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THE EFFECTS OF AMINE STRUCTURE, CHLORAMINE SPECIES AND OXIDATION STRATEGIES ON THE FORMATION OF N-NITROSODIMETHYLAMINE

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THE EFFECTS OF AMINE STRUCTURE, CHLORAMINE SPECIES AND OXIDATION STRATEGIES ON THE FORMATION OF *N*-NITROSODIMETHYLAMINE

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Environmental Engineering and Earth Sciences

---

by
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August 2014

Accepted by:

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ABSTRACT

To comply with the increasingly stringent disinfection by-product (DBP) regulations in the United States, many water treatment plants have been switching from chlorination to chloramination in the last decade. Although chloramination reduces the formation of regulated DBPs such as trihalomethanes and haloacetic acids, it causes the formation of nitrosamines. Nitrosamines are a class of compounds that are probable human carcinogens, mutagens and teratogens at concentrations as low as 0.2 ng/L. In particular, *N*-nitrosodimethylamine (NDMA) is the most frequently detected nitrosamine in distribution systems in the United States. Although, nitrosamines are currently not regulated by the USEPA, they have been recently identified as a group of contaminants highlighted for possible regulatory action.

Although several studies have investigated the formation mechanisms and important precursors for nitrosamines (especially NDMA), there is still much more to learn about their formation pathways. The main objective of this research was to systematically examine nitrosamines formation from amines to gain insight into the formation mechanisms of nitrosamines (especially NDMA) and examine the interactions of these precursors with different oxidants. Specifically, the research focused on: (i) the formation potential of nitrosamines from amino acids (AAs) under different disinfection conditions, (ii) the roles of tertiary structure on the formation of NDMA during chloramination, (iii) the importance of chloramine species in the NDMA formation, and

(iv) the interaction of various precursors with different oxidants (chlorine, chlorine dioxide and ozone) and their consequent effect on NDMA formation.

The research approach consists of three phases. First phase consisted of identifying the important nitrosamine precursors and understanding the effect of precursor structure on the conversion yield. Primary and tertiary amines were selected as the target compounds and results are presented in Chapters V and VI. Then in the second phase the roles of chloramine species in NDMA formation was examined as presented in Chapter VII. Finally, controlling NDMA formation, practically as critical as understanding the fundamentals of those reactions, was investigated using different oxidants in Chapter VIII.

AAs were selected initially as nitrosamine precursors since they are rich in nitrogen, reactive and shown to form of other classes of DBPs (trihalomethanes, halonitromethanes, etc.). Nine AAs (alanine, aspartic acid, cysteine, glutamic acid, glycine, lysine, histidine, proline and serine) were selected based on their structures (i.e., acidity vs. basic, polar vs. nonpolar, hydrophilic vs. hydrophobic), and tested under different oxidation conditions for their formation of nitrosamines. NDMA yields of all nine AAs during chloramination were below the minimum reporting levels. However, during ozonation alone and ozonation followed by chloramination, the formation of several nitrosamines (including *N*-nitrosopyrrolidine and *N*-nitroso-di-n-butylamine) at very low molar conversion yields (<0.1%) was found. Although AAs are known to form different nitrogenous DBPs (i.e., halonitromethanes, haloacetonitriles), they did not appear to be an important contributor to nitrosamines formation.

Due to very low conversion yields of nitrosamines, the research focus was directed towards tertiary amines which are more reactive nitrosamine precursors. Since, NDMA is the most frequently detected nitrosamine, potential NDMA precursors were selected for further investigation. The effect of tertiary amine structure and the influencing factors in NDMA formation were examined under chloramination conditions. Dimethylamine (DMA) and 20 different tertiary aliphatic and aromatic amines were carefully examined based on their functional groups attached to the basic DMA structure. The results indicated a wide range (0.02% to 83.9%) of NDMA yields indicating the importance of the structure of tertiary amines, and both stability and electron distribution of the leaving group of tertiary amines on NDMA formation. DMA associated with branched alkyl groups or benzyl like structures having only one carbon between the ring and DMA structure consistently gave higher NDMA yields. Compounds with electron withdrawing groups (EWG) reacted preferentially with monochloramine, whereas compounds with electron donating groups (EDG) showed a tendency to react with dichloramine to form NDMA. When the selected amines were present in natural organic matter (NOM) solutions, NDMA formation increased for compounds with EWG while it decreased for compounds with EDG. This impact was attributed to the competitions between NOM and amines for chloramine species.

After the identification of high yielding NDMA precursors, it was essential to understand the role of chloramine species in NDMA formation. The role of chloramine species in NDMA formation rate was evaluated for five amines carefully selected based on their chemical structures and exposed to varying levels of chloramine with different

ratios of mono/dichloramine. Amines (e.g., ranitidine) that prefer monochloramine reacted relatively fast to form NDMA and reached the maximum yield within 24 hours. On the other hand, the NDMA formation from amines (e.g., DMA) that prefer dichloramine was relatively slow. These reactions were limited to the decomposition of monochloramine to dichloramine. For dichloramine-sensitive amines, the presence of NOM decreased the NDMA formation rate due to competition with dichloramine; however, the NDMA formation rate increased in the presence of sulfate. In addition, pH played an important role in both chloramine and amine speciation. On the other hand, for ranitidine which is a monochloramine-sensitive amine, NOM, sulfate, and pH were less critical. In selected natural waters, dichloramine was the dominant species responsible for NDMA formation, while some NDMA formation by monochloramine was also observed.

In the last section, pre-oxidation was investigated as a control technique to minimize NDMA formation. The interaction of NDMA precursors with different oxidants (chlorine, chlorine dioxide and ozone) prior to chloramination was investigated under typical conditions used in drinking water treatment plants. Fifteen model precursors with NDMA molar yields ranging from approximately 0.1% to 90% were examined. Pre-chlorination reduced NDMA formation from most precursors by 10% to 50% except quaternary amine polymers. Pre-oxidation with chlorine dioxide and ozone achieved the same or higher deactivation of NDMA precursors (e.g., ranitidine) while increasing NDMA formation for some other precursors (e.g., daminozid). The increases with chlorine dioxide exposure were attributed to the release of oxidation products with a DMA moiety, which may form more NDMA upon chloramination than the unoxidizied

parent compound. On the other hand, chlorine dioxide was effective, if a precursor's NDMA yield were higher than DMA (i.e., without pre-oxidation). The ozone-triggered increases could be related to direct NDMA formation from DMA which was released by ozonation of amines with DMA moiety, amides or hydrazines. However, hydroxyl radicals formed from the decomposition of ozone would be also involved in decomposition of formed NDMA, reducing the overall NDMA levels at longer contact times. pH conditions significantly influenced the effectiveness of deactivation of precursors depending on the type of precursors and oxidants.

For practical applications, the key findings from this study are: (i) the structure of precursor's have a drastic effect on the NDMA formation yield. DMA moieties associated with branched alkyls or benzyl like groups had very high NDMA formation yields (>25%). Especially, strategies for controlling the discharge of those types of contaminants would lead to decreases in NDMA precursor's levels in source waters. (ii) The precursor's structure also influences the chloramine species (mono- vs. di-) responsible for NDMA formation. The dominant chloramine species responsible for NDMA formation was found as dichloramine in selected natural waters. The utilities may opt to minimize the formation of dichloramine in their distribution systems (e.g., maintaining higher pH) to control NDMA formation. However, it should be noted that some NDMA formation may still be observed due to monochloramine. (iii) Pre-oxidation strategies can be an effective method for utilities to control NDMA formation as long as the formation of regulated DBPs (trihalomethanes, haloacetic acids, chlorite and bromate) are within the allowable limits. Chlorine has shown reduction in NDMA formation for

most of the precursors (except polymers). On the other hand, chlorine dioxide and ozone may lead to decreases or increases in NDMA formation depending on the characteristics of the precursors. Preliminary testing is suggested for utilities for selecting the appropriate oxidant type, to optimum dose and contact times for controlling NDMA formation.

DEDICATION

I would like to dedicate this thesis to my parents,

Hilmi & Fügen Selbes

my relatives and all friends for their continuous

love and support.

ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. Karanfil for all that he has taught me. This work could not have been accomplished without his invaluable encouragement, support and insightful instructions. I would also like to thank Dr. Cindy Lee, Dr. David A. Ladner, and Dr. David L. Freedman for devoting time to serve in my research committee. I would like to thank my parents, Hilmi and Fügen Selbes, my brother and sister-in-law, Tunca and Sanem Selbes, and to my all other relatives, for all their love and support. Many thanks to all my friends in the lab, especially the folks of Dr. Karanfil research group.

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LIST OF ABBREVIATIONS

2-Cl-DMAN	2-Chloro-*N,N*-dimethyl-aniline
2-DMAP	2-Dimethyl-aminopyridine
4-DMAP	4-Dimehtyl-aminopyridine
AA	Amino Acid
CCL3	Contaminant Candidate List 3
C-DBP	Carbonaceous Disinfection By-Product
CH	Charleston Drinking Water Treatment Plant Water Source
CI	Chemical Ionization
Cl-DMA	Chlorinated Dimethylamine
Cl-UDMH	Chlorinated Unsymmetrical Dimethylhydrazine
CT	Concentration × Time
DBP	Disinfection By-Product
DCM	Dichloromethane
DDW	Distilled Deionized Water
DL	Detection Limit
DMA	Dimethylamine
DMAAcCN	Dimethyl-aminoacetonitrile
DMAFuOH	5-Dimethylaminomethyl-furfurylalcohol
DMAN	*N,N*-Dimethylaniline

DMAPhOH	3-Dimethylamino-phenol
DMBA	*N,N*-Dimethyl-butylamine
DMBzA	*N,N*-Dimethyl-benzylamine
DMEA	*N,N*-Dimethyl-ethylamine
DMEDA	*N,N*-Dimethyl-ethyleneamine
DMEtOH	2-Dimethyl-aminoethanol
DMEtSH	2-Dimethyl-amoniethanethiol
DMiPA	*N,N*-Dimethyl-isopropylamine
DMNZD	Daminozid
DMPhA	*N,N*-Dimethyl-phenetylamine
DMPMA	*N,N*-Dimethyl-1-(1H-pyrrol-2-yl)methanamine
DMS	*N,N*-Dimethylsulfamide
DMtBA	*N,N*-Dimethyl-tert-butylamine
DMTMA	*N,N*-Dimethylthiophene-2-methylamine
DN	Dissolved Nitrogen
DOC	Dissolved Organic Carbon
DON	Dissolved Organic Nitrogen
DPD	*N,N*-diethyl-p-phenylenediamine
DRN	Diuron
DWTP	Drinking Water Treatment Plant
EDG	Electron-Donating Group
EWG	Electron-Withdrawing Group

FAS	Ferrous Ammonium Sulfate
FP	Formation Potential
GAC	Granular Activated Carbon
GC	Gas Chromatogram
HAA	Haloacetic Acids
HAN	Haloacetonitriles
HPO	Hydrophobic
LW	Lake Water
MB	Methylene Blue
M-B	Myrtle Beach Drinking Water Treatment Plant Water Source
MIEX®	Magnetic Ion Exchange Resin
MRL	Minimum Reporting Level
MS	Mass Spectrometer
NA	Not Applicable
NDBA	*N*-nitroso-di-n-butylamine
N-DBP	Nitrogenous Disinfection By-Product
NDEA	*N*-nitrosodiethylamine
NDMA	*N*-nitrosodimethylamine
NDPA	*N*-nitroso-di-n-propylamine
NDPhA	*N*-nitrosodiphenylamine
NMEA	*N*-nitrosomethylethylamine
NMOR	*N*-nitrosomorpholine

NOM	Natural Organic Matter
NPIP	*N*-nitrosopiperidine
NPYR	*N*-nitrosopyrrolidine
PAC	Powdered Activated Carbon
PDS	Primary Diluted Stock
PolyACRYL	DMA-based polyacrylamide
PolyAMINE	Poly(dimethylamine-co-epichlorohydrin), quartenized
PolyDADMAC	Poly(diallyldimethylammonium chloride)
PPCP	Pharmaceutical and Personal Care Product
RNTD	Ranitidine
RW	River Water
SDS	Simulated Distribution System
SDWA	Safe Drinking Water Act
SM	Standard Method
SPE	Solid Phase Extraction
$SUVA_{254}$	Specific Ultraviolet light at 254 nanometer wavelength
tBA	*tert*-butyl alcohol
THM	Trihalomethanes
TMA	Trimethylamine
TPH	Transphilic
TW	Tap Water
UCMR2	Unregulated Contaminant Monitoring Rule 2

UDMH	Unsymmetrical Dimethyl Hydrazine
USEPA	United States Environmental Protection Agency
UV	Ultraviolet light
UV_{254}	Ultraviolet light at 254 nanometer wavelength
WWTP	Wastewater Treatment Plant

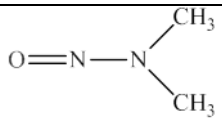
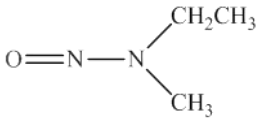
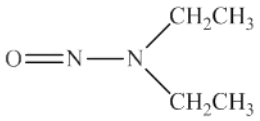
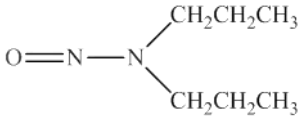
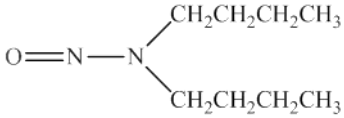
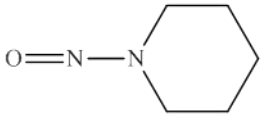
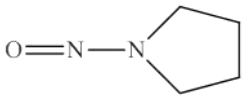
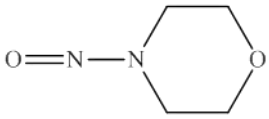
CHAPTER ONE

INTRODUCTION

Chloramination is often used to replace chlorination in order to reduce the formation of regulated disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs). Unfortunately, chloramination can lead to formation of nitrosamines (**Table 1.1**), a class of compounds which are probable human carcinogens, mutagens, and teratogens (USEPA, 1993). Although nitrosamines can pose important health risks even at ng/L concentrations (USEPA, 1993), they have not been regulated by the United States Environmental Protection Agency (USEPA). Nevertheless, five nitrosamines such as *N*-nitrosodimethylamine (NDMA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosodiethylamine (NDEA), *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodi-n-propylamine (NDPA), and *N*-nitrosodi-n-butylamine (NDBA) are covered by the Unregulated Contaminant Monitoring Rule 2 (UCMR 2) (USEPA, 2006), and NDMA, NDEA, NDPA, NPYR, and *N*-nitrosodiphenylamine (NDPhA) included in the Contaminant Candidate List 3 (CCL 3) (USEPA, 2009). The Department of Health Service in California and the Massachusetts Department of Environmental Protection has implemented an action level of 10 ng/L (MassDEP, 2004; OEHHA, 2006), and the Ontario Ministry of the Environment and Climate Change established a maximum allowable concentration of 9 ng/L for NDMA (MOE, 2003). Recently, USEPA has identified nitrosamines as one of three potential groups of contaminants highlighted for

possible regulatory action (Roberson, 2011). Therefore, new regulatory actions for nitrosamines are expected for drinking water utilities in the near future.

Table 1.1. Structures of nitrosamines that can be analyzed by USEPA method 521.

Nitrosamine	Abbreviation	Structure
N-nitrosodimethylamine	NDMA	
N-nitrosomethylethylamine	NMEA	
N-nitrosodiethylamine	NDEA	
N-nitroso-di-n-propylamine	NDPA	
N-nitroso-di-n-butylamine	NDBA	
N-nitrosopiperidine	NPIP	
N-nitrosopyrrolidine	NPYR	
N-nitrosomorpholine	NMOR	

The analysis of nitrosamine data from samples collected under UCMR2 revealed that NDMA was detected in United States drinking waters at concentrations > 2 ng/L in 10% of the samples surveyed, and 26% of systems detected NDMA in at least one sample (Russell et al., 2012). However, other nitrosamines (e.g., NDEA, NDBA, NPYR, and NMEA) were rarely detected at levels above their minimum reporting levels (MRLs) (2 ng/L). Systems with NDMA concentrations below the MRL used oxidants other than chloramines as either a primary or a secondary disinfectant, and concentrations ranged from 4 to 15 ng/L (the maximum NDMA concentration measured was 630 ng/L) (Russell et al., 2012). Therefore, among nitrosamines, NDMA has drawn the most attention due to its frequent detection in distribution systems that use chloramine as a disinfectant (Russell et al., 2012).

It can be anticipated that nitrogenous organic compounds play a key role in the formation of nitrosamines. Amines are a group of compounds present in natural, algae-impacted and wastewater-impacted sources and rich in nitrogen content (Bornick and Schmidt, 2006; Dotson and Westerhoff, 2009). These hydrophilic precursors persist through conventional water treatment stages and are likely to be present prior to post-oxidation. Amines are classified into four groups: primary, secondary, tertiary and quaternary (**Figure 1.1**). Primary amines have been found in fresh waters in a wide concentration range (5 to 2000 µg/L), in free amino acids (AAs), peptides, nucleic acids, purines, pyrimidines, and proteins (Rice and Gomez-Taylor, 1986). Secondary and tertiary amines are also found in water sources. Some of these are naturally occurring amines and found at very low concentrations (i.e., 0.1 µg/L of dimethylamine) (Bornick

and Schmidt, 2006). However, their concentrations can be much elevated depending on anthropogenic activities (i.e., 2.7 mg/L of dimethylamine [DMA]) (Bornick and Schmidt, 2006). Some of the anthropogenic sources include agricultural run-off (fungicides, pesticides, and herbicides), industrial discharges (i.e., dyes, corrosion inhibitors, vulcanizing accelerators), wastewater effluents (i.e., extracellular organic matter from microbial activities, pharmaceuticals and personal care products [PPCPs]). Finally, quartenary amines are commonly used in water and wastewater treatment as polymers in high quantities (e.g., mg/L).

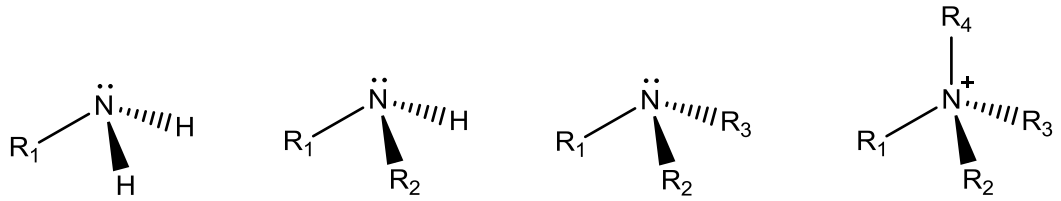


Figure 1.1. Four classes of amines. The R_x in the molecular structure indicates a radical group (e.g., $-CH_3$, $-CH_2CH_3$).

To date, several nitrosamine formation mechanisms have been proposed especially for NDMA (Choi et al., 2002; Mitch and Sedlak, 2002; Schreiber and Mitch, 2006; Bond et al., 2012; Le Roux et al., 2012b; Shah and Mitch, 2012). Generally, there are two main formation pathways. Firstly, the nitrosation reactions between amines and nitrosating agents (such as NO^+, nitrous acid, and some reactive nitrogen oxide species) leads to formation of nitrosamines (Mirvish, 1975; Challis and Kyrtopoulus, 1979; Loeppky et al., 1983; Choi and Valentine, 2003; Lee and Yoon, 2007; Walse and Mitch,

2008; Lv et al., 2009; Sun et al., 2011). The classic nitrosation mechanism usually involves nitrite which participates in the formation of a nitrosating agent in acidic solution or in the presence of hypochlorite (HOCl), carbonyl compounds, or sunlight. The formation of nitrosamines during oxidation of amines mediated by ozone or potassium permanganate are other nitrosation pathways, in which the nitrosating agent is generated from the oxidation of amines (Andrzejewski and Nawrocki, 2007; Andrzejewski et al., 2008; Yang et al., 2009; Padhye et al., 2011a). Secondly, an unsymmetrical dimethylhydrazine (UDMH) mechanism was proposed to explain NDMA formation during chloramination of DMA (Choi and Valentine, 2002; Mitch and Sedlak, 2002; Schreiber and Mitch, 2005, 2006). In this proposed mechanism, a nucleophilic substitution reaction between DMA and chloramine (NH_2Cl or $NHCl_2$) leads to formation of an UDMH or chlorinated UDMH intermediate (Cl-UDMH), and the intermediate is oxidized by dissolved oxygen to produce NDMA. However, further studies have shown that chloramination of UDMH yielded much less NDMA (<0.1%) than DMAs yield (1-3%) (Mitch et al., 2009). In addition, the presence of dichloramine has been shown to enhance NDMA formation from DMA through the formation of a chlorinated UDMH (Mitch et al., 2009). Regardless of the intermediates, some tertiary amines (such as ranitidine and *N,N*-dimethylbenzylamine) have much higher NDMA yields (i.e., >60%) as compared to DMA or UDMH (i.e., <3%) (Mitch et al., 2009; Kemper et al., 2010; Shen and Andrews, 2011a,b; Le Roux et al., 2011, 2012b). To explain the high formation yield of NDMA from ranitidine during chloramination, Le Roux et al. (2012b) hypothesized that a methylfuran moiety of ranitidine undergoes decomposition to

generate a carbocation which they supported by identifying several intermediates using an HPLC-MS technique. However, so far the formation mechanism of NDMA from amines during chloramination has not been fully explained.

Although, several studies investigated the formation mechanisms and important precursors for nitrosamines (especially NDMA), there is much more to learn about their formation pathways. Questions on what kind of amines lead to nitrosamine formation, what kind of relationship exists between the structure and reactivity of tertiary amines, why some tertiary amines have rather high NDMA yields, and what is the interaction of amines with different oxidants (including chloramine) have not been elucidated yet. The main objective of this study was to gain insight to the potential precursors' formation mechanisms of nitrosamines, especially NDMA. Specifically, the research focused on: (i) the formation potential of nitrosamines from AAs under different disinfection conditions, (ii) the roles of tertiary structure on the formation of NDMA during chloramination, (iii) the importance of chloramine species in the conversion reactions, and (iv) the interaction of these precursors with different oxidants (chlorine, chlorine dioxide and ozone) and their consequent effect on NDMA formation.

CHAPTER TWO

LITERATURE REVIEW

Occurrence of Nitrosamines

NDMA, a species of nitrosamines, is a semi-volatile organic chemical. It is highly toxic and is an industrial by-product and a probable human carcinogen. NDMA is used as an industrial solvent, an anti-oxidant, a rubber accelerator and an initiator or plasticizer (ALS, 2012). In addition, the compound has been used in the production of rocket fuel, as biocide for nematodes and an intermediate for 1,1-dimethylhydrazine to inhibit nitrification of soils (ALS, 2012). NDMA is also present in a variety of foods: cured meats, fried bacon, marine products, flour and grain products, dairy and cheese products, and alcoholic beverages including beer and whiskey (Tricker and Preussmann, 1991).

The occurrence of NDMA in drinking water was initially identified in the 1980s and 1990s in Ontario, Canada (Munoz and Sonntag, 2000). Possible sources of NDMA were thought to be anthropogenic contaminants mentioned above and microbiological transformation of those precursors or partial oxidation of hydrazines (Kim and Choi, 2002). For instance, NDMA has been detected at very high concentrations (3,000 ng/L) in a ground water near rocket engine testing facilities in Sacramento, California, and also downgradient of drinking water wells, especially in locations where wastewater effluent was used for aquifer recharge (Mitch et al., 2003a,b, 2009).

A survey by the California Department of Health Services demonstrated that NDMA occurrence was not limited to regions proximal to facilities that used rocket engine sites or UDMH-based fuels (CDPH, 2013), but also found that NDMA formed as a by-product of chlorine or chloramine disinfection of water and wastewater. Especially in locations where chlorinated wastewater effluent was reused, NDMA was detected at elevated concentrations (i.e., >100 ng/L) (Mitch et al., 2003a,b).

In 1996 the Safe Drinking Water Act (SDWA) amendment required that USEPA provide a new list of unregulated contaminants once every five years to be monitored in public water systems. Selected contaminants are known or anticipated to occur in public water systems, which may require regulation under the SDWA. The list includes, among others, pesticides, disinfection by-products, chemicals used in commerce, waterborne pathogens, pharmaceuticals, and biological toxins. This monitoring provides a basis for future regulatory actions to protect public health. Since 1999, three UCMR programs, in coordination with the CCL, have been issued (USEPA, 2006). Nitrosamines have been listed in CCL3 and monitored in UCMR2.

The analysis of nitrosamine data from samples collected under the UCMR2 revealed that NDMA was detected in United States drinking waters at concentrations > 2 ng/L in 10% of the samples surveyed, and 26% of systems detected NDMA in at least one sample (Russell et al., 2012). However, other nitrosamines (e.g., NDEA, NDBA, NPYR, and NMEA) were rarely detected at levels above their MRLs. NDMA was primarily detected in systems using chloramines, and concentrations were higher in water

systems having long contact times with chloramines (ranging from 4 to 15 ng/L (the maximum NDMA measured was 630 ng/L)) (Russell et al., 2012).

The same study also showed that systems using chloramine as disinfectant had 35% of the samples above the MRL of NDMA, compared to 3% that used chlorine. The highest NDMA concentrations (i.e., > 50 ng/L) were observed in water systems located in California, Florida, Minnesota, Oklahoma, and Texas; and these states reported the highest percent of chloramines use (Russell et al., 2012).

In another recent survey investigating the occurrence of nitrosamines in 16 drinking water treatment plant samples, the maximum concentration of nitrosamines (including NDMA) was detected in ozonated water (28.6 ng/L). In particular, NDMA (range of: 10.1-11.5 ng/L), NMOR (range of: <MRL-9.2 ng/L), NPYR (range of: <MRL-5.4 ng/L), NDPA (range of: <MRL-2.6 ng/L) and NPIP (range of: <MRL-1.3 ng/L) were detected in ozonated water followed by post-chlorination (Asami et al., 2009; Kosaka et al., 2009). Additionally, relatively high concentrations of NDMA (i.e., >10 ng/L) were reported at some ozonation plants in the western part of Japan for which the source water is the Yodo River (Oya et al., 2008; Kosaka et al., 2009).

Formation of Nitrosamines

Several pathways have been proposed for the formation of nitrosamines during drinking water treatment. In drinking water, formation of nitrosamines during chloramination is likely to be the most important pathway. Early mechanistic studies conducted by Mitch et al. (2003a) suggested a nucleophilic substitution reaction between unprotonated secondary amines (i.e., DMA) and monochloramine initiated NDMA formation (**Figure 2.1**). The UDMH intermediate that was formed that can be later oxidized to NDMA.

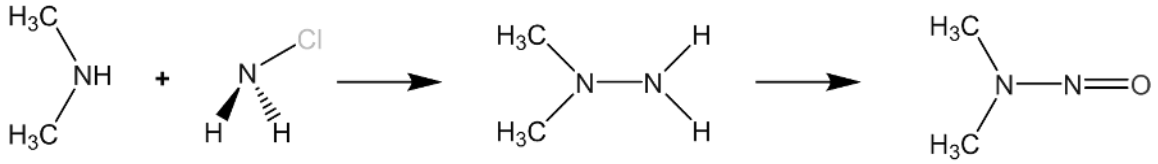


Figure 2.1. Initially proposed NDMA formation mechanism by Mitch et al. (2003a).

In later studies, it has been shown that chloramination of UDMH yielded much less NDMA (i.e., 0.1% molar conversion) than DMA (i.e., 1.5% molar conversion). Furthermore, it has been found that the presence of dichloramine was shown to enhance NDMA formation from DMA. Therefore, Schreiber and Mitch (2006) revised the proposed mechanism by Mitch and colleagues (2003a) and suggested the formation of a Cl-UDMH intermediate from a nucleophilic substitution reaction between DMA and dichloramine (**Figure 2.2**). During this reaction, the presence of dissolved oxygen played a key role. In this pathway, any quaternary or tertiary amine first reacts with chlorine or

chloramine to form DMA, and then DMA further reacts with dichloramine resulting in NDMA formation (Mitch et al., 2009). There have been several other studies that showed dichloramine could enhance NDMA formation. For instance, increased dichloramine concentrations increased NDMA formation from selected PPCPs (i.e., ranitidine [RNTD]) (Shen and Andrews, 2011a). However, recently a comprehensive study by Le Roux et al. (2012b) showed that monochloramine is responsible for NDMA formation from RNTD.

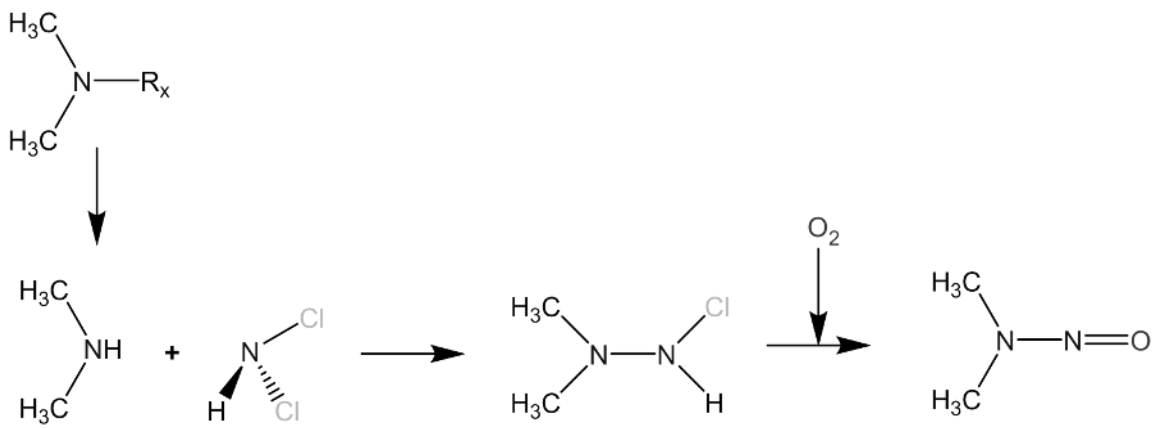


Figure 2.2. Revised NDMA formation mechanism by Mitch et al. (2006). The R_x in the molecular structure of a tertiary amine indicates the radical group (e.g., $-CH_3$, $-CH_2CH_3$).

Some tertiary amines, where one of the alkyl substituents contained an aromatic group in the β-position to the nitrogen (e.g., a benzyl functional group), such as ranitidine, exhibited far higher yields of NDMA formation than DMA during chloramination (Le Roux et al., 2011; Shen and Andrews, 2011a,b). The NDMA formation yield of RNTD was reported as 60-90% (Le Roux et al., 2011; Shen and Andrews, 2011a,b). These high yields suggest that tertiary amines can form nitrosamines

without proceeding through a secondary amine intermediate, although the specific pathway is unclear.

To explain the high formation yield of NDMA from ranitidine during chloramination, Le Roux et al. (2012b) hypothesized that a methylfuran moiety of ranitidine undergoes decomposition to generate a carbocation which has been supported by identifying several intermediates using HPLC-MS technique (**Figure 2.3**). This research provided new insight into the role of monochloramine species in the formation of NDMA from ranitidne, and highlighted that the structure of the tertiary amines is closely related with the reactivity of NDMA precursors and the preferred chloramine species.

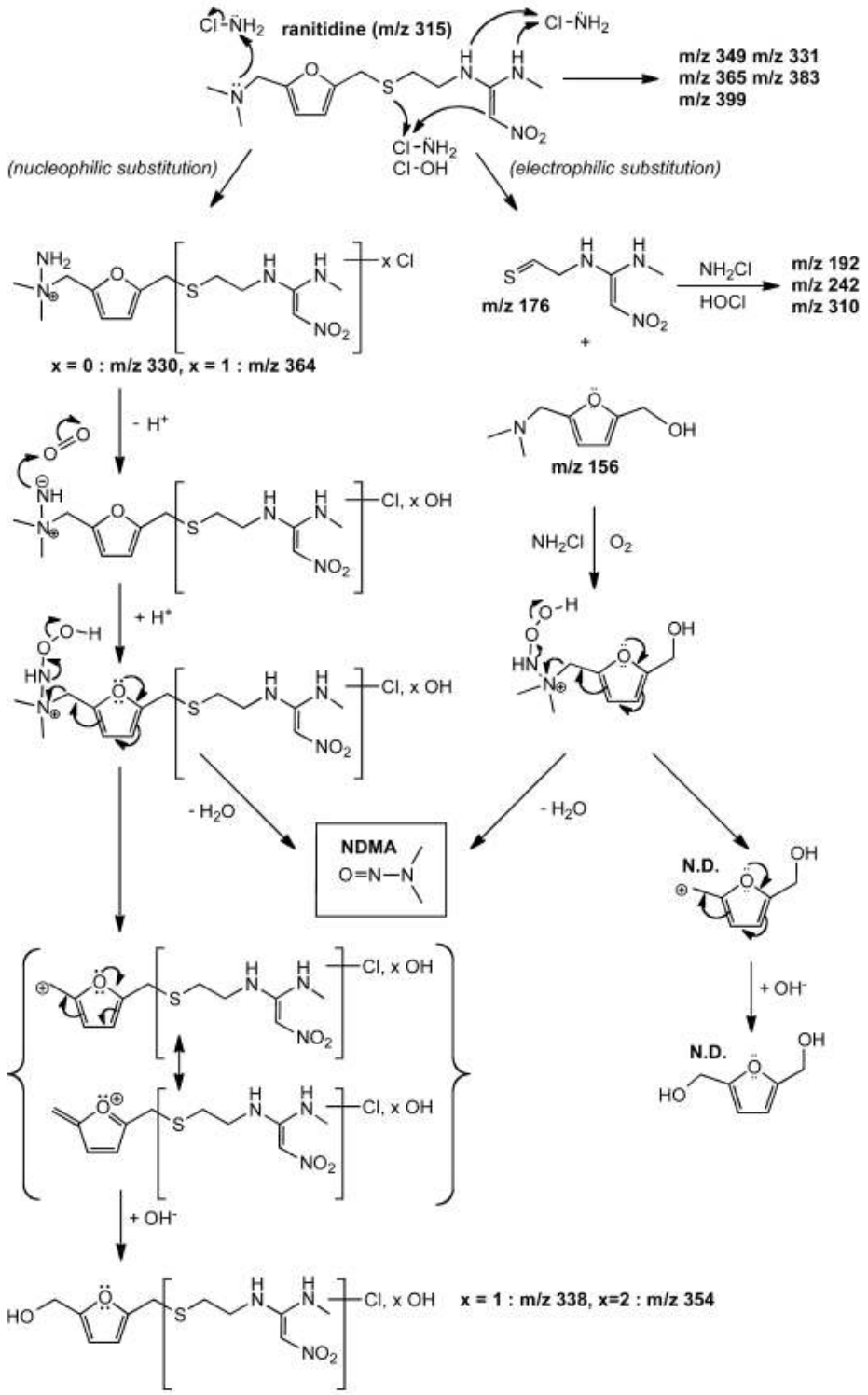


Figure 2.3. NDMA formation pathway from ranitidine during chloramination (Le Roux et al., 2012b).

Chlorination of nitrite-containing waters is another pathway of NDMA formation (Choi and Valentine, 2003). Choi and Valentine (2003) noted that NDMA forms during chlorination of nitrite-containing waters. Formation has been attributed to a dinitrogen tetraoxide (N_2O_4) intermediate, which then forms •NO which can nitrosate amines (**Figure 2.4**). The reaction yields are much lower (≈two orders of magnitude) than for the chloramination pathway. Since, nitrite concentrations in surface water sources are very low, this pathway has been especially associated with NDMA formation during chlorination of wastewater effluents (Shah and Mitch, 2012; Walse and Mitch, 2008). Nitrite is more likely to be present in a wastewater effluent if there is partial nitrification occurring in the treatment plant.

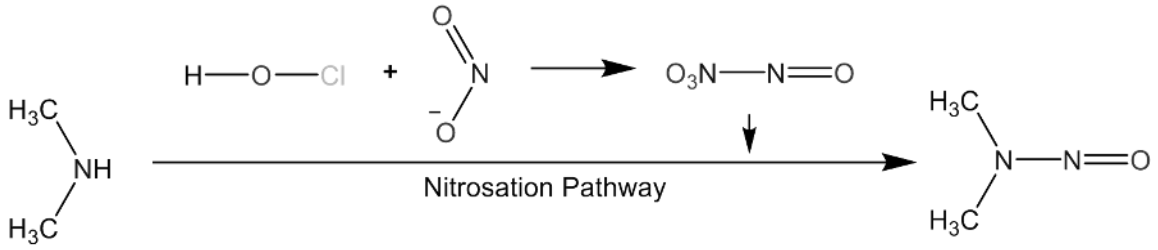


Figure 2.4. NDMA formation mechanism through nitrosation during chlorination in the presence of nitrite (pH≈3.4) (Choi and Valentine, 2003).

Ozonation of DMA forms NDMA but yields generally are < 0.02% at neutral pH (Andrzejewski et al., 2008). Another study by Yang et al. (2009) showed that NDMA can be formed from DMA at pH 3.4, through the nitrosation pathway (**Figure 2.5-A**). They also found that NDMA can be formed during ozonation at pHs greater than 7 through an

unknown pathway (**Figure 2.5-B**). Further studies investigating NDMA formation during ozonation showed that UDMH, daminozide (DMNZD) and semicarbazide, which have UDMH-like functional groups, formed NDMA at yields > 50% (Schmidt et al., 2008; von Gunten et al., 2010) (**Figure 2.6**). Ozonation of *N,N*-dimethylsulfamide (DMS), a transformation product of the fungicide tolylfluanide, formed NDMA at 52% yield (von Gunten et al., 2010). Lastly, ozonation of PolyDADMAC, a polymer used in water treatment plants can also form NDMA (Padhye et al., 2011a) (**Figure 2.7**). Ozonation of PolyDADMAC could release the DMA moiety and form hydroxylamines at the same time. Simultaneous reaction of these two products could form UDMH. Once again the formed UDMHs would be converted to NDMA in the presence of ozone.

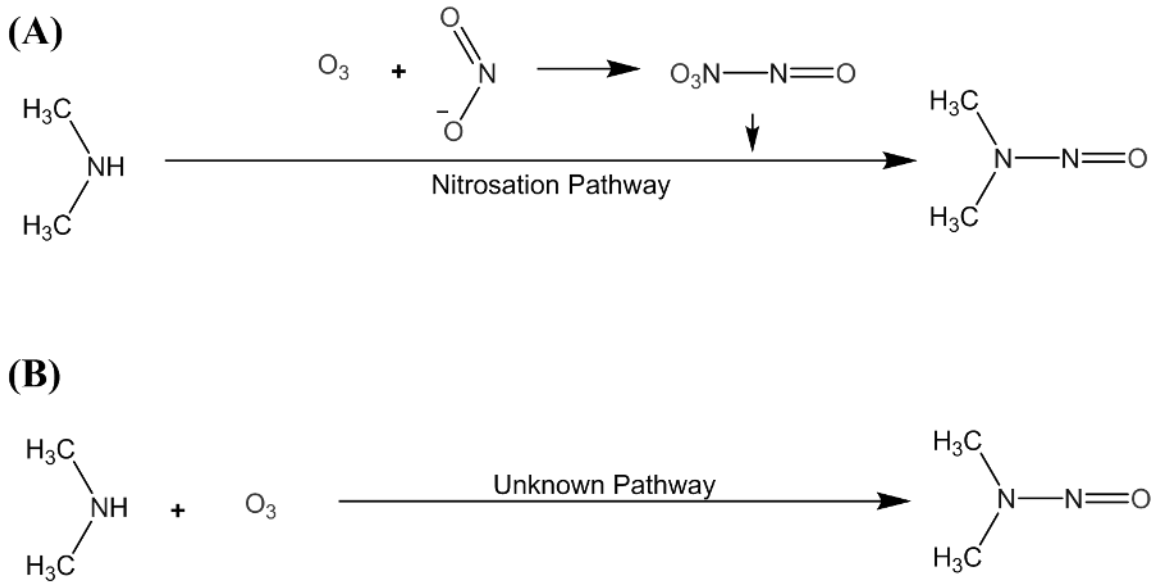


Figure 2.5. NDMA formation (A) nitrosation during ozonation (pH≈3.4), and (B) unknown pathway (pH>7).

