5-2017

Understanding N-nitrosodimethylamine Formation in Water: Chloramine Chemistry, Kinetics, and A Proposed Reaction Pathway

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Understanding *N*-nitrosodimethylamine Formation in Water: Chloramine Chemistry, Kinetics, and A Proposed Reaction Pathway

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Civil Engineering

by

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Bachelor of Science in Chemistry, 2013

May 2017
University of Arkansas

Thesis is approved for recommendation to the Graduate Council

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ABSTRACT

The formation of *N*-nitrosodimethylamine (NDMA) in drinking water systems is a concern because of its potential carcinogenicity and occurrence at toxicologically relevant levels. The postulated mechanism for NDMA formation involves a substitution between dichloramine and amine-based precursors to form an unsymmetrical dimethylhydrazine (UDMH), which is then oxidized by ground-state molecular oxygen to form NDMA. However, this latter reaction is spin forbidden, thus likely occurs at a slow rate. It is hypothesized that the reaction between monochloramine and hydroxylamine (a nitrification product) may form an intermediate, which is involved in the NDMA formation pathway. This intermediate may also be generated from dichloramine decay, in the absence of hydroxylamine. In this study, a series of batch kinetic experiments were conducted to investigate the decomposition of chloramine species at pH 8.0 to 10.0 and the concomitant formation of NDMA. Chloramine species were quantified using UV/Vis spectroscopy (Direct UV) and colorimetric methods (Hach) and compared to simulations from the unified chloramine model. NDMA was quantified using GC-MS following liquid-liquid extraction. The model captured the decay of monochloramine and dichloramine adequately, with the exception of monochloramine at pH 10.0, possibly due to an interference from a previously reported unidentified chloramine decomposition compound (UC1). NDMA formation was pH dependent with the maximum yields at pH 9.0 and the fastest kinetics at pH 10.0. A second unidentified compound (UC2), with a mass spectrum identified as UDMH, was detected only at pH 9.0 and 10.0 in batch reactors with DMA and dichloramine. Importantly, NDMA formation appeared to be insensitive to the presence or absence of UC2, suggesting UC2 was not involved in NDMA formation. Hydroxylamine accelerates the decomposition of monochloramine. The reaction between DMA and hydroxylamine formed a third unidentified compound (UC3), preliminarily identified as acetoxime, which was not observed in the presence of monochloramine.

Upon addition of hydroxylamine, NDMA yields decreased by more than half in batch reactors with DMA and monochloramine. On balance, the findings suggest the existence of a NDMA formation pathway that may not involve UDMH, and points to the need for studies with scavengers and donors of short-lived species from chloramine decay.

ACKNOWLEDGEMENT

This research was sponsored by the Vietnam Education Foundation (VEF) and the National Science Foundation (NSF) through CBET Award Number 1604820 to Dr. Wen Zhang and Dr. Julian Fairey.

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I. INTRODUCTION

N-nitrosamines are a family of extremely potent carcinogens, of which *N*-nitrosodimethylamine (NDMA) is the most commonly reported species in drinking water systems (Russell et al., 2012). NDMA forms primarily from reactions between chloramine species and amine-based precursors and is thus considered to be a disinfection byproduct (DBP). The International Agency for Research on Cancer classified NDMA as a "probable human carcinogen" (Heath, 1962; Magee and Farber, 1962), and, while *N*-nitrosamines are not regulated by the USEPA in drinking water, their cancer potencies are much higher than those of the trihalomethanes, a regulated group of DBPs. The daily tolerable limit for NDMA is 4.0-9.3 ng/(kg•day) and the WHO proposed a limit of 100 ng/L in drinking water, which corresponds to a dose of 2.9 ng/(kg•day) (Fitzgerald and Robinson, 2007). The States of California and Massachusetts have set notification levels for NDMA at 10 ng/L and California has a response level of 300 ng/L.

Human exposure routes to NDMA were initially focused on food, consumer products, and air. The attention for NDMA in drinking water systems arose after the detection of elevated concentrations of NDMA in the groundwater (as high as 400,000 ng/L on site and 20,000 ng/L offsite) at a rocket engine testing facility in Sacramento County, California that used unsymmetrical dimethylhydrazine (UDMH)-based rocket fuel. A statewide survey at drinking water facilities also indicated that NDMA occurrence was not limited to areas near facilities that used UDMH-based fuels, but was also associated with chlorine or chloramines disinfection of water and wastewater (Mitch et al., 2003). More recently, enhanced NDMA formation has been associated with the presence of nitrifying bacteria in storage facilities and distribution systems (Zeng and Mitch, 2016).

The postulated reaction mechanism for NDMA formation involves a fast nucleophilic substitution between dichloramine and unprotonated DMA to form an UDMH intermediate, which is slowly oxidized to form NDMA (Figure 1). Higher pH increases the fraction of unprotonated DMA (pK_a = 10.7) but also accelerates the breakdown of dichloramine (Hand and Margerum, 1983). With the rate constant of the UDMH oxidation (k_{di3} = 1.4 $M^{-1}s^{-1}$) 35 times less than the rate of the substitution reaction between DMA and dichloramine to form UDMH (k_{di1} = 52 $M^{-1}s^{-1}$), the former is the rate-limiting step. Mitch and Schreiber (2006) concluded that oxygen radicals did not play a significant role in the NDMA formation mechanism due to the addition of superoxide dismutase (an effective scavenger for superoxide, hydroperoxyl radical, and $^1O_2$ (Rao et al., 1988)) and t-BuOH (a specific scavenger for hydroxyl radical), neither of which had a significant effect on NDMA formation. Additionally, they concluded that the oxygen species that oxidizes UDMH to NDMA was not generated from water because incorporation of ^{18}O was not observed in NDMA when using ^{18}O-labeled water. However, Schreiber and Mitch (2006) did not test other dichloramine decay products and radicals, which may be an important part of the reaction mechanism.

Recent evidence suggests that monochloramine may react with hydroxylamine (NH_2OH, a nitrification intermediate formed during ammonia oxidation by nitrifying bacteria), to form an intermediate (Wahman et al., 2014), hypothesize to be nitroxyl, HNO – a portion of which can be oxidized by dissolved oxygen to peroxynitire, $ONOO^-$, that may play an important role in NDMA formation (Figure 2). This intermediate may also be generated from dichloramine decay, in the absence of hydroxylamine. The fractional rate order of dichloramine and monochloramine indicates the involvement of radical intermediates and branching reaction pathways, which was recently proved by Spahr et al., (2017), but only for specific precursors with electron-rich aromatic

moieties, such as ranitidine. Secondary amines like dimethylamine (DMA, a model NDMA precursor) may react to form NDMA through other reaction pathways, which could have important implications for controlling formation of this compound. The objective of this research was to investigate the stability of the chloramine species over a pH range relevant to chloramination (7.0 to 10.0) and the concomitant formation of NDMA in batch systems with DMA, monochloramine, and hydroxylamine. NDMA formation from batch kinetic experiments was measured by GC-MS. The results provide evidence for an additional NDMA formation pathway, one that is perhaps more relevant to drinking water systems.

II. CHEMICALS AND METHODS

A. CHEMICALS

High purity water (18.2 MΩ-cm) for batch kinetic experiments was generated using a Millipore Integral 3 purification system and referred to herein as Milli-Q water. All stock chemicals were used as obtained without any further purification, which included: sodium hypochlorite (VWR, ACS grade), ammonium chloride (Amresco, ACS grade), ascorbic acid (Amresco, ACS grade), potassium phosphate monobasic (Amresco, ACS grade), sodium phosphate dibasic (Fisher, ACS grade), *N*-nitrosodimethylamine (Accustandard), dimethylamine (Merck, 40% wt.% in H_2O), dichloromethane (VWR, HPLC grade), and hydroxylamine-hydrochloride (Sigma, ACS grade).

