio of 42 is due to $CH_2{=}N{=}CH_2^+$ which is formed during the characteristic fragmentation of DMA [17] and this peak was not affected by $^{15}NH_2Cl$. Hence, we conclude that the formation of NDMA in this system is from the reaction of DMA and monochloramine.

Surface and wastewaters may contain DMA or related compounds, and thus NDMA may also be formed by the reaction with monochloramine. This potential was demonstrated in secondarily treated wastewater at pH 7.2 by addition of preformed monochloramine. Addition of 0.05 and 0.5 mM monochloramine resulted in the NDMA formation of 3.6 and 111 ng/L, respectively after 24 h. None was present in the absence of monochloramine addition.

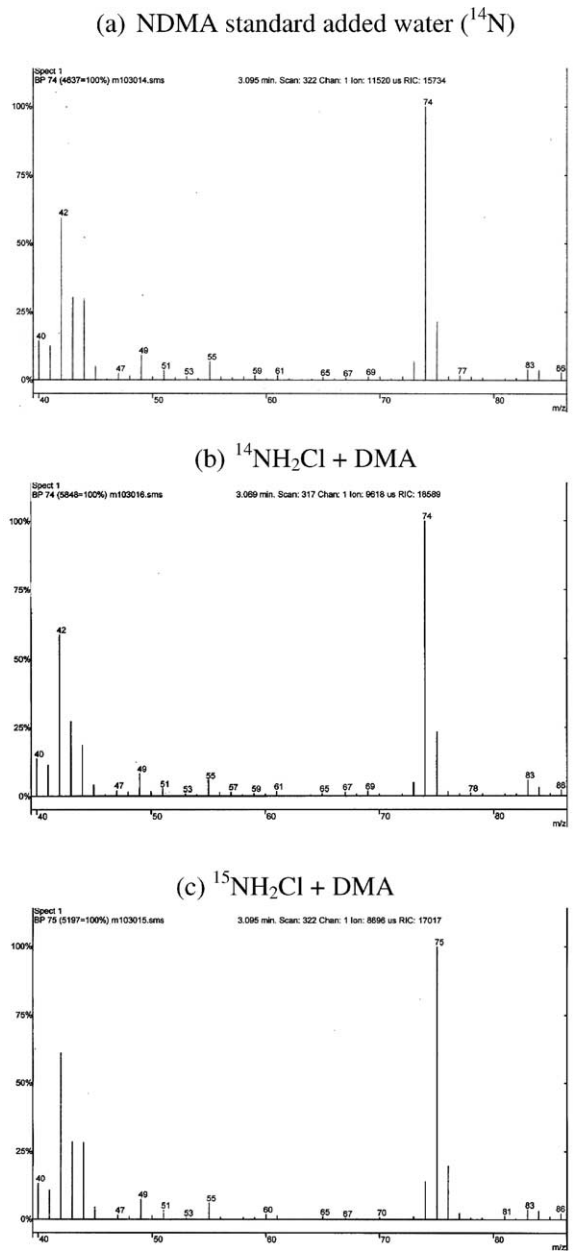

Fig. 7. The mass spectra of NDMA from (a) commercially obtained NDMA showing a parent m/z peak (M^+) at 74, (b) the reaction of $^{14}NH_2Cl$ and DMA showing a parent m/z peak (M^+) at 74, (c) the reaction of $^{15}NH_2Cl$ and DMA showing a parent m/z peak (M^+) at 75.

3.2. Proposed reaction mechanism

We propose a new NDMA formation mechanism that involves monochloramine that probably occurs in chloraminated water containing DMA or other potential precursors. This mechanism is unlike that of classical nitrosation, which requires nitrite as a nitrosating agent [7,8]. Depending on the relative stability of nitrite in the presence of monochloramine [18], however, both pathways may take place in parallel to form NDMA. The proposed key reactions when preformed monochloramine is an initial reactant are shown schematically in Fig. 8 and listed in Table 1. Also listed in Table 1 are rate constants used in the reaction modeling.

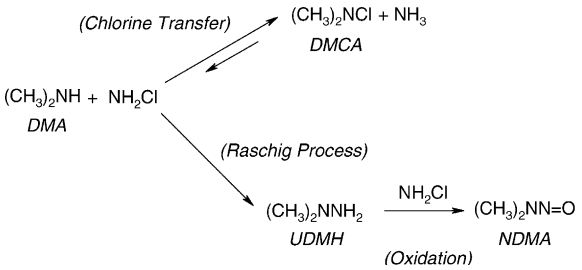

Fig. 8. Proposed reaction scheme for NDMA formation from DMA and monochloramine.

The critical NDMA formation reactions consist of (i) the formation of 1,1-dimethylhydrazine (UDMH) intermediate from the reaction of DMA with monochloramine followed by, (ii) the oxidation of UDMH by monochloramine to NDMA, and (iii) the reversible chlorine transfer reaction between monochloramine and DMA which is parallel with (i).

By means of a modification of the Raschig synthesis, it has been shown that monochloramine reacts with DMA in aqueous solution to produce UDMH (Reaction 3 in Table 1) [21–24].

The oxidation of UDMH has been studied because it is widely used in rocket propellant fuels. NDMA was found when UDMH was deliberately exposed to the atmosphere [25,26] and oxidized by sodium hypochlorite [27]. However, we hypothesize that UDMH would be preferentially oxidized by monochloramine as shown in Reaction 4 in Table 1 under these reaction conditions. Oxidation of UDMH by HOCl cannot be ruled out but its involvement is not likely due to its extremely low concentration determined by the equilibrium of monochloramine hydrolysis in the presence of excess ammonia. This is also supported by the lack of significant effect of ammonia concentration. Increasing it by a factor of 7 increased NDMA by only a factor of 2 at most (Fig. 6). The oxidation of UDMH by dissolved oxygen is also probably not significant in the presence of monochloramine. Additional studies showed that the amount of NDMA formed after 24 h was independent of oxygen content. Its formation in nitrogen- and oxygen-sparged solutions containing 0.1 mM of monochloramine and 0.1 mM of DMA was essentially identical, 11.6 and 12.1 μg/L, respectively.