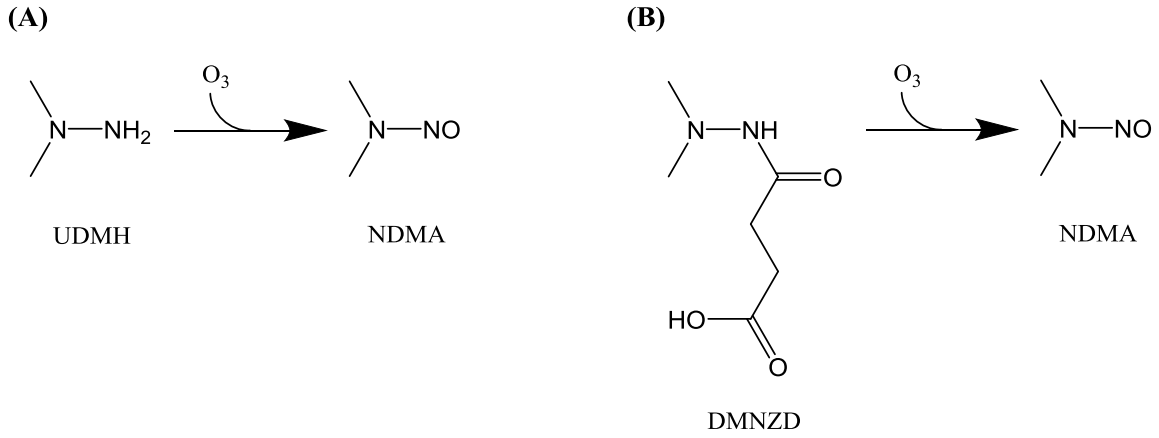


Figure 2.6. NDMA formation from (A) UDMH, and (B) UDMH-like functional groups during ozonation.

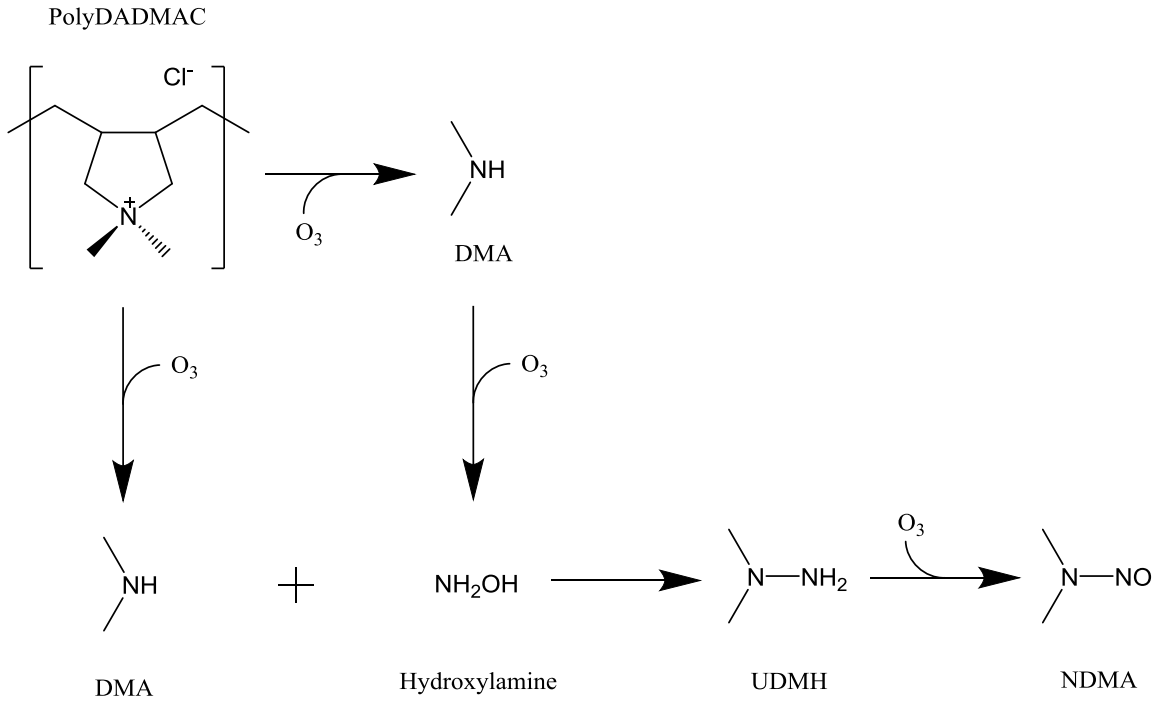


Figure 2.7. NDMA formation from PolyDADMAC during ozonation (Padhye et al., 2011a).

Nitrosamines can also be formed from catalytic transformation of secondary amines on activated carbon. Reported yields are lower than 0.3% (Padhye et al., 2010). This NDMA formation pathway involves a series of complex reactions. Reaction of oxygen with activated carbon could form reactive oxygen species, which could lead to formation of reactive nitrogen species. These reactive species can form hydroxylamines. Similar to the ozonation pathway, hydroxylamines can react with secondary amines and form NDMA. (Vorob'ev-Desyatovskii et al., 2006; Padhye et al., 2011b). Taking into consideration the yield and the occurrence of secondary amines in drinking water sources, this pathway is unlikely to be important (Krasner et al., 2013).

Lastly, sunlight photolysis of nitrite at <400 nm could form reactive nitrogen species (Lee and Yoon, 2007) and those reactive species can react with secondary amines present in surface waters. NDMA formation yields were around 0.02% from selected secondary amines. Similar findings have also been reported by Soltermann et al. (2013). Ultraviolet (UV) treatment at 254 nm of chlorinated secondary amines in the presence of monochloramine increased nitrosamine concentrations in swimming pools (Soltermann et al., 2013). However, this NDMA formation mechanism is unlikely to be important for drinking waters due to the low prevalence of secondary amines.

Factors Affecting Nitrosamine Formation

Several factors affect the formation of NDMA during drinking water treatment. Among those, chloramine speciation is suspected to be the most important factor. Chlorine reacts rapidly with ammonia to form a mixture of inorganic chloramines that

may contain monochloramine, dichloramine, or trichloramine. Some additional information about the chloramine chemistry can be found in the **Appendix A**.

The speciation of these compounds depend highly upon pH, chlorine to ammonia ratio, temperature, and contact time. At pH higher than 8, and 5:1 Cl_2:N ratio monochloramine is the dominant species. On the other hand, dichloramine is favored as the pH decreases (4 to 5) and/or the Cl_2:N ratio increases (5:1 to 7.9:1) (Diehl et al., 2000). Further a decrease in pH (pH<2), or an increase in the chlorine to nitrogen ratio leads to formation of trichloramine. However, monochloramine generally is the dominant form in drinking water disinfection with some trace concentrations of dichloramine.

As mentioned before, initial reports indicated a nucleophilic substitution reaction between monochloramine and unprotonated secondary amines formed NDMA (Mitch and Sedlak, 2002). Further research showed that dichloramine enhanced NDMA formation from DMA, some PPCPs and in few wastewater-impacted waters (Mitch et al., 2009; Farre et al., 2010). Meanwhile studies with RNTD (Le Roux et al., 2012b) showed that monochloramine is responsible for NDMA formation from ranitidine. Overall, these results suggest that NDMA formation may not always be limited to only one chloramine species.

The effect of pH on NDMA formation in drinking water has been found to increase with increasing pH levels (Mitch and Sedlak, 2002; Sacher et al., 2008; Schreiber and Mitch, 2005, 2006; Valentine et al., 2005). For example, Schreiber and Mitch (2006) found that DMAs yield was higher at pH 8–9, than at pH 6.9 that was

higher than 5.1 (Schreiber and Mitch, 2005). A similar trend was observed for natural waters (Krasner et al., 2012b).

Experiments conducted in natural waters (Sacher et al., 2008) and wastewater effluents (Hatt et al., 2013) showed an increase in NDMA formation with increasing chloramine dose. Moreover, NDMA formation reactions during chloramination are much slower than chlorines. A few days (i.e., 3 days) of contact time is needed to plateau (Sacher et al., 2008). Also, UCMR2 data showed NDMA concentrations were usually higher in longer detention distribution systems (Russell et al., 2012).

Lastly, the presence of bromide was shown to enhance NDMA formation. However, to have a distinct effect on overall NDMA formation, bromide levels should be higher than 500 μg/L (Shen and Andrews, 2011a; Shah et al., 2012; Le Roux et al., 2012a).

Precursors of Nitrosamines

Although an organic nitrogen precursor is required for NDMA formation, there is no strong correlation between dissolved organic nitrogen concentrations and NDMA formation potentials in natural waters (Pehlivanoglu-Mantas and Sedlak, 2008; Dotson et al., 2009; Aydin et al., 2012). DMA is the most studied model precursor of NDMA (Andrzejewski et al., 2008; Choi and Valentine, 2003; Lv et al., 2009; Mitch and Sedlak, 2002; Mitch et al., 2003a,b) and is ubiquitous in natural waters. However, some studies have shown that DMA concentrations present in surface waters (Gerecke and Sedlak, 2003; Lee et al., 2007a) or secondary municipal wastewaters (Mitch and Sedlak, 2004)

are inadequate to explain the amount of NDMA formation. Other than DMA, some other NDMA precursors have been identified such as tertiary and quaternary amines with DMA functional groups (Lee et al., 2007; Park et al., 2007; Kemper et al., 2010; Shen and Andrews, 2011a,b), natural organic matter (NOM) and fractions of NOM (Gerecke and Sedlak, 2003; Mitch and Sedlak, 2004; Chen and Valentine, 2007; Dotson et al., 2007; Krasner et al., 2008a), polyelectrolytes and ion-exchange resins (Gough et al., 1977; Kimoto et al., 1980; Najm and Trussell, 2001; Kohut and Andrews, 2003; Wilczak et al., 2003; Mitch and Sedlak, 2004; Nawrocki and Andrzejewski, 2011), fungicides, pesticides, and herbicides (Graham et al., 1995; Chen and Young, 2008; Schmidt and Brauch, 2008), pharmaceuticals, cosmetics (Sacher et al., 2008; Shen and Andrews, 2011a,b), and wastewater effluent/impacted waters (Krasner et al., 2004; Sedlak et al., 2005; Krasner et al., 2009; Krauss et al., 2009; Shah et al., 2012; Gan et al., 2013a,b).

Among these, wastewater-impacted waters are likely to have the highest NDMA formation and thus thought to be the most significant source of NDMA precursors (Schreiber and Mitch, 2006; Guo and Krasner, 2009; Krasner, 2009; Shah and Mitch, 2012). As expected, wastewaters contain a range of precursors. Specific precursors in wastewater-impacted water supplies have not been characterized but are likely to include tertiary amine-based pharmaceuticals, quaternary amine-based constituents of shampoos, pharmaceuticals, and potentially pesticides, fungicides, herbicides, or insecticides.

Other than the wastewater influence, some chemicals and resins used in drinking water treatment plants (DWTPs) are shown to increase NDMA formation. Cationic polymers (e.g., polyAMINE and polyDADMAC) used as coagulant or dewatering aids in

drinking water treatment can degrade to DMAs and consequently increase NDMA formation (Kohut and Andrews, 2003; Najm and Trussell, 2001; Wilczak et al., 2003). PolyAMINEs have been shown to produce more NDMA than polyDADMAC around pH 8.0 during chloramination (Padhye et al., 2011a). Additionally, ozonation of polyDADMAC yielded NDMA without sequential chloramination (Padhye et al., 2011a). NDMA yield during ozonation from polyDADMAC was several times more than polyACRYL and polyAMINE (Padhye et al., 2011a).

Similar to polymers, anion exchange units also have quaternary amine or tertiary amine based resins in their structures. Anion exchange resins (trimethylamine [TMA], dimethylethanolamine based) released NDMA likely due to shedding of manufacturing impurities (Kemper et al., 2009). Furthermore, these resins can also shed the precursors that can increase NDMA formation upon chloramination (Kemper et al., 2009; Nawrocki and Andrzejewski, 2011). Higher levels of nitrosamine precursors were observed after regeneration cycles (Singer and Flower, 2012). Similar findings have been reported for magnetic ion exchange resin (MIEX®) by Gan et al. (2013a,b). Use of MIEX® to treat wastewater effluents increased NDMA formation by at least 50% during chloramination. This increase was reported to be much less (i.e., 5%) if the wastewater impact was minimal (wastewater blended with a pristine water source, <10% by volume). Exposure of these resins to oxidants (i.e., chlorine, chloramine) produced NDMA in the effluents (Kimoto et al., 1980; Najm and Trussell, 2001; Kemper et al., 2009).

DMA moieties of PPCPs has been shown to form NDMA during chloramination (Shen and Andrews, 2011a,b). In study conducted by Shen and Andrews (2011a), 20

PPCPs were investigated and NDMA molar yields higher than 1% were observed for eight pharmaceuticals (i.e., RNTD, sumatripan, tetracycline, doxylamine, chlorphenamine, nizatidine, diltiazem, and carbinoxamine). Although, these precursors have the potential to form NDMA, their trace levels in the environment suggest (i.e., ng/L) that they may not account for the majority of the NDMA formation during the disinfection process. Among the tested pharmaceuticals, RNTD, which draws the most attention, showed the highest molar conversion (60-90%) to NDMA caused by the benzyl functional group (Le Roux et al., 2011; Shen and Andrews, 2011a,b). These higher yields suggest that these tertiary amines can form nitrosamines without proceeding through a secondary amine intermediate, although the specific pathway is unclear.

Some herbicides, pesticides, insecticides and fungicides used in agricultural applications are also shown to be NDMA precursors. These amides yielded much lower molar NDMA conversions - probably caused by the carbonyl groups - than secondary, tertiary and quaternary amines. However, ozonation of amides have been shown to form NDMA without sequential chloramination. NDMA formation from amides are rapid (<1 h) and the molar yields could be more than 50% (Kosaka et al., 2009; Schmidt and Brauch, 2008; Shen and Andrews, 2011a; von Gunten et al., 2010). Occurrence of trace amounts of DMS, a degradation product of the fungicide tolylfluanide, in several German drinking water treatment plants (Schmidt and Brauch, 2008) and similarly, anti-yellowing agents near Tokyo, Japan, resulted in NDMA formations exceeding 10 ng/L after ozonation (Kosaka et al., 2009).

Certain distribution system piping materials such as rubber seals and gaskets leached NDMA and its precursors in oxidant-free water and formed more NDMA after chloramination (Morran et al., 2011; Teefy et al., 2011). Increasing contact times (i.e., stagnation period) with these materials resulted in further increases in NDMA levels. NDMA levels resulting from leaching pipe materials were within the range of 10-25 ng/L (Morran et al., 2011).

Algal blooms can generate metabolites and increase DBP formation during those periods. Algae have been identified as a source of carbonaceous DBP (C-DBP) precursor (Hoehn et al., 1980) and nitrogenous-DBP (N-DBP) precursor (Bond et al., 2011, 2012). NDMA formation has been reported from algae-derived and -impacted sources upon chlorination or chloramination (Mitch et al., 2009; Zamyadi et al., 2010; Fang et al., 2010; Li et al., 2012). Mitch et al. (2009) reported NDMA formation within the range of 12-261 ng/L from algae-impacted source waters (algae counts ranged from 300 to 22700/mL). Further studies with laboratory cultured algae (i.e., *M. aeruginosa*) solutions had NDMA formation of 9 to 20 ng/mg C (Zamyadi et al., 2010; Fang et al., 2010; Li et al., 2012). These findings indicate that algal activity can contribute to NDMA formation; however, these values (i.e., 12-261 ng/L NDMA formation from algae-impacted sources) are much lower than the yields observed for other NDMA precursors (i.e., wastewater).

Lastly, NOM and its fractions are also shown to form NDMA during chloramination (Chen and Valentine, 2007; Dotson et al., 2007; Gerecke and Sedlak, 2003; Mitch and Sedlak, 2004). However, NDMA yields from NOM are much lower than wastewater-impacted waters, polymers, ion-exchange resins and PPCPs.

Removal of Nitrosamines and Their Precursors

Nitrosamine can be removed by activated carbon adsorption or by UV photolysis. Since nitrosamine formation kinetics are slow, nitrosamines continue to form within the distribution system unless the precursors are removed. Therefore, this section focuses on precursor removal.

Coagulation with alum or ferric chloride has limited removal efficiency for nitrosamine precursors (i.e., <10%) (Krasner et al., 2008a; Sacher et al., 2008). Similar results have been reported during the lime softening process (Mitch et al., 2009). It has been shown that the majority of NDMA precursors are associated with low molecular weight hydrophilic compounds, and these types of organics is poorly removed by coagulation (Lee and Westerhoff, 2006; Xu et al., 2011). One study involving three treatment plants found that polymers (i.e., PolyDADMAC) used during coagulation process led to an increase in NDMA formation by 43-82% (Krasner et al., 2012b) probably caused by the residual polymer in the effluent (Novak and Montgomery, 1975; Novak and Langford, 1977). Therefore, reduction in polymer dosage can reduce, but not eliminate NDMA formation. Unfortunately, almost all cationic polymers currently in use will contribute to NDMA formation because they are amine-based, but using alternate polymers can help with its management. NDMA yields from selected polymers are in the decreasing order of: PolyAMINE (DMA-based) > PolyAMINE (TMA-based) ≥ PolyDADMAC > PolyACRYL (Park et al., 2007).

Powdered activated carbons (PAC) and to lesser extent granular activated carbons (GAC) are commonly used in DWTPs in the United States to minimize taste- and odor-causing compounds. They have been shown to be effective for removal of NOM and consequently controlling the formation of C-DBPs. Initial experiments investigating removal of NDMA precursors demonstrated NDMA formation potential (FP) reduction of more than 73% in wastewater with 50 mg/L of PAC after seven days contact time (Krasner et al., 2008b). Experiments in surface waters and wastewater-impacted sources with the same contact time exposed to 5 mg/L of PAC showed 50% NDMA FP reduction, and 90% or greater with 20 mg/L (Sacher et al., 2008). Recently, Hanigan et al. (2012) reported 37% NDMA FP in a secondary wastewater effluent at 3 mg/L of PAC dose and 4 h contact time. A dose of 75 mg/L of PAC had approximately 90% removal in secondary wastewater-effluents (Hanigan et al., 2012). Similarly, studies with GACs demonstrated 60-80% reduction in NDMA FP in surface waters (Hanigan et al., 2012).

Research has demonstrated that the use of pre-oxidation such as chlorine, ozone, chlorine dioxide, permanganate, ferrate, hydrogen peroxide, UV and even sunlight can affect NDMA formation subsequent to chloramination (Charrois and Hrudey, 2007; Chen and Valentine, 2008; Lee et al., 2007a, 2008; Shah et al., 2012). Recent research by Shah et al. (2012) evaluated the reduction in NDMA formation with pre-oxidants (chlorine, ozone, chlorine dioxide, and low or medium pressure UV) applied at exposures relevant to 99.9% removal of *Giardia* with post-chloramination conducted under conditions relevant to drinking water distribution. Ozone was deemed to be the most effective pre-oxidants by achieving 50% reduction in NDMA with exposures ≤0.4 mg×min/L.

Chlorine was able to achieve similar results at exposures around 70 mg×min/L. In a few sources, it promoted NDMA formation at low exposures, but formation declined again at higher exposures which was attributed to the presence of nitrite-causing nitrosation. Chlorine dioxide and UV treatment were relatively ineffective over exposures relevant to disinfection. In some cases, chlorine dioxide promoted NDMA across the range of exposures.

There are only a few studies focusing on pre-oxidation of model compounds. Some amides (Schmidt and Brauch, 2008; von Gunten et al., 2010), anti-yellowing agents (Kosaka et al., 2009), and polymers (Padhye et al., 2011a) have been recognized to form NDMA during ozonation without sequential chloramination. Occurrence of these precursors in natural waters during ozonation actually led to the formation of NDMA (Asami et al., 2009; von Gunten et al., 2010). In another study, Lee et al. (2007) has shown that the use of ozone, and to a lesser extent, chlorine dioxide, has reduced NDMA formation from seven tertiary amines; however, this was only achieved with substantially high doses of oxidants compared to those used for drinking water treatment. Lastly, Shen and Andrews (2013b) have used chlorine as a pre-oxidant to control NDMA formation originating from selected pharmaceuticals. This pre-chlorination reduced NDMA formation from RNTD, nizatidine, and tetracycline by 50%, with a relatively low concentration×time (CT) (i.e., 10 mg×min/L). In the same study sumatripan conversely almost doubled its NDMA formation, while other pharmaceuticals had no noticeable change during pre-chlorination.

Biofiltration can partially remove NDMA precursors (Farre et al., 2011). Farre´ et al. (2011) reported about 80% reduction in NDMA FP (250 to 50 ng/L) using pilot-scale biologically active carbon columns at a wastewater reuse facility. However, some of this removal may be due to adsorption of NDMA precursors to carbons. Furthermore, it has been also shown to increase NDMA formation by transforming some precursors into more potent forms (Krasner et al., 2012a). The presence of ammonia in the influent led to higher concentrations of nitrite in the effluent. Thus, increasing nitrite concentrations at the biofilters effluent can increase NDMA FP triggered by the nitrosation pathway (Krasner et al., 2012a).

Riverbank filtration has been shown in Europe to remove nitrosamine precursors via biodegradation and/or adsorption (Sacher et al., 2008). Recently, riverbank filtration was shown to be effective at a site in the U.S. with approximately 64% reduction in NDMA FP (Krasner et al., 2012c).

Since NDMA precursors are associated with low molecular weight compounds, ultrafiltration displayed negligible reduction in NDMA FP (Pehlivanoglu-Mantas and Sedlak, 2008). For selected nitrosamine precursors such as DMA, methylethylamine, diethylamine, and dipropylamine, rejections of more than 98.5% have been reported (Miyashita et al., 2009). Furthermore, reverse osmosis demonstrated complete removal at selected wastewater treatment plants (WWTPs) in California (Mitch and Sedlak, 2004).

CHAPTER THREE

OBJECTIVES, APPROACHES, AND EXPERIMENTAL DESIGN

Objectives

Despite the significant efforts devoted to minimizing nitrosamine formation in drinking water treatment, the formation of nitrosamines is poorly understood. In this research, the main objective was to systematically examine nitrosamine formation from amines to gain insight about the formation mechanisms of nitrosamines (especially NDMA) and examine the interactions of these precursors with different oxidants. This is especially important considering the potential health effects and future regulations of nitrosamines in drinking water. Specifically, this research was carried out in the following areas:

1. To examine the formation potential of nitrosamines from selected AAs under different oxidation conditions.
2. To investigate the effect of tertiary amine structure and the influencing factors in ultimate NDMA formation.
3. To determine the factors that influence NDMA formation as a function of time.
4. To evaluate the reactivity of different oxidation techniques with NDMA precursors and the effects on NDMA conversion.

Approaches and Experimental Designs

- ***Objective 1:*** ***Examine the formation potential of nitrosamines from selected amino acids under different oxidation conditions.***

  Approach: Nine AAs (alanine, aspartic acid, cysteine, glutamic acid, glycine, lysine, histidine, proline and serine) were selected based on charge, polarity and hydrophobicity. Ten mg/L of individual AA solutions were exposed to different oxidation conditions (i.e., chloramination, and ozonation-chloramination) and their FPs were examined for nitrosamines that can be analyzed by method USEPA 521 (**Figure 3.1**).

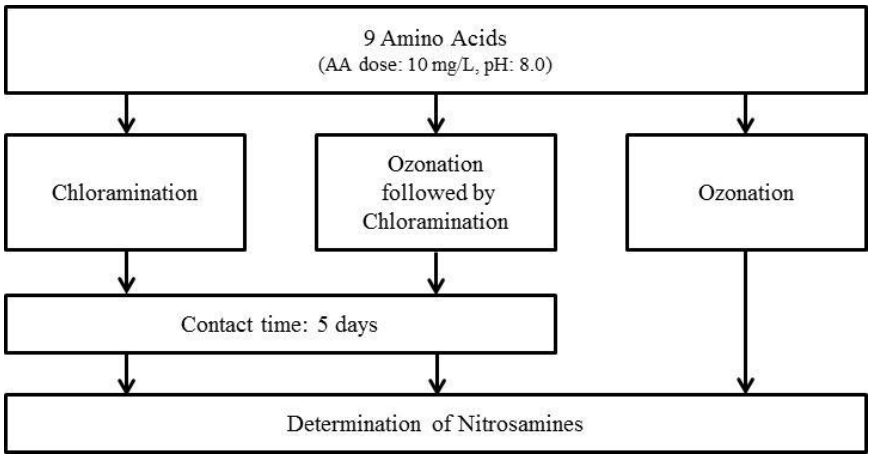


Figure 3.1. Experiments conducted for Objective 1.

- ***Objective 2:*** ***Investigate (i) the effect of tertiary amine structure, (ii) the effect of background NOM, and (iii) the roles of mono- vs. dichloramine species on NDMA formation.***

Approach: To explore the effect of tertiary amine structure, DMA and 20 different tertiary aliphatic and aromatic amines were carefully selected based on the functional groups attached to the basic DMA structure (**Figure 3.2**). Selected precursors were chloraminated individually and tested for their NDMA FP. The NOM effect was initially investigated by spiking the selected amines in solution prepared with two different NOM fractions (transphilic [TPH] and hydrophobic [HPO]) alone to eliminate the confounding effects that may come from the other constituents in the background matrices of natural waters. Finally, the selectivity and sensitivity of amine precursors to monochloramine and dichloramine species were examined for eight selected compounds by suppressing dichloramine in the presence of excess ammonia.

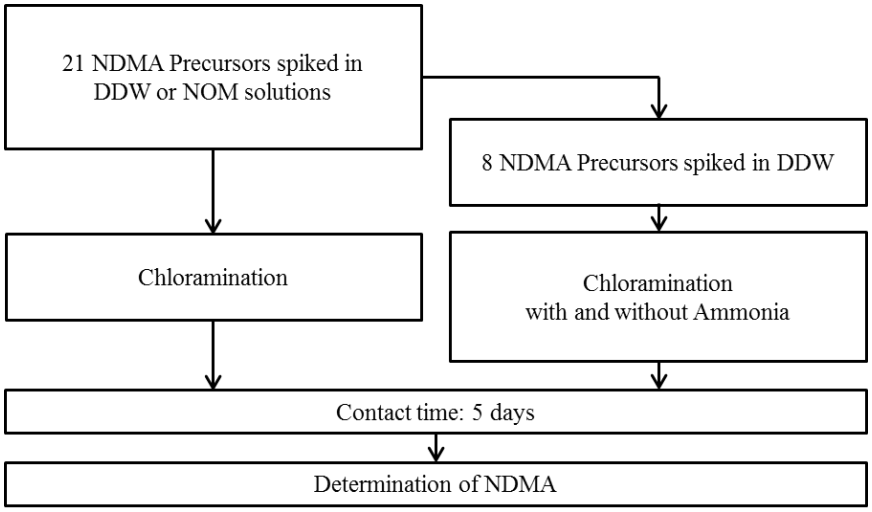


Figure 3.2. Experiments conducted for Objective 2.

- ***<u>Objective 3:</u> Examine (i) the role of chloramine species in the formation of NDMA from DMA and selected tertiary amines; (ii) the factors that influence chloramine decomposition (i.e., pH, sulfate and NOM) during NDMA formation from these model precursors; and (iii) the role of chloramine species in selected natural waters.***

  <u>*Approach:*</u> To explore objective *i*, DMA and four tertiary amines were carefully selected based on their structures. NDMA formation rates were monitored from these five model compounds in three parallel experiments with varying amounts of dichloramine. Based on the results, two amines were selected due to their extreme sensitivity to specific chloramine species and the effect of pH, sulfate and NOM were further examined to reach the second objective. A simplified diagram of the experimental design is given in **Figure 3.3**. Since chloramine speciation could also be an important factor in natural samples, the objective *iii* was to evaluate the impact of chloramine species in a selected drinking water treatment plant and a watershed.

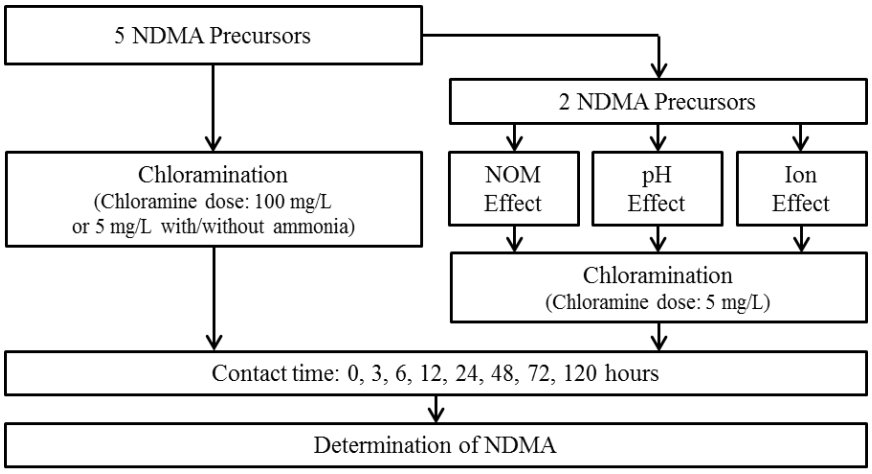


Figure 3.3. Experiments conducted for Objective 3.

- ***<u>Objective 4:</u> Examine (i) the commonly used pre-oxidants (i.e., chlorine, chlorine dioxide and ozone) in water treatment; (ii) CT values, and (iii) pre-oxidation pH effects on NDMA formation from selected precursors.***

  <u>*Approach:*</u> A total of 15 precursors with a DMA moiety in their structures were carefully selected and exposed to different oxidants (chlorine, chlorine dioxide and ozone) (**Figure 3.4**). Selected precursors included tertiary aliphatic and aromatic amines, polymers, amides, hydrazines, and a secondary amines that can be encountered during drinking water treatment. CT curves for chlorine, chlorine dioxide and ozone were generated for each compound relevant to *Giardia* and virus removal at room temperature. Then, residual oxidants were quenched and chloraminated immediately to determine the effect on NDMA conversion. Finally, from each group of precursors, a representative sub-set was chosen to

further evaluate the effect of pre-oxidation pH ranging from 5.5 to 9.5. The pH experiments were conducted for one fixed CT for each oxidant.

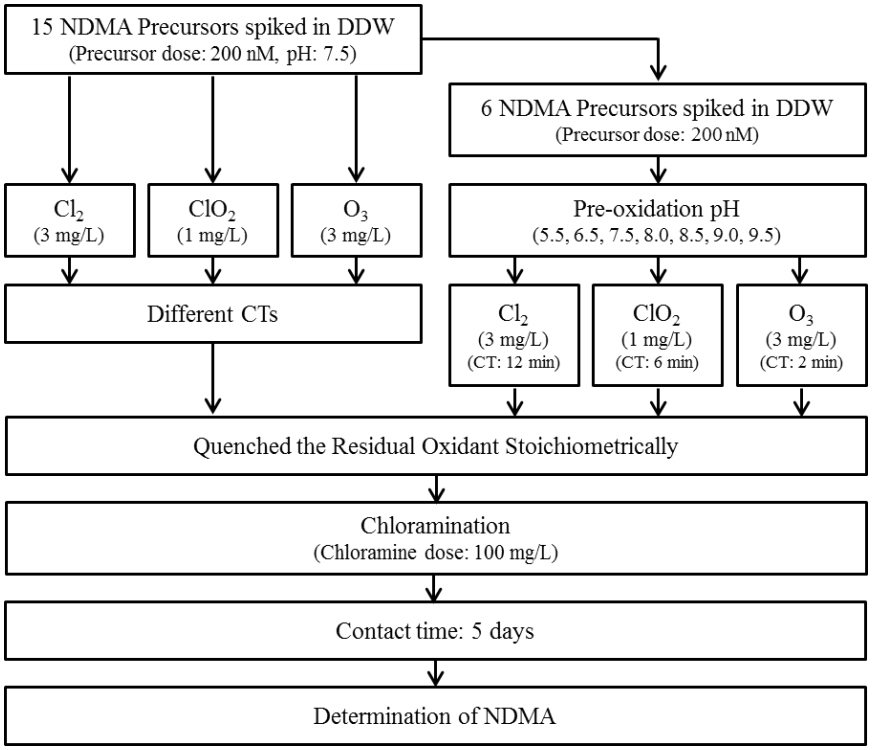


Figure 3.4. Experiments conducted for Objective 4.

The following chapter describes the details of the materials and methods used throughout this research. Chapters five, six, seven and eight present results that address objectives 1, 2, 3 and 4, respectively. Chapter nine provides a comprehensive set of conclusions and recommendations.

CHAPTER FOUR

MATERIALS AND METHODS

In this chapter, an overall description of experimental materials and methods used in this research will be provided. Since different samples and methods were involved in different phases of the study, in each chapter there will be a short experimental materials and methods section to list the precursors used and the experimental matrix conducted for a particular chapter.

Glassware, Reagent Water, & Chemical Reagents

Glassware was scrupulously cleaned by tap water and a detergent, rinsed with distilled water five times and finally five times with distilled deionized water (DDW). The glassware was dried at a temperature of least 105 ºC inside an oven to avoid any contamination and dust.

Reagent water used in the experiments was DDW produced by a Millipore water purification system. The DDW was Type I water with a resistivity of 18 MΩ-cm.

All chemicals used were purchased from certified vendors. All chemicals, except precursors, were American Chemical Society reagent grade. Solvents used in the extraction were high purity. All stock solutions and buffers were prepared at the use time; otherwise they were stored in amber borosilicate glass bottles at 4°C for up to a week.

Model Precursors

A range of nitrogenous precursors were selected for their nitrosamines formation. All precursors were purchased from certified vendors (Sigma-Aldrich, TCI, Matrix Scientific, and Santa Cruz Biotechnology) at purities ranging from 98.0% to 99.5% and used without further purification. Furthermore, some precursors were purchased as a solution (i.e., 20.0% to 45.0%). All amines were chosen based on their structure to examine the effects of several parameters, such as chain length, acidity, polarity and functional groups. A stock solution for each precursor was prepared in methanol or DDW and stored in 65 mL or 1 L amber glass bottles at 4ºC until use. Since, different precursors were used in each objective, the structures of precursors are given in each section of results and discussion.

Natural Water Samples Collection and Preservation

Most of the model precursor's DBP formations were investigated in DDW; however, selected experiments were also conducted in the presence of background NOM. To investigate the role of NOM in these reactions, 20 to 40 L of water samples were collected from selected water sources or DWTPs (Myrtle Beach [M-B] and Charleston [CH]) in South Carolina. If water was to be collected from a treatment plant, samples were collected as raw (influent to the plant) and treated [after conventional treatment processes (coagulation, flocculation, and sedimentation)]. Collected samples were transported to the lab and immediately filtered using pre-washed 0.2 or 0.45 µm Supor® membrane, and stored in a cold dark room at 4°C until experiments that were usually

performed within a week of collection. In selected experiments only isolated NOM fractions were used which were available in the lab from previous studies.

Formation Potential Tests

FP tests, designed to determine DBP precursors in a water sample, were conducted in the presence of an excess of disinfectant. Chloramines were used as the primary oxidant to investigate the formation of nitrosamines; however, ozonation, and ozonation followed by chloramination were also investigated in selected experiments.

FP tests for nitrosamine formation were performed using either 500 or 1000 mL amber bottles. Each bottle received a stir bar and was initially filled halfway with DDW or background solutions (i.e., natural waters, and NOM isolates). Model compounds were spiked in the bottle and 50 mL of fresh monochloramine stock solution was added. The remaining volume was filled with the same solutions leaving a headspace free bottle. The initial chloramine dose in the bottles was 100 mg/L. The bottles were capped and stirred on a stir plate for a couple of minutes and then stored at room temperature (21-23°C). Nitrosamine extractions were performed after five days.

For the reactors involving ozonation-chloramination, a pre-calculated volume of the test water was removed from each bottle, the volume removed being equal to the volume of the ozone stock solution to be subsequently added for ozonation. The ozone dose was variable for each objective. Ozone stock solution was directly added from a gas wash bottle to the top of the solution while minimizing the transfer time to avoid

volatilization loss. Then, samples were mixed on a stir plate for 5 min before chloramination.

Chlorine and Chloramine Production

The fresh chlorine stocks were prepared by diluting sodium hypochlorite (5-6% available free chlorine) before the experiment each time. Chlorine stock solutions were prepared to give a chlorine concentration of ≈2500 mg/L. A fresh monochloramine stock solution was prepared by mixing sodium hypochlorite (5-6% available free chlorine) and ammonium sulfate solutions at a Cl_2:N mass ratio of 3.5:1 or 4.0:1 at pH 9. Chloramine stock solutions were prepared to give a chlorine concentration of ≈1000 mg/L.

Ozone Production

For the experiments involving ozonation of water samples, ozonation was carried out by adding ozone stock solution to the samples. A gas washing bottle (1 or 2 L) containing DDW with minimal headspace was placed in an ice bath, and the solution was ozonated with a GTC-1B Griffin ozone generator fed with ultra-high purity oxygen gas. To minimize the fluctuation of ozone output of the ozonator, a glass damper was placed between the ozonator and the gas washing bottle. In a typical ozone stock preparation, approximately 30 min ozonation would saturate the solution, yielding 28-32 mg O_3/L. The ozonated samples were mixed on a stir plate for 5 min before chlorination or chloramination.

Chlorine Dioxide Production

A fresh chlorine dioxide stock was prepared via the slow acidification of $NaClO_2$ solution with H_2SO_4 (Jones et al., 2012). Chlorine dioxide stock solutions were prepared to give a chlorine dioxide concentration of ≈1500 mg/L.

Analytical Methods

A summary of the parameters, analytical methods, instruments and MRL are presented in **Table 4.1**. These methods were developed following either Standard Methods (SMs) or USEPA Methods. All experiments were conducted for two independent samples and the results presented in the tables and figures represent the averages of the duplicates.

Table 4.1. Analytical methods and minimum reporting levels.

Parameter	Unit	Measurement Method	Equipment	Minimum Reporting Levels
DOC[a]	(mg/L)	SM[b] 5310B High Temperature Combustion	TOC-V_{CSH}, Shimadzu Corp., Japan	0.10[c]
DN[d]	(mg/L)		TNM-1, Shimadzu Corp., Japan	0.10[c]
UV Absorbance[e1]	(abs)	SM 5910	Cary 50, Varian Inc., USA	0.003[e2]
Br^-, NO_3^-, NO_2^-, SO_4^{-2}	(μg/L)	USEPA Method 300	ICS-2100, Dionex Corp.	Br^-=10 NO_3^-=15 NO_2^-=20 SO_4^{-2}=25
Chlorine Dioxide	(mg/L)	SM 4500-ClO_2 E	NA	0.10
		DPD Method	HACH Test Kit	0.04
Ozone	(mg/L)	SM 4500-O_3	HACH Test Kit	0.02
Ammonia	(mg/L)	Salicylate Method	HACH Test Kit	0.02
pH		SM 4500-H^+	420A, Orion Corp., USA	±0.01[f]
Nitrosamines	(ng/L)	USEPA Method 521	Varian GC/MS/MS	3.0
Residual free/combined Chlorine	(mg/L)	SM 4500-Cl F	NA	0.05-0.15

[a]: Reagent grade potassium hydrogen phthalate was used to prepare external standards.
[b]: SM: Standard Methods.
[c]: As reported by the manufacturer.
[d]: Reagent grade potassium nitrate was used to prepare external standards.
[e1]: Measured at wavelength of 254 using a 1-cm cell.
[e2]: Photometric accuracy (absorbance units).
[f]: Accuracy (pH units).
NA: Not Applicable

Oxidant Concentration Measurements

Free and combined chlorine concentrations were measured using an N,N-diethyl-p-phenylenediamine (DPD) method (SM 4500-Cl F). Chlorine samples were diluted based on their expected residual chlorine concentration to the range of 0 to 5 mg/L as Cl_2. The sample was then poured into a flask containing 5 mL of DPD indicator solution and 5 mL of phosphate buffer. After mixing, the sample was titrated using a ferrous ammonium sulfate (FAS) solution to the end-point and titrant volumes were used to calculate chlorine concentrations. The DPD indicator solution and FAS solution were made according to SM 4500-Cl F.

The concentrations of the chlorine dioxide were measured with one of two methods. Mainly, chlorine dioxide concentrations were measured using 4500-Cl F (DPD Method) method with HACH kits. A few drops of glycine were added to a 10 mL sample, and after few seconds, DPD reagent was added. Chlorine dioxide concentrations were immediately measured with a HACH DR/820 colorimeter. SM 4500-ClO_2 E was also used to determine chlorine dioxide concentrations. One mL of phosphate buffer was added to 200 mL samples and 1 g of potassium iodide was added as indicator. The sample was titrated with a sodium thiosulfate until the end point and titrant volume was recorded as “A”. To this solution, 20 mL of hydrochloric acid was added, titrated until the end point and titrant volume was recorded as “B”. The pH of another 200 mL sample was adjusted with phosphate buffer once again. This solution was purged for 5 minutes. One gram of potassium iodide was added as indicator, titrated until the end point and titrant volume was recorded as “C”. To this solution, 20 mL of hydrochloric acid was

added, titrated until the end point and titrant volume was recorded as "D". A, B, C, and D values were used to calculate Cl_2, ClO_2, and ClO_2^- concentrations. The necessary solutions were prepared according to SM 4500-ClO_2 E.

Ozone concentration was measured using the indigo method. Approximately 40 mL of sample was transferred in a plastic beaker and a HACH ozone reagent ampul (Accuvac) containing indigo reagent was filled with the sample. The indigo reagent immediately reacted with ozone and the blue color of indigo was bleached in proportion to the amount of ozone present in the sample. Ozone in the sample was colorimetrically measured with a HACH DR/820 colorimeter.

