



The role of chloramine species in NDMA formation

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ABSTRACT

N-nitrosodimethylamine (NDMA), a probable human carcinogen disinfection by-product, has been detected in chloraminated drinking water systems. Understanding its formation over time is important to control NDMA levels in distribution systems. The main objectives of this study were to investigate the role of chloramine species (i.e., monochloramine and dichloramine); and the factors such as pH, sulfate, and natural organic matter (NOM) influencing the formation of NDMA. Five NDMA precursors (i.e., dimethylamine (DMA), trimethylamine (TMA), *N,N*-dimethylisopropylamine (DMiPA), *N,N*-dimethylbenzylamine (DMBzA), and ranitidine (RNTD)) were carefully selected based on their chemical structures and exposed to varying ratios of monochloramine and dichloramine. All amine precursors reacted relatively fast to form NDMA and reached their maximum NDMA yields within 24 h in the presence of excess levels of chloramines (both mono- and dichloramine) or excess levels of dichloramine conditions (with limited monochloramine). When the formation of dichloramine was suppressed (i.e., only monochloramine existed in the system) over the 5 day contact time, NDMA formation from DMA, TMA, and DMiPA was drastically reduced (~0%). Under monochloramine abundant conditions, however, DMBzA and RNTD showed 40% and 90% NDMA conversions at the end of 5 day contact time, respectively, with slow formation rates, indicating that while these amine precursors react preferentially with dichloramine to form NDMA, they can also react with monochloramine in the absence of dichloramine. NOM and pH influenced dichloramine levels that affected NDMA yields. NOM had an adverse effect on NDMA formation as it created a competition with NDMA precursors for dichloramine. Sulfate did not increase the NDMA formation from the two selected NDMA precursors. pH played a key role as it influenced both chloramine speciation and protonation state of amine precursors and the highest NDMA formation was observed at the pH range where dichloramine and deprotonated amines coexisted. In selected natural water and wastewater samples, dichloramine led to the formation of more NDMA than monochloramine.

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1. Introduction

Nitrosamines, a class of emerging disinfection by-products (DBPs) in drinking water, have been classified as probable human carcinogens associated with a 10^{-6} lifetime cancer risk at concentrations as low as 0.2 ng/L (US EPA, 2002). The formation of nitrosamines has been known to be commonly associated with chloraminated water distribution systems (Choi et al., 2002; Choi and Valentine, 2002a, 2002b; Mitch et al., 2003a, 2003b; Russell et al., 2012). Among nitrosamines, *N*-nitrosodimethylamine

(NDMA) has drawn the most attention due to its frequent detection and elevated concentrations (Russell et al., 2012). Although there are currently no federal regulations for nitrosamines in drinking water in the United States (US), this widespread detection of NDMA in drinking water distribution systems has prompted the California Department of Health Services and the Massachusetts Department of Environmental Protection to implement a maximum level of 10 ng/L for NDMA in drinking water (MassDEP, 2004; OEHHA (Office of Environmental Health Hazard Assessment (OEHHA), 2006). Furthermore, the US Environmental Protection Agency (US EPA) has identified nitrosamines as a group of contaminants highlighted for possible regulatory action in the near future (Khiri, 2017; Russell et al., 2017).

Dimethylamine (DMA) is one of the most commonly studied

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model precursors of NDMA (Choi et al., 2002; Choi and Valentine, 2003, 2002a, 2002b; Mitch et al., 2003b; Mitch and Sedlak, 2002; Schreiber and Mitch, 2006, 2005). Further studies have shown that in addition to DMA, tertiary and quaternary amines with the DMA moiety can lead to the formation of NDMA during chloramination (Gerecke and Sedlak, 2003; Lee et al., 2007; Mitch and Sedlak, 2004). Besides, some nitrogenous compounds with the DMA moiety which are present in natural organic matter (NOM) and anthropogenic organic materials (such as polyelectrolytes, ion-exchange resins, fungicides, pesticides, herbicides, pharmaceuticals, personal care products, cosmetics, and wastewater effluent impacted waters) have been shown to form NDMA (Bond and Templeton, 2011; Gan et al., 2013a, 2013b; Gerecke and Sedlak, 2003; Hanigan et al., 2015; Krasner et al., 2013; Lee et al., 2007; Mitch and Sedlak, 2004; Sacher et al., 2008; Selbes et al., 2013, 2014; Shen and Andrews, 2011a; Spahr et al., 2017, 2015).

Understanding the formation of NDMA as a function of time is essential to develop feasible and effective strategies for controlling NDMA and other nitrosamines in drinking water distribution systems. In the literature, dichloramine has been recognized as the reactive chloramine species to form NDMA from different precursors (Huang et al., 2018; McCurry et al., 2017; Mitch et al., 2009, 2005; Schreiber and Mitch, 2006; Shen and Andrews, 2013), and subsequent work indicated that minimizing dichloramine formation has reduced NDMA formation during drinking water and wastewater chloramination (Mitch et al., 2005; McCurry et al., 2017). Furthermore, in other studies, monochloramine was identified to lead to NDMA formation from ranitidine (RNTD) (Le Roux et al., 2012, 2011; Liu et al., 2014; Selbes et al., 2013). However, the role of mono- or dichloramine was not sufficiently examined in terms of NDMA formation rates from model precursors with different chemical structures. It has been reported that the NDMA formation in natural and wastewater impacted waters was relatively slow, and further NDMA could continue to form in distribution systems with increasing water age (i.e., a plateau was reached after 150–200 h of chloramine contact time) (Barrett et al., 2003; Charrois and Hruday, 2007; Krasner et al., 2010; Russell et al., 2012; Sacher et al., 2008). Since various precursors with different reactivity are present in source waters, it is not simple to predict which major factors would determine NDMA formation rates. Only a few studies have investigated the NDMA formation rates from model compounds (i.e., DMA, RNTD, chlorphenamine, and doxylamine) (Krasner et al., 2010; Padhye et al., 2013; Shen and Andrews, 2013, 2011b). These studies showed that the NDMA formation reached the plateau after 24 h during chloramination. Furthermore, these studies focusing on specific model compounds, have investigated the role of various factors influencing the NDMA formation: (i) the effect of temperature and pH with RNTD (Krasner et al., 2010); and (ii) the effect of NOM and pH with selected pharmaceuticals including RNTD (Shen and Andrews, 2011b). It has been reported that temperature can affect both stability and the reactivity of chloramines (Krasner et al., 2010). The NDMA formation from RNTD was found to be relatively constant independent of either temperature (5 vs. 25 °C) or pH (7 vs. 8 vs. 9) (Krasner et al., 2010). At low temperatures, due to reduced chloramine reactivity toward NOM, chloramines became more available to react with NDMA precursors. A study reported a decrease in NDMA formation from RNTD in the presence of NOM which was attributed to the decreased availability of chloramine species (Shen and Andrews, 2011b). Despite these previous studies, there is limited information on the impact of some key background water chemistry parameters (i.e., pH, NOM, temperature) on the chloramine speciation and NDMA formation as a function of time. Moreover, findings from selected model precursor compounds so far have been insufficient to explain the observed NDMA formation trends (i.e., the NDMA

formation over time and the role of chloramine species) in natural water samples.