Glassware and plastic-ware were scrubbed with mixture of Alconox soap and tap water and triple-rinsed with deionized water and Milli-Q water. Chlorine demand-free glassware was prepared by soaking cleaned glassware in a chlorine bath (at least 100 mg•L^{-1} as Cl_2) for 24 hours, triple-rinsed with deionized and Milli-Q water, and baked at 400 °C for at least 2 hours. PTFE-lined lids were rinsed with acetone and baked at 80 °C for at least 1 hour.

B. EXPERIMENTAL PROCEDURES

All *N*-nitrosamine formation kinetic experiments were performed headspace free in 25 mL amber glass vials sealed with PTFE-lined screw top lids. Dimethylamine (DMA) solutions were diluted with Milli-Q water to 25 μM DMA in a volumetric flask and adjusted with 10 mM buffer to the desired pH. Bicarbonate buffer was used for pH 10, borate buffer for pH 9, and phosphate buffer for pH 8 and 7. Monochloramine solutions at 2.0 mM were freshly prepared before each experiment following the procedure developed by Do et al., (2015) and adjusted with 10 mM buffer to the desired pH. Next, 5 mL of the monochloramine solution was added to 10 mL of 25 μM DMA at the same pH and 10 mL of the corresponding buffer at 10 mM to make it headspace

free. Dichloramine solutions were made by adjusting the pH of stock monochloramine to pH 3.7 with 2 N sulfuric acid and aging for 1 hour. The pH of the dichloramine solution was not pH adjusted before mixing with 10 μM DMA stock solution due to its fast decomposition at these conditions. Precisely 5 mL of the dichloramine solution was added to 10 mL of 25 μM DMA at the same pH and 10 mL of the corresponding buffer at 15 mM.

To assess the effect of hydroxylamine on monochloramine breakdown and concomitant NDMA formation, stock 40 mM hydroxylamine was added to 0.4 mM monochloramine at pH 7.0, 8.0, 9.0, and 10.0 to achieve a hydroxylamine to monochloramine molar ratio of 1:1.

Following the desired reaction time (up to 4 hours unless stated otherwise), 10 mL aliquots were quenched of chloramines with 0.5 g dry quenching mix containing 1.8 g ascorbic acid, 1 g KH_2PO_4 and 39 g Na_2HPO_4 (12.5 mM ascorbic acid in solution). After quenching, samples were immediately extracted with dichloromethane with 10:1 water:dichloromethane volume ratio using a back-and-forth shaker table at high speed for 15 minutes. Following a 5-minute quiescent settling period, dichloromethane was extracted with a Pasteur pipette and stored for NDMA analysis.

C. ANALYSIS

Monochloramine and dichloramine were quantified using a Shimadzu UV 2450 spectrophotometer following the procedure developed by Schreiber and Mitch (2005) by deconvoluting UV absorbance spectra at 245 and 295 nm and referred to herein as the Direct UV Method. Monochloramine was also quantified using Hach Method 10171 and total chlorine was quantified by DPD Method 8167. The difference between the total chlorine and monochloramine was assumed to be dichloramine, and referred to herein as the Hach Method.

NDMA was identified and quantified using gas chromatography–mass spectrometry (GC-MS). Splitless injections of 5 μL were used with an injector temperature was 250 °C. The separation column used was a RESTEK 12497 FAMEWAX with a length of 30 m, inner diameter 0.25 mm, with a stationary phase film thickness of 0.25 μm. Helium carrier gas was used with constant flow rate at 1.0 mL/min. The oven program was 45 °C for 3 minutes followed by a ramp of 25 °C/min to 130 °C and then 12 °C/min to 230 °C hold for 1 minute. The full scan and selected ion monitoring (SIM) mode was simultaneously run with the MS conditions stated in Table 1. Six-point NDMA standard curves (10 – 1000 μg-L^{-1}) were used to quantify the unknowns ($R^2 > 0.999$). Blanks and check standards were run after at least every ten injections. Standard solutions were prepared following the same procedure as samples.

D. NUMERICAL MODELING

The unified chloramine kinetic model programmed by Wahman and Speitel (2012), implemented in AQUASIM, was used to monitor the decay and formation of chloramine species. In particular, solutions initially containing preformed monochloramine and dichloramine were modeled as a function of pH (8.0, 9.0, and 10.0) over 2 hours in the chloramine stability experiments and 4 hours for the reactions between DMA and chloramine species, and compared to batch kinetic experimental data. In this kinetic model, the acid-base reactions were assumed to be fast and governed by their equilibrium constants.

III. RESULTS AND DISCUSSION

A. MONOCHLORAMINE AND DICHLORAMINE DECOMPOSITION

Figure 3 shows monochloramine profiles at pH 8.0, 9.0, and 10.0 and indicates monochloramine was stable over 4 hours at a concentration of approximately 30 mg•L as Cl_2. The concentrations determined by the Direct UV Method matched those measured by the Hach Method and were simulated accurately by the AQUASIM model. Similar experiments by Valentine et al. (1986) performed over longer periods of time (i.e., 400 hours compared to 4 hours) indicated monochloramine concentrations measured by the Direct UV Method were greater than those by the Hach Method at pH 6.8 and 8.0, which was attributed to the formation of an unidentified product (UC1) that had a UV absorbance spectra in the 230-270 nm range. The deviation between the methods began at approximately 25 hours at pH 8.0 and 80 hours at pH 6.8. The experiments shown in Figure 1 were not performed long enough to generate measurable concentrations of UC1 (i.e., there is no deviation between the Direct UV and Hach methods), which may play a role in NDMA formation.

Figure 4 shows dichloramine decay and the concomitant formation of monochloramine at pH 8.0, 9.0, and 10.0, with quantification of the chloramine species by the Hach and Direct UV Methods. Dichloramine decomposition occurred more rapidly as the pH increased. For instance, at pH 8.0, dichloramine (measured with the Hach method) decreased from 57 to 14 mg/L as Cl_2 over 2 hours, while at pH 9.0 it only took one hour for dichloramine to completely decay and at pH 10.0, less than 15 minutes. Similar trends were also observed in studies by Hand and Margerum (1983) and Leung and Valentine (1994).

At pH 8.0, the AQUASIM model matched the data adequately between 60- and 120 minutes; however, at 15- and 30 min, the model over predicted the measured dichloramine concentrations.

This was attributed to analytical error with regard to the dichloramine measurements as the model accurately captured the concomitant monochloramine formation at 15- and 30 minutes. At pH 9.0, the AQUASIM model matched data generated with the Hach Method adequately, but dichloramine measured by the Direct UV Method was higher by approximately a factor of three. This result was attributed to the formation of the aforementioned UC1 from dichloramine decay, which appeared to be stable and to interfere with the Direct UV Method, but not the Hach Method at pH 8.0 and 9.0.

At pH 10, the AQUASIM model only matched dichloramine measured with the Hach Method, which completely decayed within 5 minutes, an expected result. In contrast, dichloramine measured with the Direct UV Method indicated a concentration of approximately 3.0 mg/L as Cl_2. Monochloramine was measured at 27 mg/L as Cl_2 by the Direct UV method, 14 mg/L as Cl_2 by the Hach method, and 10 mg/L as Cl_2 by the AQUASIM model. These disparities in the monochloramine concentrations between Hach Method and the model were attributed to either the pH dependent redox potential of the UC1 and/or inadequate calibration of the unified chloramine model at this high pH condition.

This UC1 from dichloramine decay was discovered by Hand and Margerum (1983), and subsequently investigated by Valentine (1990). They determined that UC1 was more polar than monochloramine due to the longer retention time on HPLC and did not partition into any common organic solvent at pH 3.5-4.0 or 9.0. Because it passed through an anion exchange column, Valentine concluded that UC1 was likely an anion rather than an uncharged compound. Additionally, its maximum absorbance was near 245 nm, which is one of the wavelengths used in Direct UV Method. Lastly, they found that UC1 could serve as both a reductant and oxidant and the redox reactions were pH dependent.

The next section focuses on the formation of NDMA in reactions of DMA with monochloramine or dichloramine at pH 8.0, 9.0 and 10.0. The chloramine species concentrations were determined by the Hach Method because the unidentified product interfered with the Direct UV Method.

