ROLES OF POLYDADMACS, DITHIOCARBAMATES AND ACTIVATED CARBONS IN FORMATION OF *N*-NITROSAMINE CONTAMINANTS IN WATER

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ROLES OF POLYDADMACS, DITHIOCARBAMATES AND ACTIVATED CARBONS IN FORMATION OF *N*-NITROSAMINE CONTAMINANTS IN WATER

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[To my family]

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TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SYMBOLS AND ABBREVIATIONS

AC	Activated carbon
Cationic PAM	Cationic polyacrylamide copolymer
CDHS	California Department of Health Service
CLLE	Continuous liquid-liquid extraction
ClO_2	Chlorine dioxide
CSPE	Cartridge solid-phase extraction
DBP	Disinfection by-product
DCM	Dichloromethane
DBA	Dibutylamine
DEA	Diethylamine
DEDTC	Diethyldithiocarbamate
DI water	Deionized water
DMA	Dimethylamine
DMA-d_6	Dimethylamine-d_6
DMAEA	Dimethylaminoethyl acrylate
DMDTC	Dimethyldithiocarbamate
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
DPA	Dipropylamine
EI	Electron ionization
EPA	Environmental Protection Agency

FAC	Free available chlorine
FT-IR	Fourier transform infrared spectroscopy
GC/MS	Gas chromatography/ mass spectrometry
GC/HRMS	Gas chromatography/ high resolution mass spectrometry
HAA	Haloacetic acids
LLE	Liquid-liquid extraction
LVI	Large volume injector
Mannich polymer	Aminomethylated polyacrylamide
MAC	Maximum acceptable concentration
MCA	Monochloramine
MCL	Maximum contaminant level
MDL	Method detection limit
MEA	Methylethylamine
NDBA	*N*-Nitrosodi-n-butylamine
NDEA	*N*-Nitrosodiethylamine
NDMA	*N*-Nitrosodimethylamine
NDMA-d_6	*N*-Nitrosodimethylamine-d_6
NDPA	*N*-Nitrosodi-n-propylamine
NDPhA	*N*-Nitrosodiphenylamine
NMEA	*N*-Nitrosomethylethylamine
NMOR	*N*-Nitrosomorpholine
NOM	Natural Organic Matter
NPIP	*N*-Nitrosopiperidine

NPYR	*N*-Nitrosopyrrolidine
O_3	Ozone
PCI	Positive-ion chemical ionization
Polyamine	Poly(epichlorohydrin dimethylamine)
PolyDADMAC	Poly(diallyldimethylammonium chloride)
PYR	Pyrrolidine
SPE	Solid-phase extraction
SPME	Solid phase micro extraction
TBA	*tert*-Butanol
THMs	Trihalomethanes
UDMH	Unsymmetrical Dimethylhydrazine
UV	Ultraviolet

SUMMARY

N-Nitrosamines are an emerging group of disinfection byproducts characterized by high carcinogenic risks at ng/L levels and by their frequent detection in water and wastewater treatment systems in the U.S. and other parts of the world. The overall goal of this research is to achieve a better understanding of the roles of common nitrosamine precursors in leading to *N*-nitrosamine formation in water and wastewater treatment systems. The specific objectives of this research are: (a) To probe the mechanisms of nitrosamine formation from commonly employed water treatment polymers, particularly polyDADMACs, during ozonation, (b) To evaluate the role of dithiocarbamate compounds as nitrosamine precursors in reaction with common water disinfection oxidants, and (c) To investigate the potential enhancement effect of activated carbons (AC) to promote transformation of amines to nitrosamines and identify the involved reaction mechanism.

Results of this research show that, upon ozonation, polyDADMACs may yield *N*-nitrosodimethylamine (NDMA) at levels up to two orders of magnitude higher than current advisory guidelines for NDMA. Radical pathways may be responsible for the degradation of the quaternary ammonium ring groups in polyDADMACs to release of dimethylamine (DMA). Ozonation of released DMA through formation of reaction intermediates such as hydroxylamine and unsymmetrical dimethylhydrazine (UDMH) may be responsible for observed NDMA formation during ozonation of polyDADMACs. Study results also reveal dithiocarbamates as potent nitrosamine precursors with significant nitrosamine yields upon ozonation and monochloramination. Identification and quantification of reaction products suggest UDMH and chlorinated-UDMH oxidation as primary reaction mechanisms in nitrosamine formation from ozonation and monochloramination of dithiocarbamates compounds, respectively. This research also demonstrates that many commercial AC materials may catalyze transformation of secondary amines to yield trace levels of *N*-nitrosamines under ambient aerobic conditions. This is a novel discovery with far-reaching implications because of the widespread usage of AC materials in numerous analytical and environmental applications. The study results show that the properties of AC materials and reaction conditions play a crucial role in the catalyzed nitrosamine formation and should be carefully selected to minimize analytical errors and undesirable nitrosamine formation in water samples. Overall, the mechanistic information obtained in this research will be useful for the water industry and research communities to develop more effective strategies to control undesirable nitrosamine formation in water and wastewater treatment systems and thus better protect the public health.

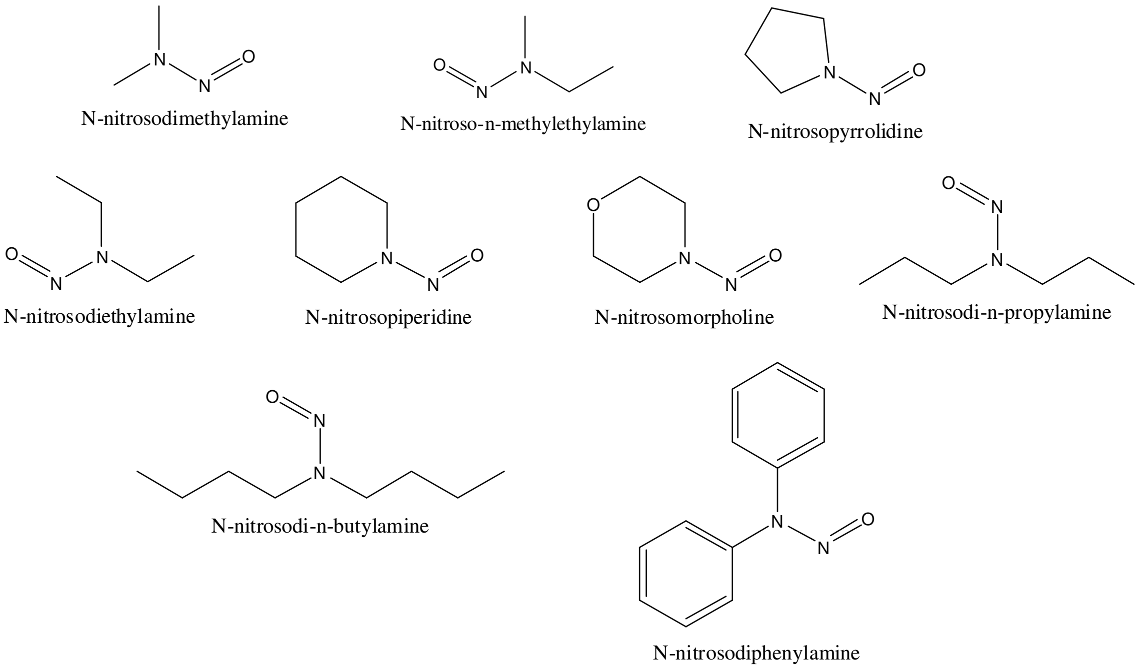
CHAPTER 1

INTRODUCTION

1.1 Background

Since the 1960s, *N*-nitrosamines have been studied by toxicologists for their carcinogenic potential. However, the main areas of focus were the food and consumer products, particularly beer, meats cured with nitrite, tobacco smoke, and rubber products (Mitch *et al.*, 2003b). However, recently it has been shown that *N*-nitrosamines are a group of emerging disinfection byproducts (DBPs) that can be generated during water disinfection processes (Richardson, 2007) and have been detected in treated drinking water in the United States (California Department of Public Health; Mitch *et al.*, 2003b) and in other parts of the world (Charrois *et al.*, 2007). Much of the recent focus on nitrosamines can be traced to recently proposed guidelines at ng/L levels in water by regulatory agencies.

Although there are no federal regulations controlling nitrosamines in drinking water in the United States or Canada, the U.S. Environmental Protection Agency (EPA) has added *N*-nitrosodimethylamine (NDMA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-*n*-butylamine (NDBA), *N*-nitrosodi-*n*-propylamine (NDPA), and *N*-nitrosomethylethylamine (NMEA) to the Unregulated Contaminant Monitoring Rule 2 (UCMR-2) (U.S. EPA, 2006) and NDMA, NDEA, NDPA, NPYR and *N*-nitrosodiphenylamine (NDPhA) to the 3rd version of the Contaminant Candidate List (CCL 3) (U.S. EPA, 2009). These nitrosamines represent 6 of 26 compounds included in the UCMR-2, signaling the importance of monitoring this class of compounds in drinking water. Figure 1.1 depicts the molecular structures of the nine nitrosamines.



N-nitrosodimethylamine
N-nitroso-n-methylethylamine
N-nitrosopyrrolidine
N-nitrosodiethylamine
N-nitrosopiperidine
N-nitrosomorpholine
N-nitrosodi-n-propylamine
N-nitrosodi-n-butylamine
N-nitrosodiphenylamine

Figure 1.1 Molecular structures of *N*-nitrosamines

Nitrosamines are potent rodent carcinogens that have been recognized to cause hepatic tumors in rats and mice (Magee and Barnes, 1956). Although no adequate studies have been reported regarding the relationship between exposure of nitrosamines and human cancer, *N*-nitroso compounds are considered potent human carcinogens due to similarities of metabolism to reactive intermediates between humans and animals (Lijinsky *et al.*, 1983). The U.S. EPA has also classified many members of nitrosamines as probable human carcinogens, with water concentrations as low as 0.2 ng/L associated with a 10^{-6} lifetime cancer risk (U.S. EPA, 2002). The maximum admissible concentrations for the above mentioned nitrosamines in drinking water determined by U.S. EPA at a cancer risk level of 10^{-6} are listed in Table 1.1. Currently, the Ontario Ministry of the Environment has a maximum allowable concentration (MAC) for NDMA of 9 ng/L (Government of Ontario, 2002) while the California Department of Public Health has established a notification level of 10 ng/L for NDMA, NDEA, and NDPA, and a public health goal (PHG) of 3 ng/L for NDMA (California Department of Public Health).

The nine nitrosamines shown in Figure 1.1 and Table 1.1 are of particular importance for nitrosamine research because they are under monitoring regulations (U.S. EPA, 2006; U.S. EPA, 2009) and have been detected at water and wastewater treatment plants in the U.S. and Canada (Mitch *et al.*, 2003b; Charrois *et al.*, 2004; Charrois *et al.*, 2007). At room temperature, these nitrosamines are in liquid state. Their polarity decreases with increasing chain length. Thus, NDMA is the most hydrophilic nitrosamine while NDPhA is the most hydrophobic followed by NDBA.

Table 1.1 U.S. EPA 10^{-6} cancer risk concentrations for six nitrosamines (U.S. EPA, 2002)

Compound	**Molecular Formula**	**Molecular Weight (g/mole)**	**10^{-6} Cancer Risk Concentration (ng/L)**
NDMA	$C_2H_6N_2O$	74.08	0.7
NMEA	$C_3H_8N_2O$	88.06	2
NPYR	$C_4H_8N_2O$	100.06	20
NDEA	$C_4H_{10}N_2O$	102.13	0.2
NPIP	$C_5H_{10}N_2O$	114.15	3.5
NMOR	$C_4H_8N_2O_2$	116.12	5
NDPA	$C_6H_{14}N_2O$	130.11	5
NDBA	$C_8H_{18}N_2O$	158.14	6
NDPhA	$C_{12}H_{10}N_2O$	198.23	7,000

Note: NMOR- *N*-nitrosomorpholine; NPIP- *N*-nitrosopiperidine

1.2 Nitrosamine Extraction and Analysis

For nitrosamine detection in foods and consumer products, analysis was usually performed by liquid-liquid extraction followed by gas chromatography mass spectrometry (GC/MS) or gas chromatography with a nitrogen phosphorus detector with detection limits at 1,000 ng/L (Mitch *et al.*, 2003b). It has been difficult to establish reliable analytical methods for measuring nitrosamines in water, because of the need for low detection limits (in ng/L) due to their higher cancer risk levels (Table 1.1). The basic analytical procedure to detect low-level nitrosamines in water consists of extraction, pre-concentration, and analysis by gas chromatography mass spectrometry (GC/MS). Extraction techniques used for NDMA analysis are mostly liquid-liquid extraction (LLE) and solid phase extraction (SPE). Based on an isotope dilution GC/MS method, a known amount of deuterated NDMA (NDMA-d_6) is added as a surrogate standard to the sample prior to extraction in order to calculate extraction recovery during LLE or SPE. Since mass spectrometry can distinguish the different mass-to-charge ratios (*m/z*) of the parent compound (NDMA) and its isotopic analogue (NDMA-d_6), the use of an isotope makes quantification accurate by precluding the uncertainty of extraction efficiency associated with the sample matrix.

In LLE used for NDMA analysis, based on U.S. EPA Method 607 and Method 3510C (U.S. EPA, 1998), NDMA is extracted using dichloromethane (DCM) and a separatory funnel. However, this method has drawbacks of varying extraction efficiency depending on sample matrix and low recoveries especially when used with wastewater effluents. Another difficulty in performing LLE is the poor separation between aqueous and non-aqueous phases due to emulsification caused by surfactant-like constituents in wastewater samples (Mitch *et al.*, 2003a; Mitch *et al.*, 2003b). Alternatively, continuous liquid-liquid extraction (CLLE) according to U.S. EPA Method 3520C (U.S. EPA, 1998) have also been tested with a larger volume of DCM (100-300 mL) and longer extraction time (approximately 6-18 h) to avoid emulsification problems encountered in wastewater samples during LLE. The CLLE method reportedly yielded extraction efficiencies up to 60% (Mitch *et al.*, 2003b). The extract from LLE or CLLE is usually preconcentrated to less than 1 mL by nitrogen blowdown or using rotary evaporator to lower the method detection limit (MDL). In addition to the inconvenience coming from labor-intensive procedures in LLE methods, the use and disposal of large volumes of organic solvents render these methods less environmentally friendly for routine sample analysis.

As an alternative extraction method, solid-phase extraction (SPE) has been used more often because it possesses several advantages over LLE such as lower costs, shorter extraction times, accommodation of more samples, ease of practice and optimization. Taguchi *et al.* (1994) developed a SPE method using a granular carbonaceous adsorbent, Ambersorb 572, which is commercially produced by pyrolysis of highly sulfonated styrene divinyl benzene ion exchange resins. The black spherical bead form of Ambersorb 572 is much easier to handle compared to the powder types of other carbonaceous adsorbent materials or DCM during the extraction. Typically, a few hundred milligrams of Ambersorb 572 are put into water samples with the surrogate standard, NDMA-d_6, and then extraction is conducted on a roller apparatus or shaker platform for 1-2 h. After NDMA adsorbs to Ambersorb 572, it is isolated from water samples by filtration, dried in air, and transferred to an autosampler vial. The vial is filled with 400-500 μL of DCM which immediately elutes NDMA from the resin. Not only does the above approach greatly reduce the amount of DCM thereby creating a more environmentally friendly method, it also results in a reduction in lowering the method detection limit without a pre-concentration step due to the large concentration factor between the water sample and extract. The NDMA extract is then mounted on an autosampler and undergoes GC/MS analysis. Extraction efficiencies as high as 60% were reported and when combined with GC/High Resolution MS (GC/HRMS), the determination of 1 ng/L levels of NDMA in water samples became possible using the above method (Taguchi *et al.*, 1994). The SPE method, however, suffers from difficulties arising from fragmentation of the resin and subsequent recovery of the extraction (Tomkins and Griest, 1996). Also, Rohm and Haas has discontinued Ambersorb 572 production (Rohm and Haas Co., 2008), leading to an increase in the use of alternate carbonaceous SPE materials including coconut shell-based (Walse and Mitch, 2008) and charcoal-based (Planas *et al.*, 2008) carbons.

1.3 Occurrence of Nitrosamines

1.3.1 Drinking Water

NDMA is the most commonly detected nitrosamine in drinking water with concentrations ranging from 0-180 ng/L (California Department of Public Health; Charrois *et al.*, 2007). The discovery of high concentrations of NDMA in treated drinking water in Ohsweken, Ontario, in 1989 resulted in a survey of 145 drinking water plants in Ontario. The results showed that the NDMA concentration in treated water from most plants was less than 5 ng/L with some plants showing higher NDMA concentrations of up to 9 ng/L (Jobb *et al.*, 1993). Subsequent expanded survey from 179 treatment plants during 1994-2002 showed that median NDMA concentrations in effluents from drinking water treatment plants using chlorine as disinfectant were less than 1 ng/L (Charrois *et al.*, 2007), while effluents from plants using chloramines and their distribution systems showed median NDMA levels of 1.3 ng/L and 2.2 ng/L, respectively. Less than 36% of effluent or distribution system samples showed NDMA more than 1 ng/L when chlorine was used as a disinfectant while that number raises to 79% for distribution systems employing chloramines as primary disinfectant. Even though maximum detected NDMA concentrations (~65 ng/L) were similar for chlorine and chloramine treated distribution systems, the above difference in occurrence of NDMA indicate the stronger tendency of chloramines than chlorine to produce NDMA. Also, the results showed higher NDMA levels for distribution systems with longer retention times, indicating slow kinetics of NDMA formation through disinfectants. In addition, survey results showed that 23 tests from five municipal drinking water treatment plants exceeded Ontario's drinking water quality standards of 9 ng/L with NDMA concentrations ranging from 9.3 - 19 ng/L.

NDMA was also detected in drinking water wells near a rocket engine testing facility in eastern Sacramento County and the San Gabriel Basin in 1998. With groundwater NDMA concentrations as high as 400,000 ng/L on site and 20,000 ng/L off site, downgradient drinking water wells were closed by California Department of Health Science (California Department of Public Health). Resulting survey conducted by California Department of Health Science in 2001 showed that 3 of the 20 chloraminated water supplies contained NDMA concentrations greater than 10 ng/L, while none of the eight water supplies that used only free chlorine disinfection exhibited NDMA levels above 5 ng/L (California Department of Public Health). One drinking water supply, employing anion exchange treatment, also showed NDMA concentrations higher than 10 ng/L.

Charrois *et al.* (2004) reported much higher NDMA concentrations in an occurrence study carried out in Alberta, Canada. NDMA concentrations detected in the study ranged from 0-180 ng/L in distribution systems while it ranged from 0-67 ng/L in finished water samples from treatment plant. In another study carried out in Alberta, Canada, four nitrosamines, NDMA, NPYR, NPIP, NDPhA, were detected in the same distribution system at four locations. NDMA was detected at highest concentration, ranging from 0 to 108 ng/L (Zhao *et al.*, 2006). NPYR, NPIP and NDPhA were also detected at maximum concentrations of 70.5, 117.8 and 1.86 ng/L, respectively. Similar to previous studies, results of this study showed an increase in nitrosamine concentrations with increasing distance from the plant in a distribution system.

1.3.2 Wastewater

Several members of nitrosamines have been detected at concentrations one or two orders of magnitude higher than their drinking water levels in the effluents of wastewater treatment plants (WWTPs) throughout the U.S. and Canada (Mitch *et al.*, 2003b; Krauss and Hollender, 2008; Padhye *et al.*, 2009). NDMA is often detected in raw sewage prior to disinfection with concentrations in µg/L levels being reported from industries (Mitch *et al.*, 2003b). Discharge of certain industrial effluents in municipal wastewater can result in high NDMA concentrations in raw sewage. For example, NDMA concentrations as high as 105,000 ng/L have been reported in effluents from printed circuit board manufacturers using dimethyldithiocarbamates to remove metals (Mitch *et al.*, 2003b).

However, due to biological treatment removal, NDMA concentrations in secondary effluents are expected to be lower than 20 ng/L (Mitch *et al.*, 2003b). In one of the NDMA occurrence studies carried out at seven wastewater treatment plants in California from 2002-2004 (Sedlak *et al.*, 2005), NDMA was detected at median concentration of 80 ng/L in untreated wastewater with maximum concentration of 790 ng/L. Secondary effluent samples also showed significant presence of NDMA with median concentration of 46 ng/L.

In another nitrosamine occurrence study carried out in sludge samples from three wastewater treatment plants in Southeastern United States (Padhye *et al.*, 2009), NDMA was detected at 678 ng/L in primary sludge samples, at 394 ng/L in waste activated sludge and at 271 ng/L in anaerobic digester mixed liquor. Apart from NDMA, NPYR was also detected at maximum concentration of 60 ng/L. NDMA has also been detected in dried municipal sewage sludge used for agricultural fertilizer (Mitch *et al.*, 2003b).

In a study carried out to understand the fate of nitrosamines and their precursors in wastewater-impacted surface waters (Schreiber and Mitch, 2006b), it was observed that the half-life of NDMA precursors originating from wastewater effluents was sufficiently long to negatively impact downstream communities. In addition, NDMA was detected in river water downstream of known effluent discharge locations that received NDMA containing wastewater effluent from one of the treatment plants.

1.4 Nitrosamine Formation Pathways

Occurrence of nitrosamines in drinking water may be related to industrial wastewater effluents due to industrial inputs and nitrosamine-contaminated chemicals in manufacturing processes (OCSD, 2002). But more importantly, formation of nitrosamines may occur at significant levels during chlorine and chloramines disinfection processes in both drinking water and wastewater (Mitch *et al.*, 2003b). Since NDMA is the most commonly detected nitrosamine in water and wastewater treatment plants, most of the research on understanding nitrosamine formation pathways in aqueous medium is focused on NDMA.

Currently, two pathways have been proposed to be responsible for most NDMA formation in drinking water and wastewater: (i) formation of NDMA via *N*-nitrosation reaction; and (ii) formation of NDMA by oxidation of a chlorinated unsymmetrical dimethylhydrazine (UDMH-Cl) intermediate. Details of these two proposed formation mechanisms are discussed as follows.

1.4.1 N-Nitrosation

Nitrosation involves the formation of nitrosyl cation or similar nitrogen-containing species, such as dinitrogen trioxide (N_2O_3), during acidification of nitrite (reactions 1.1 and 1.2, (Mirvish, 1975)). The nitrosyl cation then reacts with an amine, such as dimethylamine (DMA), to form NDMA (reactions 1.3 and 1.4, (Mirvish, 1975)). This reaction occurs most rapidly at pH 3.4, reflecting a balance between the protonation of nitrite (pKa of HNO_2 = 3.35) and the increased fraction of DMA in the reactive, deprotonated form with increasing pH (pKa of $H_2N(CH_3)_2^+$ = 10.7).

$$HNO_2 + H^+ \leftrightarrow H_2O + NO^+ \quad (1.1)$$

$$2HNO_2 \leftrightarrow N_2O_3 + H_2O \quad (1.2)$$

$$NO^+ + (CH_3)_2NH \rightarrow (CH_3)_2NNO + H^+ \quad (1.3)$$

$$N_2O_3 + (CH_3)_2NH \rightarrow (CH_3)_2NNO + HNO_2 \qquad (1.4)$$

Due to the requirement of acidic conditions for the above reactions to occur, nitrosation is not considered as a primary formation mechanism for NDMA in water treatment facilities which are operated near circum-neutral pH (Mitch *et al.*, 2003b). However, some studies have reported that *N*-nitrosation can be catalyzed at circumneutral pH by photochemical reactions (Lee and Yoon, 2007) or by formaldehyde (Keefer and Roller, 1973) and fulvic acid (Weerasooriya and Dissanayake, 1989). In another study, Choi and Valentine (Choi and Valentine, 2003) reported that the formation of NDMA from the reaction of DMA and nitrite can be greatly enhanced by the presence of free chlorine at pH 7. The authors attributed the enhancement of *N*-nitrosation even at neutral pH to the formation of a highly reactive nitrosating intermediate such as dinitrogen tetroxide (N_2O_4) during the oxidation of nitrite to nitrate by free chlorine.

1.4.2 Oxidation of Chlorinated UDMH

Choi and Valentine (Choi and Valentine, 2002) and Mitch and Sedlak (Mitch and Sedlak, 2002b) proposed that NDMA could be preferably formed via an unsymmetrical dimethylhydrazine (UDMH) intermediate during the reaction of DMA and monochloramine instead of the nitrosation pathway. The authors showed that the reaction of monochloramine and DMA formed much more NDMA compared to the reaction of nitrite and DMA at the circumneutral pH conditions encountered in drinking and wastewater treatment plants. However, NDMA formation mechanisms after the UDMH intermediate-forming step, *i.e.*, the oxidation pathways from UDMH to NDMA were not explicit at that time about how the NH_2 moiety in UDMH converts to the NO moiety in NDMA.

Later on, Schreiber and Mitch (Schreiber and Mitch, 2006a) refined the previous UDMH oxidation pathway by revealing the important role of dichloramine and dissolved oxygen with the chlorinated UDMH intermediate rather than UDMH. The authors demonstrated that dichloramine plays a major role instead of monochloramine for NDMA formation. The chlorinated UDMH intermediate then undergoes further oxidation by dissolved oxygen to form NDMA (Figure 1.2), which is in competition with oxidation by dichloramine to form other products. The authors proposed that the low concentration of dichloramine solely contributes to NDMA formation via chlorine disproportionation even in typical chloramination conditions in which monochloramine exists as the dominant chloramine species, thereby possibly explaining the low yield of NDMA formation at the treatment plants.

1.4.3 NDMA Formation from Other Oxidants

Several recent studies also show that alternative oxidants including ozone, chlorine dioxide and permanganate (Andrzejewski *et al.*, 2005; Andrzejewski and Nawrocki, 2007; Andrzejewski *et al.*, 2008; Oya *et al.*, 2008; Schmidt and Brauch, 2008) can produce low levels of nitrosamines. Andrzejewski *et al.* (2007; 2008) linked nitrosamine formation during ozonation to the formaldehyde-catalyzed nitrosation (Keefer and Roller, 1973) since formaldehyde is a common product of ozonation. In contrast, Yang *et al.* (2009) proposed two alternative pathways: (a) secondary amine precursors reacting with hydroxylamine to form unsymmetrical dialkylhydrazine intermediates, which are further oxidized to their relevant nitrosamines; and (b) a nitrosation pathway in which N_2O_4 acts as the nitrosating reagent, to be responsible for nitrosation of dimethylamine. However, nitrosamine formation mechanism from reaction of other oxidants with nitrosamine precursors is still unclear.

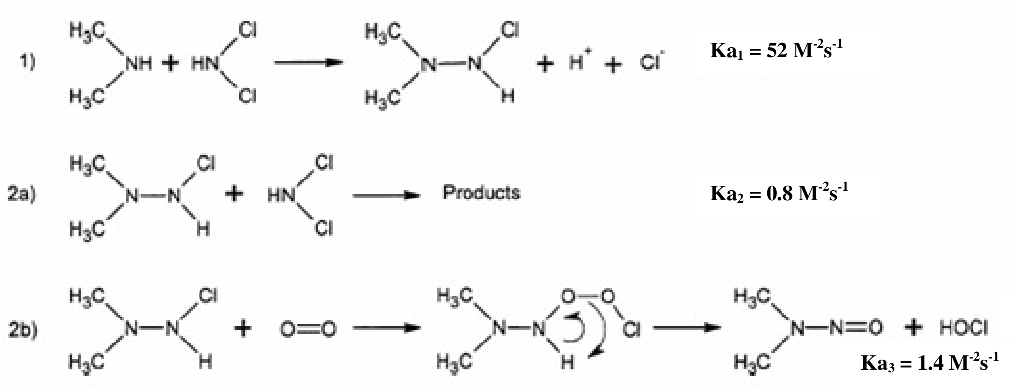


Figure 1.2 Formation mechanism of NDMA by oxidation of a chlorinated unsymmetrical dimethylhydrazine (UDMH-Cl) intermediate (figure adapted from Schreiber and Mitch (2006a))

1.5 Common Nitrosamine Precursors

1.5.1 Amines

Both the published mechanisms of NDMA formation involve reactions between an inorganic nitrogen containing species (e.g. nitrite or chloramines) and a secondary amine. Indeed, dimethylamine has been demonstrated to be the most effective organic nitrogen precursor of NDMA. Both pathways can also form NDMA from tertiary amines, however at lower concentration than dimethylamine. The lower concentration of NDMA formed from dimethylamine-containing tertiary amines as compared with dimethylamine likely is due to the extra step involved in cleavage of a C-N bond during NDMA formation (Mitch and Sedlak, 2004). The mechanism of this dealkylation reaction during chloramination may involve chlorine transfer to the nitrogen atom on the tertiary amine followed by elimination of hydrochloric acid to form an iminium ion. Hydrolysis would result in the formation of dimethylamine that could then react to form NDMA (Figure 1.3).

According to NDMA precursor tests conducted by Mitch and Sedlak (2004), the presence of DMA functional groups seems to be the prerequisite to be a significant NDMA precursor, and the structural relationship between the DMA functional group and its adjacent group in the precursors is also important to determine NDMA formation potential and rate during chloramination. For example, primary and tertiary amines which do not have DMA functional groups did not form significant levels of NDMA. Quaternary ammonium salt containing DMA or trimethylamine functional groups also did not form significant levels of NDMA due to the absence of free lone pair of electrons on the nitrogen.

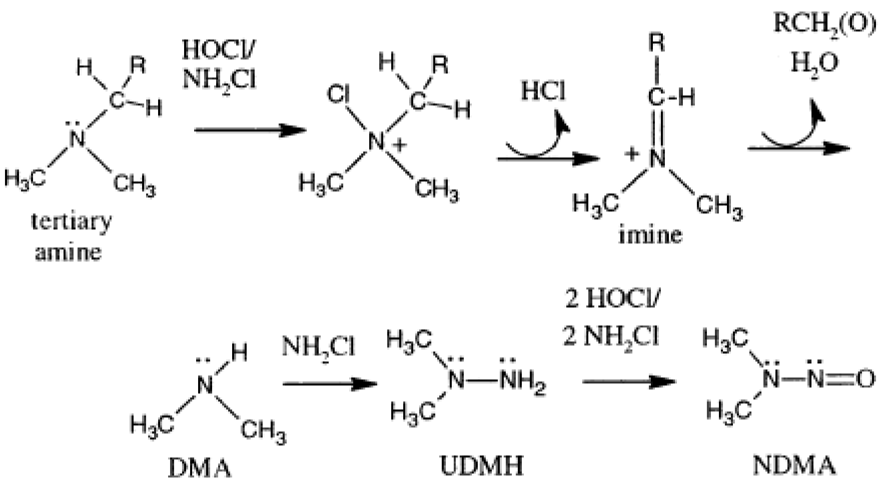


Figure 1.3 Formation mechanism of NDMA through tertiary amine (figure adapted from Mitch and Sedlak (2004))

In an earlier study carried out by Mitch and Sedlak (2002a), other nitrogen-containing molecules, including monomethylamine (primary amine), tetramethylamine (quaternary amine), and amino acids or proteins did not form significant amount of NDMA after chloramination. It has also been reported that nitrosation of quaternary amines that contained trimethylamine functional groups resulted in four orders of magnitude lower NDMA concentrations than did trimethylamine (Fiddler *et al.*, 1972). Hence, secondary amines and tertiary amines with secondary amine functional groups are thought to be major nitrosamine precursors.