Nitrosamine Measurements

EPA 521 nitrosamine mix (2000 µg/mL of each component, 98.6-99.9%) in methanol, nitrosamine calibration mix of *N*-nitrosodimethylamine-d6 (NDMA-d6, 98%) as a surrogate and *N*-nitrosodi-n-propylamine-d14 (NDPA-d14, 99%) as an internal standard (1000 µg/mL of each in dichloromethane [DCM]) were purchased from Sigma-Aldrich and Restek, respectively. Nitrosamine mix (2000 µg/ml of mix) and nitrosamine calibration mix (1000 µg/ml of NDMA-d6 and NDPA-d14) solutions served as the master stock solutions. Primary diluted stock (PDS) of each stock (~500 µg/L) was prepared by diluting them in DCM for further use in calibration curve or extractions.

NDMA and seven nitrosamine species (NPYR, NDEA, NMEA, NDPA, NDBA, NPYR, and NMOR) were analyzed following USEPA Method 521. Calibration solutions were prepared from a stock of mixed nitrosamines. Typical calibration curves were

generated from at least six standard points. For the sample analysis, 500 mL of chloraminated solutions were quenched with sodium thiosulfate. NDMA-d_6 was added to the samples as a surrogate before solid phase extraction (SPE). Samples were passed through cartridges pre-packed with 2 g of coconut charcoal purchased from UCT. Prior to sample extraction, cartridges were pre-conditioned with DCM, methanol, and DDW. After SPE, cartridges were dried with air, and then eluted with DCM. Eluted samples were passed through a column pre-packed with 6 g of sodium sulfate and concentrated to 1 mL under high purity nitrogen gas. The extracts were spiked with NDPA-d_{14} as an internal standard, and analyzed using a Varian GC 3800-MS/MS 4000 equipped with RTX-5MS (Restek 30m × 0.25mm × 0.25μm) MS using an 8 μL injection volume and chemical ionization (CI) with methanol. The temperature program is as follows: injection temperature was 35 °C holding for 0.8 minute, and then increased to 260 °C at 200 °C/min and held for 2.08 minutes. The column temperature program was as follows: 35 °C for 5 minutes, increased to 70 °C at 5 °C/min, then to 87 °C at 3 °C/min, then to 120 °C at 5 °C/min, and then to 250 °C at 40/min holding for 2.48 minutes. Nitrosamines are sufficiently thermally stable and volatile for direct analysis by gas chromatography (GC). Reference and quantifications ions of each nitrosamine and their retention times are given in **Table 4.2**. All samples and blanks were prepared and extracted in duplicates, and then each extract was analyzed on a GC equipped with a mass spectrometer (MS).

Table 4.2. Detection information of nitrosamines on GC-MS/MS.

Nitrosamine	Molecular Weight	Quantification Ion	Confirmation Ion	Retention Time (min)
NDMA	74	75.0	43.3, 47.3	6.0
NDMA-d_6	80	81.1	50.3, 49.3	6.0
NMEA	88	89.0	61.1, 43.2	8.5
NDEA	102	103.1	103.9, 75.0	10.5
NPYR	100	101.1	55.1, 102.1	16.3
NDPA-d_{14}	144	145.2	97.2, 146.3	16.3
NDPA	130	131.2	89.1, 132.1	16.6
NMOR	116	117.2	101.2, 87.0	16.5
NPIP	114	115.1	69.1, 116.2	17.9
NDBA	158	159.1	160.2, 103.1	23.4

The detection limits (DL) were estimated for all nitrosamine species by eight consecutive analyses (i.e., one injection per vial for the eight vials prepared) of mixture solutions, which contained approximately 5 ng/L of each nitrosamine compound. The following equation was used to calculate DL:

$$DL = S \times t_{(n-1,\ 1-\alpha)} \qquad \textbf{Equation 4.1}$$

where, S = standard deviation of the replicate analyses, t (n-1, 1-α) = student-t value for the 1-α with n-1 degrees of freedom (e.g., t(7, 0.99) = 2.998 for eight replicates at the 99% confidence level), n = number of replicates, and α = 0.01 (i.e., confidence level 1-α = 0.99). The MRL was established at a concentration that is three times the DL. In practice, this is the lowest point on the calibration curve that can be quantified. The DL and MRL of nitrosamines determined are presented in **Table 4.3**.

Table 4.3. DLs and MRLs of nitrosamines established at 5 ppt in DDW.

Nitrosamine	Mean Measured (ng/L)	RSD (%)	DL (ng/L)	MRL (ng/L)
NDMA	4.8	5.2	0.7	2.2
NMEA	5.1	5.7	0.9	2.6
NDEA	5.0	4.4	0.7	2.0
NPYR	5.2	4.9	0.8	2.3
NDPA	5.5	5.6	0.9	2.8
NMOR	5.0	6.7	1.0	3.0
NPIP	4.5	6.1	0.8	2.4
NDBA	4.5	6.7	0.9	2.7

Spike recovery experiments were also performed to verify that the employed analytical method would be applicable to other water matrices. This was examined by analyzing spike recoveries of nitrosamine species in two source waters with high $SUVA_{254}$ (3.6 L/mg-m) and low $SUVA_{254}$ (2.3 L/mg-m). Samples were spiked from the mix solution containing 10 ng/L of each nitrosamine species before extraction and analysis. The results are shown in **Table 4.4**. Relative standard deviation in these tests and analyzed samples were less than 20%.

Table 4.4. Spike recoveries of nitrosamines in high and low SUVA background solutions.

		Low SUVA			High SUVA		
Nitrosamine	Fortified (ng/L)	Mean Measured (ng/L)	RSD (%)	Mean Recovery (%)	Mean Measured (ng/L)	RSD (%)	Mean Recovery (%)
NDMA	10	8.85	3.5	87	9.52	5.6	93
NMEA	10	9.10	5.6	89	10.61	4.6	104
NDEA	10	9.01	7.9	89	10.88	6.6	107
NPYR	10	9.40	4.6	93	11.31	3.0	112
NDPA	10	8.64	10.8	85	9.57	10.3	95
NMOR	10	8.52	8.8	84	11.42	15.7	113
NPIP	10	7.59	8.4	75	8.11	10.9	80
NDBA	10	6.34	12.9	63	8.28	12.8	82

Dissolved Organic Carbon and Dissolved Nitrogen Measurement

Dissolved organic carbon (DOC) and dissolved nitrogen (DN) were measured using a Shimadzu TOC-V_{CHS} or TOC-L_{CHS} high temperature combustion analyzer equipped with a TN module. TOC standards were prepared by diluting 1000 mg C/L potassium hydrogen phthalate solution in the range of 0.2-15 mg C/L. TN standards were prepared by diluting 1000 mg N/L potassium nitrate solution in the range of 0.2-5 mg N/L. The MRLs for these measurements were determined to be 0.15 mg/L and 0.1 mg/L for DOC and DN, respectively.

Ammonia Measurement

Ammonia concentrations were measured using salicylate method with HACH kits. Salicylate reagent was added to a 10 mL sample, and after 3 min, cyanurate reagent was added. After 15 min reaction, ammonia in the sample was colorimetrically measured with a HACH DR/820 colorimeter.

UV_{254} Absorbance

UV absorbance at 254nm wavelength (UV_{254}) was measured using a Cary 50 UV-Vis spectrophotometer (Varian). Samples were placed in a 1 cm quartz cuvette and measured at a wavelength of 254 nm. The spectrophotometer was zeroed by measuring the absorbance of DDW after several rinses. The instrument was zeroed every ten samples, and method performance was monitored using DOC standards made with potassium hydrogen phthalate.

pH

The pH values for samples were measured using a SM 4500-H^+ pH electrode with a VWR Symphony pH meter (VWR). The pH meter and electrode were calibrated using standard pH 2, 4, 7 and pH 10 buffer solutions before use.

Bromide, Nitrite, Nitrate and Sulfate Measurements

Bromide, nitrite, nitrate, and sulfate were measured using an ion chromatography system. A Dionex ICS-2100 equipped with an AAES suppressor was used to determine these anions present in natural samples used for background NOM experiments. The mobile phase was 9 mM Na_2CO_3. A Dionex AS-HC9 column coupled with an AG-HC9 guard column was used to separate samples. The injection volume was 250 µL. A calibration curve was obtained by a series of standard concentrations (at a low range of 10-1000 µg/L) using NaBr (> 99.9%, Sigma), $NaNO_2$ (> 99.9%, Sigma), $NaNO_3$ (> 99.9%, Sigma), and Na_2SO_4 (> 99.0%, EMD) and their corresponding MRLs were 10, 20, 15, and 25 µg/L, respectively.

Dissolved Organic Nitrogen Determination

In this study, dissolved organic nitrogen (DON) concentrations were determined through subtraction as given in **Equation 4.2**.

$$DON = DN - NO_3\text{-}N - NO_2\text{-}N - NH_4^+ \qquad \textbf{Equation 4.2}$$

CHAPTER FIVE

NITROSAMINES FORMATION FROM AMINOACIDS

Introduction and Objective

Recent research has shown that emerging N-DBPs exhibit orders of magnitude higher cyto- and geno-toxicity than any of the regulated C-DBPs (Plewa et al., 2008). Therefore, it should not be surprising to see additional DBP regulations including N-DBPs in the near future. Recent research has shown that nitrogen-rich organic materials in natural waters play an important role in the formation of N-DBPs (Dotson et al, 2009; Hu et al, 2010; Mitch et al, 2009). However, the important precursors and the formation mechanisms of N-DPBs, especially NDMA, still remain largely unknown.

AAs have been found in fresh waters in a wide concentration range, 5 to 2000 µg/L, either in free or combined as peptides, nucleic acids, purines, pyrimidines, and proteins (Rice and Taylor, 1986). Thurman (Thurman, 1985) reported that total AAs, sum of the free and combined AAs, accounted for 2.6% of the dissolved organic carbon (DOC) and 35% of the DON in some lakes. Hagedorn et al. (2000) observed in catchment runoff that the total AAs accounted for 20% to greater than 75% of the DON. Elevated amino acid levels were also found during the occurrence of algae blooms (Meon and Kirchman, 2001; Sellner and Nealley, 1997). In addition, degradation of algal cells during the die-off phase can be a major contributor of dissolved AAs in natural waters (Thurman, 1985; Jørgensen 1987). In a recent survey of sixteen water treatment plants in

the United States, the average total AAs constituted 15% of DON in the source waters (Dotson and Westerhoff, 2009). The principal AAs identified in natural waters included glycine, glutamic acid, alanine, aspartic acid, leucine, proline and serine (Thurman, 1985; Münster, 1999; Chinn and Barrett, 2000; Dotson et al, 2009).

The presence of AAs in raw and treated waters exerts high chlorine demand (Trehy et al, 1986; Hureiki et al, 1994). The relative chlorine reactivity of AAs depends on the side chain groups attached to the α-carbon. Studies conducted on the reactions of AAs with chlorine have shown the formation of various classes of DBPs including haloacetaldehydes, haloacetonitriles (HANs), cyanogen chloride, THMs and HAAs (Hureiki et al, 1994; Na and Olson, 2006; Hong et al, 2009; Hu et al., 2010). As compared to C-DBPs, there is much less information on the formation of N-DBPs from amino acids, especially for nitrosamines. NDMA can form especially in drinking waters and wastewater effluents under chloramination conditions (Sacher et al, 2008). NDMA has been classified as a probable human carcinogen by USEPA (Richardson et al, 2007), and can pose important health risk even at ng/L concentrations. As a result, the Ontario Ministry of the Environment and Climate Change established a maximum allowable concentration of 9 ng/L for NDMA, and the California Department of Health Service set an interim action level of 10 ng/L. Though nitrosamines are not currently regulated at a federal level in the United States, NDMA and four other nitrosamines (NDEA, NDPA, NDPhA, and NPYR) are on the USEPA's CCL3, and have been monitored under the UCMR2 (USEPA, 2006, 2009).

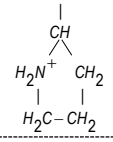
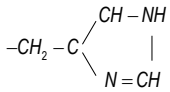
Since AAs constitute an important fraction of the organic nitrogen pool in natural waters, the objective of this study was to investigate the formation potential of nitrosamines from AAs under different oxidation conditions. As reviewed in this section, previous studies have mainly focused on the formation regulated C-DBPs (e.g., THM and/or HAA) from AAs, while significantly less attention has been placed on the nitrosamines.

Materials and Methods

Amino Acids

AAs can be classified into four categories depending upon their acidity and polarity: acidic, basic, polar, and nonpolar. For this study, nine AAs (alanine, aspartic acid, cysteine, glutamic acid, glycine, lysine, histidine, proline and serine) were selected based on charge, polarity and hydropobicity. The physicochemical characteristics and structures of the selected AAs are listed in **Table 5.1**.

Table 5.1. AAs selected for this study and their properties (Lide, 1991).

Type	Amino acid	R group	pK_1	pK_2	pK_3	Isoelectric point	Hydrophobicity Designation*
acidic	Aspartic acid	$-CH_2COO^-$	2.0	10.0	4.04	2.77	W
	Glutamic acid	$-CH_2CH_2COO^-$	2.2	9.7	4.39	3.22	W
basic	Lysine	$-CH_2CH_2CH_2CH_2NH_3^+$	2.2	9.2	11.1	9.74	W
nonpolar	Glycine	-H	2.4	9.8	-	5.97	W
	Alanine	$-CH_3$	2.3	9.9	-	6.01	N
	Proline		2.0	10.6	-	6.48	W
polar	Serine	$-CH_2OH$	2.1	9.2	-	5.68	W
	Cysteine	$-CH_2SH$	1.8	10.8	8.6	5.07	L
	Histidine		1.8	9.2	6.8	7.59	N

* Hydrophobic = L, Hydrophilic = W, Neutral = N

A stock solution (500 mg/L) of each amino acid (Sigma-Aldrich) was prepared in DDW. The stock solutions were buffered at pH 8 using 4 mM sodium bicarbonate and 1M HCl or NaOH solutions. For the formation potential tests, typical occurrence concentration of 1 mg/L was used initially which were then increased to 10 mg/L. Although these AA concentrations are higher than their typical occurrence levels in fresh waters, they were intentionally selected at these high levels to magnify and better examine the DBP formation; an approach that has been used in previous studies (Berger et al, 1999; Mitch et al, 2009). AA sample solutions were prepared with dilution from the

main stock, and the concentrations were confirmed using a TOC analyzer (Shimadzu Corp., USA).

Formation Potential Tests

The oxidation conditions that favor the formation of certain classes of DBPs were used in the FP tests. Chloramination, ozonation and ozonation-chloramination were applied for the nitrosamines FP tests. Each FP test was conducted in duplicates.

Monochloramine stock solution was prepared by mixing sodium hypochlorite (5-6% available free chlorine) and ammonium sulfate solutions at a Cl_2:N mass ratio of 4:1 (0.8:1 molar ratio) and pH 9. The dosage of chloramine was determined using the formula approach developed by Krasner et al. (2009) (NH_2Cl [mg/L] = 3 × DOC [mg/L]). The concentrations of the free chlorine and monochloramine were measured with SM 4500-Cl F (DPD Ferrous Titrimetric Method).

Ozonation was conducted by adding ozone stock solution to the samples. To prepare the ozone stock solution, a 1 L gas washing bottle containing DDW with minimal headspace was placed in an ice bath, and the solution was ozonated with an ozone generator (Model GTC-1B, Griffin Technics Incorporated, NJ) fed with ultra-high purity oxygen gas. In a typical ozone stock preparation, about 30 mg O_3/L stock solution was obtained within 30 min. Precalculated volumes of AA solutions were removed from the 125mL or 1L amber glass bottles used for the FP tests and replaced with the freshly prepared ozone stock solution. Ozone concentration in the bottles at the beginning of the experiments was approximately 4 mg/L that assured that ozone was not a limiting factor during ozonation period. After ozone addition, the samples were mixed on a stir plate for

five minutes. The residual ozone concentrations were measured before chlorine or chloramines addition to assure that there was ozone residual by the end of the ozonation period. For chloramination samples without pre-ozonation, the same volume of solutions was removed as for the ozonated samples and replaced with DDW to have the same sample composition (e.g. for DOC, DON) as the pre-ozonated samples.

Experiments for nitrosamine FP test, were conducted in the 1L amber glass bottles without headspace at room temperature (~22 ^{o}C) in the dark for five days.

Analytical Methods

N-nitrosamine samples were concentrated 500 times by SPE using 6-mL cartridge prepacked with 2g of coconut charcoal (UCT). The extracts were analyzed with a Varian GC-MS/MS 4000 under CI mode, using an RTX-5MS (Restek 30m × 0.25mm × 0.25µm) column, for eight N-nitrosamines including NDMA, NDEA, NMEA, NMOR, NDPA, NPYR, NPIP and NDBA. The MRL for each nitrosamine was 3 ng/L. DOC and DN were measured using a Shimadzu TOC-V_{CHS} high temperature combustion analyzer equipped with a total nitrogen module (TNM-1). The MRLs for DOC and DN were 0.1 mg/L. DON concentrations were equal to DN concentrations of AAs, since there was no inorganic nitrogen in the stock solutions. All analytical methods and their minimum reporting levels are given in **Table 4.1**.

Results and Discussion

Nitrosamines Formation from AAs

Initial nitrosamines FP test for three of the selected amino acids at 1 mg/L concentration did not produce measurable nitrosamines. To further confirm the results, it was decided to magnify the initial concentration of amino acids during the experiments by increasing to 10 mg/L, and three different oxidation scenarios, monochloramination, ozonation and ozonation-chloramination were tested for all nine AAs. Ozonation alone was also examined because NDMA formation has recently been reported after ozonation in laboratory studies (Andrzejewski et al, 2008; Yang et al, 2009) and in full scale ozonation plants (Planas et al, 2008; Asami et al, 2009).

Despite increasing the amino acids concentrations to 10 mg/L, in most of the cases, NDMA and NDBA FP concentrations were very low, such as 5 ng/L NDBA from lysine after chloramination (**Table 5.2**). Mitch and co-workers reported non-detectable nitrosamine (NDMA, NMEA and NDEA) formation from aspartic acid, proline and histidine during chloramination (Mitch and Sedlak, 2002); and NDMA formation of <2ng/L from glycine and tyrosine during chloramination (Mitch et al, 2006).

Table 5.2. Nitrosamine FPs of AAs tested in this study.

AA	DOC (mg C/L)	DON (mg N/L)	Chloramine NDBA (ng/L)	Ozone-Chloramine NDBA (ng/L)	Ozone-Chloramine NPYR (ng/L)	Ozone NPYR (ng/L)
Alanine	4.0	1.6	<MRL	<MRL	<MRL	<MRL
Aspartic Acid	3.6	1.1	<MRL	<MRL	<MRL	<MRL
Cysteine	3.0	1.2	<MRL	<MRL	<MRL	<MRL
Glutamic Acid	4.1	1.0	<MRL	<MRL	<MRL	<MRL
Glycine	3.2	1.9	<MRL	<MRL	<MRL	<MRL
Histidine	4.6	2.7	<MRL	<MRL	<MRL	<MRL
Lysine	4.9	1.9	5	9	<MRL	<MRL
Proline	5.2	1.2	<MRL	3	4	4
Serine	3.4	1.3	<MRL	3	<MRL	<MRL

Reported values are average of two measurements (n=2).

During ozonation-chloramination, NDBA formation of 9, 3 and 3 ng/L from lysine, proline and serine was observed, respectively. Proline also led to formation of 4 ng/L NPYR during both ozonation and ozonation-chloramination conditions. Other nitrosamines were not detectable. The formation of NPYR from proline is quite straight forward based on its structure. Once ozonation leads to the decarboxylation of proline followed by nitrosation, NPYR will be formed directly (**Figure 5.1**). It is very likely that the nitrogen of the nitrosating agent was sourced from the oxidation of the nitrogen atom. Overall, the nitrosamine yields of AAs during the FP tests were very low. Considering the occurrence concentrations of total AAs in natural waters, it is unlikely that AAs play

a role in the formation of NDMA and other nitrosamines during chloramination, ozonation, and ozonation followed by chloramination.

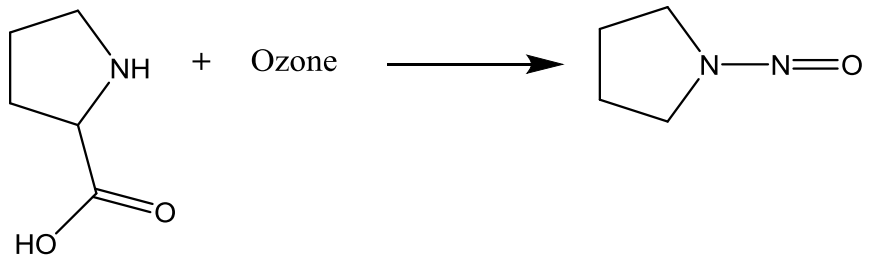


Figure 5.1. NPYR formation from proline.

Conclusions

Although the total AA concentrations in natural waters are, in general, low, their elevated concentrations during some seasonal events (e.g., algae blooms, algae die-off, run off) can result in some contributions to certain nitrosamines depending on the oxidation conditions. Only NDBA and NPYR formation was observed from the selected AAs. Since other nitrosamine formation yields of AAs were very low, the results obtained in this study suggest that AAs are not likely to contribute to nitrosamines formation.

CHAPTER SIX

THE ROLES OF TERTIARY AMINE STRUCTURE, BACKGROUND ORGANIC MATTER AND CHLORAMINE SPECIES ON NDMA FORMATION

Introduction and Objective

Nitrosamines are a group of compounds classified as probable human carcinogens in water at concentrations as low as 0.2 ng/L associated with a 10^{-6} lifetime cancer risk (USEPA, 1993). They form as DBPs in chloraminated and chlorinated drinking waters and wastewaters (Choi and Valentine, 2002a,b; Choi et al., 2002; Mitch and Sedlak, 2002, 2004). NDMA is the most commonly detected and reported nitrosamine in drinking water. Although there are currently no federal regulations for nitrosamines in drinking water in the United States, the USEPA has recently identified nitrosamines as one of three potential groups of contaminants highlighted for possible regulatory action in the near future (Roberson, 2011).

Although an organic nitrogen precursor is required for NDMA formation, there is no strong correlation between dissolved organic nitrogen concentrations and NDMA formation potentials in natural waters (Pehlivanoglu-Mantas and Sedlak, 2008; Dotson et al., 2009; Aydin et al., 2012). Research evaluating the NDMA formation potential of several compounds has encompassed DMA (Mitch et al., 2003a,b), tertiary and quaternary amines with DMA functional groups (Lee et al., 2007; Kemper et al., 2010; Shen and Andrews, 2011a,b), NOM and fractions of NOM (Gerecke and Sedlak, 2003;

Mitch and Sedlak, 2004; Chen and Valentine, 2007; Dotson et al., 2007; Krasner et al., 2008a), polyelectrolytes and ion-exchange resins (Gough et al., 1977; Kimoto et al., 1980; Najm and Trussell, 2001; Kohut and Andrews, 2003; Wilczak et al., 2003; Mitch and Sedlak, 2004; Nawrocki and Andrzejewski, 2011), fungicides, pesticides, and herbicides (Graham et al., 1995; Chen and Young, 2008; Schmidt and Brauch, 2008), pharmaceuticals, cosmetics (Sacher et al., 2008; Shen and Andrews, 2011a,b), and wastewater effluent/impacted waters (Krasner et al., 2004; Sedlak et al., 2005; Krasner et al., 2009; Krauss et al., 2009; Shah et al., 2012).

Different mechanisms have been proposed for NDMA formation with different oxidants (e.g., chlorine, chloramines and ozone), as reviewed in detail elsewhere (Bond et al., 2011; Shah and Mitch, 2012). For chloramination, NDMA formation was initially attributed to a nucleophilic substitution reaction between monochloramine and unprotonated secondary amines (e.g., DMA) to form UDMH intermediates (Mitch and Sedlak, 2002; Choi and Valentine, 2002a,b). However, further studies have shown that chloramination of UDMH yielded much less NDMA than DMA (Mitch et al., 2009). Moreover, dichloramine has been shown to enhance NDMA formation from DMA through the formation of a Cl-UDMH (Mitch et al., 2009). In the same study, Mitch and colleagues proposed that NDMA formation from quaternary or tertiary amines includes liberation of the DMA moiety via reaction of chlorine or monochloramine and released the DMA group further reacts with dichloramine resulting in NDMA formation. After testing of several compounds in recent years as listed above, there are some limitations to explain the formation of NDMA from different precursors using only this pathway during

chloramination. For example, (i) the reported NDMA conversion rates from DMA were at most 3.0% and usually 1-2% (Choi and Valentine, 2002a,b; Choi et al., 2002; Mitch and Sedlak, 2002; Schreiber and Mitch, 2005, 2006; Lee et al., 2007a; Le Roux et al., 2012a). However, some model compounds (e.g., RNTD, sumatripan) have resulted in significantly higher NDMA yields (>>5%) than DMA (Mitch et al., 2009; Le Roux et al., 2011a; Shen and Andrews, 2011a). (ii) Although the proposed pathway emphasizes the significance of dichloramine in NDMA formation, higher NDMA concentrations were observed at pH 8.8 than both pH 6.9 and 5.1 during chloramination of DMA (Schreiber and Mitch, 2005) and a similar trend was observed for natural waters (Krasner et al., 2012a). Monochloramine becomes more stable with increasing pH, and significantly less dichloramine is produced. Le Roux et al. (2011a) reported a decrease in NDMA formation from ranitidine when they switched from monochloramine to dichloramine (i.e., yield decreased from 80.2 to 46.8%). Therefore, the major NDMA formation pathway may not always be limited to dichloramine as the only chloramine species. (iii) The formation of NDMA may also be influenced from the components in the background water matrices (e.g., NOM, bromide, other ions) (Le Roux et al., 2011b; Shen and Andrews, 2011a,b; Le Roux et al., 2012a; Luh and Marinas, 2012; Shah et al., 2012). (iv) DMA concentrations detected in surface waters (Gerecke and Sedlak, 2003; Lee et al., 2007a) or secondary municipal wastewaters (Mitch and Sedlak, 2004) did not explain the observed levels of NDMA formation.

It is evident that there is still much more to learn about the formation of NDMA in natural waters. For example, the structural characteristics of quaternary or tertiary amines

with a DMA group are of importance (Shah and Mitch, 2012). The main objectives of this study were to systematically investigate (i) the effect of tertiary amine structure, (ii) the effect of background NOM, and (iii) the roles of mono vs. dichloramine species on the NDMA formation. To explore the effect of tertiary amine structure, DMA and 20 different tertiary aliphatic and aromatic amines were carefully selected based on their functional groups attached to the basic DMA structure. The NOM effect was initially investigated by spiking the selected amines in a solution prepared with one of two NOM fractions individually to eliminate the confounding effects that may come from the other constituents in the background matrices of natural waters. Experiments were also conducted with Myrtle Beach, SC, raw and treated (i.e., after conventional clarification processes) waters with negligible bromide concentrations. Finally, the selectivity and sensitivity of amine precursors to monochloramine and dichloramine species were examined for selected compounds.

Materials and Methods

Amines

DMA and 20 tertiary amines were tested for nitrosamine formation. Chemical structures and abbreviations of selected amines are given in Figure 6.1. All compounds were purchased from certified vendors (Sigma-Aldrich, TCI, Matrix Scientific, and Santa Cruz Biotechnology) and used without further purification. Tertiary aliphatic amines were chosen based on their chain length and functional groups attached to DMA

structure. Tertiary aromatic amines were also selected with variable functional groups and different heteroatoms present in the ring structures.

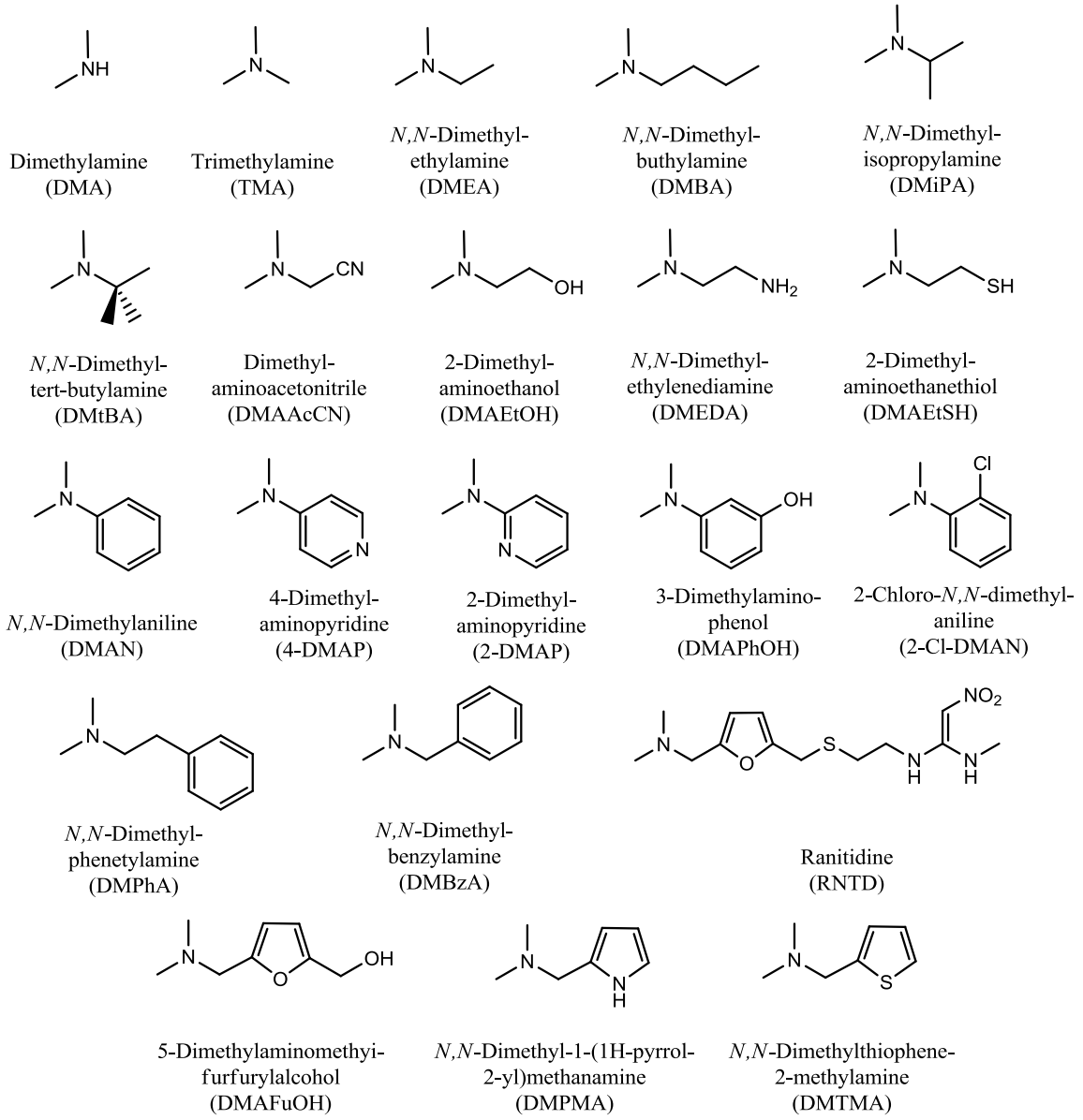


Figure 6.1. Molecular structures of selected amines

Experimental Procedure

FP tests were conducted in DDW with or without NOM. The NOM solutions were prepared using (i) two NOM fractions, M-B TPH or M-B HPO, that were available in our laboratory from a previous study (Hong et al., 2007; Karanfil et al., 2007), and (ii) water samples, source water (M-B Raw) and after conventional clarification processes before filtration (M-B Treated), were also collected from M-B in South Carolina. DOC levels of all NOM solutions were adjusted to 3 mg C/L by diluting them with DDW. NDMA levels in DDW were below 2 ng/L. NOM solutions were filtered with pre-washed 0.2 µm polyethersulfone filters prior to FP tests. The selected characteristics of NOM solutions are shown in **Table 6.1**.

Table 6.1. Selected characteristics of solutions used for NOM experiments

	DOC (mg C/L)	$SUVA_{254}$ (L/mg.m)	DN (mg N/L)	NH_3 (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	Br^- (mg/L)
M-B TPH	3.0	2.0	0.2	<MRL	<MRL	<MRL	<MRL
M-B HPO	3.0	4.2	0.1	<MRL	<MRL	<MRL	<MRL
M-B Treated	3.0	1.7	0.2	<MRL	<MRL	0.16	<MRL
M-B Raw	3.0	3.8	0.1	<MRL	<MRL	0.09	<MRL

Reported values are average of two measurements (n=2).

A stock solution (4 mM) for each amine was prepared in methanol and stored in the 65 mL amber glass bottles at 4ºC until use. Each model compound was diluted to 200 nM in DDW or in NOM solution in 1-L amber bottles capped with Teflon lined PTFE caps. The monochloramine stock solution was prepared by mixing diluted sodium hypochlorite and ammonium sulfate solutions at Cl:N mass ratio of 4:1 at pH 9. An initial chloramine concentration of approximately 1 mM (100 mg/L) was used at pH 7.5 in the

presence of 10 mM phosphate buffer which was prepared by mixing sodium phosphate monobasic and sodium phosphate dibasic. For the NOM experiments, a solution of TPH or HPO was prepared by adding each fraction in DDW with buffer prior to the addition of the target compound; and it was chloraminated under the same conditions used for the DDW experiments. For the experiments with the M-B raw and treated waters, the target amine (200 nM) was spiked directly in the waters.

The roles of monochloramine and dichloramine on NDMA formation were assessed by conducting FP test using a lower dose of chloramine (5 mg/L as Cl_2) with and without ammonia in DDW. The presence of ammonia suppresses the decomposition of monochloramine to dichloramine during FP tests (Hong et al., 2007). Some additional information about the chloramine chemistry can be found in the **Appendix A**. Therefore, two parallel FP tests were conducted: (i) Cl:N ratio of 4:1 without ammonia addition (i.e., having both mono- and dichloramine present with a maximum of 5% dichloramine content), and (ii) Cl:N ratio of 4:1 in the presence of 100 mg/L ammonia (i.e., only monochloramine in the bottles and the concentration of dichloramine was below its detection limit of 0.05 mg/L). These experiments were conducted with an initial monochloramine concentration of 5 mg/L as Cl_2 to control chloramine speciation at pH 7.5 using 4 mM carbonate buffer. The initial chloramine concentrations (i.e., either 5 or 100 mg/L) were enough to provide excess amount of chloramine for all FP tests. All the nitrosamine FP tests in this study were carried out in 1-L amber glass bottles without headspace in the dark at 22ºC and for five days of contact time.

Analytical methods

NDMA was analyzed following USEPA method 521 (USEPA, 2004). Calibration solutions were prepared from an NDMA stock. Typical calibration curves were generated from at least six standard points and the minimum reporting level was 3 ng/L. For the sample analysis, 500 mL of chloraminated amine solutions were taken and quenched with 100 mg of sodium thiosulfate. *N*-nitrosodimethylamine-d6 (NDMA-d6) was added to the samples as a surrogate before SPE. Samples were passed through cartridges pre-packed with 2 g of coconut charcoal. Prior to sample extraction, cartridges were preconditioned with DCM, methanol, and DDW. After SPE, cartridges were dried with air, and then eluted with dichloromethane. Eluted samples were passed through cartridges pre-packed with 6 g of sodium sulfate and concentrated to 1 mL under high purity nitrogen gas. The extracts were spiked with *N*-nitrosodi-n-propylamine-d14 (NDPA-d14) as an internal standard, and analyzed using a Varian GC-MS/MS 4000 equipped with RTX-5MS (Restek 30m × 0.25mm × 0.25μm) column and under the CI mode. Measured NDMA concentrations were used to calculate percent molar yield for each amine using **Equation 6.1** (**Appendix B**).

$$\text{NDMA Yield (\%)} = \left({[\text{NDMA}]\ (\text{nM})} \Big/ {[\text{Amine}]_0\ (\text{nM})} \right) \times 100 \qquad \textbf{Equation 6.1}$$

DOC and DN were determined using a Shimadzu TOC-VCSH instrument equipped with a Total Nitrogen module (TNM-1). UV_{254} absorbance of NOM samples was measured using a Varian Cary-50 spectrophotometer, and used to calculate $SUVA_{254}$ values (Karanfil et al., 2002). Ammonia concentrations were measured with a HACH spectrophotometer. Nitrite, nitrate, and bromide were measured using an ion

chromatograph (Dionex, ICS 2100). Concentrations of free chlorine, and mono- and dichloramine as free chlorine were determined following SM 4500-Cl F (APHA/AWWA/WEF, 2005). All analytical methods and their MRLs are given in **Table 4.1**. All samples and blanks were prepared and extracted in duplicates, and then each extract was analyzed on GC-MS/MS as described in Chapter Four. Error bars in all the graphs show the variability due to multiple extraction and analysis (n=4) under the same conditions.

Results and Discussion

Effect of Amine Structure on NDMA Formation

Table 6.2 shows the NDMA yields observed from the chloramination of 21 selected amines (10 aliphatic and 11 aromatic) during the FP tests along with the yields reported in the literature for the purpose of comparison. The yields obtained for DMA and RNTD in this study agree well with those reported in the literature (Lee et al., 2007a; Mitch et al., 2009; Shen and Andrews, 2011a,b; Le Roux et al., 2012a) despite some differences in the experimental conditions of FP tests (e.g., contact time, buffer type, and pH) (**Table 6.3**).

Table 6.2. Molar yields of NDMA from selected compounds in this study and in selected studies.

Compound	This Study[a] Molar Yield (%[b])	Studies Reported in DDW Yield (%[b])	Reference[c]
DMA	1.2 (0.12)[d]	3.0	Lee et al., 2007a
		0.082	Mitch et al., 2009
		1.2	Le Roux et al., 2011b
		2.3	Le Roux et al., 2012a
TMA	1.9 (0.16)	1.2	Lee et al., 2007a
		0.017	Mitch et al., 2009
DMEA	0.5 (0.09)	NA	NA
DMBA	0.3 (0.05)	NA	NA
DMiPA	83.9 (0.67)	NA	NA
DMtBA	6.2 (0.03)	NA	NA
DMAAcCN	2.4 (0.28)	NA	NA
DMEtOH	0.3 (0.14)	0.5	Lee et al., 2007a
DMEDA	0.8 (0.08)	NA	NA
DMEtSH	0.8 (0.01)	NA	NA
DMAN	0.2 (0.03)	1.2	Lee et al., 2007a
4-DMAP	0.06 (0.02)	NA	NA
2-DMAP	0.09 (0.01)	0.37	Le Roux et al., 2012a
2-Cl-DMAN	0.02 (0.02)	NA	NA
DMAPhOH	1.0 (0.05)	1.0	Le Roux et al., 2012a
DMPhA	0.4 (0.06)	NA	NA
DMBzA	83.8 (0.99)	19.63	Mitch et al., 2009
RNTD	80.5 (2.85)	80.2	Le Roux et al., 2011a
		89.9	Shen and Andrews, 2011a
		82.7	Shen and Andrews, 2011b
DMAFuOH	81.8 (1.58)	74.9	Le Roux et al., 2012a
DMPMA	25.0 (1.97)	NA	NA
DMTMA	77.6 (1.99)	NA	NA

a: Experimental conditions include compound dose of 200 nM, 100 mg/L chloramine (as Cl_2), contact time of 5 days, pH 7.5 adjusted with 10 mM phosphate buffer.
b: NDMA molar conversions calculated by **Error! Reference source not found.**.
c: Experimental conditions of studies reported in literature are summarized in **Table 6.3**.
d: Error Bars represent data range for duplicate samples.
NA: Not Applicable

Table 6.3. Experimental conditions of used in this study and the literature.

Reference	pH (Buffer)	Chloramine Dose (mM as Cl_2)	Cl:N (mol/mol)	Contact Time (day)	Background
This study	7.5 (10 mM Phosp.)	2.0	0.80:1	5	DDW, NOM, RW
Lee et al. 2007a	7.0 (10 mM Phosp.)	2.0	-	10	DDW
Mitch et al. 2009	8.0 (Phosp.)	0.26	0.80:1	3	DDW
Le Roux et al. 2012a	8.0 (10 mM Phosp.)	2.5	0.83:1	1	DDW
Le Roux et al. 2011a	8.0 (10 mM Phosp.)	2.5	0.83:1	1	DDW
Shen and Andrews, 2011a	7.0 (2 mM Phosp.)	0.55	0.84:1	1	DDW, TW
Shen and Andrews, 2011b	7.0	0.05	0.84:1	1	DDW, TW, LW, RW

TW: Tap/drinking water
LW: Lake water
RW: River water

The chain length of the alkyl group next to the nitrogen atom of DMA moiety did not significantly affect the NDMA yield (**Figure 6.2**). DMA and TMA exhibited about 1% and 2% of NDMA yields, respectively, and the yield decreased slightly as the number of carbon chain increased from $–CH_3$ (i.e., TMA) to $–CH_2CH_2CH_2CH_3$ (i.e., DMBA). These relatively low yields suggest that NDMA formation is not likely to be either enhanced or reduced by a long alkyl chain of tertiary amines. However, higher NDMA yields were observed for both DMiPA (84%) and DMtBA (6%) which have branched alkyl groups (i.e., isopropyl and tertiary butyl) next to the nitrogen atom of DMA (**Figure 6.3**). Such high NDMA yields have not been previously reported for any aliphatic amine precursor. Assuming that the nucleophilic substitution between chloramine species and

tertiary amine is the initial step of the NDMA formation, the stability of the leaving group may play a key role in the reactivity of precursor compounds. In other words, branched alkyl groups become carbocations such as $(CH_3)_2CH^+$ and $(CH_3)_3C^+$, which are more stable than unbranched ones such as CH_3^+ and $CH_3CH_2^+$ when the N-C bond is broken in aqueous solutions (Streitwieser et al., 1992). Thus, DMiPA and DMtBA, which also have a good leaving group, formed more NDMA than DMA, TMA, DMEA, and DMBA. Steric hindrance, because of a bulk tertiary butyl leaving group, may account for the lower NDMA formation from DMtBA (6%) than DMiPA (84%). The yield of NDMA from DMtBA was still significantly higher than those from unbranched aliphatic amines.