B. REACTION WITH DMA

1. Monochloramine

Figure 5 shows NDMA formation kinetics with 10 μM DMA and 0.4 mM NH_2Cl in 10 mM buffer at pH 8.0, 9.0 and 10.0 over 24 hours. The experiment was also run at pH 7.0, but the resultant NDMA concentrations were below the method detection limit and thus not reported. Nevertheless, both the reaction rate/kinetics and NDMA yield were pH dependent. The yield at pH 8 < pH 10 < pH 9, similar to the trends were observed by Schreiber and Mitch (2006). The reaction rate also increases with pH. For example, it took approximately 6 hours for NDMA formation to reach its final concentration at pH 8, compared to 1 hour at pH 9 and only 10 minutes at pH 10. However, the observed yields were at least 10 times higher than those reported by Schreiber and Mitch (2005). These data are shown in Figure 5 and indicate NDMA after 24 hours (i.e., near its final concentration) at pH 8.0, 9.0, and 10.0 was approximately 12 μg/L, 48 μg/L, and 41 μg/L, respectively; while Schreiber and Mitch (2006) did not report temporal profiles, their data indicate NDMA after 2 hours for pH 8.0, 9.0, and 10.0 was 0.9 μg/L, 1.9 μg/L, and 1.2 μg/L respectively. One possible reason for the higher NDMA yields in this work may be a result of pH-adjusting monochloramine prior to mixing with DMA.

2. Dichloramine

Figure 6 shows NDMA formation kinetics with 10 μM DMA and 0.4 mM $NHCl_2$ in 10 mM buffer at pH 7.6, 8.0, 9.0 and 10.0. Due to the anticipated interference of UC1 using the Direct UV Method (see Figure 3), the chloramine species were quantified using the Hach Method. On

balance, dichloramine concentrations were accurately predicted with the unified chloramine model as was monochloramine at pH 9.0 (Figure 5C); in contrast, at pH 7.6 and 8.0, the measured monochloramine concentrations were higher than predicted by the chloramine model prior to 2 hours, and, at pH 10.0, the model consistently underpredicted the measured concentrations by approximately 5 mg/L as Cl_2. The reason for this disparity at pH 10 is unclear, but it could be that the unified chloramine model does not account certain reactions that impact chloramine speciation at this high pH.

NDMA formation was pH dependent (Figure 6), with the yield at pH 7.6 < pH 8.0 < pH 10.0 < pH 9.0, in agreement with the trends observed by Schreiber and Mitch (2006). The NDMA formation kinetics appeared to be fastest at pH 10.0, as the reaction was complete (i.e., at its final concentration) by 0.25 hours. Interestingly, at pH 9 (i.e., the pH of the highest NDMA yield), NDMA formation continued to occur after dichloramine decayed completely (at ~1.5 hours) and continued through 3.0 hours, suggesting the existence of an NDMA formation pathway that may involve the stable decay product of dichloramine (i.e., UC1) or nitroxyl (i.e., an unstable intermediate) as opposed to dichloramine itself.

To investigate the role of UC1 in NDMA formation, DMA was periodically spiked into a solution of 0.4 mM dichloramine at pH 10 (i.e., the condition where NDMA forms most rapidly and UC1 is stable – see Figure 6D). As shown in Figure 7, DMA was spiked 4 times over 4.5 hours at 50 μM DMA each time. As there was no significant increase in NDMA upon DMA addition in the presence of UC1, it can be concluded that UC1 is not a primary reactant in NDMA formation.

The results in Figure 6D and 7 suggest the presence of more than one unidentified compound from dichloramine decay and an additional NDMA formation pathway, one that involves a reaction between a dichloramine decay product and DMA. Nitroxyl, HNO, could be the unidentified

compound (not UC1), which forms by dichloramine hydrolysis (Table 2, Reaction 7, Product "I"). Under aerobic conditions, a portion of HNO may rapidly react with O_2 to form peroxynitrite, $ONOO^-$, which has been recently experimentally proven to occur with a second-order rate constant, $k = 1.8 \times 10^4\ M^{-1}s^{-1}$ (Smulik et al., 2014). Peroxynitrite is a known nitrosating agent and, therefore, is likely to react with DMA to form NDMA and other amine-based precursors to form other *N*-nitrosamines. Therefore, dichloramine, dissolved oxygen and pH conditions likely impact the kinetics and yield of NDMA formation. The rate-limiting step in this pathway may be the generation of HNO from dichloramine decay. As pH increases, dichloramine decays more rapidly and more HNO will form, leading to the faster formation and higher yields of NDMA at higher pH. Interestingly, superoxide dismutase and t-BuOH are not scavengers for peroxynitrite, so the fact that their addition in the Schreiber and Mitch (2006) study did not impact NDMA formation is not unexpected should this additional pathway be relevant. Batch kinetic experiments with scavengers of nitroxyl, nitroxyl radical, and peroxynitrite radical could be useful in further elucidating this additional NDMA formation pathway. Experiments with nitroxyl donors, such as Angeli's salt ($Na_2N_2O_3$) and Piloty's acid ($PhSO_2NHOH$), are needed to further understand this proposed reaction pathway.

Figure 8 shows the formation of a second unidentified compound (UC2) that was detected by GC-MS at a retention time at 7.292 minutes (Figure 8B) only at pH 9.0 and 10.0, approximately one minute after elution of NDMA at a retention time of 6.424 minutes. UC2 did not appear in the blank chromatogram (extracted Milli-Q water, Figure 7A) and was observed in full scan spectrum (Figure 8B). This is unlikely to be the same compound as UC1 observed by UV-Vis because UC1 was shown by Valentine (1986) to not partition into any common organic solvent, including dichloromethane which was used in this study, and the mass spectrum indicates UC2 is an organic

compound with at least one methyl group (m/z = 15). UC2 had a similar mass spectrum as acetic acid and UDMH. However, acid acetic has a retention time of 7.248 minutes. Therefore, UC2 is unlikely to be acid acetic but a spiked sample is needed to confirm this assertion. Interestingly, UC2 was only observed at pH 9.0 and 10.0, not at pH 8.0, but its peak area did not exhibit any discernable trends with pH or reaction time (Figure 7C). However, if UC2 is in fact UDMH, it can be concluded that most NDMA formation is not through the UDMH pathway. Specifically, at pH 9.0, comparing Figure 6C to Figure 8C, NDMA forms in the presence of UDMH; however, at pH 10.0, comparing Figure 6D to Figure 8C, NDMA is at its final concentration in the presence of UDMH. Additionally, at pH 8, no UDMH was observed, but NDMA forms, albeit at lower yields (Figure 6B). This is reasonable because UDMH forms by a reaction between dichloramine and unprotonated DMA (pK_a = 10.7). A spiked sample with UDMH may help confirm the identity of UC2, which will be a focus of in upcoming experiments.

C. THE ROLE OF HYDROXYLAMINE

Figure 9 shows the effects of hydroxylamine on monochloramine stability. Due to the interference of hydroxylamine on the Hach Method coupled with the fact that hydroxylamine does not have an absorption spectra between 200-300 nm, monochloramine and dichloramine were measured by the Direct UV Method. By comparing Figure 9 to Figure 3, it can be concluded that the presence of hydroxylamine accelerates the breakdown of monochloramine and its impact is pH dependent. Lower pH favors more rapid monochloramine decay in the presence of hydroxylamine. For instance, after 3.5 hours, monochloramine concentrations were approximately 20 mg/L as Cl_2 at pH 10, 13 mg/L as Cl_2 at pH 9, and 8 mg/L as Cl_2 at pH 8, in agreement with the trends reported by Wahman et al. (2014).

