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Ozonation in Water Reuse: Formation and Mitigation of N-~nitrosodimethylamine

Erica J. Marti
University of Nevada, Las Vegas, echemie@gmail.com

OZONATION IN WATER REUSE: FORMATION AND MITIGATION OF *N*-NITROSODIMETHYLAMINE

By

Erica Jean Marti

Bachelor of Science – Chemistry
University of Illinois at Urbana-Champaign
2004

Master of Education – Curriculum and Instruction
University of Nevada, Las Vegas
2007

Master of Science in Engineering – Civil and Environmental Engineering
University of Nevada, Las Vegas
2012

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of the requirements for the

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The Graduate College

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Erica Jean Marti

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Jacimaria R. Batista, Ph.D.
Examination Committee Chair

Kathryn Hausbeck Korgan, Ph.D.
Graduate College Interim Dean

Eric Dickenson, Ph.D.
Examination Committee Member

Daniel Gerrity, Ph.D.
Examination Committee Member

David E. James, Ph.D.
Examination Committee Member

Mary Kay Orgill, Ph.D.
Graduate College Faculty Representative

ABSTRACT

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by

Erica Jean Marti

Dr. Jacimaria Ramos Batista, Examination Committee Chair
Professor, Department of Civil and Environmental Engineering and Construction
University of Nevada, Las Vegas

Formation of *N*-nitrosodimethylamine (NDMA) is a substantial concern for drinking water and water reuse. NDMA, a probable human carcinogen, is formed when water is disinfected with chloramines and ozone. This research focused on three issues regarding NDMA formation and mitigation. The first issue involved understanding the compounds (i.e., precursors) present in water and wastewater that react with ozone to form NDMA. Model precursors were identified and molar yields for NDMA formation were determined. The model precursors form high amounts of NDMA with ozone, but form very little NDMA with chloramines, which means there are two distinct groups of NDMA precursors: ozone-reactive and chloramine-reactive. An investigation into factors that affect NDMA formation resulted in understanding that bromide enhances NDMA formation for some precursors and elimination of hydroxyl radicals, which are produced during ozonation, leads to higher NDMA formation. Comparison of three oxidants, molecular ozone, hydroxyl radicals and dissolved oxygen, revealed that molecular ozone is the agent responsible for NDMA formation.

The second issue addressed the strategic use of disinfection oxidants, alone and in combination, to minimize disinfection byproduct (DBP) formation. This study compared the

formation and reduction of NDMA and two groups of regulated drinking water DBPs (trihalomethanes (THMs) and haloacetic acids (HAAs)) in treated wastewaters using seven disinfection treatment schemes. The top two treatment schemes resulting in the lowest total DBP formation, after converting concentrations to an equivalent unit based on drinking water risk, were ozonation and ozonation-chloramination. Both treatment schemes also exhibit several advantages for application in water reuse situations. It was demonstrated that pre-chlorination can reduce NDMA formation by inactivating ozone-reactive NDMA precursors, but DBP trade-offs must always be addressed because chlorination causes THM and HAA formation.

The third issue investigated non-optimized biofiltration to mitigate NDMA formation by removing NDMA precursors prior to disinfection with ozone or chloramines. NDMA precursor removal (ranitidine (RAN), daminozide (DMZD), 2-furaldehyde dimethylhydrazone (2-F-DMH) and 1,1,1',1'-tetramethyl-4,4'-(methylene-di-p-phenylene)disemicarbazide (TMDS)) and DBP formation potential (NDMA, THMs, HAAs) in treated wastewater were assessed before and after biofiltration using three anthracite-containing columns with different contact times. Precursor removal varied (RAN: 6-7%; DMZD: 73-85%; 2-F-DMH: 15-27%; TMDS: 11-24%) and was correlated to dissolved oxygen concentration or correlated to contact time for some precursors. The investigated wastewater was phosphorus-limited and had low dissolved oxygen. NDMA, THM, and HAA precursor removal may be increased through optimization of the biofilter media and the nutrients available for bacteria growth.

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2-F-DMH	2,2-Furaldehyde dimethylhydrazone
AC	Activated carbon
Acetone-DMH	Acetone dimethylhydrazone
AE	Aerobic
AN	Anaerobic
ANOVA	Analysis of variance
AOP	Advanced oxidation process
AS	Activated sludge
ATP	Adenosine triphosphate
AX	Anoxic
BAC	Biological activated carbon
BOD	Biochemical oxygen demand
BNR	Biological Nutrient Removal
BPR	Biological phosphorus removal
Br-	Bromide
CAS	Conventional activated sludge
CCL3	3rd Contaminant Candidate List
C_{eff}	Effluent concentration
CEPA	California Environmental Protection Agency
C_{inf}	Influent concentration
Cl_2	Chlorine
CLM	Chloramine
CLM-FP	Chloramine formation potential test for NDMA

CLM-UFC	Chloramine uniform formation conditions test for NDMA
Cl:N	Chlorine to nitrogen ratio
C:N:P	Carbon to nitrogen to phosphorus ratio
COD	Chemical oxygen demand
Ct	Exposure calculated as concentration integrated over time
CV	Coefficient of variation
d6-NDMA	Deuterated *N*-Nitrosodimethylamine
Da	Dalton
DBP	Disinfection byproduct
DMA	Dimethylamine
DMC-dithio	*N'*-{[(dimethylamino)carbonyl]oxy}-4-(1,3-dithiolan-2-yl)benzenecarboximidamide
DMC-phenyl	*N*-{[(dimethylamino)carbonyl]oxy}-2-phenylacetamide
DMDTC	Dimethyldithiocarbamate
DMPD	*N*,*N*-Dimethyl-p-phenylenediamine
DMS	Dimethylsulfamide
DMSC	*N*-1-(3-{[(2,2-dimethylhydrazino)carbonyl] amino}-4-methylphenyl)-2,2-dimethylhydrazine-1-carboxamide
DMST	Dimethyl-*N'*-(4-methylphenyl)-sulfamide
DMTC-phenyl	*N*-1-(4-methylphenyl)-2,2-dimethylhydrazine-1-carbothioamide
DMZD	Daminozide
DO	Dissolved oxygen
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
DPD	*N*,*N*-diethyl-p-phenylenediamine
EBCT	Empty bed contact time

EfOM	Effluent organic matter
ESI –	Negative-ion electrospray ionization
ESI+	Positive-ion electrospray ionization
FP	Formation potential
GAC	Granular activated carbon
GC	Gas chromatography
GC-MS	Gas chromatography mass spectrometry
Gy	Gray
H_2O_2	Hydrogen peroxide
HAAs	Haloacetic acids
HAA-FP	Haloacetic acid formation potential test
HCl	Hydrochloric acid
HDPE	High density polyethylene
HDMS	4,4'-hexamethylenebis(1,1-dimethylsemicarbazide)
K_d	Sorption coefficient
KH_2PO_4	Potassium dihydrogen phosphate
KI	Potassium iodide
K_{oc}	Soil sorption coefficient
K_{ow}	Partition coefficient
LC	Liquid chromatography
LC-MS/MS	Liquid chromatography tandem mass spectrometry
LLE	Liquid-liquid extraction
M	Molarity
MA	Methylamine
MBR	Membrane bioreactor

MF	Microfiltration
MGD	Million gallons per day
MRL	Method reporting limit
MS	Mass spectrometry
N	Normality
N_2O	Nitrous oxide
N_2O_4	Dinitrogen tetroxide
Na_2HPO_4	Sodium hydrogen phosphate
NDEA	*N*-Nitrosodiethylamine
NDMA	*N*-Nitrosodimethylamine
NDMA-FP	(Chloramine) formation potential test for NDMA
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
NOM	Natural organic matter
NPOC	Non-purgeable organic carbon
•OH	Hydroxyl radical
O_2	Oxygen
O_3	Ozone
O_3-FP	Ozone formation potential test for NDMA
O_3/H_2O_2	Advanced oxidation process with ozone and hydrogen peroxide
O_3:H_2O_2	Ozone to hydrogen peroxide ratio
O_3:TOC	Ozone to total organic carbon ratio
OEHHA	Office of Environmental Health Hazard Assessment
pCBA	Parachlorobenzoic acid

pKa	Acid dissociation constant using the logarithmic scale
polyDADMAC	Poly(diallyldimethylammoniumchloride)
POU	Point-of-use
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
R^2	Coefficient of determination
RLU	Relative light unit
RNTD	Ranitidine
RO	Reverse osmosis
SPE	Solid phase extraction
SRT	Solids Retention Time
SS	Suspended solids
tBA	Tert-butyl alcohol
THAAs	Total haloacetic acids
THM-FP	Trihalomethane formation potential test
THMs	Trihalomethanes
TMCH	1,1,5,5-tetramethylcarbohydrazide
TMDS	1,1,1',1'-tetramethyl-4,4'-(methylene-di-p-phenylene)disemicarbazide
TN	Total nitrogen
TTHMs	Total trihalomethanes
TOC	Total organic carbon
TOrC	Trace organic contaminant
UCMR2	2nd Unregulated Contaminant Monitoring Rule
UDMH	Unsymmetrical dimethylhydrazine or 1,1-dimethylhydrazine

UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
UV/H_2O_2	Advanced oxidation process with UV irradiation and hydrogen peroxide
UV/O_3	Advanced oxidation process with UV irradiation and ozone
WHO	World health organization
wt%	Weight percent
WW	Wastewater
WWTP	Wastewater treatment plant

CHAPTER 1

INTRODUCTION

As potable water demands rise and water shortages occur, more communities are considering reuse of wastewater as an option for increasing their overall water supply. Ozone is effective for treating pathogens and trace organic contaminants and, therefore, is a promising treatment technology for potable water reuse applications (Gerrity and Snyder 2011). However, the formation of ozone byproducts, such as *N*-Nitrosodimethylamine or NDMA (Figure 1.1), is an issue that could limit the use of ozone for potable water reuse.

Figure 1.1: Structure of NDMA.

NDMA has received substantial attention as a contaminant of concern in water and wastewater. It is classified as a B2 probable human carcinogen by the United States Environmental Protection Agency (USEPA) (USEPA 2014c). NDMA is on the Third US EPA Contaminant Candidate List (USEPA 2014a) and it was part of the second Unregulated Contaminant Monitoring Rule (UCMR2) (USEPA 2013), which are steps leading to contaminant regulation in drinking water. The E-6 (1 in 1,000,000) cancer risk level for NDMA in drinking water is 0.7 ng/L (USEPA 2016). The State Water Resources Control Board in California has set a drinking water notification level of 10 ng/L (CEPA 2014), while Health Canada has a maximum acceptable concentration of 40 ng/L (Health Canada 2011) and the World Health

Organization has a guideline of 100 ng/L for drinking water (WHO 2008). In comparison, the levels of disinfection byproducts currently regulated by the USEPA are 80 ppb for total trihalomethanes (THMs) and 60 ppb for total haloacetic acids (HAAs). At 10 ng/L or 10 ppt, NDMA might be regulated at a 1000-fold lower level due to its high toxicity.

There are two main routes by which NDMA ends up in water and wastewater: direct anthropogenic sources of NDMA and formation due to disinfection. The latter is a greater concern because disinfection is a standard process used in water treatment and formation of this carcinogen is a widespread issue in the U.S. with NDMA detected above 2 ng/L at 25% of the 1,162 utilities that participated in the UCMR2 study (Woods and Dickenson 2015). Direct sources of NDMA may be found in wastewater due to rubber and circuit board manufacturing or rocket fuel production (ATSDR 1989; Mitch et al. 2003b); however, this is a localized issue related to particular industries. NDMA formation due to disinfection is widespread and affects both drinking water and wastewater. NDMA is formed by disinfection with ozone and chloramines, either by addition of chloramines directly or by chlorination of wastewater with ammonia present (Nawrocki and Andrzejewski 2011). While the majority of the research has focused on NDMA formation with chloramines, this dissertation investigates NDMA formation due to ozonation.

The motivation for this work is to fill research gaps about the formation of NDMA due to ozonation of wastewater and to examine mitigation strategies to reduce NDMA formation with ozone. Research gaps include limited knowledge of ozone-reactive NDMA precursors, a lack of understanding of the mechanisms for NDMA formation with ozone, and techniques to prevent NDMA formation with ozone. Understanding the precursors and the reactions that lead to NDMA formation may help with water reuse source control (i.e., selecting wastewaters which do

not contain the precursors), pretreatment for precursor removal, and optimizing ozonation processes to avoid NDMA formation. Once NDMA is formed, the technologies for removal, such as reverse osmosis or ultraviolet irradiation, are costly and energy intensive (Plumlee et al. 2014). Preventing NDMA formation with mitigation strategies, like pre-chlorination and biofiltration, could save time and money. Pre-chlorination may be a simple and effective method to minimize NDMA formation during ozonation. Research has already shown that free chlorine contact substantially reduces NDMA formation caused by chloramination (Charrois and Hrudey 2007), but similar evidence for NDMA formation with ozone is lacking. On the other hand, since chlorination may also result in disinfection byproducts (DBPs), it is necessary to evaluate the trade-offs in DBP formation between these two disinfection methods. Additionally, biofiltration of wastewater prior to disinfection may reduce NDMA by eliminating NDMA precursors before ozonation and without an increase in regulated DBPs. Ultimately, this research will provide a strong foundation for understanding NDMA formation by ozonation, which is essential for furthering ozone as an effective water reuse treatment technology.

This research addresses three important issues related to NDMA formation in water reuse applications:

1.1 Issue One: Determining Ozone-reactive NDMA Precursors

While NDMA formation due to ozonation of wastewater, groundwater, and surface water has been established (Gerrity et al. 2015; Hollender et al. 2009; Kosaka et al. 2014; Schmidt and Brauch 2008; Sgroi et al. 2014; von Gunten et al. 2010), only a handful of ozone-reactive precursors have been identified in source waters (Table 1.1). These compounds include hydrazines, semicarbazides, sulfamides, and dimethylamines. In particular, compounds with dimethylamine bonded directly to a nitrogen atom or compounds with dimethylamine separated

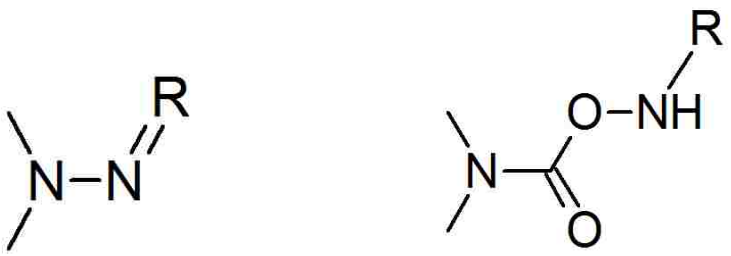
from a second nitrogen by a good leaving group (e.g., SO_2) form NDMA with significant molar conversion yields (i.e., 10-80%) (Kosaka et al. 2009; Schmidt and Brauch 2008). The chemical structures can be symbolized as $(CH_3)_2N$-N-R for the dimethylamine bonded to a nitrogen atom or $(CH_3)_2N$-L-N-R for the dimethylamine with a good leaving group between the nitrogens.

Other classes of compounds may also exhibit high NDMA formation upon ozonation. **It is hypothesized that hydrazones and carbamates with two methyl groups are ozone-reactive precursors (Figure 1.2). These compounds fit the $(CH_3)_2N$-N-R and $(CH_3)_2N$-L-N-R arrangements, respectively. Hydrazones may have a similar mechanism to hydrazines for NDMA formation, but the double bond may be more reactive.** As described in more detail in Chapter Two of this dissertation, the nitrogen atoms in dimethylsulfamide (Table 1.1) are separated by sulfur dioxide (SO_2), which leaves as a gas during the ozonation reaction. Similarly, the nitrogen atoms in carbamates are separated by carbon dioxide (CO_2). The carbamate compounds may undergo decarboxylation and lose CO_2 in order to form a nitrogen-nitrogen bond for NDMA.

It is important to distinguish between chloramine-reactive and ozone-reactive NDMA precursors. Chloramine-reactive NDMA precursors react strongly with chloramines to form NDMA and have a general structure of $(CH_3)_2N$-R, where R is a carbon atom in, for example, an alkane chain, cyclic ring or benzene ring. These compounds have very low molar yields for NDMA formation with ozone, usually less than 0.01% (Oya et al. 2008; Padhye et al. 2013). On the other hand, ozone-reactive NDMA precursors, such as those shown in Table 1.1, react strongly with ozone to form NDMA. Likewise, these compounds have much lower molar yields for NDMA formation with chloramines as compared to ozone. Because these compounds react

differently with ozone and chloramines, it is beneficial to treat them as distinct groups of NDMA precursors. More details are provided in Chapter Two.

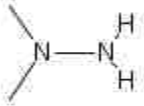
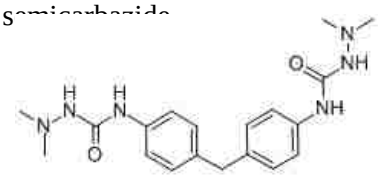
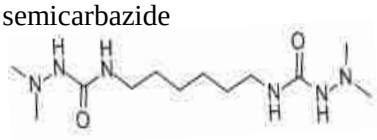
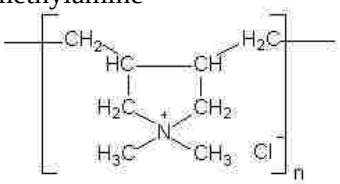
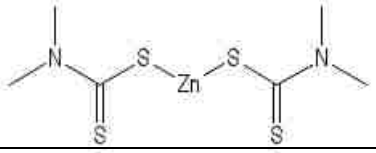
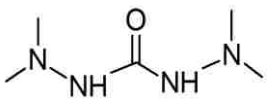
A goal in this research is to identify model compounds that are ozone-reactive NDMA precursors. These compounds will represent various chemical classes that include different structural moieties to determine the influence of chemical structure on NDMA formation. Furthermore, experimental work to address Issue One will investigate other parameters that affect NDMA formation, such as ozone dose, oxidant type (i.e., molecular ozone, hydroxyl radical and dissolved oxygen), and matrix components (e.g., presence of bromide, wastewater effluent organic matter, and natural organic matter). The information gained from these experiments will fill research gaps on the limited knowledge of ozone-reactive NDMA precursors and factors affecting NDMA formation.



hydrazone carbamate

Figure 1.2: General structures of dimethylhydrazone and dimethylcarbamate compounds that could be NDMA precursors.

Table 1.1: Structures and molar yield formations of ozone-reactive NDMA precursors that have been identified in wastewater, ground water or surface water.