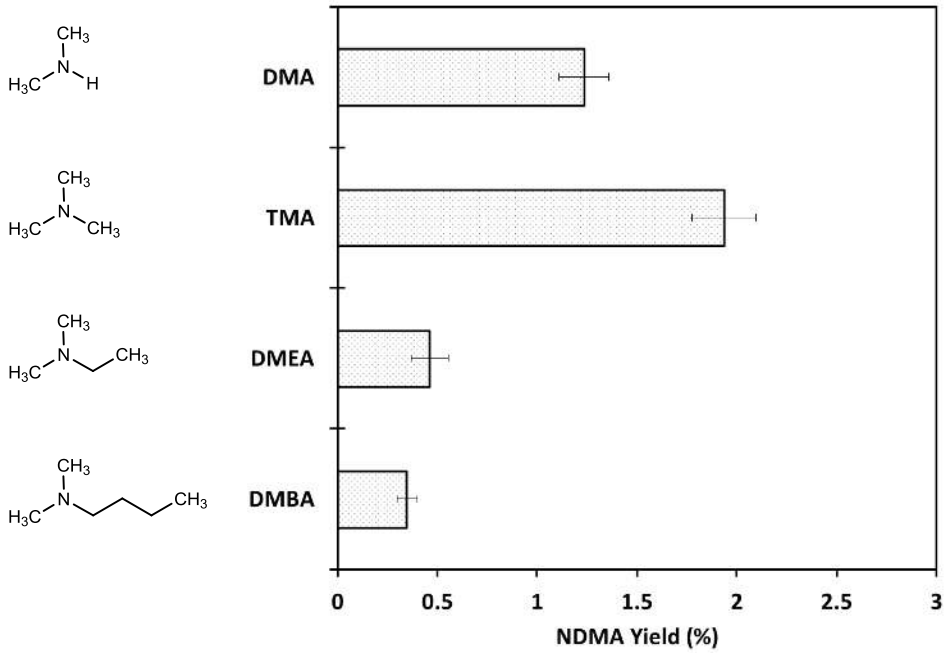


Figure 6.2. The effect of chain length (attached to DMA moiety) on NDMA formation. Error bars represent data range for duplicate samples.

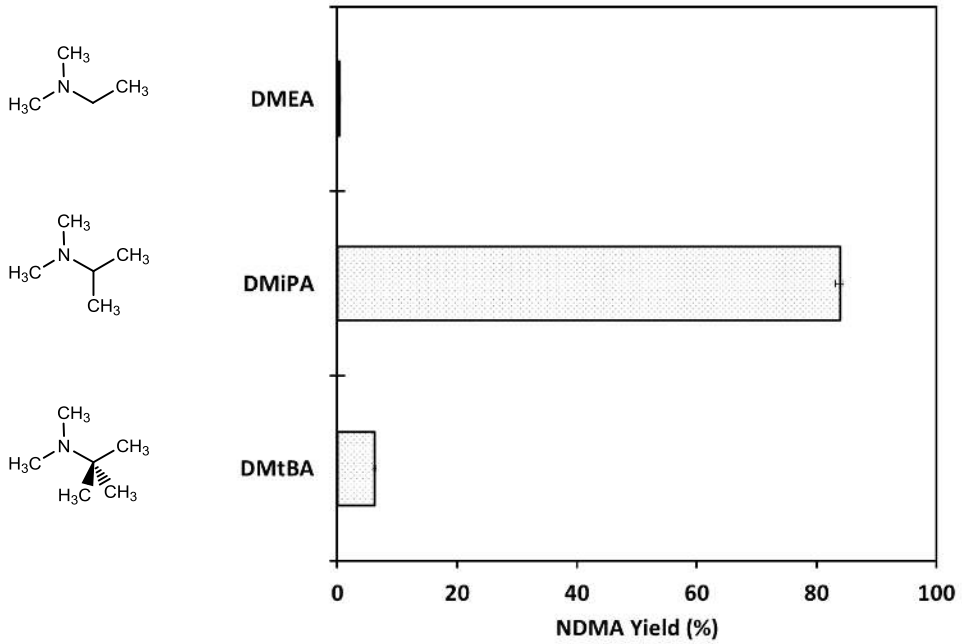


Figure 6.3. The effect of branched groups (attached to DMA moiety) on NDMA formation. Error bars represent data range for duplicate samples.

DMEA formed both NDMA and NMEA (data not shown in the graph) through N-C bond cleavage in N-CH_2CH_3 or N-CH_3, and their yields were 0.5% and 1%, respectively. Since DMEA has one N-CH_2CH_3 and two N-CH_3 in its molecular structure, it seems that there was no difference in N-C bond breaking tendency between N-CH_2CH_3 and N-CH_3. Variable functional groups such as CN, OH, NH_2, and SH located at C-1 and C-2 positions in the alkyl group attached to the DMA moiety (e.g., DMAAcCN, DMAEtOH, DMEDA, and DMAEtSH) were also investigated, and no changes in NDMA yields were observed compared to those of TMA and DMEA (**Figure 6.4**). Although very low NDMA yields were obtained for some compounds, the NDMA levels measured in extracts were always above the minimum reporting limit. Therefore, only aliphatic

tertiary amines with branched alkyl groups attached to $N(CH_3)_2$ showed a high yield of NDMA, possibly due to the stability of their leaving groups.

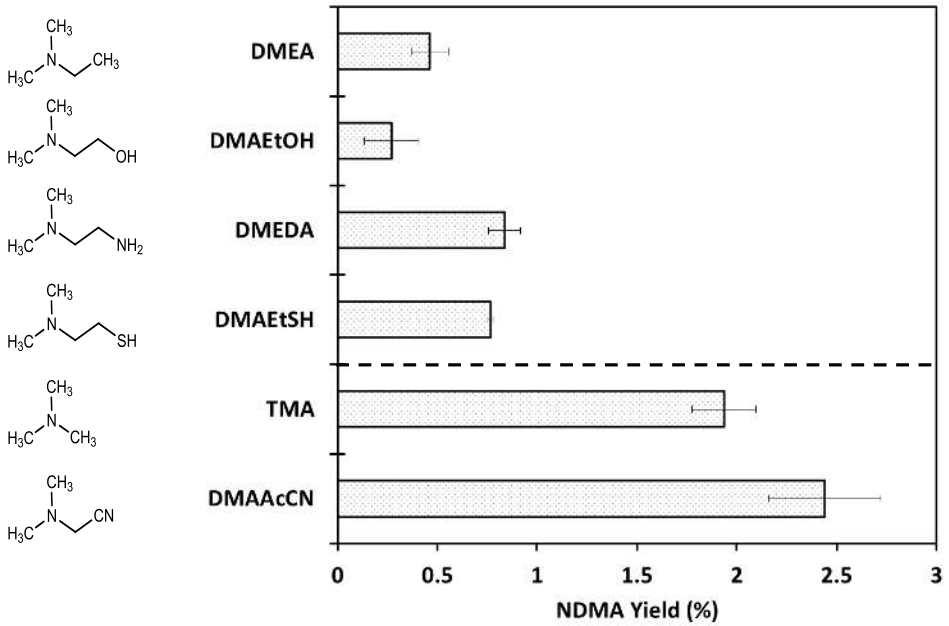


Figure 6.4. NDMA formation from DMEA and TMA and their derivatives. Error bars represent data range for duplicate samples.

Unlike aliphatic amine precursors, relatively high NDMA yields have been reported from chloramination of tertiary amines, where DMA structure is associated with benzyl-like functional groups (Lee et al., 2007a; Sacher et al., 2008; Shen and Andrews, 2011a,b). However, what causes such higher NDMA yields than DMA still remains unknown. In this study, DMBzA (84%), RTND (81%), DMAFuOH (82%), DMPMA (25%), and DMTMA (78%), which have only one carbon between the ring and the DMA structure, formed high levels of NDMA compared to the other compounds with two carbons (i.e., DMPhA) or no carbon (i.e., DMAN, 4-DMAP, 2-DMAP, DMAPhOH, and

2-Cl-DMAN) between them (**Figure 6.5**). The leaving groups from the former compounds (one carbon distance) are carbocations which can be greatly stabilized by resonance, whether heteroatoms (e.g., O, N, and S) are present or not in their rings. However, the latter group of compounds (zero or two carbon distance) which formed low NDMA do not have such advantages to stabilize carbocation intermediates. Thus, again, the stability of the leaving groups may be a critical factor controlling the reactivity of precursors towards NDMA formation. However, neither the assistance of an electron donating heteroatom nor the order of reactivity among N, S, and O was not observed in our experiments. Although, Sacher et al. (2008) conducted experiments under different conditions, their findings also showed that precursors with one carbon between the ring and the DMA structure had consistently high NDMA conversions (≥50%). On the other hand, compounds with DMA groups directly attached to a benzene ring gave NDMA yields lower than 10%.

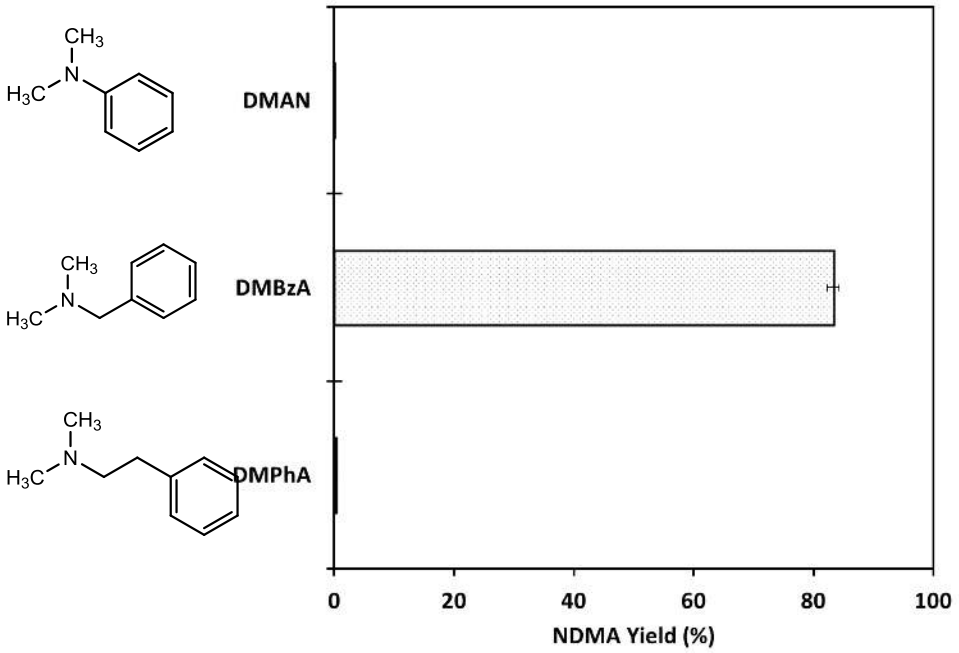


Figure 6.5. The effect of distance of the benzene ring (attached to DMA moiety) on NDMA formation. Error bars represent data range for duplicate samples.

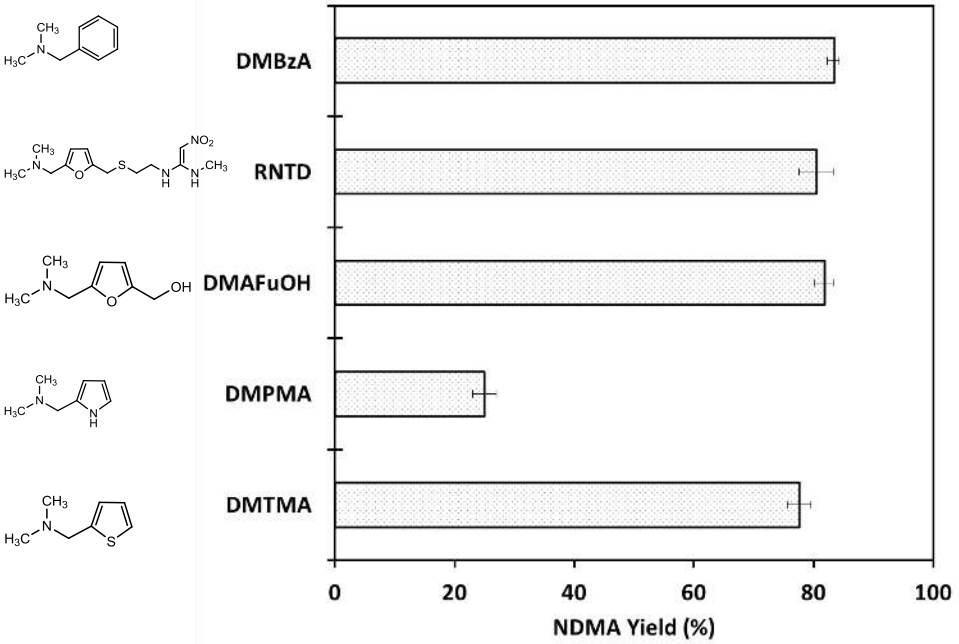


Figure 6.6. The effect of heteroatom in the benzyl group (attached to DMA moiety) on NDMA formation. Error bars represent data range for duplicate samples.

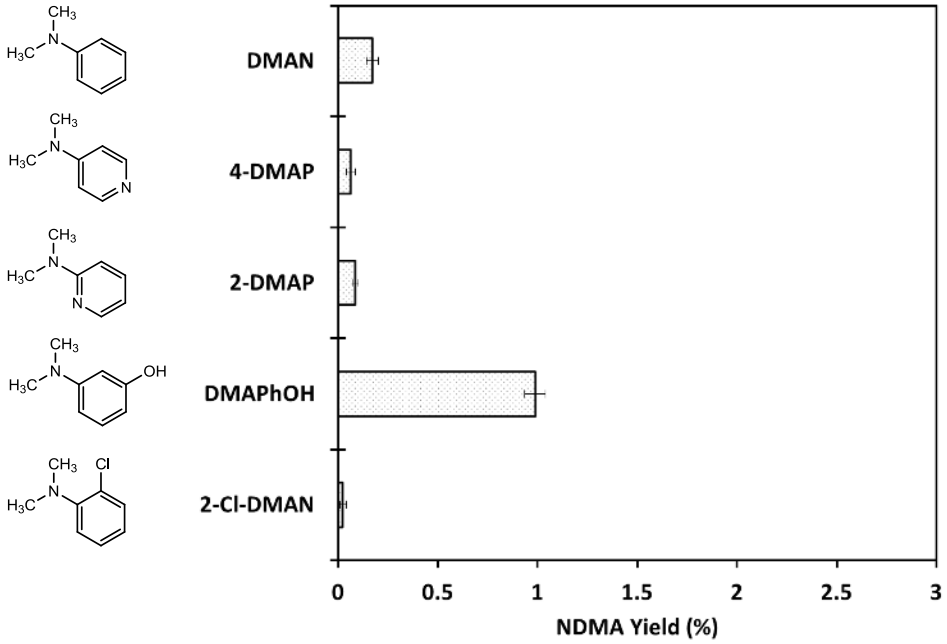


Figure 6.7. NDMA formation from DMAN and its derivatives. Error bars represent data range for duplicate samples.

The nitrogen atom in 5- (e.g., DMPMA) and 6-membered (e.g., 2- and 4-DMAP) ring structures is likely to reduce the electronegativity of aromatic rings, and consequently the NDMA yields decreased compared to their corresponding compounds (i.e., RNTD and DMAN). It was also observed that NDMA formation from DMAPhOH was higher than that of 2-Cl-DMAN.

In NDMA formation, the pK_a of precursors can be a factor for overall conversion. Deprotonated amines are expected to be more prone to reactions than protonated amines. However, the experimental results did not support this expectation. NDMA yields of TMA (pK_a of 9.8) and DMAAcCN (pK_a of 4.2) were very similar with NDMA yields of 1.9 and 2.4%, respectively. Similarly, DMAN, 4-DMAP, and DMAPhOH with pK_a of

5.1, 9.5, and 10.2, respectively, all showed NDMA yields lower than 1%. Although pK_a of the tertiary amine can have a role in NDMA formation, the stability of the structure appeared to govern the overall NDMA formation for the compounds examined in this study. Since the design (experiments were conducted at pH 7.5) and compound selection for this study were intended to examine mainly the structure effect, further research is warranted to examine the effect of pK_a.

Overall, these results suggest that the stability of leaving groups of both aliphatic and aromatic tertiary amines may play an important role in NDMA formation, which will allow us to understand the high yields of NDMA from certain precursor compounds based on information from their chemical structure. The NDMA formation yields determined for many compounds in this study (DMEA, DMBA, DMiPA, DMtBA, DMAAcCN, DMEDA, DMAEtSH, 4-DMAP, 2-Cl-DMAN, DMPhA, DMPMA, and DMTMA) are reported for the first time.

The Effect of NOM on NDMA formation

For practical applications in water and wastewater treatment, it is important to understand the interactions of the background matrix with NDMA precursors and their roles in NDMA formation. To test the NOM effect, two fractions of NOM were used which were available in our laboratory. HPO fraction of NOM contains organics high in aromaticity which are hydrophobic. TPH fraction of NOM contains organics low in aromaticity which transphilic. HPO fraction was used as a representative of the raw water; whereas, TPH fraction was used as a representative for the water after conventional treatment (i.e., coagulation/flocculation/sedimentation). The NDMA yields

for selected precursors in TPH and HPO solutions are given in **Figure 6.8** and **Figure 6.9**. NDMA formation in TPH (29 ng/L) was higher than in the HPO (7 ng/L) fraction which was consistent with the literature (Chen and Valentine, 2007; Dotson et al., 2009). These values were taken into account during calculation of NDMA yields of model compounds in NOM solutions. NDMA conversion from DMA and selected aliphatic tertiary amines showed a decrease in the presence of NOM. However, there was no significant change in NDMA yields for DMEA, DMBA and DMAEtOH (**Figure 6.8-A** and **-B**). The impact of NOM was higher in derivatives of DMEA and TMA (i.e., DMEDA, DMAEtSH, DMAAcCN) than other aliphatic compounds (**Figure 6.8-B**). In most cases, the least NDMA formation was observed in the presence of the TPH fraction. Unlike aliphatic compounds, NDMA formation from aromatic tertiary amines generally increased in the presence of both NOM fractions with the exception of DMPMA, DMTMA, and DMAPhOH (**Figure 6.9-A** and **-B**). Among aromatic tertiary amines that showed an increase, NDMA formation was higher in the presence of HPO than TPH fraction with the only exception of DMBzA which formed higher NDMA in TPH than in HPO solution. Although DMAN and its derivatives had no significant difference between the background of DDW and TPH solutions, NDMA yields from some of these compounds in HPO solution increased up to five times. Only DMAPhOH among DMAN derivatives showed lower NDMA yields in both NOM solutions than in DDW.

To date, the NOM effect on NDMA formation has not been systematically investigated except for RNTD. Shen and Andrews (2011a) have reported that NDMA yields from RNTD were 89.9% and 94.2% in DDW and tap water, respectively. These

results are consistent with the NDMA yields observed in this study, which were higher in the presence of NOM (89.1% in TPH and 91.7% in HPO) than in DDW (80.5%) (**Figure 6.9-A**). In another study by Shen and Andrews (2011b), the presence of NOM decreased formation of NDMA reaction rate within a 24 hour incubation period and the yield in NOM was lower than in DDW. The decrease in the reaction rate and NDMA yields in NOM background was attributed to a temporary reversible covalent bond formation between aromatic amines and functional groups of NOM (such as, carbonyls and quinones). Moreover, the researchers stated that NDMA conversion could still reach maximum levels, if enough reaction time was provided.

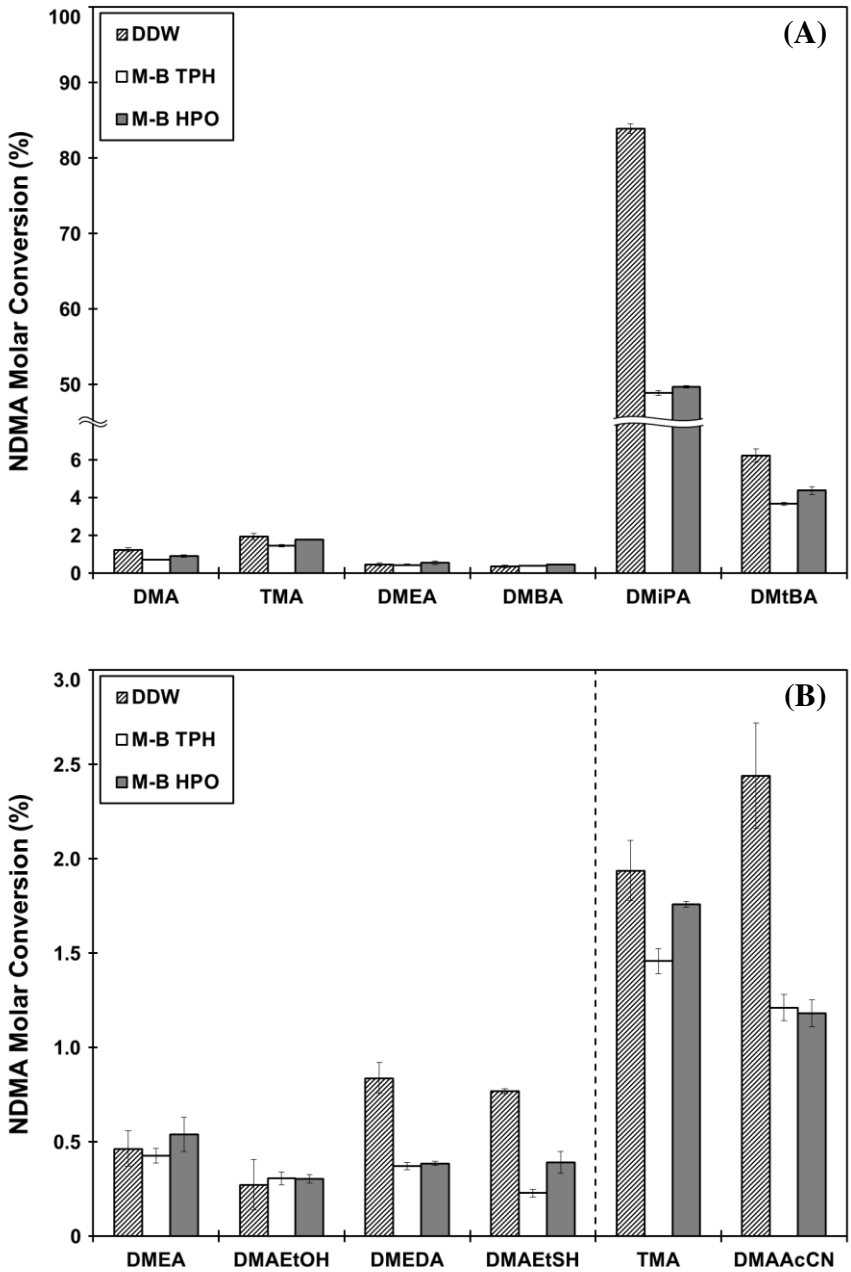


Figure 6.8. NDMA FPs for DMA and tertiary amines in DDW, M-B TPH and M-B HPO solutions. (A) Aliphatic amines with different chain lengths and branches. (B) DMEA and its derivatives and TMA and its derivative. Error bars represent data range for duplicate samples.

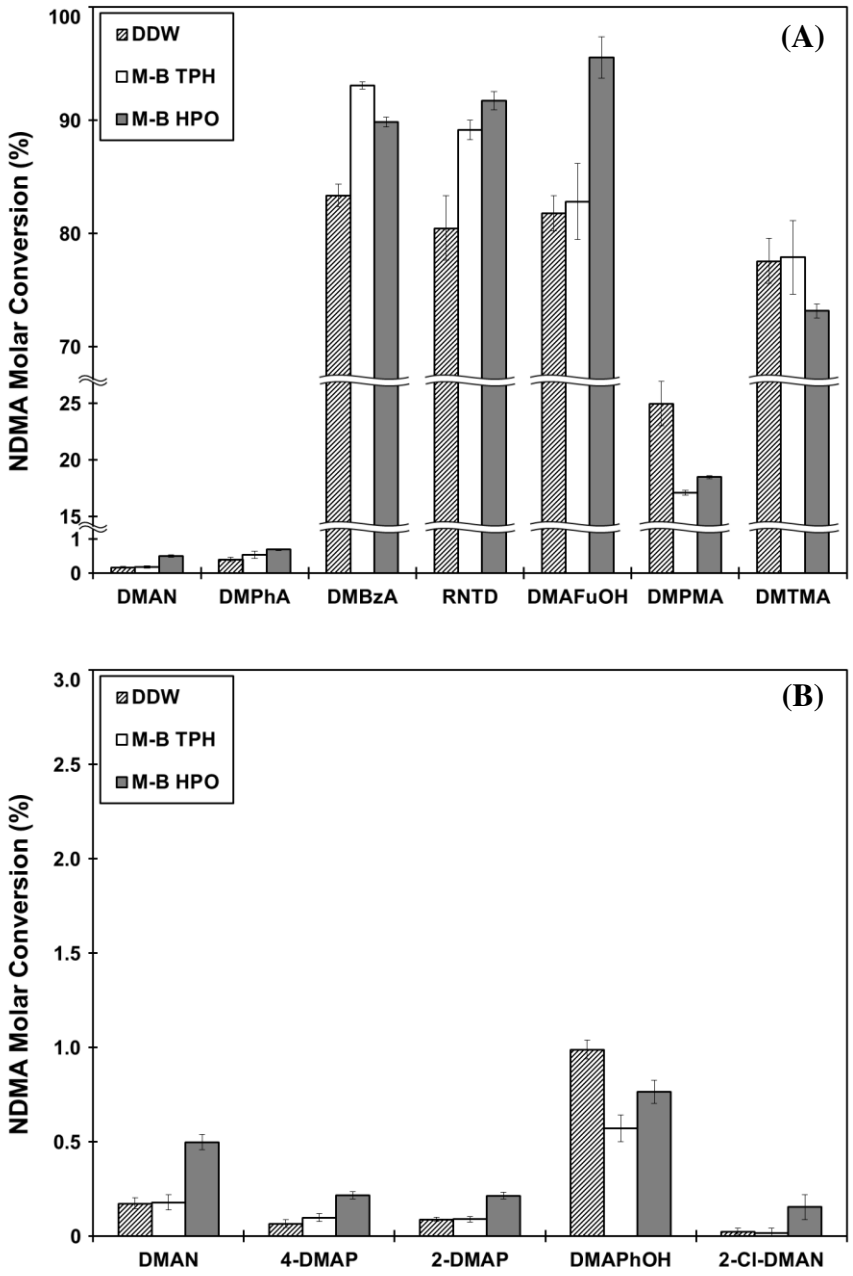


Figure 6.9. NDMA FPs for DMA and tertiary amines in DDW, M-B TPH and M-B HPO solutions. (A) Aromatic amines for comparison of distance of carbon ring and presence of heteroatom in carbon ring. (B) DMAN and its derivatives. Error bars represent data range for duplicate samples.

For selected compounds (i.e., DMA, TMA, DMiPA, DMBzA, and RNTD), the NOM effect was also tested in natural waters (M-B Raw and M-B Treated water), and the results are provided in **Figure 6.10**. Highest NDMA yields from DMA, TMA, and DTMiPA were observed in M-B Raw water, while DMBzA and RNTD formed the highest NDMA in M-B treated water, which was in good agreement with the results of the HPO/TPH experiments. Therefore, the effect of inorganic components in M-B water on NDMA formation appear to be negligible.

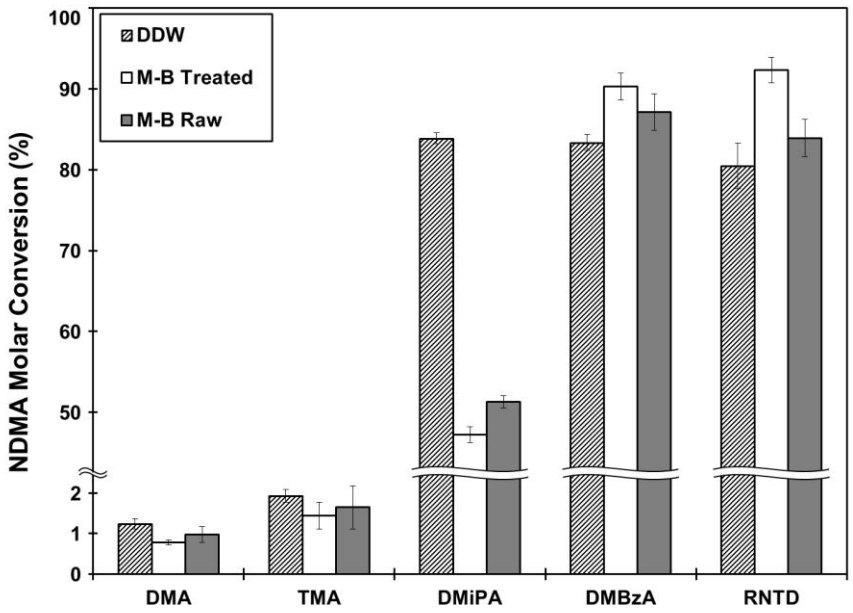


Figure 6.10. NDMA molar conversion of selected amines in DDW, M-B Treated and M-B Raw background solutions. Error bars represent data range for duplicate samples.

RNTD and other aromatic compounds which have electron-withdrawing groups (EWGs) such as methyl furan and benzyl exhibited higher NDMA yields in the presence of NOM. On the contrary, DMPMA and aliphatic tertiary amine compounds with electron-donating groups (EDGs) such as methyl pyrrole and alkyl formed less NDMA in the presence of NOM. This is probably because of competition between precursors and negatively charged NOM in the reaction matrixes for chloramine species. However, the NOM effect was not obvious in the case of DMTMA which has a methyl thiophene (an EWG). NDMA formation from DMTMA increased in TPH and decreased in HPO solution. Therefore, the interactions between NDMA precursors and NOM need to be considered as an important factor affecting NDMA formation in natural waters.

Both mono- and dichloramine have been shown to react with different compounds (phenols, organophosphates, etc.) at different rates (Heasley et al., 2004; USEPA, 2008). Therefore, different chloramine reactivity with different moieties can create competition in the presence of amines. In our experiments, dichloramine was always detected (2-3 mg/L) due to decomposition of monochloramine at pH 7.5 in DDW control bottles. The observation of lower dichloramine levels in TPH and HPO waters as compared to DDW can be attributed to the reactions of dichloramine with NOM. Since the reaction of DMA with dichloramine has been known as a major pathway to form NDMA (Schreiber and Mitch, 2005, 2006; Mitch et al., 2009), a competition for dichloramine in the presence of NOM could account for the differences observed in overall NDMA conversions.

The Effect of Chloramine Species on NDMA Formation

Although monochloramine is dominant at pH 7.5, trace level of dichloramine is also present and NDMA formation may be affected by the reaction of dichloramine with DMA. To further investigate the effect of chloramine species on the formation of NDMA, an excess amount of ammonia was used to minimize the formation of dichloramine according to **Equation 6.2**.

$$2\ NH_2Cl + H^+ \leftrightarrow NHCl_2 + NH_4^+ \qquad \textbf{Equation 6.2}$$

In the samples spiked with ammonia, dichloramine was not observed during five days of contact time as shown in **Figures C.1-C.3**, thus NDMA formation in these samples were mainly attributed to monochloramine. Eight tertiary amines (TMA, DMiPA, DMtBA, DMBzA, RNTD, DMAFuOH, DMPMA, and DMTMA) were selected and FP tests were conducted with and without ammonia addition. The effects of chloramine speciation on NDMA conversion from these compounds are presented in **Figure 6.11**. By addition of ammonia, the NDMA yield from DMA decreased from 1.7% to 0.97% which indicates the importance of dichloramine but also involvement of monochloramine in NDMA formation. The change in NDMA FP in the presence of background ammonia was drastic for TMA, DMiPA and DMtBA as their yields decreased from 0.43% to 0.03%, 61.2% to 5.8% and 1.84% to 0.07%, respectively, indicating that dichloramine was more important species than monochloramine to form NDMA. However, for DMBzA, DMAFuOH, and DMTMA which are aromatic tertiary amines producing high yields (>90%) of NDMA, the effects of dichloramine on NDMA yields were less than the aliphatic precursors. Therefore, DMBzA, DMAFuOH, and

DMTMA reacted with both mono- and dichloramine, but mostly with monochloramine to form NDMA. Interestingly, RNTD showed an insignificant change in NDMA formation with and without ammonia addition probably because of its high monochloramine-reactive nature. This observation is also consistent with study by Le Roux et al. (2011, 2012b) that showed monochloramine was responsible for NDMA formation from RNTD. DMA, TMA, DMiPA, and DMtBA which were sensitive to dichloramine have EDGs in their structures, whereas DMBzA, RNTD, DMAFuOH, and DMTMA which have EWGs attached to the DMA moiety were sensitive to monochloramine. The results support the hypothesis that the reactivity of tertiary amines with chloramines (mono- and di-) toward NDMA formation is dependent on the electron distribution of precursors.

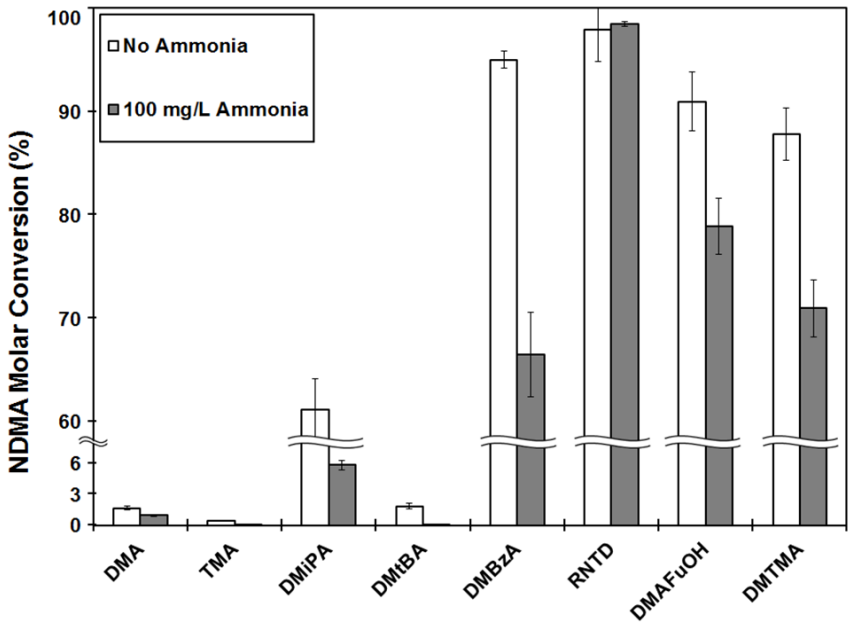


Figure 6.11. NDMA formations from selected compounds reacted with monochloramine in the presence of excess ammonia and with mixture of mono- and dichloramine under regular chloramination conditions. Error bars represent data range for duplicate samples.

Considering the observation that tertiary amine precursor compounds react with both mono- and dichloramine to form NDMA, and the preference of chloramine species depends on the structure of the leaving group attached to the nitrogen atom of the DMA moiety, we postulate that the initial step of NDMA formation is nucleophilic attack of amines on chloramines and the preference of the chloramine species depends on the electron densities of the precursors and oxidants (**Figure 6.12**). Electron poor nitrogen of tertiary amines with EWG reacts with monochloramine which has electron rich nitrogen to form the N-N bond. Likewise, electron rich nitrogen of tertiary amines reacts with dichloramine with electron poor nitrogen to form the N-N bond. The reaction proceeds with the release of the leaving group forming a carbocation which was reported for the NDMA formation from RNTD by Le Roux et al. (2012b). Hence, a stable leaving group would facilitate these reactions towards NDMA formation. Both electronegativity and stability of the leaving group in tertiary amines are closely related with the reactivity of NDMA precursors and the preferred chloramine species involved in the NDMA formation reactions.

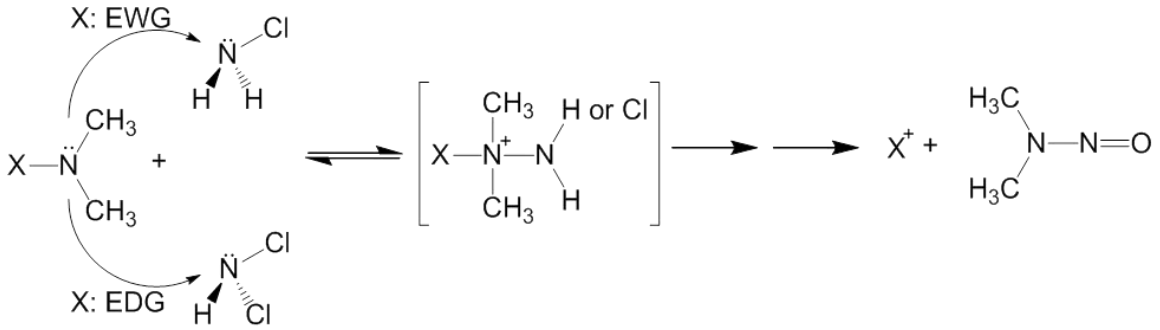


Figure 6.12. Schematic diagram depicting interaction of tertiary amine with chloramine followed by end products such as carbocation and NDMA.

Conclusions

A fairly wide range (0.02% to 83.9%) of NDMA formation from 21 selected amines indicated the importance of the structure of tertiary amines on NDMA formation. The results showed that both stability and electron distribution of the leaving group of the tertiary amines have an important role in NDMA formation. The DMA moiety associated with branched alkyl groups or benzyl like structures, which have only one carbon between the ring and DMA structure, consistently gave high yields of NDMA formation (>25%). Compounds with EWG reacted preferentially with monochloramine, whereas compounds with EDG showed a tendency to react with dichloramine to form NDMA. These findings indicated that characteristics of tertiary amines would determine the responsible chloramine species for NDMA formation. Tertiary amines can form NDMA with or without degradation to DMA, and the overall yield depends on the stability of the leaving group. When the amines were present along with NOM in solution, NDMA formation increased for compounds with EWG while it decreased for compounds with EDG. This impact was attributed to the competition between NOM and amines for chloramine species.

CHAPTER SEVEN

THE ROLE OF CHLORAMINE SPECIES IN NDMA FORMATION

Introduction and Objective

Nitrosamines are considered as an emerging DBP in drinking water, as they are classified as probable human carcinogens associated with a 10^{-6} lifetime cancer risk at concentrations as low as 0.2 ng/L (USEPA, 1993). Nitrosamine formation is commonly associated with water distribution systems that apply chloramine as the post-oxidant (Choi and Valentine, 2002a,b; Choi et al., 2002; Mitch et al., 2003a,b; Russell et al., 2012), and among the nitrosamines, 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, 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, 2006). Furthermore, USEPA has recently identified nitrosamines as one of three potential groups of contaminants highlighted for possible regulatory action in the near future (Roberson, 2011).

DMA has been the most commonly studied model precursor of NDMA (Mitch et al., 2003a; Bond and Templeton, 2011) and frequently detected in natural waters. However, several studies have shown that DMA concentrations in surface waters

(Gerecke and Sedlak, 2003; Lee et al., 2007a) or secondary municipal wastewaters (Mitch and Sedlak, 2004) were inadequate to explain the observed levels of NDMA. Rather than DMA, tertiary or quaternary amines with the DMA moiety (Lee et al., 2007a; Kemper et al., 2010; Shen and Andrews, 2011a), NOM (Gerecke and Sedlak, 2003; Mitch and Sedlak, 2004; Chen and Valentine, 2007; Dotson et al., 2007; Krasner et al., 2008a), and anthropogenic organic materials have been shown to form NDMA. Potential anthropogenic sources of NDMA precursors include polyelectrolytes and ion-exchange resins (Gough et al., 1977; Kimoto et al., 1980; Najm and Trussell, 2001; Kohut and Andrews, 2003; Wilczak et al., 2003; Mitch and Sedlak, 2004; Nawrocki and Andrzejewski, 2011; Gan et al, 2013a,b), fungicides, pesticides, and herbicides (Graham et al., 1995; Chen and Young, 2008; Schmidt and Brauch, 2008), pharmaceuticals, personal care products, and cosmetics (Sacher et al., 2008; Shen and Andrews, 2011a), and wastewater effluent impacted waters (Sedlak et al., 2005; Krauss et al., 2009; Shah et al., 2012; Gan et al, 2013a,b).