A control experiment with hydroxylamine was conducted with 0.4 mM NH_2OH and 10 μM DMA in 10 mM buffer solution at pH 8.0, 9.0 and 10.0. As expected, in the absence of ozone (Yang et al., 2009), no NDMA was formed over 24 hours. However, a peak was detected with retention time of 6.464 minutes (UC3 in Figure 10A), close to retention time of NDMA (6.424 minutes). To confirm the observed peak was not NDMA, 100 μL of 5 ppm NDMA was added to 10 mL of reaction solution, extracted, and analyzed. The shoulder peak emerged at 6.424 minutes (Figure 10B) indicating that UC3 was not NDMA, but a product formed by DMA and hydroxylamine. The product has the same mass spectrum as acetoxime (Figure 10C), which is distinct from NDMA (Figure 10D). However, acetoxime has not been reported in the NDMA literature and its importance is unknown at this stage.

Figure 11 shows NDMA formation with 10 μM DMA and 0.4 mM NH_2Cl with and without the addition of 0.4 mM NH_2OH in 10 mM buffer at pH 9.0 and 10.0 after 24 hours. The experiment was also run at pH 8.0 but the resultant NDMA concentrations were below the method detection limit and thus not reported. The presence of hydroxylamine with DMA and monochloramine decreased the NDMA yields by more than half. This was attributed to competition reactions, which included monochloramine and DMA, monochloramine and hydroxylamine, and DMA and hydroxylamine. Interestingly, UC3 was not observed in these samples at both pH 9.0 and 10.0. There are two hypotheses for this phenomenon: (1) the reaction between DMA and hydroxylamine is slow in comparison to the reactions between DMA and monochloramine and hydroxylamine and monochloramine, thus inhibiting the formation of UC3 or (2) after the formation of UC3 it reacts with monochloramine to form other product which may or may not be NDMA. A batch kinetic experiment with monochloramine, DMA, and hydroxylamine is needed to more fully understand the impact of hydroxylamine on NDMA formation.

IV. CONCLUSIONS

The significant findings of this research are:

- The unified chloramine model implemented in AQUASIM accurately simulated monochloramine stability over 4 hours at pH 8.0, 9.0 and 10.0; in solutions of dichloramine, the AQUASIM model adequately captured dichloramine decay at pH 8.0, 9.0, and 10.0 and the concomitant formation of monochloramine at pH 8.0 and 9.0 only; however, the model consistently underpredicted monochloramine at pH 10.0, indicating there was either an interference in the experimental measurements or the model is not calibrated accurately for this high pH condition.
- Dichloramine decay occurred more rapidly as the pH increased from 8 to 10; the formation of unidentified product (UC1) was observed at pH 9.0 (by interference with the Direct UV Method) and pH 10.0 (by interference with the Direct UV Method and possibly the Hach Method).
- NDMA formation was pH dependent for both monochloramine and dichloramine, with the highest yields at pH 9.0 and the fastest formation kinetics at pH 10.0.
- The unidentified compound that interfered with UV-Vis measurements of dichloramine decay (i.e. UC1) does not have significant role in NDMA formation.
- In reactions between dichloramine and DMA, a second unidentified compound (UC2) formed that has a mass spectrum similar to UDMH; while the identity of UC2 needs to be confirmed, this species did not appear to play an important role in NDMA formation.
- Hydroxylamine accelerates the decomposition of monochloramine, which occurs more rapidly at lower pH; the reaction between hydroxylamine and DMA did not form NDMA, an expected result in the absence of ozone; however, another compound (UC3), tentatively

identified as acetoxime, was detected that disappeared in the presence of monochloramine; the precise role of UC3 in NDMA formation is unclear.

- The presence of hydroxylamine added at equal molar concentrations with monochloramine in the presence of DMA decreased the NDMA yields by more than half.

V. FUTURE WORK

The results from this study point to the need for the following:

- Identify UC1, which is likely not a NDMA precursor, but could be an inorganic nitrogenous DBP that may exert toxicity.
- Confirmation of the identities of UC2 and UC3 by analyzing spiked samples with UDMH and acetoxime by GC-MS.
- A series of batch experiments to further investigate the role of UDMH in NDMA formation; these experiments would need to included UDMH and monochloramine, UDMH and dichloramine, and UDMH and a HNO donor (i.e., Angeli's salt).
- Monitoring hydroxylamine concentrations (Frear and Burrell, 1955) and dosing hydroxylamine throughout the kinetics experiments with monochloramine and dichloramine in the presence of DMA could help elucidate the role of hydroxylamine on monochloramine and dichloramine decay and NDMA formation.
- A series of kinetics experiments with DMA and dichloramine in the presence of nitroxyl and peroxynitrite radical scavengers and Angeli's salt (i.e., a nitroxyl donor) could provide evidence of an additional NDMA formation pathway.
- A unified NDMA kinetic model that includes the relevant formation pathways and short-lived species related to chloramination conditions.

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Table 1. Gas chromatography mass spectroscopy conditions for the identification and quantification of *N*-nitrosodimethylamine (NDMA)

Full Scan Mode			
Tune		Standard Spectrum autotune	
Scan Range		5 – 200 amu	
Threshold		150	
Solvent Delay		5 minutes	
MS Temperature		150 ºC (Quad) 230 ºC (Source)	
Selected ion monitoring Mode			
		Selected Ions	
Group	Start Time (min)	1	2
NDMA	5.0	74	43

Table 2. Monochloramine decay reactions and associated reaction rates and equilibrium constants at 25 ºC (Vikesland et al., 2001)

	Reaction	Reaction rate/ equilibrium constant (25 ºC)	Rate expression
1	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	$1.5 \times 10^{10}\ M^{-1}h^{-1}$	$k_1[HOCl][NH_3]$
2	$NH_2Cl + H_2O \rightarrow HOCl + NH_3$	$7.6 \times 10^{-2}\ M^{-1}h^{-1}$	$k_2[NH_2Cl]$
3	$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	$1.0 \times 10^{6}\ M^{-1}h^{-1}$	$k_3[HOCl][NH_2Cl]$
4	$NHCl_2 + H_2O \rightarrow HOCl + NH_2Cl$	$2.3 \times 10^{-3}\ h^{-1}$	$k_4[NH_2Cl]$
5	$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$	$2.5 \times 10^{7}\ M^{-1}h^{-1}$	$k_5[NH_2Cl]^2$
6	$NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$	$2.2 \times 10^{8}\ M^{-2}h^{-1}$	$k_6[NH_2Cl][NH_3]H^+]$
7	$NHCl_2 + H_2O \rightarrow I$	$4.0 \times 10^{5}\ M^{-1}h^{-1}$	$k_7[NH_2Cl][OH^-]$
8	$I + NHCl_2 \rightarrow HOCl$ + products	$1.0 \times 10^{8}\ M^{-1}h^{-1}$	$k_8[I][NHCl_2]$
9	$I + NH_2Cl \rightarrow$ products	$3.0 \times 10^{7}\ M^{-1}h^{-1}$	$k_9[I][NH_2Cl]$
10	$NH_2Cl + NHCl_2 \rightarrow$ products	$55.0\ M^{-1}h^{-1}$	$k_{10}[NH_2Cl][NHCl_2]$
11	$HOCl \rightarrow H+ + OCl^-$	pKa = 7.5	
12	$NH_4^+ \rightarrow NH_3 + H^+$	pKa = 9.3	
13	$H_2CO_3 \rightarrow HCO_3^- + H^+$	pKa = 6.3	
14	$HCO_3^- \rightarrow CO_3^{2-} + H^+$	pKa = 10.3	

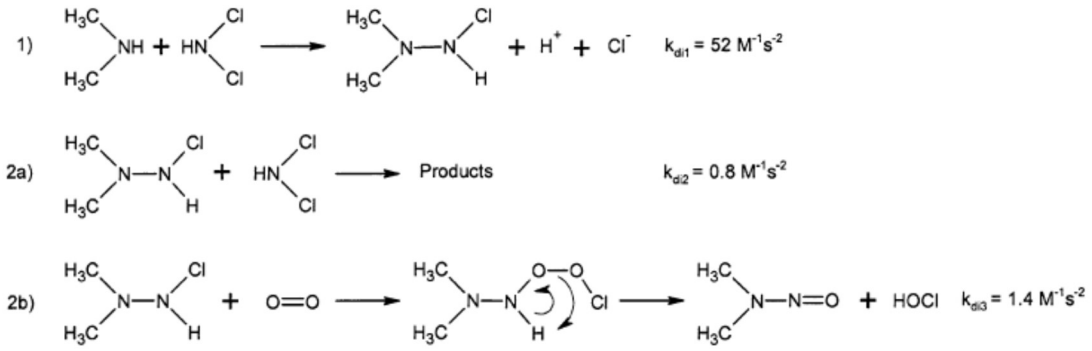

Figure 1. Nitrosation pathway for NDMA formation proposed by Schreiber and Mitch (2006) with corresponding reaction rates; the products in reaction 2a indicate unspecific products.