Compound Name [Molar Yield]	**Structure**	**Description**	**Reference**
Dimethylsulfamide (DMS) [52%]	sulfamide 	Decomposition product of fungicide tolylfluanid	Schmidt and Brauch 2008
Daminozide [55%]	hydrazi 	Plant growth regulator	Schmidt and Brauch 2008
1,1-dimethylhydrazine (UDMH) [80%]	hydrazine 	Rocket fuel, decomposition product of daminozide	Schmidt and Brauch 2008
1,1,1′,1′-tetramethyl-4,4′-(methylene-di-p-phenylene) disemicarbazide (TMDS) [27%]	s 	Yellow inhibitor and light stabilizer for polyamide resins	Kosaka et al. 2009
4,4'-hexamethylenebis(1,1-dimethylsemicarbazide) (HDMS) [10%]	semicarbazide 	Yellow inhibitor and light stabilizer for polyamide resins	Kosaka et al. 2009
polyDADMAC [Not available]	dimethylamine 	Coagulant	Padhye et al. 2011
Zinc dimethyldithiocarbamate (DMDTC) or Ziram [0.008%]	dimethylamine 	Root-control fungicide, metal precipitation	Padhye et al. 2013
1,1,5,5-tetramethylcarbohydrazide (TMCH) [146%]	hydrazine 	Used to prevent deterioration of paper	Kosaka et al. 2014

1.2 Issue Two: Investigating Pre-chlorination as a Mitigation Strategy for NDMA Formation

Chloramine-reactive NDMA precursors can be deactivated with pre-oxidation by disinfectants such as chlorine, chlorine dioxide, and ozone (Charrois and Hrudey 2007; Shah et al. 2012). **A similar investigation for ozone-reactive NDMA precursors would be valuable, but has not been performed to date**. A bench-scale study for nitrosamine formation and mitigation investigated eleven different treatment trains, but pre-chlorination and ozonation was not reported (Zhao et al. 2008). Recently, Selbes et al. (2014), examined pre-oxidation of various chloramine-reactive and ozone-reactive NDMA precursors by chlorine, chlorine dioxide and ozone prior to chloramine disinfection (e.g., chlorine-chloramine, ozone-chloramine). **However, additional oxidant combinations (e.g., chlorine-ozone and chlorine-ozone-chloramine) were not studied and, to the author's knowledge, have not been investigated for ozone-reactive precursors.**

Chlorine is a strong, non-selective oxidant that reacts with a wide variety of organics. **It is hypothesized that chlorine will react with ozone-reactive NDMA precursors and that subsequent ozonation will result in reduced NDMA formation.** Table 1.2 lists the options that will be investigated to reveal the differences in NDMA formation due to single and combined oxidants. Certain combinations (e.g., ozone-chlorine, ozone-chlorine-chloramine, ozone-chloramine-chlorine) will not be examined because it is known that NDMA formation will be high if ozone-reactive precursors are not pre-treated.

Since chlorination results in the formation of regulated DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs), it is important to look at the overall DBPs formed by each treatment. Along with NDMA analysis, THMs and HAAs will be quantified for the parallel tests.

It is hypothesized that concentrations of THMs and HAAs will be increased with pre-chlorination of wastewater, while NDMA concentrations will be decreased due to reaction of the precursors with chlorine prior to ozonation.

It is expected that there will be increases and decreases in the DBPs formed by the different treatments. For example, chlorination may increase THMs while reducing NDMA formation. THMs, HAAs, and NDMA vary in toxicity. Therefore, the DBP concentrations will not be summed directly, but rather normalized to a common unit based on toxicity. This approach will allow for an examination of the trade-offs in DBP formation as a result of the different treatments.

Table 1.2: Single and combined oxidation treatments for investigating NDMA formation with ozone-reactive NDMA precursors.

Cl_2	Cl_2-O_3	Cl_2-O_3-CLM
O_3	O_3-CLM	
CLM	Cl_2-CLM	

Cl_2 = chlorination; CLM = chloramination; O_3 = ozonation

1.3 Issue Three: Investigating Anthracite Biofiltration for NDMA Precursor Removal

Biodegradation is effective for removing a variety of compounds (van Agteren et al. 1998). Full-scale biological activated carbon filters have been shown to reduce NDMA formation potential (NDMA-FP) by 80% (Farre et al. 2011a), where NDMA-FP is a test to establish the maximum level of NDMA formed by chloramines over ten days. The NDMA-FP test also provides a general sense of the amount of chloramine-reactive NDMA precursors present in the

water. Biodegradation of several chloramine-reactive precursors (dimethylamine, ranitidine, trimethylamine, dimethylformamide, N-dimethyldithiocarbamate, dimethylaminobenzene, doxylamine) in activated sludge systems has been studied (Jelic et al. 2011; Radjenovic et al. 2007; Wang and Li 2015), along with change in NDMA-FP during activated sludge treatment (Krauss et al. 2010). Other studies have also shown a decrease in NDMA in wastewater as a result of biological sand filtration (Hollender et al. 2009; Zimmermann et al. 2011). While several biofiltration studies have targeted chloramine-reactive NDMA precursors (Bond et al. 2012; Krasner et al. 2013), no studies have specifically focused on removal of ozone-reactive NDMA precursors by biofiltration.

Like pre-chlorination, biofiltration has the potential to remove NDMA precursors prior to ozonation or chloramination. This mitigation strategy would reduce NDMA formation in the first place, rather than destroy it after it has already been formed. There are limited studies on NDMA precursor removal by biofiltration where specific compounds are monitored, as compared to studies investigating bulk NDMA precursors with NDMA-FP. Dimethylamine (DMA) was well removed (> 90%) in a microcosm study utilizing a mixed culture from a drinking water biofilter (Liao et al. 2015). Pilot-scale biological activated carbon successfully removed several chloramine-reactive NDMA precursors (doxylamine, roxithromycin, tramadol and venlafaxine) by more than 98% (Farre et al. 2011b). A comparative study with ozone-reactive NDMA precursors has not been completed.

While biofiltration has been shown to remove some chloramine-reactive NDMA precursors, knowledge gaps remain, including: the process responsible for precursor removal (e.g., sorption to media, sorption to biofilm, biodegradation) and the extent of removal for specific NDMA precursors. This research task will focus on using biofiltration to remove both chloramine-

reactive (ranitidine, DMA) and ozone-reactive (daminozide, TMDS, 2-furaldehyde dimethylhydrazone) NDMA precursors. Based on previous studies involving biodegradation in wastewater and soil, **it is hypothesized that DMA and daminozide will be removed to a high extent by biofiltration** (Liao et al. 2015; Carlsen et al. 2008)**, while ranitidine will have moderate to low removal** (Vasiliadou et al. 2013)**.** There is no prior information on TMDS or 2-furaldehyde dimethylhydrazone (2-F-DMH). TMDS is a semicarbazide and an anti-yellowing agent. **It is hypothesized that this compound will be poorly removed by biofiltration since it persists after wastewater treatment and is found in wastewater-impacted surface waters in Japan** (Kosaka et al. 2009)**.** Although there is no information on 2-F-DMH degradation, 2-furaldehyde undergoes anaerobic biodegradation (Rivard and Grohmann 1991) and dimethylamine is biodegraded easily (Rappert and Müller 2005). **Therefore, since the components that form 2-F-DMH are biodegradable, it is hypothesized that 2-F-DMH will be removed by biofiltration.**

Several factors affect compound removal by biofiltration, including contact time, media type, and temperature. To gain a better understanding of the precursor removal, two parameters will be considered: biofilter empty bed contact time (i.e., average time the compounds remain in the biofilter) and sorption to filter media. Three empty bed contact times (EBCTs) will be examined to see if there is a substantial difference in removal of the precursors. Anthracite will be the media used in the biofilters. Unlike activated carbon, sorption of organics to this media is relatively low, which means biodegradation or sorption to the biofilm will be the key removal mechanisms. Other factors involved in optimizing biofiltration (e.g., dissolved oxygen concentration, temperature, nutrients) are not addressed in this research due to time constraints and the already established biofiltration column set-up.

Several analyses will be conducted to identify removal by biofiltration. Concentration change will be monitored before and after biofiltration for the specific precursors, NDMA formation potential (ozone and chloramine), and THM/HAA formation potential. Ultimately, results will show the extent of removal for the specific precursors, as well as the opportunity for combined precursor removal (i.e., NDMA, THMs/HAAs) during biofiltration.

1.4 Objectives

Overall, the research encompassed in this dissertation involves understanding the formation of NDMA due to ozonation and how to prevent the formation from occurring (i.e., mitigation strategies). The specific objectives of this research are to:

1. Identify compounds that form NDMA upon ozonation.
2. Determine the influence of ozone dose, oxidant type (molecular ozone, hydroxyl radical, dissolved oxygen), and matrix components on NDMA formation with ozone.
3. Evaluate pre-chlorination as a mitigation strategy to reduce NDMA formation with ozone.
4. Determine trade-offs in disinfection byproduct formation resulting from various combinations of disinfectants.
5. Evaluate the removal of NDMA precursors during non-optimized biofiltration at various empty bed contact times.

CHAPTER 2

STATE OF THE KNOWLEDGE

2.1 Disinfection Byproducts

Water and wastewater are disinfected in order to destroy or inactivate pathogens. When chemical oxidants are used for disinfection, they can react with organic and inorganic matter in the water. These unintentional reactions form disinfection byproducts (DBPs). The first DBPs were discovered in the 1970s as a result of chlorine disinfection or chlorination (Bellar et al. 1974). The two classes of organic DBPs regulated in U.S. drinking water are trihalomethanes (THMs) and haloacetic acids (HAAs), and they are formed through chlorination (USEPA 2014b). THMs and HAAs are carcinogenic and regulated in drinking water at total concentrations of 80 μg/L and 60 μg/L, respectively. Many water treatment plants switched to chloramines as an alternative disinfectant to reduce THM and HAA formation. However, other DBPs are formed with chloramines, including *N*-Nitrosodimethyalmine (NDMA) and other nitrogeneous DBPs. Another alternative disinfectant, ozone, forms bromate and NDMA as DBPs (Karanfil et al. 2008; Richardson 2003). Changing disinfectants has only led to the formation of different DBPs, rather than eliminating DBPs.

2.2 NDMA Occurrence

2.2.1 Drinking Water

The national Unregulated Contaminant Monitoring Rule (UCMR2) study provides comprehensive data about NDMA and other nitrosamines in U.S. drinking water. As shown by UCMR2 data, NDMA is more associated with chloramination than chlorination and was detected in 34% of treatment plants using chloramines (Russell et al. 2012). Overall, 25% of the treatment

plants in the UCMR2 study had detectable NDMA with an average of 9.0 ng/L and reaching a maximum of 630 ng/L. NDMA was detected at treatment plants in all but six states and with higher frequency for small and medium utilities. Surface water sources resulted in higher NDMA formation as compared to groundwater sources (Woods and Dickenson 2015). NDMA concentrations are often higher within the distribution system compared to effluent leaving the drinking water treatment plant because of longer chloramine exposure time (Boyd et al. 2011).

2.2.2 Wastewater

Chlorination of wastewater containing ammonia and chloramination of wastewater can form high NDMA concentrations. In one occurrence survey with 23 wastewaters, NDMA concentrations as high as 3,165 ng/L were found in chloraminated systems and the median concentration was 11 ng/L (Krasner et al. 2009a). Another study of 12 wastewaters found NDMA concentrations from <10 to 80 ng/L in influents and formation increase (relative to influent concentration) up to 298% after ozonation (Yoon et al. 2011). A recent study focusing on wastewater treatment plants (WWTPs) utilizing ozone found NDMA formation at seven out of eight WWTPs, with final concentrations ranging from 5.2 ng/L to 143 ng/L (Gerrity et al. 2015).

2.3 NDMA Formation

Many different reactions are responsible for nitrosamine formation during drinking water and wastewater treatment. Several formation mechanisms have been identified, but many others require more investigation. The three main formation pathways include chloramination, nitrosation and ozonation.

2.3.1 Formation Pathways

Chloramination

Previous research has focused on chloramination as the main disinfection process that forms NDMA. This process can be direct chloramination or chlorination of wastewater containing ammonia. Originally, the reaction was thought to be nucleophilic substitution between monochloramine and a secondary amine (Figure 2.1a). This reaction resulted in unsymmetrical dimethylhydrazine (UDMH), which was subsequently oxidized by chloramines to form NDMA (Choi and Valentine 2002; Mitch and Sedlak 2002). Subsequent research into the pathway provided evidence on reaction rates and intermediates, which caused the mechanism to be revised (Figure 2.1b). The modified pathway involves the reaction of dichloramine and a model secondary amine, dimethylamine (DMA), which forms chlorinated unsymmetrical dimethylhydrazine (Cl-UDMH) as an intermediate. Dissolved oxygen oxidizes Cl-UDMH to NDMA (Schreiber and Mitch 2006). Consequently, NDMA formation may be greater in aerated processes for water and wastewater treatment. The conversion yield of DMA to NDMA varies in the literature, but it is < 3% molar yield when controlling the order of ammonia and chlorine addition (Mitch et al. 2005). Although DMA appears to be an intermediate for precursors such as polyDADMAC (Padhye et al. 2011), the high molar yields for other tertiary amines (i.e., 90% for ranitidine) indicate there may be other mechanisms leading to NDMA formation that do not have a DMA intermediate.

Nitrosation

Nitrosation involves the reaction of nitrite and chlorine. At a low pH, hypochlorous acid and nitrite form one of two dinitrogen tetroxide (N_2O_4) tautomers (Figure 2.1c), which are isomers that interconvert into one another easily. One tautomer reacts with DMA to form NDMA, while

the other tautomer results in the nitrated-amine. The impact of the nitrosation reaction is minor due to the very low molar yield (< 0.0007%) and this formation pathway is more likely to occur in wastewater than in drinking water due to the availability of nitrite (Shah and Mitch 2012).

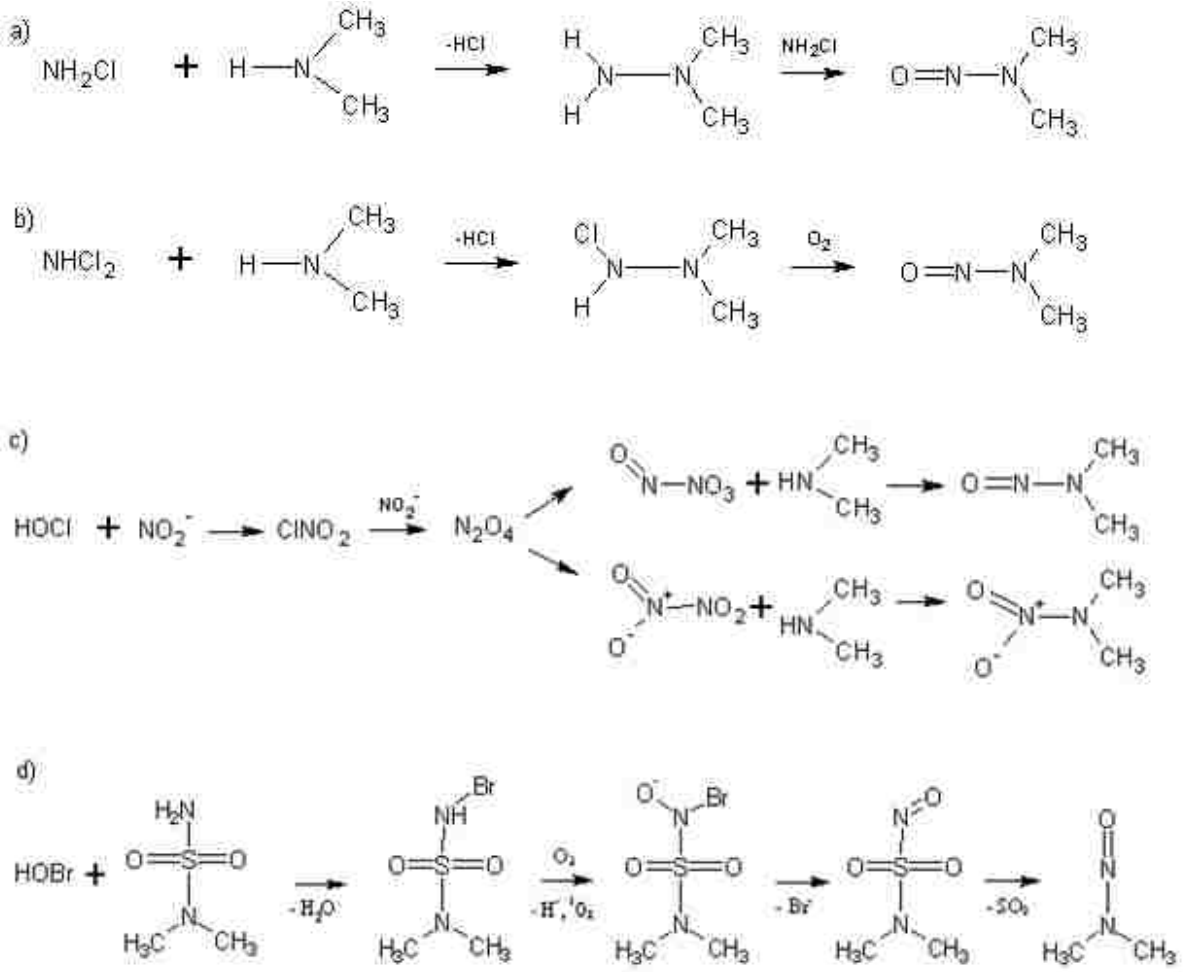


Figure 2.1: Proposed mechanisms for NDMA formation via a) chloramination of dimethylamine, b) revised chloramination of dimethylamine, c) nitrosation of dimethylamine, and d) ozonation of dimethylsulfamide (Shah and Mitch 2012).

Ozonation

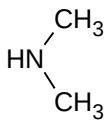
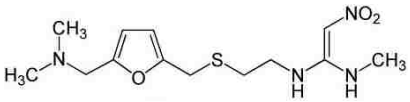
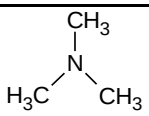
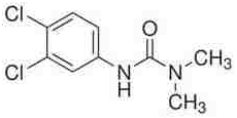
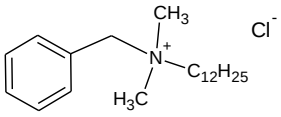
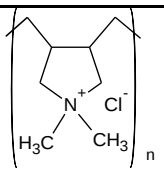
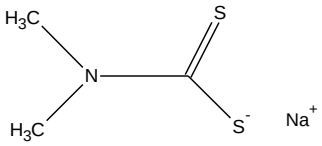
More recently, oxidation by ozone has been shown to directly form NDMA when precursors are present (Hollender et al. 2009; Kosaka et al. 2009; Kosaka et al. 2014; Marti et al. 2015; Oya et al. 2008; Schmidt and Brauch 2008; Zimmermann et al. 2011;). Very little is known about the formation pathway and any intermediates that are formed; however, it is unlikely that DMA is an intermediate since the molar yield for DMA with ozone is < 0.4% (Andrzejewski et al. 2008) and some of the known precursors (i.e., UDMH, daminozide and dimethylsulfamide) have molar yields above 50%. Also, ozonation of tertiary amines mainly results in the formation of aldehydes (Munoz and von Sonntag 2000). Von Gunten et al. (2010) proposed a mechanism for NDMA formation from dimethylsulfamide (DMS) (Figure 2.1d). The mechanism is bromide-catalyzed and results in the loss of $–SO_2$ as a leaving group, after which the two nitrogen atoms are joined. Recent quantum chemical calculations suggest a pathway involving two brominated intermediates and rule out pathways involving Br-UDMH or ozonide complexes as intermediates (Trogolo et al. 2015). UDMH conversion to NDMA is likely simple oxidation, but formation mechanisms for other precursors have not been identified.

2.3.2 Precursors and Molar Yields

Chloramine-reactive and ozone-reactive NDMA precursors differ in structure. Chloramine-reactive precursors, such as diuron and ranitidine, have a tertiary dimethylamine moiety. Some of the most frequently studied chloramine-reactive precursors are shown in Table 2.1. One research group looked at 20 pharmaceutical compounds and found eight with > 1% NDMA molar yield (Shen and Andrews 2011). Some quaternary amines are also chloramination precursors for NDMA, such as the coagulant polymer poly(diallyldimethylammonium chloride) or

polyDADMAC and benzalkonium chloride, which is a compound used as a surfactant in detergents and as a biocide in personal care products (Kemper et al. 2010).

Table 2.1: Examples of chloramine-reactive NDMA precursors.