Secondary amines are present in foods, human excreta, in municipal sewage as well as in surface waters. Previous studies reported DMA concentrations ranging from 1,000-3,000 ng/L (Sacher *et al.*, 1997) in surface waters to up to 235,0000 ng/L in rivers that receive considerable discharge of wastewater effluents (Abalos *et al.*, 1999). Similarly, diethylamine (DEA) was detected in surface waters at 9,000-13,000 ng/L (Neurath *et al.*, 1977; Abalos *et al.*, 1999). High incidence of multiple secondary amines in wastewaters has been documented in numerous studies with concentrations of DMA and other amines at 20,000-1,000,000 ng/L (Mitch *et al.*, 2003b; Sedlak *et al.*, 2005; Pehlivanoglu-Mantas and Sedlak, 2006; Padhye *et al.*, 2009).

1.5.2 Water Treatment Polymers

Based on the above two NDMA formation mechanisms, DMA has been demonstrated by many studies to be the most effective NDMA precursor (Choi and Valentine, 2002; Mitch and Sedlak, 2002b). However, the effort to identify other potential NDMA precursors has been continuously conducted because several studies have shown that DMA alone cannot explain all the concentrations of NDMA measured in wastewater and drinking water treatment plants (Mitch *et al.*, 2003a; Mitch and Sedlak, 2004; Chen and Valentine, 2007; Padhye *et al.*, 2009).

Among potential NDMA precursors, cationic amine-based water treatment polymers containing DMA moiety (Figure 1.4) have been reported to form NDMA during chlorination or chloramination (Najm, 2004; Park *et al.*, 2009). NDMA formation from reaction of water treatment polymers and chlorine was first reported by Child *et al.* (1991). In their study, when 5,000 mg/L of poly(diallyldimethylammonium chloride) coagulant (polyDADMAC) was reacted with 5,000 mg/L of hypochlorite for one hour, it resulted in NDMA formation at concentration of 310 ng/L.

Nitrosamine detection has been particularly linked with facilities using quaternary amine-based treatment polymers like polyDADMACs (Mitch *et al.*, 2009). In a survey of U.S. drinking water treatment plants, final effluent NDMA concentrations were correlated to the dosage of quaternary amine-based polyDADMACs (Figure 1.4). Wilczak *et al.* (2003) also observed a correlation between polyDADMAC dose and NDMA formation in pilot- and full-scale water treatment plants employing chloramination. A treatment plant utility employing anion exchange exhibited the highest effluent NDMA concentration in another drinking water plant survey (Valentine *et al.*, 2005). Most anion exchange resins are made up of quaternary amine-based polymers.

An in-depth investigation on the mechanisms of how polyDADMACs and polyamines, two amine-based polymers commonly used in potable water treatment, behave as NDMA precursors during chloramination has also been reported (Park *et al.*, 2009). However, there exists a knowledge gap in the literature about behavior of these polymers when reacted with different disinfectant other than chlorine or chloramines.

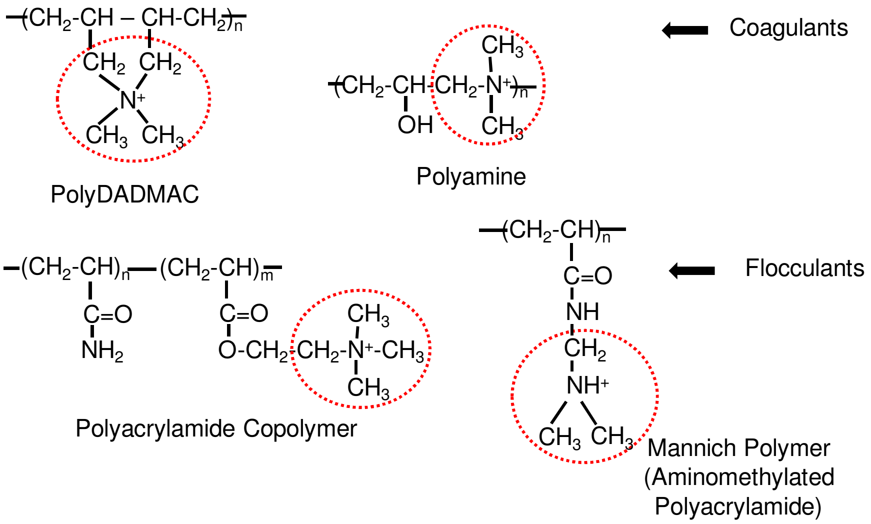


Figure 1.4 Commonly employed water treatment polymers with amines as a moiety in their structures

1.5.3 Dithiocarbamates

Based on the structure with DMA as a moiety, one of the other groups of potential nitrosamine precursors is dithiocarbamates. Large quantities of dithiocarbamates are used in agriculture as fungicides on almond trees, stone fruits, and vegetables. Dithiocarbamates also are used as rodent repellents, vulcanization additives in rubber manufacturing, and additives in lubricants. As fungicides, the most commonly used compound is dimethyldithiocarbamate (DMDTC), which is applied as Ziram, $Zn(DMDTC)_2$ (Figure 1.5). Nearly 1400 tons of DMDTCs are applied in the United States annually (Weissmahr *et al.*, 1998). One of the other uses of DMDTCs includes its use to enhance the precipitation of metals in wastewater treatment and pretreatment systems.

With the above knowledge of the ubiquitous applications of dithiocarbamates, it is not surprising that these compounds have been detected at ppb levels in surface water run-offs (Kesari and Gupta, 1998) and in wastewaters in the United States (Engel *et al.*, 1985). After it is released into the environment, DMDTC can form strong complexes with trace elements such as Cu(II) (Weissmahr and Sedlak, 2000). The pH, type, and concentration of trace metals and ligand-to-metal ratio will determine the fraction of DMDTC that is present as free ligands, positively charged 1:1 metal-DMDTC complexes, or uncharged and hydrophobic metal-$(DMDTC)_2$ complexes. Because each of these DMDTC species will behave differently, environmental conditions will affect the fate, transport, and toxicity of the DMDTCs. More importantly, with secondary amine as a moiety in their structures, dithiocarbamates are suspected nitrosamine precursors. The literature regarding reactions of these compounds with water disinfectants is scarce and further information is needed to understand their nitrosamine formation potential in surface water and wastewater.

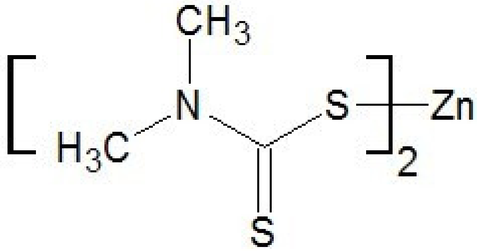


Figure 1.5 Molecular structure of Ziram

1.6 Removal of Nitrosamines

Due to high vapor pressure, moderate solubility in water, and low octanol-water partition coefficient (K_{ow}) values, nitrosamines are difficult to remove from water. Due to the presence of polar functional groups, nitrosamines are also adsorbed poorly to soils, sediments and activated carbon. Since NDMA has been reported to be the most prevalent of all nitrosamines in water, the flowing discussion uses NDMA as a representative model for nitrosamines.

Currently, the most commonly used NDMA treatment in water is photolysis by ultraviolet (UV) radiation (Mitch *et al.*, 2003b). NDMA absorbs light strongly between 225 and 250 nm (with max at 228 nm). This wavelength is at the lower end of the transparency of water to UV radiation. The absorption results in a *p* to *p** transition followed by cleavage of the N—N bond, most likely via hydrolysis to DMA and nitrous acid, or by forming nitroso and DMA radicals as shown in Figure 1.6. Evidently, the major products of NDMA photolysis are DMA and nitrite while minor products may include nitrate, formaldehyde, formate and methylamine. The quantum yield for the reaction shown in Figure 1.6 is 0.13 at pH 7. DMA is resistant to photolytic reaction while nitrite gets oxidized to nitrate. NDMA also has a secondary absorption band between 300-350 nm which results in NDMA's photolysis in direct sunlight. Under conditions typically encountered in drinking water treatment systems, the required UV dosage for an order of magnitude decrease in NDMA concentration is approximately 1,000 mJ/cm^2, which is an order of magnitude higher than UV dosage requirements for equivalent viral removal. Hence, UV treatment for NDMA is cost prohibitive for many treatment plants. Also, UV treatment suffers from a disadvantage of regeneration of NDMA precursor, DMA, upon treatment.

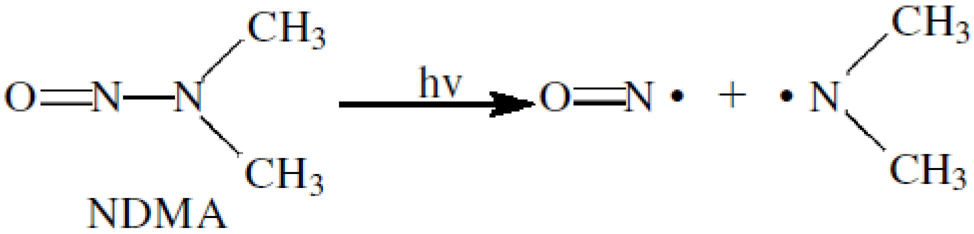


Figure 1.6 UV treatment for removal of NDMA in drinking water

Strong oxidants such as ozone and hydrogen peroxide do not appear to react with NDMA, and hence cannot be employed as NDMA treatment alternatives (Mitch *et al.*, 2003b). Hydroxyl radicals which are byproducts of ozone and hydrogen peroxide degradation can be used to remove NDMA. However, efficiency of ozonation and other advanced oxidation processes will be hindered by the presence of hydroxyl radical scavenger. Recently it has also been shown that nanofiltration and reverse osmosis membranes have poor rejection for lower molecular weight nitrosamines like NDMA (Miyashita *et al.*, 2009) limiting their use in nitrosamine removal.

Out of prevalent treatments for NDMA removal, biotransformation seems to be a promising option. NDMA has been shown to degrade by both aerobic and anaerobic pathways (Sharp *et al.*, 2005). A recent study by Chung *et al.* (2008) showed that NDMA can be used as an electron acceptor and reduced to ammonia and DMA by microorganisms using H_2 as the electron donor in a hydrogen-based membrane biofilm reactor, and concluded that NDMA reduction kinetics is controlled by electron donor availability and NDMA reduction competes directly with nitrate reduction. Moreover, the NDMA biotransformation pathway may involve the reduction of the nitroso group and subsequent N-N cleavage, which results in the formation of DMA and ammonia.

In fact, not only H_2 but also fermentation products of complex organics, such as long-chain or short-chain fatty acids and alcohols, may serve as an electron donor in nitrosamine biotransformation during the wastewater treatment. Indeed, in one of the recent studies (Padhye *et al.*, 2009), lower molecular weight nitrosamines were anaerobically biotransformed in sludge matrix. Removal of nitrosamines required carbon addition and was found to be directly related to the chemical oxygen demand (COD) consumption. However, utilization of the available electron donors via fermentation (acid and alcohol fermentation), and methanogenesis (acetoclastic and hydrogenotrophic methanogenesis) may compete with their use for nitrosamine biotransformation, which may hinder complete removal of nitrosamines.

Hence, the best strategy for minimizing occurrence of nitrosamines in water may lie in preventing or minimizing their formation. This can be achieved through identification of nitrosamine precursors and understanding reaction mechanisms that govern nitrosamine formation. This research is designed to address some of these needs. Chapter 2 explains the specific research objectives for this study.

CHAPTER 2

RESEARCH OBJECTIVES

Complexity and high costs associated with treatment technologies for removal of nitrosamines from water is a motivation to develop methods to prevent formation of these compounds in water treatment systems. To realize this goal requires understanding of pathways by which nitrosamines are formed, identifying the sources and nature of nitrosamine precursors, and determining technologies and reaction conditions that can be effective in minimizing risk of nitrosamine formation.

2.1 Overall Research Goal

The overall goal of this research is to achieve a better understanding of the roles of common nitrosamine precursors in leading to *N*-nitrosamine formation in water and wastewater treatment systems, and to propose more effective strategies to control *N*-nitrosamine formation.

2.2 Research Objectives

The specific objectives of this study are:

(a) To probe the mechanisms of nitrosamine formation from commonly employed water treatment polymers, particularly polyDADMACs, during ozonation,

(b) To evaluate the role of dithiocarbamate compounds as nitrosamine precursors in reaction with common water disinfection oxidants, and

(c) To investigate the potential enhancement effect of activated carbons (AC) to promote transformation of amines to nitrosamines and identify the involved reaction mechanism.

Chapter 3 delineates the role of polyDADMACs in NDMA formation upon ozonation. PolyDADMACs are amine-based polymers commonly used as coagulant aids in potable water treatment and are discovered in this study to form NDMA upon ozonation. Results of this research show that, upon ozonation, polyDADMACs yield NDMA at levels up to two orders of magnitude higher than current advisory guidelines for NDMA. Radical pathways are shown to be responsible for the release of DMA from polyDADMACs while the role of nitrosation pathway to form NDMA from released DMA is highlighted. Finally, suggestions are made based on the findings to reduce NDMA formation risks associated with polyDADMACs.

Chapter 4 investigates the role of commonly employed water treatment disinfection oxidants, monochloramine, free chlorine, chlorine dioxide, and ozone, in transforming two dithiocarbamates, dimethyldithiocarbamate (DMDTC) and diethyldithiocarbamate (DEDTC), to corresponding nitrosamines. These dithiocarbamate compounds are widely used insecticides and metal complexing agents in various applications. Study results reveal dithiocarbamates as potent nitrosamine precursors with significant nitrosamine yields upon ozonation and monochloramination. Identification and quantification of reaction products suggest nitrosation and chlorinated-UDMH oxidation as primary reaction mechanisms in nitrosamine formation from ozonation and monochloramination of dithiocarbamates compounds, respectively.

Chapter 5 demonstrates the enhancement effect of AC particles to transform secondary amine to *N*-nitrosamines under ambient aerobic conditions. This is a novel discovery that has not been widely recognized previously. This discovery also has significant implications because of the widespread use of AC materials in analytical and environmental applications. This study systematically investigated the influence of AC materials on the formation of nitrosamines from amine precursors under water analysis and water treatment conditions with the objective to obtain a mechanistic understanding of the involved reactions. The study results show that the properties of AC materials and reaction conditions play a crucial role in the catalyzed nitrosamine formation and should be carefully selected to minimize analytical errors and undesirable nitrosamine formation in water samples. The mechanism of the catalyzed amine transformation to nitrosamine on AC surfaces was probed with various techniques.

Chapter 6 presents the conclusions based on the results obtained from this research. Recommendations are made to reduce risks of nitrosamine formation in water treatment systems. Furthermore, environmental and water treatment conditions encouraging and inhibiting these risks are highlighted. In the end, future research avenues in this area are discussed.

CHAPTER 3

FORMATION OF NDMA FROM OZONATION OF POLYDADMACS: REACTION KINETICS AND MECHANISM

3.1 Introduction

In one of the recent findings, nitrosamine detection was found to be particularly evident at facilities employing quaternary amine-based treatment polymers, in which final effluent NDMA concentrations were correlated to the dosage of polyDADMAC (Mitch *et al.*, 2009). Amine-based water treatment polymers have been previously established as potent nitrosamine precursors upon chlorination and chloramination (Najm and Trussell, 2001; Wilczak *et al.*, 2003; Mitch and Sedlak, 2004; Najm, 2004; Park *et al.*, 2009). There are also attempts made to detail the mechanism of NDMA formation from chloramination of polyamines and polyDADMACs (Park *et al.*, 2009; Kemper *et al.*, 2010). However, there exists a knowledge gap regarding the interaction of polymers with alternative disinfecting agents used in water treatment systems.

Ozone is increasingly used as a disinfectant of choice in water treatment, since it is much more effective in inactivating various pathogenic microorganisms of public health concern, including *Cryptosporidium parvum* oocysts and *Giardia lamblia* cysts, compared to chlorine-based disinfectants (Gottschalk *et al.*, 2000). Recent studies have indicated that ozonation of DMA (Andrzejewski *et al.*, 2008) as well as commonly used plant protection agent, tolylfluanid, and its metabolites, *N*,*N*-dimethyl-*N*'-(4-methylphenyl)-sulfamide (DMST) and *N*,*N*-dimethylsulfamide (DMS) (Schmidt and Brauch, 2008), can result in the formation of NDMA. Andrzejewski *et al.* (2008) proposed formaldehyde-catalyzed nitrosation (Keefer and Roller, 1973) as a possible pathway for NDMA formation from ozonation of DMA based on the observation of nitrite formation as one of reaction products. However, products other than NDMA were not quantified and formaldehyde-catalyzed nitrosation pathway was unable to explain observed increase in NDMA yield with pH increase. Hence, Yang *et al.* (2009) proposed an alternative mechanism involving reaction of hydroxylamine, ozonation product of DMA, with DMA to explain NDMA formation via unsymmetrical dimethylhydrazine (UDMH) pathway in neutral and alkaline pH. However, the above reaction pathways were not verified in ozonation experiments and mechanisms for NDMA formation from ozonation of DMA are still uncertain.

This study examined the reactions of ozone with common amine-based water treatment polymers and DMA with particular emphasis on assessing their potential for NDMA formation as well as formation mechanisms. Among the tested polymers, polyDADMACs exhibited the highest potential to release DMA and consequently form the greatest amount of NDMA during ozone treatment. Hence, polyDADMACs were selected for further detailed mechanism study. Suggestions were made to water treatment utilities employing ozonation for reducing NDMA formation risks associated with the use of polyDADMACs.

3.2 Synthesis of Amine-based Water Treatment Polymers

Three amine-based water treatment polymers were included in this study: poly(epichlorohydrin-dimethylamine) (polyamine), poly(diallyldimethylammonium chloride) (polyDADMAC) and cationic polyacrylamide (cationic PAM). The structures of these three polymers are shown earlier in Figure 1.4. Although Mannich polymer, a common flocculant for wastewater sludge dewaterng, is also shown in Figure 1.4, it was not included in this current study because Mannich polymer has relatively high tendency to decompose in water and contains high background DMA and formaldehyde concentrations as a result of reversible Mannich reaction (Park, 2008). In contrast, polyamine, polyDADMAC and cationic PAM are stable polymers in typical water conditions and their syntheses and characteristics are briefly described below.

Polyamine is commonly employed as coagulant in drinking water treatment. As evident from Figure 1.4, polyamine has quaternary ammonium ionic groups integrated all along the backbone of the polymer chain. Polymerization involves two steps. In the first step, DMA is added to epichlorohydrin at low temperature, or vice versa, to make a DMA-epichlorohydrin adduct. In the second step, DMA-epichlorohydrin adduct undergoes condensation polymerization at high temperature to produce polyamine polymer (Figure 3.1) (Schwoyer, 1986).

PolyDADMAC is widely used in water treatment as coagulant aid and in wastewater treatment for sludge thickening purposes. It is effective in flocculating, decoloring, killing algae and removing natural organic matter from water. DADMAC, which is a monomer of polyDADMAC, is synthesized by reaction of allyl chloride and DMA. Non-conjugated diene of DADMAC is then subjected to cyclopolymerization to form quaternary amine ring structure of polyDADMAC in pendent position (Figure 3.2) (Shalaby *et al.*).

Cationic PAM copolymer is used as a flocculant in a wide variety of municipal and industrial wastewater treatment applications. First, quarternized dimethylaminoethyl acrylate (DMAEA) is prepared by the reaction of DMAEA with methyl chloride. It is then subjected to copolymerization with acrylamide to yield cationic polyacrylamide (Figure 3.3). The ratio of the acrylamide and chloromethylated DMAEA determines the cationic molar proportion of the copolymer, yielding varying cationic charge density between 0% and 100% (Ishigaki *et al.*, 1981). The ester group of this copolymer is sensitive to pH and may hydrolyze at pH above 6.

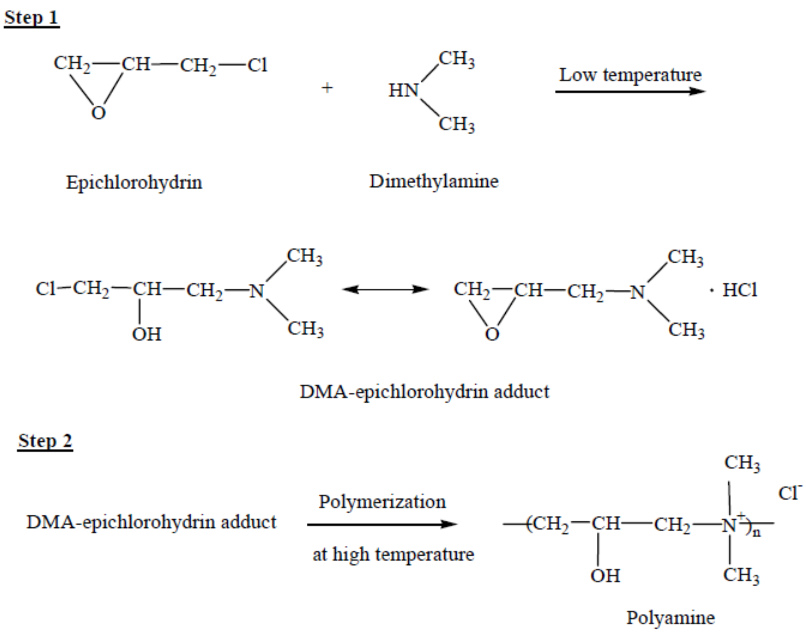


Figure 3.1 Synthesis of polyamine (figure adapted from Park (2008))

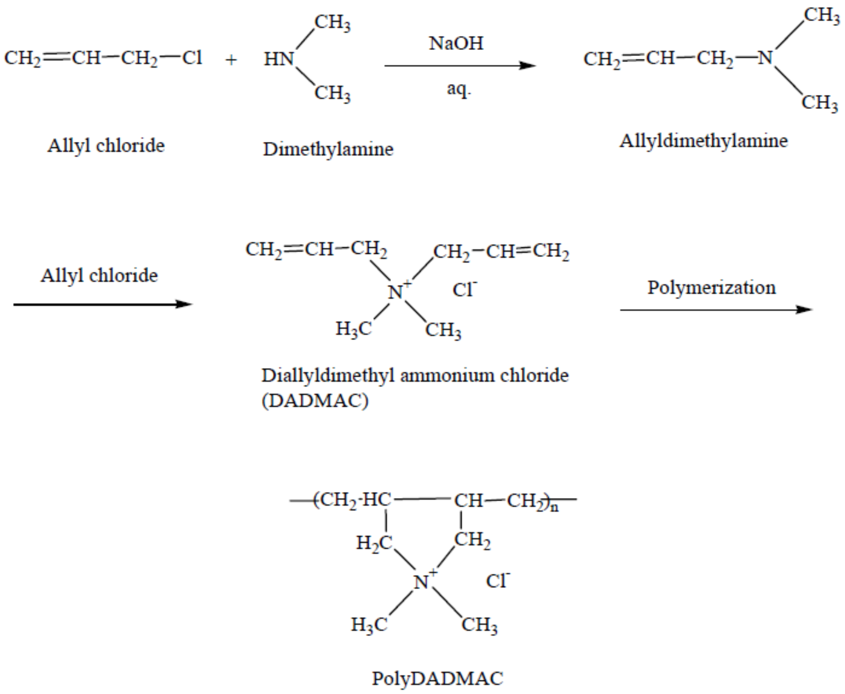


Figure 3.2 Synthesis of polyDADMAC (figure adapted from Park (2008))

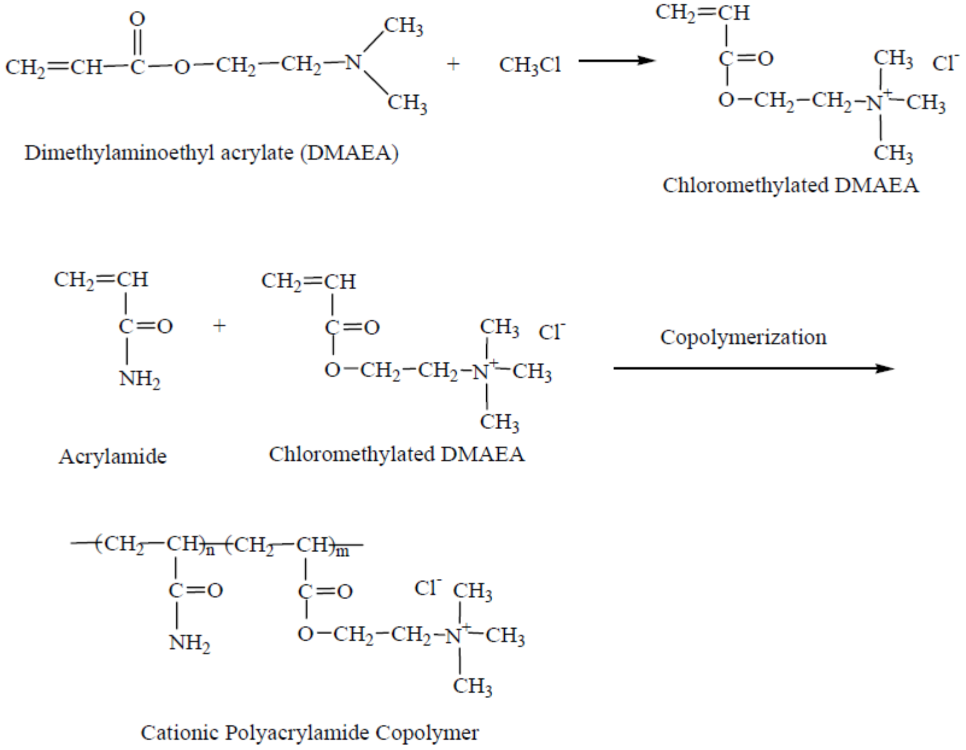


Figure 3.3 Synthesis of cationic polyacrylamide copolymer (figure adapted from Park (2008))

3.3 Materials and Methods

3.3.1 Chemicals

Standard-grade *N*-nitrosodimethylamine, dimethylamine hydrochloride, sodium nitrite, sodium nitrate, hydroxylamine (50% in water), *N,N*-dimethylformamide, sodium bromide, unsymmetrical dimethylhydrazine (UDMH), disodium ethylenediamine tetraacetate (EDTA), L-ascorbic acid, sodium thiosulfate, *tert*-butyl alcohol, benzene sulfonylchloride, methoxy-benzene sulfonylchloride, ferrous ammonium sulfate, *N*-(1-naphthyl)ethylenediamine dihydrochloride, hydrogen peroxide, diallyldimethyl ammonium chloride (DADMAC), sulfanilamide, 2,4-dinitrophenylhydrazine (DNPH), phosphoric acid, acetone, methanol, methylene chloride (DCM), indigo-5,5′-disulfonic acid disodium salt, ammonium chloride, sodium phosphate monobasic and dibasic, and sodium borate were obtained at >98% purity from Sigma-Aldrich (St. Louis, MO) or Fisher Scientific (Pittsburgh, PA). All reagents were used without further purification. The isotopes NDMA-d_6 and DMA-d_6 hydrochloride were obtained from Cambridge Isotope Laboratories (Andover, MA). Low molecular weight (LMW) polyDADMAC (molecular weight 100,000-200,000 g/mol, 20 % by weight in water), medium molecular weight (MMW) polyDADMAC (molecular weight 200,000-350,000 g/mol, 20 % by weight in water), Poly(dimethylamine epichlorohydrin) (polyamine, 50 % by weight in water) and Poly(acrylamide-*co*-diallyldimethylammonium chloride) (cationic polyacrylamide, 10 % by weight in water), were obtained from Sigma-Aldrich, stored at room temperature, and used without further purification. Ambersorb 572 resins for solid phase extraction (SPE) were obtained from Supelco (St. Louis, MO).

3.3.2 Experimental Protocol

All glassware was cleaned with a laboratory detergent, rinsed with acetone and DI water, and baked at 300 °C for 3 hours prior to use. All batch experiments, unless mentioned otherwise, were conducted using pH 7.6 buffer solution containing 5 mM phosphate and 1 mM carbonate, prepared using ultrapure water (Milli-Q Water Purification system). All experiments with polyDADMAC were carried out with LMW polymer except for the study involving different molecular weights (Section 3.4.2). Reaction solutions were contained in amber borosilicate bottles with Teflon-lined caps to which polymer was added at dosage ranging from 5 to 10 mg/L as the amount of active ingredient. For comparative experiments, 2.25 mg/L (0.05 mM) DMA was added instead of polyDADMAC. Freshly prepared ozone stock was used to achieve initial ozone concentrations ranging from 1 mg/L (0.02 mM) to 10 mg/L (0.21 mM). Experiments were conducted at room temperature (23 ± 1 °C) under mild agitation and each bottle represented a single data point. All experiments were triplicated, unless mentioned otherwise. Selected experiments were performed using Fenton's reagent, which was prepared by adding 100 μM ferrous ammonium sulfate (FAS) and 500 μM H_2O_2. Solution pH was adjusted at 4.6 by HCl and NaOH for optimum production of •OH (Bishop *et al.*, 1968). The solution containing either 5 mg/L polyDADMAC, 2.25 mg/L DMA, or 6.3 mg/L DADMAC was allowed to react with the Fenton's reagent for 30 min at room temperature.