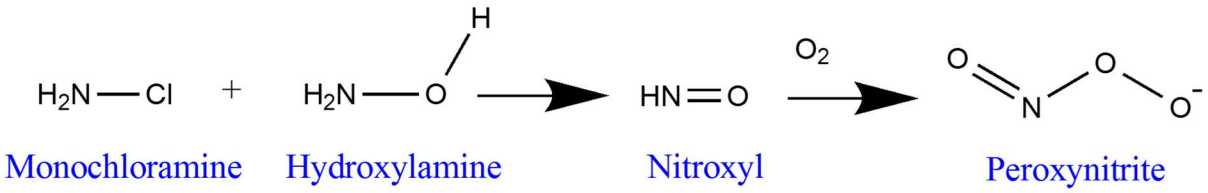

Figure 2. The proposed decay pathway of monochloramine in the presence of hydroxylamine and dissolved oxygen.

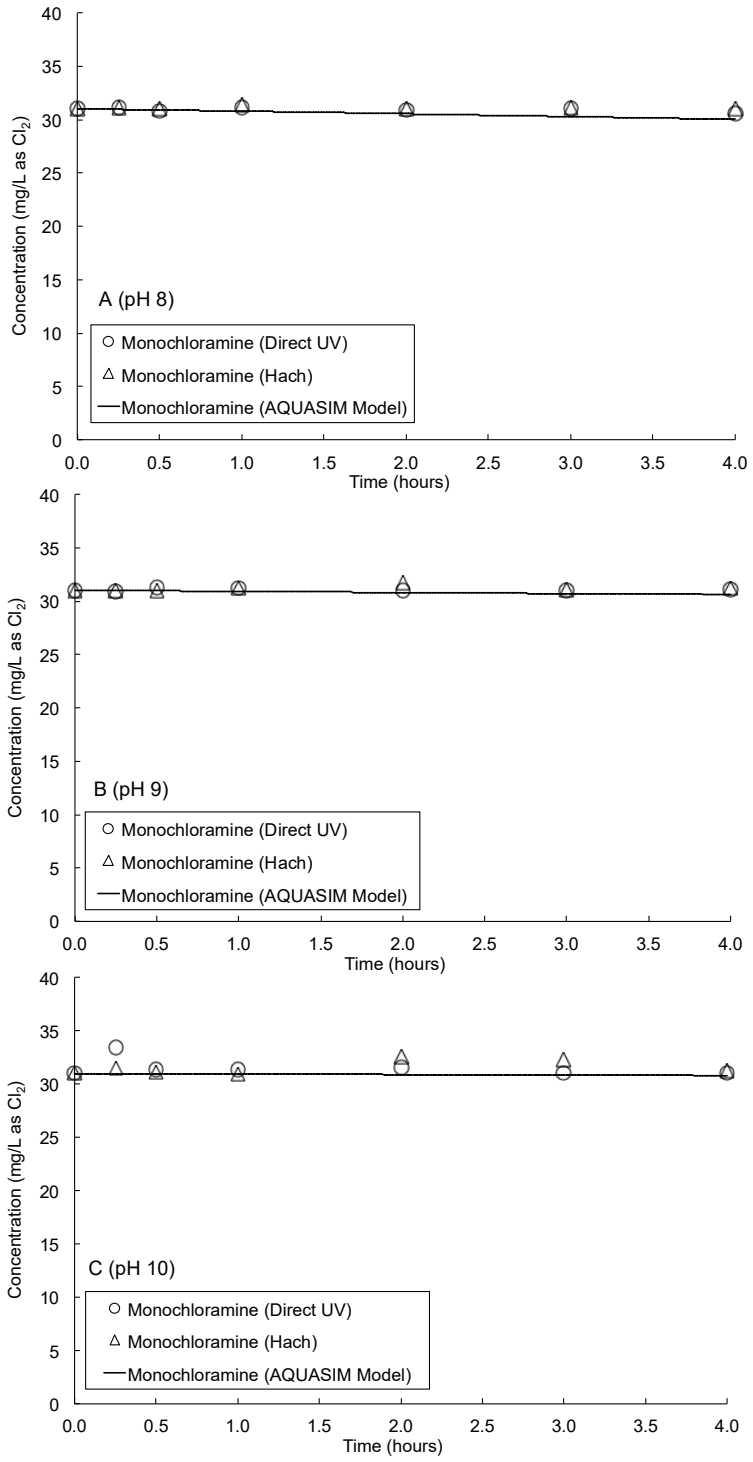

Figure 3. Experimental data and AQUASIM model simulations for monochloramine decomposition at (A) pH 8, (B) pH 9, and (C) pH 10. Monochloramine was quantified using the Hach Method and Direct UV Method. No dichloramine was detected by the Direct UV Method.