Understanding formation kinetics is essential to develop strategies for controlling NDMA and other nitrosamines in drinking water distribution systems. It has been reported that NDMA formation in natural and wastewater impacted waters was relatively slow, and further NDMA could continue to form in distribution systems as water age increased (i.e., a plateau was reached after 150-200 hours of chloramine contact time) (Barrett et al., 2003; Charrois and Hrudey, 2007, Sacher et al., 2008; Krasner et al., 2010; Russell et al., 2012). Since various precursors with different reactivity are present in source waters, it is not simple to explain what causes this slow NDMA formation. Only a

few studies, focusing on specific model compounds, have investigated the following factors which may control the NDMA formation rate: (i) the effect of temperature and pH on RNTD (Krasner et al., 2010); and (ii) the effect of NOM and pH on selected pharmaceuticals including RNTD (Shen and Andrews, 2011b, 2013a). Although, these factors had some influence on the NDMA formation rate, the NDMA formation reached its maximum yield within a relatively short time (i.e., plateau reached after 24 hours with RNTD). Thus, findings from selected model precursor compounds so far are insufficient to explain the observed trends in natural water samples. Overall, data regarding the NDMA formation rate both in real water samples, and from model compounds are largely lacking.

The main objective of this study was to investigate: (i) the role of chloramine species (i.e., mono- and dichloramine) in the formation of NDMA from DMA and selected tertiary amine precursors; (ii) the factors that may influence dichloramine levels (i.e., pH, sulfate and NOM); and (iii) the role of mono- and dichloramine during NDMA formation in selected natural waters. Four tertiary amines were selected based on their structures. NDMA formation rates (i.e., time to reach the plateau) were monitored from selected model compounds in three parallel experiments with varying amounts of dichloramine. Based on the results, two amines were selected due to their extreme sensitivity to specific chloramine speciation and the effects of pH, sulfate and NOM were further examined. Since chloramine speciation could also be an important factor in natural samples; the impact of chloramine species was examined in water from a watershed, and in water from a drinking water treatment plant.

Materials and Methods

Amines

DMA and four tertiary amines were selected as model precursors based on their electron distribution and sensitivity to chloramine species as demonstrated in the previous chapter. Chemical structures and abbreviations of selected amines are given in **Figure 7.1**. All compounds were purchased from Sigma-Aldrich, and TCI and used without further purification.

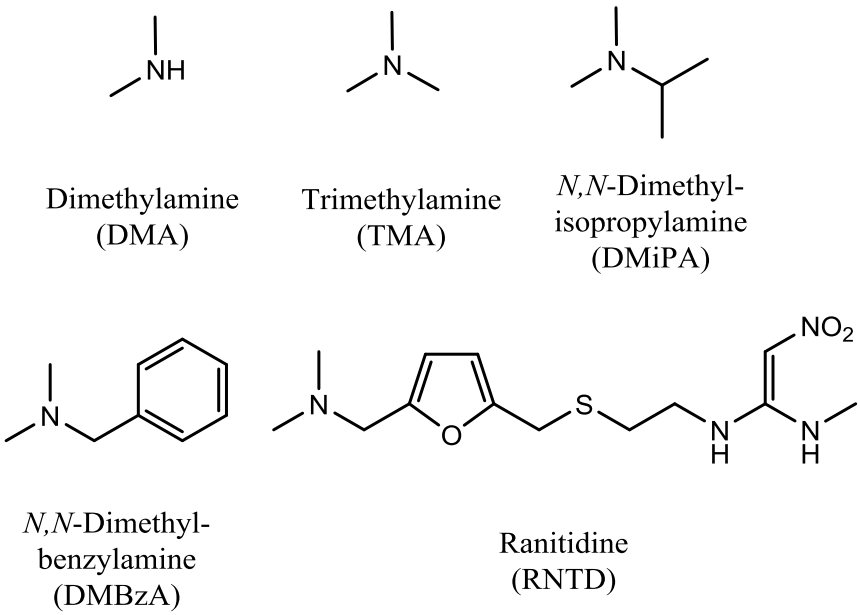


Figure 7.1. Molecular structures of selected amines.

Experimental Procedure

A stock solution (4 mM) for each amine was prepared in methanol and stored in a 65 mL amber glass bottle at 4ºC until use. Each model compound was diluted to 200 nM in DDW. The role of chloramine species was investigated by conducting three parallel experiments under the following conditions: (i) FP experiments with an initial chloramine dose of 100 mg/L, (ii) simulated distribution system (SDS) experiments with an initial dose of 3 mg/L chloramine, and (iii) SDS experiments with an initial dose of 3 mg/L in the presence of 100 mg/L ammonia to suppress the formation of monochloramine to dichloramine (**Equation 6.2**) (Some additional information about the chloramine chemistry can be found in the **Appendix A**). In these experiments to keep the pH constant at 7.5, 10 mM phosphate buffer was used in FP experiments and 4 mM carbonate buffer was used in SDS experiments. The preformed chloramine stock solution was prepared by mixing diluted sodium hypochlorite and ammonium sulfate solutions at Cl:N mass ratio of 4:1 at pH 9 and spiked to the samples. After the injection of chloramine solution into eight identical amber bottles, bottles were opened at 3, 6, 12, 24, 48, 72, and 120 hours to measure NDMA formation and residual chloramine.

The factors that may influence chloramine decomposition and speciation were assessed under SDS conditions for two amines (DMiPA and RNTD). First, the effect of NOM was investigated in background solutions that were prepared using raw water, and treated water collected after coagulation/flocculation/sedimentation processes before filtration from the Charleston (CH) DWTP in South Carolina. Water samples were filtered immediately with pre-washed 0.2 µm polyethersulfone filters. DOC levels of all

NOM solutions were adjusted to 1.5, 3.0 and 6.0 mg C/L by diluting with DDW. The selected characteristics of NOM solutions are shown in **Table 7.1**. Second, the pH effect was investigated by adjusting the pH of DDW to 6.5 and 8.5. And lastly, the effect of sulfate was investigated in DDW by spiking sodium sulfate to achieve 10, 25 and 50 mg/L sulfate concentrations.

Table 7.1. Selected water quality parameters of the natural water samples.

	DOC (mg C/L)	$SUVA_{254}$ (L/mg.m)	DN (mg N/L)	NH_3 (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	SO_4^{-2} (mg/L)	Br^- (µg/L)
CH Raw[a]	6.3	3.3	0.3	<MRL	<MRL	0.35	6.3	75
CH Treated[b]	2.8	1.7	0.2	<MRL	<MRL	0.28	36.8	75
Upstream	1.5	3.0	0.6	<MRL	<MRL	2.25	1.2	19
WW Effluent	7.8	1.9	18.2	<MRL	0.195	73.50	52.0	162
Downstream	2.0	2.8	2.7	<MRL	<MRL	11.19	6.1	33

a: In background NOM experiments this water was diluted to DOC of 1.0, 2.5, & 5.0 mg C/L using DDW.
b: In background NOM experiments this water was diluted to DOC of 1.0, & 2.5 mg C/L using DDW.
Reported values are average of two measurements (n=2).

CH Raw and CH Treated were used without any dilution. For a case study, a wastewater-impacted creek was selected and samples were collected at three different positions (i.e., upstream of a 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., 2013b). Selected characteristics of natural water samples are also given in **Table 7.1**. 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 in this study were conducted in 1-L amber glass bottles without headspace in the dark at ~22°C.

Analytical methods

NDMA was analyzed following USEPA method 521 (USEPA, 2004), consisting of SPE using coconut charcoal followed by GC-MS/MS analysis. Analytical details can be found in the previous section and a brief summary follows. For the sample analysis, 500 mL of chloraminated amine solutions were quenched with sodium thiosulfate and NDMA-d_6 was added as a surrogate before SPE. Samples were passed through coconut charcoal cartridges preconditioned with DCM, methanol, and DDW. The cartridges were dried with air, and then eluted with DCM. Eluents were passed through sodium sulfate columns to remove residual moisture, then concentrated to 1 mL under a gentle stream of high purity nitrogen gas. The extracts were spiked with NDPA-d_{14} as an internal standard, and analyzed using a Varian GC-MS/MS 4000 under the CI mode. Percent molar yield of each amine was calculated using **Equation 6.1** (**Appendix B**).

DOC and DN were determined using a Shimadzu TOC-V_{CSH} instrument equipped with a Total Nitrogen module (TNM-1). UV_{254} absorbance of NOM samples was measured using a Varian Cary-50 spectrophotometer, and used to calculate $SUVA_{254}$ values. Ammonia concentrations were measured with a HACH spectrophotometer. Nitrite, nitrate, bromide, and sulfate were measured using ion chromatography (Dionex, ICS 2100). Concentrations of free chlorine, and mono- and dichloramine as free chlorine were determined following SM 4500-Cl F (APHA/AWWA/WEF, 2005). All analytical methods and their MRLs are given in **Table 4.1**. All samples and blanks were prepared, extracted and analyzed in duplicates. Error bars in all the graphs show the variability due to multiple analysis (n=2).

Results and Discussion

NDMA Conversion from Selected Model Compounds

Figures 7.2 through **7.6** shows the NDMA molar conversion from DMA and four tertiary amines over reaction time under three different chloramination conditions: FP, SDS, and SDS in the presence of excess ammonia. Residual chloramine concentrations are given **Appendix D**. In FP tests, an excessive dose of chloramine (i.e., 100 mg/L) was used to produce both monochloramine (~95%) and dichloramine (~5%) at a given pH and each chloramine species was enough to form NDMA from selected amines. Thus, under FP test conditions, the NDMA conversion rates from all model compounds were relatively fast. The maximum NDMA formation was achieved within 24 hours of chloramination and no additional formation was observed. The NDMA yields obtained at 120 hours from these precursors were in a good agreement with those reported by other research groups (Lee et al., 2007a; Sacher et al., 2008; Mitch et al., 2009; Shen and Andrews, 2011a,b; Le Roux et al., 2012b) despite some differences in experimental conditions (**Table 6.3**).

For DMA, NDMA conversion yields under SDS conditions did not decrease significantly compared to FP tests (**Figure 7.2**). However, overall NDMA yield after 120 hours of reaction time decreased from 1.1% in FP test to 0.8% under SDS conditions. Even though the difference is trivial, this change could be caused by the limited availability of the dichloramine. Further decreases in dichloramine concentration in the presence of excess ammonia resulted in only 0.2% NDMA molar conversion after 120

hours. Although the reaction with dichloramine via the Cl-UDMH pathway is the most commonly accepted pathway for the NDMA formation from DMA, the observed slow and low NDMA conversion yields in the presence of ammonia indicate the NDMA formation via nucleophilic substitution reactions between monochloramine and DMA via UDMH intermediates could be an alternative pathway to form NDMA (Mitch and Sedlak, 2002; Choi and Valentine, 2002a,b; Mitch et al., 2009).

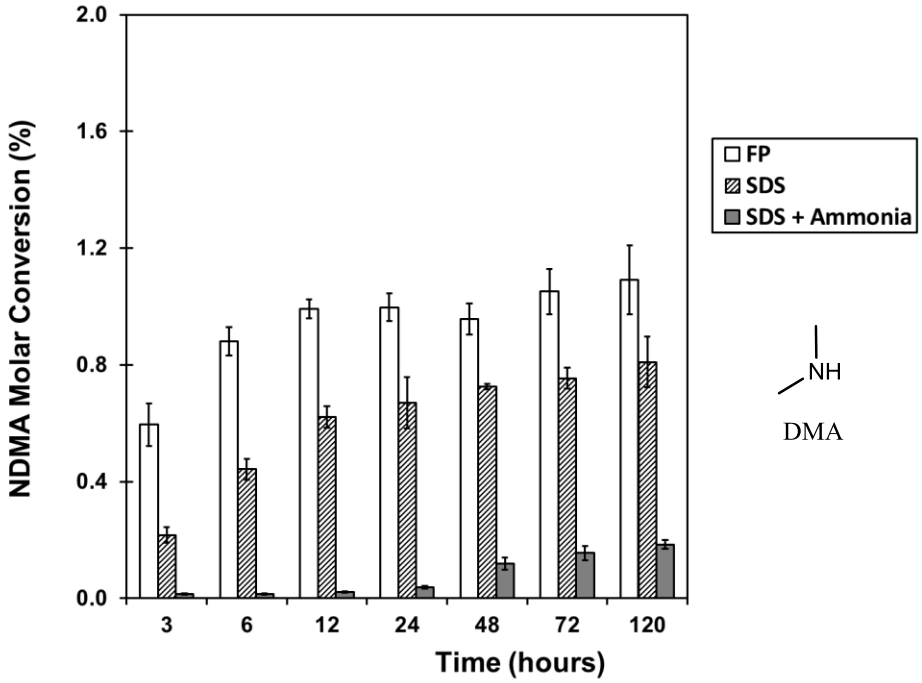


Figure 7.2. NDMA formation from DMA tested under three chloramination conditions: FP, SDS, and SDS in the presence of excess ammonia. Error bars represent data range for duplicate samples.

The NDMA formation rates from DMiPA and TMA both decreased significantly under SDS chloramination conditions compared to FP tests (**Figure 7.3** and **7.4**). Methyl or isopropyl functional group is likely to donate electrons to the nitrogen atom. Therefore, the electron-rich nitrogen atoms in DMiPA and TMA tend to react with dichloramine species where the electron density of nitrogen is reduced by two chlorine atoms rather than monochloramine which has only one chlorine to withdraw electrons. Consequently, NDMA formation from both amines is expected to be limited by the availability of dichloramine species. Since dichloramine concentration was much lower in the SDS test than FP, the transformation of monochloramine to dichloramine would be a limiting factor for NDMA formation. Conversion of monochloramine to dichloramine is a reversible reaction. However, the forward reaction from monochloramine to dichlroamine can be suppressed by an excess amount of ammonia. In the presence of excess ammonia under SDS conditions, the NDMA conversion yields from DMiPA and TMA were 0.3 and 0.1% at 120 hours, respectively, indicating that dichloramine is the dominant species in the NDMA formation from these two amines.

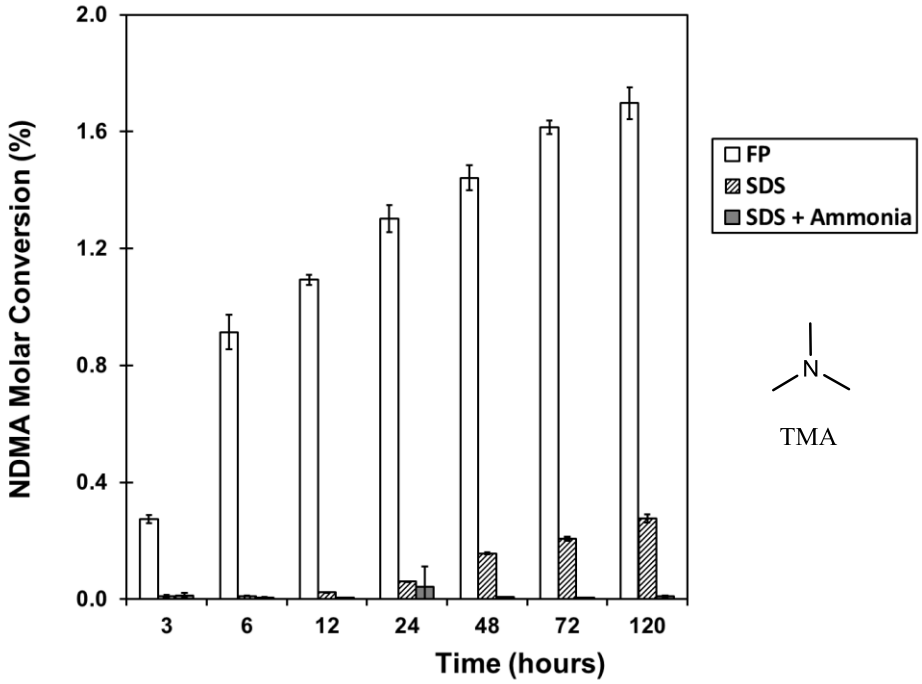


Figure 7.3. NDMA formation from TMA tested under three chloramination conditions: FP, SDS, and SDS in the presence of excess ammonia. Error bars represent data range for duplicate samples.

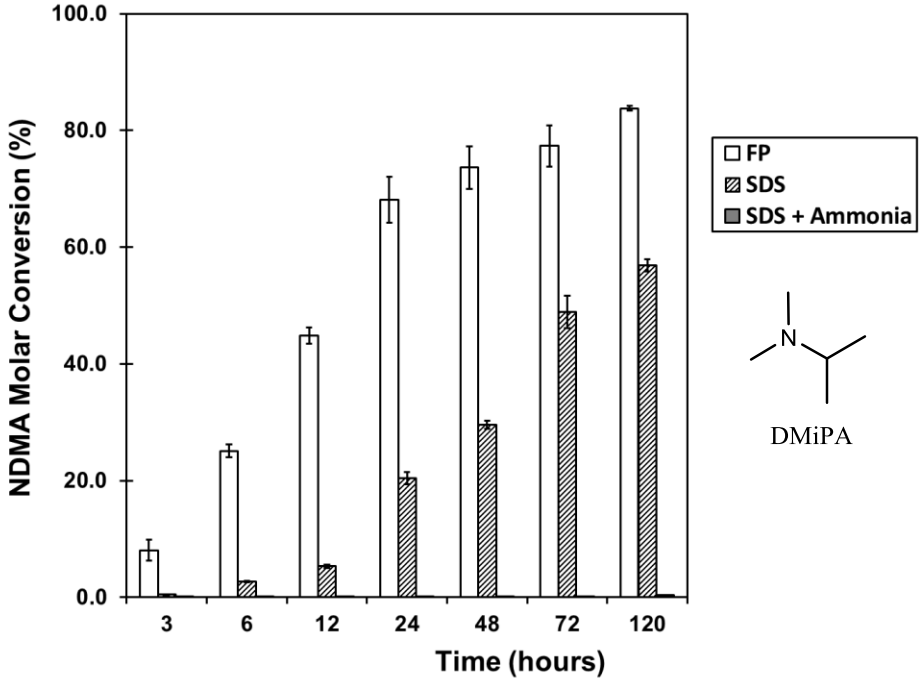


Figure 7.4. NDMA formation from DMiPA tested under three chloramination conditions: FP, SDS, and SDS in the presence of excess ammonia. Error bars represent data range for duplicate samples.

Under FP or SDS conditions, the NDMA conversion yield from DMBzA reached at its maximum (~80%) within 24 hour of chloramination (**Figure 7.5**). However, the NDMA yield reduced to 36.2% at 120 hours under SDS conditions in the presence of excess ammonia. During nucleophilic substitution reactions, benzyl group ($C_6H_5CH_2$-) of DMBzA could be a good leaving group resulting in high NDMA formation yields. The decrease in the NDMA conversion yields in the presence of excess ammonia indicates that dichloramine was a more important species than monochloramine toward NDMA formation from DMBzA.

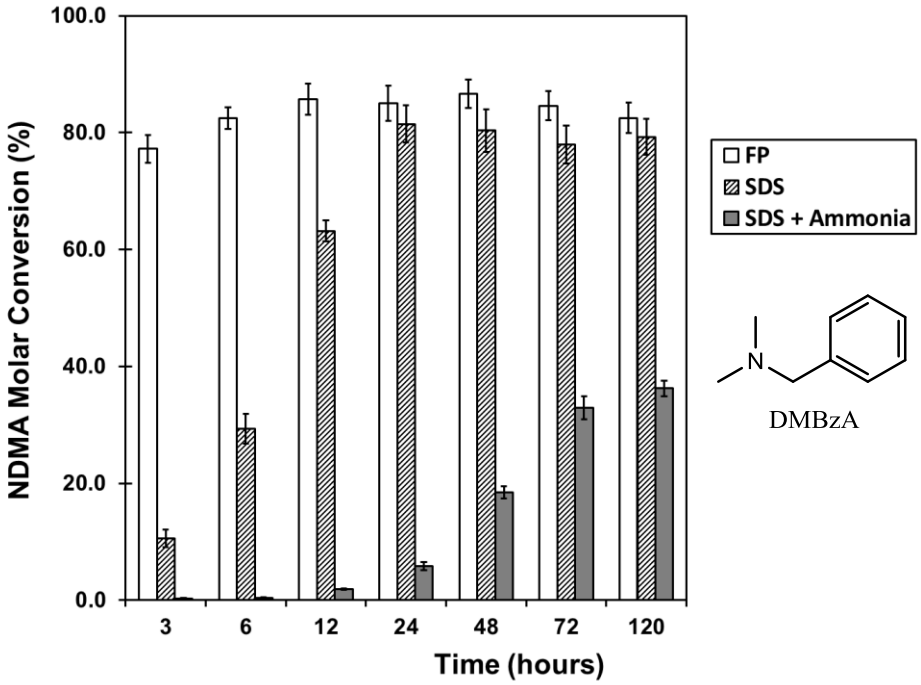


Figure 7.5. NDMA formation from DMBzA tested under three chloramination conditions: FP, SDS, and SDS in the presence of excess ammonia. Error bars represent data range for duplicate samples.

The furan ring next to the DMA moiety of RNTD is also a good leaving group, and thus RNTD is likely to react with monochloramine having electron-rich nitrogen rather than dichloramine as indicated in the previous section. It has been reported that RNTD formed NDMA via nucleophilic substitution by monochloramine (Le Roux et al., 2012b). The NDMA conversion yield under both FP and SDS conditions reached its maximum (~80%) within 24 hours and remained until 120 hours (**Figure 7.6**). Since monochloramine is the dominant chloramine species under SDS conditions at the given pH, there was no distinguished change observed in the NDMA conversion yields from RNTD between FP and SDS conditions. Therefore, further changes in the NDMA formation by suppression of dichloramine with excess ammonia were not expected and overall yields under three different chloramination conditions were almost same. However, the NDMA conversion yield within initial 24 hours of chloramination with ammonia was only 62.9% and it took longer time to reach its maximum. The results indicate that monochloramine, a dominant species, is more important to form NDMA than dichloramine, but dichloramine may also make contribution to NDMA formation from RNTD to some extent. This is consistent with findings from an ongoing project that the activation energy of the reaction of monochloramine with RNTD is more favorable than with dichloramine but dichloramine is still capable of reacting with RNTD to form NDMA (Liu et al., 2014).

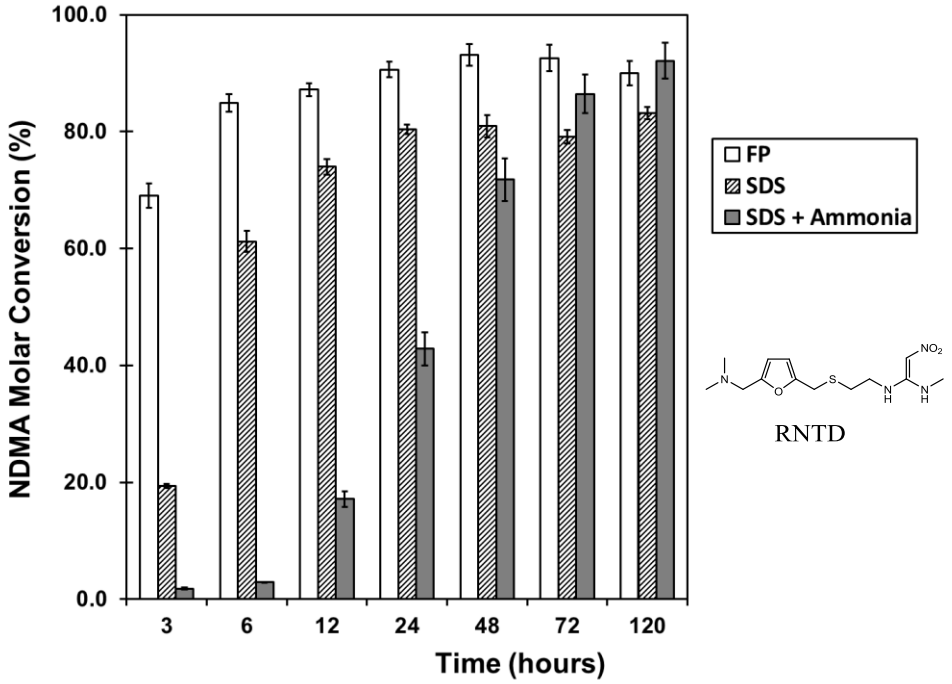


Figure 7.6. NDMA formation from RNTD tested under three chloramination conditions: FP, SDS, and SDS in the presence of excess ammonia. Error bars represent data range for duplicate samples.

Overall, the results suggest that the NDMA formation from the reaction of amine compounds with chloramines is dependent on the electron distribution of the leaving group of amines. Based on the structure, the theoretical electron densities of leaving groups in the selected amines is expected to follow the order of DMiPA>TMA>DMA>DMBzA>RNTD. This trend was also reflected in the sensitivity to chloramine species, which will allow us to understand the NDMA conversion yields from certain precursor compounds based on their chemical structure information.

Factors that Influence the NDMA Conversion over Time

NOM Effect: To investigate the NOM effect on the NDMA formation, water samples collected from CH DWTP were used as background matrix. It is well known that HPO is a major fraction of NOM in raw waters, while NOM in treated waters (i.e., after coagulation/flocculation/sedimentation) contains mostly TPH and hydrophilic fractions (Croue et al., 1993; Kim and Yu, 2005; Karanfil et al., 2007). Thus, selected amines spiked in raw and treated waters could interact with NOM fractions (i.e., HPO and TPH) toward NDMA formation. It is crucial to understand possible interactions of background NOM with NDMA precursor compounds, because various characteristics of NOM 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 over reaction time at different DOC levels of CH raw and treated waters are given in **Figure 7.7** and **7.8**.

In the case of RNTD, it has been known that, monochloramine is the dominant chloramine species responsible for NDMA formation (Le Roux et al, 2012b). At the DOC levels of 1.0 and 2.5 mg C/L of CH treated water, there were no significant changes in NDMA conversion yields indicating that TPH-dominated NOM did not compete with RNTD for monochloramine (**Figure 7.7-A**). On the other hand, the NDMA conversion yields from DMiPA were reduced drastically in the presence of TPH-dominated NOM (**Figure 7.7-B**). The NDMA yields at 120 hours decreased from 56.9% in DDW to 32.0 and 9.1% in the presence of 1.0 and 2.5 mg C/L DOC, respectively. These decreases

resulted probably from the competition of NOM with DMiPA for dichloramine. Similar NOM effects have been observed even under FP conditions (i.e., chloramine dose of 100 mg/L) in the previous section. NOM can facilitate monochloramine consumption (Vikesland et al., 1998). Since the electron density on the nitrogen atom of dichloramine is less than on the monochloramine's nitrogen, dichloramine could be the preferential species to react with negatively charged NOM. Thus, the interaction between dichloramines and NOM could reduce available dichloramine to react with amines to form NDMA.

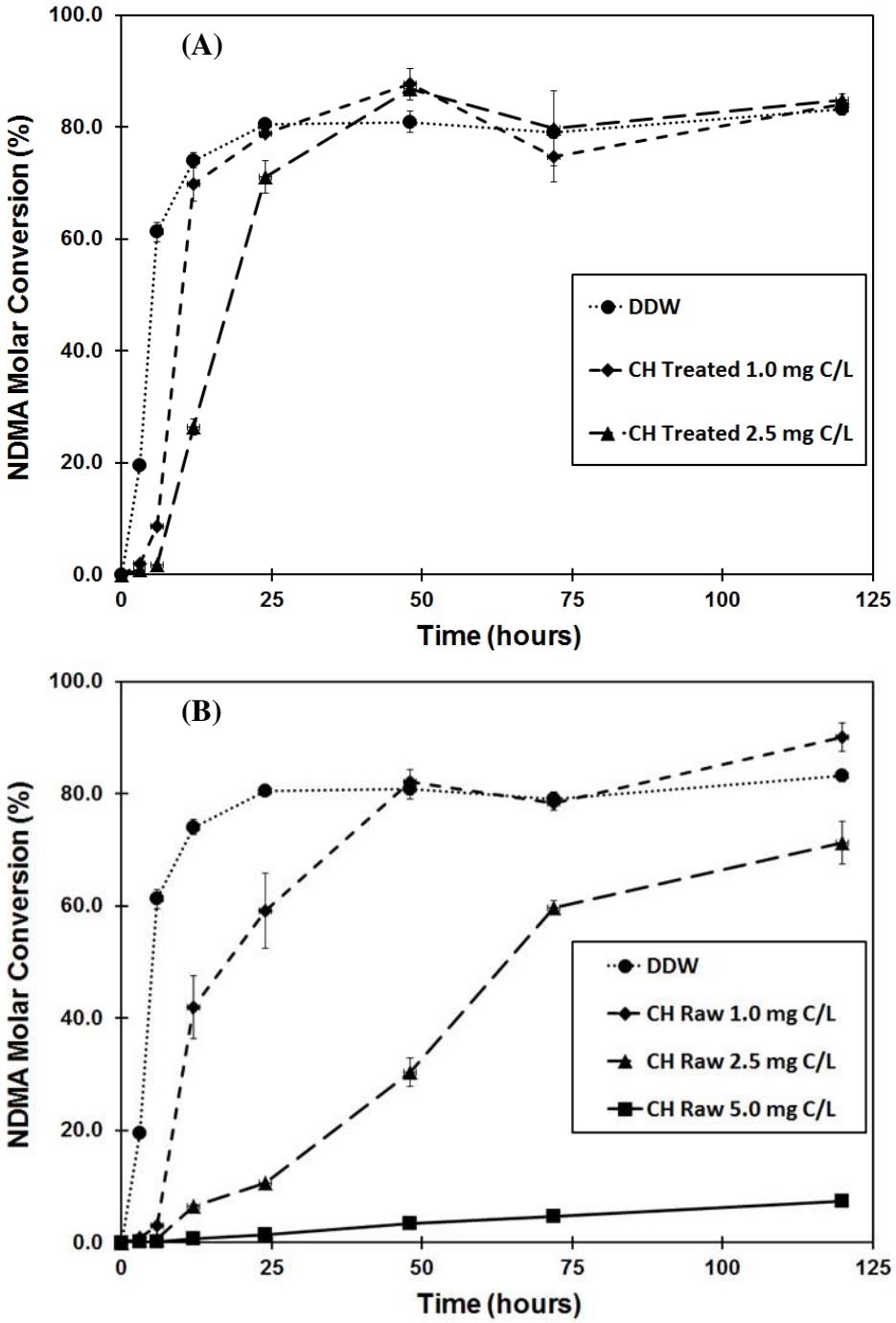


Figure 7.7. The effect of NOM in NDMA formation from RNTD under SDS conditions. Background solutions for (A) were obtained by diluting CH treated water to DOC levels of 1.0 and 2.5 mg C/L. Background solutions for (B) were obtained by diluting CH raw water to DOC levels of 1.0, 2.5, and 5.0 mg C/L. Error bars represent data range for duplicate samples.

When CH raw water containing HPO-dominated NOM was used as the background matrix, the NDMA conversion yield from RNTD decreased as DOC levels increased (**Figure 7.8-A**). The NDMA conversion yield from RNTD without NOM reached the maximum (~85%) within 24 hours, while slightly slower conversion was observed 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 after 120 hours of reaction 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 hours of chloramination. The results show that the NDMA conversion yield from RNTD was consistent and independent of NOM in treated water, but NOM in raw water caused decreases in the NDMA conversion yield, indicating that NOM characteristics in natural water may either increase or decrease the NDMA formation from a certain type of precursor compound. CH raw water has a higher content of aromatic components than CH 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 influence the NDMA formation during chloramination of amines. Shen and Andrews (2011b) reported similar decreases in the NDMA formation rate when river water with 6.2 mg C/L of DOC and 2.3 L/mg.m of $SUVA_{254}$ was used. However, the changes of the NDMA conversion rates in their study were not as drastic as the results in this study, which may be due to the difference in the $SUVA_{254}$ values of NOM. 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 (Parris, 1980; Thorn et al., 1996; Weber et al., 1996; Chen, 2007), and consequently their initial contact with chloramine species can be hindered (Shen and Andrews, 2011b). Some additional information about the quinone-tertiary amine chemistry can be found in the **Appendix E**.

The NDMA molar conversion of DMiPA (**Figure 7.8-B**) showed slightly higher inhibition in the presence of CH raw water than CH treated water. The NDMA yields at 120 hours decreased from 56.9 % in DDW to 21.8, 3.7, and 0.3% in the presence of 1.0, 2.5, and 5.0 mg C/L DOC, respectively. These trends were very similar to the results in CH treated, which is probably because of less interaction between DMiPA, an aliphatic amine, and HPO fraction of the NOM than between RNTD, an aromatic amine, and HPO. However, the NOM effects on the NDMA conversion and the interaction of NOM fractions with both aliphatic and aromatic amines need to be further verified with various precursors in different water matrices a to understand the NDMA formation mechanism in natural water systems.

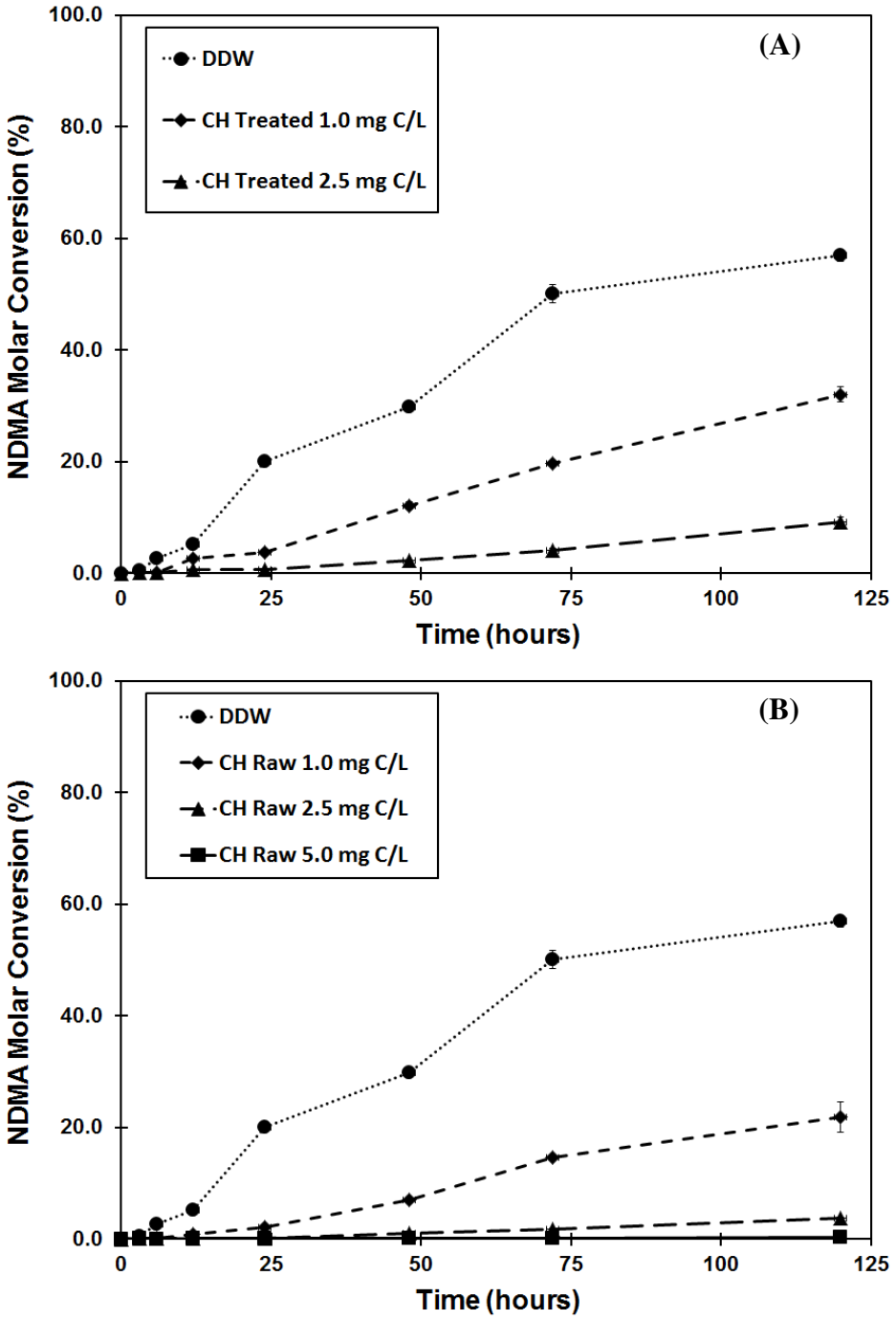


Figure 7.8. The effect of NOM in NDMA formation from DMiPA under SDS conditions. Background solutions for (A) were obtained by diluting CH treated water to DOC levels of 1.0 and 2.5 mg C/L. Background solutions for (B) were obtained by diluting CH raw water to DOC levels of 1.0, 2.5, and 5.0 mg C/L. Error bars represent data range for duplicate samples.

Overall, these results suggest that the presence of NOM would be beneficial in the control of NDMA in distribution systems when precursors such as RNTD and DMiPA are present. Rather than TPH, HPO fraction of NOM could have benefits in the reduction of NDMA formation probably due to its covalent binding capability with aromatic amines. Although the majority of the HPO fraction can be removed during coagulation/flocculation/sedimentation processes, the remaining TPH fraction of NOM may also decrease the NDMA formation from non-aromatic amine precursors by competing for the reaction with dichloramine. For both NOM fractions, higher DOC levels would be more beneficial –resulting in more competition for dichloramine leading to reducing NDMA formation as long as the formation of C-DBPs (i.e., THMs and HAAs) are maintained under the regulated limits if free chlorine is applied prior to ammonia addition.

pH Effect: The effect of pH (6.5-8.5) on the NDMA conversion from RNTD and DMiPA was investigated and the results are given in **Figure 7.9**. The NDMA formation from RNTD was not affected by pH, while DMiPA showed noticeable changes in the NDMA formation rate and yields after 120 hours of chloramination. For the pH range of 6.5-8.5, Shen and Andrews (2013a) reported minor pH effects on the NDMA formation rate from RNTD. However, the NDMA conversion yields from DMiPA at 120 hours decreased as pH decreased from 8.5 to 6.5 in this study. NDMA yields at 120 hours were 7.6, 56.9, and 35.4% for pH 6.5, 7.5, and 8.5, respectively. Assuming that NDMA forms

via nucleophilic substitution of dichloramine with deprotonated amines (i.e., DMiPA) (Schreiber and Mitch, 2006; Mitch et al., 2009), 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 toward the NDMA formation (Shen and Andrews, 2011b, 2013a). The mid-point of both reactants' pK_a values (~4.0 for dichloramine and ~10.3 for deprotonated DMiPA) is slightly above pH 7. Therefore, the highest yield of NDMA from DMiPA was observed at pH 7.5, which corresponds to the optimal condition for the maximum coexistence of dichloramine and deprotonated DMiPA. However, this trend was not observed for RNTD since the NDMA conversion from RNTD was from the reaction with monochloramine which is the dominant chloramine species at pH 6.5-8.5. Moreover, RNTD's pK_a (8.2) is lower than DMiPA's, which leads to more deprotonated amines at the given pH range.