3.3.3 Chemical Analysis

3.3.3.1 NDMA Extraction and Analysis

Concentrations of NDMA in samples were analyzed by liquid-liquid extraction (LLE) for all experiments except preliminary ozonation study for polymers (Section 3.4.1) where solid phase extraction (SPE) using Ambersorb 572 resins (Padhye *et al.*, 2009) was used. For LLE, 100 mL of sample was fortified with NDMA-d_6 at 500 ng/L as a surrogate standard. The isotope-labeled surrogate was used to correct for nitrosamine extraction efficiency and matrix effect in the isotope dilution method (Taguchi *et al.*, 1994; Padhye *et al.*, 2009; Park *et al.*, 2009). After addition of surrogate standard, sample was extracted twice with 20 mL of DCM by vigorous shaking on platform shaker for 1 hour. The DCM layer was separated, concentrated down to 0.5 mL by evaporating under vacuum, and analyzed for nitrosamines by GC/MS.

3.3.3.2 DMA Extraction and Analysis

One hundred µg/L of DMA-d_6 from a 10 mg/L freshly prepared aqueous stock solution was added as a surrogate standard to 2 mL of sample aliquot that was adjusted to pH 9.0 by using 10 mM borate buffer. The sample then received 0.1 mL of methoxy-benzenesulfonyl chloride solution, and was stirred by a magnetic stir bar for 2 hours and extracted with 2 mL of dichloromethane for 2 minutes. The extracts were analyzed for derivatized secondary amines by the GC/MS system described below.

3.3.3.3 GC/MS Conditions

Samples were analyzed by an Agilent GC/MS (6890/5973) system equipped with a HP-5MS column (30 m × 250 μm × 0.25 μm) and a large volume injector (LVI). Solvent vent mode injections of 25 μL and 5 μL were used with an initial injection port temperature of 0 ˚C or 30 ˚C for nitrosamine and secondary amine analysis, respectively, which was rapidly increased to 220 ˚C after 0.3 seconds. The temperatures of the MS ion source and transfer line were 150 and 260 ˚C, respectively. For nitrosamine analysis, GC oven temperatures were 35 ˚C held for 1 min followed by ramping at 10 ˚C/min to 170 ˚C, then ramping at 15 ˚C/min to a final temperature of 240 ˚C held for 2 min. For secondary amine analysis, GC oven temperatures were 40 ˚C held for 1 min followed by ramping at 20 ˚C/min to a final temperature of 260 ˚C held for 5 min.

3.3.3.4 DADMAC Analysis

DADMAC was analyzed using the method adopted from Park *et al.* (2009). An Agilent LC/MS system with electrospray ionization (ESI) in positive ion mode was utilized for analysis of aqueous DADMAC monomer solution. An Agilent Zorbax RX-C18 column was used for the analysis of DADMAC. The flow rate of 0.25 mL/min was used with mixture of acetonitrile and 5 mM heptafluorobutyric anhydride (HFBA) aqueous solution as the mobile phase. Gradient elution was performed with a linear gradient change from 99.5% A (5mM HFBA, pH 4.2) and 0.5% B (acetonitrile) to 60% A and 40% B in 10 min and then held isocratic for 2 min, followed by a stepwise elution to 0% A and 100% B. The nitrogen gas flow rate (drying gas flow) for desolvation was at

10 L/min at 350°C, the nebulizer pressure was at 25 psi, and the capillary voltage was at 4500 V. DADMAC was quantified by SIM using its molecular ion (*m/z* 126.3).

3.3.3.5 Ozone Generation and Monitoring

A stock solution of dissolved ozone with concentrations ranging from 16 to 20 mg/L (0.33 to 0.42 mM) was prepared in a 500-mL gas-washing cylinder at 4 ˚C, by bubbling gaseous ozone produced from extra dry grade (minimum purity of 99.8%) oxygen using a PCI-Wedeco Model GSO 10 ozone generator (Herford, Germany) through DI water. The ozone concentration was determined by the indigo colorimetric method (Bader and Hoigne, 1981). The decrease in absorbance due to the decolorization of indigo trisulfonate at 600 nm as a result of its reaction with ozone was measured by a UV-visible spectrophotometric detector (Agilent 8453 UV/VIS). Equation 3.1 was used to calculate the ozone concentration

$$\text{mg O}_3\,/\,\text{L} = \frac{100 \times \Delta\text{A}}{f \times b \times V} \tag{3.1}$$

Where,

ΔA = difference in absorbance between sample and bank (at 600 nm),

b = path length of cell, cm (1 cm),

V = volume of sample, mL (125 mL), and

f = absorption coefficient for aqueous ozone (0.42)

3.3.3.6 Reaction Product Analysis

Nitrite was quantified based on a reddish azo dye which forms at pH 2.0 to 2.5 via coupling of diazotized sulfanilamide with *N*-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride) in the presence of nitrite (Eaton, 1998). Nitrate was analyzed by measuring the absorbance of sample at 220 and 275 nm (Eaton, 1998). Formaldehyde was derivatized with 2,4- dinitrophenylhydrazine (DNPH) and quantified using HPLC (Soman *et al.*, 2008). Dimethylformamide (DMF) was quantified using GC/MS. GC/MS conditions were the same as those used for NDMA analysis. PolyDADMAC degradation was monitored through a Fourier Transform Infrared spectrometer using an Attenuated Total Reflection mode (FT-IR/ATR). IR-ATR spectra were recorded from 4000-400 cm^{-1} using a Bruker Equinox 55 Fourier transform (FT-IR) spectrometer (Bruker Optics Inc., Billerica, MA). The spectrometer was equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector (Infrared Associates, Stuart, FL) and an in-compartment horizontal ATR unit (Gateway, Specac Inc., Woodstock, GA) with trough top plate and six-reflection trapezoidal ZnSe (n_D=2.43 at $\lambda = 5\ \mu m$) ATR crystal (MacroOptica, Moscow, Russia).

3.4 Results and Discussion

3.4.1. NDMA Formation from Ozonation of PolyDADMAC and Other Polymers

Results of preliminary ozonation experiments conducted using three common water treatment polymers, polyDADMAC, polyamine, and cationic polyacrylamide (PAM), are shown in Figure 3.4. As shown in Figure 3.4A, ozonation of polyDADMAC yielded 3 and 4 times more NDMA compared to PAM and polyamine, respectively. It is noteworthy that all three polymers contained some levels of DMA even before ozonation, *i.e.*, termed $[\mathrm{DMA}]_{\mathrm{initial}}$ (Figure 3.4B), which constitute 0.2 to 1.2 % of the initial polymer mass. However, polyDADMAC showed considerably more DMA released upon ozonation; $[\mathrm{DMA}]_{\mathrm{final}} - [\mathrm{DMA}]_{\mathrm{initial}}$ for polyDADMAC was an order of magnitude greater than those for polyamine and PAM (wherein $[\mathrm{DMA}]_{\mathrm{final}}$ is the amount of DMA measured at the end of ozonation). Since DMA is a structural moiety in the quaternary ammonium groups of these polymers, release of DMA might indicate the extent of polymer degradation. These results, therefore, suggest that polyDADMAC is more susceptible to oxidation by ozone than the other two polymers. This apparent different reactivity towards ozone oxidation can be rationalized based on differences in polymer structures. In contrast to polyDADMAC's pendent quaternary ammonium groups (Figure 3.2), polyamine's quaternary ammonium groups are integrated along the polymer backbone (Figure 3.1). PAM, on the other hand, has fewer quaternary ammonium ring groups on the weight basis because this group originates from only one of the two monomers that comprise PAM (Figure 3.3). Based on the highest risk to form NDMA among tested polymers, polyDADMAC was chosen for further mechanistic evaluation on NDMA formation upon ozonation.

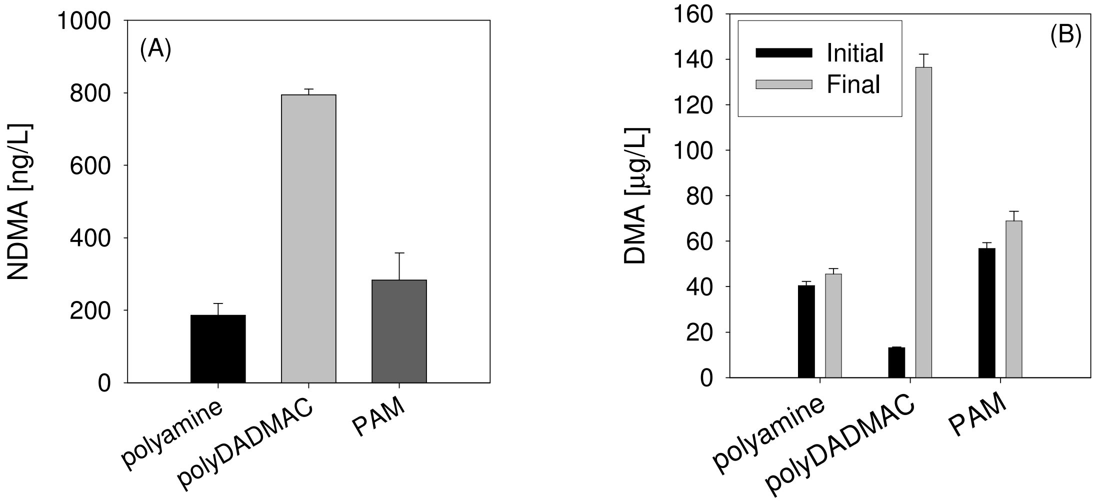


Figure 3.4 (A) NDMA formation potential and (B) DMA release for commonly employed water treatment polymers upon ozonation. Polymers with active ingredient concentrations of 10 mg/L were reacted with initial ozone dose of 0.141 mM (6.7 mg/L) for 30 minutes in a batch reactor at pH 7.6 and room temperature. The initial and final represent DMA concentration at the beginning and the end of 30 minutes of reaction time, respectively. (Error bars represent one standard deviation of the means)

3.4.2 Effect of PolyDADMAC's Molecular Weight

LMW and MMW PolyDADMACs were ozonated to evaluate the impact of polymer molecular weight on the NDMA formation potential. This investigation allows evaluation of the role of polymer chain ends versus polymer backbone in the overall NDMA formation potential. For the same mass of the polymer, LMW polyDADMACs are of shorter chain length and thus contain a greater number of chain ends compared to MMW polyDADMACs. As can be seen from Figure 3.5, NDMA formation potential and DMA release for both LMW and MMW polyDADMAC solutions were similar. The lack of significant difference in either DMA release or NDMA formation between these two different MW polyDADMACs suggests that polymer chain ends may not be playing a critical role during degradation of polyDADMAC upon ozonation, nor in the formation of NDMA.

Consistent with the above observations were results from ozonation of DADMAC, a monomer of polyDADMAC (Figure 3.2). When 50 μM (8.05 mg/L) of DADMAC was ozonated by 0.1 mM (4.8 mg/L) of initial ozone dosage for 30 minutes at pH 7.5, 142 ± 17 μg/L of DMA was released from DADMAC. Initial DMA impurity in 50 μM of DADMAC was determined to be 14 ± 4 μg/L. These results further confirm that DMA release from polyDADMAC by ozonation is related to the quaternary ammonium group in polyDADMAC and not to the chain ends of polymer.

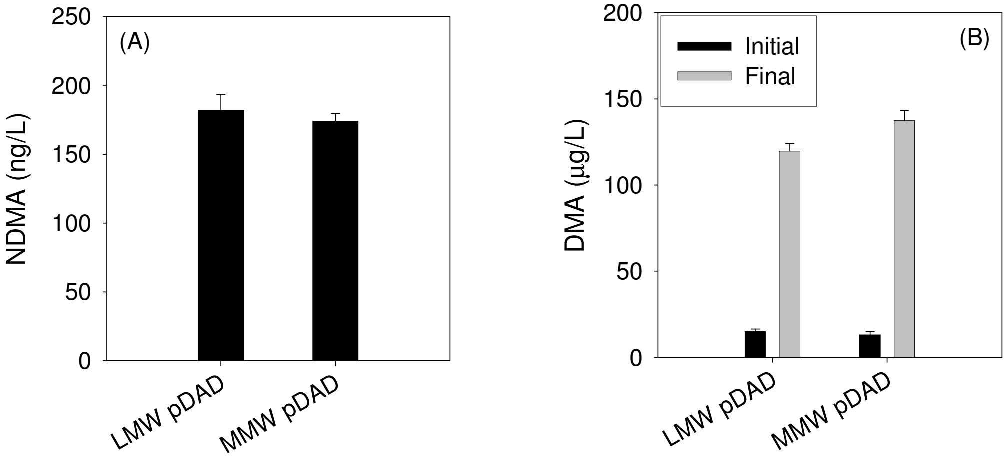


Figure 3.5 (A) NDMA formation potential and (B) DMA release for 5 mg/L LMW and 5 mg/L MMW polyDADMAC solutions upon ozonation. Initial ozone concentration was 0.1 mM (4.8 mg/L). (Error bars represent one standard deviation of the means)

3.4.3 Effect of pH on Ozonation of PolyDADMAC and DMA

Effects of pH on NDMA formation and DMA released (shown as the amount measured at the end of the ozonation) during ozonation of polyDADMAC are shown in Figures 3.6A and 3.6B. Results of comparative experiments performed using DMA are also shown in Figures 3.6C and 3.6D. Note that, since the experiments were carried out in batch reactors and ozone decays more rapidly at higher pH, *CT* (*i.e.*, ozone concentration × contact time) values (von Gunten, 2003) were different at different pHs even for the same exposure time. Figure 3.7 compares the kinetics of ozone decay at pH 5 and pH 9 in solutions containing polyDADMAC. *CT* values were calculated by integrating the area under each curve. Then, the experimental results of NDMA and DMA concentrations measured at each pH were normalized with *CT* values in Figure 3.6. Similar data treatment was conducted for the results of ozonation of DMA (ozone decay curves not shown).

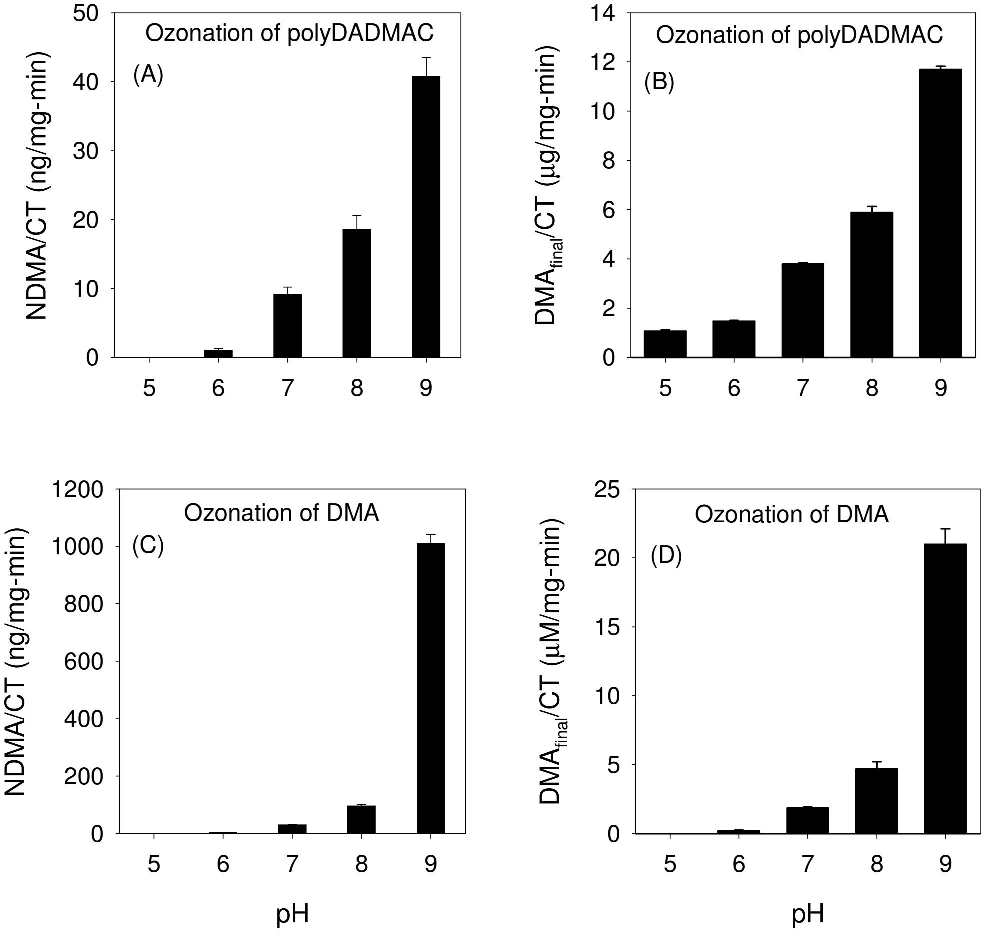


Figure 3.6 Effect of pH on (A) NDMA formed for 5 mg/L polyDADMAC solution, (B) final DMA remaining for 5 mg/L polyDADMAC solution, (C) NDMA formed for 50 μM (2.25 mg/L) DMA solution, and (D) DMA consumed for 50 μM (2.25 mg/L) DMA solution upon ozonation. Initial ozone concentration was 0.1 mM (4.8 mg/L). (Error bars represent one standard deviation of the means)

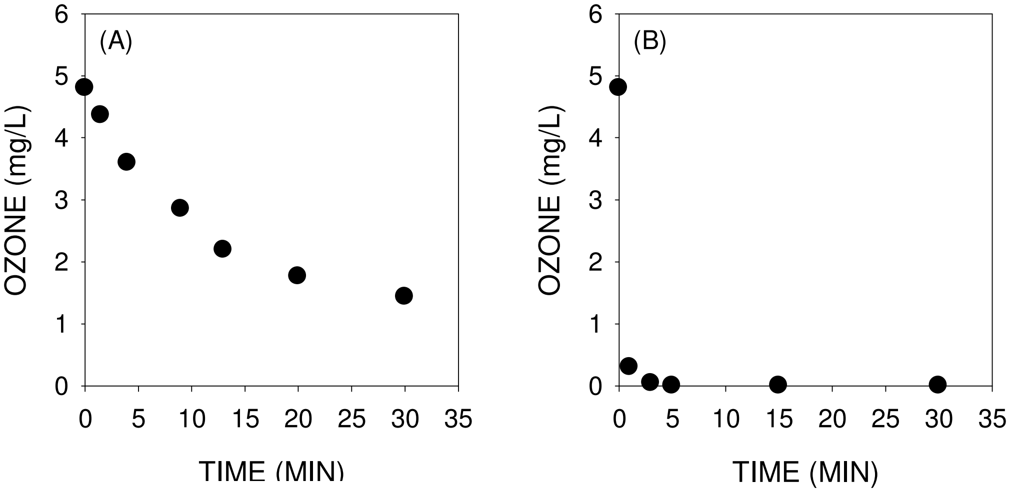


Figure 3.7 Kinetics of ozone decomposition in 5 mg/L polyDADMAC solution at (A) pH = 5 and at (B) pH = 9. Initial ozone concentration was 0.1 mM (4.8 mg/L).

For the ozonation of polyDADMAC, NDMA formed and DMA remaining after ozonation ($[DMA]_{final}$) followed the similar trend; both increased as pH increased. These trends were also similar to the trend observed with ozonation of DMA (Figure 3.6C). Since ozone can react only with deprotonated form of DMA (von Gunten, 2003), more DMA, released from polyDADMAC, would be consumed at higher pHs, as shown in Figure 3.6D. Therefore, it is likely that the actual amount of DMA released from polyDADMAC was significantly underestimated in Figure 3.6B, especially at higher pHs.

3.4.4 Significance of Hydroxyl Radicals in Degradation of polyDADMAC

Ozone decomposes in water to produce a range of radical species including highly reactive •OH (Tomiyasu *et al.*, 1985). When 0.1 mM of *tert*-butanol (TBA) (von Gunten, 2003) was added to polyDADMAC solution as •OH scavenger, the amount of DMA remaining after ozonation was decreased by more than 40% and the NDMA formation was decreased by more than 70% (Figure 3.8). These results imply that •OH plays an important role on DMA release from polyDADMAC and subsequent NDMA formation. These results were consistent with results shown in Figure 3.6, since at higher pH, more •OH are formed due to faster ozone decay.

Consistently, both polyDADMAC and DADMAC released a significant amount of DMA after reaction with Fenton's reagent, an alternative way to induce •OH exposure (Figure 3.9B). This massive DMA release from DADMAC was accompanied by significant degradation of DADMAC (Figure 3.9A). PolyDADMAC solution initially contained only a small amount (0.07 μM) of residual DADMAC and no significant amount of DADMAC was found after the reaction with Fenton’s reagent. In control experiment performed with hydrogen peroxide alone or with ferrous ammonium sulfate alone, degradation of DADMAC or polyDADMAC or release of DMA from either source was not observed. Since DADMAC and polyDADMAC share the same quaternary ammonium ring moiety, the above results suggest that •OH attacks the quaternary ammonium site of polyDADMAC to release DMA.

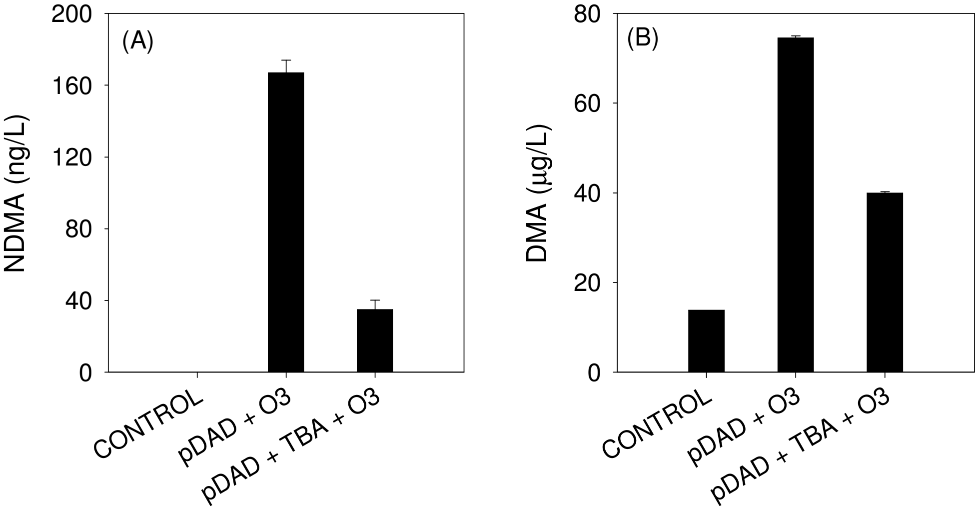


Figure 3.8 Effect of 0.1 mM *tert*-butanol on (A) NDMA formed and (B) final DMA remaining for 5 mg/L polyDADMAC solution upon ozonation. Initial ozone concentration was 0.1 mM (4.8 mg/L). (Error bars represent one standard deviation of the means)

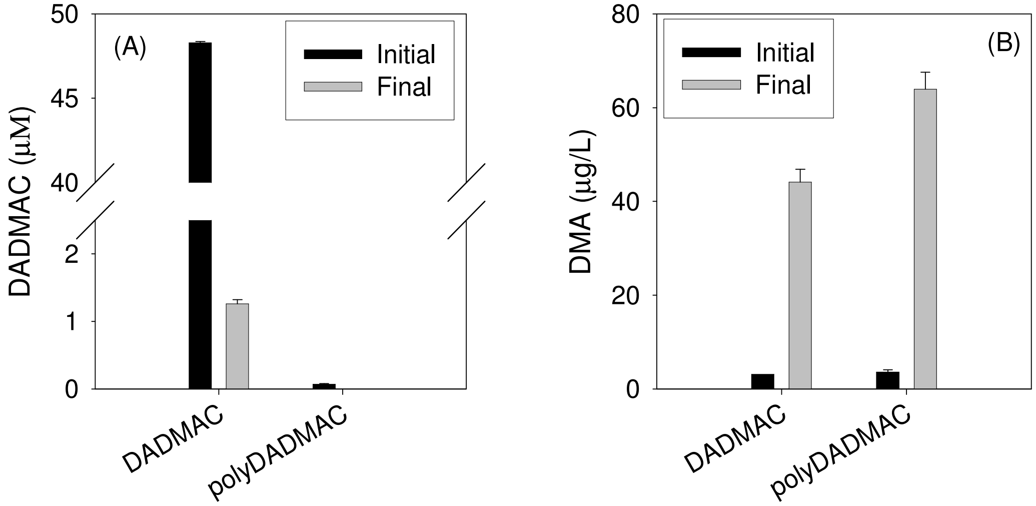


Figure 3.9 Effect of Fenton's reagent on (A) DADMAC and (B) DMA concentrations for 50 µM (6.3 mg/L) DADMAC and 5 mg/L polyDADMAC solutions. Initial and final represent DADMAC and DMA concentrations at the beginning and at the end of 30 minutes of reaction time, respectively. (Error bars represent one standard deviation of the means)

3.4.5 Effect of Initial Ozone Concentration

The amount of NDMA formed and DMA measured after ozonation with varying initial ozone concentrations are shown in Figure 3.10 for polyDADMAC and DMA. NDMA formation from polyDADMAC increased sharply up to 2 mg/L of initial ozone concentration after which the formation plateaued (Figure 3.10A). Similar trend was observed for $[DMA]_{final}$ wherein higher initial ozone concentrations resulted in only small increase in $[DMA]_{final}$ (Figure 3.10B). In contrast, during ozonation of DMA, NDMA formation continuously increased (Figure 3.10C) and $[DMA]_{final}$ continuously decreased (Figure 3.10D) with increasing initial ozone concentration.

When polyDADMAC was exposed to different initial concentrations of Fenton's reagent ($[FAS]:[H_2O_2]$ = 10:50, 20:100, 40:200, 100:500, or 200:1000 μM/μM), $[DMA]_{final}$ also plateaued at higher •OH exposure (Figure 3.11). Note that 5 mg/L as active ingredient of polyDADMAC contains approximately 30 μM of monomeric unit and, hence, could release maximum of 30 μM (1.35 mg/L) of DMA. This suggests that only a small fraction (approximately 2 to 4%) of DMA remained after •OH attack (Figure 3.11), similar to the observation made with ozonation, where only approximately 3 to 5% of DMA from polyDADMAC remained (Figure 3.10B). These might have resulted since some of DMA moiety sites on polyDADMAC may not be accessible to oxidants such as •OH and ozone. It is also possible that some of DMA released might have formed other products or even mineralized, especially under excessive oxidant exposure condition (Andrzejewski *et al.*, 2008). It is therefore noteworthy that the initial ozone to DMA ratio at higher ozone dosage was 20 to 50 times higher for polyDADMAC ozonation (Figure 3.10B) than that for DMA ozonation (Figure 3.10D).

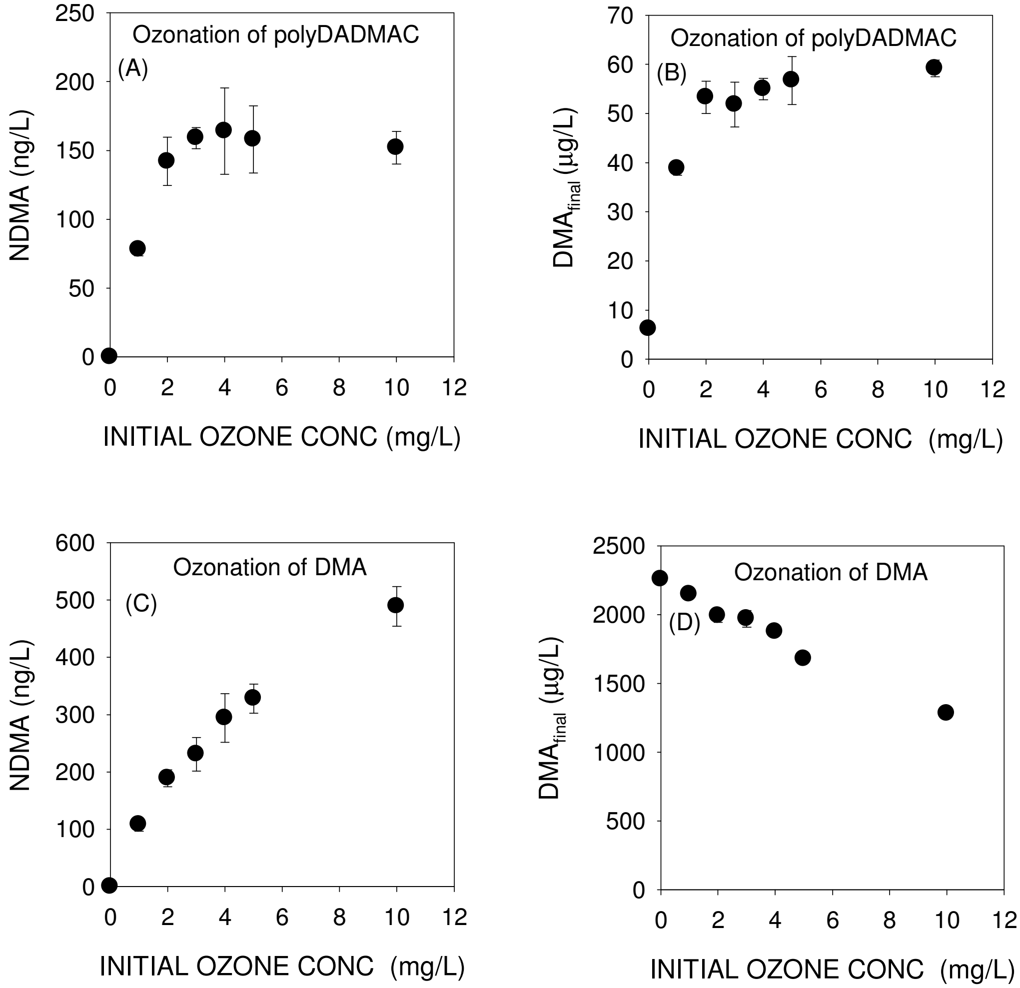


Figure 3.10 Effect of initial ozone concentrations on (A) NDMA formed for 5 mg/L polyDADMAC solution, (B) final DMA remaining for 5 mg/L polyDADMAC solution, (C) NDMA formed for 50 µM (2.25 mg/L) DMA solution, and (D) final DMA remaining for 50 µM (2.25 mg/L) DMA solution upon ozonation. Initial ozone concentrations varied from 1 to 10 mg/L (0.02-0.21 mM) at pH 7.6 in batch reactors. (Error bars represent one standard deviation of the means)

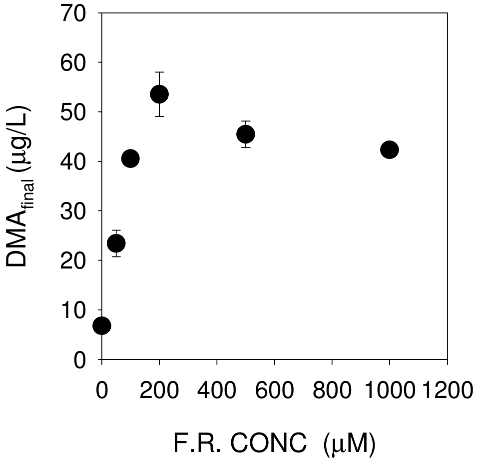


Figure 3.11 DMA release from 5 mg/L polyDADMAC as a function of Fenton's reagent (F.R.) concentrations

3.4.6 Kinetics of NDMA Formation and DMA Release from Ozonation of PolyDADMAC

As shown in Figure 3.12A, both $[DMA]_{final}$ and NDMA formation increased till about 10 min and then plateaued during the course of polyDADMAC ozonation. The 10 min time correlated well with the ozone depletion time in polyDADMAC solution (Figure 3.12C). Hence, the presence of ozone is termed responsible not only for DMA release, but also for the majority of the NDMA formation. These results were similar to those observed during ozonation of DMA (Figure 3.12B), in which ozone depleted within 5 min (Figure 3.12D). Most of the DMA degradation and NDMA formation also occurred during the period of ozone depletion. These results indicate that the presence of ozone is essential, not only for DMA release from polyDADMAC, but also for the formation of NDMA from DMA.