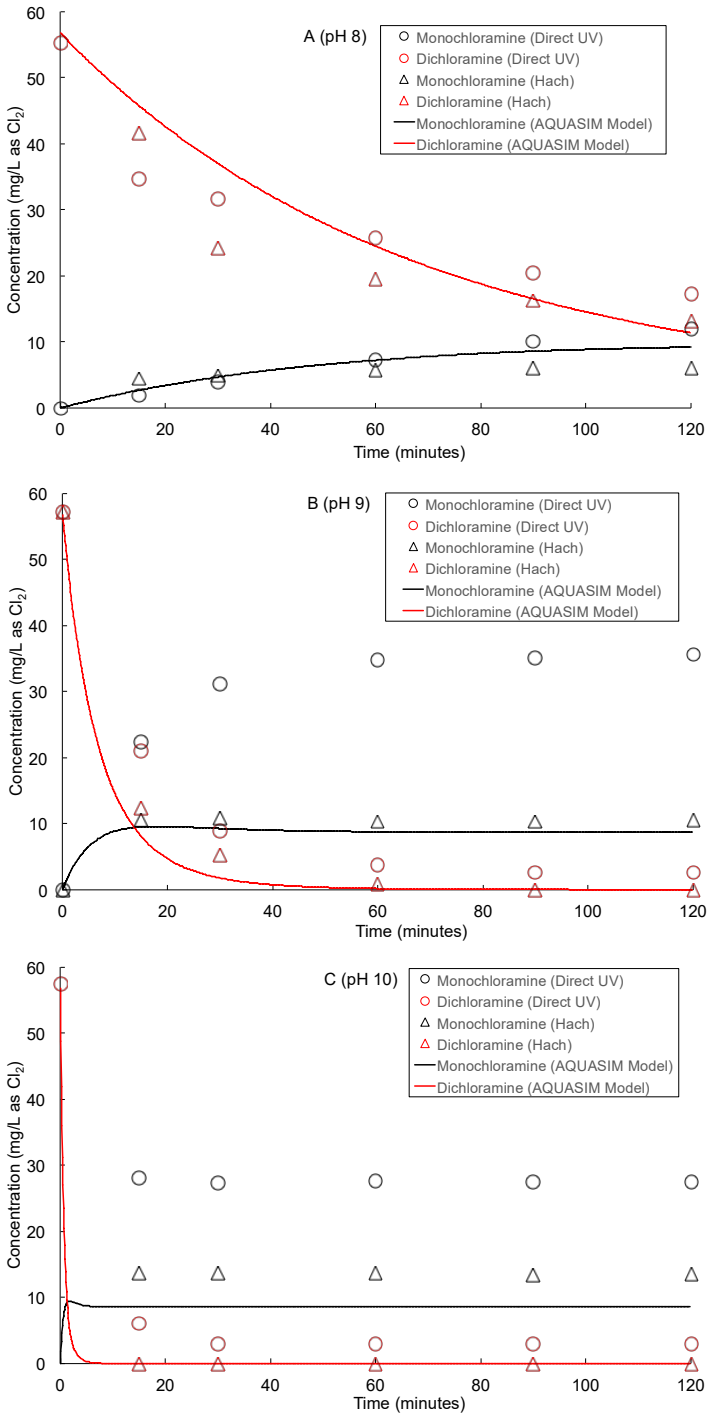

Figure 4. Experimental data and AQUASIM model simulations for dichloramine decomposition and monochloramine formation at (A) pH 8 (B) pH 9 and (C) pH 10. For the Hach Method, total chloramine and monochloramine were quantified and the difference was assumed to be dichloramine. In the Direct UV Method, monochloramine and dichloramine concentrations were obtained through deconvolution of UV absorbance at 245 and 295 nm.

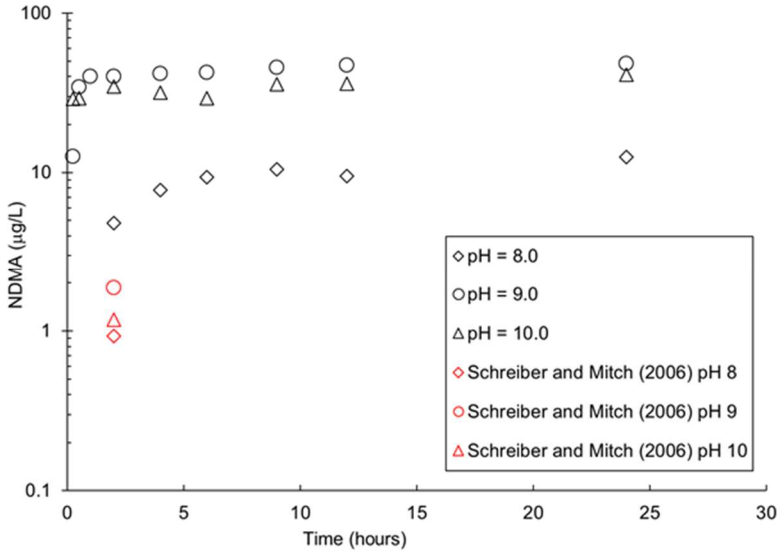

Figure 5. NDMA formation kinetics with 10 µM DMA and 0.4 mM NH_2Cl over 24 hours in 10 mM buffer at pH 8.0, 9.0, and 10.0; phosphate buffer was used for pH 8.0, borate buffer for pH 9.0, and carbonate for pH 10. Data from Schreiber and Mitch (2006) is shown for comparison.

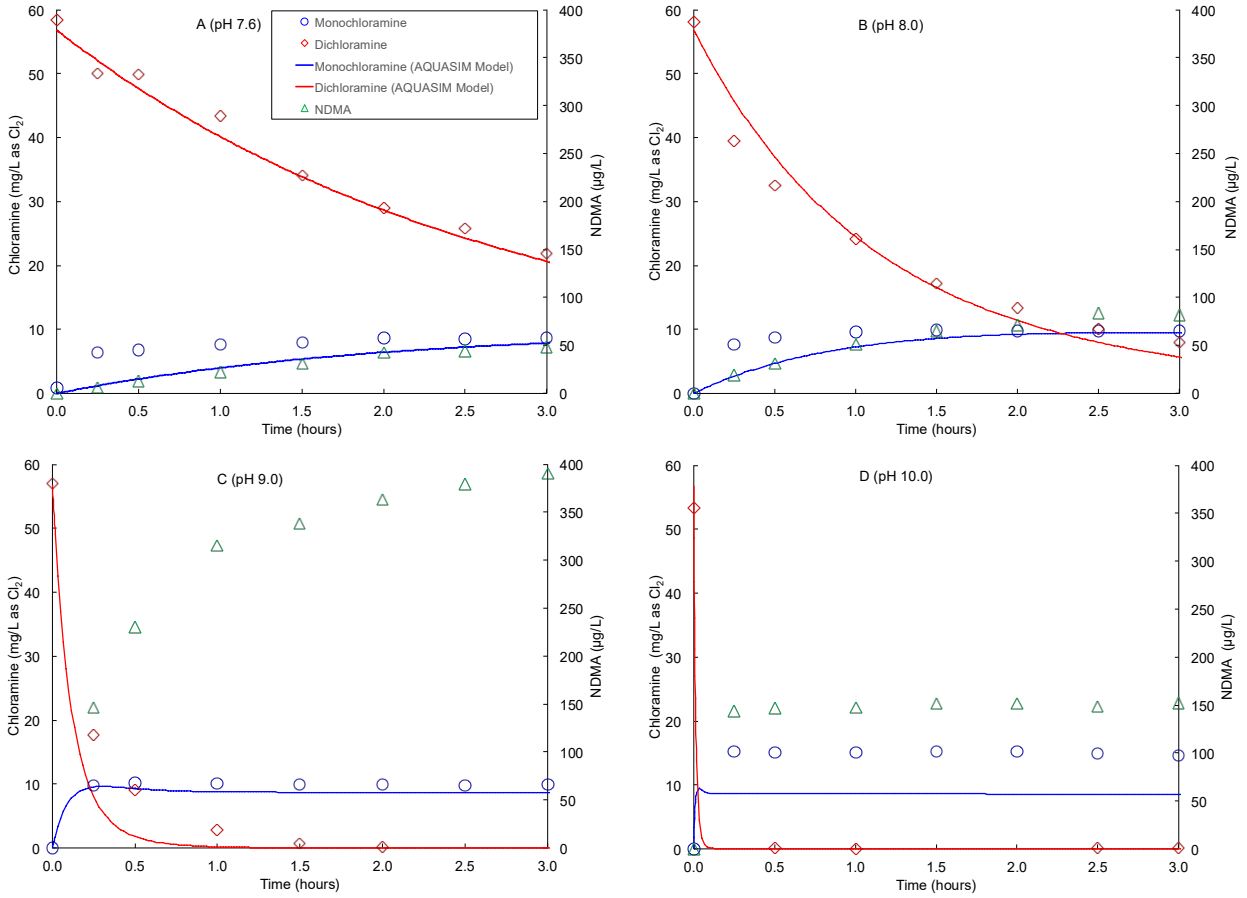

Figure 6. NDMA formation kinetics with 10 µM of DMA and 0.4 mM $NHCl_2$ over 4 hours in 10 mM buffer at (A) pH 7.6, (B) pH 8.0, (C) pH 9.0, and (D) pH 10.0; phosphate buffer was used for pH 7.6 and 8.0, borate for pH 9.0 and carbonate for pH 10. Total chloramine and monochloramine were quantified using the Hach Method and the difference was assumed to be dichloramine.