The main objective of this study was to investigate the roles of chloramine species (i.e., monochloramine vs. dichloramine) and selected background water matrix components (i.e., pH, sulfate and NOM) in the formation of NDMA from DMA and selected tertiary amine precursors. DMA and four tertiary amines were carefully selected based on their chemical structures, and the NDMA formation as a function of time was monitored during four parallel experiments with varying amounts of dichloramine. Then, given their reactivity with each chloramine species, two amines were selected to examine the effects of pH, sulfate and NOM on the NDMA formation. Chloramine speciation can be an important factor controlling the NDMA formation rate in natural water samples with a variety of precursors present. Thus, the role of monochloramine vs. dichloramine was also investigated in selected natural waters: a drinking water system (i.e., before and after treatment) and a wastewater (WW) impacted water system (i.e., before and after WW confluence).

2. Materials and methods

2.1. Amine precursors

The selected amines for the study are shown in Fig. 1. All compounds were purchased from Sigma-Aldrich and TCI, and used without further purification. The purities of DMA, TMA, DMiPA, DMBzA and RNTD were 40%, 25%, 99%, 99% and 99%, respectively. Among the selected amines, RNTD was in the hydrochloride solid/powder form, while the other amines were in liquid form.

2.2. Experimental procedure

A stock solution (4 mM) of each amine was prepared in methanol and stored in an amber glass bottle at 4 °C until use. Each model compound was diluted to 200 nM in distilled and deionized water (DDW). The role of chloramine species was investigated by conducting four parallel experiments: (i) formation potential (FP) experiments with an initial monochloramine dose of 100 mg/L; (ii) simulated distribution system (SDS) experiments with an initial dose of 3 mg/L monochloramine; (iii) SDS experiments with an initial dose of 3 mg/L monochloramine in the presence of 100 mg/L background ammonia which was added to suppress the transformation of monochloramine to dichloramine (Eq. (1)); and (iv)

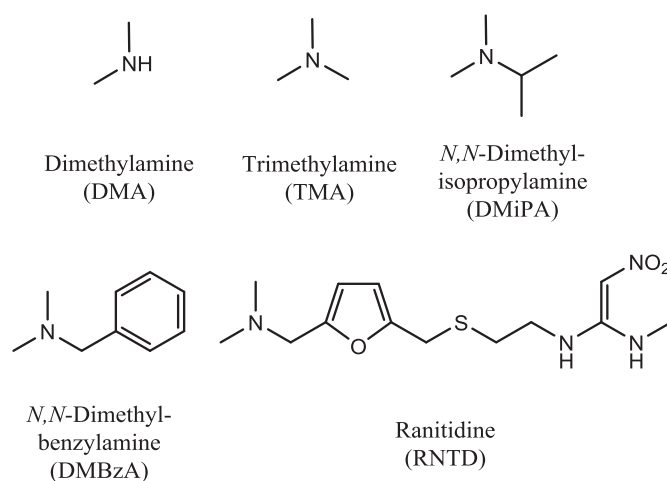


Fig. 1. Molecular structures of selected NDMA precursors.

SDS experiments with an initial dichloramine dose of 3 mg/L. Additional information about the chloramine chemistry is provided in the supporting information (Text S1). Since sulfate can contribute to decay of chloramines (Vikesland et al., 2001), ammonium chloride was used in all of the SDS experiments to achieve excess ammonia and in the preparation of chloramine stock. Chloramine species and their concentrations in DDW during the experiment are provided in Figs. S1–S4.



pH was adjusted at 7.5 with 10 mM phosphate buffer for the FP experiments and 4 mM carbonate buffer for the SDS experiments. The preformed monochloramine stock solution was prepared by mixing diluted sodium hypochlorite and ammonium chloride solutions at Cl₂:N mass ratio of 4:1 at pH 9. To prepare dichloramine stock solutions, monochloramine stock solution was prepared as described above, followed by gradual adjustment of its pH to 3.5–4.0 by using hydrochloric acid. Pre-determined amount of preformed chloramine solution (monochloramine or dichloramine) was spiked into eight identical amber bottles, which were opened at 3, 6, 12, 24, 48, 72, and 120 h to measure NDMA formation and residual chloramines.

The factors that may influence chloramine decomposition and speciation were assessed under SDS conditions for two model precursors (DMiPA and RNTD). The effect of NOM was investigated in background solutions that were prepared using raw (collected from the influent) and treated waters (collected between coagulation/flocculation/sedimentation and filtration) obtained from a drinking water treatment plant (DWTP). Water samples were filtered immediately with pre-washed 0.2 µm polyethersulfone filters. Dissolved organic carbon (DOC) levels of the NOM solutions were adjusted to 1.5, 2.5 and 5.0 mg C/L by diluting with DDW. Selected characteristics of NOM solutions are shown in Table 1. For the pH effect on NDMA formation, SDS tests were conducted at pH 6.5, 7.5, and 8.5. The effect of sulfate was investigated in DDW by spiking sodium sulfate to achieve 10, 25 and 50 mg/L sulfate concentrations.

In order to investigate the NDMA formation in natural waters, DWTP raw and treated water samples were used without any dilution. Moreover, a WW impacted creek was selected and samples were collected at three different locations (i.e., upstream of a wastewater treatment plant (WWTP), WWTP-effluent, and 8.4 km downstream from the WW discharge point). Further details of the watershed can be found elsewhere (Gan et al., 2013a, 2013b). Selected characteristics of natural water samples are also given in Table 1. The initial chloramine concentrations (i.e., either 3 or 100 mg/L) were enough to provide an excess amount of chloramine for all tests (i.e., DDW or natural samples) during the 5 day reaction time. All of the NDMA formation tests were conducted in 1-L amber glass bottles without headspace and stored in the dark at ~22 °C.