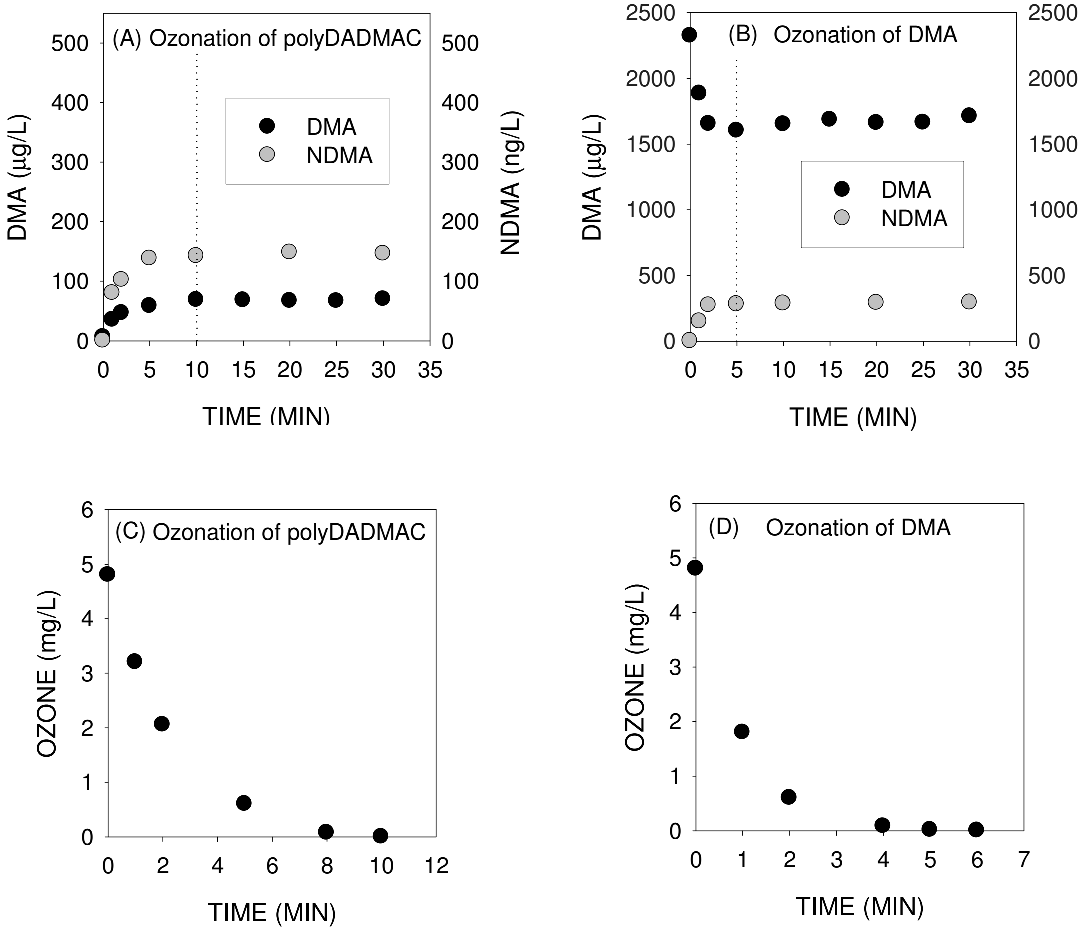


Figure 3.12 (A) Kinetics of NDMA formation and final DMA remaining for 5 mg/L polyDADMAC solution upon ozonation at pH = 7.6, (B) Kinetics of NDMA formation and final DMA remaining for 50 μM (2.25 mg/L) DMA solution upon ozonation at pH = 7.6, (C) Kinetics of ozone decomposition in 5 mg/L polyDADMAC solution at pH = 7.6, and (D) Kinetics of ozone decomposition in 50 μM (2.25 mg/L) DMA solution at pH = 7.6. Initial ozone concentration was 0.1 mM (4.8 mg/L).

3.4.7 Polymer Structural Change and Ozonation Product Characterization

Results of FT-IR analysis on polyDADMAC prior and after ozonation provided insights on the structural changes in the polymer's backbone (Figure 3.13). After ozonation, FT-IR spectra displayed decreased C-N stretching (1137 cm^{-1}), which is characteristic of quaternary amine group, suggesting ring opening (Park *et al.*, 2009). The formation of DMA after ozonation was also evident with the appearance of N-H stretch (3000-3200 cm^{-1}) representative of secondary amine (Socrates, 2007). The appearance of formaldehyde was clearly seen in the polyDADMAC spectra after ozonation as C=O stretch at 1750 cm^{-1} (Socrates, 2007). Additionally, the appearance of DMF could be attributed to a strong absorption at 1650 cm^{-1}, representative of C=O stretch and C-N stretch at 1000 to1350 cm^{-1} (Socrates, 2007). Moreover, an increase in CH_3 deformations in 1300 to 1400 cm^{-1} region further confirmed the presence of secondary and tertiary amines (Durig and Cox, 1982).

Amounts of reaction products including NDMA, DMA, DMF, formaldehyde, DADMAC, nitrite, and nitrate, formed during ozonation of polyDADMAC, DADMAC and DMA at different pHs (5, 7.6 and 9) results are presented in Table 3.1. Significant amounts of nitrite and formaldehyde were detected from ozonation of DMA, DADMAC, and polyDADMAC. The nitrite concentration increased significantly as the solution pH increased, confirming that nitrite was one of major products of ozonation of deprotonated DMA. Among the products quantified, formaldehyde was present at significantly higher concentrations than DMF, nitrite, and NDMA. In contrast, DADMAC was not observed to be a product of ozonation of polyDADMAC. When NDMA yields were compared based on the mass basis for polyDADMAC and on the molar basis for DMA and DADMAC, NDMA showed increase in yields with increase in pH.

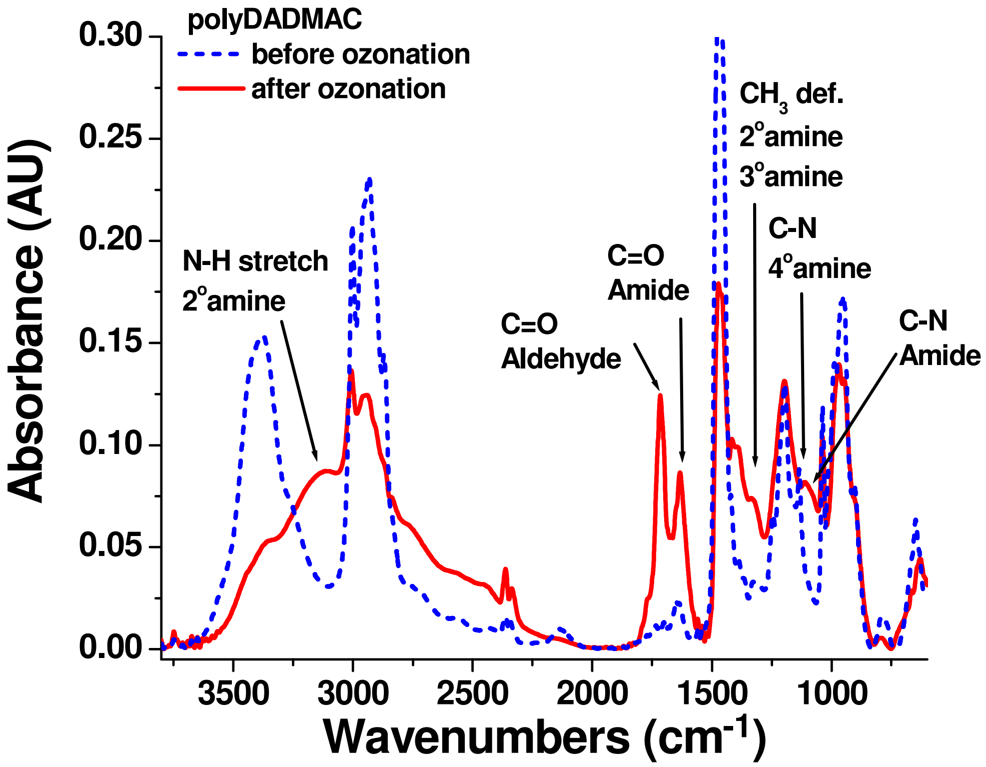


Figure 3.13 FT-IR spectra for 50 mg/L polyDADMAC solution before and after ozonation (CT = 150 mg.min/L) at pH 7.6.

Table 3.1 Ozonation products for 5 mg/L polyDADMAC, 50 µM (6.3 mg/L) DADMAC and 50 µM (2.25 mg/L) DMA at pH 5, 7.6, and 9 with initial ozone dose of 0.1 mM

Sample	**DMA (i) (µM)**	**DMA (f) (µM)**	**DMC (i) (µM)**	**DMC (f) (µM)**	**DMF (µM)**	**Nitrite (µM)**	**FAld (µM)**	**NDMA (ng/L)**	**NDMA Yield[a] (%)**
pDAD pH 5	0.10	1.71	0.07	0.00	0.05	0.01	4.99	ND	0.000
pDAD pH 7.6	0.10	1.44	0.07	0.00	0.04	0.09	6.00	152	0.003
pDAD pH 9	0.10	0.77	0.07	0.00	0.04	0.18	4.05	225	0.005
DMC pH 5	0.04	0.19	50	12.35	0.05	0.01	25.46	ND	0.000
DMC pH 7.6	0.04	0.94	50	13.50	0.04	0.08	41.56	167	0.004
DMC pH 9	0.04	1.42	50	16.30	0.04	0.16	16.53	237	0.006
DMA pH 5	50.00	40.72	NA	NA	0.03	0.05	12.43	ND	0.000
DMA pH 7.6	50.00	34.87	NA	NA	0.04	0.20	5.35	354	0.010
DMA pH 9	50.00	29.99	NA	NA	0.04	0.80	11.77	1480	0.040

[a] NDMA yield is calculated on mass basis for initial concentration (5 mg/L) of polyDADMAC and on molar basis for initial concentration of DADMAC and DMA (50 µM).

Notes: pDAD – polyDADMAC; DMC – DADMAC; DMF – dimethylformamide; FAld – formaldehyde; NA – Not Applicable; i – initial concentration before ozonation; f – final concentration after ozonation; ND – Non detectable, Method detection limit for NDMA = 20 ng/L.

3.4.8 Possible Reaction Mechanisms

3.4.8.1 Mechanism of DMA Release from polyDADMAC

The above results collectively suggest that •OH plays a critical role in degradation of polyDADMAC and release of DMA during ozonation. One of the predominant modes of •OH attack is H-atom abstraction from a C-H bond (Goshe *et al.*, 2000). For organic macromolecules, it has been established that H-atom abstraction by •OH from C-H bonds in the backbone is a rare event compared to reaction with the side chains (Goshe *et al.*, 2000). Hence, the quaternary ammonium rings in polyDADMAC pendent position would be the primary sites for the radical attacks. Experiments conducted to test the effect of different molecular weights of polyDADMAC (Figure 3.5) and ozonation of DADMAC monomer established that the backbone and chain ends of polyDADMAC did not play an important role in the observed concentrations of DMA released, and the amount of DMA released can be attributed to the quaternary ammonium ring structure at the pendent position of polyDADMAC. It is likely that •OH preferentially attacks α-carbon of quaternary ammonium ring, resulting in H-abstraction and subsequent C-N bond cleavage and formation of tertiary amine. Additional H-abstraction at α-carbon of tertiary amine would result in the release of secondary amine. Presence of electron-donating alkyl groups (*i.e.* polymer backbone) is believed to render H-abstraction from α-carbon of quaternary amine rings in polyDADMAC more feasible.

3.4.8.2 Mechanism of NDMA Formation from polyDADMAC and DMA

NDMA yield, expressed in terms of the amount of NDMA formed normalized by the amount of DMA consumed, from ozonation of DMA experiments at pH 7.6 was only approximately 0.03% (Table 3.1). If the same yield were applied, based on the observed NDMA formation at pH 7.6 (Table 3.1), polyDADMAC would have released at least 6 μM of DMA. However, the amount of DMA remaining was much smaller at 1.4 μM after ozonation (Table 3.1). This difference resulted since the amount of DMA remaining reflected the DMA released from polyDADMAC as well as DMA consumed during ozonation. In addition, the ratio of ozone to DMA was high during polyDADMAC ozonation. Since the ratio is expected to be higher, NDMA yield was also expected to be higher for polyDADMAC (Figure 3.10C). Also, results from this study show that NDMA formation from polyDADMAC was strongly correlated to DMA release during ozonation indicating that NDMA formation may be the result of ozonation of released DMA from polyDADMAC.

Detection of a significant amount of nitrite after polyDADMAC and DMA ozonation (Table 3.1) suggests the possibility of nitrosation pathway for NDMA formation. Andrzejewski *et al.* (2008) proposed that the presence of nitrite and formaldehyde (*i.e.*, both are ozonation products of DMA) can catalyze NDMA formation at circumneutral pH. However, this pathway cannot explain observed increased yield on NDMA with increasing pH (Table 3.1). In addition, our kinetic study results along with ozonation product characterization contradict this hypothesis. After ozone depletion, formaldehyde, nitrite and DMA all remained in the solution (Table 3.1), but NDMA formation ceased (Figure 3.12).

In contrast, transformation of DMA to NDMA seems to involve both nitrite and •OH. In an additional experiment performed with 20 mM nitrite and 20 mM DMA, a twice more NDMA (3.54 ± 0.06 μM) was formed with the addition of Fenton's reagent

(50 μM FAS and 200 μM H_2O_2) at pH 4.6, compared to nitrite and DMA only (1.62 ± 0.03 μM NDMA formed). In the absence of nitrite, both DMA and polyDADMAC, did not yield any detectable amount of NDMA when exposed to Fenton's reagent. Since nitrosation is expected to be a dominant mechanism at lower pH (4.6), higher yield of NDMA in the presence of Fenton's reagent may indicate a role of •OH in transforming nitrite to more potent nitrosating agent such as dinitrogen tetroxide (Yang *et al.*, 2009). However, no further increase in NDMA formation was observed when nitrite was added additionally during ozonation of DMA (Table 3.2), indicating that contribution of nitrosation pathway is minimal and cannot explain the observed NDMA yield for the conditions employed in this study.

There may be a possibility of other ozonation products of DMA not quantified in this study, such as hydroxylamine (Yang *et al.*, 2009), reacting with DMA to form NDMA. However, when 50 μM of hydroxylamine and 50 μM of DMA were reacted at pH 7.6 for 30 min in the absence of ozone, NDMA formation was below the method detection limit of 20 ng/L. Yet, when 10 μM hydroxylamine was added externally during ozonation of 50 μM DMA, NDMA yield was tripled (Table 3.2), indicating that presence of ozone was critical. When ^{15}N-DMA was reacted with hydroxylamine in the presence of ozone, significant formation of ^{15}N-NDMA was observed (Table 3.2) suggesting that hydroxylamine may be contributing one nitrogen atom to NDMA. When UDMH, a proposed intermediate of reaction between hydroxylamine and DMA (Yang *et al.*, 2009), was ozonated, it formed 3 orders of magnitude more NDMA than in the absence of ozone (Table 3.2). Above results, coupled with results from kinetic study, indicate that presence of ozone is critical during reaction of hydroxylamine with DMA to yield NDMA.

Table 3.2 Assessing NDMA formation pathways from DMA during ozonation

Samples	**NDMA (ng/L)**	**^{15}N-NDMA (ng/L)**	**^{15}N,^{15}N-NDMA (ng/L)**
DMA + Ozone	240 ± 29	ND	ND
DMA + NH_2OH + Ozone	660 ± 27	ND	ND
^{15}N-DMA + Ozone	ND	ND	194 ± 6
^{15}N-DMA + NH_2OH + Ozone	ND	500 ± 13	106 ± 4
DMA + NO_2 + Ozone	190 ± 15	ND	ND
DMA + ^{15}N-NO_2 + Ozone	191 ± 6	ND	ND
UDMH + Dissolved Oxygen	5,200 ± 850	ND	ND
UDMH + Ozone	1,500,000 ± 80,000	ND	ND

Notes: DMA (50 µM), NO_2 (10 µM), NH_2OH (10 µM), UDMH (100 µM), Ozone (100 µM), pH 7.6 with reaction time of 30 minutes; ND – Non detectable, Method detection limit for NDMA = 20 ng/L. Mean ± standard deviation (*n* = 2)

3.4.9 Environmental Significance

Results of this study suggest that, upon ozonation, polyDADMAC may yield NDMA at significantly higher levels than current advisory guidelines for NDMA in drinking water, for the polymer dosage ranging from 5 to 10 mg/L and initial ozone concentration of 5 mg/L (*CT* ~ 12 mg-min/L) at pH 7.6. These concentrations are comparable to the optimum dosages of polymer required for coagulation (2-4 mg/L) (Faust and Aly, 1983) and recommended ozone dosage for disinfection (*CT* = ~ 2-10 mg-min/L at 20 °C for 0.5-3 log inactivation of *C. Parvum* oocysts) (Rakness, 2005) Since coagulation and flocculation are typically followed by sedimentation and filtration processes, only trace levels of polyDADMAC are expected to still persist in water after the above mentioned treatment processes and before disinfection. However, NDMA formation results from this study are significant for utilities employing high concentration of polyDADMACs or where pre-oxidation by ozone is employed before coagulation. In addition, for wastewater treatment plants, where an order of magnitude higher dosage of polyDADMAC for sludge thickening operations is not uncommon, practicing tertiary treatment of ozone disinfection can form significant amounts of NDMA. Also the risk of NDMA formation from ozonation of polyDADMAC and DMA present in water could potentially be enhanced by constituents such as hydroxylamine or bromide in real water matrices. Our preliminary experiments with bromide suggest that it may significantly increase the yield of NDMA formation during ozonation of polyDADMAC and DMA (Table 3.3 and Table 3.4), for example, 3 times more NDMA was formed when 100 μM of bromide is present during ozonation of 50 μM DMA and 5 mg/L polyDADMAC.

Table 3.3 Effect of bromide on NDMA formation from ozonation of DMA and polyDADMAC

Samples	**NDMA** (ng/L)
DMA + Ozone	187 ± 17
DMA + Bromide + Ozone	546 ± 55
polyDADMAC + Ozone	95 ± 11
polyDADMAC + Bromide + Ozone	302 ± 16

Notes: DMA (50 μM), polyDADMAC (5 mg/L), Bromide (100 μM), Ozone (100 μM), pH 7.6 with reaction time of 30 minutes, Mean ± standard deviation (*n* = 2)

Table 3.4 Effect of varying concentrations of bromide on NDMA formation from ozonation of DMA

Samples	**NDMA** (ng/L)
DMA + Ozone (No Bromide)	165 ± 16
DMA + 2 μM Bromide + Ozone	209 ± 12
DMA + 10 μM Bromide + Ozone	263 ± 26
DMA + 20 μM Bromide + Ozone	318 ± 29
DMA + 50 μM Bromide + Ozone	508 ± 11
DMA + 100 μM Bromide + Ozone	859 ± 36

Notes: DMA (50 μM), Ozone (100 μM), pH 7.6 with reaction time of 30 minutes, Mean ± standard deviation (*n* = 2)

In brief, avoiding direct contact of ozone with polyDADMAC will reduce the risk of NDMA formation during water and wastewater treatment. In addition, suppressing solution pH will help reduce DMA release from polyDADMAC. Lowering pH will also reduce NDMA formation risks because ozone and hydroxylamine reacts only with deprotonated DMA. Treatment plants employing advanced oxidation processes (AOPs), such as Fenton’s Reagent, can also be at increased risk of NDMA formation due to generation of •OH. To minimize NDMA formation risk at such treatment processes, it is advised to remove NDMA precursors such as polyDADMAC and DMA as much as possible before oxidation step.

CHAPTER 4

OXIDATION OF DITHIOCARBAMATES TO YIELD *N*-NITROSAMINES BY WATER DISINFECTION OXIDANTS

4.1 Introduction

Dithiocarbamate compounds are used widely in agriculture as fungicides. They are also used as rodent repellents, vulcanization additives in rubber manufacturing, and additives in lubricants. There have been a few studies that investigated the toxicity of dithiocarbamate compounds in water. For example, presence of Ziram (Figure 1.5) has been linked to toxic effects of water collected from the Sacramento River in California (Weissmahr *et al.*, 1998), while hydrophobic metal complexes of many dithiocarbamates have been shown to significantly increase trace metal uptake by aquatic organisms (Phinney and Bruland, 1994). In addition, the potential estrogenic effects and chronic toxicity of dithiocarbamates to other animals is an environmental concern (Maita *et al.*, 1997).

Given the widespread usage of dithiocarbamates, their frequent occurrence in water sources and the presence of secondary amine as a moiety in their structures, this study focused on evaluating the potential role of dithiocarbamates as nitrosamine precursors once they enter water and wastewater treatment systems and are subjected to water disinfection processes. While there has been some limited amount of experimental data showing the NDMA formation potential of dithiocarbamates primarily in reaction with monochloramine (Mitch and Sedlak, 2004; Lee *et al.*, 2007), a detailed study has not yet been carried out to understand the impact of different disinfection agents and reaction conditions that facilitate or reduce the nitrosamine formation potential of dithiocarbamates in water and wastewater treatment plants. Two most commonly used dithiocarbamates pesticides, dimethyldithiocarbamate (DMDTC) and diethyldithiocarbamate (DEDTC) (Figure 4.1), were examined in this study to evaluate their potential to form nitrosamines when in contact with various water disinfection oxidants including monochloramine, free chlorine, chlorine dioxide and ozone. Also, the study evaluated the effects of reaction conditions in order to obtain a better understanding of the reaction mechanism governing nitrosamine formation. Finally, several suggestions were made based on the study results to reduce the risks of nitrosamine formation from dithiocarbamates in water and wastewater treatment systems.

Dimethyldithiocarbamate (DMDTC) Diethyldithiocarbamate (DEDTC)

Figure 4.1 Molecular structures of DMDTC and DEDTC

4.2 Materials and Methods

4.2.1 Chemicals

Standard-grade sodium dimethyldithiocarbamate (40% in water) and sodium diethyldithiocarbamate (in solid form) were obtained at ≥97% purity from Sigma-Aldrich (St. Louis, MO). Other chemical reagents including NDMA, NDEA, DMA hydrochloride, DEA, copper(II) sulfate, 1-hexanesulfonic acid sodium salt (HSA), sodium nitrite, disodium ethylenediamine tetraacetate (EDTA), *N,N*-diethyl-p-phenylenediamine oxalate, L-ascorbic acid, sodium thiosulfate, benzene sulfonylchloride, methoxy-benzene sulfonylchloride, N-(1-naphthyl)ethylenediamine dihydrochloride, ferrous ammonium sulfate, hydrogen peroxide, sulfanilamide, 2,4-dinitrophenylhydrazine (DNPH), phosphoric acid, acetone, methanol, methylene chloride, indigo-5,5′-disulfonic acid disodium salt, ammonium chloride, sodium phosphate monobasic and dibasic, and sodium borate were obtained at >98% purity from Sigma-Aldrich (St. Louis, MO) or Fisher Scientific (Pittsburgh, PA). The isotopes NDMA-d_6, NDEA-d_{10}, NDPA-d_{14} and DMA-d_6 hydrochloride were obtained from Cambridge Isotope Laboratories (Andover, MA). All reagents were used directly without further purification. All experiments were carried out in nano-pure distilled water from a Millipore Milli-Q water purification system. Ambersorb 572 resins for solid phase extraction (SPE) were obtained from Supelco.

4.2.2 Experimental Protocol

All batch experiments were conducted in deinoized nanopure water using amber borosilicate bottles with Teflon-lined caps at room temperature (23 ± 1 ˚C). Prior to use, all glassware was cleaned with laboratory detergent, rinsed with acetone and DI water, and baked at 300 ˚C for 3 hours. Dithiocarbamates concentrations ranged from 20 to 50 µM for the study while initial oxidant concentrations applied in the aqueous phase were from 100 to 200 µM. All experiments were carried out at pH 7.5 using 10 mM phosphate buffer. For samples that were subjected to ozonation, bicarbonate buffer at 1 mM along with 5 mM phosphate buffer (pH = 7.6) was used for all batch reactors to simulate ozone decay kinetics in real water (Section 3.3.2). Reaction was carried out for 24 hours for chlorine dioxide, free chlorine, and monochloramine, while the time of contact for ozone was 30 minutes. At the end of reactions, 1 mM sodium thiosulfate was added to quench residual oxidants. All experiments were conducted in duplicates for controls and triplicates for samples.

4.2.3 Oxidant Preparation

4.2.3.1 Monochloramine Stock Preparation

For all experiments, monochloramine stock was prepared freshly at approximately 1,000 mg as Cl_2/L by slow addition of a 5% sodium hypochlorite solution into an ammonium chloride solution at a Cl/N molar ratio of 0.7 and with continuous stirring. To minimize disproportionation of monochloramine to dichloramine, the pH was maintained above 8.5 using 10 mM phosphate buffer. After 30 minutes of stirring in the amber bottle, covered with aluminium foil to protect from light, preformed monochloramine stock was aged in the dark for one hour and used for experiments within one day. Final free chlorine and monochloramine concentrations were determined prior to each experiment by *N,N*-diethyl-p-phenylenediamine-ferrous ammonium sulfate (DPD-FAS) titration method specified in the Standard Methods (Eaton, 1998).

4.2.3.2 Chlorine Dioxide Stock Preparation

Chlorine dioxide stock was prepared by a procedure modified from the literature (Pitochelli, 2006). In a reactor equipped with an inlet and an outlet for bubbling air, sulfuric acid (H_2SO_4) was slowly added to sodium chlorite ($NaClO_2$) solution with constant stirring by using a stir bar. The reaction between 100 mL of 8.0 N sulfuric acid and 250 mL of 160 g/L sodium chlorite resulted in chlorine dioxide gas, which was captured in solution by passing through chilled nanopure water. The capturing of chlorine dioxide gas was continued until a desired amount of chlorine dioxide was collected in the same chilled nanopure water trap. The final yellow solution of chlorine dioxide was then stored into an amber glass bottle and refrigerated. The final concentration of chlorine dioxide was determined by titrating with sodium thiosulfate in the presence of potassium iodide, acid and starch indicator as specified in the Standard Methods (Eaton, 1998).

4.2.3.3 Ozone Generation and Monitoring

Ozone was generated and monitored as described in the Section 3.3.3.5.

4.2.4 Reactant and Product Analysis

4.2.4.1 Nitrosamine Extraction and Analysis

The same NDMA extraction and analytical procedure was employed as described in Section 3.3.3.1. For NDEA analysis, similar analytical protocol was followed except

NDEA-d_{10} was used as a surrogate standard. Description of GC/MS conditions is given in Section 3.3.3.3.

4.2.4.2 Secondary Amine Extraction and Analysis

The same DMA extraction and analytical procedure was employed as described in Section 3.3.3.2. For DEA analysis, similar analytical protocol was followed as for DMA. Description of GC/MS conditions is given in Section 3.3.3.3.

4.2.4.3 Dithiocarbamate Analysis

Analysis of dithiocarbamates was conducted according to the method described by Weissmahr *et al.* (1998) with some modifications. All samples were analyzed by a HPLC 1100 system equipped with an auto sampler (Agilent Technologies, Palo Alto, CA, USA). Eclipse XDB-C18 (Agilent Technologies, Palo Alto, CA, USA) reverse phase column was used for chromatography, while UV-VIS detector at 260 and 385 nm was used to detect and quantify dithiocarbamates. The mobile phases used consisted of methanol (45%) and acetate buffer (55%). The buffer typically contained 2-3 mM sodium acetate (pH adjusted to a value between 4 and 5), 100-200 μM $CuSO_4$, and 2-4 mM HSA ion-pairing reagent. The hydrolysis of most dithiocarbamates is fast at low pH. However, the $CuDMDC^+$ complex is very stable, and complexation of DMDC with Cu(II) present in the mobile phase prevents the degradation of DMDC during the analysis (Weissmahr *et al.*, 1998). Before analysis, the column was equilibrated for at least 30 min with mobile phase. Equilibration was complete when a breakthrough of Cu(II) species was detected at 260 nm. To remove Cu(II) from the column after each day of analysis, the HPLC system was flushed with 50 mL of water/methanol (70:30), 50 mL of 10 mM EDTA/methanol (80:20), and again followed by 50 mL of water/methanol (70:30).

4.2.4.4 Reaction Product Analysis

Nitrite, nitrate, formaldehyde, and dimethylformamide (DMF) were analyzed by same analytical methods as described in Section 3.3.3.6.

4.3 Results and Discussion

4.3.1 Hydrolysis Rate of DMDTC and DEDTC

Dithiocarbamates can undergo hydrolysis in aqueous solution under environmental conditions to yield corresponding secondary amines and CS_2 (Aspila *et al.*, 1969) as shown in Figure 4.2. Hence, without addition of any external oxidant, dithiocarbamates can yield direct precursors of nitrosamines in the form of secondary amines. The rate of hydrolysis depends on pH, with faster hydrolysis at more acidic conditions. Dithiocarbamates have a strong tendency to complex with metal ions and their rate of hydrolysis can be slowed by metal complexation (Weissmahr and Sedlak, 2000); however, only copper(+II) ion was found to have significant impact in this regard under environmental conditions.