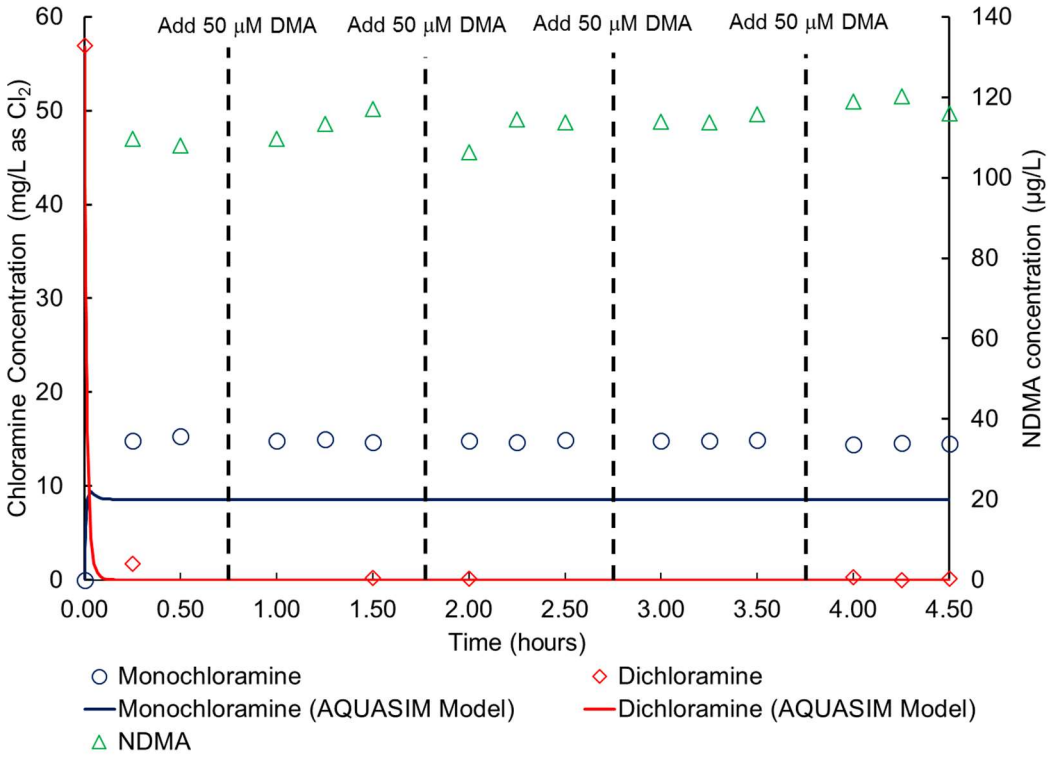

Figure 7. NDMA formation kinetics with DMA and 0.4 mM $NHCl_2$ over 4.5 hours in 10 mM total phosphate buffer at pH 10.0 with DMA spiked at 10 μM at time zero and thereafter at 50 μM as indicated by the vertical dashed lines. Total chloramine and monochloramine were quantified using the Hach Method and the difference was assumed to be dichloramine.

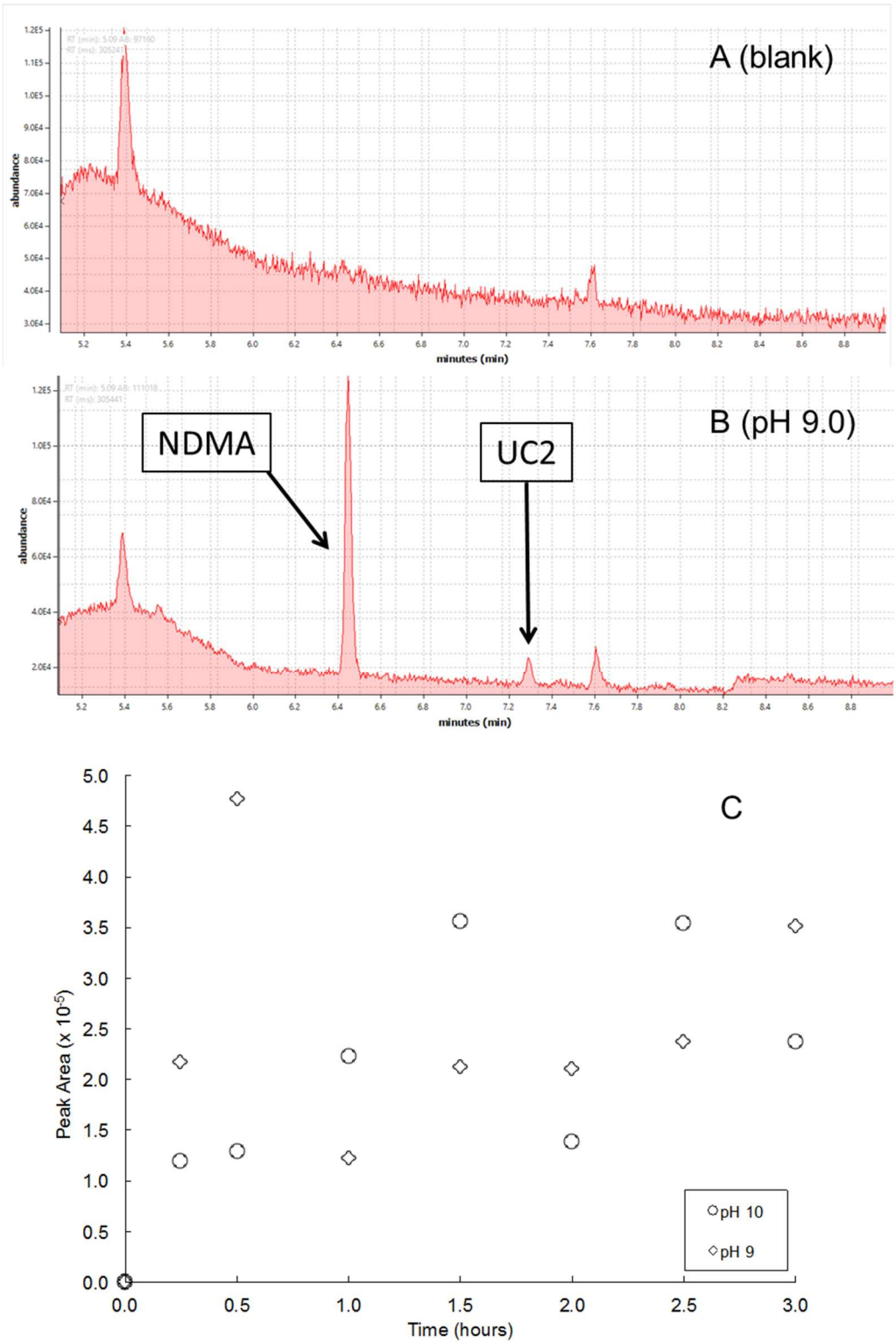

Figure 8. A blank GC-MS chromatogram (Panel A) and the second Unidentified Compound (UC2) observed by GC-MS at a retention time of 7.292 minutes (Panel B, pH 9.0 only) for the reaction between 0.4 mM dichloramine and 10 μM DMA. Panel C shows peak areas for UC2 at pH 9 and 10.