2.3. Analytical methods

NDMA was analyzed following US EPA method 521 (US EPA, 2004), consisting of solid-phase extraction using coconut charcoal tubes followed by GC/MS/MS analysis. Analytical details can be found elsewhere (Selbes et al., 2014, 2013) and a brief summary is as follows. For the analysis after chloramination, 500 mL amine solutions were quenched with sodium thiosulfate and NDMA-d₆ was added as a surrogate before solid phase extraction. Samples were passed through coconut charcoal cartridges preconditioned with dichloromethane, methanol, and DDW. The cartridges were dried with air, and then eluted with dichloromethane. Eluents were passed through sodium sulfate columns to remove residual

moisture, and then concentrated to 1 mL under a gentle stream of high purity nitrogen gas. The extracts were spiked with NDPA-d₁₄ as an internal standard, and analyzed using a Varian GC 3800-MS/MS 4000 under the chemical ionization mode. Percent molar yield of each amine was calculated using Eq. (2). The NDMA concentrations corresponding to the yields can be found in Table S1.

$$\text{NDMA Yield (\%)} = \left(\frac{[\text{NDMA}](\text{nM})}{[\text{Amine}]_0 (\text{nM})} \right) \times 100 \quad (2)$$

DOC and dissolved nitrogen (DN) were determined using a Shimadzu TOC-V_{CSH} instrument equipped with a Total Nitrogen module. UV absorbance of NOM samples was measured using a Varian Cary-50 spectrophotometer, and used to calculate SUVA₂₅₄ values. Ammonia concentrations were measured with a HACH spectrophotometer. Nitrite, nitrate, bromide, and sulfate were measured using an ion chromatography (Dionex, ICS 2100). Concentrations of free chlorine, monochloramine, and dichloramine as free chlorine were determined following Standard Method 4500-Cl F (APHA et al., 2005). The concentrations of monochloramine and dichloramine were examined with chloramine formation and decay software available via web application (<https://usepaord.shinyapps.io/Unified-Combo/>) (Wahman, 2016). In the web application, the chemical addition scenario was selected as “preformed chloramines” at a pH of 7.5 with a water temperature of 22 °C and the total organic carbon set to zero. Monochloramine, dichloramine and ammonia inputs to the web application were changed for each SDS test conditions. Example outputs of the web application are provided in Fig. S5 and Fig. S6. Furthermore, for selected samples, chloramine concentrations were also measured with UV spectrophotometer by using a 5-cm cuvette (Schreiber and Mitch, 2005) to confirm the chloramine residuals determined by the Standard Method 4500-Cl F. An example figure for the comparison of Standard Method 4500-Cl F, UV spectrophotometer method and web application for chloramine formation and decay is presented in Fig. S9 (other data not shown). Due to interference from background NOM, UV spectrophotometer method for chloramine species was used for the tests conducted in DDW in the absence of NOM. All analytical methods and their minimum reporting levels (MRL) are given in Table S2. All samples and blanks were prepared, extracted and analyzed in duplicates. Error bars in all the graphs show the minimum and maximum measurements (i.e., range of analysis) due to multiple analysis (n = 2). ANOVA was performed using Origin Pro to assess the statistical differences between the results of data sets (examples of the analysis are provided in Text S4).

3. Results and discussion

3.1. NDMA conversion from selected model compounds

Fig. 2 shows the NDMA molar conversion yields from DMA and four tertiary amines over reaction time under four different chloramination conditions: FP, SDS, SDS with monochloramine (in the presence of excess background ammonia) and SDS with dichloramine. In the FP tests, an excessive dose of chloramine (i.e., 100 mg/L) resulted in sufficient levels of both monochloramine (~95%) and dichloramine (~5%) at pH 7.5 to form NDMA from selected amines. Under the FP test conditions, the NDMA formation rates from all five model compounds were relatively fast; in general, the maximum NDMA formation was achieved within 24 h of chloramination, although further increases up to 120 h were observed only from TMA (Fig. 2B) and DMiPA (Fig. 2C). The NDMA yields obtained at 120 h of contact time for the five model precursors