Compound Name	Structure	Description	Reference
Dimethylamine		Commonly found in wastewater, feces, urine, algae and plants; can be found in herbicides	Mitch et al. 2003b
Ranitidine		Stomach acid inhibitor; pharmaceutical	Shen and Andrews 2011
Trimethylamine		Commonly found in wastewater, feces and urine	Mitch et al. 2003b
Diuron		Herbicide	Chen and Young 2008
Benzalkonium chloride		Quaternary amine used in personal and consumer products	Kemper et al. 2010
PolyDADMAC		Coagulation polymer	Park et al. 2009
Dimethyl-dithiocarbamate (DMDTC)		Used in manufacturing to remove metals and for root-control in sewers	Padhye et al. 2013

A commonly used method to determine the amount of chloramine-reactive precursors is the NDMA formation potential (NDMA-FP) test. It involves adding a high concentration of chloramine to the sample and allowing it to react at room temperature for ten days (Mitch et al. 2003a). This simulates the potential NDMA formation that could occur in a water distribution system with long retention times. In a similar manner, the amount of ozone-reactive NDMA precursors can be assessed through a formation potential test (O_3-FP) by reacting the sample with a high concentration of ozone. Since ozone-reactive NDMA precursors have not been researched as much, this FP test is not frequently applied and a consistent protocol has not been implemented.

Natural organic matter (NOM) includes nitrogen-containing compounds which may form NDMA. Chen & Valentine (2007) concentrated NOM and analyzed various fractions to determine NDMA-FP. The hydrophilic and basic fractions showed the strongest NDMA-FP per unit mass, but the hydrophobic acidic fraction had a much greater total mass and contributed the largest portion (71%) of the NDMA-FP. Neutral compounds provided only 1.6% of the total NDMA-FP, which indicates that the chloramine-reactive precursors tend to be charged compounds (Chen and Valentine 2007). In another fractionation experiment, researchers found that half of the NDMA precursors in wastewater influent were sorbed to particles, suggesting that many precursors are hydrophobic and sorb readily (Krauss et al. 2010). A study on dissolved organic nitrogen (DON) in wastewater indicated that NDMA precursors are low-molecular weight compounds (< 1 kDa), but not amino acids (Pehlivanoglu-Mantas and Sedlak 2008).

High molar yield ozone-reactive precursors contain the dimethylamine attached to an additional nitrogen (e.g. R-N-N$(CH_3)_2$ rather than R-N$(CH_3)_2$). An exception is DMS, which has the dimethylamine separated from the nitrogen by SO_2. Compounds with a dimethylamine

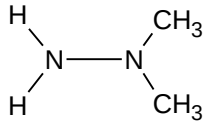
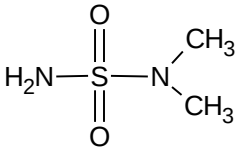
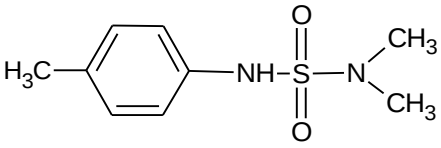
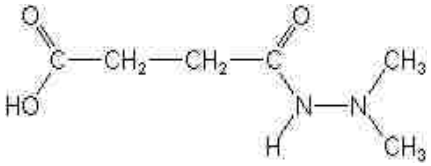
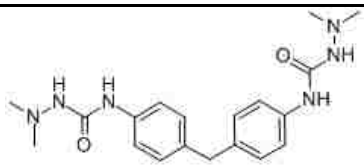
moiety only and no additional nitrogen are not significant precursors for NDMA with ozonation, which differs from chloramination precursors. For example, various organic dyes with tertiary dimethylamines were shown to have NDMA molar yields < 0.001% (Oya et al. 2008). Dimethyl-dithiocarbamate (DMDTC) has been shown to form NDMA through oxidation with monochloramine and ozone at the same low molar yield, 0.008% (Padhye et al. 2013).

Much less is known about the precursors forming NDMA through ozonation (Table 2.2) than chloramine-reactive NDMA precursors. There are no published fractionation studies that identified precursor characteristics (e.g., hydrophobic or hydrophilic) as it relates to NDMA formation. Chemical structure (i.e., presence of dimethylamine and additional nitrogen) appears to be the most relevant characteristic in predicting NDMA formation. Details for the NDMA precursors, including structures and molar yields, are provided in Appendix A.

2.3.3 Factors Affecting NDMA Formation for Ozone-reactive Precursors

Certain factors have been shown to impact NDMA formation with ozone, including the presence of dissolved ions, ozone dose and, the presence of hydroxyl radicals (•OH). For example, bromide has been shown to catalyze the reaction of DMS with ozone (von Gunten et al. 2010) and bromide can enhance or inhibit NDMA formation with chloramine at different pH (Luh and Mariñas 2012). NDMA formation is also dependent on ozone dose. In a model compound study, two precursors were individually reacted with ozone at doses ranging from 0.1 to 1.5 mM O_3 in buffered ultrapure water. One precursor showed increased NDMA formation from 0.1 to 0.5 mM O_3 and then NDMA concentration leveled off. Another precursor showed a linear correlation (R^2 = 0.98) between NDMA formation and ozone dose in the tested range. However, it appears that a maximum molar conversion yield was not reached for this compound (Marti et al. 2015).

Table 2.2: Known ozone-reactive NDMA precursors.

Compound Name	Structure	Description	Reference
Unsymmetrical dimethylhydrazine (UDMH)		Rocket fuel component; intermediate in NDMA formation	Schmidt and Brauch 2008
Tolylfluanid		Fungicide	Schmidt and Brauch 2008
Dimethylsulfamide (DMS)		Decomposition product of tolylfluanid	Schmidt and Brauch 2008; von Gunten et al. 2010
***N,N*-dimethyl-*N*'-(4-methylphenyl)-sulfamide (DMST)**		Tolylfluanid metabolite	Schmidt and Brauch 2008
Daminozide		Plant growth additive	Schmidt and Brauch 2008
1,1,1′,1′-tetramethyl-4,4′-(methylene-di-*p*phenylene) disemicarbazide (TMDS)		Anti-yellowing agent	Kosaka et al. 2009

The presence or absence of hydroxyl radicals affects NDMA formation. Hydroxyl radical quenching with tert-butyl alcohol (tBA) was shown to increase NDMA formation from DMS. It was presumed that the presence of •OH can 1) result in reactions that form products other than NDMA or 2) enhance bromate formation, which limits the catalytic bromide pathway for NDMA formation with DMS. Therefore, •OH scavenging with tBA diminishes two pathways that hinder NDMA formation (von Gunten et al. 2010). Similarly, Marti et al. (2015) performed parallel ozonation tests for ozone-reactive NDMA precursors in buffered ultrapure water with and without tBA and found that higher molar yields were obtained when •OH were scavenged. Hydroxyl radical quenching could also explain why NDMA molar conversion yields for several model compounds were significantly greater in a wastewater matrix compared to ultrapure water (Marti et al. 2015). Effluent organic matter in wastewater is known to scavenge •OH (McKay et al. 2011).

2.4 NDMA and NDMA Precursor Mitigation Strategies

Several techniques have been attempted to remove NDMA or prevent its formation. Strategies include biodegradation, UV irradiation and photolysis, chemical oxidation and advanced oxidation processes (AOP), membranes and reverse osmosis, and adsorption. Since NDMA and NDMA precursors vary in size and polarity, mitigation strategies may be effective for some compounds, but not for all.

2.4.1 Biodegradation

Biodegradation will eliminate NDMA (Sharp et al. 2005) and some of its polar or charged chloramine-reactive precursors (Krauss et al. 2010). In biological secondary level wastewater treatment, NDMA removal is highly variable (0-75%) and there is no clear relationship between

NDMA-FP and wastewater characteristics (i.e., BOD, COD, SS, nitrate, NH_4^+, total N) (Krasner et al. 2009b; Sedlak et al. 2005; Yoon et al. 2011). Groundwater contaminated with NDMA from rocket fuel production was remediated with an intercept-and-treat system. In 30 days, up to 60% was biodegraded with facultative bacteria, but only after the groundwater was treated with granular activated carbon (GAC) (Gunnison et al. 2000). NDMA biodegradation is a co-metabolic process and no microorganisms have been identified that can use NDMA as their sole carbon source (Krauss et al. 2010). Initial NDMA concentration is an important factor. If the concentration is very low, removal does not occur (Gunnison et al. 2000).

Biofiltration is an application of biodegradation and may be used in drinking water or wastewater treatment. Biofiltration, whether intentional or unintentional, occurs when disinfection is not applied directly before filtration and microorganisms grow on the media. Contaminant removal may occur through biodegradation, sorption to the media or sorption to the biofilm attached to the media. Biofiltration is possible with many media types, including sand, anthracite, and activated carbon. An advantage of biological activated carbon (BAC), compared to normal GAC operation, is the possibility of bioregeneration, where adsorbed contaminants are biodegraded and the sorption capacity of the activated carbon is restored (Aktaş and Çeçen 2007).

Biofiltration is effective at decreasing chloramine-reactive NDMA precursors, as well as NDMA. In a study that compared different treatment steps using the same influent (i.e., post dissolved air flotation and sand filtration), biofiltration alone reduced NDMA-FP by 80% while ozonation alone reduced NDMA-FP by 66%. Consequently, biofiltration may be more effective at eliminating chloramine-reactive NDMA precursors than ozonation (Farre et al. 2011a). Another biofiltration study used activated carbon and immobilized bacteria species, *Arthrobacter*

and *Paracoccus*, to remove several amines (i.e., dimethylamine, trimethylamine, methylamine) from an air stream (Ho et al. 2008). These bacteria species could be useful for eliminating NDMA precursors. Other studies showed a decrease in NDMA in wastewater as a result of biodegradation through biological sand filtration (Hollender et al. 2009; Zimmermann et al. 2011).

2.4.2 Ultraviolet Irradiation and Photolysis

Ultraviolet (UV) photolysis is effective at eliminating NDMA (Sharpless and Linden 2005). NDMA has a strong UV absorption band at 230 nm and a weaker band at 330 nm (Plumlee 2008). UV irradiation at 254 nm will degrade NDMA, but only at around 10-fold the dose to inactivate viruses (Mitch et al. 2003b). A pilot-plant study determined that a UV dose of 540 mJ/cm^2 was needed to reduce organic contaminants, including NDMA, by 80%. This was five times greater than the disinfection dose needed to inactivate spores (Kruithof et al. 2007). A higher UV dose makes this type of treatment costly. Natural photochemical attenuation by sunlight is possible due to the NDMA's weak absorption band at 330 nm. In a previous study, NDMA was degraded by 42% in 83 minutes under solar light exposure. Photolysis was hindered by dissolved organic matter (DOM) due to light screening (Plumlee 2008).

Although UV irradiation reduces NDMA effectively, there are a few issues in implementing this treatment. A potential problem with UV treatment is that NDMA is degraded to DMA and subsequent chloramination, for disinfection purposes, could reform NDMA (Zhao et al. 2008), albeit at low concentrations. The UV dose needed to treat NDMA and its associated cost is influenced by water quality. Pretreatment with ultrafiltration (UF) and ion-exchange to remove hydroxyl scavengers, such as nitrate and NOM, may be needed to reduce energy costs and to eliminate NDMA precursors as well (Martijn et al. 2010). Additionally, the presence of

hypochlorite, chloramines, aqueous ferric iron, and ozone decrease UV transmittance, which negatively impacts the UV dose delivered (Cushing et al. 2001).

Xu et al. (2009a) investigated factors affecting UV destruction of NDMA. Complete degradation occurred at any initial concentration, but the reaction rate decreased with increasing initial concentration. Lower pH resulted in greater photodegradation, which was attributed to higher quantum yields. NDMA destruction was greater for solutions saturated with oxygen as compared to nitrogen and hindered by humic acid, which may be the result of decreased UV transmittance (Xu et al. 2009).

2.4.3 Chemical Oxidation

Typical oxidants used in water and wastewater treatment are chlorine, ozone, hydrogen peroxide and hydroxyl radicals. Fenton reagent ($Fe(II)/H_2O_2$) and electrochemical oxidation are other possibilities, but these are not employed at full-scale treatment plants. Chlorination above breakpoint is known to reduce NDMA formation with respect to chloramine-reactive NDMA precursors, but this oxidation process can also result in the formation of regulated chlorination DBPs (Charrois et al. 2007; Chen and Valentine 2008). An equivalent study has not been completed for ozone-reactive NDMA precursors.

Rate constants for NDMA destruction with ozone and hydroxyl radical are 1.0×10^{1} and 3.3×10^{8} $M^{-1}s^{-1}$, respectively (Suthersan and Payne 2004). While ozone is not effective for destroying NDMA already formed, it can reduce NDMA-FP (Lee et al. 2007a; Pisarenko et al. 2012; Shah et al. 2012), which again is with respect to chloramine-reactive NDMA precursors. Depending on the types of precursors in the water, ozone can result in direct NDMA formation or mitigate NDMA formation, which makes it difficult to predict the net effect. Hydroxyl radicals are far more efficient at destroying NDMA; however, constituents in the water (e.g.,

bicarbonate, effluent organic matter, natural organic matter) may quench hydroxyl radicals and in real water matrices the reaction intermediate can transfer its electron and regenerate NDMA. This means that actual NDMA destruction by hydroxyl radicals will be lower than expected (Mezyk et al. 2004).

2.4.4 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) include ozone, ozone with hydrogen peroxide (O_3/H_2O_2), UV with hydrogen peroxide (UV/H_2O_2) and UV with ozone (UV/O_3). Most of these treatments hinge on the hydroxyl radical as a non-selective oxidant that will react with more constituents than UV or ozone alone.

Adding hydrogen peroxide with ozone does not appear to improve NDMA removal. In a pilot-scale study by Pisarenko et al., (2012) O_3/H_2O_2 had little effect on direct NDMA formation or NDMA-FP compared to ozone alone. Another study also showed no significant difference between ozone and O_3/H_2O_2 for NDMA oxidation (Lee et al. 2007b). On the other hand, Yang et al. (2009) observed a large decrease (88%) in NDMA formation potential with chloramines after treating DMA in deionized water with O_3/H_2O_2 (Yang et al. 2009). While there is no benefit in preventing ozone-derived NDMA, increased •OH from hydrogen peroxide may be useful in reducing NDMA-FP by destroying DMA.

AOPs are influenced by operational factors, such as initial concentration and pH. For example, in UV/O_3 and UV/H_2O_2 systems, it was shown that reaction rates were negatively affected by increasing the initial concentration (De et al. 1999; Xu et al. 2010). Another operational factor, pH, affects AOP performance because species may be protonated or deprotonated depending on the pH and hydroxyl radical reactions are pH dependent (Hoigne and

Bader 1976). In a study on the destruction of NDEA, UV alone showed high removal with acidic and neutral pH, while UV/O_3 worked well at any pH (Xu et al. 2010).

Degradation products may differ with AOP treatments. Increasing the ozone dose resulted in higher concentrations of nitrate and lower DMA, but it did not affect the reaction rate. Hydroxyl radical reactions favored methylamine (MA) formation over DMA, which is useful in preventing regeneration of NDMA (Xu et al. 2009). Adding 1 mM H_2O_2 to ozone increased DMA removal by 30% and decreased NDMA-FP by 88% (Yang et al. 2009). The authors hypothesize that the drop in NDMA-FP is because the hydroxyl radical eliminates hydroxylamine, which inhibits an NDMA formation pathway. A comparison of UV and UV/ H_2O_2 revealed that hydrogen peroxide does not enhance NDMA degradation due to light screening (Sharpless and Linden 2003); however, there was a difference in the transformation products formed. Even though NDMA destruction isn't improved through this particular process, UV/ H_2O_2 may still have advantages in removing other micropollutants while simultaneously removing NDMA (Swaim et al. 2008). Chen et al. (2011) investigated DMA formation and NDMA-FP with UV and UV/ H_2O_2. The authors found that increasing the H_2O_2 dosage and increasing the contact time resulted in less DMA formation and consequently lower NDMA-FP (Chen et al. 2011).

The water quality prior to AOP treatment will influence NDMA formation. Zhao et al. (2008) investigated 11 parallel disinfection treatment trains with seven surface waters. NDMA formation varied for waters subjected to the same treatment and this was attributed to a difference in precursors (Zhao et al. 2008). In comparing secondary effluents after activated sludge and membrane bioreactor (MBR) treatments, the ozonated MBR effluent had a much lower NDMA concentration (Pisarenko et al. 2012). This suggests that more extensive secondary

wastewater treatment, such as membrane bioreactors, may increase the removal of NDMA precursors.

2.4.5 Membrane Filtration and Reverse Osmosis

Membranes will effectively remove some nitrosamines and precursors. Microfiltration (MF) and UF do not remove NDMA precursors (Farre et al. 2011a). In fact, NDMA may increase in wastewater treated with microfiltration-reverse osmosis because chloramination is used to prevent membrane biofouling (Plumlee et al. 2008). The need to use chloramines for biofouling prevention may limit the overall effectiveness of NDMA removal in wastewater by membranes. Reverse osmosis (RO) will remove many NDMA precursors (Farre et al. 2011a), but only about 50% of NDMA due to its small size (Plumlee et al. 2008).

Many factors affect membrane performance. In one study, ionic strength and pH did not influence RO rejection, but artificial fouling with alginate significantly decreased rejection (Steinle-Darling et al. 2007). Changes in the feed water may cause fouling, and this will, in turn, affect RO rejection (Plumlee et al. 2008). Rejection of NDMA by reverse osmosis and nanofiltration is challenging due to NDMA's low molecular weight and hydrophilic properties; thus, other treatment strategies have to be considered for NDMA removal (Yangali-Quintanilla et al. 2010).

2.4.6 Adsorption

Activated carbon is moderately beneficial for removing NDMA precursors, but not NDMA itself. NDMA does not adsorb as strongly as other organic compounds, which is seen by its Freundlich isotherm constants (K = 1.07-9.08 µg/g and 1/n = 0.744-1.11) (Kommineni et al. 2003). Groundwater at Rocky Mountain Arsenal, a rocket fuel production site, was remediated with GAC, carbonaceous resins (synthetic carbon adsorbent, e.g., Ambersorb), zeolite, silica,

acidic hydrolysis, and metal complexation. GAC and the carbonaceous resins removed 99% of NDMA after equilibrium was achieved, while zeolite and silica removed 15-20%. Metal complexation and hydrolysis were not effective (Fleming et al. 1996). At the same site, another study found that NDMA adsorbed to the soil very little and was quickly desorbed in the presence of water (Gunnison et al. 2000). GAC was shown to remove chloramine-reactive NDMA precursors 60-90% even after dissolved organic carbon breakthrough. (Hanigan et al. 2012). However, one group reported that activated carbon can act as a catalyst to form trace levels of NDMA from secondary amines (Padhye et al. 2010). This is important to consider because many analytical methods use activated carbon cartridges during solid phase extraction.

A typical problem with activated carbon after breakthrough (i.e., no more capacity to remove the targeted contaminant) is its replacement or regeneration. If GAC is not regenerated, it must be replaced and this increases the treatment cost. On the other hand, regeneration may lead to deterioration of the carbon. Kommineni et al. (2003) used Fenton's reagent to destroy adsorbed NDMA (99% destruction) and regenerate GAC at pH 2-3. The regeneration cost was low ($0.10/lb GAC) and very little capacity was lost (< 3.8%). Unfortunately, NDMA precursors vary greatly, and not all precursors will sorb strongly to activated carbon (Hanigan et al. 2012), which means other mitigation strategies are needed to prevent or reduce NDMA formation.