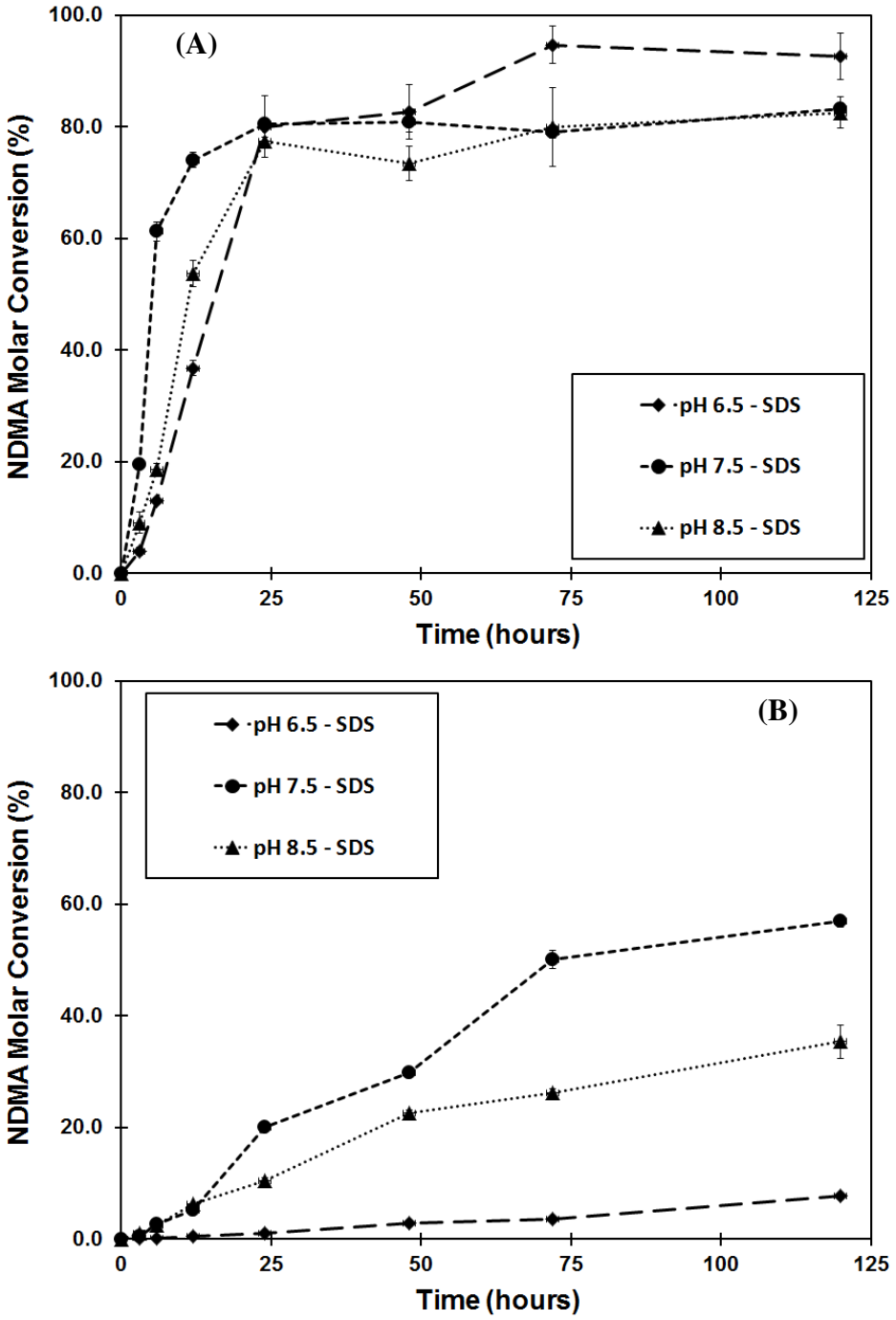


Figure 7.9. The effect of pH in NDMA formation from (A) RNTD and (B) DMiPA under SDS conditions. Error bars represent data range for duplicate samples.

Sulfate Effect: It has been known that sulfate, bicarbonate, and phosphate can facilitate decomposition of monochloramine (Valentine and Jafvert, 1988; Vikesland et al., 2001). The presence of those ions would increase dichloramine concentrations, and consequently the NDMA conversion from some amine precursors, which prefer dichloramine to form NDMA, would be affected. To investigate the anion effect on the NDMA formation, sulfate was selected and SDS tests were performed in the presence of sulfate at three different concentrations (i.e., 10, 25, and 50 mg/L) for both RNTD and DMiPA (**Figure 7.10**). The results showed that sulfate did not affect the NDMA formation from RNTD, because RNTD would react with monochloramine, the dominant species to form NDMA rather than dichloramine and consequently, the chloramine decomposition caused by sulfate would not influence overall NDMA molar conversion. On the contrary, dichloramine is more important than monochloramine in the formation of NDMA from DMiPA and consequently, increasing sulfate would lead to more dichloramine by the chloramine decomposition and increase the NDMA formation from DMiPA (**Figure 7.10-B**). NDMA formation from DMiPA increased with increasing sulfate concentration. Similar patterns of conversion curves at different sulfate concentrations indicate that the NDMA formation from DMiPA is still limited by dichloramine concentration. Furthermore, overall NDMA yield at 120 hours increased from 56.9% to 70.6, 71.7, and 79.4% when sulfate was added at 10, 25, and 50 mg/L, respectively. Although the initial chloramine dose in the SDS tests was much lower than the FP experiments, the NDMA conversion yield from DMiPA after 120 hours in the

presence of 50 mg/L sulfate reached ~80% which is the maximum level observed from the FP test. These results indicate that introducing sulfate during coagulation, or phosphate during pH adjustment or bicarbonate during recarbonation may increase the chloramine decomposition (Valentine and Jafvert, 1988; Vikesland et al., 2001) and the NDMA formation may increase or decrease depending on precursors' properties. Even though no additional precursors are introduced during water treatment processes, the NDMA formation may increase in distribution systems due to anion effects and long detention times. Therefore, such processes must be optimized to reduce possible chloramine decomposition in distribution systems.

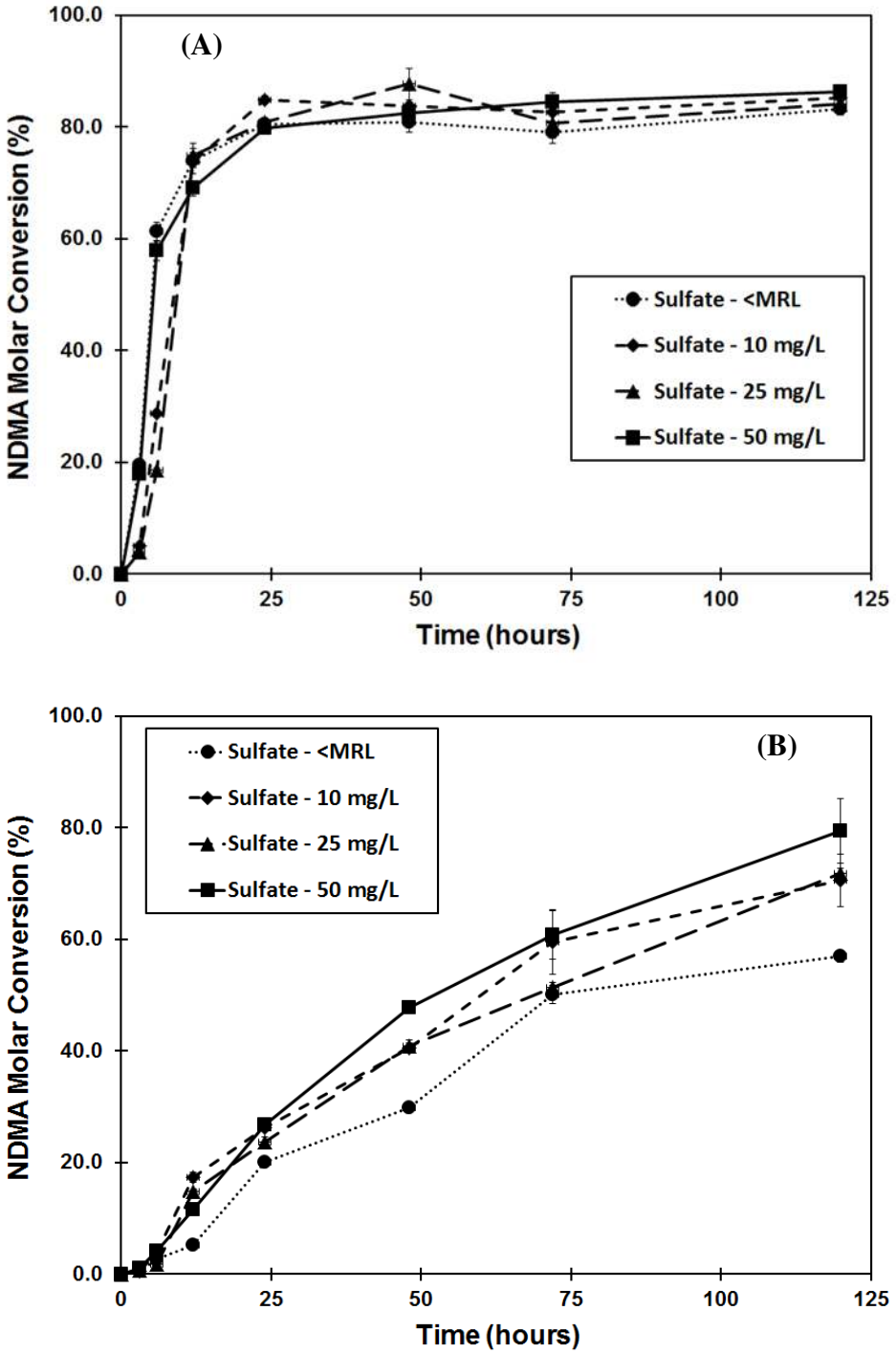


Figure 7.10. The effect of sulfate in NDMA formation from (A) RNTD and (B) DMiPA under SDS conditions. Error bars represent data range for duplicate samples.

Case Studies

CH Drinking Water Treatment Plant: As a case study, the NDMA formation rate was examined with CH raw and treated water under three different chloramination conditions (i.e., FP, SDS, and SDS in the presence of excess ammonia) and the results are given in **Table 7.2**. In the FP experiment with both waters, the NDMA formation yield reached its maximum within the initial 24 hours of chloramination. The NDMA formation rate decreased gradually for the next 48 hours. And at last, the NDMA formation reached the plateau after 72 hours of chloramination yielding 59 and 45 ng/L of NDMA at 120 hours from CH raw and treated, respectively. The difference in NDMA FP values of CH raw and CH treated waters corresponds to a ~24% reduction in NDMA precursors. This was found consistent with the ongoing project for three DWTPs, where coagulation/flocculation/sedimentation (without any polymer influence) resulted in 9-23% reduction in NDMA FP (Uzun et al., 2012).

The NDMA formation in CH raw water under SDS conditions was below MRL. However, NDMA formation was observed in CH treated water reaching up to 9 ng/L at 120 hours of chloramination. Since DOC of the raw water decreased from 6.3 mg C/L to 2.8 mg C/L after coagulation/flocculation/sedimentation, the competition between NOM and amines for dichloramine decreased and consequently, dichloramine could be more available for reactions with amines leading to higher NDMA formation. In addition, since alum was used in this DWTP as the coagulant, sulfate concentration increased from 6.3 to 36.8 mg/L. This increase in the sulfate level could also contribute to dichloramine levels

leading to higher NDMA formation under SDS conditions. To confirm this alum effect on the NDMA formation, CH 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; indicating that introduction of sulfate in the coagulation process did not affect the NDMA formation. This suggests that only DOC removal could be the reason for the NDMA formation observed in CH treated water. The importance of DOC and the NDMA formation curve over the reaction time under SDS conditions indicate that: (i) the 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. In both samples, the NDMA levels were below MRL under SDS conditions in the presence of excess ammonia. Thus, precursors which are sensitive to monochloramine must have been negligible in this water source. If a water source has negligible amounts of precursors which are sensitive to monochloramine, the dichloramine would be the key player for NDMA formation.

Table 7.2. NDMA formation (ng/L) over time from selected DWTP.

		Time (hours)						
		3	6	12	24	48	72	120
CH Raw	FP	7	14	22	38	46	55	59
	SDS	<3	<3	<3	<3	<3	<3	<3
	SDS + Ammonia	<3	<3	<3	<3	<3	<3	<3
CH Treated	FP	8	12	21	26	33	42	45
	SDS	<3	<3	<3	4	6	7	9
	SDS + Ammonia	<3	<3	<3	<3	<3	<3	<3

Reported values are average of two measurements (n=2).

Wastewater-Impacted Watershed: The NDMA formation rates of the samples collected from the watershed are given in **Table 7.3** and the yields obtained at 120 hours for these three locations in this study agree well with the previous study conducted by Gan et al. (2013b). The sample collected from the upstream of the discharge location represented a pristine source with minimal anthropogenic impact. The NDMA FP at this location was 23 ng/L after 120 hours. Under SDS conditions, 5 ng/L of NDMA formed within the first 3 hours and slowly increased to 7 ng/L after 120 hours. In the presence of excess ammonia, 5 ng/L of NMDA formed within the first 3 hours, but remained constant afterwards. This indicates that monochloramine could be more important for the NDMA formation in this type of source water than dichloramine.

Table 7.3. NDMA formation (ng/L) over time from selected watershed.

		Time (hours)						
		3	6	12	24	48	72	120
Upstream	FP	7	10	12	15	21	21	23
	SDS	5	5	5	5	7	7	7
	SDS + Ammonia	5	5	5	6	5	5	5
Wastewater Effluent	FP	1316	1365	1532	1567	1641	1654	1659
	SDS	5	5	8	11	11	14	16
	SDS + Ammonia	7	5	7	8	6	8	7
Downstream	FP	94	108	114	127	126	139	149
	SDS	5	5	15	33	74	87	102
	SDS + Ammonia	4	5	5	5	5	4	6

Reported values are average of two measurements (n=2).

The NDMA FP at the wastewater discharge point was 1567 ng/L within the initial 24 hours of chloramination. Further chloramination for another 24 hours resulted in additional of NDMA formation (i.e., 74 ng/L) and NDMA FP remained constant afterwards. Under SDS conditions, only 5 ng/L of NDMA formed within the first 3 hours and NDMA formation slowly increased to 16 ng/L after 120 hours. This yield was much lower than expected and in attempting to explain this anomaly the WW was diluted with DDW and examined under SDS conditions. The results showed that with the increasing number of dilutions, NDMA yields of SDS experiments got closer to FP tests (**Figure 7.11**). These dilutions watered down the background organic matter (i.e., DOC) and since initial chloramine dose was constant the competition for dichloramine species decreased.

Thus, dichloramine was more available to react with NDMA precursors. The NDMA formation by monochloramine was fast and yielded 7 ng/L within 24 hours. These findings indicate that dichloramine was the key player for NDMA formation from this wastewater.

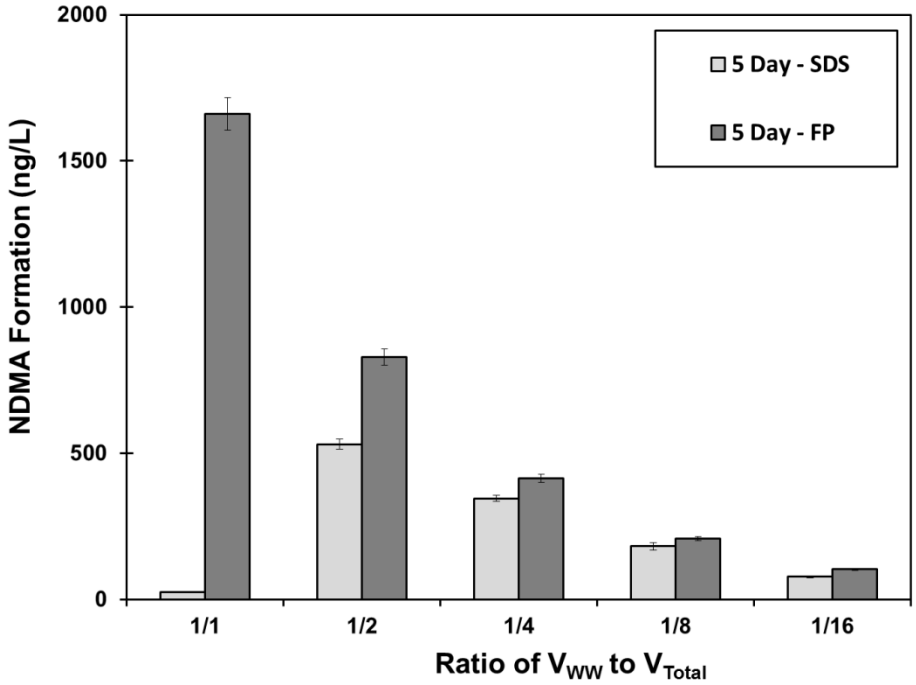


Figure 7.11. NDMA formation from wastewater under different dilution ratios. Error bars represent data range for duplicate samples.

At the downstream location NDMA FP was 127 ng/L within 24 hours of chloramination and additional NDMA formed with further exposure to chloramine. For this location, monochloramine seemed more important for the NDMA formation due to the results from SDS test in the presence of excess ammonia. However, NDMA formed constantly under SDS test conditions without ammonia reaching 102 ng/L after 120

hours. This observed difference in NDMA formation indicated that NDMA formation was probably limited to the presence of available dichloramine. It should be noted that the NMDA concentrations of FP and SDS are somewhat comparable. Once again, this is probably caused by the dilution of organic matter (i.e., DOC) reducing the competition for dichloramine, highlighting its importance for NDMA formation. With samples collected at this location, the factors (e.g., sulfate, and pH) that might influence chloramine decomposition and speciation were investigated under SDS conditions. Increasing concentrations of sulfate increased NDMA formation slightly (**Figure 7.12**), but the yield after 120 hours remained the same. On the other hand, there was a distinct pH effect (**Figure 7.13**). Lowest NDMA formation rate and overall yield were observed at pH 8.5 where a minimum amount of dichloramine was present. There was no distinct difference in formation rate and overall yield between pH 6.5 and 7.5. Since dichloramine could be a key player in NDMA formation at this location, within this pH range the trade-off between chloramine speciation and amine's proton state might be comparable. This indicates that pH can be an effective for controlling NDMA formation in distribution systems.

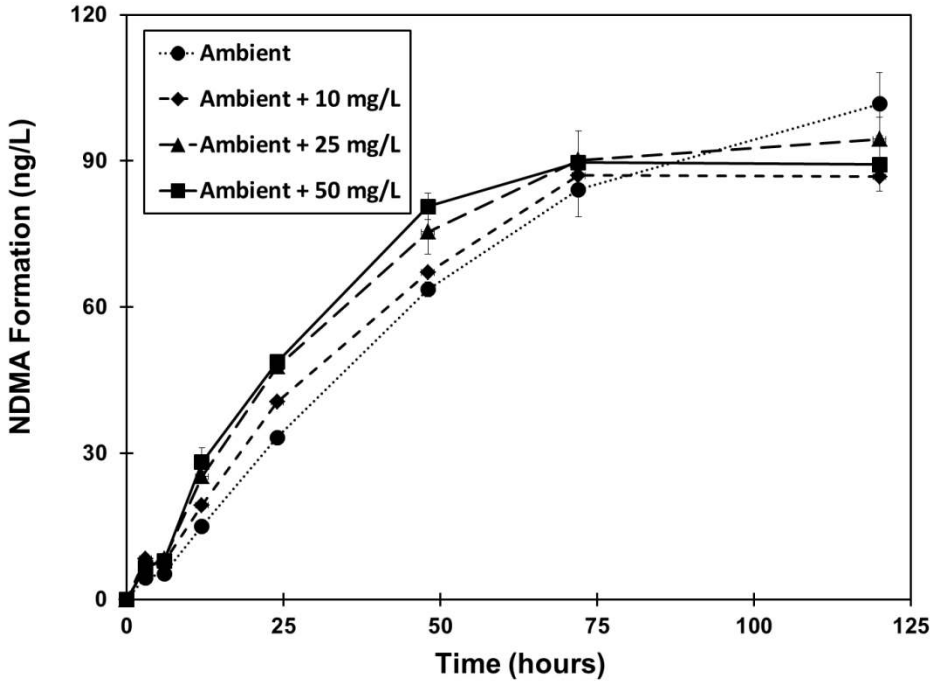


Figure 7.12. The effect of sulfate in NDMA formation under SDS conditions from downstream sample collected from the wastewater impacted watershed. Error bars represent data range for duplicate samples.

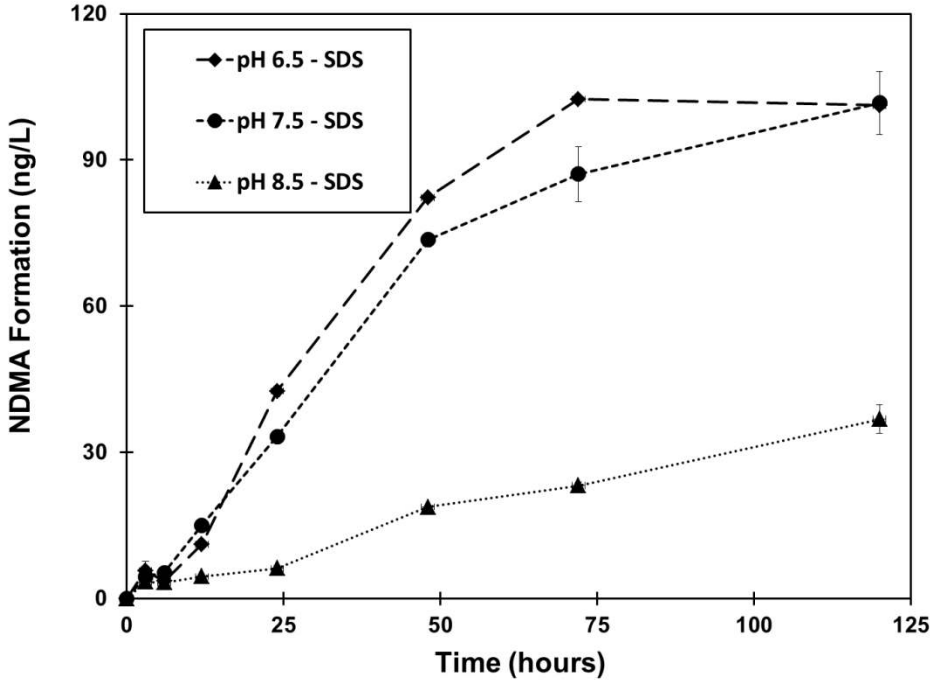


Figure 7.13. The effect of pH in NDMA formation under SDS conditions from downstream sample collected from the wastewater impacted watershed. Error bars represent data range for duplicate samples.

Conclusions

NDMA formation rate from DMA and four tertiary amines was determined under three chloramination conditions (i.e., FP, SDS, and SDS in the presence of excess ammonia). The results showed that the electron distribution of the tertiary amine determines the reactive chloramine species. Compounds with EWG (i.e., RNTD) reacted preferentially with monochloramine, whereas compounds with EDG (i.e., DMiPA) reacted preferentially with dichloramine to form NDMA. Since monochloramine is the abundant species at pH 7.5, NDMA formation rate from amines with EWGs were relatively fast and reached a plateau approximately within 24 hours of chloramine application in all three test conditions. On the other hand, the NDMA formation rate from compounds with EDG was highly dependent on the dichloramine concentration. In the NDMA FP tests, compounds with EDG also had a relatively fast reaction and reached a plateau approximately within 24 hours of chloramination. However, the NDMA formation rate from those was limited by the transformation of monochloramine to dichloramine under SDS conditions and had a relatively low rate. Further suppression of dichloramine - in the SDS tests by spiking excess ammonia - resulted in negligible NDMA formation from these compounds.

The presence of NOM decreased the NDMA formation rate and overall conversion due to competition for dichloramine and consequently, drastic decreases were noticed for DMiPA. Only the HPO fraction of the NOM was found to decrease the NDMA formation from RNTD which could be caused by its aromatic structure leading to

a binding with NOM. In NDMA formation, pH plays a key role as it influences both chloramine speciation and protonation state of the amine. Thus, the more profound effect was observed on the dichloramine sensitive DMiPA, whereas RNTD did not show a distinct difference. Lastly, the presence of sulfate that can increase the chloramine decomposition was found to increase NDMA formation from DMiPA, but had no effect on RNTD.

Investigating two case studies showed that some NDMA can be formed by monochloramine; however, dichloramine was observed to be the dominant species responsible for NDMA formation in both systems. The NDMA formation was found to be limited by the transformation of monochloramine to dichloramine, and thus relatively slow NDMA formation rates were observed under SDS conditions. It is likely that the presence of high levels of NOM could be beneficial to reduce the NDMA formation rate due to competition for the dichloramine species. However, it should be noted that it is not desirable to have high levels of NOM in the distribution system as it can lead several issues (i.e., formation of THMs and HAAs during pre-chlorination, increased microbial activity in the distribution system). While NOM may hinder NDMA formation, presence of chloramine decomposing ions (i.e., sulfate, phosphate, bicarbonate) may work against this effect. Also, since dichloramine is the key player for NDMA formation, pH can be an effective tool to control NDMA formation as it influences both chloramine speciation and protonation state of the amine.

CHAPTER EIGHT

THE EFFECT OF PRE-OXIDATION ON OVERALL NDMA FORMATION, AND THE INFLUENCE OF PH

Introduction and Objective

Chloramination has become increasingly used among drinking water utilities in the US to comply with DBP regulations, such as THMs and HAAs. Unfortunately, chloramination can lead to the formation of nitrosamines (Choi and Valentine, 2002a,b; Choi et al., 2002; Mitch et al., 2003a,b), which are probable carcinogens, mutagens, and teratogens (USEPA, 1993). Among nitrosamines, NDMA has drawn the most attention due to its frequent detection in drinking water systems and high lifetime cancer risk level (USEPA, 1993). Although there are currently no federal regulations concerning nitrosamines in drinking water in the United States, the USEPA has listed nitrosamines as one of three potential groups of contaminants highlighted for possible regulation in the near future (Roberson, 2011).

NDMA preferentially forms upon chloramination via a nucleophilic substitution reaction between chloramine (mono- or di-) and amines (Schreiber and Mitch, 2006; Mitch et al., 2009; Le Roux et al, 2012b). NDMA can also form during chlorination in the presence of nitrite, especially under acidic conditions (Choi and Valentine, 2003) and during ozonation (Andrzejewski et al., 2008; Oya et al., 2008; Schmidt and Brauch, 2008). The precursors that have been reported to form NDMA upon oxidation include, but are not limited to, DMA, and tertiary and quaternary amines with a DMA moiety in

their molecular structures (Lee et al., 2007a; Kemper et al., 2010; Shen and Andrews, 2011a,b), such as fungicides, pesticides, herbicides (Graham et al., 1995; Chen and Young, 2008; Schmidt and Brauch, 2008), pharmaceuticals, cosmetics (Sacher et al., 2008; Shen and Andrews, 2011a), wastewater effluent organic matter (Sedlak et al., 2005; Krauss et al., 2009; Shah et al., 2012; Gan et al, 2013a,b), and NOM (Gerecke and Sedlak, 2003; Mitch and Sedlak, 2004; Chen and Valentine, 2007; Dotson et al., 2007; Krasner et al., 2008a). NDMA formation was also found to increase in the presence of polymers and ion-exchange resins (Kimoto et al., 1980; Najm and Trussell, 2001; Kohut and Andrews, 2003; Wilczak et al., 2003; Mitch and Sedlak, 2004; Nawrocki and Andrzejewski, 2011; Gan et al, 2013a,b).

The use of pre-oxidants for either transforming or eliminating NDMA precursors prior to chloramination can be a viable strategy for water utilities to control the NDMA levels. Chlorine is the most commonly applied pre-oxidant in water treatment; however, due to the formation of regulated C-DBPs from chlorine (i.e., THMs and HAAs), the use of chlorine dioxide and ozone to control simultaneously both regulated C-DBPs and nitrosamines has received attention within the last decade (Shah et al., 2012).

Previous studies with chlorine, chlorine dioxide, and ozone have provided some promising results to reduce NDMA formation, despite some observations that the same pre-oxidants enhanced NDMA formation in some cases (Charrois and Hrudrey, 2007; Lee et al., 2007a; Chen and Valentine, 2008; Krasner et al, 2012a; Shah et al., 2012; Shen and Andrews, 2013b). In general, the research indicated that ozone and chlorine are effective oxidants for controlling NDMA precursors, likely due to their high reaction rate

constants with amines, especially in their deprotonated forms (von Gunten, 2003; Ternes and Joss, 2006; Lee and von Gunten, 2010; Krasner et al., 2012a). For example, ozone reduced NDMA formation by over 50% within a very short contact time (i.e., CT ≤0.5 mg×min/L) (Lee et al., 2007a; Chen and Valentine, 2008; Shah et al., 2012), and only in a few cases did ozonation actually lead to the formation of NDMA (Asami et al., 2009; von Gunten et al., 2010). Chlorine was also able to achieve the same level of deactivation as ozone at longer contact times (i.e., CT ~50 mg×min/L), while increases in NDMA formation occurred at low exposure levels (i.e., CT ≤25 mg×min/L) in a few wastewater-impacted sources, due to the nitrosation pathway facilitated by the presence of nitrite (Chen and Valentine, 2008; Shah et al., 2012). Although chlorine dioxide has the potential to control NDMA formation (Lee et al., 2007a), it may increase the overall NDMA formation like ozone (Shah et al., 2012).

The effects of pre-oxidant on the reactivity of a few types of NDMA precursors have been investigated in a few studies: (i) some amides (Schmidt and Brauch, 2008; von Gunten et al., 2010), anti-yellowing agents (Kosaka et al., 2009), and polymers (Padhye et al., 2011a) were recognized to form NDMA during ozonation without chloramination; (ii) the use of ozone and chlorine dioxide reduced NDMA formation from seven tertiary amines; however, it is noted that substantially high doses of oxidants compared to typical doses for drinking water treatment were used (Lee et al., 2007a); and (iii) pre-chlorination reduced NDMA formation from RNTD, nizatidine, and tetracycline by 50%, at a relatively low contact time (i.e., CT ~10 mg×min/L) (Shen and Andrews, 2013b).

The main objective of this study was to systematically investigate the impact of commonly-applied pre-oxidants on the formation of NDMA during chloramination from a suite of carefully selected NDMA precursor to: (i) investigate the effects of pre-oxidants on NDMA formation (either by increasing, decreasing, or remaining constant); (ii) determine the optimum CT values to minimize the NDMA formation from each precursor, and (iii) examine the effect of pH. Fifteen precursors with a DMA moiety in their structures, such as secondary amine, tertiary aliphatic and aromatic amines, polymers, amides, and hydrazines, were selected. The CT curves for the effect of pre-oxidation with chlorine, chlorine dioxide and ozone were obtained for each compound and an overall comparison was made. A representative compound was chosen from each group of precursors to further evaluate to the effect of pre-oxidation pH.

Materials and Methods

NDMA Precursors

Selected amines, amides, and polymers were tested for NDMA formation to cover a wide range of precursors which might be encountered during drinking water treatment. Chemical structures and abbreviations of these compounds are given in **Figure 8.1**. All compounds were purchased from Sigma-Aldrich, SP^2, and TCI, and used without further purification.

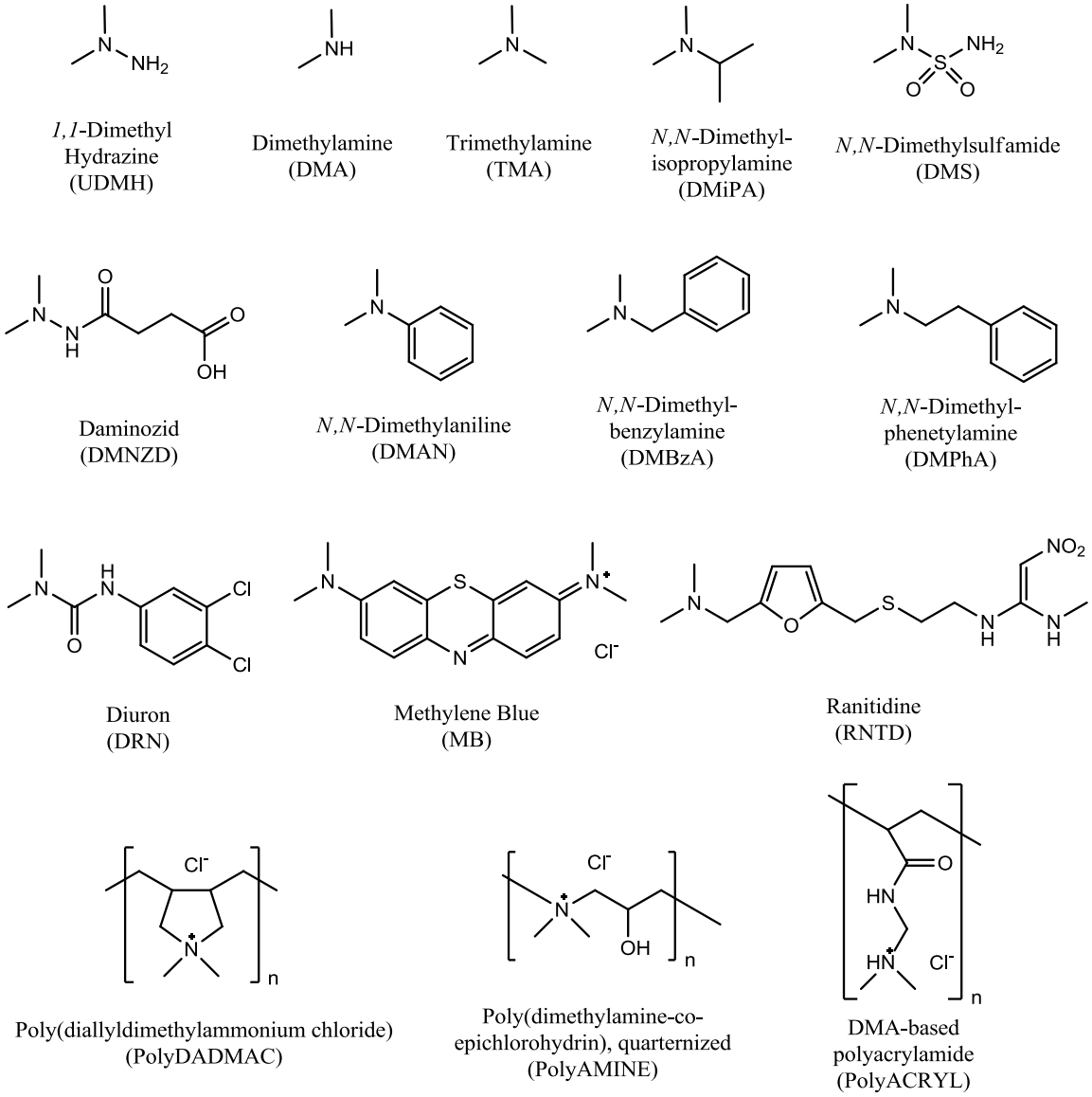


Figure 8.1. Molecular structures of selected precursors.

Experimental Methods

A stock solution (4 mM) of each precursor, except the polymers, was prepared in methanol and stored in a 65 mL amber glass bottle at 4ºC until used. Each of these model compounds was diluted to 200 nM in DDW and buffered with 2 mM phosphate solution to adjust the pH at 7.5. A stock solution of 200 mg/L for each polymer was prepared in DDW and spiked at predetermined concentrations to buffered DDW to induce NDMA formation within the range of 100 to 150 ng/L (**Figure 8.2**).

For pre-oxidation with chlorine, chlorine dioxide, and ozone, their doses were targeted to capture CT exposures ranging from zero to levels capable of *Giardia* cyst and virus removal at room temperature (USEPA, 1999). CT values were calculated by multiplying the residual oxidant concentrations by contact time. Initial oxidant concentrations for chlorine, chlorine dioxide, and ozone were 3.0 mg/L, 1.0 mg/L, and 3.0 mg/L, respectively. Following injection of oxidants, bottles were periodically analyzed for residual oxidants at desired contact times ranging from a few minutes to maximums (T_{Max}) of 60, 30, and 10 minutes, for chlorine, chlorine dioxide, and ozone, respectively (**Table 8.1**). Generally, chlorine dioxide residual is removed by purging the solution. However, since such strong oxidants have the potential to form volatile free DMA (Lee et al, 2007a; Mitch and Schreiber, 2008) and purging could cause unintentional loss of NDMA precursors (**Figure 8.3**), all residual oxidants were quenched by stoichiometric doses of sodium thiosulfate at the end of each pre-oxidation scenario.

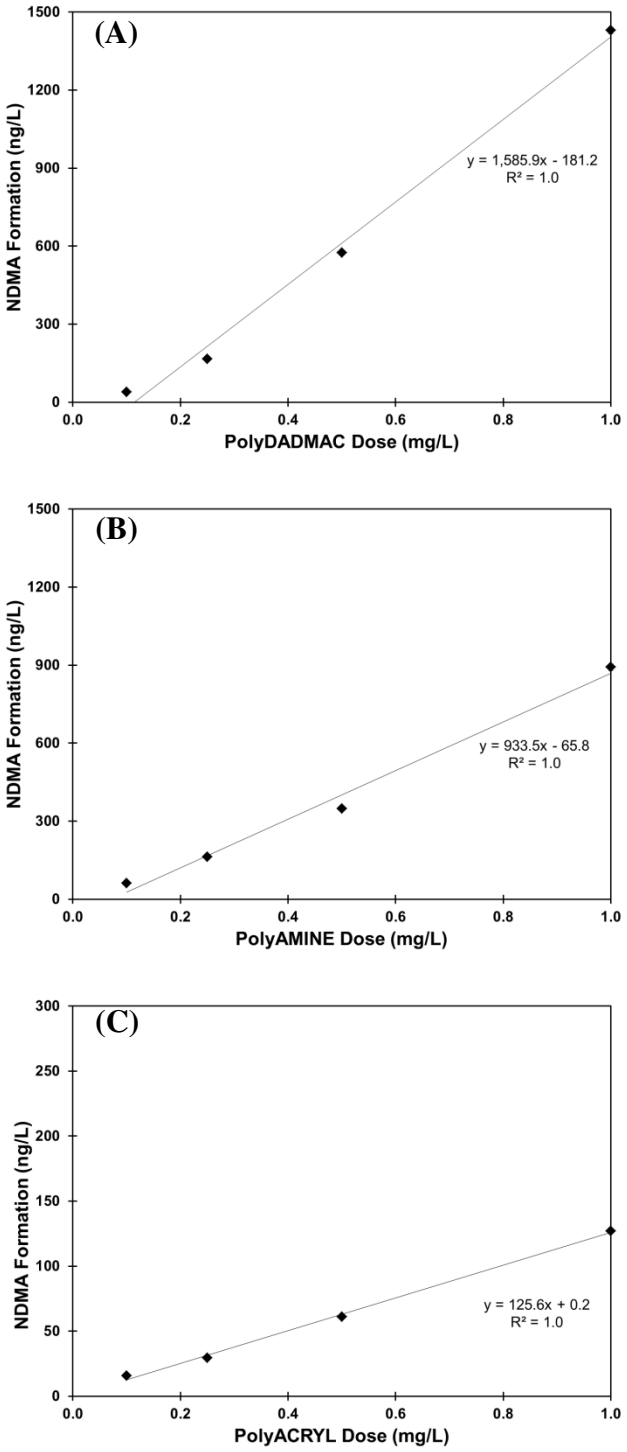


Figure 8.2. NDMA formation from (A) PolyDADMAC, (B) PolyAMINE, and (C) PolyACRYL as a function of polymer dose.

Table 8.1. Pre-oxidation contact times with Cl_2, ClO_2, and O_3.

Oxidant (Conc.)	Cl_2 (3 mg/L)	ClO_2 (1 mg/L)	O_3 (3 mg/L)
Contact Time (min)	0	0	0
	5	5	1
	10	10	2
	15	15	3
	30	20	5
	45	30	10
	60		
T_{Max} =	60	30	10

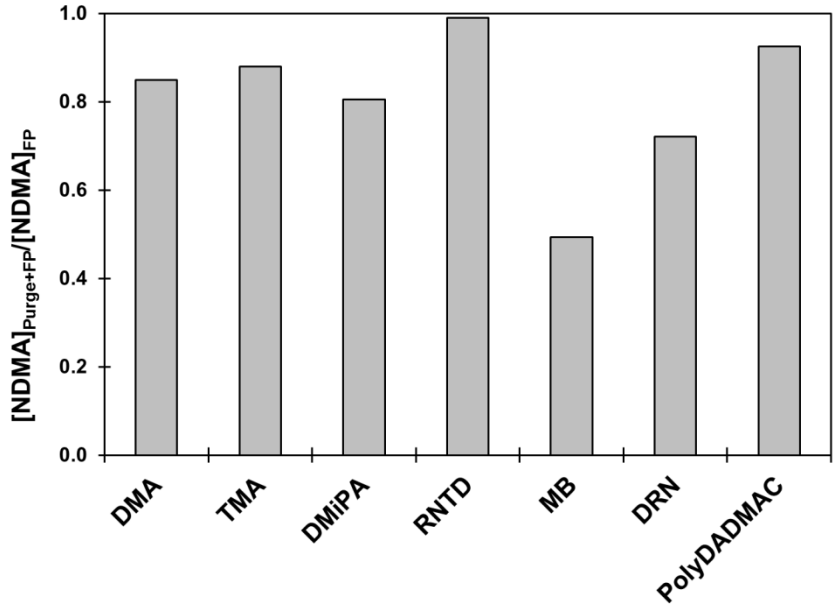


Figure 8.3. Effect of 5 minute purging on selected amines and their consequent NDMA FPs. Reported values are average of two measurements (n=2).

To investigate the effect of pre-oxidation pH, precursor solutions diluted in DDW were buffered with 2 mM phosphate solution to adjust the pH at 5.5, 6.5, 7.5, 8.0, 8.5, 9.0 and 9.5. Chlorine, chlorine dioxide, and ozone were injected at the same concentrations used to obtain the CT curves. At T/T_{Max} of 0.2 for each oxidation scenario (i.e., 12 min for chlorine, 6 min for chlorine dioxide, and 2 min for ozone) oxidation of precursors were quenched with stoichiometric doses of sodium thiosulfate.