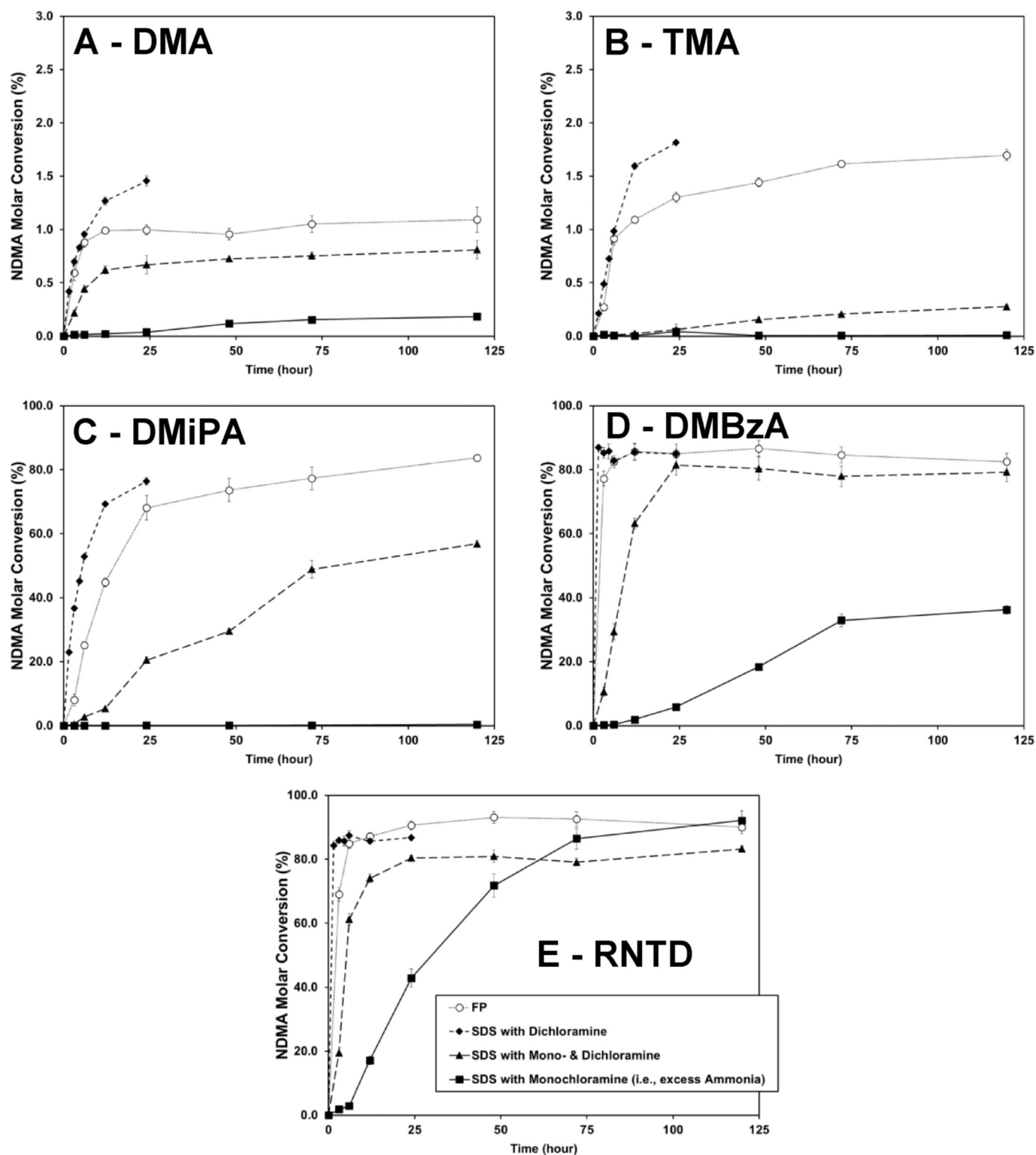


Fig. 2. NDMA formation as a function of time from (A) DMA, (B) TMA, (C) DMiPA, (D) DMBzA and (E) RNTD. Experimental conditions: i) FP ($[\text{NH}_2\text{Cl}]_{\text{initial}} = 100 \text{ mg Cl}_2/\text{L}$), ii) SDS with dichloramine ($[\text{NH}_2\text{Cl}]_{\text{initial}} = 3 \text{ mg Cl}_2/\text{L}$), iii) SDS with mono- and dichloramine ($[\text{NH}_2\text{Cl}]_{\text{initial}} = 3 \text{ mg Cl}_2/\text{L}$), and iv) SDS with monochloramine (in the presence of excess ammonia) ($[\text{NH}_2\text{Cl}]_{\text{initial}} = 3 \text{ mg Cl}_2/\text{L} + 100 \text{ mg NH}_4^+/\text{L}$); pH = 7.5 and $T \sim 22^\circ\text{C}$.

were comparable to those reported in the literature (Huang et al., 2018; Le Roux et al., 2012; Lee et al., 2007; Mitch et al., 2009; Sacher et al., 2008; Selbes et al., 2014, 2013; Shen and Andrews, 2011a, 2011b; Spahr et al., 2017). The differences of NDMA yields observed in our study vs. those reported in the literature were

attributed to some differences in experimental conditions (e.g., reaction time, chloramine dose, buffer, stoichiometric ratio of oxidant to precursor, etc.).

The NDMA formation rates for DMA (Fig. 2A), TMA (Fig. 2B), and DMiPA (Fig. 2C) were significantly affected by dichloramine

concentrations. The higher NDMA yields were observed in the SDS with dichloramine and FP test experiments (i.e., more dichloramine was present). In the FP experiment, the decomposition of monochloramine formed a maximum of 5 mg/L dichloramine. Along with the formation rates, the NDMA conversion yields also decreased as dichloramine levels decreased (e.g., 57% and 84% for DMiPA, 0.3% and 1.7% for TMA, 0.8% and 1.1% for DMA under SDS and FP conditions, respectively). On the other hand, under SDS conditions in the presence of excess background ammonia where almost no dichloramine existed in the system, NDMA barely formed from those three amine precursors (DMiPA, TMA, and DMA), suggesting that dichloramine is the more favorable species to form NDMA than monochloramine, and the NDMA formation was controlled by the decomposition of monochloramine to dichloramine. The NDMA formation rates for these three amines dramatically increased under SDS with dichloramine only. Especially for TMA (Fig. 2B) and DMA (Fig. 2C), their NDMA molar conversions were even greater than those under the FP tests within 24 h. On the contrary, the NDMA formation rates for DMBzA (Fig. 2D) and RNTD (Fig. 2E) showed very similar patterns in both FP and SDS tests although slightly higher yields were achieved under FP conditions at the end of 5 days contact time. In the absence of dichloramine (i.e., dichloramine formation suppressed by excess background ammonia), considerable NDMA formed from DMBzA and RNTD, suggesting monochloramine reacts with these amines to form NDMA. Similarly, it has been reported that RNTD can form NDMA by the reaction with monochloramine (Le Roux et al., 2012; Liu et al., 2014; Selbes et al., 2013). However, the NDMA formation from DMBzA and RNTD was slower than those when dichloramine was present (i.e., SDS test). Interestingly, under SDS with preformed dichloramine, NDMA formed very fast from DMBzA and RNTD. The formation rates were comparable with those under FP tests, indicating that the reaction rates of dichloramine with any amine precursors are always faster than those of monochloramine, and only some amine precursors (e.g., DMBzA and RNTD) can also react with monochloramine to form NDMA. Although the formation rate for the reaction between monochloramine and RNTD was slower than that between dichloramine and RNTD (Fig. 2E), the NDMA conversion yield in the FP test was almost same as that in the SDS test in the presence of excess ammonia at 120 h contact time, indicating that both monochloramine and dichloramine can react with RNTD to form NDMA with different reaction rates.

It is important to note that all chloramine species including, mono-, di- and trichloramine, are in equilibrium reactions and trace concentrations of dichloramine can be present even if dichloramine is not detected (i.e., SDS test with monochloramine in the presence of excess ammonia). The Standard Method 4500-Cl F method and UV spectrophotometer (5-cm cuvette) used for the detection of dichloramine have minimum reporting levels of 0.05 mg/L dichloramine. It is possible that some trace concentrations of dichloramine may be present even under the conditions of the SDS test in the presence of excess ammonia which may have contributed to some NDMA formation from RNTD and DMBzA. However, if trace amounts of dichloramine were resulting in NDMA formation from RNTD and DMBzA, this effect would have been observed in other precursors such as in DMiPA (Fig. 3C – SDS in the presence of excess background ammonia). Given that NDMA barely formed from DMiPA, TMA, and DMA under the SDS conditions in the presence of excess background ammonia, the high NDMA yields observed from RNTD and DMBzA under the same test conditions would be mainly formed by monochloramine. Therefore, the findings of our study indicate that dichloramine is more reactive species to form NDMA from tertiary amine precursors as reported in the literature (Huang et al., 2018; McCurry et al., 2017; Mitch et al., 2005; Schreiber and Mitch, 2006; Shen and Andrews, 2013);

however, NDMA can also form from the reactions with monochloramine depending on the precursor structure (Le Roux et al., 2012, 2011; Liu et al., 2014; Selbes et al., 2013). In our previous research, we found that in SDS tests with and without ammonia DMA, TMA and DMiPA were dichloramine reactive while DMBzA and RNTD were monochloramine reactive (Selbes et al., 2013). Consistently, in the present study DMA, TMA and DMiPA were found to be dichloramine reactive, and the additional data collected over 120 h in different mono- and dichloramine conditions allowed us to further refine the findings and show that both mono- and dichloramine can contribute to NDMA formation from DMBzA and RNTD.