CHAPTER 3

METHODOLOGY

3.1 Experimental Approach Overview

This chapter covers the methods used in investigating each of the three issues comprising this research. Issue one deals with the identification of model precursors that can potentially lead to the formation of NDMA upon ozonation. The hypothesis is that hydrazones and carbamates with two methyl groups are ozone-reactive precursors. Secondarily, it is hypothesized that other factors (i.e., ozone dose, oxidant type, and wastewater matrix components) affect NDMA formation and that ozone-reactive precursors are less reactive with chloramine than ozone. To investigate the initial hypothesis, model precursors were spiked into an aqueous matrix and ozonated at a consistent dose through the addition of ozone-saturated water. Samples were analyzed for NDMA and molar yields for NDMA formation were calculated based on the initial concentration of the precursors spiked into the aqueous matrix. The second hypothesis was investigated by varying the experimental design to control ozone dose, the type of oxidant available (e.g., molecular ozone, hydroxyl radical, dissolved oxygen), and dissolved constituents (e.g., bromide, effluent organic matter, natural organic matter). Samples were analyzed for NDMA and results were compared to determine the impacts of ozone dose, oxidant type, and dissolved constituents on NDMA formation.

Issue two involves investigating combinations of chlorine, ozone and chloramine to minimize NDMA formation. The hypothesis is that chlorination ahead of ozonation and chloramination will reduce NDMA formation. Several treated wastewaters, collected from actual wastewater plants, were chlorinated, ozonated, and chloraminated individually and in series in the laboratory. In one situation, parallel tests were completed where the wastewater was spiked with

model precursors to further ascertain the impact of pre-chlorination on ozone-reactive NDMA precursors. Chlorine, ozone and chloramine concentrations were measured and overall oxidant exposure was calculated based on contact time and concentration. Samples were analyzed for NDMA, ammonia (to determine breakpoint chlorination), total organic carbon (to determine an appropriate ozone dose), and chlorination disinfection byproducts (i.e., trihalomethanes, haloacetic acids).

Issue three looks at removal of NDMA precursors via biofiltration using treated wastewater effluent. Varying degrees of precursor removal were hypothesized based on known information about biodegradability and sorption of the compounds (i.e., daminozide, 2-F-DMH, TMDS, ranitidine, DMA). Three biofiltration columns containing anthracite and with different empty bed contact times (5, 10, and 20 minutes) were acclimated to tertiary-treated wastewater effluent. Next, the biofiltration columns were subjected to precursor-infused wastewater to examine if biofiltration was able to remove NDMA precursors. The performance of the system was monitored by total organic carbon (TOC), chemical oxygen demand (COD), and dissolved oxygen (DO). Adenosine triphosphate (ATP) was measured at the start and end of the test period as a means to determine general microbial activity for biofilm attached to the media. Influent and column effluent samples were analyzed for individual precursors, total nitrogen (TN), NDMA, THMs and HAAs. In a separate test, sorption of the precursors to anthracite was determined in order to establish which mechanisms (i.e., sorption to media, sorption to biofilm, biodegradation) were responsible for precursor removal.

3.2 Experimental Methods for Issue One

3.2.1 Model Precursors

A variety of chemicals were chosen as model compounds for ozone-reactive NDMA precursors (Table 3.1). The term "model" is used because these compounds represent different functional groups (i.e., moieties) and will serve as models in understanding the relationship between NDMA formation and that functional group. The full names, CAS registry numbers, and compound uses are shown in Table 4.2. The list consists of already established ozone-reactive NDMA precursors and previously untested compounds, which were chosen based on chemical structure. Chloramine-reactive NDMA precursors were included for confirmation that tertiary amines without an additional nitrogen, R-N(CH_3)$_2$ vs. R-N-N(CH_3)$_2$, do not form NDMA in high yields during ozonation.

Table 3.1: List of model precursors selected to be tested for NDMA formation with ozone.

Established ozone-reactive NDMA precursors	**Untested compounds**	**Established chloramine-reactive NDMA precursors**
UDMH	Acetone-DMH	Ranitidine
TMDS	2-F-DMH	DMA
Daminozide	DMC-phenyl	Ziram
DMS	DMTC-phenyl	
	DMC-dithio	
	DMSC	
	Dacarbazine	
	Atazanavir	
	Streptozocin	
	N-Nitrososarcosine	

3.2.2 Experimental Plans

Table 3.2 shows the experimental plan to test if the selected compounds are ozone-reactive NDMA precursors. Briefly, an aqueous matrix containing the compounds was subjected to ozonation and then analyzed for NDMA. Phosphate-buffered (1 mM) ultrapure water (18.2 MΩ·cm) at pH 7 was used as the baseline aqueous matrix. Several matrix components were varied to determine their impact on NDMA formation. The investigated matrix components included: bromide, effluent organic matter (in wastewater), and natural organic matter (NOM). Bromide was added at two doses (50 and 1250 ppb) in phosphate-buffered ultrapure water and compared against the condition where no bromide was present. NOM was added at 3 mg/L as organic carbon by dissolving Suwannee River fulvic acid into phosphate-buffered ultrapure water. Wastewater effluent from a membrane bioreactor was used in replacement of the phosphate-buffered ultrapure water for the wastewater matrix.

Table 3.2: Experimental plan to investigate potential NDMA precursors in several matrices (Issue One).

	Precursor Conc. (mM)	Ozone Conc. (mM)	Matrices				
			Buffered Ultrapure Water				Wastewater
			0 ppb Br^-	50 ppb Br^-	1250 ppb Br^-	3 mg/L NOM	0 ppb Br^-
Example Precursor	0.10	1.0	-	-	-	-	-

Note: Br^- = bromide; NOM = natural organic matter.

Additional tests were performed on selected compounds that formed NDMA (Table 3.3). These tests included ozone dose and oxidant type. Ozone dose was tested at four concentrations (0.1-1.5 mM) in phosphate-buffered ultrapure water with a constant precursor concentration.

Oxidant type was tested by isolating each oxidant. Samples were exposed to dissolved oxygen (O_2) by adding an aliquot of oxygen-saturated water in replacement of ozone-saturated water. Molecular ozone (O_3) was isolated through the addition of 100 mM tert-butyl alcohol (tBA), which reacts quickly with hydroxyl radicals, but has no effect on molecular ozone (Anipsitakis and Dionysiou 2004). Hydrogen peroxide (H_2O_2) was added at two doses (0.35, 0.70 mM) to test the impact of increased hydroxyl radical concentration (•OH) on NDMA formation. Hydroxyl radicals were produced without ozone via gamma radiolysis (Peller et al. 2003).

Parachlorobenzoic acid (pCBA) was used as a probe to determine what level of gamma irradiation was needed to produce a similar concentration of •OH for radiolysis as found during ozonation. Also, to verify •OH quenching by tBA, pCBA samples with and without 100 mM tBA were ozonated. Quenching was confirmed since pCBA concentration decreased without tBA (i.e., pCBA was destroyed by •OH), but it remained constant in the presence of tBA. Analysis of pCBA is described in section 3.5.12.

Table 3.3: Experimental plan to investigate ozone dose and oxidant type for selected ozone-reactive NDMA precursors (Issue One).

	Precursor Conc. (mM)	O_3 and •OH						O_3 only	•OH only	O_2
		Ozone Dose (mM)				H_2O_2 Dose (mM) [1.0 mM ozone]		Ozone (mM) and 100 mM tBA	Radiolysis (Gy)	Dissolved Oxygen (mg/L)
		0.1	0.5	1.0	1.5	0.35	0.70	1.0	38.6	8
2-F-DMH	0.10	-	-	-	-	-	-	-	-	-
TMDS	0.10	-	-	-	-	-	-	-	-	-

Note: O_3 = molecular ozone; •OH = hydroxyl radicals; O_2 = oxygen; tBA = tert-butyl alcohol; H_2O_2 = hydrogen peroxide; Gy = gray (unit for radiation).

Finally, NDMA formation was compared for ozonation and chloramination. Precursors were added to phosphate-buffered ultrapure water, as before, and then spiked with a high chloramine dose. A parallel test was completed where the precursors were first ozonated and then chloraminated (Table 3.4). The chloramination step occurred 24 hours after ozonation to ensure that there was no ozone residual remaining.

The precursor concentration (0.1 mM) used in these tests is higher than anticipated in treated wastewater effluents. The purpose of the high concentration was to eliminate the need for sample extraction and therefore reduce the time and materials needed for analysis.

Table 3.4: Experimental plan to compare NDMA formation from ozonation and chloramination of model precursors (Issue One).

	Precursor Conc. (mM)	Ozone Conc. (mM)	Chloramine Conc. (mg/L)	Tests		
				Ozone only	Chloramine only	Ozone + Chloramine
Example Precursor	0.10	1.0	140	-	-	-

3.2.3 Generation of Ozone Stock Solution

Ozonation was performed by generating a stock solution of ozone-saturated water and adding an aliquot to the aqueous matrix containing the precursors. The ozone set-up (Figure 3.1) included an ozone generator (model CFS-1A, Ozonia North America, Inc., Elmwood Park, NJ, USA) where ozone is produced from oxygen gas and bubbled into cold, ultrapure water. An aliquot of the ozone-saturated water (typically 70 mg O_3/L) was removed via a stopcock and immediately added to the precursor solution, as described in the next paragraph, and allowed to react until all ozone residual was dissipated. At the ozone doses used in these experiments (up to

1.5 mM), a zero ozone residual was observed in less than one hour for wastewater and less than six hours for ultrapure water; however, a 24 hour reaction time was allowed as a precaution against opening a container and being exposed to ozone. For safety, ozone gas escaping from the system (i.e. exhaust flow) was quenched with a potassium iodide solution (20 g/L), and ozone generation was performed in a fume hood. Ozone concentration was measured as described in section 3.5.7.

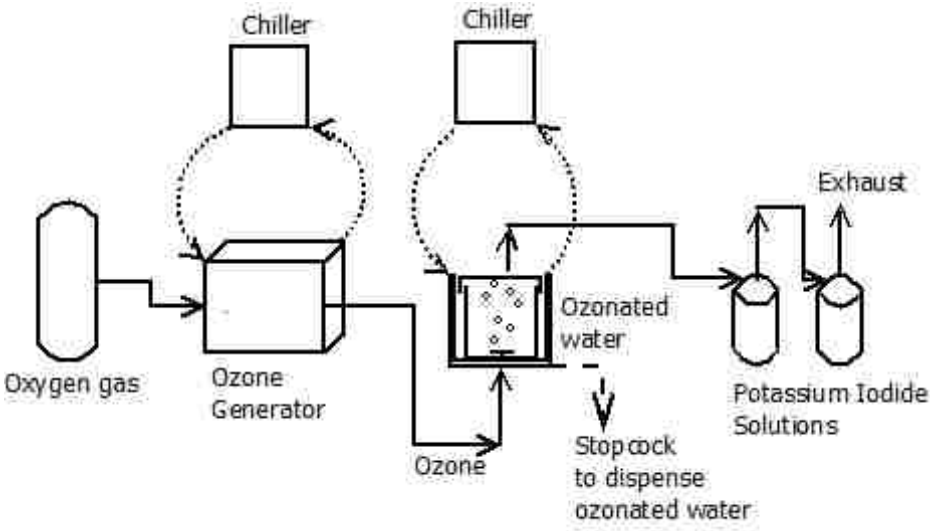


Figure 3.1: Diagram illustrating how ozone-saturated water is prepared for ozonation experiments.

3.2.4 Ozonation Procedure

Bench-scale ozonation was performed to identify compounds as ozone-reactive precursors and to evaluate impacts of other factors on NDMA formation. To start, the precursors were spiked into the aqueous matrix along with additional chemicals (bromide or tBA) and ozonated with a tenfold molar excess of ozone (Figure 3.2) via addition of ozone-saturated water. The ten-

fold molar excess of ozone was used to achieve a high level of NDMA formation. Although this may not give the maximum NDMA molar yield for each compound, it did show whether or not the compound was an ozone-reactive precursor and the consistent ratio (0.1 mM precursor: 1 mM O_3) provided a way to compare NDMA formation among the precursors.

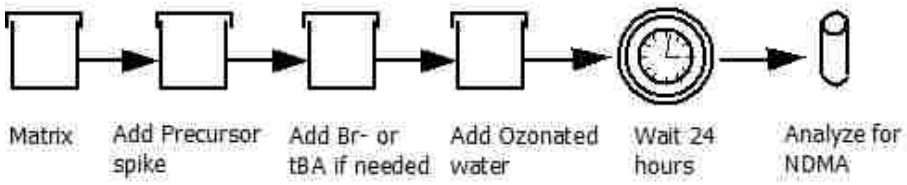


Figure 3.2: Experimental procedure for ozonation tests to identify ozone-reactive NDMA precursors.

3.2.5 Chloramination – Formation Potential

Chloramination was performed at 140 mg/L as Cl_2 for ten days according to a frequently used NDMA formation potential test (Mitch et al. 2003a). The sample was spiked with a monochloramine solution (14 g/L as Cl_2) that was freshly prepared from a cold ammonium chloride solution adjusted to pH 9 with sodium hydroxide and the slow addition of sodium hypochlorite at a Cl:N mass ratio of 3.3 to 1. Chloramine concentration was measured as described in sections 3.5.5 and 3.5.6. After ten days at room temperature, sodium thiosulfate was added to the samples to quench the chloramine residual. Figure 3.3a illustrates the procedure for chloramination only, while Figure 3.3b illustrates the procedure for ozonation followed by chloramination.

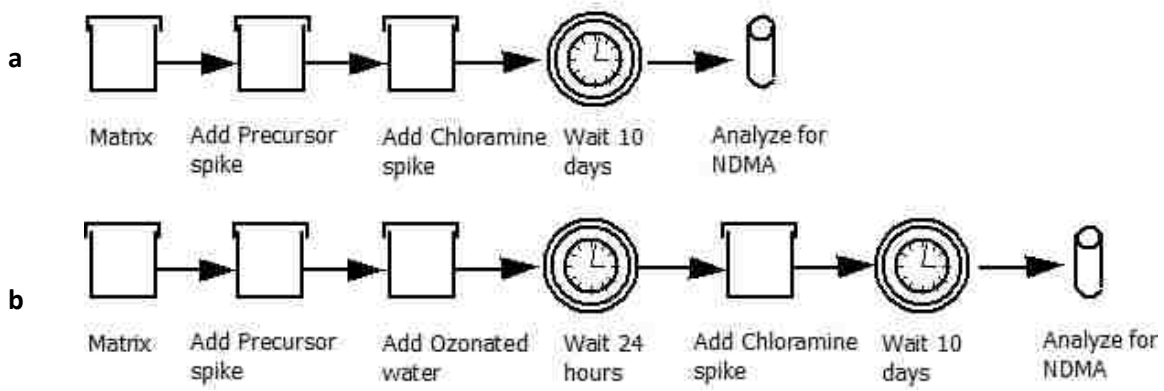


Figure 3.3: Experimental procedures for chloramination of ozone-reactive NDMA precursors.

3.3 Experimental Methods for Issue Two

3.3.1 Experimental Plans

Issue Two deals with mitigation of NDMA by precursor removal with different oxidant combinations. Briefly, chlorination, ozonation and chloramination alone and in combination with each other were performed with different water matrices. Chlorination was based on the chlorine breakpoint of the wastewater, while ozonation was conducted at an ozone to total organic carbon (O_3:TOC) ratio of 0.8 based on the TOC present in the wastewater. The goals were to demonstrate pre-chlorination as a NDMA mitigation strategy for ozone-reactive precursors and to determine trade-offs between NDMA mitigation and chlorination byproduct formation. Samples were analyzed for trihalomethanes (THMs) and haloacetic acids (HAAs), as well as NDMA. Details of the analyses are described in sections 3.5.3, 3.5.4, and 3.5.2, respectively. Details for each test procedure are shown in Figure 3.4.

The process was repeated for several wastewaters with and without ammonia (Table 3.5) in order to identify trends in NDMA mitigation. Ammonia was an important factor since free

chlorine combines with ammonia to produce chloramine, which can form NDMA. To minimize the presence of chloramine, free chlorine was added beyond the chlorine breakpoint, above which chloramines are destroyed.

Another concern was the presence of free chlorine during ozonation. Ozone reacts with free chlorine, which makes ozone less effective for reacting with the NDMA precursors. In addition, free chlorine interferes with the analytical method used to measure ozone. To abate this problem, ozonation was delayed until the free chlorine residual had reached zero.

For greater confirmation of NDMA mitigation, one of the wastewaters was spiked with NDMA precursors. This provided a much higher change in NDMA formation potential because the precursor concentrations were several times greater than those typically found in the wastewater. For example, it was possible to see a change in NDMA formation of several hundred ng/L in the precursor-spiked wastewater as compared to less than 100 ng/L at precursor concentrations typically found in treated wastewater effluent.

Table 3.5: Experimental plan for parallel tests with single and combined disinfection processes to investigate NDMA mitigation and THM/HAA formation (Issue Two).

Tests	O_3:TOC ratio (mg/L)	Wastewater			
		WW1 with ammonia	WW2 without ammonia	WW3 without ammonia	WW3 spiked with precursors
Cl_2	N/A	-	-	-	-
O_3	0.8	-	-	-	-
CLM	N/A	-	-	-	-
Cl_2-O_3	0.8	-	-	-	-
O_3-CLM	0.8	-	-	-	-
Cl_2-CLM	N/A	-	-	-	-
Cl_2-O_3-CLM	0.8	-	-	-	-

Note: Cl_2 = pre-chlorination; O_3 = ozonation; CLM = chloramination; TOC = total organic carbon; WW = wastewater; N/A = not applicable.

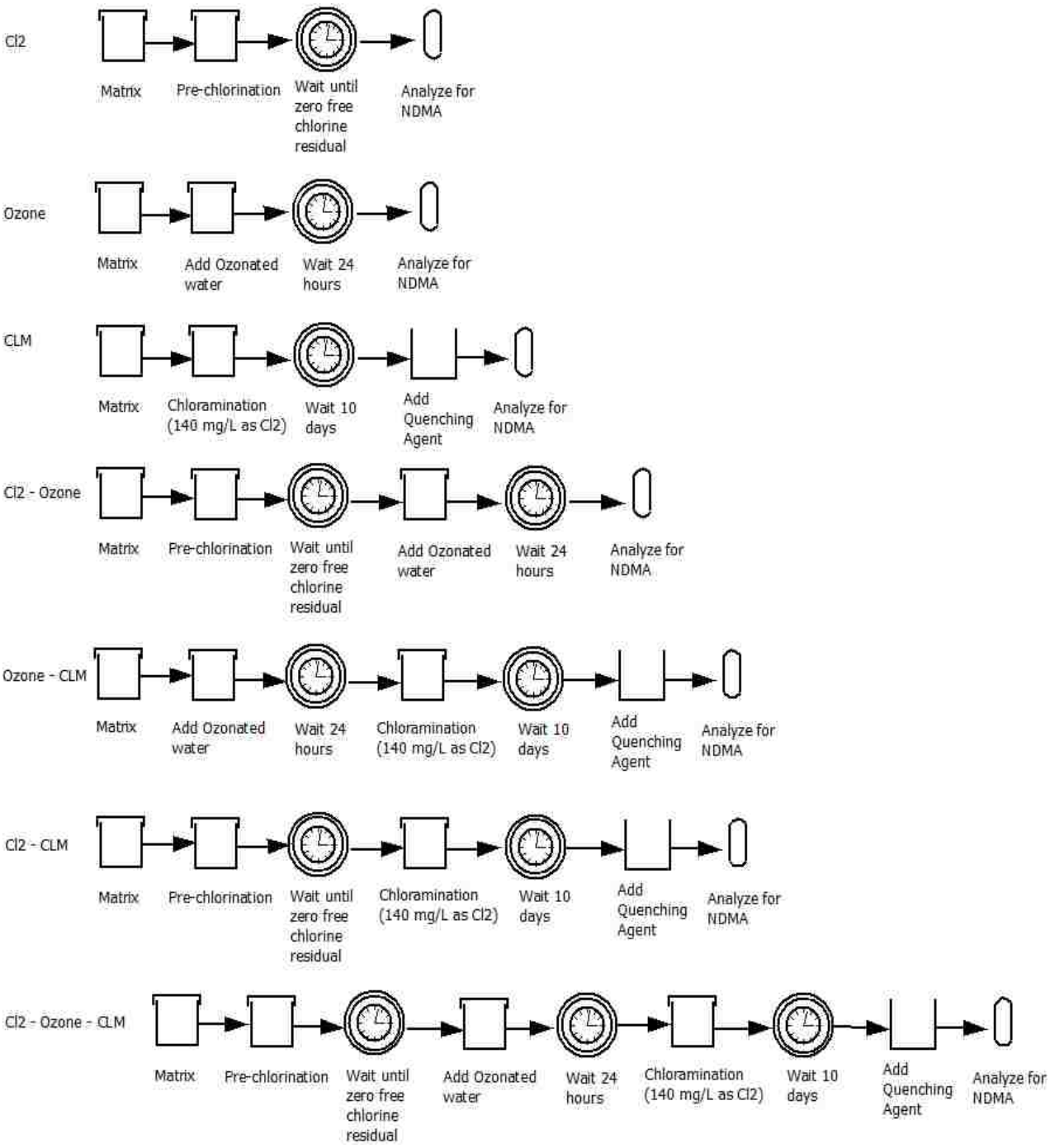


Figure 3.4: Experimental procedures for parallel tests with chlorination (Cl_2), ozonation, and chloramination (CLM) to investigate NDMA mitigation.