It was necessary to understand the stability of DMDTC and DEDTC in water with regard to hydrolysis before studying the reactions of these two dithiocarbamates with common water disinfection oxidants. The hydrolysis rates of DMDTC and DEDTC in pH 7.5 water was monitored from 30 minutes to up to 5 days as shown in Figure 4.3. The concentration versus time curve was fit to pseudo-first-order decay kinetics to obtain the hydrolysis rate constant. The obtained rate constants corresponded to a half-life of about 121.4 hours (~5 days) for DMDTC and about 60.3 hours (~2.5 days) for DEDTC at pH 7.5. These results agree with the rate constant values reported in the literature (Aspila *et al.*, 1969).

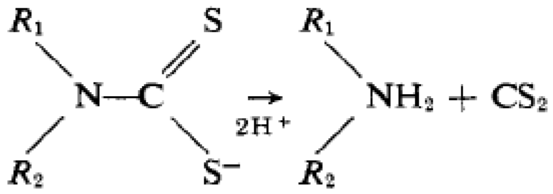


Figure 4.2 Hydrolysis of dithiocarbamates catalyzed by acids

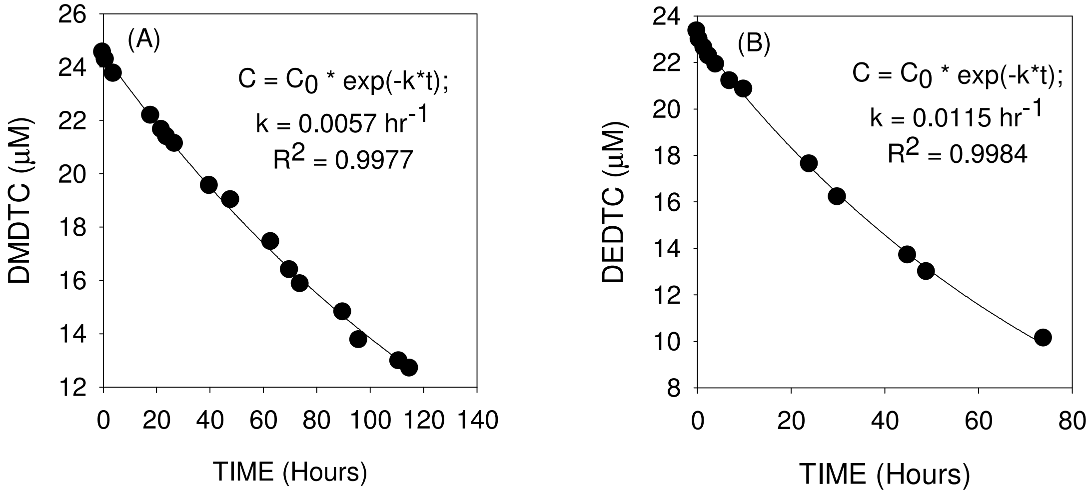


Figure 4.3 Hydrolysis and corresponding rate constants of (A) DMDTC and (B) DEDTC at pH 7.5.

The acid-catalyzed hydrolysis of dithiocarbamates (DTC) proceeds via decomposition of the protonated species. Protonation-deprotonation reactions are fast compared to hydrolysis rate of dithiocarbamates and are assumed to reach equilibrium quickly (Joris *et al.*, 1970).

$$\mathrm{DTC^- + H^+ \xleftrightarrow{K_a} DTCH \xrightarrow{k_1} CS_2 + Secondary\,amine} \tag{4.1}$$

where,

k_1 = Limiting hydrolysis rate constant

K_a = Acid dissociation constant

It has been shown that the hydrolysis rate of dithiocarbamates depends only on its fraction of protonated ligand in solution (Joris *et al.*, 1970). Therefore, the pH-dependence of the acid-catalyzed hydrolysis (Figure 4.2) can be described by the following equation (Weissmahr and Sedlak, 2000):

$$R = \frac{k_1 \times [H^+]}{[H^+] + K_a} \times [DTC]_{total} = k_{app} \times [DTC]_{total} \tag{4.2}$$

where,

R = Rate of transformation of DTC

$[DTC]_{total}$ = Total dithiocarbamate concentration, and

k_{app} = Apparent rate constant

Based on equation 4.2 and by knowing k_{app} for a specific pH ($k_{app} = 5.70\times10^{-3}$ for DMDTC and 1.15×10^{-2} for DEDTC at pH 7.5) and K_a values for DMDTC and DEDTC ($K_a = 10^{-3.6}$ for DMDTC and 10^{-4} for DEDTC) (Aspila *et al.*, 1969), we can predict k_{app} values for different pH. Table 4.1 lists k_{app} values and half-lives ($t_{1/2}$) for DMDTC and DEDTC at pH ranging from 5 to 9.

Table 4.1 Calculated hydrolysis rate constants and half-lives for DMDTC and DEDTC at pH ranging from 5 to 9.

pH	**DMDTC** k_{app} (hr^{-1})	**DMDTC** $t_{1/2}$ (hrs)	**DEDTC** k_{app} (hr^{-1})	**DEDTC** $t_{1/2}$ (hrs)
5	1.7	0.4	3.3	0.2
6	1.8×10^{-1}	3.9	3.6×10^{-1}	1.9
7	1.8×10^{-2}	38.4	3.6×10^{-2}	19.1
7.5	5.7×10^{-3}	121.4	1.2×10^{-2}	60.3
8	1.8×10^{-3}	383.9	3.6×10^{-3}	190.6
9	1.8×10^{-4}	3838.4	3.6×10^{-4}	1905.5

As pH decreases, rate constants increase by an order of magnitude for every unit drop in the pH and vice versa within the pH range of 2-9 (Aspila *et al.*, 1969). Evidently, pH and possibly the trace metal content in surface water and wastewater will significantly influence the stability of dithiocarbamates (Weissmahr and Sedlak, 2000). If pH is acidic, DMDTC and DEDTC will hydrolyze to form DMA and DEA, direct precursors of NDMA and NDEA, respectively. Hence, water treatment plants that operate at lower pH will experience much more significant formation of secondary amines from dithiocarbamates if these compounds are present in the water sources. Note that based on the obtained rate constants, about 14% of DMDTC and 28% of DEDTC will be lost due to hydrolysis at pH 7.5 after reaction time up to 24 hours, the employed reaction time in subsequent studies for the reactions of dithiocarbamates with monochloramine, free chlorine and chlorine dioxide. However, less than 1% of DMDTC and DEDTC will be lost due to hydrolysis at pH 7.5 after 30 minutes, the employed reaction time for the studies with ozone. Thus, for the majority of the experiments that were conducted at pH 7.5, hydrolytic loss of the dithiocarbamates can be neglected in the experiments with ozone, but may play a role in the experiments with the other three oxidants due to longer reaction time.

Table 4.1 shows that the rate of hydrolytic decomposition of DEDTC is more rapid than that of DMDTC. Hydrolysis rate of dithiocarbamates is a function of the bulkiness of the substituent alkyl groups on the nitrogen atom (Joris *et al.*, 1970). One of the reasons for this observed steric effect can be the increasing size of alkyl chain which introduces a strain on the N-C bond as a result of an interaction with the relatively large sulfur atoms in the molecule. Another point to consider is the inductive effect of the bulky alkyl groups which would enhance the nucleophilic character of the nitrogen atom (Joris *et al.*, 1970).

4.3.2 Nitrosamine Formation Potential of DMDTC and DEDTC with Disinfection Oxidants

The nitrosamine formation potentials of DMDTC and DEDTC were evaluated at pH 7.5 in reactions with monochloramine, free chlorine, chlorine dioxide and ozone. Initial oxidant concentration was 100 μM while initial dithiocarbamate concentration was 50 μM. Contact times were 24 hours for monochloramine, free chlorine and chlorine dioxide and 30 minutes for ozone. As shown in Figure 4.4, monochloramine and ozone generated the highest amounts of NDMA from DMDTC and NDEA from DEDTC, followed by chlorine dioxide and free chlorine. Secondary amines were also monitored at the end of the reaction with the reaction with monochloramine showing the lowest amount of remaining DMA and DEA (Figure 4.5). Parent compounds were also quantified at the end of the reaction, with ozone, free chlorine and chlorine dioxide reactors showing no residual dithiocarbamates, indicating that ozone, free chlorine and chlorine dioxide are sufficiently strong oxidants to break down dithiocarbamates readily. In contrast, monochloramine reactor had 42% of parent DMDTC and 31% of parent DEDTC remaining at the end of 24 hour reaction. Compared to the expected hydrolytic loss of 13% of DMDTC and 24% of DEDTC after 24 hours at pH 7.5, reaction with monochloramine oxidant causes still greater loss of dithiocarbamtaes than hydrolysis. For the risk of generating nitrosamines, the study results clearly indicate that the reactions of dithiocarbamates with monochloramine and ozone are particularly problematic. Further studies were conducted to better understand the factors governing nitrosamine formation for those two reactions.

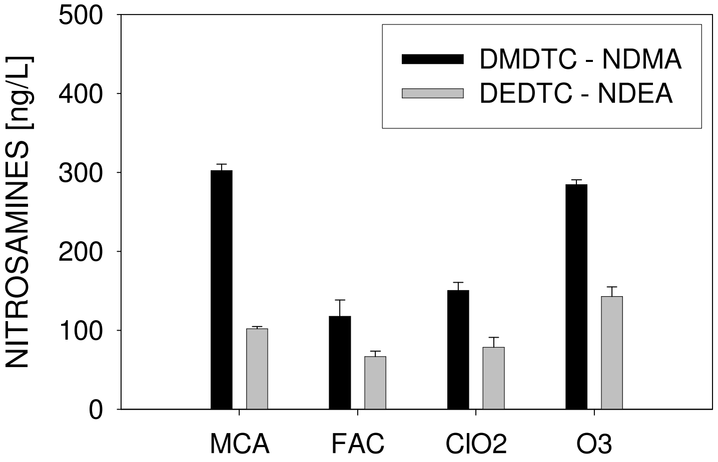


Figure 4.4 Formation of NDMA from DMDTC and NDEA from DEDTC in reactions with various oxidants. At pH 7.5, 0.05 mM of DMDTC and DEDTC were reacted with 0.1 mM of preformed monochloramine (MCA), free chlorine (FAC) and chlorine dioxide (ClO_2) for 24 hours and with 0.1 mM of ozone (O_3) for 30 minutes. (Error bars represent one standard deviation of the means)

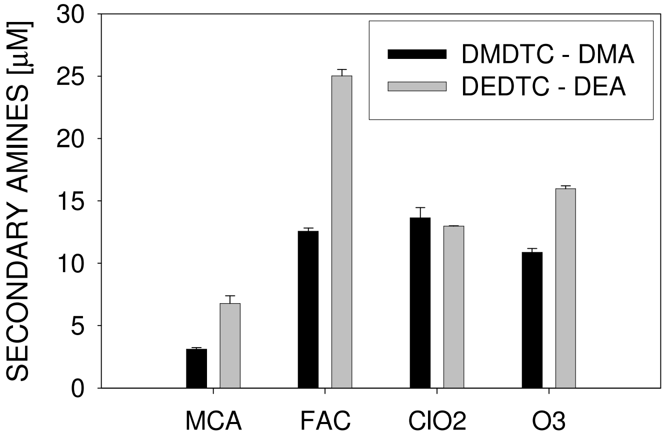


Figure 4.5 Concentration of DMA from DMDTC and DEA from DEDTC in reactions with various oxidants. At pH 7.5, 0.05 mM of DMDTC and DEDTC were reacted with 0.1 mM of preformed monochloramine (MCA), free chlorine (FAC) and chlorine dioxide (ClO_2) for 24 hours and with 0.1 mM of ozone (O_3) for 30 minutes. (Error bars represent one standard deviation of the means)

The results in Figure 4.5 show that the amount of DEA remained in the solution after reaction was higher, by different degrees, than the amount of DMA remained in the solution for all oxidants except ClO_2, for which it was similar. Note that the amount of amine detected at the end of reaction time is influenced by how much of the dithiocarbamate is degraded to release amine, as well as the stability of the released amine to the oxidant employed in the reaction. The faster hydrolysis of DEDTC than hydrolysis of DMDTC probably contributed modestly to the greater amount of remaining DEA than DMA observed in the monochloramination experiments.

However, the NDEA yield from DEDTC was always lower, by different degrees, than NDMA yield from DMDTC for all four oxidants (Figure 4.4), despite that more or similar amount of DEA was available compared to DMA. When 200 µM of monochloramine was reacted with 20 µM of DMA and 20 µM of DEA for 24 hours at pH 7.5, the yield of DEA to form NDEA based on the amount of DEA consumed (0.5%) was observed to be significantly lower than the yield of DMA to form NDMA based on the amount of DMA consumed (1.5%). Similar observations are reported elsewhere for ozonation of DMA and DEA (Andrzejewski *et al.*, 2008). The lower yield of DEA to form NDEA than the yield of DMA to form NDMA in reactions with oxidants of monochloramine and ozone may be attributed to steric hindrance associated with bulkier reaction intermediate that are more difficult to be further oxidized to form nitrosamine.

4.3.3 Effect of Oxidant Dosage

Figures 4.6A and 4.6B show the effect of oxidant dosage on the nitrosamine formation from DMDTC and DEDTC by monochloramination and ozonation, respectively. In general, the yield of nitrosamines increased with the oxidant dosage for both monochloramination and ozonation. For monochloramination of dithiocarbamates, the increase in nitrosamine appeared to taper off at the highest monochloramine (MCA) to dithiocarbamate (DTC) ratio (Figure 4.6A). This is similar to monochloramination of DMA, in which NDMA formation also reaches a plateau at higher MCA/DMA ratio (Choi, 2002). Nitrosamine formation continued to increase with increase in ozone dosage in the ozonation of dithiocarbamates (Figure 4.6B), similar to DMA's trend of NDMA formation with increased ozone dosage (Figure 3.10C). Hence, results from this experiment are consistent with the NDMA formation trends from DMA by monochloramination and ozonation.

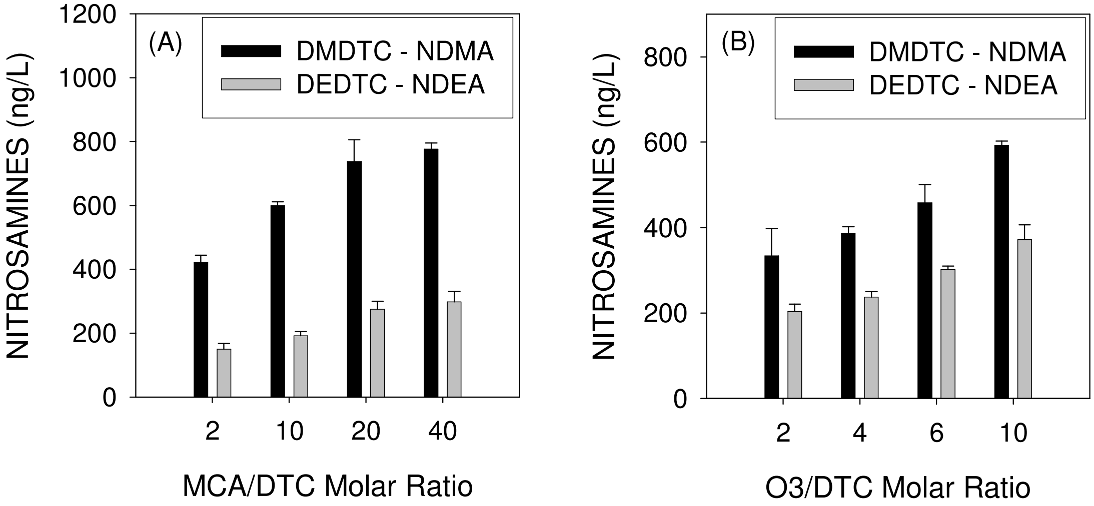


Figure 4.6 Nitrosamine yield from reaction of 0.05 mM DMDTC and DEDTC with (A) preformed monochloramine (MCA) and (B) ozone (O_3) as a function of oxidant concentration (Error bars represent one standard deviation of the means)

4.3.4 Effect of pH

Solution pH is expected to influence protonation of dithiocarbamates (pKa ~ 4), the degradation rate of dithiocarbamates, protonation of secondary amine products (pKa ~ 10.5), speciation of chloramines, stability of ozone, and transformation of secondary amine to form nitrosamine during reactions with monochloramine and ozone.

Figure 4.7A shows the effect of pH on the nitrosamine yield from monochloramination of DMDTC and DEDTC. As can be seen, nitrosamine yield decreased significantly with increasing pH from pH 5 to 7. However, from pH 7 to 9, nitrosamine yield increased slightly and then decreased with increasing pH. Figure 4.7B shows the nitrosamine yield from monochloramination of DMA and DEA. As can be seen, nitrosamine yield was highest near pH 7.5 to 8 and decreased on either side. This trend is attributed to balance between deprotonation of secondary amines (pKa ~ 10.5) and formation of dichloramine from disproportionation of monochloramine at lower pH. Since dichloramine is significantly more efficient in transforming deprotonated secondary amine to nitrosamine, yield of nitrosamines from monochloramination of secondary amines follow the observed bell shaped curve (Schreiber and Mitch, 2006a). At pH 5 and 6, dithiocarbamates will hydrolyze completely (Table 4.1) to yield secondary amines within 24 hours of reaction time. This may be a reason for the observed higher yield of nitrosamine at lower pH for dithiocarbamates. As pH increases, hydrolysis rate decreases, with less significant difference in amount of secondary amine released. The observed trend then can be explained in similar terms as that of secondary amines at higher pH.

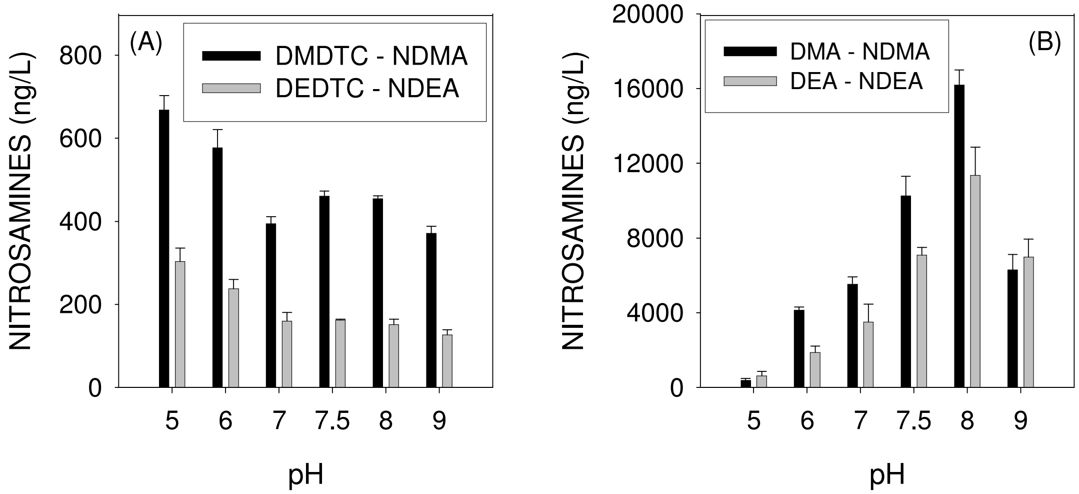


Figure 4.7 Nitrosamine yield from (A) reaction of 0.05 mM DMDTC and DEDTC with 0.1 mM of preformed monochloramine (MCA) after 24 hours and (B) reaction of 0.01 mM DMA and DEA with 0.1 mM of preformed monochloramine (MCA) after 24 hours as a function of pH (Error bars represent one standard deviation of the means)

The effect of pH on the nitrosamine yield from ozonation of DMDTC and DEDTC was also investigated. Since the experiments were carried out in batch reactors, the *CT* (i.e., ozone concentration × contact time) values (von Gunten, 2003) for ozone varied at different pH. Ozone decomposes rapidly under basic pH conditions and hence, has a shorter half-life under basic than acidic conditions. Hence, the experimental results were corrected by normalizing NDMA concentrations with respect to *CT* values for ozone exposure measured at respective pH. For ozonation, nitrosamine yield was highest at basic pH and it decreased with decrease in pH (Figure 4.8A). These results were found to be consistent with the pH trend of NDMA formation from ozonation of DMA (Figure 4.8B).

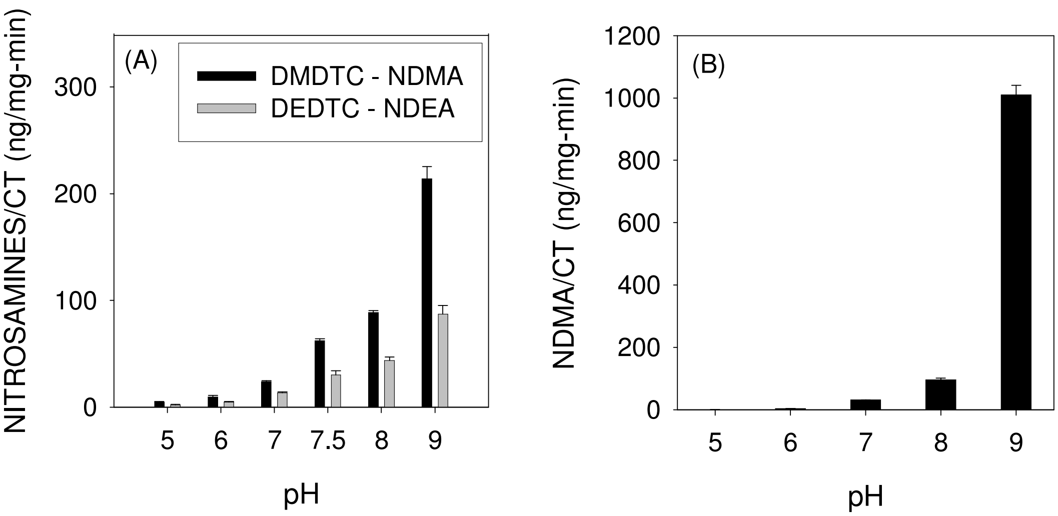


Figure 4.8 Nitrosamine yield from (A) reaction of 0.05 mM DMDTC and DEDTC with 0.1 mM of ozone after 30 minutes and (B) reaction of 0.05 mM DMA with 0.1 mM of ozone after 30 minutes as a function of pH (Error bars represent one standard deviation of the means)

4.3.5 Kinetic Study for Monochloramination of DMDTC

Because monochloramination of dithiocarbamates involves complex reactions including hydrolysis of dithiocarbamates, degradation of dithiocarbamates by monochloramine, and the reaction of amine products to generate nitrosamines, further study was carried out to examine the trends of DMDTC degradation, DMA release and NDMA formation with monochloramine to better understand the reaction mechanism,. Reactions were carried out at pH 7.5. Contact time was up to 125 hours (~5 days). Initial monochloramine concentration was 200 μM while initial DMDTC concentration was 20 μM.

As can be observed from the data points in Figure 4.9A, DMDTC degraded significantly over time. However, DMA concentrations (Figure 4.9B) increased initially and then decreased with time. NDMA concentrations (Figure 4.9C), on the other hand, increased continuously throughout the reaction period. If degradation of DMDTC releases DMA, the concentration of DMA is expected to increase over time; however, DMA amount may be counter-balanced by its consumption through reaction with monochloramine. Thus, a complex DMA concentration trend over time could be expected. Another observation is that DMDTC degradation was more than the hydrolysis alone could explain (shown as the smooth curve in Figure 4.9A), particularly during the initial reaction period. For example, for reaction time of up to 24 hours, 14% (2.8 μM) of the initial DMDTC is expected be lost due to hydrolysis. However, 66% (13.2 μM) of DMDTC was consumed after 24 hours of reaction in monochloramine solution, indicating that monochloramine reacts with DMDTC and causes it to degrade. This conclusion was also supported by the rapid loss of monochloramine (Figure 4.9D) during initial reaction period. About 70% (140 μM) of MCA was consumed after 24 hours of reaction time. While there was 66% (13.2 μM) loss of DMDTC after 24 hours, the amount of DMA detected was only in the range of 2.1-2.8 μM (Figure 4.9B), far less than the concentration of DMDTC consumed.

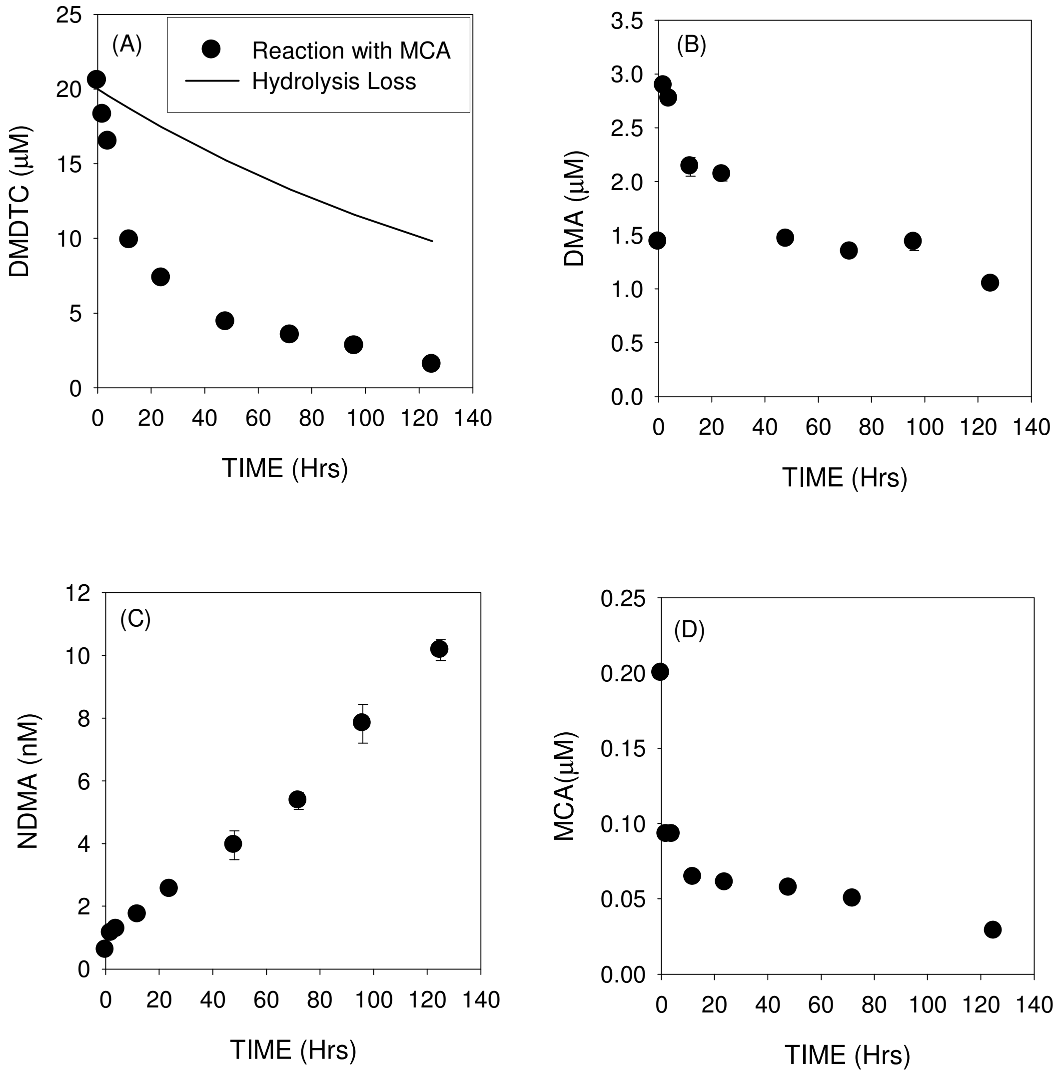


Figure 4.9 (A) DMDTC decay, (B) DMA concentration, (C) NDMA yield, and (D) monochloramine decay from reaction of 0.02 mM DMDTC with 0.2 mM of preformed monochloramine (MCA) at pH 7.5 as a function of time. (Error bars represent one standard deviation of the means)

Separate experiments were conducted to investigate reaction of DMA with monochloramine over time. Reactions were carried out at pH 7.5 with contact time up to 100 hours (~4 days). Initial monochloramine concentration was 200 μM while initial DMA concentration was 20 μM. As shown in Figure 4.10A, significant loss of DMA occurred during the first 48 hours, and then reached a very low concentration after that. The NDMA formation (Figure 4.10B) increased over time and then plateaued after 48 hours, reasonably well correlated with the loss of DMA over time. Monocnloramine concentration decreased steadily over time, with about 35% loss occurred during the first 24 hours (Figure 4.10C). Based on the experimental results in Figure 4.10A, about 25% of the initial DMA remained in water after 24 hours of reaction with monochloramine at pH 7.5. So even considering the loss of DMA due to reaction with monochloramine, the amount of DMA observed in the experiments with DMDTC (Figure 4.9B) cannot explain much of DMDTC consumption. Thus, it can be hypothesized that monochloramine reacts quickly with DMDTC, effectively competing with hydrolysis of DMDTC, but likely yields products other than DMA.

The observed NDMA yield at the end of 24 hours for DMDTC was 2.5 nM (Figure 4.9C). Considering that the yield of NDMA is 1.5% of the amount of DMA consumed after monochloramination for 24 hours (Section 4.3.2), the amount of DMA consumed would be about 0.17 μM for formation of 2.5 nM of NDMA. This is within the same range of observed consumption of DMA at 0.74 μM in 24 hours (Figure 4.9B).