The higher reactivity of dichloramine to form NDMA can be attributed to more partial positive charge on nitrogen atom due to two neighboring chlorine atoms than that of monochloramine with only one chlorine (Fig. S5). Nitrogen atom of tertiary amines would always be partially negative due to two neighboring methyl functional groups. During a nucleophilic substitution, therefore, bonding between nitrogen atoms of amine and dichloramine would form first because of partially more positive charge on nitrogen of dichloramine. Overall, the results suggest that the NDMA formation from the reaction of amine compounds with chloramines is dependent on the dichloramine concentration, and higher concentrations of dichloramine increases NDMA formation rates. However, monochloramine can also form NDMA depending on the precursor's structure, if available dichloramine is limited. In the literature, several NDMA formation pathways have been proposed involving either monochloramine (Le Roux et al., 2012, 2011; Liu et al., 2014; Selbes et al., 2013) or dichloramine (Huang et al., 2018; McCurry et al., 2017; Mitch et al., 2009; Schreiber and Mitch, 2006; Shen and Andrews, 2013); and in all studies, the first reaction is the nucleophilic substitution. Findings of our study, indicate a potential reactivity of RNTD with both monochloramine and dichloramine. The questions to how both chloramine species can react with RNTD are still outstanding. Further research is required to examine formation pathways and identify the intermediates formed during the reactions.

3.2. Factors influencing NDMA conversion yields

3.2.1. The NOM effect

To investigate the NOM effect on the NDMA formation rates, raw and treated water samples collected from a DWTP were used as background matrices. Hydrophobic (HPO) organic matter is typically the major fraction of NOM in raw waters, while NOM in treated waters (i.e., after coagulation/flocculation/sedimentation) contains mostly transphilic (TPH) and hydrophilic (HPI) organic matter (Croué et al., 1993; Karanfil et al., 2007; Kim and Yu, 2005). Thus, selected amines spiked in raw and treated waters could react and/or compete with NOM (i.e., HPO, TPH and HPI) toward NDMA formation. NOM characteristics may play an important role in either enhancement or reduction of NDMA formation in natural water systems. The NDMA molar conversion yields from RNTD and DMiPA as a function of reaction time at different DOC levels of raw and treated waters are given in Fig. 3. For DWTP treated water, there was a slight decrease in NDMA conversion yields from RNTD as DOC increased (Fig. 3A). The formation of NDMA from RNTD proceeded faster in DDW than in the presence of 1.0 mg C/L and 2.5 mg C/L of DOC, particularly during the first 24 h of reaction time. For instance, the NDMA yields were 61%, 9% and 2% for DDW, treated 1.0 mg C/L and treated 2.5 mg C/L at 6 h, respectively. While these conversion rates were 74%, 70% and 26% at 12 h (Fig. 3A). The maximum yield from RNTD occurred at 24 h for DDW and treated 1.0 mg C/L while it happened at 48 h for treated 2.5 mg C/L. Despite the slower conversion rate, the presence of DOC caused no