Chloramine FP tests were conducted immediately after pre-oxidation experiments (quenched with stoichiometric doses of sodium thiosulfate) spiked with chloramine and a phosphate buffer. Residual concentrations of the pre-oxidants can be found in **Figures F.1** through **F.3**. Chloramine stock solution was prepared by mixing diluted sodium hypochlorite and ammonium sulfate solutions at Cl:N mass ratio of 4:1 at pH 9. An initial chloramine concentration of 100 mg/L as Cl_2 was used at pH 7.5 in the presence of the 10 mM phosphate buffer, prepared by mixing sodium phosphate mono- and dibasic. NDMA FP tests were carried out in 1-L amber glass bottles without headspace, in the dark at 21-23°C, for 5 days of contact time. Typical chloramine concentrations can be found **Figure F.4**.

Analytical methods

NDMA was analyzed following USEPA method 521 (USEPA, 2004), consisting of SPE using coconut charcoal followed by GC-MS/MS analysis. Analytical details can be found in the previous sections and a brief summary is as follows. For the sample analysis, 500 mL of chloraminated amine solutions were quenched with sodium thiosulfate and NDMA-d_6 was added as a surrogate before SPE. Samples were passed

through coconut charcoal cartridges which were preconditioned with DCM, methanol, and DDW. The cartridges were dried with air, and then eluted with DCM. 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-d_{14} as an internal standard, and analyzed using a Varian GC-MS/MS 4000 under the CI mode. Percent molar yield of each precursor was calculated, except polymers, using **Equation 6.1** (**Appendix B**)Error! Reference source not found..

Ozone gas, generated by a GTC-1B Griffin ozone generator fed by ultra-high purity oxygen, was purged into DDW cooled to 4ºC to produce ozone stock solutions. Throughout the experiments, the ozone concentrations of stock solutions and samples were measured with the HACH spectrophotometer. Chlorine dioxide stock solutions were prepared via the slow acidification of $NaClO_2$ solution with H_2SO_4 (Jones et al., 2012). Residual chlorine dioxide concentrations were monitored by the SM 4500-ClO_2 E method (APHA/AWWA/WEF, 2005), as well as by the HACH spectrophotometer. Concentrations of free chlorine, and mono- and dichloramine reported as free chlorine, were determined following SM 4500-Cl F (APHA/AWWA/WEF, 2005). All analytical methods and their MRLs are given in **Table 4.1**. All samples and blanks were prepared, extracted and analyzed in duplicates. Error bars in all the graphs show the variability in duplicate analysis (n=2).

Results and Discussion

Pre-oxidation with Chlorine

The NDMA molar conversions from selected precursors during pre-chlorination are shown in **Figure 8.4**. The NDMA formation from DMA decreased from 1.6% to 1.1% within 5 minutes (i.e., CT of 15 mg×min/L) of contact time with chlorine. It has been known that DMA has high reactivity with chlorine (k_{app} at pH 7 ≈ 10^4 M^{-1} s^{-1}), rapidly forming chlorinated DMA (Cl-DMA) (Deborde and von Gunten, 2008; Lee and von Gunten, 2010; Solterman et al., 2013). However, increased chlorine contact time (i.e., CT of 180 mg×min/L) did not lead to further decreases in the NDMA formation from DMA. Therefore, formed Cl-DMA could remain in the solution and still form NDMA during sequential chloramination. It is noted that NDMA levels yielded from Cl-DMA were approximately two thirds of DMA yields. Assuming that NDMA formation is initiated by nucleophilic substitution (Schreiber and Mitch, 2006; Le Roux et al., 2012b), the electron density on the nitrogen atom of precursors would significantly influence the overall NDMA yield. Forming a bond between chlorine and nitrogen of DMA would decrease the electron density on the nitrogen atom. As a result, during sequential chloramination the nucleophilic substitution to form NDMA would be less favorable. This phenomenon will also explain the results from chlorination of tertiary amines, leading to the formation of partial positive charge on the nitrogen atom of amine (Abia et al., 1998; Deborde and von Gunten, 2008). Pre-chlorination of TMA, DMiPA, DMBzA, RNTD, and DMAN led to reduction in NDMA molar conversions as expected by changes in charge density. Their NDMA yields decreased from 1.8, 74.2, 78.4, 87.6, and

0.3% to 1.2, 38.1, 30.0, 37.4, and 0.1%, respectively, within the CT of 180 mg×min/L. For DMAN, similar results were observed: reduction of NDMA formation was achieved within 5 minutes (15 mg×min/L) and further contact time (i.e. 180 mg×min/L) did not show any changes in the NDMA formation. On the other hand, gradual decreases in the NDMA formation from TMA, DMiPA, DMBzA and RNTD were observed as CT values increased. Relatively sharp decreases were observed especially within the initial 15 minutes of contract time (i.e., CT of 0 to 45 mg×min/L). A similar trend was reported by Shen and Andrews (2013b) during pre-chlorination of RNTD in DDW. For MB and DMPhA, relatively constant NDMA yields were observed during pre-oxidation with chlorine regardless of changing CT values indicating that chlorine does not deactivate effectively such precursors.

During pre-chlorination, the NDMA formation from hydrazine (UDMH), and amide (DMNZD) decreased from 0.30 and 0.14% to 0.12 and 0.03%, respectively. Decreases in the NDMA formation form UDMH happened within the initial 5 minutes (i.e., CT of 15 mg×min/L) of pre-chlorination, and no further decreases were observed for the rest of contact times (5 to 60 minutes). For DMNZD, relatively gradual decreases in NDMA formation were observed, which are similar to tertiary amines such as TMA, DMiPA, DMBzA, and RNTD. On the other hand, pre-chlorination showed almost no effect on the NDMA formation from DRN or led to a slight increase in NDMA formation from DMS. It is likely that neighboring carbonyl or sulfonyl groups can withdraw electrons and decrease the electron density of the nitrogen atom, thus nucleophilic substitution by chlorine may become less favorable. For quaternary amine polymers such

as PolyDADMAC, PolyAMINE, and PolyACRYL, pre-chlorination showed almost no effect on overall NDMA formation (**Figure 8.5-A**). This is probably because nucleophilic substitution could be hindered by the positive charge on the nitrogen atoms of polymers (Krasner et al., 2013). Therefore, the reaction of chlorine with quaternary amines would be limited, and consequently the NDMA formation from polymers with such structures is expected to remain constant during pre-chlorination.

Pre-chlorination's efficiency for NDMA control on a wide array of precursors has not been reported in the literature before. These findings are important to identify the interactions between chlorine and precursor's structure and the consequence on NDMA yield during sequential chloramination. Overall NDMA formation from selected polymers and compounds with either carbonyl or sulfonyl groups remained constant. For other precursors NDMA formation decreased to approximately half of the initial yield ($[\text{NDMA FP}]_{\text{CT-0}}/[\text{NDMA FP}]_{\text{CT-180}}$) during pre-chlorination. Similar decreases have been reported in the pre-chlorination of natural waters (Chen and Valentine, 2008; Shah et al., 2012), where NDMA formation reduced by half at CT of 50 mg×min/L (Shah et al., 2012). In a few cases in the literature, increases in NDMA formation were reported in the presence of nitrite (Shah et al., 2012) through chlorine-triggered nitrosation pathway (Shah and Mitch, 2012). However, the effect of ions (i.e., nitrite) was not within the scope of this study, and was not further investigated.

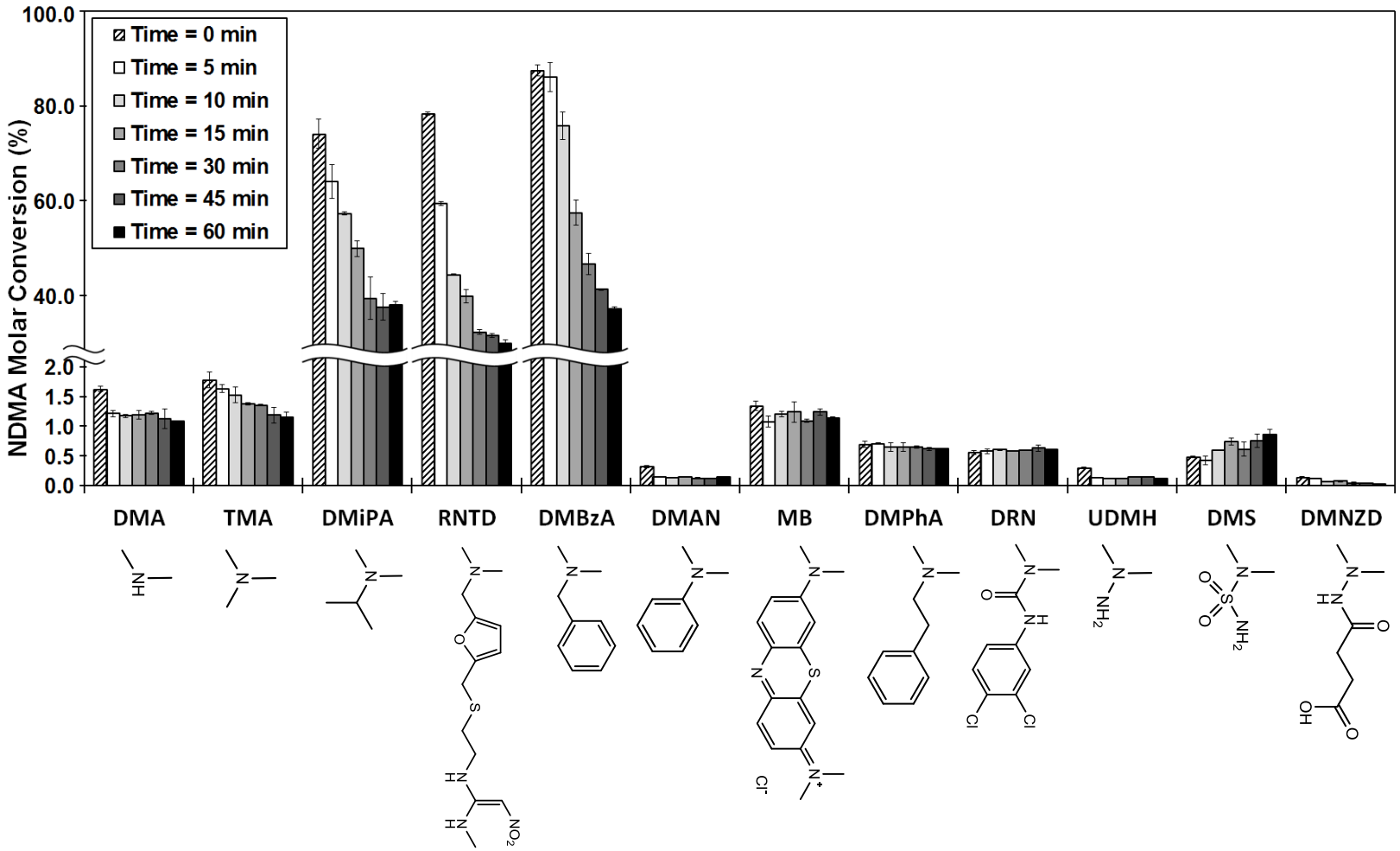


Figure 8.4. NDMA formation from selected precursors upon pre-oxidation with chlorine, followed by chloramine disinfection for different pre-oxidation contact times. $[\text{Precursor}]_0$ = 160 nM, $[Cl_2]_0$ = 3 mg/L, $pH_{\text{Pre-oxidation}}$ = 7.5 (2 mM phosphate buffer), pH_{FP} = 7.5 (10 mM phosphate buffer). Time = 0 min shows no pre-oxidation. Error bars represent data range for duplicate samples.

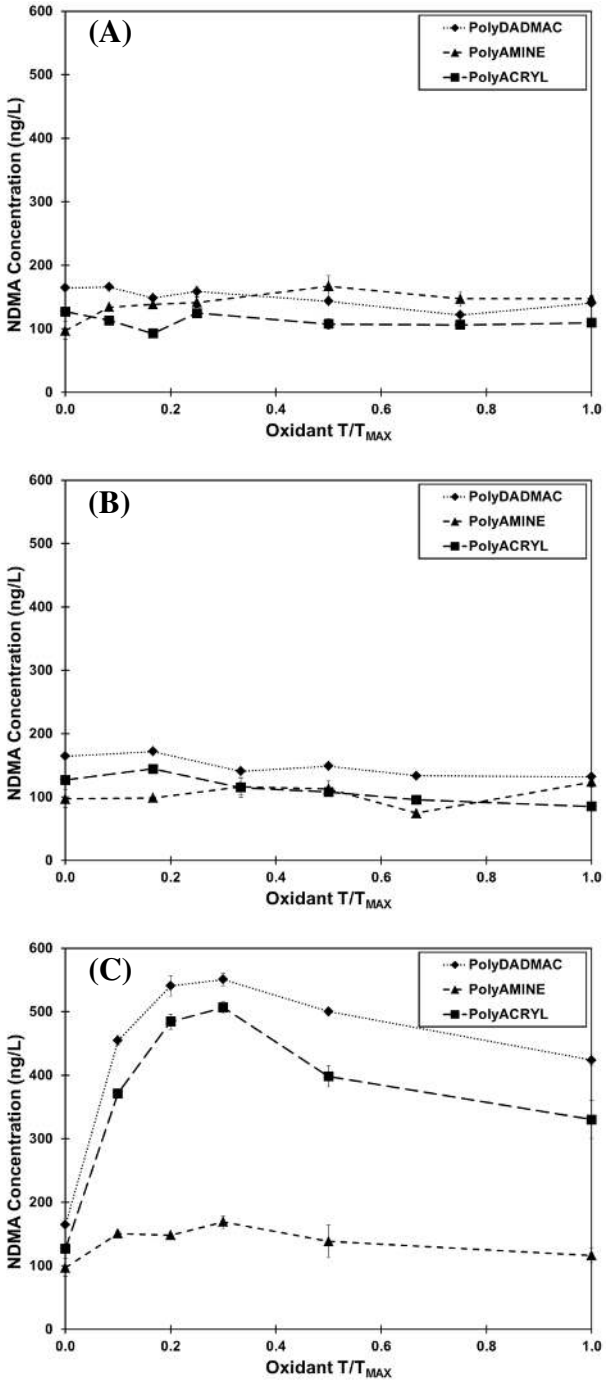


Figure 8.5. NDMA formation from selected polymers upon pre-oxidation with (A) chlorine, (B) chlorine dioxide, and (C) ozone followed by chloramine disinfection for different pre-oxidation contact times. $[\text{PolyDADMAC}]_0 = 0.2$ mg/L, $[\text{PolyAMINE}]_0 = 0.2$ mg/L, $[\text{PolyACRYL}]_0 = 1.0$ mg/L. $T/T_{MAX} = 0$ shows no pre-oxidation. Error bars represent data range for duplicate samples.

Pre-oxidation with Chlorine Dioxide

The molar conversions of NDMA from selective precursors exposed to chlorine dioxide as a pre-oxidant were plotted with different contact times in **Figure 8.6**. The NDMA yield from DMA (1.6%) did not change regardless of the contact time with chlorine dioxide. Lee et al. (2007a) reported that DMA, a secondary amine, has very low reactivity with chlorine dioxide (Lee and von Gunten, 2010). For DMiPA, RNTD, and DMBzA which showed relatively high NDMA formation (≈80%) during chloramination due to their stable intermediates as shown in the previous section, their NDMA molar conversions were reduced distinctively upon exposure to chlorine dioxide. At CT of 5 mg×min/L, the NDMA molar conversion from each of them was around 15%, dropping to 4% at CT of 15 mg×min/L. When CT reached 30 mg×min/L, the NDMA molar conversions were 0.6, 2.3, and 1.4% for DMiPA, RNTD, and DMBzA, respectively. These drastic changes in NDMA formation after pre-oxidation with chlorine dioxide imply that chlorine dioxide can be effectively used to control NDMA formation from these types of precursors.

On the contrary, for DMAN, MB, UDMH, and DMNZD which showed relatively low NDMA formation (<2%) during chloramination, their NDMA molar conversions increased after exposure to chlorine dioxide. At CT of 5 mg×min/L, overall NDMA formation from these precursors increased up to 2% not showing any significant changes afterwards.

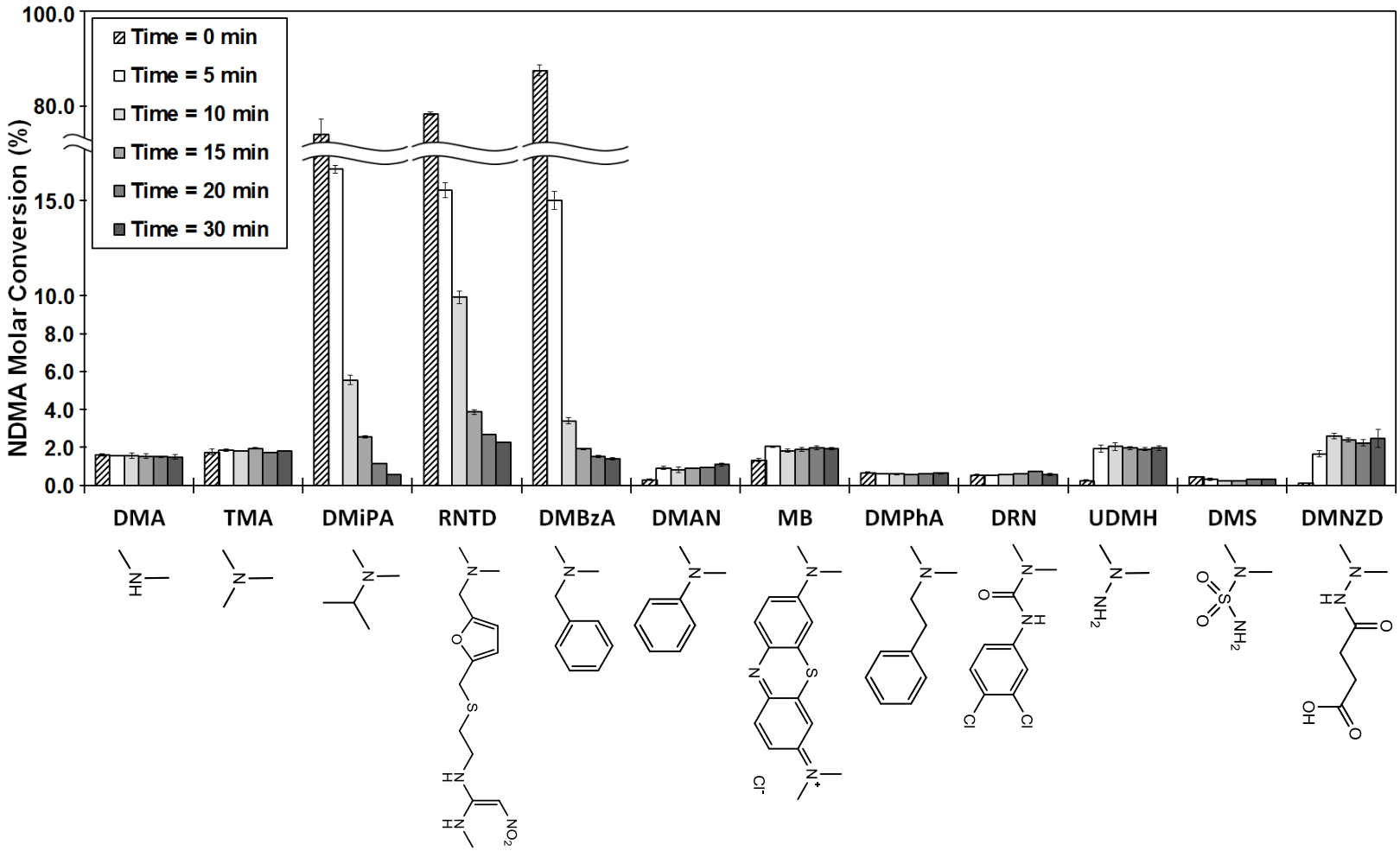


Figure 8.6. NDMA formation from selected precursors upon pre-oxidation with chlorine dioxide followed by chloramine disinfection for different pre-oxidation contact times. $[\text{Precursor}]_0$ = 160 nM, $[Cl_2]_0$ = 3 mg/L, $pH_{\text{Pre-oxidation}}$ = 7.5 (2 mM phosphate buffer), pH_{FP} = 7.5 (10 mM phosphate buffer). Time = 0 min shows no pre-oxidation. Error bars represent data range for duplicate samples.

However, TMA, DMPhA, DRN, and DMS did not show any noticeable change in NDMA conversions after pre-oxidation with chlorine dioxide. Likewise, all of the selected polymers (i.e., PolyDADMAC, PolyAMINE, and PolyACRYL) remained relatively constant in their NDMA formation after pre-oxidation with chlorine dioxide (**Figure 8.5-B**). As an electron acceptor, chlorine dioxide reacts mainly through an electron transfer reaction. Thus, it is likely that reactions with chlorine dioxide would be less favorable due to electron deficient nitrogen atom of quaternary amine polymers.

Unlike pre-chlorination, pre-oxidation effects of chlorine dioxide on overall NDMA formation depended highly on precursors. The NDMA formation from high NDMA yielding compounds such as DMiPA, RNTD, and DMBzA drastically decreased upon contact with chlorine dioxide. On the other hand, low NDMA yielding compounds such as DMAN, MB, UDMH, and DMNZD showed increases in NDMA formation after pre-oxidation with chlorine dioxide. Interestingly, although these two trends seem contradictory, the NDMA conversion yields from the selective precursors which were oxidized with chlorine dioxide reached 1.5-2.0% at CT of 30 mg×min/L. Such conversion rates are very close to that of DMA which was constant for various contact times with chlorine dioxide. This pattern has not been previously reported in the literature for model compounds upon exposure to chlorine dioxide.

Lee et al. (2007a) reported that oxidation of tertiary amines with chlorine dioxide could release DMA or products with DMA moiety, but chlorine dioxide would not react further with such oxidation products with DMA moieties. According to their findings, oxidized amines with DMA moiety released by pre-oxidation with chlorine dioxide may further react with chloramine to produce NDMA. Therefore, both high and low NDMA yielding precursors could be decomposed to either DMA or oxidation products with DMA moiety by chlorine dioxide, and their final NDMA conversion rates become similar to that of DMA. Shah et al. (2012) have reported that the NDMA formation after pre-oxidation with chlorine dioxide decreased or increased and the results depended on different types of precursors present in different water sources. However, based on the findings from our study, it is more likely that different deactivation efficiencies of precursors may be attributed to one single major product, namely DMA, during pre-oxidation with chlorine dioxide. Consequently, the application of chlorine dioxide as a pre-oxidant to control NDMA formation could be effective in source waters containing high NDMA yielding precursors (i.e., >5%). The application would be redundant for source waters containing DMA or lower NDMA yielding precursors than DMA (i.e., <1%) as major precursors.

Pre-oxidation with Ozone

The molar conversions of NDMA from selective precursors exposed to ozone as a pre-oxidant were plotted with different contact times in **Figure 8.7**. When DMA was pre-oxidized with ozone, overall NDMA formation from DMA increased. This is consistent with the findings reported by Andrzejewski et al. (2008) and Yang et al. (2009). In the latter study, it was revealed that ozonation by itself can form NDMA from DMA through a nitrosation pathway at pH 3.4. They also noted that NDMA formation also occurred at pH 7.0 or greater via an unknown pathway (Yang et al., 2009). In our study, however, the highest NDMA formation (molar conversion of 2.3%) from DMA occurred within 1-2 min of contact time with ozone, while further contact led to overall decreases (molar conversion of 1.8%).

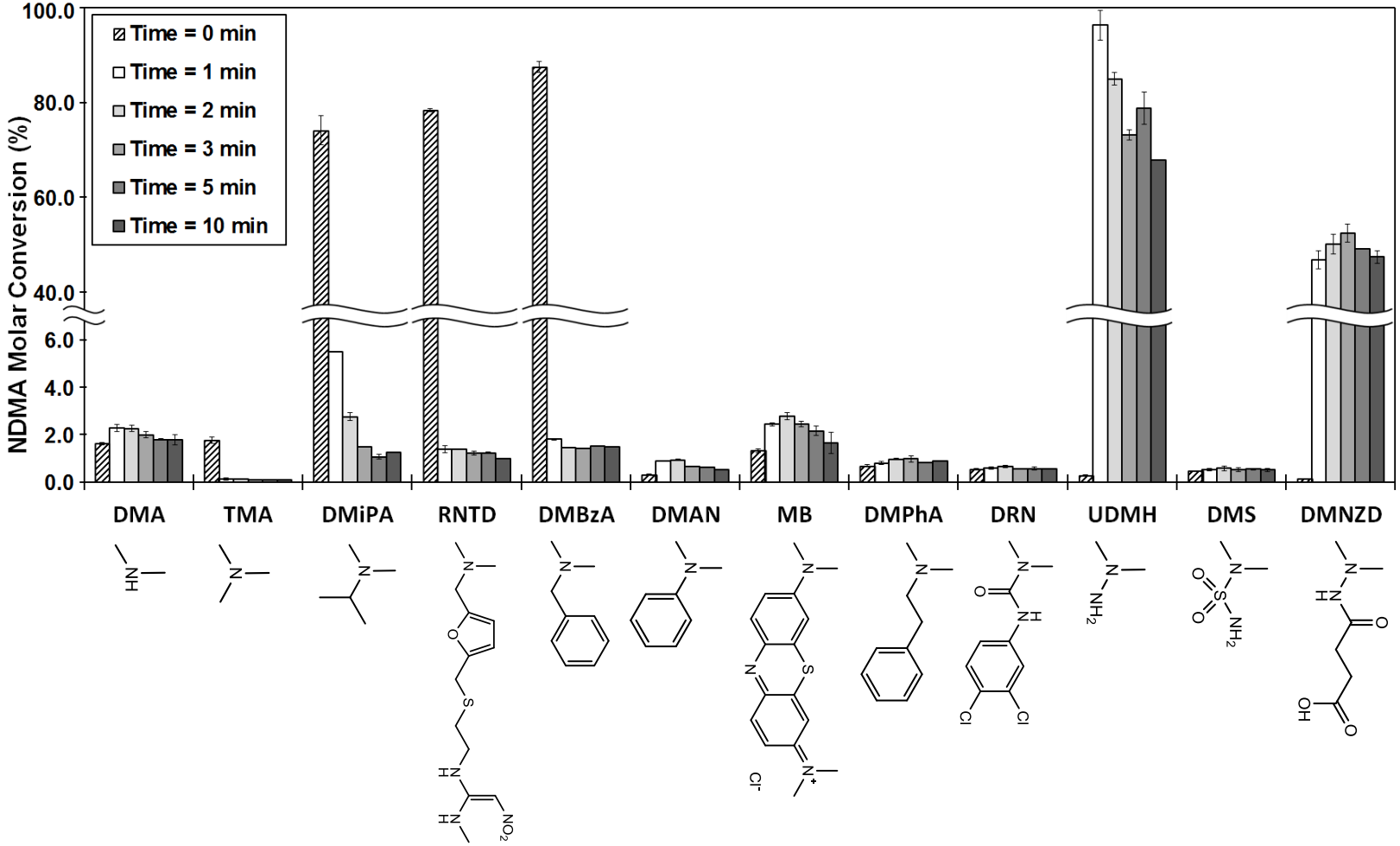


Figure 8.7. NDMA formation from selected precursors upon pre-oxidation with ozone followed by chloramine disinfection for different pre-oxidation contact times. $[\text{Precursor}]_0$ = 160 nM, $[Cl_2]_0$ = 3 mg/L, $pH_{\text{Pre-oxidation}}$ = 7.5 (2 mM phosphate buffer), pH_{FP} = 7.5 (10 mM phosphate buffer). Time = 0 min shows no pre-oxidation. Error bars represent data range for duplicate samples.

For DMAN, MB, and DMPhA, pre-oxidation with ozone also led to increases in NDMA formation. Like DMA, these compounds had the highest NDMA yields within 1-2 min (i.e., T/T_{Max} of 0.1 – 0.2), and overall NDMA formation decreased as CT values increased. Since tertiary amines may release DMA as an intermediate (Lee et al., 2007a) upon oxidation with ozone, released DMA which could produce more NDMA than the parent compounds (i.e., DMAN, MB, and DMPhA) may increase the NDMA formation observed during initial 1-2 min (T/T_{Max} of 0.1 – 0.2) during chloramination. However, the subsequent decreases with the increasing CT have not been previously reported in the literature. One possible explanation is the hydroxyl radicals formed during ozonation contributing to the decomposition of formed NDMA. To investigate this hypothesis, an NDMA stock solution of 200 ng/L was prepared and ozonated with and without *tert*-butyl alcohol (used as a hydroxyl radical scavenger) at pH 7.5 and 9.5 (**Figure 8.8**). In the presence of *tert*-butyl alcohol NDMA concentrations remained constant, while a sharp decrease in NDMA was observed without hydroxyl radical scavenger. As hydroxyl radical formation increased with increasing pH, more decreases in NDMA at pH 9.5 than at pH 7.5 were observed. This indicates that hydroxyl radicals released from ozonation would decompose NDMA. In a recent study conducted by Lv et al. (2013), similar findings have been reported. In that study it has been shown that hydroxyl radicals can decompose NDMA to DMA and some other nitrogenous compounds (i.e., methylamine, nitromethane and ammonia) which were identified and quantified by a GC/MS. Based on

the findings of our study and previous studies in the literature (Lee et al., 2007a; Andrzejewski et al., 2008; Yang et al., 2009; Padhye et al., 2011; Lv et al., 2013), ozone or hydroxyl radicals can react with the NDMA precursors and either destroy these precursors or release the DMA moiety or form NDMA. However, hydroxyl radicals can decompose DMAs and NDMAs. Consequently, NDMA formation may be not only enhanced by the reaction of DMA with ozone, but also reduced due to NDMA decomposition by hydroxyl radicals (**Figure 8.9**), which would explain the increasing, then decreasing NDMA conversion patterns observed during ozonation.

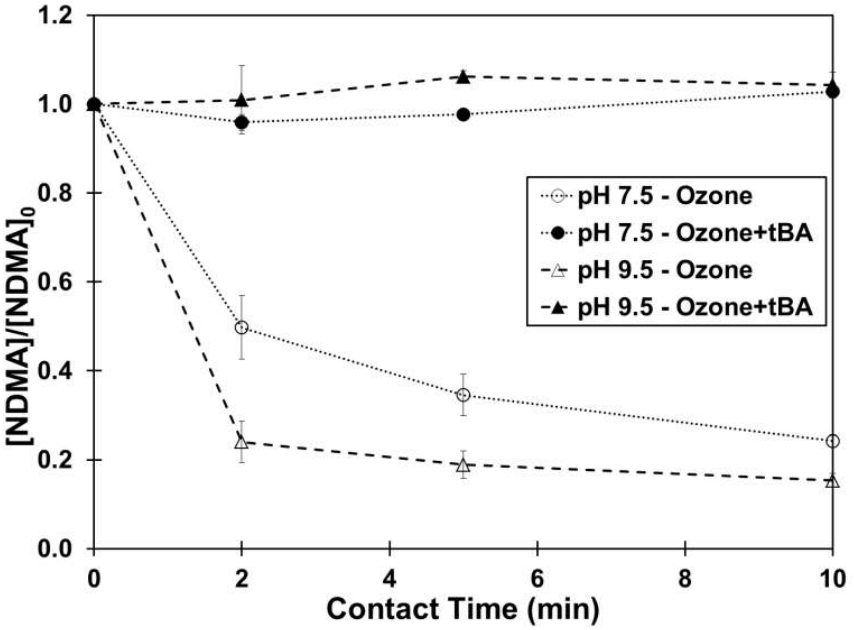


Figure 8.8. Effect of ozone versus hydroxyl radicals on NDMA decomposition. $[NDMA]_0$ = 200 ng/L, $[O_3]_0$ = 3 mg/L, [tBA] = 1 mM, phosphate buffer of 10 mM at pH 7.5 or 9.5. Time = 0 min shows no pre-oxidation. Error bars represent data range for duplicate samples.

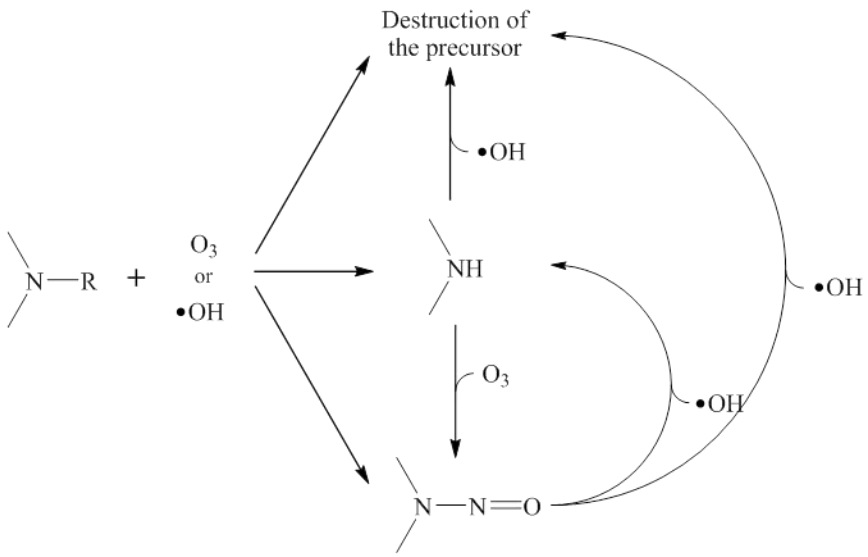


Figure 8.9. Reaction of tertiary amines with ozone and hydroxyl radicals.

For TMA, pre-oxidation with ozone was able to reduce NDMA formation significantly (from 1.8% to 0.2% for 1 min contact time), which is in good agreement with the findings of Lee et al. (2007a). Ozonation was also effective to control NDMA formation from high NDMA yielding compounds such as DMiPA, RNTD, and DMBzA. Only 3 minutes of contact with ozone (i.e., CT ≈7.2 mg×min/L) reduced NDMA formation from these compounds to approximately 2%.

For selected polymers, pre-ozonation led to increases in NDMA formations (**Figure 8.5-C**). For 3 minutes of exposure to ozone, NDMA formation from PolyDADMAC and PolyACRYL increased from 164 and 127 ng/L to 551 ng/L and 507 ng/L, respectively. These changes were less drastic for PolyAMINE; NDMA formation increased from 97 to 169 ng/L after pre-oxidation with ozone. Under chloramination without any pre-oxidation, the NDMA formation from these polymers was very low (≈0.2%), due to hindrance of the nucleophilic substitution by positive charge on the

nitrogen atom (Krasner et al., 2013). It has been known that DMA could be released from PolyDADMAC by ozonation (Padhye et al., 2011a) with an approximate yield of 1.5-2.0%. Therefore, sequential chloramination may enhance NDMA formation from PolyDADMAC. Without chloramination, NDMA can also be formed from PolyDADMAC (Padhye et al., 2011a) through the simultaneous formation and reaction of released hydroxylamine and DMA. The NDMA formation from the other two polymers could be explained in the same way, since similar trends in data were observed for PolyAMINE and PolyACRYL. Hydroxyl radicals formed by the decomposition of ozone may be the reason for decreases in NDMA levels after 3 minutes of contact time for these polymers.

Compared to other precursors, amides and hydrazines (i.e., DMNZD and UDMH) yielded significant amounts of NDMA when pre-oxidized with ozone. At approximately 3 mg×min/L of CT, NDMA yields jumped from 0.3 to 96.4% and 0.1 to 46.9% for UDMH and DMNZD, respectively. In another set of experiments where ozone was applied without subsequent chloramination, comparable NDMA was formed from these compounds, which is consistent with the study conducted by Schmidt and Brauch (2008). This suggests that only ozone accounted for the NDMA formation from these compounds. Like the compounds described above, the NDMA formation from these precursors also decreased with increasing contact time. Once again this can be attributed to ozone decomposition and formation of hydroxyl radicals, which can destroy NDMA after its initial formation.

On the other hand, DRN and DMS did not show any change in NDMA formation in spite of pre-ozonation. DRN remained relatively constant regardless of contact time. The NDMA formation from DMS under pre-ozonation was different from previous studies conducted by von Gunten et al. (2010). But the presence of bromide was shown to be an essential factor to form NDMA from DMS in their study. To verify bromide effect on NDMA formation from DMS, a pre-ozonation experiment was conducted with 200 μg/L of background bromide, and the subsequent NDMA yield was found to be 56.7% (±2.3). This result was consistent with the findings of Schmidt and Brauch (2008) and von Gunten et al. (2010). However, since the effect of ions (i.e., bromide) was not within the scope of this study, further investigation was not made.

Effect of pH on Pre-oxidation

In water treatment process, the pH of water is subject to change after each stage. Since reactions between amines and oxidants have been observed to be pH dependent (von Gunten et al., 2010), the overall NDMA formation from amine precursors could be largely influenced by oxidation pH, which was not previously studied. Different pH conditions during pre-oxidation were investigated with selected precursors to cover typical conditions of different stages for the water treatment process: (i) non-adjusted raw water pH, (ii) pH after the coagulation/flocculation process (pH ≈6.5), and (iii) pH after softening with lime/soda ash (pH ≈9.0). The NDMA FP results from the selected precursors after pre-oxidation at different pH conditions are given in **Table 8.2**.

For chlorination, NDMA FPs of DMA and TMA showed slight decreases with increasing pre-oxidation pH. Increasing pH has been known to facilitate reaction kinetics

and achieve higher precursor deactivation (Lee and von Gunten, 2010). Pre-chlorination of DMiPA which is a high NDMA yielding precursor resulted in at least 10% reduction of NDMA conversion at pH 5.5-9.5. As pre-oxidation pH increased from 5.5 to 8.5, NDMA FP from DMiPA decreased from 74.7% to 54.4%. However, NDMA formation increased again to 67% at pH 9.0. The lowest NDMA FP was observed at pH 8.5, which is close to the mid-point (8.9) of the two reactants' pK_a (7.5 for chlorine and 10.3 for DMiPA). HOCl reacts with deprotonated amines; the mid-point of pK_a of the two reactants will represent an optimum pH for the oxidation since both species may coexist at the highest concentrations, and thus enhance the reaction kinetics. Another high NDMA yielding precursor, RNTD was deactivated more by chlorine at lower pre-oxidation pH. Unlike DMiPA, RNTD has two pK_a values: 8.2 for the DMA moiety and 2.7 for the diaminonitroethene group. At low pH, chlorine would attack the diaminonitroethene group rather than the DMA moiety of RNTD, which would lessen the stability of the leaving group, which would make NDMA formation unfavorable (previous chapter). In the case of DMNZD, increasing pre-chlorination pH slightly increased NDMA formation. Lastly, NDMA FP of PolyDADMAC remained relatively constant at varying pH values due to hindrance caused by the positive charge on the nitrogen atom (Krasner et al., 2013).

Table 8.2. Molar NDMA yields of selected precursors after pre-oxidation under different pH conditions (Pre-oxidant T/T_{Max} = 0.2).

Precursor (pK_a)	Oxidant	NDMA Yields (%)						
		Pre-oxidation pH						
		5.5	6.5	7.5	8.0	8.5	9.0	9.5
DMA (10.6)	Cl_2	1.3	1.0	1.0	0.8	0.7	0.6	0.5
	ClO_2	1.0	1.0	1.1	1.1	1.0	1.1	1.2
	O_3	0.9	1.1	1.4	1.3	1.4	1.9	1.5
TMA (9.8)	Cl_2	1.5	1.5	1.8	1.5	1.5	1.0	0.9
	ClO_2	1.8	1.4	1.2	1.3	1.5	1.2	1.1
	O_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1
DMiPA (10.3)	Cl_2	74.7	66.4	61.8	59.4	54.4	58.8	67.0
	ClO_2	56.2	40.8	14.7	3.7	0.3	0.2	0.2
	O_3	18.7	10.0	7.3	4.9	6.2	6.6	5.9
RNTD (2.7 & 8.2)	Cl_2	38.2	40.7	45.9	52.8	54.6	63.3	71.8
	ClO_2	82.9	59.8	18.9	4.5	2.2	1.8	1.6
	O_3	6.4	2.2	1.3	0.7	0.5	0.3	0.3
DMNZD (4.7)	Cl_2	0.1	0.1	0.3	0.3	0.4	0.4	0.3
	ClO_2	0.2	0.4	1.3	1.7	2.0	2.1	2.0
	O_3	66.7	64.0	54.5	43.8	43.3	38.9	43.3
PolyDADMAC* (NA)	Cl_2	114	134	128	119	113	107	124
	ClO_2	136	116	137	112	114	111	110
	O_3	402	382	499	519	530	476	480

*: NDMA concentration (ng/L) formed from 0.2 mg/L of PolyDADMAC.
Reported values are average of two measurements (n=2).
NA: Not Available.