3.3.2 Pre-chlorination

An important component of this experiment was having similar free chlorine exposures among the different wastewaters in order to directly compare the results. Therefore, it was necessary to determine a suitable chlorine dose before actual experiments began. A chlorine demand curve (Figure 3.5) was developed for each wastewater in order to identify the chlorine breakpoint, after which a free chlorine residual is present. Then, a 24-hour chlorine decay test was performed for each wastewater in order to estimate free chlorine exposure at three chlorine doses above the breakpoint (Table 3.6). The final dose was selected so that free chlorine exposure (i.e., Ct) was similar for all wastewaters (e.g., 130 mg·min/L). Free chlorine exposure was determined during the actual experiment rather than relying on the estimated chlorine exposure from the original decay test. Free and total chlorine were measured as described in section 3.5.5.

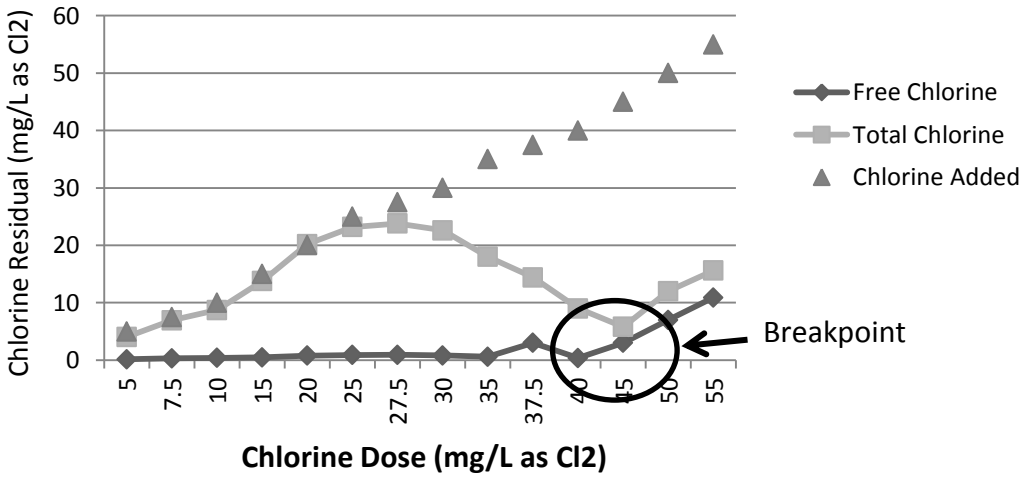


Figure 3.5: Example of a chlorine demand curve for determining the chlorine breakpoint.

Table 3.6: Sampling schedule for 24-hour chlorine decay tests to determine free chlorine exposure.

Chlorine (mg/L as Cl_2)	Time (min)															
	1	3	5	7	10	15	20	30	45	60	120	180	300	480	1200	1440[a]
Dose 1																
Dose 2																
Dose 3																

[a]Sampling continued until the free chlorine residual was zero.

3.3.3 Ozonation

Ozonation was conducted at a common O_3:TOC ratio (0.8) for all wastewaters. O_3:TOC ratios were based on the TOC of the original sample (e.g., non-chlorinated wastewater) and took into account sample dilution through the addition of ozone-saturated water. Ozone exposure was determined by completing an ozone decay curve for both the non-chlorinated and chlorinated samples (Table 3.7). Ozone concentration and TOC were measured as described in sections 3.5.7 and 3.5.10, respectively.

Table 3.7: Sampling schedule for ozone decay tests to determine ozone exposure for chlorinated and non-chlorinated wastewater samples.

Ozone (mg O_3/L)	Sample	Time (min)								
		0.5	0.75	1	1.5	2	3	5	7	10[a]
O_3:TOC = 0.8	Non-chlorinated									
	Chlorinated									

[a]Sampling continued until the ozone residual was zero.

3.3.4 Chloramination – Uniform Formation Conditions

In contrast to the formation potential (FP) test, which expresses a maximum level of disinfection byproduct (DBP) that might be reached, the uniform formation conditions test is meant to represent DBP formation under realistic conditions in a distribution system. The chloramine uniform formation conditions (CLM-UFC) test involves spiking chloramine in a 0.4 mM borate-buffered sample to achieve at least a 2.5 mg/L as Cl_2 residual after three days (Shah et al. 2012). Each sample was spiked with a monochloramine solution (1 g/L as Cl_2) prepared as described in section 3.2.5. Typically, an initial concentration of 5 mg/L as Cl_2 was high enough to achieve the desired residual. After three days at room temperature, sodium thiosulfate was added to the samples to quench the chloramine residual. Chloramine concentration was measured as described in section 3.5.5.

3.4 Experimental Methods for Issue Three

3.4.1 Pilot Plant set up and Operation of the Biofiltration Columns

Biofiltration columns, located at a wastewater treatment facility, were used for investigating NDMA precursor removal using actual tertiary-treated effluent from the plant. The three columns were operated at the same flow rate and contained different amounts of anthracite media, which corresponded to empty bed contact times (EBCTs) of 5, 10, and 20 minutes. EBCT is the average time the water stays in contact with the media and was calculated by dividing the volume of the media in the column by the wastewater flow rate through the column. Hydraulic loading rate was calculated as flow rate divided by the area of the column. Column design parameters are shown in Tables 3.8 and 3.9. Figure 3.6 shows the experimental setup for the biofiltration columns. Prior to starting the NDMA removal experiments, the columns were

acclimated to tertiary-treated wastewater in alternating cycles of recirculating batch mode and flow-through mode for 11 weeks as part of a related experiment. Before commencing the NDMA precursor removal test, the columns were run in flow-through mode for 10 days, which corresponds to a minimum of 720 EBCTs. Biofilm growth was visible on the anthracite and confirmed through solid-phase measurement of adenosine triphosphate (ATP), which indicates general microbial activity for biofilm attached to the media.

Columns were in operation continually during the preparation phase and test period, with the exception of one day during the preparation phase when the feedwater tank ran dry. No backwashing occurred. Instead, between the 10-day preparation phase and test period, the columns were shaken to fluidize the media and unattached particulates were flushed off the top layer of the media. During the 14-day test period, the feedwater (tertiary-treated wastewater) was spiked with a mixture of NDMA precursors. The wastewater and NDMA precursor mixture were pumped into a tank for blending. Complete mixing was not established; therefore, sampling ports were added to each feed line instead of assuming a homogeneous mixture and sampling directly from the tank. Peristaltic pumps (Cole Palmer, Masterflex with Easy Load Pump Head) were used to maintain a constant flow of 100 mL/min to the columns. The performance of the system was monitored by measuring total organic carbon (TOC), chemical oxygen demand (COD), and dissolved oxygen (DO) in the influent and effluent of the columns. DO was not regulated and varied depending on the feedwater. ATP was measured at the start and end of the test period. Feedwater and column effluent samples, collected at sampling ports before and after each column, were analyzed for individual precursors, total nitrogen (TN), NDMA, THMs and HAAs, as described in sections 3.5.15, 3.5.13, 3.5.1, 3.5.3, and 3.5.4, respectively.

All connecting tubing was periodically replaced due to biofilm growth. New ¼ inch inner diameter Tygon tubing was used for the feedwater lines at the start of the test period and these were replaced on day 11 of the test period because biofilm was sloughing off the tubing interior and accumulating at the top of the columns. Biofilm also clogged the waste lines and those were replaced during the test period, but this had no impact on precursor removal. Biofilm in the feedwater lines may have increased precursor removal; however, the tubing lengths were similar for the columns, so all columns should have been affected equally.

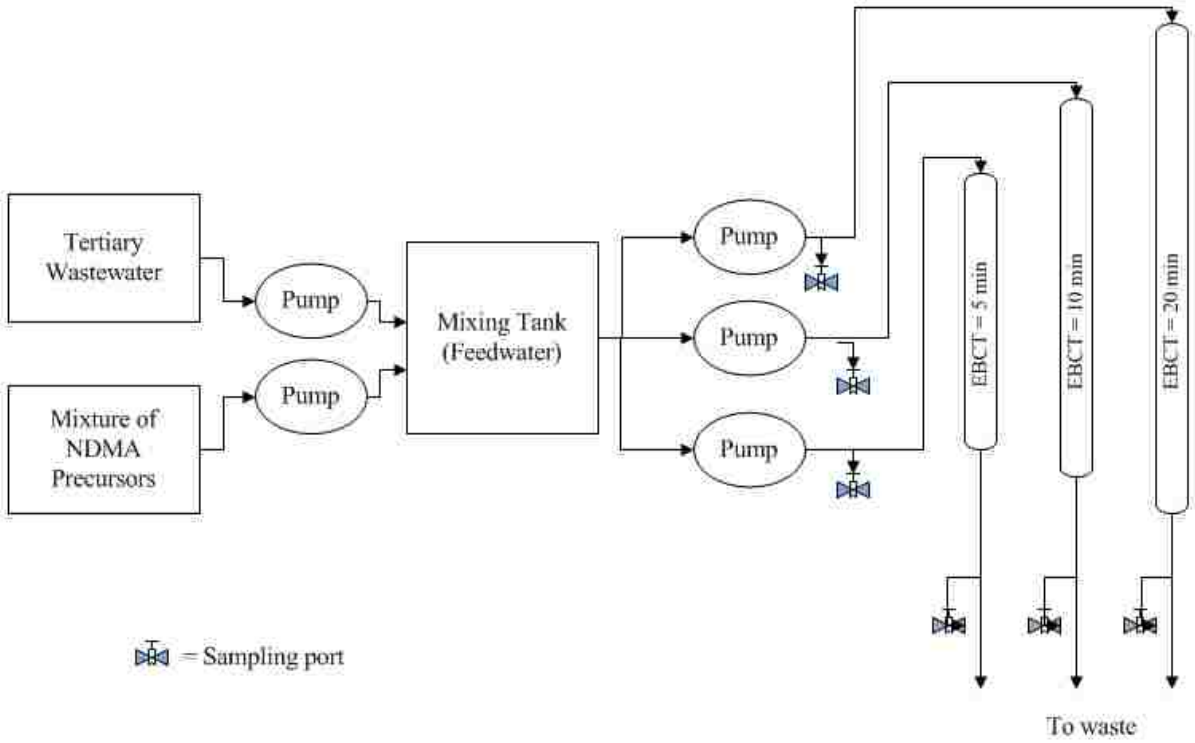


Figure 3.6: Schematic of the anthracite biofiltration columns set-up used to investigate Issue Three.

Table 3.8: Parameters used in the design of the biofiltration columns.

Parameter	Value	Value
Column Diameter	5 cm	0.164 ft
Column Area	19.63 cm^2	0.021 ft^2
Hydraulic Loading Rate	5.0 mL/min·cm^2	1.2 gpm/ft^2
Flow Rate	100 mL/min	0.026 gpm

Table 3.9: Empty bed contact times (EBCTs) and media parameters for the biofiltration columns.

Column	EBCT	Media Height	Media Volume
1	5 min	25 cm	0.49 L
2	10 min	50 cm	0.98 L
3	20 min	100 cm	1.96 L

3.4.2 Preparation of NDMA Precursors Mixture

Individual stock solutions of five NDMA precursors were prepared from neat standards. Amounts were weighed out to make 500 mL of 1 or 10 mM solution (Table 3.10). 2-F-DMH was diluted from the neat liquid (75.414 mM). TMDS was prepared in 50/50 acetonitrile/water because of its low solubility in water. All other precursor stock solutions were made with ultrapure water.

Batches of the NDMA precursor mixture were generated daily. First, equal aliquots of the stock solutions were mixed together and diluted by approximately 300-fold with tap water. This diluted mixture was then pumped into a 125 gallon high density polyethylene (HDPE) tank and mixed with the tertiary wastewater by approximately 30-fold. A precursor concentration of 0.1 μM (1 μM for DMA) was targeted in the feedwater in order to have an initial concentration within the LC-MS/MS analytical range and without the need to concentrate the sample.

Table 3.10: Specifications for the NDMA precursor stock solutions for biofiltration.

Precursor	Molecular Weight (g/mol)	Mass weighed out (g)	Stock Solution Concentration (mM)
TMDS	368.48	184 mg	1
Daminozide	160.17	80 mg	1
2-F-DMH	138.17	N/A	1
Ranitidine	314.4	175 mg	1
DMA	45.08	407 mg	10

3.4.3 Sample Collection, Preservation, and Analysis

Samples were collected throughout the 10-day preparation phase and the 14-day test period according to Table 3.11.

3.4.4 Experimental Procedures

Collected influent and effluent samples underwent ozonation, chloramination UFC, and THM/HAA formation potential (THM/HAA-FP) testing. Ozonation and chloramination UFC procedures are explained in sections 3.3.3 and 3.3.4, respectively.

THM/HAA-FP testing involved determining an initial chlorine demand, spiking multiple samples with chlorine, and then choosing the sample with an appropriate residual. First, 60 mL was dosed at 100 mg/L as Cl_2 and 10 mM phosphate buffer at pH 7. The sample was kept at room temperature and in the dark. After 24 hours, the chlorine residual was measured using the DPD method (section 3.5.5) and the chlorine demand was calculated as the difference between the original concentration (100 mg/L) and the chlorine residual. Next, a series of samples (n = 6) were dosed with chlorine (ranging from 15-60 mg/L as Cl_2 depending on the chlorine demand) and kept in the dark at room temperature. After 7 days, the chlorine residual was measured and the sample that fell in the range of 3-5 mg/L as Cl_2 was used for analysis of THMs and HAAs.

Table 3.11: Sample schedule for the biofiltration columns during the (a) 10-day preparation phase and (b) 14-day test period. An 'x' indicates samples were collected for that test.

(a) Analysis	**Preparation Phase - Day**									
	1	2	3	4	5	6	7	8	9	10**
*NDMA: ambient						x				
*NDMA: O_3-FP						x				
*NDMA: CLM-UFC						x				
TOC	x	x	x	x	x	x	x	x	x	x
COD	x	x	x	x	x	x	x	x	x	x
DO	x	x	x	x	x	x	x	x	x	x
Precursors										
THM/HAA-FP						x				
ATP										x

(b) Analysis	**Test Period - Day**													
	1**	2	3	4	5	6	7	8	9	10	11	12	13	14
*NDMA: ambient				x							x			x
*NDMA: O_3-FP				x							x			x
*NDMA: CLM-UFC				x							x			x
TOC	x	x	x	x	x	x	x	x	x	x	x	x	x	x
COD	x	x	x	x	x	x	x	x	x	x	x	x	x	x
DO	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Precursors	x	x	x	x	x	x	x	x	x	x	x	x	x	x
THM/HAA-FP				x							x			x
ATP														x

*NDMA tests: ambient = NDMA present in the sample without any additional treatment; O_3-FP = NDMA analysis after ozonation; CLM-UFC = NDMA analysis after chloramination at uniform formation conditions. **Same calendar date.

3.4.5 Testing for Adsorption of the NDMA Precursors to Anthracite

Sorption of the precursors to anthracite was determined in order to establish which mechanisms (i.e., sorption to media, sorption to biofilm, biodegradation) were responsible for

precursor removal. Batch adsorption tests were performed using 125 mL borosilicate glass serum bottles and fresh anthracite media. The anthracite and bottles were sterilized by autoclaving (20 min at 250 °C). Anthracite was weighed and added to the glass bottles, along with the aqueous matrix, as indicated in Table 3.12. The bottles were sealed with a rubber septum and crimped closed with an aluminum ring (Wheaton, Vernon Hills, IL). Next, the bottles were attached to a rotating shaker and mixed constantly at 20 rpm for 24 or 48 hours. The following control samples were included: blank (deionized water with 2.0 g anthracite), control (precursor-spiked wastewater and no anthracite), and negative control (wastewater without precursors and 2.0 g anthracite). After the desired contact time, bottles were opened and samples were filtered through a pre-rinsed syringe filter (Whatman 0.7 μM GF/F with GMF) to remove suspended anthracite particles. The filtrate was analyzed for the individual precursors.

Table 3.12: Experimental plan for anthracite sorption test with NDMA precursors used in biofiltration columns.

Sample ID	Time	Aqueous Matrix	Anthracite (g)
Blank	48 hr	100 mL deionized water	2.0
Control	48 hr	100 mL WW + precursors	0
Negative Control	48 hr	100 mL WW	2.0
A1	24 hr	100 mL WW + precursors	0.10
A2	24 hr	100 mL WW + precursors	0.20
A3	24 hr	100 mL WW + precursors	0.30
A4	24 hr	100 mL WW + precursors	0.40
A5	24 hr	100 mL WW + precursors	0.50
A6	24 hr	100 mL WW + precursors	2.0
B1	48 hr	100 mL WW + precursors	0.10
B2	48 hr	100 mL WW + precursors	0.20
B3	48 hr	100 mL WW + precursors	0.30
B4	48 hr	100 mL WW + precursors	0.40
B5	48 hr	100 mL WW + precursors	0.50
B6	48 hr	100 mL WW + precursors	2.0

WW = wastewater

3.5 Analytical Procedures

3.5.1 NDMA Analysis – High Level

Aqueous samples were analyzed by direct injection (20 µL) with liquid chromatography tandem mass spectrometry (LC-MS/MS) using isotope dilution with d6-NDMA (Cambridge Isotope Laboratories, Tewksbury, MA). A Luna C18(2) column (Phenomenex, Torrance, CA) was used for separation with the LC system (Agilent 1100 LC with binary pump and CTC PAL autosampler). The mobile phases 5 mM ammonium acetate in water (A) and methanol (B) were run at 0.8 mL/min on a gradient starting at 10% B, stepped to 65% B at 0.5 min, increased linearly to 100% B until 7 min and returned to 10% B over 3 min. The mass spectrometer (API 4000 triple quad, Applied Biosystems) was operated via multiple reaction-monitoring in positive-ion electrospray ionization (ESI+) mode with a source temperature of 375 °C. Two transitions were monitored for NDMA (75/43 and 75/58) and d6-NDMA (81/46 and 81/64). The reporting limit (0.34 µM or 25 µg/L) was set at five times the signal to noise ratio and based on the instrument detection limit (n = 12).