Table 1
Proposed reactions and rate constants for NDMA formation from DMA and monochloramine

	Reaction	Rate constant at pH 7 (25°C) ($M^{-1}s^{-1}$)	Reference
(1)	$NH_2Cl + (CH_3)_2NH \rightarrow^{k_1} (CH_3)_2NCl + NH_3$	$k_1 = 1.4 \times 10^{-1}$	[19]
(2)	$(CH_3)_2NCl + NH_3 \rightarrow^{k_2} NH_2Cl + (CH_3)_2NH$	$k_2 = 5.83 \times 10^{-3}$	[20]
(3)	$NH_2Cl + (CH_3)_2NH \rightarrow^{k_3} (CH_3)_2NNH_2 + H^+ + Cl^-$	$k_3 = 1.28 \times 10^{-3}$	This model
(4)	$(CH_3)_2NNH_2 + 2NH_2Cl + H_2O \rightarrow^{k_4} (CH_3)_2NNO + 2NH_4^+ + 2Cl^-$	$k_4 = 1.11 \times 10^{-1}$	This model

Aside from NDMA formation, the reaction of UDMH with monochloramine may form other products such as tetramethyltetrazene, methylenedimethylhydrazine, and formaldehyde dimethylhydrazone [28]. However, due to lack of data, we have not included the formation of these products. Including the formation of these products may affect the apparent rate constants characterizing UDMH formation (k_3) and oxidation to NDMA (k_4) in the model (Table 1).

Instead of UDMH formation, the reaction between monochloramine and DMA also leads to reversible chlorine transfer from monochloramine to DMA to form dimethylchloramine (DMCA) [19,20,29,30] as shown in reactions (1) and (2) in Table 1. Thus, DMCA formation by chlorine transfer would play a significant role in the kinetics and serve to reduce the rate of NDMA formation. The transfer of active chlorine between monochloramine and DMA can occur by direct chlorine transfer or by chloramine hydrolysis with subsequent N-chlorination [20]. Since direct chlorine transfer is subject to general acid catalysis especially in the near neutral and acidic pH range [29,30], the rate of chlorine transfer reaction is expected to increases as pH decreases. In this simplified model, chlorine transfer via chloramine hydrolysis is not considered. However, the pathways involving chloramine hydrolysis may be important under other reaction conditions especially when free chlorine addition is practiced.

A reaction of DMCA with ammonia producing UDMH, although possible [31,32], is probably not significant under these reaction conditions. Otherwise, NDMA formation would also continue to increase (instead of reaching a plateau, Fig. 3) under conditions where essentially all of the DMA is converted to DMCA.

3.3. Kinetic modeling

The reactions shown in Table 1 and corresponding rate expressions were used to develop the set of differential rate expressions describing the reaction mechanism. We assumed that reactions (1)–(3) were elementary and could be described by simple second order reactions. Reaction 4 is clearly not elementary. We assumed, however, that the rate limiting reaction is first order in both DMA and monochloramine. Presumably any intermediates would be rapidly oxidized to NDMA.

The rate constants in Table 1 were obtained either from literature or estimated from the data. The direct acid catalyzed chlorine transfer rate constant (k_1) applicable at pH 7 was obtained from the literature [19]. The rate constant characterizing chlorine transfer from DMCA to ammonia (k_2) was estimated using the value for methylamine [20] and a correlation between rate constants and the basicity [19,20]. The rate constants characterizing the formation of UDMH (k_3) and its oxidation to NDMA (k_4) were estimated simultaneously by minimizing the errors between measured and predicted NDMA concentrations on the data sets shown in Figs. 2 and 3. Finally, the set of differential equations was solved using Scientist™.

The model appears to adequately predict NDMA concentrations within about 20% of the measured values over a 40 h time period (Fig. 2). The model predicted a plateau in NDMA formation with monochloramine concentration (Fig. 3) consistent with the expected limitation of DMA concentration due to DMCA formation (DMA limiting). It also captured the maximum in NDMA formation occurring near the ratio of DMA to monochloramine of approximately 1 (Figs. 4 and 5). The maximum is hypothesized to occur because when the DMA to monochloramine ratio becomes approximately greater than 1, the amount of monochloramine available to oxidize UDMH is rapidly exhausted with increasing DMA due to chlorine transfer (monochloramine limiting).

4. Conclusions

NDMA can be directly formed by the reaction of monochloramine with DMA. Given that drinking waters and wastewaters may contain DMA or related compounds as well as ammonia, NDMA should, therefore, be considered a potential disinfection by-product. This was demonstrated by observing NDMA formation from the addition of monochloramine to a secondarily treated wastewater. Both this reaction and classical nitrosation reactions are therefore potentially important pathways for the formation of NDMA. These findings

suggest that any test developed to ascertain the NDMA formation potential should consider the reaction with monochloramine in addition to the reaction with nitrite. Since a variety of related nitrogenous substances are quite common in some waters, the formation of nitrosamines other than NDMA is also suspected.

The model is simplified but captures several important aspects. These include the rate limiting formation of UDMH and its subsequent oxidation to NDMA. Additionally, the chlorine transfer reaction and the formation of DMCA must play a significant role in the kinetics by consuming both monochloramine and DMA, which would act to eventually reduce NDMA formation. Consideration of additional reactions will be required to provide a more detailed description of this model system and its applicability to water and wastewater treatment systems.

Acknowledgements

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