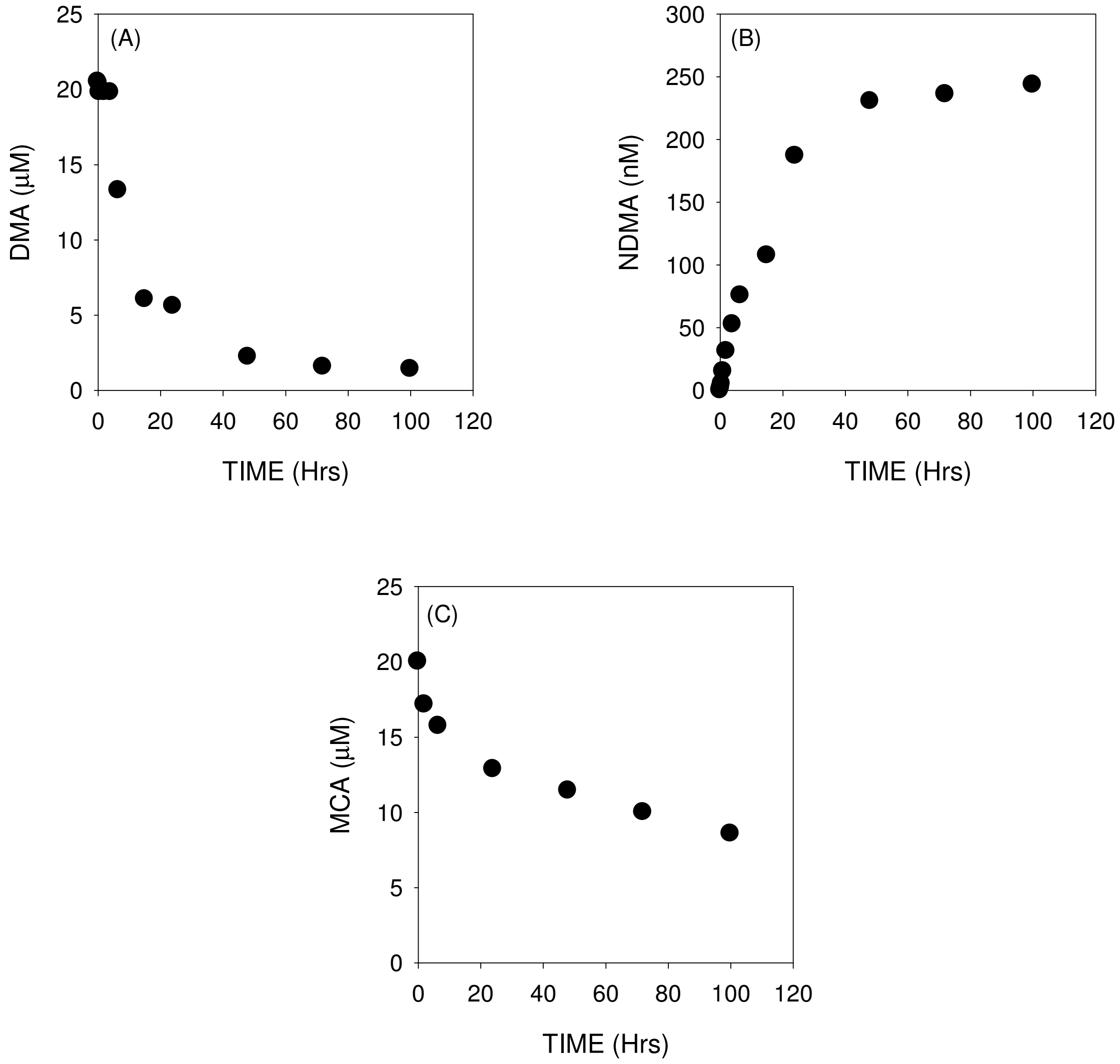


Figure 4.10 (A) DMA decay, (B) NDMA yield and (C) monochloramine decay from reaction of 0.02 mM DMA with 0.2 mM of preformed monochloramine (MCA) at pH 7.5 as a function of time.

4.3.6 Identification of Reaction Products

To understand the reaction products that may be generated from monochloramination and ozonation of DMDTC, experiments were carried out with initial concentrations of DMDTC at 50 μM and monochloramine or ozone at 0.1 mM, respectively. In addition to DMA and NDMA, other possible reaction products from monochloramination and ozonation of DMDTC including DMF, formaldehyde, nitrite and nitrate were measured and the results are summarized in Table 4.2. As is evident from Table 4.2, nitrite, formaldehyde and DMF were detected for ozonation of DMDTC, while these products were not detected for monochloramination of DMDTC. Furthermore, the yield of nitrite increased with increasing pH for ozonation of DMDTC. Presence of similar products from ozonation of DMA (Table 3.1) hints that observed NDMA and other products may be from ozonation of DMA released from DMDTC.

Table 4.2 Reaction products from monochloramination (MCA) and ozonation (O_3) of DMDTC. Note: (i) and (f) denotes at the beginning and at the end of the reaction, respectively. Reaction time was 24 h for monochloramination and 30 min for ozonation.

Sample	**DMA (i) (µM)**	**DMA (f) (µM)**	**DMDTC (i) (µM)**	**DMDTC (f) (µM)**	**DMF (µM)**	**Nitrite (µM)**	**Form-aldehyde (µM)**	**NDMA (µM)**
DMDTC + MCA(pH 7.5)	0.15	3.13	50	21.20	ND	ND	ND	0.005
DMDTC + O_3 (pH 5)	0.15	28.37	50	0.00	0.24	0.00	1.35	0.001
DMDTC + O_3 (pH 7.5)	0.15	7.71	50	0.00	0.23	0.10	1.95	0.004
DMDTC + O_3 (pH 9)	0.15	4.80	50	0.00	0.23	0.17	1.26	0.005

4.3.7 Possible Nitrosamine Formation Mechanisms

Dithiocarbamates, in which secondary amine functional groups are adjacent to electron-withdrawing thiocarbonyl functional groups, have been previously assumed to be relatively unreactive to monochloramine (Mitch and Sedlak, 2004). However, our study results show that all four oxidants (monochloramine, free chlorine, chlorine dioxide and ozone) can oxidize dithiocarbamates albeit monochloramine was the weakest reacting oxidant. Although DMDTC reacts with monochloramine readily, the reaction did not yield much DMA. The observed NDMA yield during monochloramination of DMDTC could be mostly attributed to DMA produced through hydrolysis of DMDTC and the reaction of DMA with monochlorine through chlorinated UDMH pathway (Schreiber and Mitch, 2006a). Results from this study indicate that the dithiocarbamates were not significant direct precursors of nitrosamines during reaction with monochloramine, but rather nitrosamines were from reaction of monochloramine with the amine hydrolytic product of dithiocarbamates.

For ozonation, dithiocarbamates react rapidly with ozone ($K_{O3} = 3.9\times10^{6}\ M^{-1}\ s\text{-}^{1}$) (Lee *et al.*, 2007). Results from reaction product analysis indicate that secondary amines may be a product of ozonation of dithiocarbamates since hydrolysis rate is too slow to account for the observed amount of secondary amines at the end of 30 minutes of ozonation. The results also show similar nitrosamine formation trend at varying pH as reaction of secondary amines with ozone. The presence of significant amounts of nitrite and other reaction products similar to ozonation of DMA suggest that nitrosamine formation mechanism may be similar to that described in Section 3.4.8.2. Thus, dithiocarbamates serve as direct precursors of nitrosamines during ozonation, in which ozone decomposes dithiocarbamates to release secondary amines that can further react with ozone to form nitrosamines possibly through an enhanced nitrosation mechanism.

4.3.8 Environmental Significance

Results of this study show that dithiocarbamates may serve as nitrosamine precursors, by release of secondary amines through hydrolysis or through reactions with oxidants (particular with ozone, free chlorine and chlorine dioxide). Hence, emphasis should be placed on reducing secondary amine formation from dithiocarbamates. Increasing the pH would decrease hydrolysis rate of dithiocarbamates; however it increases nitrosamine formation through ozonation of secondary amines. Decreasing the pH is beneficial to remove toxicity associate with dithiocarbamates themselves since decreasing the pH results in more hydrolysis of dithiocarbamates. However, in addition to more amine release from hydrolsis, lower pH may result in more nitrosamine formation through monochloramination due to more disproportionation of monochloramine to dichloramine, a more potent nitrosamine precursor (Schreiber and Mitch, 2006a). The results of this study indicate that, based on the oxidant uses, treatment conditions need to be modified to reduce nitrosamine formation risks from dithiocarbamates.

CHAPTER 5

TRANSFORMATION OF SECONDARY AMINES TO *N*-NITROSAMINES ON ACTIVATED CARBONS

5.1 Introduction

Trace level analysis of nitrosamines in water requires pre-concentration steps such as solid-phase extraction (SPE) or liquid-liquid extraction (LLE) followed by high resolution or tandem GC/MS or LC/MS analysis. SPE is more commonly employed than LLE for nitrosamine analysis in recent years because it uses less hazardous solvents (Jenkins *et al.*, 1995). Table 5.1 summarizes the AC adsorbents that have been commonly used for nitrosamine extraction in the literature. These adsorbents include synthetic as well as coconut shell-based and charcoal-based carbonaceous particles. Taguchi *et al.* (1994) were the first to demonstrate the synthetic Ambersorb 572 (Rohm and Haas, Philadelphia, PA) as an effective SPE adsorbent for nitrosamines. It soon became the preferred choice for extraction of nitrosamines in aqueous media as demonstrated by numerous studies conducted using this adsorbent (Table 5.1).

EPA's Method 521 (Munch, 2004) for nitrosamine analysis uses coconut shell-based carbonaceous adsorbents for SPE. A number of other carbonaceous adsorbents (Table 5.1) have been reported for SPE of nitrosamines in water as well as in foods and beverages with lower extraction efficiencies than Ambersorb 572. However, Ambersorb 572 became unavailable from most commercial suppliers in the recent two years due to discontinuation of production of Ambersorb 572 by Rohm and Haas (Rohm and Haas Co., 2008), leading to an increase in the demand for alternate carbonaceous SPE materials including coconut shell-based (Walse and Mitch, 2008) and charcoal-based (Planas *et al.*, 2008) carbons.

Table 5.1 Carbonaceous adsorbents used for nitrosamine analysis in water and wastewater

	Nitrosamine Extraction Material (Source)	**Properties**	**Cited Literature**
1	Ambersorb 572 (Rohm and Haas)	Synthetic carbonaceous, spherical beads, produced by pyrolysis of highly sulfonated styrene divinyl benzene ion exchange resins Size: 0.841 - 0.297 mm Surface Area: 1100 m^2/g	(Jenkins *et al.*, 1995; Fleming *et al.*, 1996; Choi, 2002; Choi and Valentine, 2002; Schreiber and Mitch, 2005; Chen and Valentine, 2006; Cheng *et al.*, 2006; Schreiber and Mitch, 2006a; Charrois *et al.*, 2007; Charrois and Hrudey, 2007; Chen and Valentine, 2007; Chen and Young, 2008; Planas *et al.*, 2008; Zhao *et al.*, 2008)
2	Ambersorb 563 (Rohm and Haas)	Synthetic carbonaceous, spherical beads Size: 0.841 - 0.297 mm Surface Area: 550 m^2/g	(Fleming *et al.*, 1996)
3	Ambersorb XE 340 (Rohm and Haas)	Hydrophobic carbonized resin beads Size: 0.841 - 0.354 mm Surface area: 460 m^2/g	(Kimoto *et al.*, 1981)
4	Coconut Charcoal Cartridge (Anspec, Ohio)	Size: 0.177 mm – 0.125 mm Other info not available	(Munch, 2004; Munch and Bassett, 2006; Dillon *et al.*, 2008)
5	Coconut Charcoal EPA 521 Cartridge (Restek)	Size: ≤ 0.149 mm Other info not available	(Munch, 2004; Planas *et al.*, 2008)
6	Carboxen 564 (Supelco)	Carbonaceous adsorbent, spherical beads Size: 0.841 - 0.354 mm Surface area: 400 m^2/g	(Jenkins *et al.*, 1995)
7	conut shell-based carbon cartridge (UCT ENVIRO-CLEAN®; approved for EPA Method 521)	Carbon information not published	(Walse and Mitch, 2008)

Table 5.1 (continued)

8	Coconut shell-based activated carbon particles (Calgon)	Information not available	(Fleming *et al.*, 1996)
9	Carbon disks (3M)	Disk size: 47 and 90 mm Surface area: > 1100 m^2/g	(Tomkins and Griest, 1996; Munch and Bassett, 2006)
10	Resprep graphitized carbon particles (Restek)	Information not available	(Munch and Bassett, 2006)
11	Spherical carbonaceous sorbent (JT Baker Bakerbond Carbon)	Spherical carbon particles Size: 0.200 - 0.450 mm Surface area: 1300 m^2/g	(Lee *et al.*, 2007; Krauss and Hollender, 2008; Schmidt and Brauch, 2008)
12	Activated carbon fiber felt KF Type 1500 (Toyobo, Osaka, Japan)	Length: 0.3 mm Diameter: 0.014 – 0.023 mm Surface area: 1500 m^2/g	(Kawata *et al.*, 2001)
13	F-400 activated carbon particles (Calgon)	Bituminous coal-based activated carbon Size: 0.55 -0.75 mm Iodine no: 100 mg/g	(Dietrich *et al.*, 1986; Fleming *et al.*, 1996)

AC materials are also widely used in drinking water and wastewater treatment, primarily for removal of small molecular weight organic compounds. Liquid-phase applications of AC constitutes 80% of the total AC demand in the U.S. (>500 million pounds), of which the removal of water contaminants represents the major market (55%) (Marsh and Rodríguez-Reinoso, 2006). Of the total U.S. water treatment market for AC adsorbents, about 50% is in drinking water, 40% is in wastewater, and the rest is in groundwater applications (Marsh and Rodríguez-Reinoso, 2006). Potable water is the largest end-use market for activated carbon, accounting for more than 100 million pounds. Demand for activated carbon in public service water is expected to grow at approximately 4.5 percent annually (The Innovation Group, 2002).

AC materials are also frequently used as catalyst supports or in some cases catalysts in various industrial processes including hydrogenation, oxidation, polymerization and halogenation (Abotsi and Scaroni, 1989; Radovic and RodriguezReinoso, 1997). For example, the production of phosgene (carbonyl chloride) and oxidation of pollutant gases in air pollution control employ AC catalysts. ACs are less used as catalysts for the abatement of organic pollutants in the liquid phase. However, the use of ACs for catalytic wet air oxidation (CWAO) of organic pollutants in waste streams is developing. CWAO of phenolic compounds has been studied in detail (Stuber *et al.*, 2005). Apart from phenols, ACs have been shown as effective catalysts for CWAO of ammonia, aniline, dimethylamine, methylamine, 1,3,6-naphthalene trisulphonic acid, hydrogen peroxide, *N*-phosphonomethyliminodiactic acid, and cyclohexanone (Stuber *et al.*, 2005; Gomes *et al.*, 2008).

As to be documented in this study, while examining various AC materials for SPE of *N*-nitrosamines, it was discovered that many ACs can catalyze transformation of secondary amines to form *N*-nitrosamine under ambient aerobic conditions. Because of the widespread applications of AC materials in water analysis and water treatment, this finding has significant implications in a broad range. This is also a novel discovery since to the best of our knowledge, only one prior work by Dietrich et al. (1986) reported that AC particles can catalyze nitrosation of a secondary amine (*N*-methylaniline) with nitrite to form *N*-nitroso-methylaniline. Currently, there is little information in literature regarding the transformation of secondary amines on AC surfaces to form nitrosamines, the potential role of AC in catalyzing nitrosamine formation, the impact of reaction conditions, or the involved reaction mechanisms. Without such knowledge, nitrosamine analysis will continue to be susceptible to this potential error. Furthermore, understanding the roles of AC materials and water treatment conditions on nitrosamine formation will be important to assess the significance of these findings for practical applications.

As an initial effort to address the important information need on this topic, we systematically examined the formation of nitrosamines from amine precursors on various AC surfaces under typical nitrosamine analysis conditions with the objective to identify critical factors influencing this reaction. This study reports the reaction yields in reagent and real water matrices, and the factors including AC properties, amine properties and environmental conditions that influence the nitrosamine formation.

5.2 Materials and Methods

5.2.1 Chemicals

Standard-grade NDMA, NMEA, NPYR, NDEA, NDPA NDBA, methylethylamine (MEA), pyrrolidine (PYR), DEA, di-*n*-propylamine (DPA), di-*n*-butylamine (DBA), sodium nitrite, hydroxylamine (50% in water), hydrogen peroxide (30% in water), sodium thiosulfate ($Na_2S_2O_3$), *tert*-butanol, superoxide dismutase, hydrochloric acid, sulfuric acid, 4-methoxybenzenesulfonyl chloride, acetone, dichloromethane, sodium phosphate monobasic and dibasic, sodium borate, sodium carbonate, sodium bicarbonate, sodium hydroxide, sulfanilamide and *N*-(1-naphthyl)-ethylenediamine dihydrochloride were obtained at >98% purity from Sigma-Aldrich (St. Louis, MO) or Fisher Scientific (Pittsburgh, PA). DMA was obtained in the form of DMA hydrochloride from both Sigma-Aldrich and Fisher Scientific, and in the form of 40% solution in water) from Sigma-Aldrich. The isotopes DMA-N_{15}, sodium nitrite-N_{15}, NDMA-d_6, NDEA-d_{10}, NDPA-d_{14} and DMA-d_6 hydrochloride were obtained from Cambridge Isotope Laboratories (Andover, MA). All reagents were used without further purification. High purity deionized water was generated from a Millipore (Billerica, MA) Milli-Q® water purification system and used to prepare reaction solutions. HPLC-grade water was also purchased from Fisher Scientific and used in some experiments.

5.2.2 Activated Carbons, Modifications and Characterization

The suite of activated carbon particles and fibers used in this study included: (i) synthetic Ambersorb 572 particles from Rohm and Haas (Philadelphia, PA), (ii) coconut shell-based activated carbons: Prominent Systems carbon (PSC) from Prominent Systems

Inc. (City of Industry, CA), Siemens Aquacarb carbon (AqC) from Siemens Water Technologies (Warrendale, PA), OLC from Calgon Corporation (Pittsburgh, PA), and UCT carbon particles from United Chemical Technologies Inc. (Bristol, PA), (iii) a bituminous coal-based carbon, F400, from Calgon Corporation, (iv) a lignite coal-based carbon, HD4000, from Norit Americas (Marshall, TX), (v) three phenol formaldehyde-based activated carbon fibers (ACF10, ACF15, ACF20H) from American Kynol (Pleasantville, NY), and (vi) a granular activated carbon (GAC) (manufacturer not known) from a local wastewater treatment plant. The UCT particles were obtained from dissembling a UCT ENVIRO-CLEAN® carbon cartridge and used in this study in order to be compared with the other carbon particles in a similar analytical protocol. All ACs were used as received from the manufacturers unless specified otherwise.

These AC materials were selected to represent ACs of different origins, uses, and properties. They are also widely used in environmental applications. For example, Ambersorb 572 and UCT represent AC particles used for SPE of nitrosamines, AqC, PSC and GAC represent carbons that are supplied to water and wastewater treatment plants by leading AC suppliers, F400, OLC and HD4000 have been commonly employed in adsorption studies of organic compounds, and carbon fibers possess special properties such as more uniform pore size distribution.

Four types of ACs were also pretreated using different approaches to modify their surface characteristics, which may provide insight to the roles of activated carbons in the catalyzed nitrosamine formation. For PSC, three different pretreatment techniques were used: (i) PSC particles were treated with acids (H_2SO_4 or HCl) by immersing 2 g of particles in 50 mL of concentrated acid solutions for 30 minutes followed by rinsing with deionized water and air-drying prior to use in experiments; (ii) PSC particles were subjected to an aqueous ozone solution at measured ozone dose of *CT* = 900 mg-min/L and then air-dried; and (iii) PSC particles were baked at 600 °C in a standard oven for 6 hours and then cooled to room temperature prior to use in experiments. For F400, OLC and HD4000, two pretreatment methods were used. One method was the heat treatment at 1173K for 2 h under hydrogen flow to remove a large portion of surface functional groups. The second method was oxidation in 4 M nitric acid at 90°C for 1 h to add surface functional groups. More details about the pretreatment methods employed for F400, OLC and HD4000 have been previously reported (Dastgheib *et al.*, 2004; Bansal and Goyal, 2005; Karanfil *et al.*, 2007).

Various characterization methods were employed to determine physical and chemical characteristics of both untreated and treated ACs. Physical characteristics, surface areas, pore volumes and pore size distributions, were determined from nitrogen adsorption isotherms using Brunauer-Emmet-Teller (BET) equation, t-plot method, and the Density Functional Theory (DFT) model. Chemical characteristics were determined with pH of zero point of charge (pH_{zpc}) measurements and elemental analysis. Details of the characterization methods have been previously described elsewhere (Dastgheib *et al.*, 2004; Karanfil *et al.*, 2007).

5.2.3 Drinking Water and Wastewater Effluent Samples

Grab samples of surface water (SW) and wastewater effluent (WW) were collected from a municipal drinking water treatment plant (DWTP) and a wastewater treatment plant (WWTP) in the Southeastern U.S. SW sample was collected from the reservoir supplying source water to the DWTP. WW sample was collected after activated sludge secondary treatment and gravity filtration, but prior to chlorine-based disinfection process.

Characterization of the water samples was conducted at the water and wastewater treatment plants where samples were collected and the available parameters are listed below:

- Surface water sample: pH 6.3, iron 0.048 mg/L, color 5 C.U., alkalinity 17 mg/L, dissolved oxygen 9 mg/L, calcium hardness 9 mg/L as $CaCO_3$, total hardness 14 mg/L as $CaCO_3$, turbidity 1.6 NTU, nitrate 0.3 mg/L as N, and nitrite non-detectable.
- Wastewater sample: pH 6.9, total phosphate 0.12 mg/L, ammonia < 0.1 mg/L, TSS 6 mg/L, VSS 2 mg/L, nitrate 8.4 mg/L as N and nitrite of 0.4 mg/L as N.

5.2.4 Experimental Protocol

Batch experiments were conducted in either deionized water or natural waters (i.e., SW or WW) using amber borosilicate bottles with Teflon-lined caps. Experiments followed the literature-established protocol (Taguchi *et al.*, 1994): AC particles (150–200 mg) were added to 100 mL of DMA or other secondary amine solution (at 1–444 μM) containing 31.25 nM (or 1.25 nM in real water experiments) of NDMA-d_6 or NDPA-d_{14} surrogate standard and 10 mM phosphate buffer. The isotope-labeled surrogates are used to correct for nitrosamine extraction efficiency and matrix effect in the isotope dilution method (Taguchi *et al.*, 1994; Padhye *et al.*, 2009; Park *et al.*, 2009). The above amine concentrations were selected in order to obtain substantial differences in nitrosamine formation from different AC particles, as well as to assess factors influencing nitrosamine formation. The amine+AC solution was shaken on a platform shaker at 200-250 rpm for 1.5–2 h at room temperature (22.5 ºC) and filtered through a glass-fiber filter (Millipore, Jaffrey, NH). The collected carbon particles were air dried for 3–6 h, transferred to a GC vial, and 0.5 mL dichloromethane (DCM) was added to desorb nitrosamines from the particles. Then, the DCM layer was analyzed for nitrosamines by GC/MS. For control experiments (samples without AC particles), LLE was used to extract nitrosamines, in which 100 mL (deionized water) or 500 mL (real water) of reaction solution as described above was extracted with 25 mL or 100 mL DCM, respectively, by vigorous shaking for two minutes. The DCM layer was separated, concentrated down to 0.5 mL by evaporating under vacuum, and analyzed for nitrosamines by GC/MS.

For secondary amines, two mL of reaction aliquot were taken before the filtration step and spiked with DMA-d_6 at 1.96 μM from a freshly prepared aqueous stock. The sample aliquot was adjusted to pH 9.0 by 10 mM borate buffer and added with 5 mM 4-methoxybenzenesulfonyl chloride as derivatizing agent. The resulting solution was agitated for 2 h and extracted with 2 mL DCM for 2 min. The extracts were analyzed for derivatized secondary amines by GC/MS.

5.2.5 GC/MS Conditions

Samples were analyzed by an Agilent GC/MS (6890/5973) system equipped with a HP-5MS column (30 m × 250 μm × 0.25 μm) and a large volume injector (LVI). Solvent-vent mode injections of 5-25 μL were used with an initial injection port temperature of 0 ˚C or 30 ˚C for nitrosamine and secondary amine analysis, respectively, which was rapidly increased to 220 ˚C after 0.3 sec. The temperatures of the MS ion source and transfer line were 150 and 260 ˚C, respectively. For nitrosamine analysis, GC oven temperatures were 35 ˚C held for 1 min followed by ramping at 10 ˚C/min to 170 ˚C, then ramping at 15 ˚C/min to a final temperature of 240 ˚C held for 2 min. For secondary amine analysis, GC oven temperatures were 40 ˚C held for 1 min followed by ramping at 20 ˚C/min to a final temperature of 260 ˚C held for 5 min. Nitrosamines and derivatized secondary amines were analyzed by electron ionization (EI) mode using selected ion monitoring (SIM). Compounds were confirmed by chromatographic retention time, parent ion, daughter ion, and parent-daughter ion ratio as described previously (Padhye *et al.*, 2009; Park *et al.*, 2009). Quantification of compounds was based on their parent ions.

Instrument Detection Limit (IDL) for NDMA was determined to be 0.32 μg/L or 0.1 pico moles based on 25 μL injection volume which corresponds to 2 pico moles of total mass of NDMA in the final 500 μL DCM extract after SPE procedure. The 0.32 μg/L was determined from the standard deviation of 7 repeated injections of a 2 μg/L NDMA standard multiplied by student t-value of 3.143. There was no significant difference in IDL for NDMA in different water matrices tested in this study. The Method Detection Limit (MDL) for NDMA was estimated to be around 1.6 or 8 ng/L, after taking into account the concentration factor of 1000 (initial sample volume = 500 mL; final extract volume = 0.5 mL) or 200 (initial sample volume = 100 mL; final extract volume = 0.5 mL), respectively, and average 20% extraction recovery of NDMA among the carbons. The MDL of NDMA by LLE was near 3.2 or 16 ng/L for concentration factors of 1000 or 200, respectively, at average 10% extraction recovery of NDMA. The IDL for derivatized secondary amines was determined to be around 0.01 pico moles based on 5 µL injections of a 0.1 µg/L derivatized secondary amine standard. The MDL for secondary amines was estimated to be 100 ng/L based on a concentration factor of 1 (initial sample volume = final sample volume = 2 mL) and identical derivatization efficiency for secondary amine samples and standards.

5.2.6 Reaction Product Analysis

Nitrite, nitrate and dimethylformamide (DMF) were analyzed by same analytical methods as described in Section 3.3.3.5.

5.3 Results and Discussion

5.3.1 AC-Catalyzed Nitrosamine Formation

Experimental results unambiguously showed that secondary amines can transform to *N*-nitrosamines in the presence of AC particles. This phenomenon was observed, to different extent, on all AC particles and AC fibers tested in this study (Table 5.2). When 100 mL of DMA-containing (200-222 µM) solutions were subjected to SPE using AC particles at pH 7.5, 0.16 to 2.14 nano moles of NDMA were formed (Table 5.2), approximately 0.001% to 0.01% of initial amount of DMA in water. In contrast, no nitrosamine formation was detected when the amine solution was subjected to LLE without using AC. These results corresponded to 118-1,584 ng/L of NDMA in mass concentrations. Further, if NDMA concentration was quantified by isotope dilution method with NDMA-d_6 which corrected for NDMA extraction efficiency, as is the current practice for SPE protocol, the above NDMA concentrations increased by an order of magnitude to 627-11,337 ng/L (Table 5.2). Since the carbon-catalyzed NDMA formation from DMA varied significantly among the AC materials (Table 5.2), the results indicated that AC properties play a role in the NDMA formation. While Ambersorb 572 and AC fibers exhibited the lowest yields, Siemens Aquacarb particles (AqC) showed the highest yield.

Table 5.2 NDMA formation from DMA in the presence of AC materials

Carbon Materials	**Specific Surface Area S_{BET} (m^2/g)**	**pH_{zpc}**	**Test Conditions**	**NDMA (nano moles)**	**NDMA (ng/L)**	**NDMA (ng/L) by NDMA-d_6 Isotope Dilution**
Ambersorb 572	1020	7.0	a	0.45 ± 0.33*	333 ± 244	972 ± 702
AqC	1202	9.6	a	2.14 ± 0.18	1584 ± 133	11337 ± 954
PSC	1114	9.7	a	0.57 ± 0.07	422 ± 52	4971 ± 618
UCT	NA	NA	a	1.68 ± 0.09	1243 ± 67	4463± 249
GAC	819	7.4	a	0.28 ± 0.03	207 ± 22	2316 ± 258
F400	1044	9.2	b	0.61 ± 0.08	451 ± 59	3773 ± 509
OLC	983	9.3	b	0.86 ± 0.02	636 ± 15	5794 ± 141
HD4000	706	6.6	b	0.60 ± 0.01	444 ± 7	4459 ± 74
ACF 10	972	7.3	b	0.17 ± 0.01	126 ± 7	1275 ± 73
ACF 15	1520	8.9	b	0.21 ± 0.01	155 ± 7	1558 ± 71
ACF 20H	1740	9.5	b	0.16 ± 0.02	118 ± 15	627 ± 80

(a) 222 μM DMA, 200 mg carbon, 2 h suspension shaking time, 3 h carbon drying time; (b) 200 μM DMA, 150 mg carbon, 1.5 h suspension shaking time, 6 h carbon drying time. *: Experiments were conducted with regenerated Ambersorb 572 particles which were washed with methanol and then dichloromethane, followed by drying in an 100 °C oven. All reaction suspensions were buffered at pH 7.5 by 10 mM phosphate buffer. Instrument detection limit for NDMA = 2 pico moles; Mean ± standard deviation (*n* = 3); NA = not available; pH_{zpc}: zero point of charge.

These findings were carefully verified with a number of control experiments. Extractions of secondary amine stocks and carbon particles by DCM showed no nitrosamine contamination. Furthermore, similar levels of NDMA formation were observed when the same experiments using AqC and Prominent Systems carbon (PSC) particles were conducted in commercial HPLC-grade water instead of the deionized water available in our lab. Because AC has the potential to catalyze nitrosation of secondary amines with nitrite to yield nitrosamines (Dietrich *et al.*, 1986), nitrite was measured using a colorimetric method (Eaton, 1998) and found to be below the method detection limit (MDL ~ 70 nM) in the deionized water used in the experiments and in DMA stocks. Spiking various amounts of ^{15}N-nitrite in solutions showed that ^{15}N-NDMA formation compared to ^{14}N-NDMA formation was not significant at least until nitrite concentration reached 1,000 nM (0.046 mg/L) (Table 5.3). These results confirmed that nitrite at concentrations below the MDL, if existed in the deionized water, was not a contributing factor to the observed NDMA formation.