3.5.2 NDMA Analysis – Low Level with Extraction

One liter samples underwent automated solid phase extraction with a Dionex Autotrace 280 workstation (Thermo Scientific) by the Southern Nevada Water Authority Laboratory (Holady et al. 2012). Conditioned activated charcoal cartridges were used and extracts were eluted with dichloromethane and dried under nitrogen to 0.5 mL. Water was removed with sodium sulfate DryDisks, and the final concentration factor was 1:2000. Extracts were injected (2 µL) in splitless mode through a 30 m x 0.32 mm ID x 1.4 µm DB624 column with helium flow and into the GC-MS (Agilent 7000C). Parent (m/z = 75) and product ions (m/z = 47, 44, 58) were

monitored, and the reporting limit (2.5 µg/L) was set at three to five times the calculated method detection limit.

3.5.3 Total Trihalomethanes (THMs)

THMs were quantified using EPA method 524.3 by the Southern Nevada Water Authority Water Quality Chemistry Laboratory. Four THMs (bromoform, bromodichloromethane, chloroform, chlorodibromomethane) were measured. A Stratum PTC purge and trap concentrator with AQUATek 100 autosampler (Teledyne Tekmar) were used for THM extraction of a 40 mL sample. THM analysis used a Thermo Scientific TRACE gas chromatograph with Electronic Pressure Control and a Split/Splitless injection port coupled to a Thermo Scientific ISQ mass spectrometer. Samples were separated on a RTX-VMS GC column (Restek).

3.5.4 Total Haloacetic acids (HAAs)

HAAs were quantified using EPA method 552.2 by the Southern Nevada Water Authority Water Quality Chemistry Laboratory. Five haloacetic acids (bromoacetic acid, dibromoacetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid) were measured from a 60 mL sample. HAA analysis used a Varian CP-3800 gas chromatograph with dual Electron Capture Detectors and a CTC Analytics CombiPal Autosampler. Samples were separated with a J&W DB-1701 GC column (Agilent) and spectra were quantified with Dionex/Thermo Chromeleon version 6.8 software.

3.5.5 Free and Total Chlorine and Monochloramine – Low Concentration

Free and total chlorine were measured by the DPD method using a Hach kit with a handheld colorimeter (Hach Pocket Colorimeter II – Chlorine). 10 mL of sample was added to the vial to provide a zero absorbance reference. A pillow containing DPD (N,N-diethyl-pphenylenediamine) for free chlorine test or DPD and iodide for the total chlorine test was added

and the sample was mixed. Color change was measured by absorbance and color intensity was proportional to the chlorine concentration. The analysis range was 0.1 to 2.2 mg/L as Cl_2.

Chloramine was measured using a Hach kit and a spectrophotometer (Hach DR 5000). A pillow containing Monochlor F was added to 10 mL of sample and absorbance was measured after a 5 min reaction time. The analysis range was 0.04 to 4.50 mg/L as Cl_2.

3.5.6 Total Chlorine – High Concentration

Total chlorine above 10 mg/L as Cl_2 was measured by iodometric titration. A 0.2 M sodium thiosulfate solution was standardized using a known concentration of potassium iodate solution. A known volume of the sample containing chlorine was added to a flask with 3 mL aliquots of 3 M HCl and 10 g/L KI. The sodium thiosulfate titrant was added dropwise with a burette while swirling the flask until the solution became clear (i.e., yellow color disappeared). Stoichiometric calculations were used to determine the chlorine concentration based on the amount of titrant added to the solution.

3.5.7 Ozone Concentration

Ozone concentration was measured using the indigo method, Standard Method 4500-O_3 (Rice et al. 2012), with modifications that used sample weight (Rakness et al. 2010). Empty flask masses and the initial absorbance of the indigo solution were determined. Then, a 0.5 mL aliquot of the ozone stock solution was added to a flask containing indigo solution. The total mass and absorbance were input into a spreadsheet that accounts for sample dilution (by mass) and the ozone residual was determined as mg/L ozone.

3.5.8 Dissolved Oxygen (DO)

Dissolved oxygen was measured by luminescence using a portable probe (Hach sensION+ DO6). The probe was calibrated once with water-saturated air at the start of the biofiltration

study. The probe reading was confirmed (0.5 mg O_2/L) on one occasion with the Hach dissolved oxygen method (Method 8166) that utilizes the indigo carmine method, AccuVac ampules, and DR 6000 spectrophotometer.

3.5.9 Ammonium (NH_4^+)

Ammonium was measured using the AmVer™ Salicylate Test 'N Tube™ Method (Hach Method 10031). A 0.1 mL aliquot of the sample was added to the reagent vial containing chlorine. One pillow each containing ammonia salicylate reagent powder and ammonia cyanurate reagent powder were added to the vial. After mixing, the sample was allowed to sit and analyzed after twenty minutes using a spectrophotometer (Hach DR 5000) with a pre-programmed method at 655 nm. The analysis range was 0.4-50.0 mg/L as NH_4^+-N.

3.5.10 Total Organic Carbon (TOC) Analysis

A 40 mL sample was collected in an amber glass vial and acidified to pH less than 3 with hydrochloric acid (HCl) for TOC analysis with a Shimadzu TOC-V analyzer (Shimadzu Scientific Instruments, Carlsbad, CA). Samples were acidified within a few hours of collection and stored at 4 °C for up to 48 hours before analysis. Calibration standards (0-20 mg C/L) were prepared from a 1000 mg C/L glucose stock solution and a 100 mg C/L working stock solution. The stock solution was replaced every two months and calibration standards were prepared fresh for every analysis. Blanks were prepared by acidifying deionized water with HCl to pH < 3. One standard was analyzed every 6-8 samples as a calibration check.

3.5.11 Chemical Oxygen Demand (COD)

Chemical oxygen demand was measured using Hach low range (3-150 mg/L) COD digestion vials by the reactor digestion method (Method 8000) with dichromate. A 2 mL sample was added the vial and digested in a DRB 200 reactor for 120 minutes at 150 °C. Absorbance was measured

at 420 nm for the cooled sampled using a Hach DR 5000 spectrophotometer. The instrument was zeroed for each analysis with a blank prepared from deionized water.

3.5.12 Parachlorobenzoic Acid (pCBA)

Analysis of pCBA followed a previously published method (Vanderford et al. 2007) using an LC-MS/MS system (Agilent 1100 LC binary pump, CTC PAL autosampler, Applied Biosystems API 4000 triple quadrupole MS) equipped with a 10 µL sample loop. Gradient separation at 0.8 mL/min flowrate using a Phenomenex Luna C18(2) 150 x 4.60 mm, 5 µm column was performed with mobile phases 5 mM ammonium acetate in water (A) and methanol (B). The gradient started at 10% B, stepped up at 0.5 min to 60% B, increased linearly to 100% B until 5 min, and was held at 100% B for 2 min to finish the run. The mass spectrometer parameters were ESI negative-ion (ESI-) mode, a flow rate of 5 µL/s, and a source temperature of 550 °C. Three transitions were monitored (155/111, 155/35 and 157/37) and the analytical range was 1.0 µg/L to 100 µg/L.

3.5.13 Total Nitrogen (TN)

Total nitrogen was measured using the low range Persulfate Digestion Test 'N Tube™ Method (Hach Method 10071). A 2 mL aliquot of the sample was added to the Total Nitrogen Hydroxide Digestion reagent vial along with a pillow containing persulfate reagent and mixed. The sample was digested in a DRB 200 reactor for 30 minutes at 105 °C. After cooling, a Total Nitrogen reagent pillow A was added and allowed to react for three minutes, followed by Total Nitrogen reagent pillow B and a two minute reaction time. Then 2 mL of the treated, digested sample was transferred to a Total Nitrogen reagent C vial. After mixing, the sample was allowed to sit and was analyzed after five minutes using a spectrophotometer (DR 5000, Hach) with a pre-programmed method at 410 nm. The analysis range was 0.5-25.0 mg/L as N. The instrument

was zeroed with a blank prepared from deionized water and treated in the same manner as the sample.

3.5.14 Adenosine Triphosphate (ATP)

ATP was analyzed using a Deposit and Surface Analysis test kit (LuminUltra Technologies Ltd), which is designed for measuring ATP in biofilm and on biological filter media. The test uses firefly luciferase enzyme to produce light in the presence of ATP and the light is measured in a luminometer as Relative Light Units (RLU). Calibration was performed with 100 µL of UltraCheck 1. Luminase enzyme was rehydrated and tested to ensure a reading of >5,000 RLU. Media samples were gently rinsed with ultrapure water to remove unattached growth and dried with vacuum filtration. 1 g of media was transferred to 5 mL of UltraLyse 7 for extraction. After vigorous mixing and at least five minutes for extraction, the sample was diluted by transferring 1 mL to a 9 mL UltraLute Dilution Tube. Then 100 µL of the diluted sample was mixed with 100 µL of rehydrated luminase enzyme in an assay tube, swirled, and measured in the luminometer (PhotonMaster^{TM} Luminometer, LuminUltra, New Brunswick, Canada). LuminCalc software was used to calculate the total ATP (pg tATP/g sample) from the measured RLU value.

3.5.15 NDMA Precursors

Individual precursors were analyzed by direct injection with LC-MS/MS and monitored for the one or two mass transitions (Table 3.13). Except for UDMH and DMA, precursors were analyzed using a method similar to the NDMA analysis (ESI positive, Luna C18(2) column) with the following exceptions: 10 µL sample loop, source temperature of 500 °C, and the mobile phases consisted of 0.1% formic acid (A) and methanol (B). The gradient was 10% B for 5 minutes, increased linearly to 90% B until 10 minutes and held until 15 minutes. An external calibration with 7 points for each precursor was used. R^2 values of 0.995 or better were observed

for all compounds. Reporting limits were set at greater than five times the signal to noise ratio and were based on the instrument detection limit (n = 12) for individual precursors. There was no matrix suppression for the phosphate buffer.

UDMH and DMA were analyzed by direct injection LC-MS/MS using a separate method with a 10 µL sample loop and 5 µL/s injection flow rate. The mobile phases were 5 mM ammonium formate adjusted to pH 3 with formic acid (A) and acetonitrile (B) at a flow rate of 0.400 µL/min. The gradient was as follows: 10% A held for 2 minutes, linearly increased to 90% A until 12 minutes, and held at 90% A until 16 minutes. A 4 minute equilibration step at 10% A at the start of each run resulted in a 20 minute total run time. A SeQuant ZIC-HILIC 150 x 2.1 mm, 5 µm column (EMD Millipore, Billerica, MA) was used for separation.

Table 3.13: Parameters for LC-MS/MS analysis of NDMA precursors.

Precursor	**Analytical Range (µM)**	**Transitions**	**Column**	**Retention Time (min)**
TMDS	0.0025 – 0.125	371.2 / 285.2	Luna C18(2)	12.6
Daminozide	0.0075 – 0.20	161.0 / 143.1	Luna C18(2)	2.84
DMS	0.010 – 0.50	124.9 / 107.9	Luna C18(2)	3.78
2-F-DMH	0.005 – 0.25	139.0 / 96.1	Luna C18(2)	11.68
DMC-phenyl	0.005 – 0.25	223.1 / 105	Luna C18(2)	11.64
DMTC-phenyl	0.005 – 0.25	210.1 / 108.0	Luna C18(2)	12.51
DMC-dithio	0.005 – 0.25	312.0 / 223.1	Luna C18(2)	12.28
Ranitidine	0.0005 – 0.10	315.3 / 176.2	Luna C18(2)	8.75
UDMH	0.010 – 1.5	60.9 / 45.0	ZIC HILIC	7.59
DMA	0.100 – 5.0	46.0 / 31.1	ZIC HILIC	7.46

3.6 Sample Collection and Preservation

The three research issues required collection and preservation of various wastewaters, stock solutions and samples pending analysis. Table 3.14 summarizes the information for bulk wastewaters, stock solutions and experimental procedures. Table 3.15 summarizes the information for sample preservation and analytical holding times.

Table 3.14: Summary of bulk water collection and storage, stock solution storage, and conditions for samples during experimental procedures.

Item	Preservation Technique
Wastewater collected from local municipal wastewater treatment facility	Wastewater was transported in a cooler on ice and stored at 4 °C until used
Wastewater collected from non-local municipal wastewater treatment facility	Wastewater was shipped overnight on ice and stored at 4 °C until used
Wastewater with ammonia collected from municipal wastewater treatment facility	Wastewater was stored at 4 °C and used within two days while ammonia was still present
Chlorinated, chloraminated, and ozonated wastewater samples (NDMA)	Kept at room temperature during reaction time, then 4 °C until analysis
Chlorinated wastewater samples (THM/HAA-FP)	Kept at room temperature during reaction time, then 4 °C until analysis
Stock solutions in ultrapure water	Stored at 4 °C
Stock solutions in methanol (d6-NDMA)	Stored at -20 °C

Table 3.15: Techniques for sample preservation and holding times for analyses.

Test	Preservation	Holding Time
*NDMA: ambient	80 mg/L Sodium thiosulfate 1 g/L Sodium azide Store at 4 °C	Extraction within 7 days
*NDMA: O_3-FP	80 mg/L Sodium thiosulfate Store at 4 °C	Extraction within 7 days
*NDMA: CLM-UFC	80 mg/L Sodium thiosulfate Store at 4 °C	Extraction within 7 days
TOC	Adjust sample pH to < 3 with HCl Store at 4 °C	Analysis within 48 hours
COD	Store at 4 °C	Analysis within 48 hours
DO	None	Immediate analysis
Precursors	Store at 4 °C	Analysis within 7 days
THM/HAA-FP	Ammonium chloride Sodium thiosulfate No headspace and store at 4 °C	Analysis within 14 days
ATP	None	Immediate analysis
TN	Store at 4 °C	Analysis within 20 days
pCBA	Store at 4 °C	Analysis within 7 days
Free/Total Chlorine	None	Immediate analysis
Monochloramine	None	Immediate analysis
Ozone	None	Immediate analysis
Ammonia/Ammonium	None	Immediate analysis

*NDMA tests: ambient = NDMA present in the sample without any additional treatment; O_3-FP = NDMA analysis after ozonation; CLM-UFC = NDMA analysis after chloramination at uniform formation conditions.

3.7 Data Analysis and Interpretation

3.7.1 Issue One – Molar Yields

Molar yield (%) of NDMA formed was based on the assumed concentration (100 μM) of the precursor (Equation 1). Individual precursor concentrations were not determined and molar yields do not take into account compounds with structures that may lead to formation of more than one molecule of NDMA.

Equation 1: Calculation of NDMA molar yield per mole of precursor.

$$Molar\ Yield\ (\%) = \frac{moles\ of\ NDMA\ formed}{moles\ of\ precursor}\ x\ 100$$

Molar yields were plotted on bar graphs to determine trends in NDMA formation for each precursor based on bromide concentration (0, 50, or 1250 ppb), aqueous matrix constituents (ultrapure water, effluent organic matter or natural organic matter), ozone dose (0.5-1.5 mM), and hydroxyl radical scavenging (tBA or no tBA).

3.7.2 Issue Two – Oxidant Exposure, Significance and DBP Trade-offs

Oxidant exposure was calculated in Excel using the trapezoidal rule (Equation 2) to determine the area under the chlorination curve or ozone decay curve. Time steps were based on sample collection (Table 3.6 and Table 3.7).

Equation 2: Trapezoidal rule used to calculate oxidant exposure from concentration and contact time.

$$Area = \int_a^b f_x dx = (b-a)\frac{f(a)+f(b)}{2}$$

NDMA concentrations were plotted on bar graphs and compared among the parallel tests. Significant differences were based on Student's t-test calculations if duplicate values were available.

NDMA mitigation and THM/HAA formation were discussed together (qualitatively) in order to examine trade-offs in DBP formation. A quantitative comparison for mitigation/formation was made based on the available USEPA drinking water unit risks (Table 3.16).

Table 3.16: Drinking water unit risk values for NDMA, THMs, and HAAs.

Compound		**Drinking water unit risk (µg/L)***	**Average drinking water unit risk (µg/L)**
NDMA		1.4 E-3	1.4 E-3
THMs	Chloroform	1.7 E-7	1.15 E-6
	Bromodichloromethane	1.8 E-6	
	Dibromochloromethane	2.4 E-6	
	Bromoform	2.3 E-7	
HAAs	Dichloroacetic acid	1.4 E-6	1.7 E-6
	Trichloroacetic acid	2.0 E-6	
	Monochloroacetic acid	N/A	
	Bromoacetic acid	N/A	
	Dibromoacetic acid	N/A	

*Sources: USEPA 2016b; Office of Environmental Health Hazard Assessment (OEHHA) 2007
Note: THMs = trihalomethanes; HAAs = haloacetic acids; N/A = not available

3.7.3 Issue Three – Precursor Removal by Biofiltration

Precursor, TOC, COD, and DO concentrations were plotted on bar graphs and compared for the different columns (i.e., EBCTs). Significant differences for TOC, COD, and precursor removal among columns were determined using one-way analysis of variance (ANOVA).

Correlation between precursor removal and DO was examined by linear regression and checked for significant differences among EBCTs using a two-sample Student's t-test. For all statistical analyses, a 95% confidence level was used ($\alpha = 0.05$).

3.8 Quality Assurance / Quality Control

3.8.1 Quality Assurance

The potential sources of error in the experimental procedures include: unclean glassware, improper LC-MS/MS and GC-MS calibration, operator error, deterioration of samples or stock solutions, incorrect starting concentrations for stock solutions, and incorrect volume measurements for spikes. To ensure the quality of the data, the following precautions were taken:

- Clean, pre-silanized amber glass bottles were used for samples whenever possible. Reused glassware was cleaned as follows: soaked at least 24 hours in a solution of Micro-90® solution, rinsed with tap water, rinsed with deionized water, air-dried, and heated for one hour at 450 °C.
- NDMA analytical methods used isotopic dilution for accurate quantitation. Multiple product ion transitions were monitored for LC-MS/MS and GC-MS. Calibration was performed prior to each batch of samples to be analyzed. Sample injection was performed with an autosampler for consistency.
- Multiple product ion transitions were monitored for pCBA by LC-MS/MS.
- Indigo stock solutions for measuring ozone concentration met a minimum absorbance threshold, as recommended by the method.
- Duplicates samples were included at a minimum of 10% of samples.
- Equipment, such as pipettes, DO meters and spectrophotometers, was calibrated.

- Samples were preserved and stock solutions refrigerated. Thermometers were in each refrigerator and checked daily to verify constant temperature.
- Sodium hypochlorite, used for chlorination and chloramination, was standardized with each use since its concentration changes as it ages.
- Calculations were carefully checked for errors leading to incorrect concentrations of stock solutions, spike volumes, or dilution factors.

3.8.2 Quality Control

LC-MS/MS and GC-MS Analysis

A set of standards (minimum: n = 7) was used to calibrate the LC-MS/MS and GC-MS for NDMA, precursor and pCBA analysis. Linearity of the calibration curves was based on least squares and R^2 values always exceeded 0.995. Method reporting limits were set at 3-5 times the method detection limit (n = 12). Precision was evaluated based on duplicate samples (see Quality Assurance) and occasional duplicate analysis of a sample (5% of analyses). A sequence of blank-standard-blank was inserted every 6-8 analyses to ensure calibration was maintained over time. Analysis included a matrix spike for all matrices other than ultrapure water (e.g., wastewater) in order to evaluation matrix suppression or interference.

TOC Analysis

A set of freshly prepared standards (n = 6) was used for TOC calibration. Linearity of the calibration curves was based on least squares and R^2 values always exceeded 0.991. Precision was evaluated based on duplicate samples during each run and < 10% variation was verified. A sequence of blank-standard-blank was inserted every 6-8 analyses to ensure calibration was maintained over time.

TN, COD, and NH_4^+ Analysis

Hach test kits were used for TN, COD and NH_4^+ analysis. Blanks were prepared with deionized water and test tubes were wiped clean prior to measuring absorbance. Precision was verified by < 10% variation for duplicate samples.