Pre-oxidation with chlorine dioxide did not affect the NDMA formation from DMA, due to low reactivity between them (Lee and von Gunten, 2010). For TMA, slight decreases in NDMA FP were observed at increasing pre-oxidation pH. And once again, much more drastic decreases in NDMA FP were observed for high NDMA yielding

compounds (i.e., DMiPA and RNTD). For TMA, DMiPA and RNTD, as pre-oxidation pH increased and approached their pK_a values, the reaction rate constants increased according to the findings of Lee and von Gunten (2010). Thus, within the same contact time (6 min) their NDMA FPs decreased more at higher pH. This is consistent with the results of Lee and von Gunten (2010) that chlorine dioxide reacted faster with deprotonated amines than protonated ones. However, further increases in pre-oxidation pH would not change the reaction rate constants, and thus the NDMA FP remained constant. These findings imply that chlorine dioxide would be more effective at higher pH, since amines generally have high pK_a values. For DMNZD, increases in NDMA FP at higher pH were also observed. However, PolyDADMAC was not affected by various pre-oxidation pH conditions during pre-oxidation with chlorine dioxide.

It has been known that ozone reacts faster with deprotonated amines (Lee and von Gunten, 2010), which means that the pK_a values of amine precursors could play a key role in NDMA formation. Thus, higher reaction rate constants are expected under alkali conditions (Lee and von Gunten, 2010). As well, an unknown pathway has been reported for higher NDMA formation from DMA at pH higher than 7 during ozonation (Yang et al., 2009) within 2 minutes of contact time. On the contrary, the NDMA formation from high NDMA yielding compounds such as DMiPA and RNTD decreased as pH increased. However, TMA and DMNZD showed somewhat different behaviors from other precursors. TMA was not affected by pH during ozonation. For DMNZD, since its pK_a is 4.7, rapid reactions between ozone and DMNZD were expected. However, the formation of hydroxyl radicals has an adverse effect. Therefore, overall decreases of NDMA FP

were observed as pH increased. Finally, the NDMA formation from PolyDADMAC increased along with increasing pH, and showed a peak at pH 8.5, and then decreased again at higher pH. Selection of appropriate ranges of oxidation pH must be considered together with selection of proper oxidants for NDMA control in the presence of various types of precursors in water matrices.

Conclusions

A fairly wide range of different NDMA precursors has shown the importance of the effect of oxidants prior to chloramination on NDMA formation. For the 15 precursors tested in this study, the use of chlorine as a pre-oxidant led to the reduction of overall NDMA FP, except polymers. Therefore, chlorine can be used to effectively control NDMA formation during drinking water treatment, as long as the formation of carbonaceous-DBPs is under the regulated levels. Chlorine dioxide was also effective in reducing NDMA formation from high NDMA yielding precursors. However, for low NDMA yielding precursors, the NDMA formation may increase due to the release of DMA and subsequent reactions between DMA and chloramines. Similar to chlorine dioxide, the use of ozone as a pre-oxidant may result in contrasting effects on NDMA formation. While ozone may stimulate NDMA formation, simultaneously produced hydroxyl radicals may also work against this effect. Thus, neither chlorine dioxide nor ozone is an independently effective pre-oxidant for controlling NDMA (i.e, coumpounds with yields <1% or amides). Instead, the effectiveness of both is highly depending on the characteristics of the existing precursors in source waters. During pre-oxidation, pH is an

important factor in deactivating NDMA precursors. Since deprotonated amines are more susceptible to the reaction with oxidants, the pK_a of both amines and oxidants are key players. In this way, optimized pH conditions for pre-chlorination must be determined for the best treatability. However, ozone and chlorine dioxide would reach and sustain their maximum effectiveness at a pH above the amines' pK_a values.

CHAPTER NINE

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The important conclusions for each objective of this study are summarized below.

Objective 1: ***Examine the formation potential of nitrosamines from selected amino acids under different oxidation conditions.***

- Even at 10 mg/L concentration, nitrosamine yields from all nine AAs during chloramination, ozonation and ozonation-chloramination conditions were very low (<10 ng/L) or below the minimum reporting levels.
- Since nitrosamine formation yields of AAs were very low, AAs would not likely to be a contributor to nitrosamines formation.

Objective 2: ***Investigate (i) the effect of tertiary amine structure, (ii) the effect of background NOM, and (iii) the roles of mono- vs. dichloramine species on the NDMA formation.***

- A fairly wide range (0.02% to 83.9%) of NDMA formation from the 21 selected amines indicates the importance of the structure of tertiary amines on NDMA formation.
- The results showed that both stability and electron distribution of the leaving group of tertiary amines have an important role in NDMA formation.

- DMA associated with branched alkyl groups or benzyl like structures which have only one carbon between the ring and DMA structure consistently gave higher yields of NDMA formation.
- Compounds with EWG reacted preferentially with monochloramine, whereas compounds with EDG showed a tendency to react with dichloramine to form NDMA.
- When the amines were present along with NOM in solution, NDMA formation increased for compounds with EWG while it decreased for compounds with EDG. This impact was attributed to the competition between NOM and amines for chloramine species.

<u>Objective 3:</u> Examine (i) the role of chloramine species in the formation of NDMA from DMA and selected tertiary amines; (ii) the factors that influence chloramine decomposition (i.e., pH, sulfate and NOM) during NDMA formation from these model precursors; and (iii) the role of chloramine species in selected natural waters.

- The results showed that electron distribution of the tertiary amine determines the reactive chloramine species. Compounds with EWG (i.e., RNTD) reacted preferentially with monochloramine, whereas compounds with EDG (i.e., DMiPA) showed a tendency to react with dichloramine to form NDMA.
- NOM would be beneficial in the control of NDMA in distribution systems. The presence of NOM decreased the NDMA formation from DMiPA (dichloramine sensitive precursor) due to competition created for dichloramine species. Furthermore, HPO fraction of NOM could also lead to some decreases in NDMA

formation probably due to its covalent binding capability with aromatic amines (i.e., RNTD).

- In NDMA formation, pH plays a key role as it influences both chloramine speciation and protonation state of the amine. Highest NDMA yield is expected to be observed at an optimum pH (mid-point of both reactants' pK_a) where both dichloramine and deprotonated amine species may coexist.
- The presence of chloramine decomposing components (sulfate, phosphate, carbonate, etc.) can increase the fraction of dichloramines and consequently lead to higher NDMA formation.
- Investigating two case studies showed that dichloramine was observed to be the dominant species responsible for NDMA formation in both systems. The NDMA formation was found to be limited by the transformation of monochloramine to dichloramine, and thus relatively slow NDMA formation rates were observed.

<u>Objective 4:</u> Examine (i) the commonly used pre-oxidants (i.e., chlorine, chlorine dioxide and ozone) in water treatment; (ii) CT values, and (iii) pre-oxidation pH's effects on NDMA formation from selected precursors.

- A fairly wide range of different NDMA precursors has shown the importance of the effect of oxidants prior to chloramination on NDMA formation.
- Among the tested precursors, the use of chlorine as a pre-oxidant led to a reduction in overall NDMA FP, with the exception of polymers and tertiary amines with carbonyl or sulfonyl groups.

- The use of chlorine dioxide could also be effective in reducing NDMA formation for source waters that contain precursors with high NDMA yields (>5%). However, it can be detrimental, increasing NDMA formation if the precursor's yield is less than <1.0%, due to the release of the DMA moiety.
- Similar to chlorine dioxide, the use of ozone as a pre-oxidant has a potential for contrasting outcomes. While ozone may stimulate NDMA formation, the simultaneously produced hydroxyl radicals would work against this effect.
- Chlorine can be used as an effective strategy in controlling NDMA formation during drinking water treatment, as long as C-DBP formation is within the regulated levels. On the other hand, the effectiveness of chlorine dioxide and ozone is determined by the characteristics of the existing precursors in source waters.
- During pre-oxidation, pH is an important factor in deactivating NDMA precursors. Since deprotonated amines are more susceptible to the reaction with oxidants, the pK_a of both amines and oxidants are key players. In this way, optimized pH conditions for pre-chlorination must be determined for the best treatability.

Recommendations for Practical Applications

- The structure of the NDMA precursor plays a critical role in NDMA formation. Strategies for controlling the discharge of DMA moieties associated with branched alkyls or benzyl like groups (i.e., pharmaceutical companies) would lead

to decreases in NDMA precursor's levels. This would decrease the stress created in downstream DWTPs.

- The dichloramine was the important chloramine species responsible for NDMA formation. The utilities can try to minimize the formation of dichloramine in their distribution systems (e.g., higher pH conditions) to control NDMA formation. However, it should be noted that there are some precursor that may form NDMA with monochloramine. Formation potential tests conducted with and without background ammonia, as performed in this study, can be used to determine mono or dichloramine sensitivity of NDMA precursor in a source water.
- Pre-oxidation strategies can be an effective tool for utilities to control NDMA formation. Chlorine has shown reduction in NDMA formation for most of the precursors (except polymers). This indicates that chlorine could be useful as a pre-oxidant as long as C-DBP formation is within the regulated levels. On the other hand, chlorine dioxide and ozone may lead to decreases or increases in NDMA formation depending on the characteristics of the precursors. Preliminary testing is suggested for utilities determining the best oxidant type, dose and contact time for particular applications to control NDMA formation. Furthermore, the pre-oxidation reactions were found to be highly dependent on the pH. To maximize the removal of NDMA precursors within the same CT, bench-scale testing is recommended to determine the optimum pH.

Recommendations for Future Research

- Different types of amines can be tested for their NDMA formation to develop correlations between NDMA yields and structural characteristics (i.e., linear free energy relationship).
- Density functional theory models can be developed to assess the reactivity of NDMA precursors to minimize experimental testing.
- Further research is needed to identify the intermediates that can be formed during the formation of NDMA from different types of precursors (e.g., amines, amides, hydrazines).
- NOM was observed to have an important effect on NDMA formation. The interactions of NOM with amines and also chloramines species can be investigated to gain further insight.
- Presence of ions (i.e., nitrite, bromide) is necessary to be investigated to evaluate the impacts on both NDMA formation and their interactions with pre-oxidants.

APPENDICES

Appendix A

Chloramines are disinfectants used to treat drinking water (Li, 2011). They are formed by mixing chlorine with ammonia. Although chloramine is a weaker disinfectant than chlorine, it is more stable and provides longer-lasting oxidant residual in the distribution system. Chloramines have been used by water utilities for almost 90 years, and their use is closely regulated (USEPA, 1999). Approximately 35% of the utilities implement chloramine as their disinfection method (Li, 2011). This corresponds to approximately a population of 68 million consuming chloraminated water (Li, 2011).

When chlorine is dispersed in water, a rapid hydrolysis occurs. The equilibrium constant (K_{eq}) at 25°C is 3.94×10^{4} M^{-1} for this reaction (USEPA, 1999). Hypochlorous acid (HOCl) is a weak acid that dissociates to OCl^- (USEPA, 1999). Simplified reactions are given below:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl_2 \qquad \text{(Hydrolysis of chlorine)}$$

$$HOCl \rightarrow OCl^- + H^+ \qquad \text{(Dissociation of chlorine)}$$

Relative proportions of HOCl and OCl^- are dependent upon pH ($pK_a = 7.6$). Both of the chlorine species in the above reaction are powerful oxidants, capable of reacting with many substances present in water (USEPA, 1999). In aqueous solutions with pH 7.0 to 8.5, HOCl reacts rapidly with ammonia to form inorganic chloramines in a series of competing reactions. Chlorine and ammonias mixing may yield the formation of monochloramine (NH_2Cl), dichloramine ($NHCl_2$), or trichloramine (NCl_3) (Valentine et

al., 1998; Karanfil et al., 2007). The simplified stoichiometry of chlorine-ammonia reactions are as follows:

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \qquad \text{(monochloramine)}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \qquad \text{(dichloramine)}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \qquad \text{(trichloramine)}$$

These competing reactions, and several others, are highly dependent on pH and controlled to a large extent by the chlorine: nitrogen (Cl_2:N) ratio (USEPA, 1999). Temperature and contact time also play a role. **Figure A.1** shows the typical relationships between the chloramine species at various Cl_2:N ratios for the neutral pH zone (6.5 to 8.5) (USEPA, 1999). This figure depicts that monochloramine is the dominant species when the applied Cl_2:N ratio is less than 5:1 by weight (1:1 molar ratio). As the applied Cl_2:N ratio increases to 7.6:1 (1.5:1 molar ratio), breakpoint reaction occurs, reducing the residual chlorine level to a minimum. Breakpoint chlorination results in the formation of nitrogen gas, nitrate, and trichloramine. At Cl_2:N ratios above 7.6:1 (1.5:1 molar ratio), free chlorine and trichloramine are present. **Figure A.2** shows the relationship between chloramine species as the pH changes (USEPA, 1999). The Figure shows that dichloramine becomes a dominant species at pH 3.5 - 4.5. At pH's lower than 3.0, trichloramine becomes dominant.

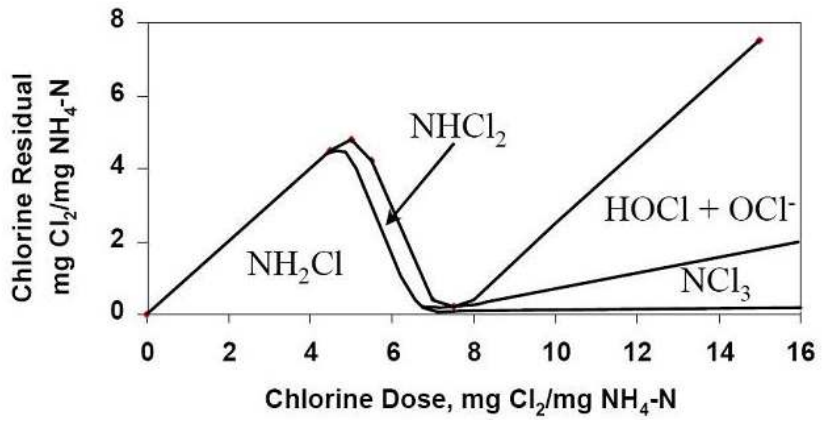


Figure A.1. Theoretical breakpoint curve.

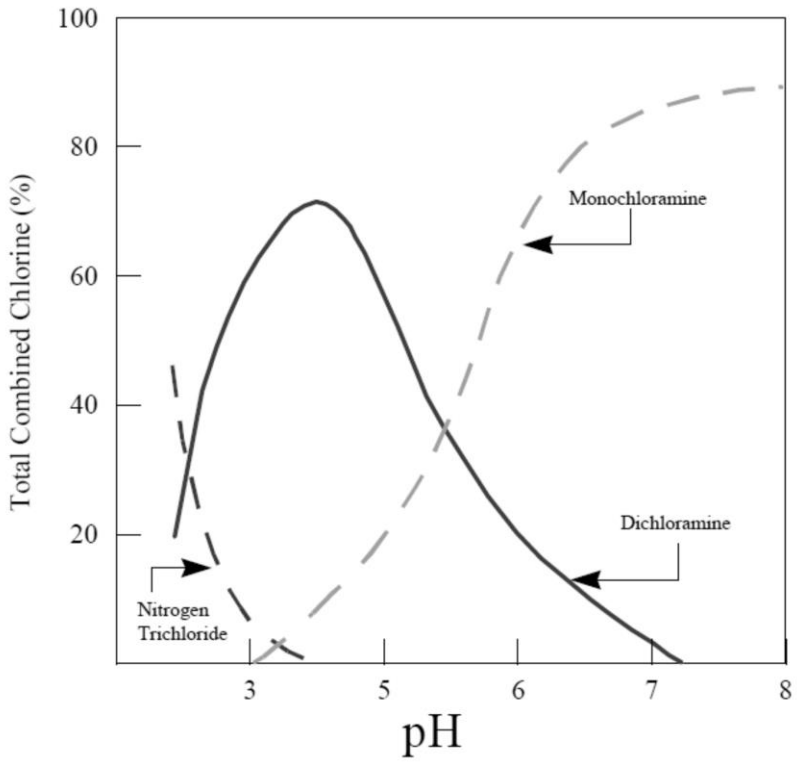


Figure A.2. Chloramine speciation with pH.

To avoid breakpoint reactions, utilities need to maintain a Cl_2:N ratio between 3 and 5 by weight. Therefore, a Cl_2:N ratio of 4 is typically accepted as optimal for chloramination.

While chloramines are considered as less-reactive, they are inherently unstable due to auto-decomposition (Vikesland et al., 2001). At a constant Cl_2:N ratio, there are several factors that can contribute to auto-decomposition of chloramines which includes NOM, carbonate, sulfate, phosphate, nitrite, bromide, and acetic acid (Vikesland et al., 2001; Karanfil et al., 2007). Furthermore, all of these reactions are dependent on pH (Valentine et al., 1998).

Appendix B

NDMA formation concentrations (ng/L) and their corresponding yields ($[Precursor]_0 = 200$ nM).

NDMA Concentration (ng/L)	Molar Conversion (%)
15	0.1
75	0.5
150	1
750	5
1500	10
3750	25
7500	50
11250	75
15000	100

Appendix C

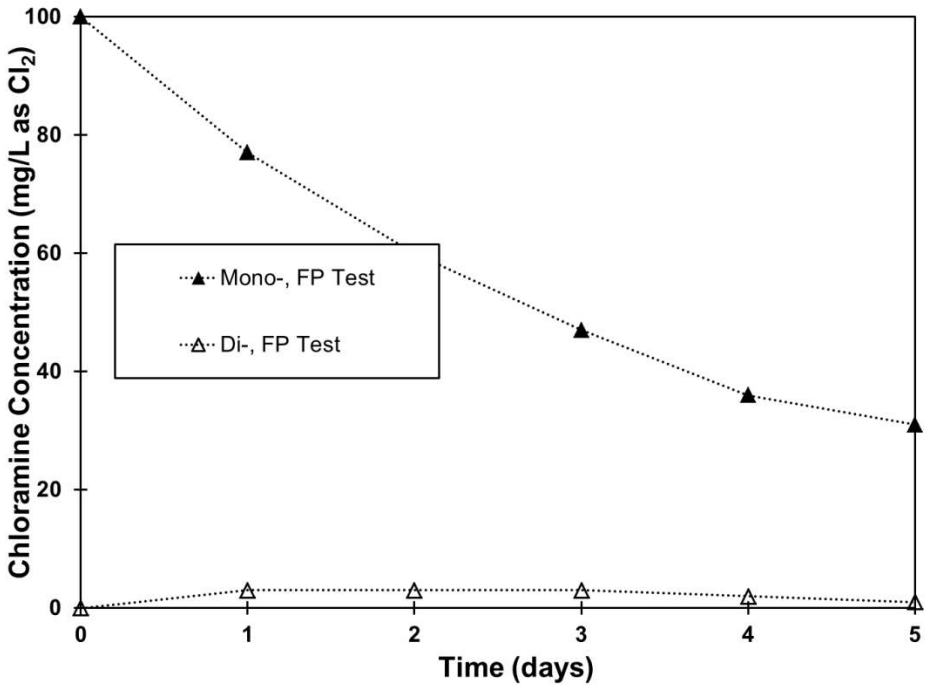


Figure C.1. Typical chloramine residuals measured in NDMA FP tests at 100 mg/L initial dose.

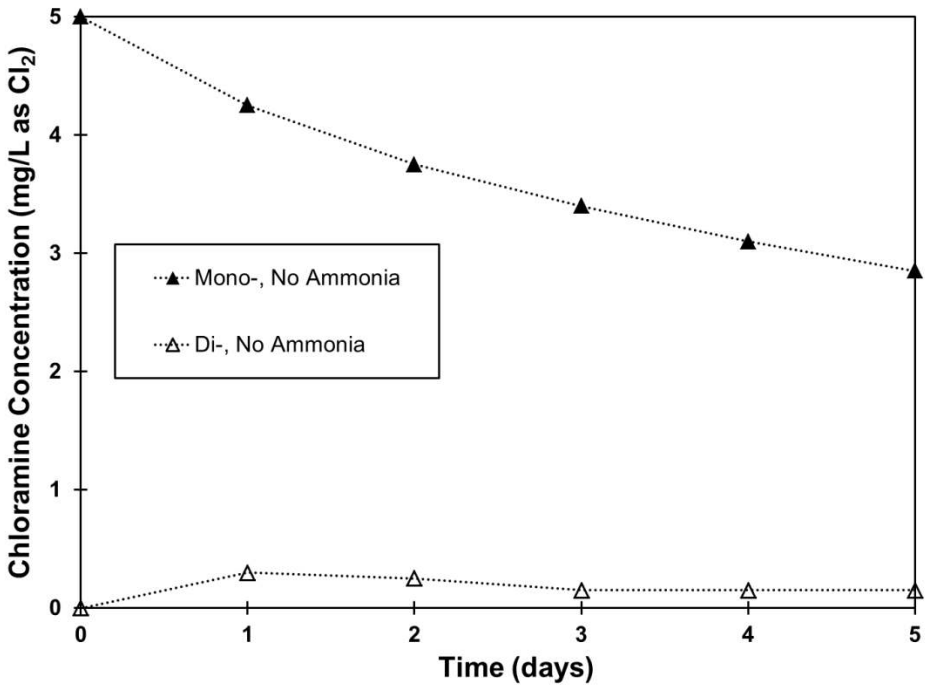


Figure C.2. Typical chloramine residuals measured in NDMA FP tests at 5 mg/L initial dose.

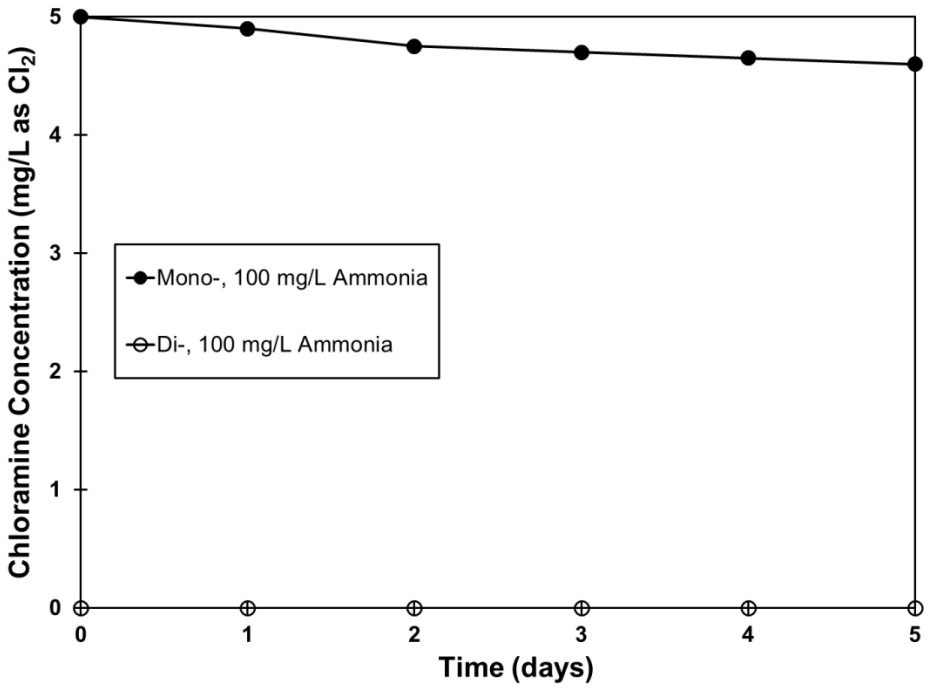


Figure C.3. Typical chloramine residuals measured in NDMA FP tests at 5 mg/L initial dose in the presence of 100 mg/L ammonia.

Appendix D

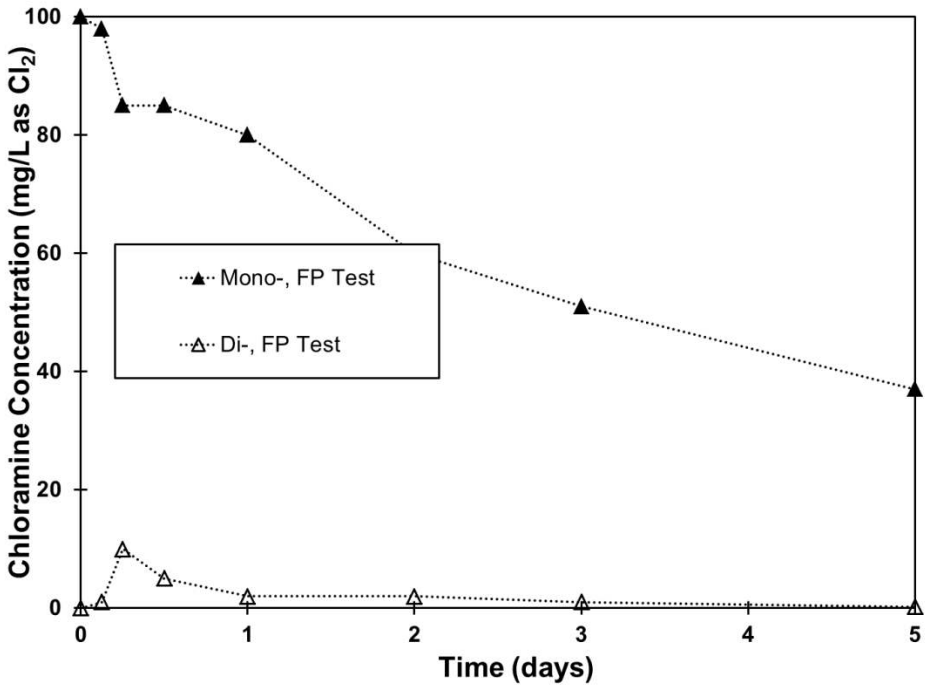


Figure D.1. Typical chloramine residuals measured in NDMA FP tests at 100 mg/L initial dose (pH=7.5).

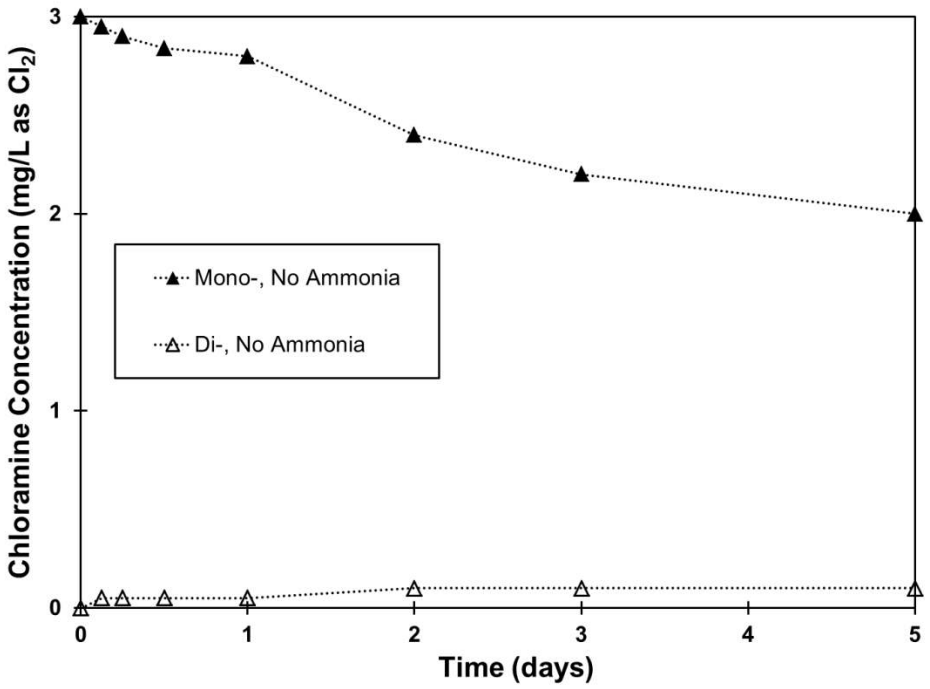


Figure D.2. Typical chloramine residuals measured in NDMA SDS tests at 3 mg/L initial dose (pH=7.5).

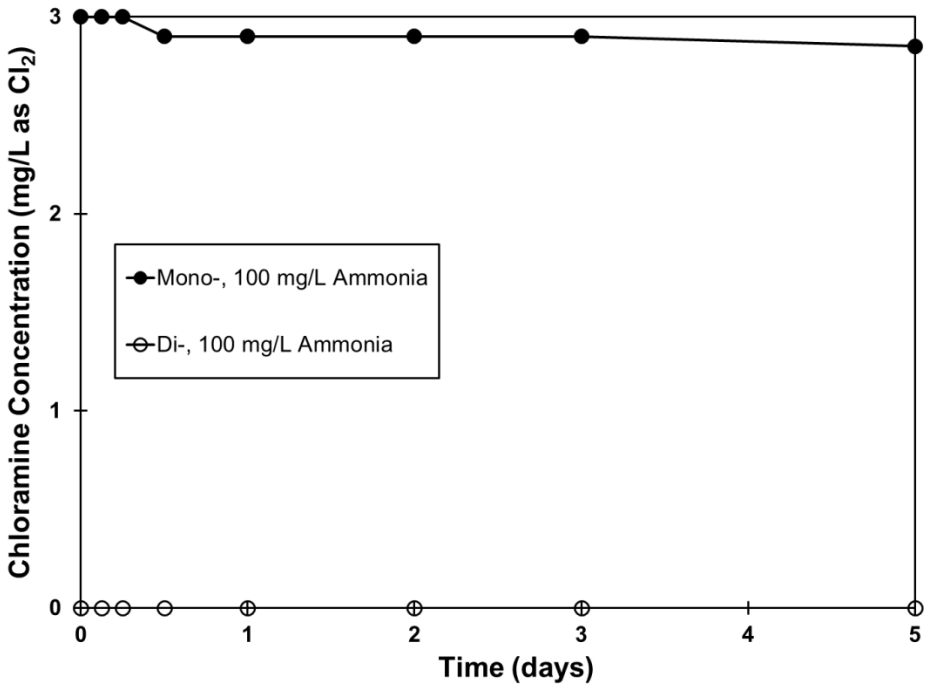


Figure D.3. Typical chloramine residuals measured in NDMA SDS tests at 3 mg/L initial dose in the presence of 100 mg/L ammonia (pH=7.5).

Appendix E

Covalent binding of aromatic amines with the constituents of the NOM are thought to be an important process in aquatic systems (Chen, 2007). Nucleophilic addition of the amine to the carbonyl moieties and/or quinoid groups is proposed to be responsible for the covalent binding (Chen, 2007). Quinones - which occur naturally in many systems and constitute a significant portion of humic acids - have been frequently used to mimic the carbonyl functional groups that may be present in humic acids (Chen, 2007).

Among the family of aromatic amines, aniline is the simplest compound and thus, it has drawn significant research interest. Parris (1980) investigated the reactions of several ring-substituted anilines with humate in aqueous solution and observed biphasic binding. Initially, a rapid, reversible equilibrium (phase I) was established, and a slow irreversible reaction (phase II) subsequently followed. The formation of imine linkage with the humate carbonyls (1,2-nucleophilic addition) was postulated to be responsible for the fast reaction (phase I) between aniline and quinones (Weber et al., 1996). The slower irreversible reaction (phase II) was proposed to result from the 1,4-nucleophilic addition (Weber et al., 1996). The possible pathways are given in **Figure E.1**.

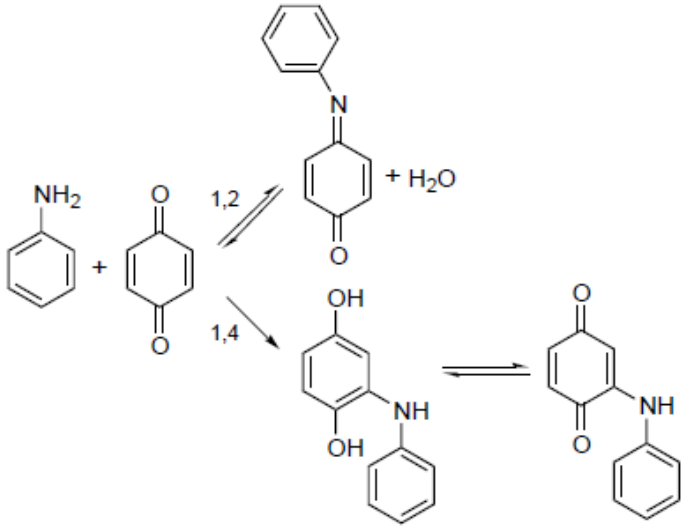


Figure E.1. The proposed pathways for the covalent binding of amines with quinones (Weber et al., 1996).

In addition to aniline, many other aromatic amine chemicals, such as dichloroaniline, *N*-methylaniline, chloroaniline, 1-naphthylamine, 4-methylaniline, and benzidine have also exhibited the similar biphasic sorption in the presence of quinones (Chen, 2007).

Appendix F

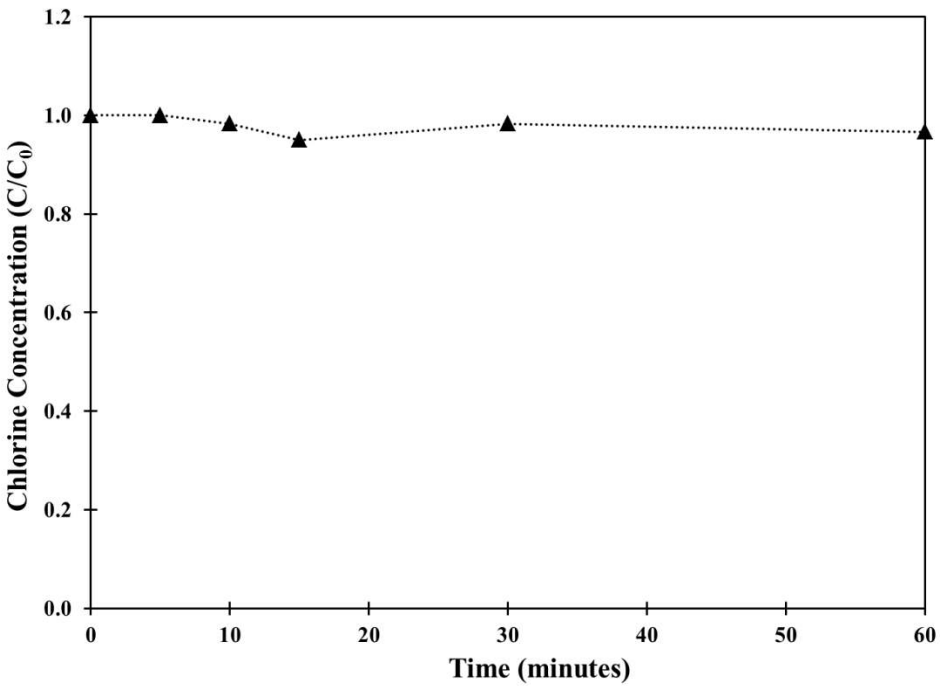


Figure F.1. Typical chlorine residuals measured during pre-oxidation tests at 3 mg/L initial dose (pH=7.5).

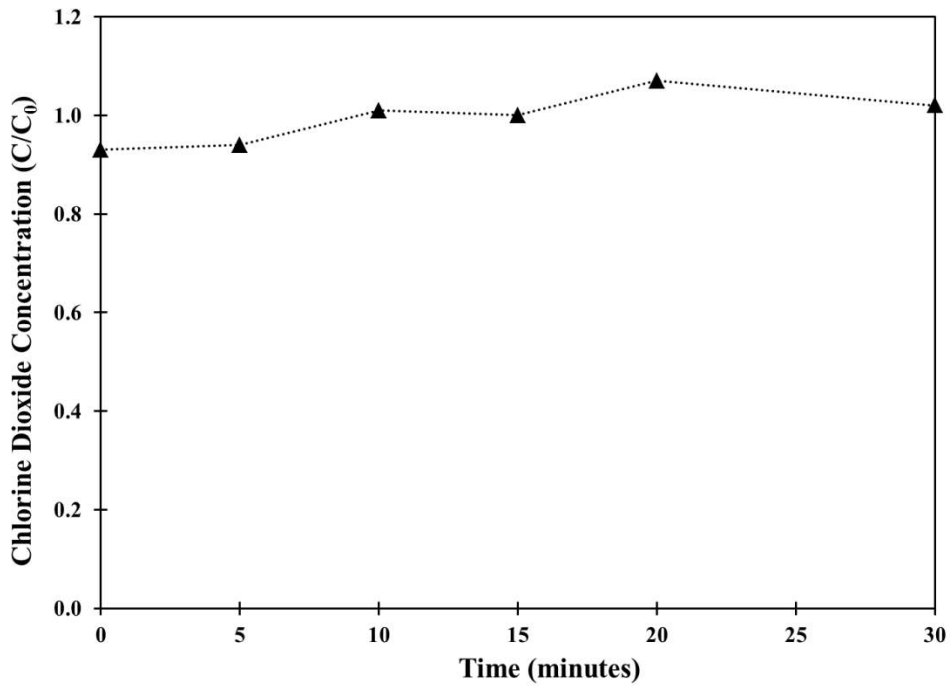


Figure F.2. Typical chlorine dioxide residuals measured during pre-oxidation tests at 1 mg/L initial dose (pH=7.5).

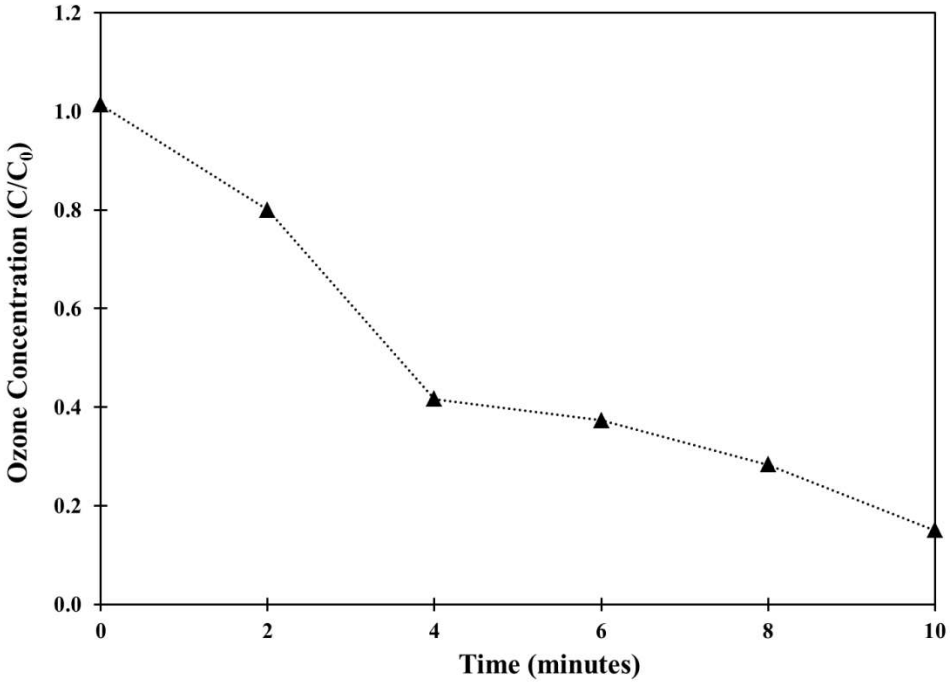


Figure F.3. Typical ozone residuals measured during pre-oxidation tests at 3 mg/L initial dose (pH=7.5).

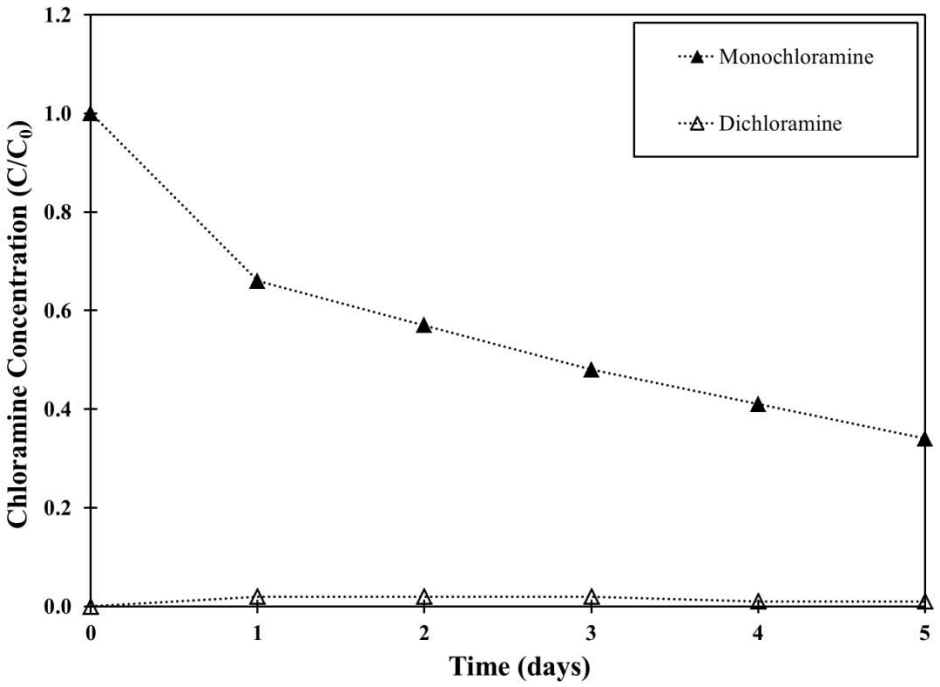


Figure F.4. Typical chloramine residuals measured after pre-oxidation tests at 100 mg/L initial dose (pH=7.5).

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