Table 5.3 Potential enhanced *N*-nitrosation by AC particles to form NDMA: Dependence on nitrite concentration

Samples	**NDMA (nano moles)**	^{15}N-**NDMA (nano moles)**
DMA (no nitrite)	0.53 ± 0.01	0.00 ± 0.00
DMA+ 50 nM ^{15}N-Nitrite	0.58 ± 0.01	0.00 ± 0.00
DMA + 100 nM ^{15}N-Nitrite	0.57 ± 0.00	0.00 ± 0.00
DMA+ 500 nM ^{15}N-Nitrite	0.55 ± 0.04	0.03 ± 0.00
DMA + 1,000 nM ^{15}N-Nitrite	0.43 ± 0.03	0.09 ± 0.00
DMA+ 100,000 nM ^{15}N-Nitrite	0.45 ± 0.00	9.78 ± 0.14

Experiments were conducted at pH 7.5, using 222 μM DMA, 200 mg AqC carbon, 3 h particle drying time; Instrument detection limit for NDMA = 2 pico moles; Mean ± standard deviation (*n* = 3)

The AC-catalyzed nitrosamine formation could occur (i) while in the suspension state when carbon particles were immersed in solution, and (ii) during drying of carbon particles after filtration. To distinguish the contributions from these two different steps, the amount of nitrosamine formed while in the suspension state was determined by the following procedures: water in the amine+AC aqueous suspension was decanted to collect the carbon particles; DCM was immediately added to the carbon particles in a centrifuge tube followed by centrifugation; afterwards, the DCM layer was analyzed for nitrosamines by GC/MS. The amount of nitrosamine formed during carbon drying was then determined by subtracting the amount formed while in the suspension state from the overall nitrosamine formation. It was found that more nitrosamine formed during drying of AC particles. For example, results with the PSC particles showed that 0.05 ± 0.00 nano moles of NDMA were formed during shaking (1.5 hours) of amine+AC suspension, while total NDMA formation for air-dried AC particles, including contribution during shaking (1.5 hours shaking and 1.5 hours drying), was 0.44 ± 0.03 nano moles. Hence, more than 90% of total NDMA formation occurred during drying of AC particles. It is for this reason that the nitrosamine concentrations to be presented later in all Figures were direct measurements, not quantified by isotope dilution method that corrected for extraction recoveries. In this way, the amount of nitrosamine reported is likely lower than the real amount and thus represents a conservative estimate.

5.3.2 Surface Water and Wastewater Samples

To examine the significance of the above results obtained in deionized water, experiments were also conducted in SW and WW samples. A larger sample volume (500 mL) was subjected to SPE to achieve a lower MDL for NDMA. Samples were extracted by two different carbons (Calgon F400 and Siemens AqC) using procedures described above. AqC and F400 were used in these experiments because they represent ACs with high and low capability to catalyze NDMA formation, respectively, based on our results (Table 5.2). For comparison, the natural water samples were also fortified with DMA (1 µM (45 µg/L) in SW and 10 µM (450 µg/L) in WW) before SPE. The selected spiking concentrations represent the upper concentration ranges of DMA and other secondary amines found in environmental samples. Previous studies reported DMA concentrations ranging from 1-3 µg/L (Sacher *et al.*, 1997) in surface waters to up to 235 µg/L in rivers that receive considerable discharge of wastewater effluents (Abalos *et al.*, 1999). Similarly, diethylamine (DEA) was detected in surface waters at 9-13 µg/L (Neurath *et al.*, 1977; Abalos *et al.*, 1999). High incidence of multiple secondary amines in wastewaters has been documented in numerous studies with concentrations of DMA and other amines at 20-1,000 µg/L (Mitch *et al.*, 2003b; Sedlak *et al.*, 2005; Pehlivanoglu-Mantas and Sedlak, 2006; Padhye *et al.*, 2009). Secondary amines have also been employed at varying concentrations as high as 180 mg/L (Choi, 2002; Choi and Valentine, 2002) in laboratory studies involving AC particles for extraction of nitrosamines.

A total of five sets (Table 5.4) were analyzed for each sample with the first set being controls (marked as blank) which employed LLE to quantify residual concentrations of secondary amines and nitrosamines in the SW and WW samples. In the others sets, 200 mg of AC particles were used to extract samples. Both SW and WW had residual NDMA levels below MDL (2-3 ng/L). DMA was not detected (< 0.1 µg/L) in SW, while WW had 0.8 µg/L of DMA. For SW, NDMA did not form above MDL when DMA was not added to the sample, while 3 ng/L (or 59 ng/L by NDMA-d_6 isotope dilution) of NDMA formed with AqC particles when 1 µM DMA was added. For WW not fortified with DMA, 9.1 ± 0.0 and 15.4 ± 2.5 ng/L of NDMA formed with F400 and AqC particles, respectively. When WW was fortified with 10 µM DMA, 10-50 ng/L (or 210-686 ng/L by NDMA-d_6 isotope dilution) of NDMA formed (Table 5.4). WW samples showed higher NDMA yields than SW samples when normalized by the spiked DMA concentration. This might be partly due to the presence of residual nitrite (0.4 mg/L) in the wastewater samples and nitrosation was catalyzed by AC. The AqC consistently showed higher NDMA yield than F400, as observed in deionized water matrix. These results further confirm that ACs can catalyze nitrosamine formation from amine precursors in natural water matrices and the choice of SPE carbons can significantly impact the analytical results of nitrosamine measurements.

Table 5.4 NDMA Formation in Surface Water and Wastewater Effluent in the Presence of AC Particles

Sample	**Water pH**	**Initial DMA (µg/L)**	**NDMA (nano moles)**	**NDMA (ng/L)**	**NDMA (ng/L) by NDMA-d_6 Isotope Dilution**
SW blank	6.3	ND	ND	ND	ND
SW + F400	6.4	ND	ND	ND	ND
SW + AqC	6.9	ND	ND	ND	ND
SW + DMA (1 µM) + F400	6.6	45.8 ± 0.9	0.002 ± 0.000	0.3 ± 0	8 ± 0
SW + DMA (1 µM) + AqC	7.3	46.3 ± 4.1	0.022 ± 0.007	3.2 ± 1	59 ± 15
WW blank	6.9	0.8 ± 0.0	ND	ND	ND
WW + F400	7.1	0.6 ± 0.1	0.003 ± 0.001	0.4 ± 0	10 ± 0
WW + AqC	7.1	0.6 ± 0.1	0.006 ± 0.003	0.9 ± 0	16 ± 3
WW + DMA (10 µM) + F400	7.3	459.2 ± 0.8	0.071 ± 0.002	10.6 ± 0	210 ± 30
WW + DMA (10 µM) + AqC	7.3	457.1 ± 4.7	0.340 ± 0.007	50.3 ± 1	686 ± 66

SW: Surface Water; WW: Wastewater
Experiments used 200 mg carbon (F400 or AqC) and conditions (a) in Table 1 except that the water pH was not adjusted.
Instrument detection limit for NDMA = 2 pico moles; ND = non-detectable; Mean ± standard deviation (*n* = 2)

5.3.3 Effect of Reaction Conditions

The AC-catalyzed nitrosamine formation was further evaluated for the impact of reaction conditions including secondary amine concentration and structure, solution pH, and presence of oxygen and nitrogen. PSC particles were used in most of this part of study for consistency. PSC was selected because it formed intermediate levels of NDMA among the ACs (Table 5.2) and was abundantly available in our lab. AqC particles were also used to evaluate the effect of oxygen and nitrogen.

5.3.3.1 Role of Amine

The effect of amine concentration was evaluated using the same nitrosamine SPE protocol described above by spiking DMA from 1 to 444 μM to solutions buffered at pH 7.5. Two hundred mg of PSC particles were added for extraction of NDMA. As shown in Figure 5.1A, the amount of NDMA formed was linearly ($R^2 = 0.97$) correlated with DMA concentration in the solution. Control experiment without DMA addition showed non-detectable amount of NDMA formation.

Similar experiments were also conducted on four other secondary amines, MEA, DEA, DPA, and DBA, using 222 μM initial amine concentration and 200 mg PSC particles at pH 7.5. The secondary amines formed corresponding *N*-nitrosamines, i.e., MEA to NMEA, DEA to NDEA, DPA to NDPA, and DBA to NDBA (Figure 5.1B). Each amine formed only its corresponding *N*-nitrosamine and no nitrosamines formed in the absence of AC. A linear relationship between NDBA formation and DBA concentration in the solution was also observed (Figure 5.2). In general, the amount of nitrosamine formed was higher for higher molecular weight secondary amines (Figure

5.1B), possibly due to their increased hydrophobicity and, hence, increased adsorption efficiency on AC particles. Experiments showed that the amount of amine adsorbed to the PSC particles, determined based on the difference between the initial and final (after shaking) amine concentrations, was 1.4%, 2.7%, 3.2%, 6.8%, and 67.6% for DMA, MEA, DEA, DPA and DBA, respectively. The yield of nitrosamine formation was calculated based on the amount of nitrosamine formed divided by the amount of adsorbed amine (both in nanomoles) on PSC particles. At pH 7.5, the nitrosamine yield was around 0.10% for the above five secondary amines for the PSC particles. Similarly, the nitrosamine formation yield was calculated to be around 0.05%, 0.07%, 0.19%, and 0.29% for F400, HD4000, OLC and AqC, respectively, based on the amount of NDMA formed divided by the amount of DMA adsorbed at pH 7.5.

These results confirm that secondary amines are precursors of nitrosamines in the AC-catalyzed nitrosamine formation, and the concentration and structure of amine strongly influence the reaction. However, the similar patterns of the AC-catalyzed nitrosamine formation from different amines suggest that the involved reaction mechanisms are likely similar.

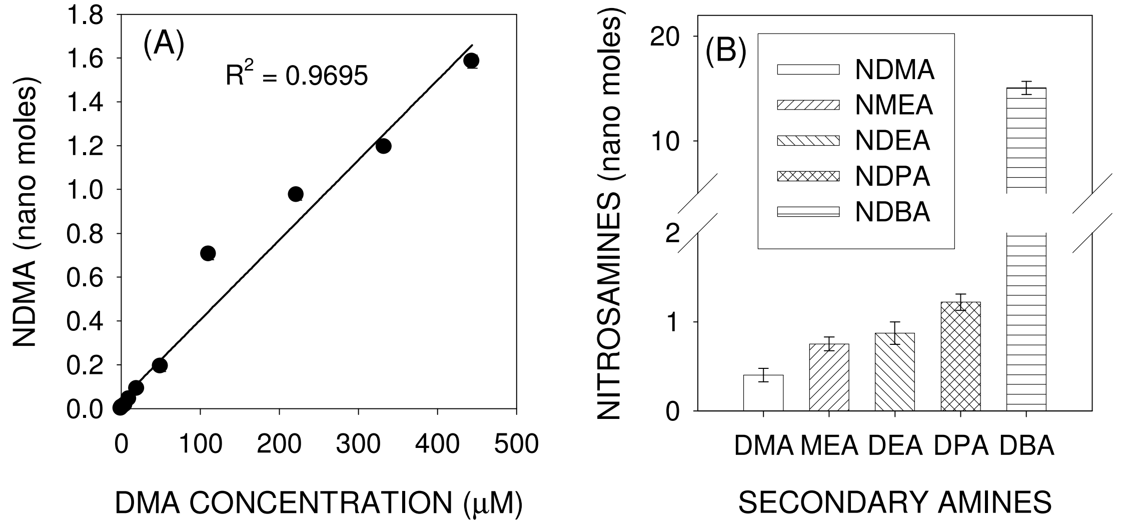


Figure 5.1 Nitrosamine formation from secondary amine in the presence of AC particles: (A) NDMA formation as a function of DMA concentration, (B) Formation of corresponding nitrosamines from five secondary amines. Experiments used 200 mg PSC particles and conditions (a) in Table 5.2 except that the DMA concentration varied and the carbon drying time was 6 h in (A). (Nitrosamine concentration was not corrected by isotope surrogate recovery; Error bars represent one standard deviation of the means; n =3)

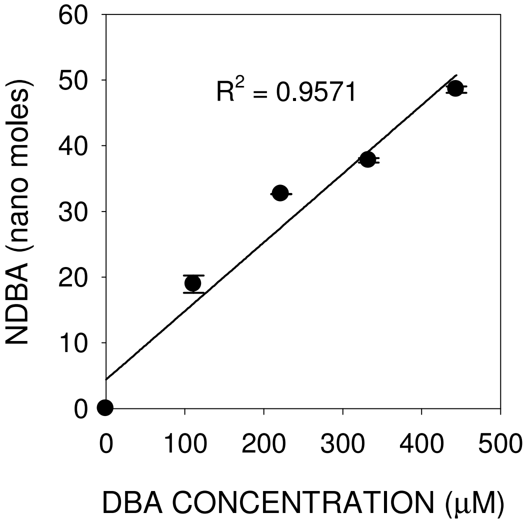


Figure 5.2 NDBA formation as a function of DBA concentration in the presence of AC particles. Experiments were conducted at pH 7.5 using 222 μM DBA, 200 mg PSC particles and 3 h carbon drying time. (NDBA concentration was not corrected by isotope surrogate recovery; Error bars represent one standard deviation of the means; n =3)

5.3.3.2 Effect of pH

The effect of pH was studied at pH 6.0, 7.0, 7.5, 8.0 and 9.0 (buffered by 10 mM phosphate buffer and NaOH) using 222 μM secondary amine and 200 mg of PSC particles. NDMA formation increased non-linearly with increase in pH and was particularly higher at pH 9 (Figure 5.3A). Similar pH trend was observed for NDBA formation from DBA in the presence of AC (Figure 5.4A). The increased nitrosamine formation at higher pH is likely related to greater adsorption of secondary amines to the AC surfaces as at higher pH more of the amines are in the unprotonated forms (pKa ~ 10-11 for aliphatic secondary amines (Hall, 1957)) and, hence, are more susceptible to adsorption by PSC with zero-point-of-charge (pH_{ZPC}) of 9.7 (Table 5.5). Indeed, the amount of DMA or DBA adsorbed increased with increase in pH (Figures 5.3B and 5.4B). However, amine adsorption alone could not fully explain the amount of nitrosamine formed at different pH as the formation yield (amount of nitrosamine formed/amount of amine adsorbed) was doubled from pH 6.0 (0.1%) to pH 9.0 (0.2%). Other mechanisms also play a role and require further study to fully understand the pH effect. Also, the observed pH trend contradicts with the acidic conditions favored by nitrosation involving nitrite with or without the presence of AC (Mirvish, 1975; Dietrich *et al.*, 1986), further supporting that a different mechanism than nitrosation is responsible for the observed catalyzed nitrosamine formation.

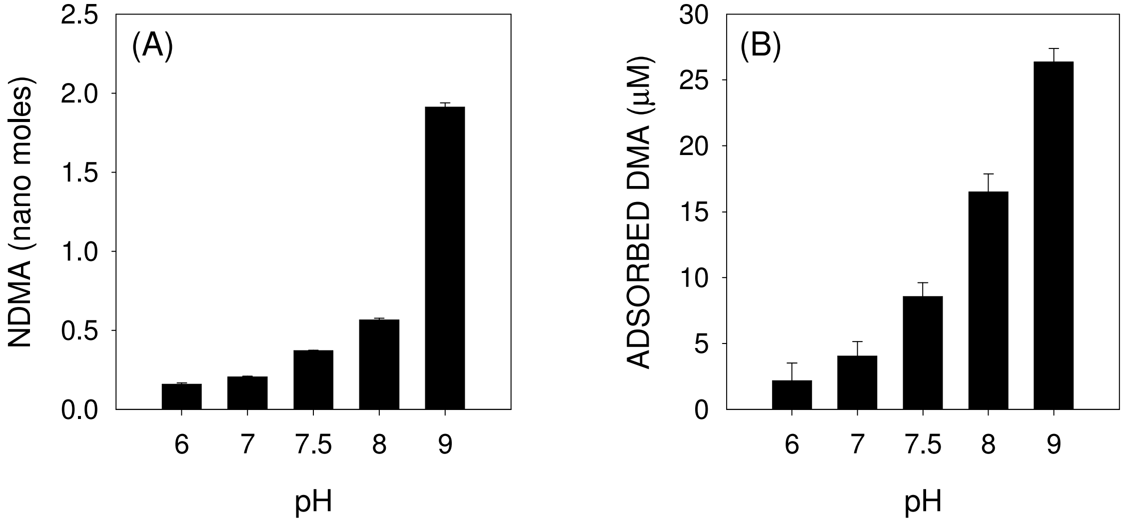


Figure 5.3 Effect of solution pH on: (A) NDMA formation from DMA in the presence of AC particles, (B) Adsorption of DMA to AC particles. Experiments used 200 mg PSC particles and conditions (a) in Table 5.2. (NDMA concentration was not corrected by NDMA-d_6 recovery; Error bars represent one standard deviation of the means; n =3)

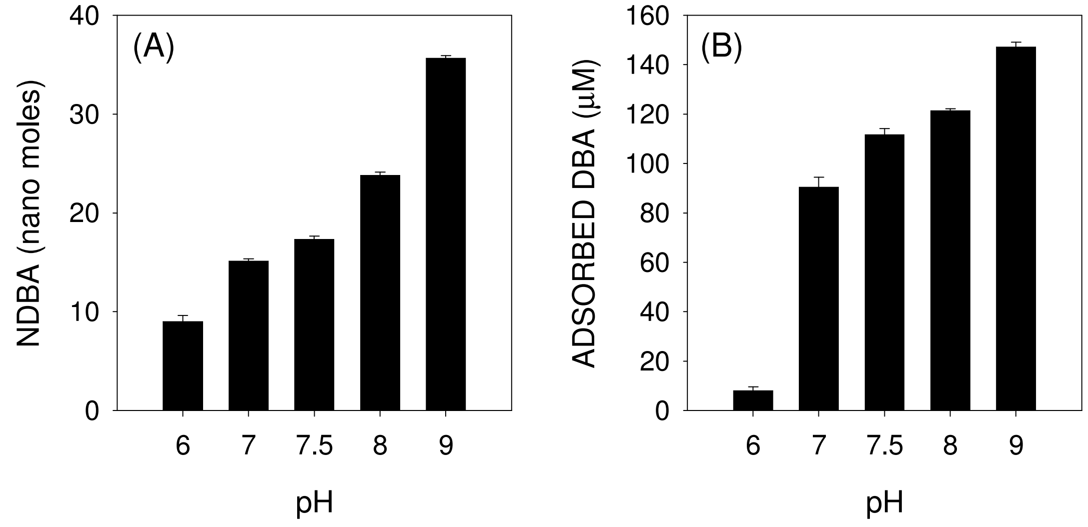


Figure 5.4 Effect of solution pH on: (A) NDBA formation from DBA in the presence of AC particles, (B) Adsorption of DBA to AC particles. Experiments used 222 μM DBA, 200 mg PSC particles and 3 h carbon drying time. (NDBA concentration was not corrected by isotope surrogate recovery; Error bars represent one standard deviation of the means; n =3)

5.3.3.3 Effect of Oxygen

As mentioned earlier, more nitrosamine was formed during the drying step of AC particles than in aqueous suspension. As the drying time increased, nitrosamine formation also increased (Figure 5.5A); the correlation was linear ($r^2 > 0.99$) until up to 12 hours and deviated from linearity at longer drying duration. Further, it was observed that significantly less amount of nitrosamine formed when drying of AC particles was conducted under pure nitrogen gas instead of air. Thus, oxygen gas was suspected to play an active role in transformation of secondary amines to nitrosamines. Hence, subsequent experiments were conducted to test the effect of oxygen flow on nitrosamine formation in a controlled environment during drying of AC particles. DMA was spiked at 222 μM in a pH 7.5 buffered solution and 200 mg PSC particles were added for SPE. After 2 hours of shaking, particles were filtered and then transferred to 125 mL glass reactors. Reactors were immediately sealed with rubber stoppers and aluminum crimps upon transferring of the AC particles. An inlet and outlet were supplied in the reactor for oxygen circulation. Pure oxygen was employed for drying of AC particles at three different flow rates of 50, 100 and 200 mL/min for the duration of 3 hours after which NDMA formed was quantified. When oxygen velocity was increased, nitrosamine formation was also increased, with a preliminary linear relationship ($R^2 > 0.99$) between oxygen velocity and NDMA formation (Figure 5.5B). The impact of particle drying time and oxygen gas flow rate on the AC-catalyzed NDBA formation from DBA showed very similar trends as those for NDMA formation (Figure 5.6). Based on these results, oxygen exposure is determined to be a critical factor for the AC-catalyzed nitrosamine formation from secondary amines.

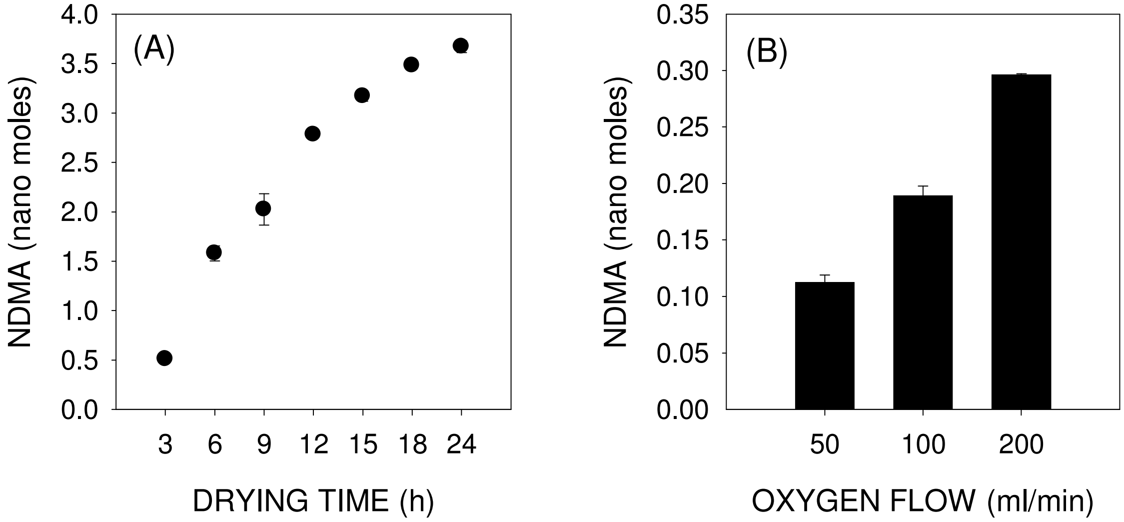


Figure 5.5 Effect of oxygen during drying of AC particles: (A) NDMA formation as a function of drying time, (B) NDMA formation as a function of oxygen flow. Experiments used 200 mg PSC particles and conditions (a) in Table 1. (NDMA concentration was not corrected by NDMA-d_6 recovery; Error bars represent one standard deviation of the means; n =3)

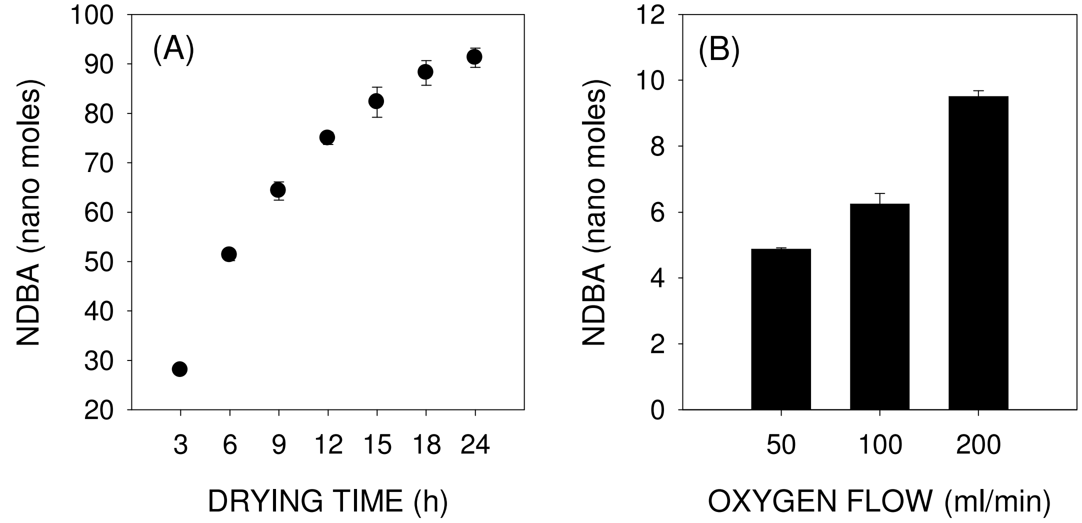


Figure 5.6 Effect of oxygen during drying of AC particles: (A) NDBA formation as a function of drying time, (B) NDBA formation as a function of oxygen flow. Experiments were conducted at pH 7.5, using 222 µM DBA, 200 mg PSC particles, and 3 h carbon drying time for (B). (NDBA concentration was not corrected by isotope surrogate recovery; Error bars represent one standard deviation of the means; n =3)

5.3.3.4 Effect of Nitrogen

As mentioned previously, it was observed that significantly less amount of nitrosamine formed when drying of AC particles was conducted under pure nitrogen gas instead of air. Also, from experiments in the previous section, the importance of oxygen was identified to be critical for the AC-catalyzed nitrosamine formation. However, NDMA formation in the case of drying the PSC particles under pure oxygen (Figure 5.5) was only 20-30% of the NDMA formation when the particles were dried in air (Table 1). There can be two possible reasons to explain this result; either insufficient amount of oxygen was provided during the experiment of drying particles in pure oxygen or exclusion of nitrogen gas limited NDMA formation.

Hence, to evaluate the above two potential reasons, experimental protocol was modified to completely eliminate the presence of external nitrogen source altogether and to ensure sufficient oxygen flow rate. To achieve this objective, DMA was spiked at 222 μM in nanopure water, previously purged with pure oxygen at the rate of 5 L/min for 15 minutes to remove dissolved nitrogen, and 200 mg AqC particles were added for SPE. The total volume of solution was 125 ml with no head space. After 2 hours of shaking, particles were filtered and then transferred to 500-mL gas-washing cylinder with an inlet and outlet for oxygen circulation. The particles were dried in pure oxygen gas at a flow rate of 12 L/min for the duration of 1.5 hours after which NDMA formed was quantified. Control experiment was also carried out in a similar way except that the aqueous solution was not purged with oxygen and drying of particles was conducted in the presence of air. This experiment differs from the previous experiment (Figure 5.5) in two major ways. First, the presence of dissolved nitrogen in the aqueous solution was completely eliminated for the current study which was not the case previously. Secondly, the oxygen flow rate was increased by nearly two orders of magnitude to ensure that oxygen was not a limiting factor responsible for low yield of NDMA observed previously.

Results of this experiment show that NDMA formation decreased by an order of magnitude for particles dried under pure oxygen and in the absence of dissolved nitrogen. Only 0.19 ± 0.01 nano moles of NDMA was formed compared to the control in which 1.79 ± 0.15 nano moles of NDMA formation was observed. These findings highlight the importance of external nitrogen source in the formation of NDMA. To further probe the source of the second nitrogen in the formation of NDMA, ^{15}N isotope-labeled DMA (^{15}N-DMA) was utilized in NDMA formation experiment as described next.

5.3.4 Study with Isotope-Labeled DMA

Experiments were conducted by spiking ^{15}N-DMA at 222 μM in 100 mL nanopure water and 200 mg AqC particles were added for SPE. After 1.5 hours of shaking, particles were filtered and then air dried for 3.5 hours. Afterwards, the NDMA formed was quantified. Control experiments were carried out simultaneously with unlabeled DMA. The solution pH of control and isotope experiments was at 9.2. Results showed that 6.47 ± 0.43 nano moles of ^{15}N-NDMA (m/z = 75) was formed in the experiments with ^{15}N-DMA, while no regular NDMA (m/z = 74) or ^{15}N,^{15}N-NDMA (m/z = 76) were detected. The amount of ^{15}N-NDMA formed was similar to the amount (6.85 ± 0.71 nano moles) of regular NDMA formed in the experiments with unlabeled DMA. The above results indicate that DMA is responsible for yielding only one nitrogen in

NDMA formation, and the source of second nitrogen of the nitroso group of NDMA is either atmospheric, dissolved, or through carbon.

5.3.5 Role of Radicals in NDMA Formation

The above experimental evidence that oxygen and nitrogen from the atmosphere are involved in the formation of NDMA from DMA on AC surfaces suggests radical reactions may be involved. The ability of activated carbon surfaces to react with oxygen is well documented in the literature. Previous studies have suggested that interaction between oxygen and AC surface reactive sites can generate reactive oxygen species (ROS) such as superoxide radical anion (which can lead to other secondary ROS including hydroxyl radical and hydrogen peroxide) and even superoxo anion via charge transfer from carbon to the adsorbed oxygen (Zawadzki and Biniak, 1988; Vorob'ev-Desyatovskii *et al.*, 2006; Pichugina *et al.*, 2008). The ability of activated carbons to interact with nitrogen was discussed by a few studies (Vorob'ev-Desyatovskii *et al.*, 2006; Pichugina *et al.*, 2008). In those studies, the authors observed fixation of atmospheric nitrogen onto carbon surfaces when the carbons were in contact with water that was saturated with air at room temperature. The reaction between oxygen and carbon surfaces in generating ROS was suggested to be critical in the redox reaction of nitrogen fixation.

Therefore, experiments were conducted to evaluate the importance of ROS in NDMA formation using radical scavengers. Experiments were conducted using similar protocol described above that spiked 222 μM DMA into 100 mL nanopure water and added 200 mg AqC particles for SPE. Superoxide dismutase (SOD) at 3,000 units/L and *tert*-butanol (TBA) at 10 mM were added as scavengers of superoxide radical and hydroxyl radical, respectively, in separate reactors. Control experiments without addition of radical scavengers were also carried out simultaneously. The pH of controls as well as radical scavenger solutions was 9.2.

In experiments with SOD, NDMA was quantified after 1.5 hours of shaking and 3 hours of drying of particles. There was no significant difference observed in the amount of NDMA formed for reactors containing SOD (1.79 ± 0.15 nano moles) and for controls without SOD (1.43 ± 0.18 nano moles). The results show that superoxide radicals do not play an important role as far as formation of NDMA is concerned from DMA in the presence of carbon particles.

In the experiments with TBA, after 1.5 hours of shaking, one set of samples were analyzed for NDMA formation in the suspension state with no drying of particles. The amount of nitrosamine formed while in the suspension state was determined following the procedures described in Section 5.3.1. The second set of samples was filtered and the particles were air-dried for 2 hours and NDMA formation was measured at the end of drying. For both sets, samples amended with TBA showed lower NDMA formation than controls. In suspension state, 0.07 ± 0.01 μM of NDMA was formed in the controls while only 0.04 ± 0.00 μM of NDMA formed in the TBA-spiked samples. The overall (suspension plus drying phases) NDMA formation was 1.62 ± 0.01 μM in the control, but was only 0.62 ± 0.06 μM in the TBA-spiked samples.