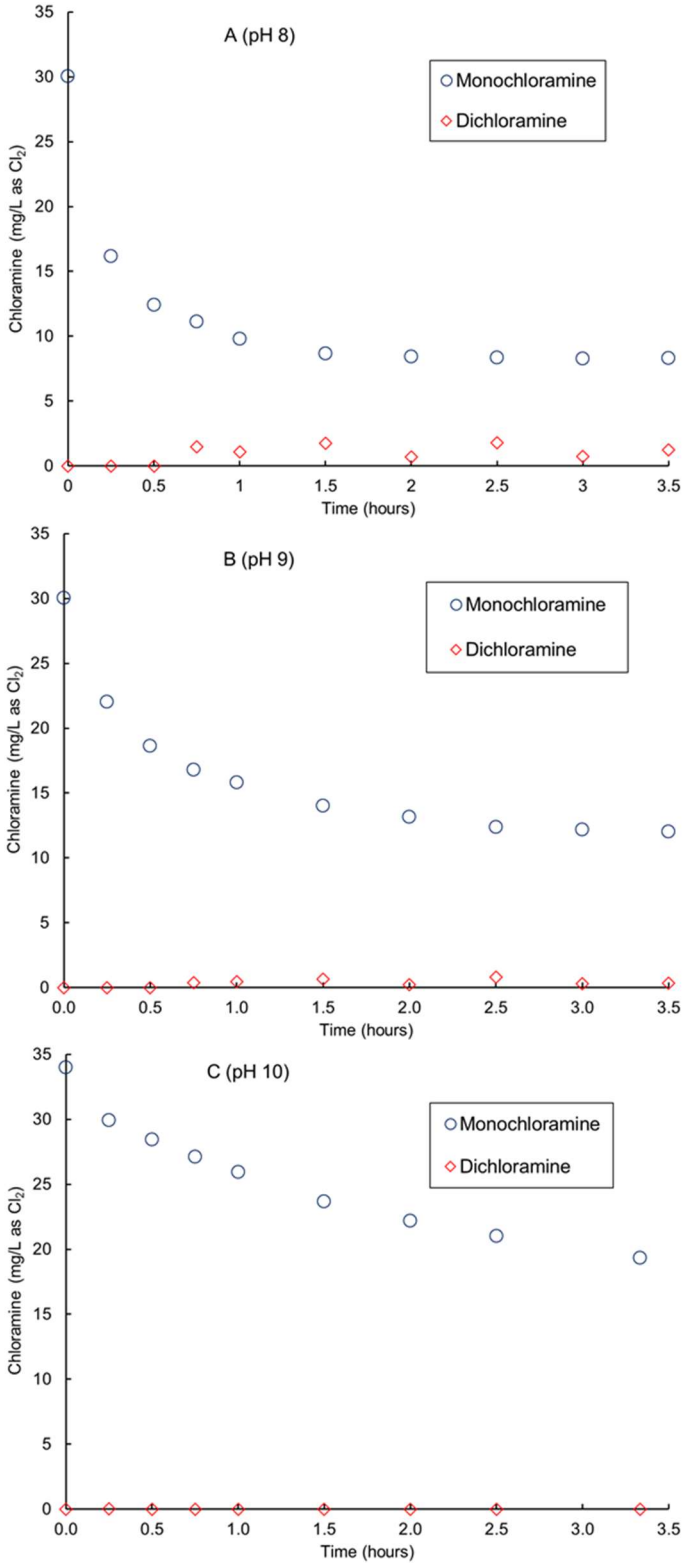

Figure 9. Effects of 0.4 mM hydroxylamine on stability of 0.4 mM monochloramine solutions at (A) pH 8 (B) pH 9 and (C) pH 10. Monochloramine and dichloramine concentrations were obtained through deconvolution of UV absorbance at 245 and 295 nm.

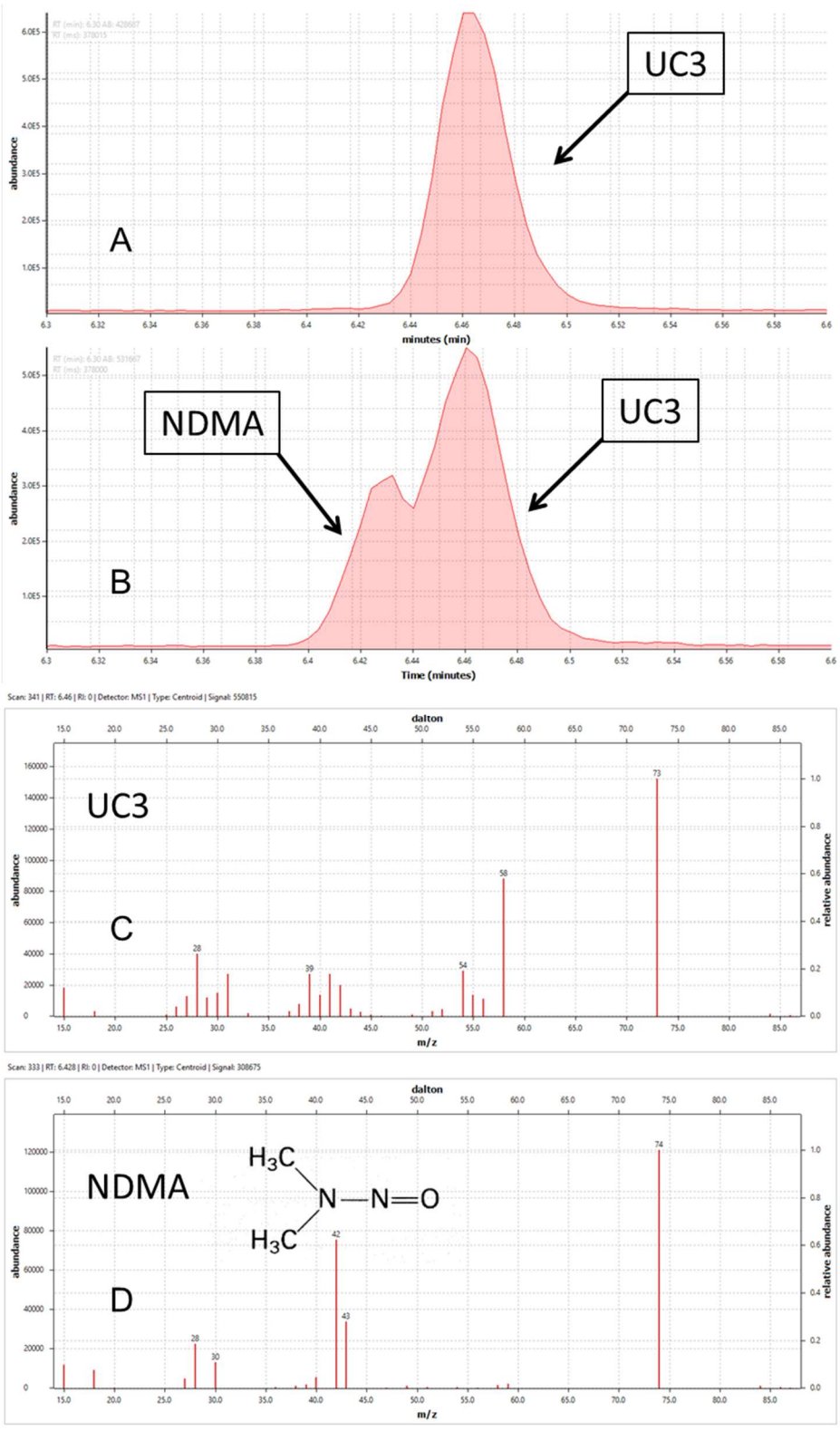

Figure 10. Total ion chromatogram (TIC) of 10 µM DMA and 0.4 mM NH_2OH reaction products at pH 10 after 24 hours (A) and a 50 µg/L NDMA spiked sample (B). Mass spectrums for UC3 (C) and NDMA (D).

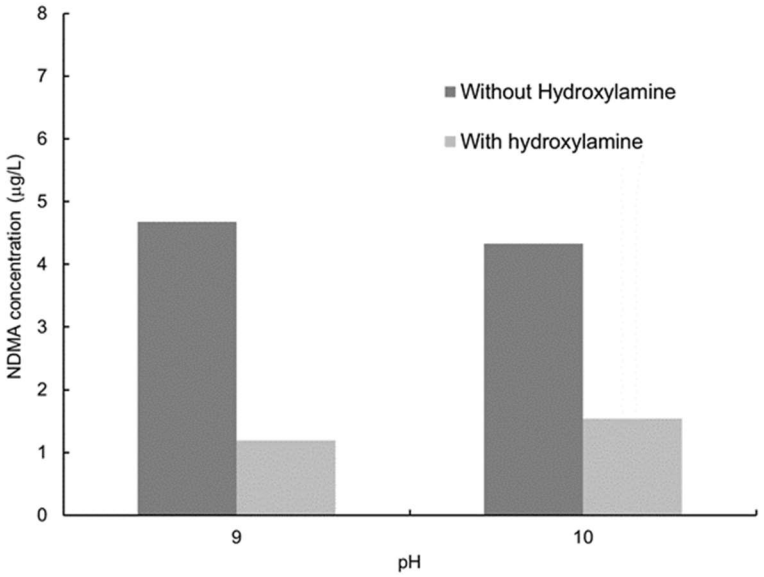

Figure 11. NDMA formation with 10 μM DMA and 0.4 mM NH_2Cl with and without 0.4 mM NH_2OH at pH 9.0 and 10.0 after 24 hours.