Control samples

Controls (no treatment) and blanks (ultrapure water) were included with all experimental plans. In addition, all precursor stock solutions were analyzed for NDMA to ensure it was not present prior to experimental procedures.

CHAPTER 4

IDENTIFICATION OF OZONE-REACTIVE NDMA PRECURSORS

4.1 Abstract

Nitrosamines are a class of toxic disinfection byproducts commonly associated with chloramination, of which several were included on the most recent U.S. EPA Contaminant Candidate List. Nitrosamine formation may be a significant barrier to ozonation in water reuse applications, particularly for direct or indirect potable reuse, since recent studies show direct formation during ozonation of natural water and treated wastewaters. Only a few studies have identified precursors which react with ozone to form *N*-nitrosodimethylamine (NDMA). In this study, several precursor compound solutions, prepared in ultrapure water and treated wastewater, were subjected to a 10 molar excess of ozone. In parallel experiments, the precursor solutions in ultrapure water were exposed to gamma radiation to determine NDMA formation as a byproduct of reactions of precursor compounds with hydroxyl radicals. The results show six new NDMA precursor compounds that have not been previously reported in the literature, including compounds with hydrazone and carbamate moieties. Molar yields in ultrapure water were 61-78% for 3 precursors, 12-23% for 5 precursors and < 4% for 2 precursors. The presence of bromide was important for three compounds (1,1-dimethylhydrazine, acetone dimethylhydrazone and dimethylsulfamide), but it did not enhance NDMA formation for the other precursors. NDMA formation due to chloramination was minimal compared to formation due to ozonation, suggesting distinct groups of precursor compounds for these two oxidants. Hydroxyl radical reactions with the precursors will produce NDMA, but formation is much greater in the presence of molecular ozone. Also, hydroxyl radical scavenging during ozonation led to increased NDMA formation. Molar conversion yields were higher for several precursors in wastewater as

compared to ultrapure water, which could be due to catalyzed reactions with constituents found in wastewater or hydroxyl radical scavenging.

4.2 Introduction

Nitrosamines, particularly *N*-Nitrosodimethylamine (NDMA), have received a great deal of attention as emerging water contaminants of concern. NDMA is classified as a B2 carcinogen by the U.S. Environmental Protection Agency, it is listed on the third Contaminant Candidate List (USEPA 2014a), and it was part of the Unregulated Contaminant Monitoring Rule 2 (USEPA 2013). Although no federal regulations have been established for NDMA, the California Department of Public Health has set a drinking water notification level of 10 ng/L (CEPA 2014). The E-6 (1 in 1,000,000) cancer risk level for drinking water is 0.7 ng/L (USEPA 2016). In addition to many direct anthropogenic sources (e.g., rubber manufacturing, circuit board manufacturing and rocket fuel production), NDMA is formed as a disinfection byproduct (DBP) in drinking water and wastewater treatment (Mitch et al. 2003).

As potable water demands and shortages rise, more communities are considering reuse of wastewater as an option for increasing the overall water supply. Ozone is effective for treating pathogens and trace organic contaminants (Gerrity and Snyder 2011; Ikehata et al. 2008; Sonntag and von Gunten 2012) and, therefore, is a promising treatment technology for potable water reuse applications. Other advantages of ozone use include: treatment versatility for pre- and post-disinfection, decolorization, taste and odor removal, coagulation assistance, and zero residual generation. However, the formation of ozone byproducts, such as NDMA, could be a barrier to the use of ozone in potable water reuse applications.

NDMA formation is commonly associated with chloramination (Choi and Valentine 2002; Mitch et al. 2003), but recent studies indicate that direct formation during ozonation also occurs (Gerrity et al. 2015; Hollender et al. 2009; Kosaka et al. 2009; Nawrocki and Andrzejewski 2011; Oya et al. 2008; Padhye et al. 2013; Pisarenko et al. 2012; Schmidt and Brauch 2008; von Gunten et al. 2010; Yoon et al. 2011). Initially, the chloramination pathway was thought to involve nucleophilic substitution between monochloramine and a secondary amine (Choi and Valentine 2002; Mitch and Sedlak 2002). This reaction resulted in unsymmetrical dimethylhydrazine (UDMH), which was subsequently oxidized by chloramines to form NDMA. The modified pathway involves the reaction of dichloramine and a model secondary amine, dimethylamine (DMA), which forms chlorinated unsymmetrical dimethylhydrazine (Cl-UDMH) as an intermediate. Dissolved oxygen oxidizes Cl-UDMH to NDMA (Schreiber and Mitch 2006). On the other hand, very little is known about the NDMA formation pathway and any intermediates that are formed with ozonation. Von Gunten et al. (2010) proposed a mechanism for NDMA formation from dimethylsulfamide (DMS), which is a degradation product of the fungicide tolylfluanid. The mechanism is bromide-catalyzed and results in the loss of $–SO_2$ as a leaving group and N-N bond formation. While UDMH conversion to NDMA is likely a basic oxidation reaction, additional pathways for other precursors' reactions with ozone have not been identified.

In order for NDMA to form as a disinfection byproduct from ozonation, certain compounds must be present in the water. Besides DMS and other metabolites of tolylfluanid, a few other precursors have been identified, including: daminozide; UDMH; 1,1,1',1'-Tetramethyl-4,4'-(methylenedi-p-phenylene)disemicarbazide (TMDS); dimethyldithiocarbamate (DMDTC); poly(diallyldimethylammoniumchloride) (polyDADMAC); *N*,*N*-Dimethyl-*p*-phenilenediamine

(DMPD); methylene blue; 4,4′-hexamethylenebis(1,1-dimethylsemicarbazide) (HDMS); and. 1,1,5,5-tetramethylcarbohydrazide (TMCH) (Kosaka et al. 2009; Kosaka et al. 2014; Mitch and Sedlak 2004; Oya et al. 2008; Schmidt and Brauch 2008; Padhye et al. 2011; Padhye et al. 2013; von Gunten et al. 2010). The chemical structures of these compounds include hydrazines, semicarbazides, sulfamides, and dimethylamines. In particular, compounds with dimethylamine bonded directly to a nitrogen atom or separated from another nitrogen by a good leaving group (e.g., $-SO_2$) form NDMA with significant molar conversion yields (i.e., 10-80%) (Kosaka et al. 2009; Schmidt and Brauch 2008; von Gunten et al. 2010). Precursors with the dimethylamine and no additional nitrogen may also form NDMA upon ozonation, but the yields are < 0.01% (Oya et al. 2008; Padhye et al. 2011; Padhye et al. 2013).

In more complex water matrices, certain factors have been shown to impact NDMA formation with ozone, including dissolved ions, pH, and hydroxyl radicals. For example, bromide ions catalyze the reaction of DMS with ozone (von Gunten et al. 2010). Oya et al. (2008) found that NDMA formation by ozonation of dimethylamine dyes increased in river water compared to ultrapure water. They also noticed increased NDMA formation with increased pH; however, this was attributed to changes in the reaction mechanism at different pH values. Dissolved molecular ozone and hydroxyl radicals can be involved in both formation (Andrzejewski et al. 2008, Schmidt and Brauch 2008) and destruction of NDMA (Lee et al. 2007b; Mezyk et al. 2004). However, the extent of each oxidant's role is not well understood.

The goal of this study was to identify specific organic structures that may contribute to the direct formation of NDMA by ozonation. Only a few precursors have been identified in literature, and there is much to gain in understanding which compounds lead to NDMA

formation. If model precursors can be identified, then specific strategies can be utilized to remove them prior to ozonation, thereby limiting the production of NDMA.

4.3 Materials and Methods

4.3.1 Tested Waters and Equipment

The tested water matrices included ultrapure water and wastewater effluent from a pilot-scale membrane bioreactor (0.032 MGD). The ultrapure water was buffered at neutral pH with phosphate buffer (1 mM or 5 mM final concentration). The wastewater came from a municipal source with treatment consisting of primary sedimentation with ferric chloride addition, biological secondary treatment with partial nitrification, and tertiary membrane microfiltration (0.40 µm nominal pore size). Table 4.1 contains water quality information and key treatment parameters for the wastewater effluent. No additional filtration was performed, and wastewater was stored at 4 °C for preservation prior to bench-scale work.

Ozonated water was generated using an oxygen-fed generator (model CFS-1A, Ozonia North America, Inc., Elmwood Park, NJ, USA) to diffuse ozone into cold, ultrapure water as described previously (Wert et al. 2009). Oxygenated water was produced when the ozone generator was switched off. The ozone stock solution was typically between 65 and 85 mg/L as O_3 and the oxygenated water was 8 mg/L as O_2. Aliquots of the ozonated or oxygenated water were measured in a graduated cylinder and quickly poured into the amber glass bottle (125 mL) with the test water. The containers were capped and inverted to mix the sample. Dilution factors based on addition of the ozone or dissolved oxygen stock aliquots were accounted for in all measurements.

Table 4.1: Water quality for membrane bioreactor effluent. Analysis occurred during the week in which the wastewater was collected for bench-scale tests.

Parameter	Unit	Value
pH	-	6.7-7.1
Ammonium	mg-N/L	2
Total organic carbon	mg-C/L	5-8*
Total nitrogen	mg-N/L	4-8*
Bromide	mg/L	0.157
Alkalinity	mg/L as $CaCO_3$	125
Nitrite	mg-N/L	0.064

*Range of measured values for monthly tests.

4.3.2 Analytical Methods and Reagents

The following chemicals were purchased as potential NDMA precursors: 2-Furaldehyde 2,2-dimethylhydrazone (2-F-DMH) from Alfa Aesar (Heysham, Lancashire, United Kingdom); acetone dimethylhydrazone (acetone-DMH), *N*,*N*-dimethylsulfamide (DMS), and Dacarbazine from TCI (Toyko, Japan); TMDS from TCI America (Portland, OR); Streptozocin and Ranitidine hydrochloride (RNTD) from Sigma (St. Louis, MO); UDMH and Dimethylamine hydrochloride (DMA) from Aldrich (St. Louis, MO); Ziram from Sigma-Aldrich (St. Louis, MO); *N*-Nitrososarcosine and Atazanavir from Toronto Research Chemicals (Ontario, Canada); Daminozide from Fluka (Steinheim, Germany); *N*-{[(dimethylamino)carbonyl]oxy}-2-phenylacetamide (DMC-phenyl), *N*-1-(4-methylphenyl)-2,2-dimethylhydrazine-1-carbothioamide (DMTC-phenyl), *N'*-{[(dimethylamino)carbonyl]oxy}-4-(1,3-dithiolan-2-yl)benzenecarboximidamide (DMC-dithio), and *N*-1-(3-{[(2,2-dimethylhydrazino)carbonyl] amino}-4-methylphenyl)-2,2-dimethylhydrazine-1-carboxamide (DMSC) from Maybridge (Cornwall, United Kingdom). Chemical structures are shown in Table A.1.

Neat standards of the precursors were individually dissolved in ultrapure water and/or acetonitrile (for solubility) at 10 mM, except for DMC-phenyl, DMSC, DMC-dithio, DMTC-phenyl and Atazanavir which were dissolved at 3.2-4.8 mM (1000 mg/L) due to a limited supply. These solutions were kept at 4 °C in amber vials to limit the potential for hydrolysis or photolysis. Phosphate buffer solution (1 M) was prepared from equal molar amounts of KH_2PO_4 and Na_2HPO_4 and adjusted to pH 7. Bromide solution (4.18×10^{-4} M or 33.4 mg/L as Br^-) was prepared from sodium bromide. A concentrated (34 wt%) hydrogen peroxide solution was diluted to 0.1 wt% (1000 mg/L) for use as a spike solution. Parachlorobenzoic acid (pCBA) solution was prepared from sodium parachlorobenzoate (500 mg/L as pCBA). Tert-butyl alcohol (tBA) was diluted slightly to make a 10.04 M solution that would remain liquid at room temperature. All solutions were prepared using ultrapure water (18.2 MΩ·cm). The phosphate salts were obtained from Fisher Scientific (Fair Lawn, NJ), sodium bromide was from Sigma-Aldrich (St. Louis, MO), pCBA was from Pfaltz & Bauer (Waterbury, CT), tBA was from Acros Organics (Fair Lawn, NJ), and the hydrogen peroxide solution was from EnviroTech Chemical Services (Modesto, CA).

Precursors were individually spiked into the test water (30 mL) at 100 µM in amber glass bottles. Bromide, hydrogen peroxide, parachlorobenzoic acid (pCBA) or tert-butyl alcohol (tBA) spikes were added to the samples next, as appropriate. Ozone-saturated water was added to give a final concentration of approximately 1 mM (48 mg O_3/L), which is at least a 10-fold molar excess (compared to the precursor concentration) to ensure the reaction is not limited by ozone. Oxygen-saturated water was added to give a final concentration of approximately 0.25 mM (8 mg O_2/L), which was the maximum concentration possible for the given equipment. Samples were capped and mixed by inverting after addition of ozonated or oxygenated water and left

undisturbed at room temperature (23 °C) overnight in the dark. Based on an ozone decay curve for ultrapure water, the ozone residual (1.52 mM initially) was less than 1.67 x 10^{-2} mM after three hours. Therefore, leaving the bottles to sit overnight was sufficient to eliminate the ozone residual. Ozone concentration was measured using the indigo method (Rakness et al. 2010).

Chloramine NDMA formation potential (CLM-FP) was evaluated based on a previously published method (Mitch and Sedlak 2002). Prior research uses the abbreviation NDMA-FP; however, this does not distinguish between chloramine and ozone-reactive NDMA precursors. Therefore, CLM-FP is used instead. Samples were spiked with preformed monochloramine at 2 mM (140 mg/L) as Cl_2 and stored at room temperature (23 °C) in the dark. Ozonated samples were allowed to sit overnight to ensure there was no ozone residual prior to chloramination. Samples were quenched after ten days with 150 µL of 0.2 M sodium thiosulfate from EMD Chemicals, Inc (Gibbstown, NJ), and absence of chlorine residual was verified using a Hach DPD test kit. The preformed monochloramine stock solution was prepared by adding sodium hypochlorite to a rapidly stirring solution of ammonium chloride with a few drops of 5 N sodium hydroxide to maintain pH above 8 and prevent monochloramine decomposition during initial mixing (Mitch and Sedlak 2002). Sodium hypochlorite from Sigma-Aldrich (St. Louis, MO), 10-14 wt% free available chlorine, was standardized using iodometric titration prior to use. Ammonium chloride was obtained from Sigma-Aldrich (St. Louis, MO) and sodium hydroxide from Fisher Scientific (Fair Lawn, NJ).

Radiolysis tests were conducted to isolate the impact of hydroxyl radicals on NDMA formation. Phosphate buffered (1 mM) ultrapure water was saturated with nitrous oxide (N_2O gas) for one hour. Aqueous electrons and •OH are formed by direct gamma radiolysis of the water (Peller et al. 2003). Aqueous electrons are scavenged by N_2O to form N_2O^-, which

decomposes to N_2 and $O^{\bullet -}$. The $O^{\bullet -}$ is subsequently protonated by water to form •OH. Samples were shipped overnight on ice in amber glass containers to the Radiation Laboratory at the University of Notre Dame. The samples were subjected to gamma irradiation at 1.93 Gy/min (Gy = Gray = Joule of radiation absorbed per kilogram of matter) with a Shepherd 109 ^{60}Co source for specific time lengths (2-20 min) corresponding to different hydroxyl radical concentrations (Peller et al. 2003).

NDMA analysis was performed by liquid chromatography tandem mass spectrometry (LC-MS/MS) using isotope dilution with d6-NDMA purchased from Cambridge Isotope Laboratories (Andover, MA, USA). An Agilent 1100 LC binary pump and a CTC PAL autosampler equipped with a 20 µL sample loop were used for all analyses. A 30 µL sample was injected at a flow rate of 5 µL/s. The mobile phase consisted of a binary gradient of 5 mM ammonium acetate from J.T. Baker (Philipsburg, NJ) in water (A) and 100% methanol (B) from Honeywell Burdick & Jackson (Muskegon, MI) at a flow rate of 800 µL/min. The gradient was as follows: 10% B held for 0.50 minutes, stepped to 65% B at 0.51 minutes and increased linearly to 100% B until 7 minutes. A 3 minute equilibration step at 10% B at the start of each run resulted in a 10 minute total run time. A Luna C18(2) 150 x 4.60 mm, 5 µm column (Phenomenex, Torrance, CA) was used for separation. The mass spectrometer was operated via multiple reaction-monitoring in positive-ion mode with a source temperature of 375 °C. Two transitions were monitored for NDMA (75/43 and 75/58) and d6-NDMA (81/46 and 81/64). NDMA standards were purchased from Ultra Scientific (Kingstown, RI, USA). An eight point calibration curve for NDMA (25-3000 ppb or 0.34-40.5 µM) was prepared in ultrapure water and linear regression for the calibration curve always exceeded 0.995. Calibration standards were kept at 4 °C in amber vials. The reporting limit (0.34 µM or 25 µg/L) was set at greater than five times the signal to noise

ratio and was based on the instrument detection limit (n = 12, concentration = 25 µg/L). There was no matrix suppression for the phosphate buffer. Recovery for the wastewater matrix spike was 102% and NDMA in the ozonated wastewater was below the reporting limit.

Individual precursors were analyzed by with LC-MS/MS and monitoring corresponding mass transitions for: TMDS (371.17/285.2), Daminozide (161/143.1), DMS (124.9/107.9), 2-F-DMH (139/96.1), DMC-phenyl (223.1/105), DMTC-phenyl (210.1/108), DMC-dithio (312/223.1), Ranitidine (315.3/176.2; 315.3/130.1), UDMH (60.9/45) and DMA (46/31.1). Except for UDMH and DMA, precursors were analyzed using a method similar to the NDMA analysis with the following exceptions: 10 µL sample loop, source temperature of 500 °C, and the mobile phases consisted of 0.1% formic acid (A) and methanol (B). The gradient was 10% B for 5 minutes, linearly increased to 90% B until 10 minutes and held until 15 minutes. UDMH and DMA were analyzed by LC-MS/MS using a separate method with a 10 µL sample loop and 5 µL/s injection flow rate. The mobile phases were 5 mM ammonium formate adjusted to pH 3 with formic acid (A) and acetonitrile (B) at a flow rate of 0.400 µL/min. The gradient was as follows: 10% A held for 2 minutes, linearly increased to 90% A until 12 minutes, and held at 90% A until 16 minutes. A 4 minute equilibration step at 10% A at the start of each run resulted in a 20 minute total run time. A SeQuant ZIC-HILIC 150 x 2.1 mm, 5 µm column (EMD Millipore, Billerica, MA) was used for separation. An external calibration with 7 points for each precursor (0.005 to 0.25 µM) was used. R^2 values of 0.995 or better were observed for all compounds. Reporting limits were set at greater than five times the signal to noise ratio and were based on the instrument detection limit (n = 12) for individual precursors. There was no matrix suppression for the phosphate buffer.

4.3.3 Selection of Model NDMA Precursors

The literature suggests that certain structures are more likely to form NDMA by ozonation, as mentioned in the introduction. Therefore, the search for model precursors was based on structural moieties, such as a dimethylamine group, hydrazine, sulfamide, hydrazone and carbamate. The selected compounds contain the dimethylamine group and at least one other nitrogen, which forms the building block for NDMA. In some compounds, the building block is located on the end of the structure (e.g., DMSC) and for other compounds it is more centrally located (e.g., Atazanavir). In most compounds, the dimethylamine is bonded to an additional nitrogen; however, the carbamates have a $–CO_2$ group separating the nitrogens. *N*-nitrososarcosine already is a nitrosamine and would form NDMA with the loss of $–CO_2$. The precursors were identified using online structure search tools (e.g., eMolecules, Sigma-Aldrich and Ryan Scientific substructure search, ChemSpider structure search and DrugBank ChemQuery) for compounds available for purchase, which is not necessarily an indication of commercial or industrial use or their potential presence in treated wastewater effluents. Table 4.2 lists the abbreviations and characteristics of the precursors selected in this study. Appendix A contains a detailed list of precursors found in the literature, their structures and molar yields of NDMA formation.