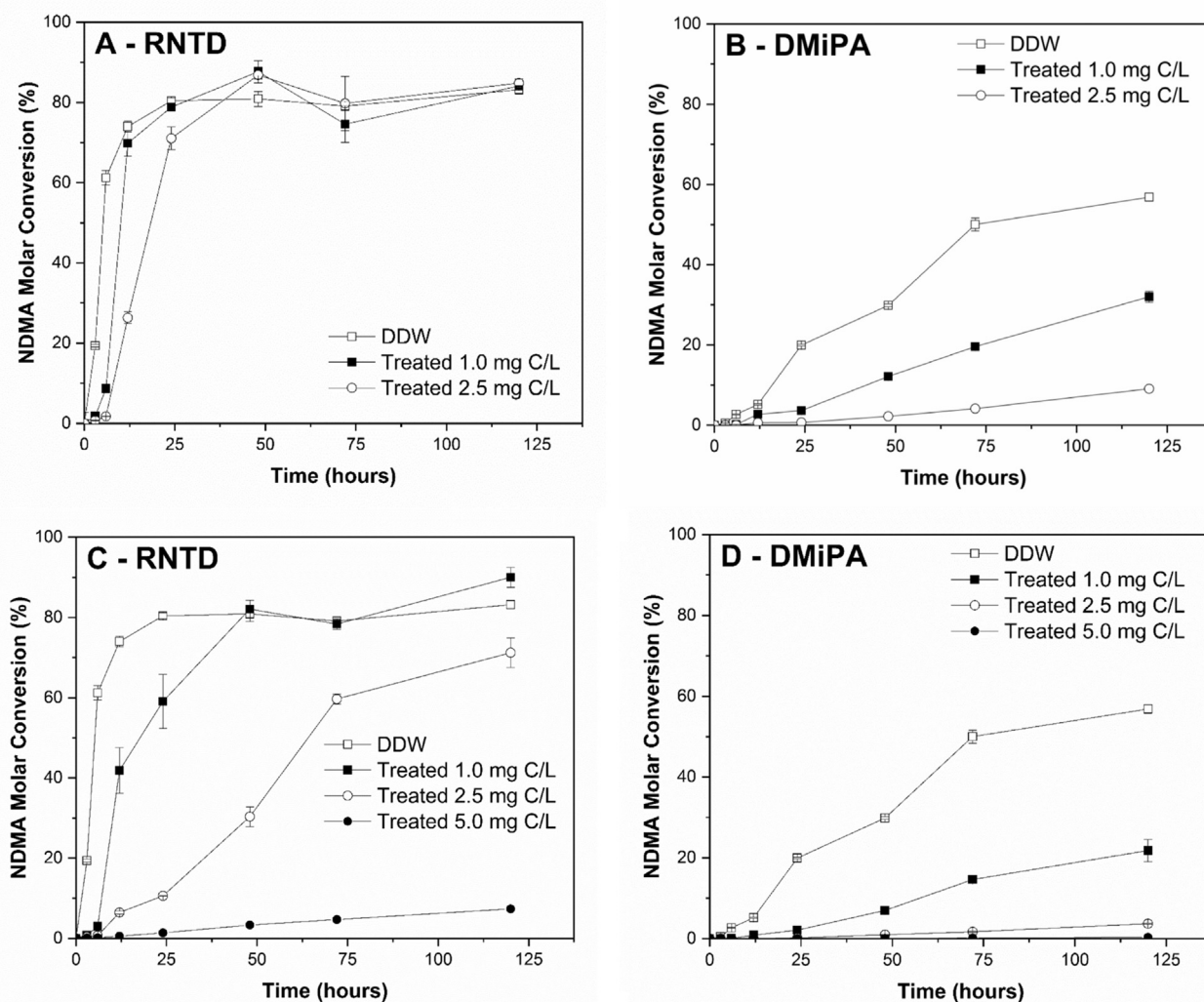


Fig. 3. The effect of NOM in NDMA formation as a function of time from RNTD (A and C) and DMiPA (B and D). Experimental conditions: i) SDS conditions ($[\text{NH}_2\text{Cl}]_{\text{initial}} = 3.0 \text{ mg Cl}_2/\text{L}$, $\text{pH} = 7.5$, $T = 22^\circ\text{C}$); ii) DWTP treated water was diluted to 1.0 mg C/L DOC and 2.5 mg C/L DOC and used as background solution for A and B; iii) DWTP raw water was diluted to 1.0 mg C/L DOC, 2.5 mg C/L DOC, and 5.0 mg C/L DOC and used as background solution for C and D.

significant effect on the formation of NDMA from RNTD. During the experiment, enough monochloramine was available and the concentration of dichloramine remained $\leq 0.10 \text{ mg/L}$ (Table S6). On the other hand, the NDMA conversion yields from DMiPA were reduced drastically in the presence of TPH- and HPI-dominated NOM (Fig. 3B). The NDMA yields for 120 h of contact time decreased from 56.9% (which was in DDW) to 32.0% and 9.1% at 1.0 and 2.5 mg C/L DOC, respectively. More specifically, decreases in NDMA yields are probably due to the competition of NOM with DMiPA for dichloramine. Since RNTD could also react with monochloramine to form NDMA, the drastic reduction of NDMA formation was observed only from DMiPA. Overall, these results indicate that NOM could reduce available dichloramine resulting in less NDMA formation. This NOM effect, however, can be insignificant for certain precursors which can react with both monochloramine and dichloramine to form NDMA.

When DWTP raw water containing HPO-dominated NOM was used as the background matrix, the NDMA conversion yield from RNTD decreased as DOC levels increased (Fig. 3C). The NDMA conversion yield from RNTD in the absence of NOM reached the maximum (~85%) within 24 h, while slightly slower conversion was

observed in the presence of NOM at 1.0 mg C/L of DOC. When the DOC concentration increased to 2.5 mg C/L , the maximum yield (~71%) of NDMA did not reach the level (~85%) observed in DDW even after 120 h of contact time. At 5.0 mg C/L of DOC; however, the NDMA conversion was significantly suppressed and its maximum was only 7.4% after 120 h of chloramination. NOM in raw water caused more drastic decreases in the NDMA conversion yield from RNTD than NOM in treated water, indicating that NOM characteristics in natural water also influence the NDMA formation. Slightly higher decay of chloramines was observed in raw water than treated water (Table S6). DWTP raw water had higher aromatic components than the treated water according to their SUVA_{254} values (3.3 and 1.7 L/mg-m , respectively). Therefore, the concentration of aromatic compounds in natural water may also influence the NDMA formation during chloramination of amines. Similar decreases in the formation of NDMA were reported when river water with 6.2 mg C/L of DOC and 2.3 L/mg m of SUVA_{254} was used (Shen and Andrews, 2011b). However, the changes of the NDMA conversion in their study were not as drastic as the results in our study, which may be due to the difference in the SUVA_{254} values. As for the importance of SUVA_{254} in the NDMA formation, it has been

found that aromatic amines can undergo reversible covalent bonding with carbonyls and quinones which are present in NOM (Text S2) (Chen, 2007; Parris, 1980; Thorn et al., 1996; Weber et al., 1996), and consequently the precursor initial contact with chloramines can be hindered (Shen and Andrews, 2011b). Some preliminary data supporting this hypothesis are given in Text S3. It should be noted that there are other functional groups in NOM that may have caused this hindrance, which would require further research.

The NDMA molar conversion of DMiPA was slightly higher in treated water (Fig. 3B) than in raw water (Fig. 3D). The NDMA yields at 120 h decreased as DOC increased in both treated and raw waters indicating that there is less interaction between HPO fraction of NOM and DMiPA, an aliphatic amine, than between HPO and RNTD, an aromatic amine. The NOM effect on the NDMA conversion and the interaction of NOM fractions with aliphatic and aromatic amines warrants further investigations with various precursors in different water matrices to better understand the NDMA formation mechanism in natural water systems.

Overall, these results suggest that the presence of NOM may decrease the formation of NDMA in distribution systems when certain precursors are present (e.g., DMiPA). HPO fraction of NOM can be more effective than THP to reduce the NDMA formation probably due to its covalent binding capability with aromatic amines and also creating a competition for dichloramine. Although the majority of the HPO fraction is removed during coagulation/flocculation/sedimentation processes, the remaining TPH fraction of NOM may also decrease the NDMA formation by competing with precursors toward dichloramine. For both NOM fractions, higher DOC levels showed more decreases in the NDMA formation (via covalent binding or creating a competition for dichloramine). However, high DOC levels are associated with the formation of regulated carbonaceous DBPs such as trihalomethanes and haloacetic acids during free chlorine application prior to ammonia addition.

3.2.2. The pH effect

The effect of pH (6.5–8.5) on the NDMA conversion from RNTD and DMiPA was investigated and the results are shown in Fig. 4. Changing pH did not cause statistically meaningful changes in the

NDMA formation from RNTD probably due to RNTD's high NDMA formation within the first 24 h under SDS conditions (Table S3). The NDMA formation from RNTD at pH 7.5 was slightly faster than at pH 6.5 or 8.5, which is in good agreement with a previous study (Shen and Andrews, 2013). On the other hand, distinct changes were observed for the NDMA formation from DMiPA under different pH conditions. The NDMA conversion yields from DMiPA at 120 h were highest (56.9%) at pH 7.5. An increase or decrease in pH adversely affected the NDMA formation rate. The NDMA yield was decreased to 7.6% and 35.4% when pH was changed from 7.5 to 6.5 and 8.5, respectively. Assuming that NDMA forms via nucleophilic substitution of dichloramine with deprotonated amines (RNTD and DMiPA) (Mitch et al., 2009; Schreiber and Mitch, 2006), the highest NDMA yield is expected to be observed at an optimum pH where both dichloramine and deprotonated amine species may coexist, and consequently enhancing the reaction kinetics towards the NDMA formation (Shen and Andrews, 2013, 2011b). For example, dichloramine is the dominant chloramine species at pH 3.0–4.0 (Text S1) and pKa of DMiPA is ~10.3 (Selbes et al., 2014). Therefore, the highest NDMA yield from DMiPA was achieved at pH 7.5 which is an optimal pH condition for the maximum coexistence of dichloramine and deprotonated DMiPA.