Furthermore, in another study, effect of pretreatment of AC particles with TBA on NDMA formation was examined. Two hundred mg of AqC particles were suspended in aqueous solution of 135 mM of TBA and were shaken at 250 rpm for 2 hours. After shaking was completed, particles were filtered and air dried for one hour. When these pretreated particles were used for SPE in the similar experimental setup, NDMA formation was reduced by more than 50% compared to untreated AqC particles. These results indicate that hydroxyl radicals play a role in the formation of NDMA from DMA in the presence of carbon particles.

5.3.6 Role of Surface Functional Groups of AC

The above results together established that AC can induce transformation of secondary amines in the presence of air to generate *N*-nitrosamines, and the reaction occurs on the AC surfaces as adsorption of secondary amines to AC surfaces is a critical factor. Owing to different properties of ACs, nitrosamine formation varied with different AC materials (Table 5.2). However, no specific correlation was found between nitrosamine formation and the specific surface area of ACs. On the other hand, carbons with lower pH_{ZPC} appeared to be weaker at catalyzing nitrosamine formation than carbons with higher pH_{ZPC}, suggesting the composition of carbon's surface functional groups may be important.

To further evaluate AC's capability to catalyze transformation of secondary amines to form nitrosamine, some of the AC particles were subjected to different pretreatments to modify carbon's surface composition. As shown in Table 5.5, pre-treating PSC particles with H_2SO_4 or ozone significantly lowered AC's capability to catalyze nitrosamine formation, while baking the carbon particles at 600 ˚C prior to usage resulted in carbons that were stronger at catalyzing nitrosamine formation. Pre-treatment of F400, OLC, and HD4000 particles under hydrogen atmosphere at high temperature resulted in greater nitrosamine formation for all three carbons, while pretreatment of carbons with nitric acid lowered nitrosamine formation for F400 and OLC. It was also found that the carbon-catalyzed nitrosamine formation was greater when thiosulfate was present in the sample, a reductant frequently added to drinking water or wastewater samples to quench residual disinfection oxidants.

Treating AC particles with H_2SO_4 or ozone oxidizes surface functional groups resulting in more carboxylic groups, while baking carbon particles at higher temperature liberates oxygen from surface functional groups and makes carbon surface more basic (Boehm, 2002). Heat treatment under hydrogen flow removes considerable portion of oxygen surface functionalities, reduces surface functional groups and decreases the surface acidity of carbons, while treatment with nitric acid oxidizes carbon's surfaces and increase the surface acidity (Dastgheib *et al.*, 2004; Bansal and Goyal, 2005; Karanfil *et al.*, 2007). These modifications are evident from the pH_{zpc} values measured for the modified carbons (Table 5.5). In contrast, the carbon modifications did not result in significant change in carbon's specific surface area (Table 5.5). Notably, acid treatment of carbons actually resulted in greater adsorption of DMA to the carbon surfaces, while the carbon-catalyzed nitrosamine formation was significantly lowered for OLC and did not increase for F400 and HD4000. Although not characterized in this study, acid treatment also reduces inorganic impurities on carbon surfaces. Thus, these results suggest that the composition of surface oxygen functional groups and maybe also inorganic impurities on AC surfaces play a role in the carbon-catalyzed nitrosamine formation reactions.

Table 5.5 Effect of pretreatment of AC particles on NDMA formation from DMA in the presence of AC particles

Carbon Particles	**Specific Surface Area S_{BET} (m^2/g)**	**pH$_{zpc}$**	**Test Conditions**	**Adsorbed DMA (micro-moles)**	**NDMA (nano moles)**	**NDMA (ng/L)**	**NDMA (ng/L) by NDMA-d$_6$ Isotope Dilution**
PSC_untreated	1114	9.7	a	0.55 ± 0.02	0.57 ± 0.07	422 ± 52	4971 ± 618
PSC_untreated (w/ $Na_2S_2O_3$)	1114	9.7	c	NA	0.86 ± 0.02	636 ± 15	5815 ± 145
PSC_H_2SO_4 treated	1134	2.5	a	0.77 ± 0.01	ND	ND	ND
PSC_HCl treated	NA	NA	a	NA	0.51 ± 0.12	377 ± 89	4450 ± 1051
PSC_O_3 treated	1088	6.9	a	0.59 ± 0.00	0.26 ± 0.02	192 ± 15	2285 ± 183
PSC_baked at 600 ˚C	NA	NA	a	0.64 ± 0.05	1.16 ± 0.10	858 ± 74	10109 ± 873
F400_untreated	1044	9.2	b	1.93 ± 0.11	1.01 ± 0.04	747 ± 30	6224 ± 815
F400_H_2 treated	1075	10.2	b	1.59 ± 0.18	1.30 ± 0.17	962 ± 126	10701 ± 1410
F400_HNO_3 treated	980	3.7	b	1.69 ± 0.19	0.66 ± 0.02	488 ± 15	5461 ± 179
OLC_untreated	983	9.3	b	0.45 ± 0.03	0.84 ± 0.04	622 ± 30	6011 ± 248
OLC_H_2 treated	1080	10.2	b	0.69 ± 0.07	1.22 ± 0.11	903 ± 81	9073 ± 822
OLC_HNO_3 treated	1030	3.5	b	2.79 ± 0.04	0.28 ± 0.01	207 ± 7	2103 ± 81
HD400_untreated	706	6.6	b	0.90 ± 0.06	0.63 ± 0.03	466 ± 22	4783 ± 92
HD4000_H_2 treated	838	9.9	b	1.10 ± 0.07	1.80 ± 0.19	1332 ± 140	13338 ± 1409
HD4000_HNO_3 treated	714	3.2	b	2.64 ± 0.03	0.65 ± 0.04	481 ± 30	4823 ± 306

(a) 222 µM DMA, 200 mg carbon, 3 h carbon drying time; (b) 222 µM DMA, 200 mg carbon, 12 h carbon drying time; (c) similar to (a) conditions but also with 222 µM $Na_2S_2O_3$. Reaction suspensions were buffered at pH 7.5 by 10 mM phosphate and shaken for 2 h prior to filtration. pH$_{zpc}$:Zero Point of Charge Instrument detection limit for NDMA = 2 pico moles and for DMA = 0.01 pico moles; ND = non-detectable; NA = not available; Mean ± standard deviation ($n = 3$)

Based on the above results, the composition of surface oxygen functional groups of several carbon samples were characterized using titration method and to evaluate possible correlations with NDMA formation potential. Four AC particles were chosen for this part of study: untreated PSC, ozonated PSC representing oxidized surfaces, PSC particles baked at 600 ˚C representing reduced surfaces, and AqC particles. NDMA formation potential for these particles was evaluated by spiking DMA at 222 μM in a pH 7.5 buffered solution and 200 mg AC particles were added for SPE. Shaking time of 1.5 hours was adopted, and particles were then filtered and air-dried for 3 hours. The acidic surface oxygen functional group content was evaluated by adopting Boehm's titration method as described by Tessmer *et al.* (1997). Two grams of the above mentioned four AC particles were equilibrated in seventy mL each of 0.05 N NaOH, $NaHCO_3$ and Na_2CO_3 and 0.25 N NaOH solutions for 3 days. At the end of the 3 days, filtrate was titrated against 0.25 N H_2SO_4 to determine carbonyl, carboxyl, lactone, and phenolic hydroxyl group content for each of the four different AC particles. Results of the functional group characterization are shown in Figure 5.7.

It was found that there was a significant correlation between the amount of NDMA formed and the carbonyl group content on the surfaces of these four carbon samples (Figure 5.8). For carbons with higher carbonyl group content on their surfaces, their NDMA formation potential was also higher. No significant correlations could be established between NDMA formation and the other functional group types. When NDMA formation was normalized by the amount of amine adsorbed on the carbons, there was still a strong correlation to the carbonyl content of the carbons (Figure 5.9), indicating that carbonyl group's contribution is not to increase amine adsorption. Instead, carbon’s surface carbonyl groups may play an active role in the transformation of DMA to NDMA. Further studies will be needed to identify the specific role of surface carbonyl groups in the range of redox reactions involved in the AC-catalyzed nitrosamine formation.

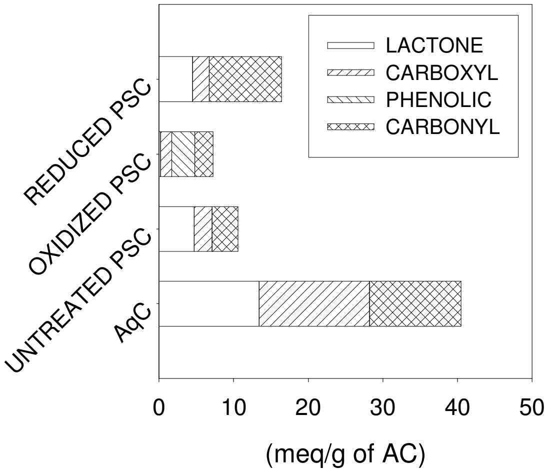


Figure 5.7 Functional group characterizations of four carbons

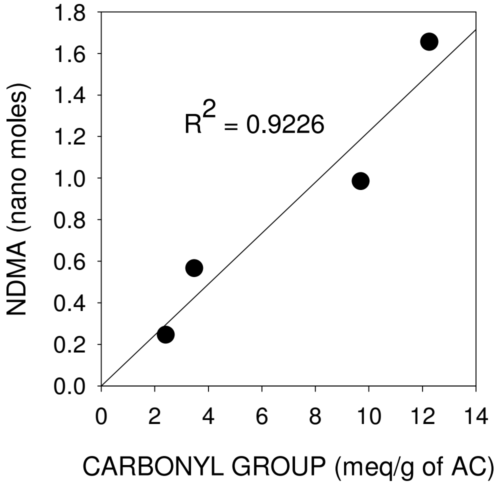


Figure 5.8 Relationship between the amounts of NDMA formation and the carbonyl group content on the surfaces of four different activated carbons samples (shown in Figure 5.7). NDMA formation experiments were conducted at pH 7.5, using 222 µM DMA, 200 mg carbon particles, and 3 h carbon drying time. (NDMA concentration was not corrected by isotope surrogate recovery)

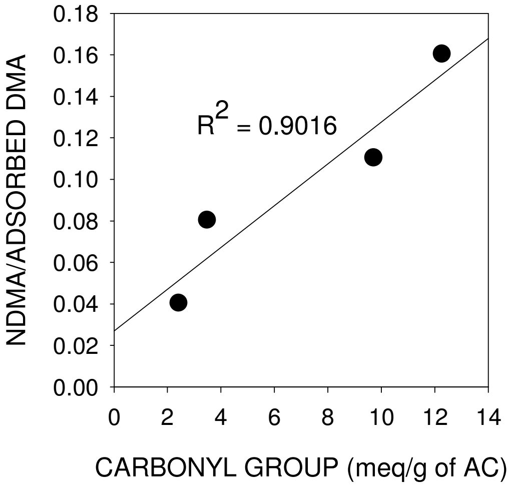


Figure 5.9 Relationship between the amounts of NDMA formation normalized by adsorbed DMA and the carbonyl group content on the surfaces of four different activated carbons samples (shown in Figure 5.7). NDMA formation experiments were conducted at pH 7.5, using 222 μM DMA, 200 mg carbon particles, and 3 h carbon drying time. (NDMA concentration was not corrected by isotope surrogate recovery)

5.3.7 Possible Reaction Mechanisms

While literature is scarce regarding carbon-catalyzed transformation of amines under ambient aerobic conditions, our experimental results show some similarity with AC-based catalytic wet air oxidation (CWAO) of amines. In the work by Aguilar *et al.* (2005) that utilized ACs as catalysts in the CWAO (at 195 °C and 16 atm) of methylamine and DMA, the authors found that the quinone surface groups (releasing CO by temperature programmed decomposition (TPD)) on ACs were responsible for the catalytic activity, while carboxylic, lactone and anhydride groups (releasing CO_2 in TPD), were responsible for a catalytic activity inhibition, despite that the latter groups exhibited stronger adsorption of the amines. Methylamine and DMA were oxidized to nitrogen, water, CO_2 and traces of nitrite and nitrate under the employed CWAO conditions. In another study by Gomes *et al.* (2008), AC-based CWAO of aniline generated a range of byproducts including nitrosobenzene and azobenzene. The authors proposed that the oxidizing species are oxygen either in the bulk or adsorbed and hydroxyl radicals readily formed under CWAO's high temperature and pressure conditions, and the catalytic removal of aniline was related to the presence of quinone-type surface functional groups.

Furthermore, it has been well documented in the literature that some activated carbon surfaces can catalyze oxidation of adsorbed phenolic compounds under environmental oxic conditions, leading to the so-called "irreversible adsorption" of phenols on AC surfaces (Vidic *et al.*, 1993; Terzyk, 2003; Dabrowski *et al.*, 2005). The oxidation of phenols results in dimers and higher polymeric products (Grant and King, 1990). Dissolved oxygen is involved in the above reaction. It has been proposed that radical species formed from interactions of oxygen with carbon surfaces oxidize the phenols (Vidic *et al.*, 1993; Terzyk, 2003). The presence of acidic surface functional group inhibits the ability of AC to adsorb phenolic compounds under oxic conditions by reducing its effectiveness in promoting adsorption via oxidative coupling reactions, while the presence of basic surface functional groups promote irreversible adsorption (Tessmer *et al.*, 1997).

Based on our results and comparison to the above studies, it can be hypothesized that AC surfaces can catalyze oxidation of adsorbed amines in the presence of oxygen and nitrogen to yield nitrosamines. Previous studies (Vorob'ev-Desyatovskii *et al.*, 2006; Pichugina *et al.*, 2008) have observed formation of oxygen- and nitrogen-containing fragments on the surface of carbon when carbon was in contact with air in water at room temperature. The authors proposed that the reactions of carbon surface defects with water dissolved oxygen could generate ROS, including hydroxyl radicals. The ROS generated or carbene centers created by reactions of ROS on carbon surfaces were responsible for nitrogen fixation by reacting with water-dissolved N_2 molecules to form nitrogen species like N_2O or diazo intermediates. Indeed, the direct gas-phase reaction of N_2 with an excited hydroxyl radical has been shown to give rise to N_2O (Estupinan *et al.*, 2001). From the thermodynamic viewpoint, two-electron reductants are able to convert N_2O into ammonia via an H_2N_2O intermediate (Shestakov and Shilov, 2001). Further reduction of the latter can provide hydroxylamine (NH_2OH) molecules and other NH-containing species or radicals.

In another set of experiments carried out in our laboratory, hydroxylamine was found to substantially enhance NDMA formation from DMA in the presence of AC particles, but not in the absence of AC particles. Thus, it may be possible that hydroxylamine is an important intermediate product formed during nitrogen fixation reactions on the surface of AC and contributes to transformation of DMA to NDMA through reactions catalyzed by AC surfaces. Our results that NDMA formation was lowered in the presence of TBA is consistent with the above mechanistic hypothesis since TBA quenches hydroxyl radical and hence, may prevent formation of N_2O, and thus hydroxylamine and NDMA. The observed pH trend can also be explained based on longer life time of ROS and reactive nitrogen species (RNS) at higher pH, and thus increased formation of NH_2OH. For carbon surface that is more reduced, formation of ROS is more favorable, so is the formation of N_2O and conversion of N_2O to NH_2OH, and thus more NDMA can be formed. Based on the discussion to this point, the presence of oxygen and nitrogen have been confirmed to be critical for the AC-catalyzed nitrosamine formation from secondary amine and may contribute to one N and O atom in the NDMA molecule, although the latter was not directly proven by experiments. Overall, more research is still needed to better understand the mechanisms of how carbon surface characteristics influence the radical reactions and the catalyzed amine transformation and nitrosamine formation.

5.3.8 Analytical and Environmental Significance

Overall, the findings in this study are highly relevant for both nitrosamine analysis and water treatment operations. The NDMA yield observed with a variety of ACs at pH 7.5 ranged from 0.001% to 0.01% based on the molar ratio of NDMA concentration to the initial aqueous DMA concentration. Thus, for water that contains 0.1

μM of DMA (4.5 μg/L), AC-based SPE may generate about 0.07-0.74 ng/L of NDMA. If the NDMA concentration is corrected by NDMA-d_6 recovery as would normally be conducted in nitrosamine analysis by isotope dilution, up to 3-4 ng/L of NDMA can be reported assuming 20% extraction efficiency. Thus, the AC's catalytic effect alone could contribute to the trace levels of nitrosamines detected. It's important to note that the above estimation is only an example and will be influenced by the type of AC, the amount of DMA in the water and water matrix. The results show that this analytical artifact is important for natural water samples, particularly in wastewater, where higher amounts of amine precursors, nitrite and other unknown constituents are present. This analytical error is also greater for higher molecular weight nitrosamines, and can become significant in laboratory studies that often employ elevated amine concentrations. Not evaluated in this study, SPE cartridges with packed AC particles are also currently being used for nitrosamine extraction. In those cases, nitrosamine formation may be lower due to less exposure of carbons to air but will depend on the adopted SPE protocol. Our evaluation on the impact of carbon surface characteristics offers useful information in selecting carbon pre-treatment methods to minimize this analytical error.

While relevant, the implications on water treatment operations are probably less than those in analytical methods considering that most surface water contains only low concentrations of amines, the typical contact time during AC processes (in PAC or GAC mode) are rather short, and the formation of nitrosamines was significantly higher during drying phase than in the solution. However, it is possible for amines to accumulate on AC surfaces (used in water treatment processes or in household water filtration device) over time and gradually transform to yield nitrosamines due to the catalytic effect of AC in the presence of oxygen. Furthermore, AC-based processes are commonly coupled with pre-oxidation by ozone or other oxidants. Such pre-oxidation processes may generate intermediates such as nitrite that can contribute to nitrosamine formation via catalyzed nitrosation by AC surfaces. More research is needed to further understand the practical implications of findings obtained in this study.

CHAPTER 6

CONCLUSIONS

Since current technique of UV treatment for removal of *N*-nitrosamines from water is expensive and not feasible for large scale treatment utilities, more attention is needed in preventing nitrosamine formation rather than relying on alternate treatment options. To curb the formation of nitrosamine carcinogens in water, it is necessary to attain understanding of their precursors as well as reaction mechanisms responsible for formation of nitrosamines in drinking water and wastewater. In this thesis, research was focused on probing the role of several commonly encountered chemicals and materials in water and wastewater treatment plants with respect to their nitrosamine formation potential under prevalent treatment practices. By altering reaction conditions, adding external chemicals, varying concentrations of reactants, and subjecting reactions to analyses for identification of products and intermediates, significant progress was made in understanding and detailing mechanisms responsible for nitrosamine formation. With the enhanced knowledge about precursors and factors influencing nitrosamine formation, recommendations were made to water utilities on how to reduce the risk of nitrosamine formation.

6.1 Formation of NDMA from Ozonation of PolyDADMACs: Reaction Kinetics and Mechanism

When water treatment polymers of polyamine, polyDADMAC and cationic polyacrylamide (PAM) were screened with respect to their NDMA formation risks upon ozonation, polyDADMAC exhibited the highest potential to form NDMA. PolyDADMAC also showed significant release of DMA, a direct precursor of NDMA, upon ozonation, indicating that it is particularly more vulnerable to oxidation by ozone than the other two polymers tested. Even though concentrations of polyDADMAC and ozone employed in this study were comparable to the optimum levels of these compounds employed in treatment plants for coagulation and disinfection, respectively, direct contact of ozone with polyDADMAC at the studied concentrations is not expected at treatment plants. Since coagulation and flocculation is typically followed by sedimentation and filtration processes, only trace levels of polyDADMAC are expected to still persist in water after the above mentioned treatment processes and before disinfection. However, NDMA formation results from this study are significant for utilities employing high concentration of polyDADMACs or where pre-oxidation by ozone is employed before coagulation. In addition, for wastewater treatment plants, where an order of magnitude higher dosage of polyDADMAC for sludge thickening operations is not uncommon, practicing tertiary treatment of ozone disinfection can form significant amounts of NDMA as evident from results of this study. In brief, avoiding direct contact of ozone with polyDADMAC will reduce the risk of NDMA formation at treatment plants.

From results related to mechanistic investigation of NDMA formation in this study, it is evident that the amount of NDMA observed at the end of ozonation can be correlated to the amount of DMA released from polyDADMAC. The pendent quaternary ammonium ring in polyDADMAC is particularly vulnerable to attacks by hydroxyl radicals, product of ozone decay in aqueous solutions, leading to quaternary ammonium ring group opening, DMA release, as well as aldehyde and amide formation. Presence of electron-donating alkyl groups nearby the methylene groups in quaternary ammonium ring of polyDADMAC renders it an easier target for hydrogen abstraction by hydroxyl radicals. Even though nitrite and formaldehyde were detected as ozonation products of DMA and polyDADMAC, contribution of formaldehyde-enhanced nitrosation pathway was found to be insignificant in NDMA formation. Augmenting hydroxylamine, one of products from ozonation of DMA, significantly enhanced NDMA formation and was shown to contribute one nitrogen atom towards NDMA, while DMA being the source of the other nitrogen. However, the presence of ozone was critical for the reaction of hydroxylamine with DMA and for oxidation of its reaction intermediates to yield NDMA, since no significant NDMA formation was observed in the absence of ozone.

Based on the knowledge of NDMA formation mechanism gained from this study, several recommendations can be made to water utilites to reduce NDMA formation risks. Since hydroxyl radicals are more abundant at higher pH, keeping treatment conditions more acidic will not only help reduce DMA release from polyDADMAC, but also minimize conversion of released DMA to NDMA. Also, addition of external radical scavengers during ozonation may prove to be an effective strategy that will not only enhance disinfection process due to inhibition of ozone decay through radicals, but can also help reduce risk of NDMA formation. Treatment plants employing advanced oxidation processes (AOPs), such as Fenton's Reagent, can also be at increased risk of NDMA formation due to generation of hydroxyl radicals. To minimize NDMA formation risk at these treatment processes, it is advisable to treat influent with respect to NDMA precursors of polyDADMAC and DMA before subjecting it to oxidation.

Even though conditions used in this study were similar to water treatment plants, in terms of reactant concentrations, pH, temperature, reaction time etc., it employed batch reactor set-up with nano-pure water matrix. Presence of other constituents in real water matrices may impact NDMA formation since the presence of NOM and other radical scavengers may reduce exposure of radicals to polyDADMAC and hence, reducing its NDMA formation potential. Therefore, further study is warranted to evaluate behavior of polyDADMAC in treatment plants in regard to its NDMA formation potential. One such approach is to study the fate of polyDADMAC and DMA release along different water treatment processes at water treatment plants by tracing polymer and DMA residues. These concentrations can then be used in either bench or pilot-scale tests employing real water matrices to assess the formation risks of NDMA. In addition, similar pilot-scale tests are also recommended to simulate reaction conditions for treatment plants equipped with ozone pre-oxidation. While this study also examined NDMA formation mechanism from ozonation of DMA, further delineation of formation of nitrosating agents, the exact role of hydroxyl radicals in nitrosation pathway, and identification of other reaction intermediates is recommended.

6.2 Oxidation of Dithiocarbamates to Yield *N*-Nitrosamines by Water Disinfection Oxidants

Two most commonly used dithiocarbamate pesticides, dimethyldithiocarbamate (DMDTC) and diethyldithiocarbamate (DEDTC), were examined in this thesis to evaluate their potential to form nitrosamines in aqueous media. DMDTC and DEDTC undergo hydrolysis in water to produce DMA and DEA, respectively. Hence, without addition of any external oxidant, dithiocarbamates yield direct precursors of nitrosamines in the form of secondary amines. As pH decreases, hydrolysis rate constants for dithiocarbamates increase by an order of magnitude for every unit drop in the pH and vice versa within the pH range of 2-9. Hence, water treatment plants that operate at lower pH will experience much more significant formation of secondary amines from dithiocarbamates if these compounds are present in the water sources.

When DMDTC and DEDTC were evaluated for their nitrosamine formation potential in reactions with monochloramine, free chlorine, chlorine dioxide and ozone, the reactions of dithiocarbamates with monochloramine and ozone were found to be particularly problematic in the risk of generating nitrosamines, though all four oxidants tested formed nitrosamines. Results from this study show that dithiocarbamates can serve as nitrosamine precursors, by release of secondary amines through hydrolysis or through reactions with oxidants particularly ozone, free chlorine and chlorine dioxide. Even though concentrations of dithiocarbamates tested in this study were on the higher end of the spectrum of literature-reported dithiocarbamate concentrations in surface waters and wastewaters, the observed nitrosamine formation was significantly higher than their current advisory guidelines. So even at lower concentrations of dithiocarbamates, their nitrosamine formation risk cannot be neglected.

Evidently for both monochloramination and ozonation of dithiocarbamates, trend observed for *N*-nitrosamine formation was similar to trend observed for monochloramination and ozonation of secondary amines, respectively, indicating that nitrosamine formation may be attributed to secondary amines produced during reactions. The observed NDMA yield during monochloramination of DMDTC could be mostly attributed to DMA produced through hydrolysis of DMDTC and the reaction of DMA with monochlorine. Thus, dithiocarbamates are not direct precursors of nitrosamines during reaction with monochloramine, but rather nitrosamines were from reaction of monochloramine with the amine hydrolytic product of dithiocarbamates. The above information can be useful to treatment plant operators, since monochloramination does not seem to transform dithiocarbamates into nitrosamines or direct precursors of nitrosamines. Hence, for treatment plants practicing monochloramination, maintaining higher pH can potentially reduce the risk of nitrosamine formation from dithiocarbamates because of slower hydrolysis rates of dithiocarbamates and consequently reduced tendency to form secondary amines at higher pH.

For ozonation, results from reaction product analysis indicate that secondary amines may be a product of ozonation of dithiocarbamates since hydrolysis rate is too slow to account for the observed amount of secondary amines at the end of 30 minutes of ozonation. The presence of significant amounts of nitrite and other reaction products similar to ozonation of secondary amines suggest that nitrosamine formation may be the result of ozonation of secondary amines produced through oxidation of dithiocarbamates. Thus, dithiocarbamates serve as direct precursors of nitrosamines during ozonation, in which ozone decomposes dithiocarbamates to release secondary amines that can further react with ozone to form nitrosamines. Hence, for treatment plants practicing ozonation, maintaining lower pH can potentially reduce the risk of nitrosamine formation from dithiocarbamates because dithiocarbamates can hydrolyze rapidly at lower pH and resulting secondary amines have lower yields to form nitrosamines during ozonation at lower pH.

Even though dithiocarbamates have been detected at ppb levels in surface water runoff from agricultural fields as well as in wastewater effluent, the fate of these compounds during different treatment processes at water treatment plants is unclear due to scarcity of data from the literature. Hence, the fate of these compounds in water treatment plants still needs to be evaluated. Dithiocarbamates have strong tendency to complex with metal ions and metal complexation can facilitate stability in terms of hydrolysis which can make dithiocarbamates persist in the environment even at circumneutral pH. The potential impact of metal complexation on the reactivity of dithiocarbamates toward reactions with disinfection oxidants has not been evaluated. More research is needed to understand nitrosamine formation potential of dithiocarbamates when in the form of metal complexes. Also, bench-scale and pilot-scale tests are recommended to simulate real water conditions and matrices with respect to dithiocarbamate concentrations, obtained from the proposed studies above, oxidant dosage and contact time to understand the risk of nitrosamine formation at treatment plants from these compounds.

6.3 Transformation of Secondary Amines to *N*-Nitrosamines on Activated Carbons

AC is the most common solid phase extraction material used for analysis of nitrosamines in water. It is also widely used for the removal of organics in water and wastewater treatment and as a catalyst or catalyst support in some industrial applications. It was discovered in this study that AC materials can catalyze transformation of secondary amines to form trace levels of *N*-nitrosamines under ambient aerobic conditions. This is a novel discovery that has significant implications in a broad range because of the widespread environmental applications of AC materials. It was also observed that this reaction is strongly influenced by carbon properties, amine properties and reaction conditions such as pH, exposure to atmospheric oxygen and nitrogen, and presence of radical scavengers.

Based on the results of this study and comparison to studies from literature, it is hypothesized that AC surfaces catalyze oxidation of adsorbed amines in the presence of oxygen and nitrogen to yield nitrosamines. The reactions of carbon surface defects with water dissolved oxygen could generate ROS, including hydroxyl radicals, which can fix dissolved nitrogen to form nitrogen species. These nitrogen species can undergo redox reactions on the surface of carbon to generate intermediate nitrogen species like hydroxylamine which in turn can react with DMA to form NDMA.

Overall, the findings in this study are highly relevant for both nitrosamine analysis and water treatment operations. The results show that the analytical artifact created by use of AC in SPE of nitrosamines is important for natural water samples, particularly in wastewater, where higher amounts of amine precursors, nitrite and other unknown constituents are present. This analytical error is also greater for higher molecular weight nitrosamines, and can become significant in laboratory studies that often employ elevated amine concentrations. Based on results from this study, it is recommended to not use AC materials for SPE of nitrosamines when presence of secondary amines is suspected in water matrix. This is particularly significant for water utilities which employ ACs for trace level analysis of nitrosamines for surface waters which may contain residual amount of secondary amines with other unknown constituents. The analytical artifact can be minimized by carefully choosing AC materials with more acidic surface (i.e., lower pH_{zpc}) for SPE of nitrosamines.

While relevant, the implications on water treatment operations are probably less than those in analytical methods considering that most surface water contains only low concentrations of amines and the typical contact time during AC processes (in PAC or GAC mode) are rather short. However, it is possible for amines to accumulate on AC surfaces (used in water treatment processes or in household water filtration device) over time and gradually transform to yield nitrosamines due to the catalytic effect of AC in the presence of oxygen. Furthermore, AC-based processes are commonly coupled with pre-oxidation by ozone or other oxidants. Such pre-oxidation processes may generate reaction intermediates such as nitrite that can contribute to nitrosamine formation via catalyzed nitrosation by AC surfaces. However, more research is needed to further understand the practical implications of findings obtained in this study.

Also, future research is needed to understand the mechanism of nitrogen fixation on the surface of carbon, role of ROS, and influence of carbon surface properties on transformation of secondary amines to nitrosamines. Another potential research avenue is to study the impact of water treatment processes employing AC on nitrosamine formation in treatment plants. For this part of study, tracing secondary amine concentrations through AC-based treatment processes will be useful in estimating potential nitrosamine concentrations in water. In addition, bench or pilot scale study can be set up to study the impact of pre-oxidation processes combined with AC-based processes in order to estimate nitrosamine formation risks.

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