3.2.3. The sulfate effect

It has been known that sulfate, bicarbonate, and phosphate can facilitate transformation of monochloramine to dichloramine (Valentine and Jafver, 1988; Vikesland et al., 2001). The presence of those ions would increase dichloramine concentrations, and consequently the NDMA conversion yields could also increase from some amine precursors which react preferentially with dichloramine to form NDMA. To investigate the anion effect on the NDMA formation, sulfate was chosen since it is introduced during coagulation with alum in conventional drinking water treatment. SDS tests were performed in the presence of sulfate at three different concentrations (i.e., 10, 25, and 50 mg/L) with RNTD and DMiPA, and the results are presented in Fig. 5. Sulfate did not cause statistically significant changes in the NDMA formation from RNTD probably due to RNTD's high NDMA formation within the first 24 h under SDS conditions (Table S4). Similarly, sulfate caused no significant changes in the formation of NDMA from DMiPA (Text S5) (Fig. 5). Similar patterns of conversion curves observed at different sulfate concentrations indicate that the NDMA formation from DMiPA was still limited by dichloramine concentration. The overall NDMA yields at 120 h increased up to 79.4% as sulfate was added. Although the initial chloramine dose in the SDS tests was much lower than the FP experiments, the NDMA conversion yield from DMiPA after 120 h in the presence of 50 mg/L sulfate reached ~80% which is close to the maximum level observed from the FP test. These results suggest that introducing sulfate during coagulation, or phosphate during corrosion inhibitor addition, or bicarbonate addition during recarbonation may increase the NDMA formation as a result of enhanced chloramine decomposition (Valentine and Jafver, 1988; Vikesland et al., 2001).

3.3. Case studies

The NDMA formation as a function of time was also examined in natural water samples under three different chloramination conditions (i.e., FP, SDS, and SDS in the presence of excess ammonia) (Table 2).

3.3.1. Drinking water treatment plant

In the FP experiment with both raw and treated waters, the NDMA formation was rapid within the initial 24 h of chloramination and then increased gradually until 120 h of chloramination

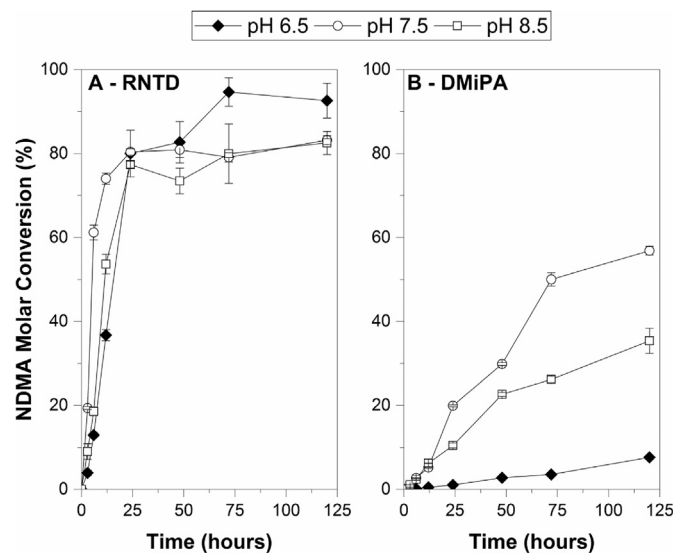


Fig. 4. The effect of pH in NDMA formation as a function of time from (A) RNTD and (B) DMiPA. Experimental conditions: SDS conditions ($[\text{NH}_2\text{Cl}]_{\text{initial}} = 3.0 \text{ mg Cl}_2/\text{L}$, pH = 7.5, $T \sim 22^\circ\text{C}$).

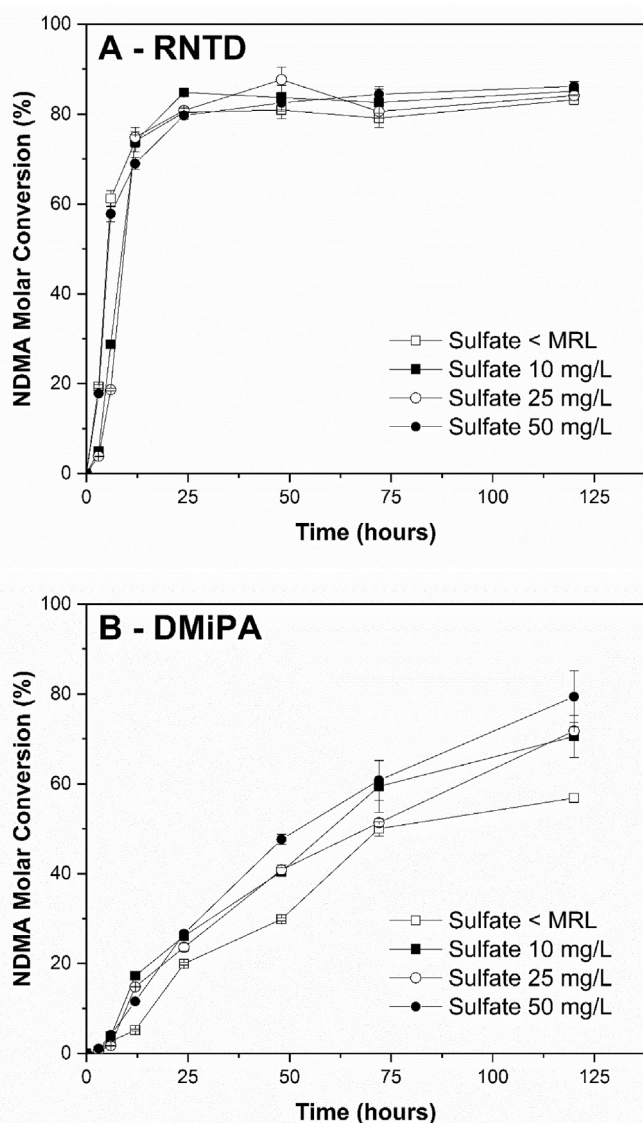


Fig. 5. The effect of sulfate in NDMA formation as a function of time from (A) RNTD and (B) DMiPA under SDS conditions. Experimental conditions: i) SDS conditions ($[\text{NH}_2\text{Cl}]_{\text{initial}} = 3.0 \text{ mg Cl}_2/\text{L}$, $\text{pH} = 7.5$, $T = 22^\circ\text{C}$), ii) $[\text{SO}_4^{2-}] = 10, 25, \text{ and } 50 \text{ mg/L}$.

yielding 59 and 45 ng/L of NDMA, respectively. The difference in NDMA FP values of raw and treated waters corresponds to a ~24% reduction in NDMA precursors. This is in good agreement with a recent study reporting that coagulation/flocculation/sedimentation (without any polymer influence) resulted in 9–23% reduction in NDMA FP (Uzun et al., 2017).

The NDMA formation in raw water under SDS conditions was below MRL, while up to 9 ng/L of NDMA was observed in treated water at 120 h of chloramination. DOC decreased from 6.3 mg C/L to 2.8 mg C/L after coagulation/flocculation/sedimentation, and thus the competition between NOM and amine precursors toward dichloramine might also decrease and consequently, more dichloramine could be available leading to higher NDMA formation. In addition, since alum was used at this DWTP as the coagulant, increased sulfate (6.3 mg/L in raw and 36.8 mg/L in treated water) could also contribute to dichloramine levels leading to higher NDMA formation under SDS conditions. To further examine the alum effect on the NDMA formation, DWTP raw water was spiked with 50 mg/L of sulfate and was subjected to the SDS test. In the

presence of sulfate; however, the NDMA formation was still below MRL (data not shown); indicating that introduction of sulfate in the coagulation process did not affect the NDMA formation. This suggests that DOC was more responsible than sulfate for the NDMA formation in the treated water used in the present study. The importance of DOC and the NDMA formation curve over the contact time under SDS conditions indicate that (i) the NDMA formation is limited by the transformation of monochloramine to dichloramine and (ii) NDMA can continue to form as long as there is residual chloramine present. Under SDS conditions in the presence of excess ammonia, the NDMA formation in both raw and treated water samples was below MRL indicating that in this water source there are a negligible amount of precursors which can potentially react with monochloramine.

3.3.2. Wastewater impacted watershed

With samples collected from three sampling locations (i.e., upstream, discharge, and downstream) of a WWTP, the formation of NDMA was monitored as a function of time. Upstream samples represented pristine source water with minimal anthropogenic impact. The NDMA FP for this location was 23 ng/L after 120 h of chloramination, while under SDS conditions only 7 ng/L of NDMA formed. In the presence of excess ammonia, 5 ng/L of NDMA formed within the first 3 h and remained constant afterwards.

On the other hand, very high levels of NDMA FP were observed in the samples collected at WW discharge point (1316 ng/L and 1659 ng/L at 3 h and 120 h of chloramination, respectively). Under SDS conditions; however, only 5 ng/L of NDMA formed within the first 3 h and NDMA formation increased to 16 ng/L after 120 h. Since this yield was much lower than expected, a WW sample was diluted with DDW at several different ratios and chloraminated under SDS conditions in attempting to explain this anomaly. More dilution resulted in more NDMA yields getting closer to the values under FP tests (Fig. S6). Reduced concentration of organics (i.e., DOC) due to dilution would lead to less competition with precursors toward dichloramine. Consequently, more available dichloramine would react with precursors to form more NDMA. The NDMA formation caused by monochloramine (i.e., under SDS with excess ammonia) was 7 ng/L at 3 h and remained until 120 h. These findings indicate that dichloramine was more important species than monochloramine for the NDMA formation in this WW matrix, which is consistent with the findings reported in the literature (Mitch et al., 2005; McCurry et al., 2017).

Downstream NDMA FP was 94 ng/L at 3 h of chloramination and additional NDMA (up to 149 ng/L) formed with further exposure to chloramine. Under SDS test conditions without ammonia, NDMA formed gradually over contact time reaching 102 ng/L at 120 h, which was close to NDMA FP (149 ng/L). The NDMA formation caused by monochloramine (i.e., under SDS with excess ammonia) was 5 ng/L at 3 h and remained the same until 120 h. Once again, these findings indicate that dichloramine is more important species than monochloramine for the NDMA formation. However, monochloramine may also lead to formation of some NDMA.

4. Conclusions

The NDMA formation as a function of time from DMA and four tertiary amines was examined under four chloramination conditions (i.e., FP, SDS, SDS in the presence of excess ammonia, and SDS with preformed dichloramine) to understand the role of chloramine species in the NDMA formation. During FP test and SDS test with preformed dichloramine having sufficient dichloramine concentrations in the system, the NDMA formation rates were relatively fast reaching a plateau approximately within initial 24 h of chloramination. However, when much lower level of dichloramine

was applied (i.e., SDS test), the NDMA formation rates from DMA, TMA, and DMiPA were noticeably reduced, while the effect of dichloramine on DMBzA and RNTD was less significant. When only monochloramine existed (i.e., dichloramine formation suppressed by excess ammonia) in the system, the NDMA formation from DMA, TMA, and DMiPA was negligible. The NDMA formation rates were reduced with monochloramine from DMBzA and RNTD indicating that dichloramine is more important chloramine species for NDMA formation from these precursors as well. Over the extended contact time monochloramine reacted with RNTD and DMBzA to form NDMA reaching comparable yields to dichloramine present conditions, but the reaction rates for dichloramine was faster than those for monochloramine. From the experiments with selected model precursors, dichloramine was found to be more reactive species to form NDMA from the selected precursors. However, monochloramine can also lead to the NDMA formation from certain precursors such as RNTD and DMBzA, even in the absence of dichloramine.

The NDMA formation from both DMiPA and RNTD was reduced in the presence of NOM probably due to less available dichloramine caused by the reactions between NOM and dichloramine and/or precursors' binding with NOM. pH played a key role as it influenced both chloramine speciation and protonation state of amine precursors. Sulfate had no effect on NDMA formation from DMiPA and RNTD. Dichloramine limited conditions, therefore, would be beneficial to control the NDMA formation from precursors which react exclusively with dichloramine. Dichloramine also lead to higher NDMA formation than monochloramine in both drinking water and wastewater impacted water systems tested in this study.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.watres.2018.04.033>.

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