4.4 Results and Discussion

4.4.1 Molar Yields in Buffered Ultrapure Water

Each of the selected precursor compounds were individually reacted with a 10-fold molar excess of ozone in 5 mM phosphate buffered ultrapure water. Figure 4.1 shows the molar yields of NDMA formed with ozonation. In parallel tests with dissolved oxygen (8 mg O_2/L), NDMA

was detected for UMDH, RNTD, and daminozide, but concentrations were well below the MRL. Molar yields (mole NDMA / mole calculated precursor amount) varied widely, from 0-78%. There was no NDMA formation observed for *N*-nitrososarcosine, atazanavir, dacarbazine and streptozocin. Ozone may react with these compounds, but not in a manner that results in NDMA. As expected, DMS and DMA did not result in NDMA formation. The reaction between ozone and DMS is catalyzed by bromide (von Gunten et al. 2010), which was not present in the ultrapure water matrix. DMA reacts with dichloramine to form NDMA, but ozonation of amines mainly results in the formation of aldehydes (Munoz and von Sonntag 2000). Very low molar yields (< 0.4%) for ozonation of DMA have been reported (Andrzejewski et al. 2008; Yang et al. 2009), but the reaction may be due to nitrosation rather than ozonation. Ziram and RNTD formed NDMA, but at low molar yields (< 0.03%) and below the MRL. These results were expected based on another study with Ziram (Padhye et al. 2013) and because the compounds have a similar structure to dyes containing a DMA group, but no additional nitrogen (Oya et al. 2008).

Table 4.2: Compounds in this study tested as NDMA precursors.

Compound Name	Abbreviation	CAS #	Moieties	Notes	Additional References
Acetone Dimethylhydrazone	Acetone DMH	13483-31-3	Hydrazone + DMA	Synthesis building block	
2-Furaldehyde 2,2-Dimethylhydrazone	2-F-DMH	14064-21-2	Hydrazone + DMA	Synthesis building block	
N-1-(3-{[(2,2-dimethyl hydrazino) carbonyl]amino}-4-methylphenyl)-2,2-dimethylhydrazine-1-carboxamide	DMSC	unavailable	Urea + DMA	No known uses	
N-1-(4-methylphenyl)-2,2-dimethylhydrazine-1-carbothioamide	DMTC-phenyl	unavailable	Thiourea + DMA	No known uses	
N'-{[(dimethylamino) carbonyl]oxy}-4-(1,3-dithiolan-2-yl) benzenecarboximidamide	DMC-dithio	unavailable	Carbamate + DMA	No known uses	
N-{[(dimethylamino)carbonyl]oxy}-2-phenylacetamide	DMC-phenyl	unavailable	Carbamate + DMA	No known uses	
Atazanavir		198904-31-3	Hydrazine (centrally located)	Antiretroviral drug for HIV	
Dacarbazine		4342-03-4	Hydrazone + DMA	Antineoplastic agent for melanoma	a
N-nitrososarcosine		13256-22-9	NDMA	Probable carcinogen found in tobacco products and in cooked foods with sodium nitrite	b, c
Streptozocin		18883-66-4	NDMA	Antibiotic produced by Streptomyces achromogenes	
Dimethylsulfamide	DMS	3984-14-3	Sulfamide + DMA	Decomposition product of fungicide tolylfluanid	a, d
Daminozide		1596-84-5	Hydrazine + DMA	Plant growth regulator	a
1,1-Dimethylhydrazine	UDMH	57-14-7	Hydrazine + DMA	Rocket fuel component, decomposition product of daminozide	a
1,1,1′,1′-tetramethyl-4,4′-(methylene-di-p-phenylene) disemicarbazide	TMDS	85095-61-0	Urea + DMA	Yellow inhibitor and light stabilizer for polyamide resins	e
Ranitidine Hydrochloride	RNTD	66357-59-3	DMA	Histamine-2 blocker for treating and preventing stomach ulcers	f, g, h
Dimethylamine Hydrochloride	DMA	506-59-2	DMA	Present in wastewater	i, j, k, l

[a]Schmidt and Brauch 2008; [b]Wu et al. 2012; [c]Wu et al. 2014; [d]von Gunten et al. 2010; [e]Kosaka et al. 2009; [f]Shen and Andrews 2011; [g]Shen and Andrews 2013; [h]Le Roux et al. 2012; [i]Mitch and Sedlak 2002; [j]Andrzejewski et al. 2008; [k]Yang et al. 2009; [l]Bond and Templeton 2011

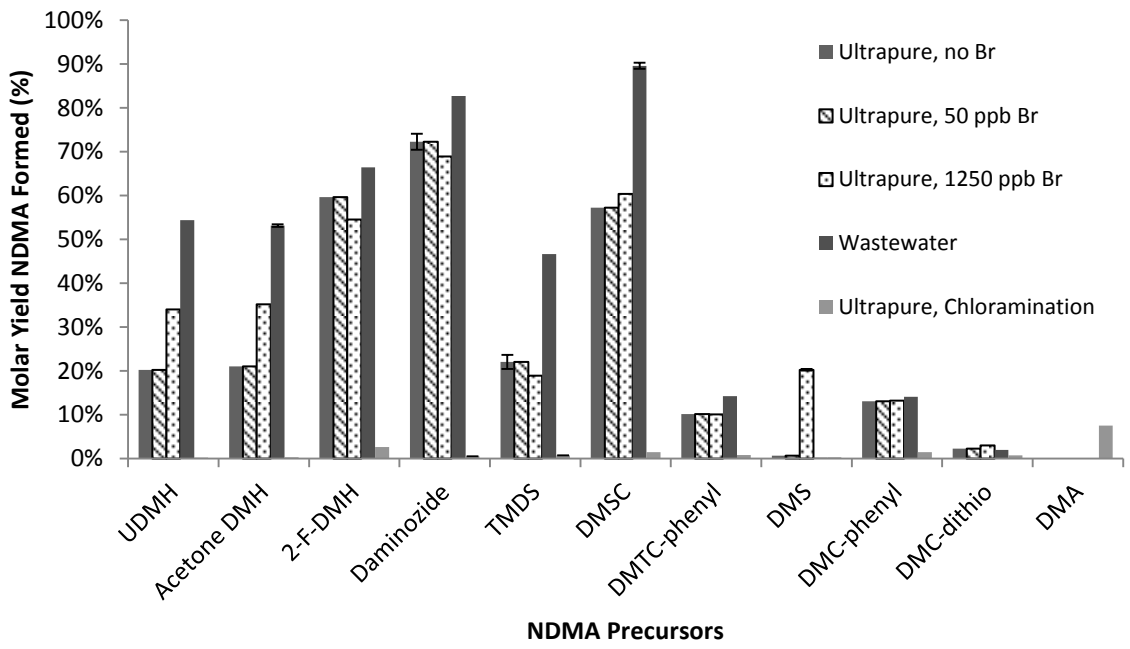


Figure 4.1: Molar yield of NDMA formed by ozonation (O_3 = 1 mM) of precursors in buffered ultrapure water at pH 7 with and without bromide (Br) addition (0, 50, 1250 ppb), by ozonation in wastewater, and by chloramination (140 mg/L or 2 mM as Cl_2) in buffered ultrapure water.

Several of the model compounds formed NDMA upon ozonation. The hydrazones, acetone-DMH and 2-F-DMH, are similar to the known precursor UDMH. However, these compounds have a double bond which makes them potentially more reactive with ozone (e.g., ozonolysis reaction). DMSC and DMTC-phenyl are similar to the known precursor TMDS. DMC-phenyl and DMC-dithio are related to DMS in that the nitrogen atoms are separated by a good leaving group (e.g., $–SO_2$, $–CO_2$). These carbamate compounds differ from DMDTC, which was previously reported to form NDMA (Padhye et al. 2013; Sedlak et al. 2005). Although the mechanism for NDMA formation with ozone is not fully understood, it seems rearrangement

with the loss of a small molecule, CO_2, results in the nitrogen-nitrogen bond. Consequently, other dimethylcarbamate compounds may potentially be precursors.

Acetone-DMH was found to be unstable in water. Through LC-MS/MS analysis, it was confirmed that acetone-DMH degraded rapidly to UDMH, which explains the very similar results between these two compounds. In addition, UDMH slowly degraded in water, so calibration standards were prepared fresh every two weeks. No other compounds showed short-term instability in water; however, NDMA was detected in old stock solutions (> 1 yr) for 2-F-DMH, UMDH, and TMDS. NDMA was present in fresh solutions of 2-F-DMH and Ziram, which suggests there may be residual NDMA from synthesis. DMA was detected in old stock solutions for 2-F-DMH, UMDH, DMC-dithio, DMC-phenyl and DMS, which may be due to slow hydrolysis of these precursors.

4.4.2 Influence of Bromide on Molar Yields

The ozonation bench-scale experiments in 5 mM phosphate buffered ultrapure water were repeated with two different bromide spikes. Molar yields for some compounds are enhanced by bromide, while others remain constant (Figure 4.1). Although there is a slight decrease in molar yield for 2-F-DMH, daminozide, and TMDS, this is probably the effect of an increased ozone demand caused by the bromide spike at 1250 ppb. A greater ozone demand could result in lower NDMA formation.

In agreement with work by von Gunten et al. (2010), there was considerably more NDMA formed in solutions of DMS containing bromide. Bromide concentration was also significant for NDMA formation in solutions of UDMH and acetone-DMH. DMC-phenyl and DMC-dithio, which have the $–CO_2$ leaving group, did not show increased formation with bromide. This suggests that the reaction pathway for these compounds is different than the bromide-catalyzed,

–SO_2 leaving reaction for DMS. It appears that there are multiple reaction pathways for NDMA precursors that react with ozone which need further investigation.

4.4.3 Effect of Hydrogen Peroxide Addition and Ozone Dose

The effects of hydrogen peroxide and ozone dose on NDMA formation were investigated for two compounds (TMDS and 2-F-DMH) in 5 mM phosphate buffered ultrapure water at pH 7. Hydrogen peroxide was added at O_3:H_2O_2 mg/L ratios of 1:0.25 and 1:0.50 (or mM ratios 1:0.35 and 1:0.70). As seen in Figure 4.2, the addition of hydrogen peroxide had minimal impact on NDMA level. This was also reported by Oya et al. (2008).

The two precursor compounds were individually reacted with ozone at doses ranging from 0.1 to 1.5 mM O_3 in buffered ultrapure water. Initial ozone dose affected the extent of NDMA formation. For 2-F-DMH, NDMA formation increased from 0.1 to 0.5 mM O_3 and then leveled off (Figure 4.3). The maximum molar conversion yield was 70%. Likely, increasing the ozone dose above 0.5 mM did not cause more NDMA formation because the precursor had reacted completely to form NDMA and other transformation products. In the case of TMDS, there was a linear correlation (R^2 = 0.98) between NDMA formation and ozone dose in the tested range. No maximum molar conversion yield was achieved at these ozone doses.

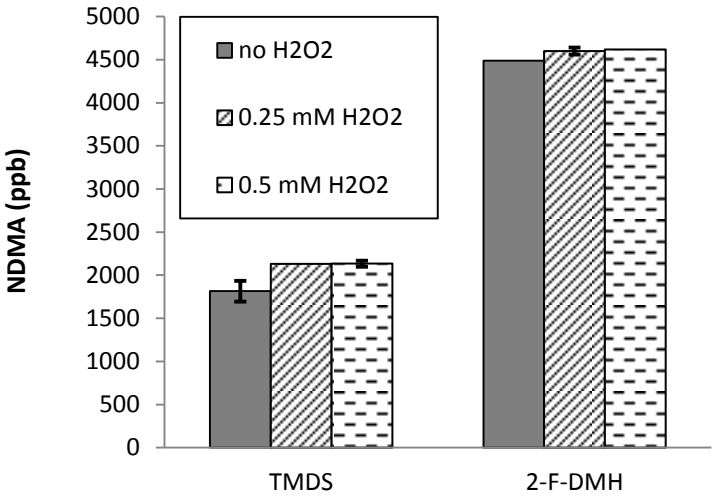


Figure 4.2: Effect of hydrogen peroxide (H_2O_2) on NDMA formation by ozonation (O_3 = 1 mM) in buffered ultrapure water at pH 7. Error bars represent one standard deviation (n = 2).

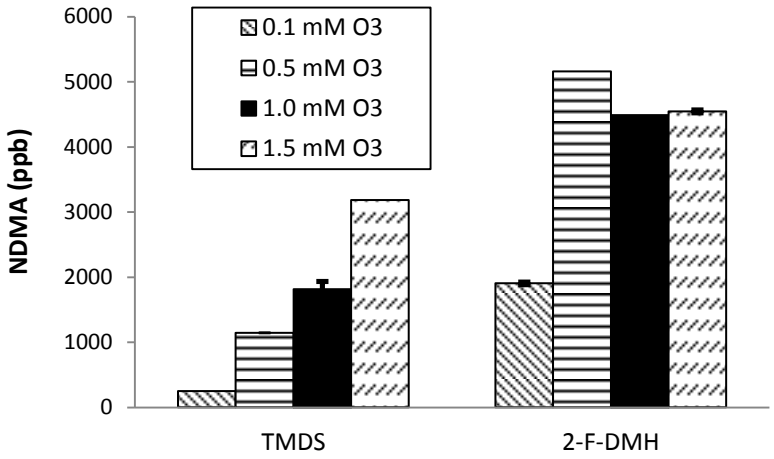


Figure 4.3: Effect of ozone (O_3) dose on NDMA formation by ozonation in buffered ultrapure water at pH 7. Error bars represent one standard deviation (n = 2).

4.4.4 NDMA Formation Potential with Chloramination

Chloramine NDMA formation potential is a test to quantify precursors that react with chloramine to form NDMA. At a high chloramine dose, the test serves as a way to determine the maximum formation potential for NDMA. In this study, CLM-FP for the targeted precursors was investigated through 10-day tests in 5 mM phosphate buffered ultrapure water before and after ozonation. Experimental parameters were kept the same for comparison to previous tests. One set of samples was spiked with preformed monochloramine (140 mg/L as Cl_2). The other set of samples was ozonated and allowed to react for 24 hours before spiking with preformed monochloramine.

A comparison of NDMA formation in buffered ultrapure water after ozonation only and ozonation followed by chloramination can be seen in Figure 4.4. The NDMA molar conversion yields are summarized in Table A.2. With the exception of DMA, all yields for chloramination were below 3% and most were below 1.5%. The precursors have a much higher NDMA formation with ozone as compared to chloramines, making these precursors distinctly different from other dimethylamine-containing compounds. As expected, DMA had the highest molar conversion yield with chloramines (7.5%). CLM-FP decreased 30% after ozonation for DMA, which agrees with previous research that ozonation can reduce CLM-FP associated with chloramination (Pisarenko et al. 2012).

Molar yields for UDMH and acetone-DMH increased slightly for chloramination following ozonation (Figure 4.4). This suggests that transformation products from the ozonation reaction may be NDMA chloramination precursors. Ozonation of tertiary amines can result in DMA formation (Lee et al. 2007a), which would result in NDMA formation with subsequent chloramination.

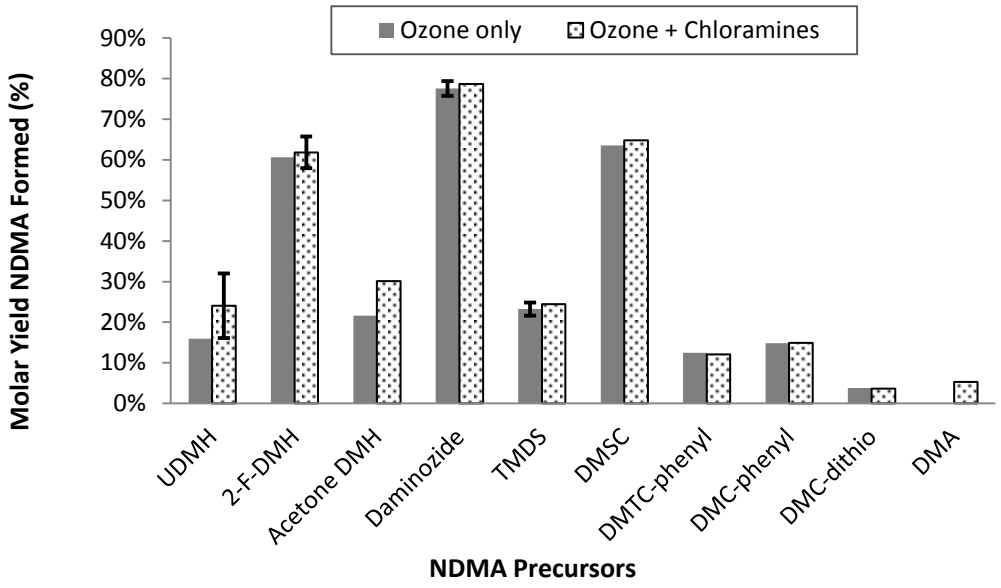


Figure 4.4: Comparison of NDMA formation with ozonation only (O_3 = 1 mM) and ozonation-chloramination (O_3 = 1 mM; 140 mg/L as Cl_2) in buffered ultrapure water at pH 7. Error bars represent one standard deviation (n = 2).

4.4.5 Comparison of Molecular Ozone and •OH as Oxidants for NDMA Formation

Gamma radiolysis of three precursors (DMTC-phenyl, 2-F-DMH, and TMDS) was performed in 1 mM phosphate buffered ultrapure water in order to isolate the effect of •OH reactions on NDMA formation. As a control test, buffered ultrapure water spiked with NDMA was irradiated in parallel with the precursor-containing solutions, and slight NDMA destruction due to •OH was measured. Therefore, results for the gamma radiation experiments are a combination of NDMA formation from the precursors reacting with •OH and subsequent NDMA destruction by •OH, though the latter was negligible.

NDMA was formed by all three precursors (Figure 4.5) at low molar yields (0.2-4.3%), which were calculated based on the amount of precursor that degraded after 20 min (38.6 Gy).

Due to low NDMA concentration, samples underwent solid phase extraction and GC-MS/MS analysis (Holady et al. 2012). DMTC-phenyl was spiked at 1 µM and reacted entirely within 6 minutes (11.6 Gy). 2-F-DMH and TMDS were spiked at 100 µM and showed different degrees of degradation by •OH reactions (Figure 4.6).

Parachlorobenzoic acid (pCBA) was used as a •OH probe and tert-butyl alcohol (tBA) was used to scavenge •OH. Based on pCBA concentrations before and after radiolysis, [•OH] from gamma irradiation was similar to what was produced during ozonation. Since radiolysis resulted in low NDMA formation, molecular ozone is the main oxidant responsible, whereas the •OH may play a minor role in NDMA formation for these model precursors. While a 100 mM tBA spike was able to scavenge •OH effectively for pCBA (data not shown) and TMDS, the same spike was not effective for DMTC-phenyl and 2-F-DMH (Table 4.3). This suggests that DMTC-phenyl and 2-F-DMH react faster with •OH than tBA. Overall, the low molar yields indicate that •OH reacts with the precursor to form products other than NDMA.

The presence of hydroxyl radicals may be more likely to hinder NDMA formation than to increase it because of side reactions and increased ozone decay. For example, hydroxyl radical quenching with tBA was shown to increase NDMA formation from DMS by reducing •OH reactions that either formed products other than NDMA or resulted in bromate formation, which limited bromide catalysis (von Gunten et al. 2010). Similarly, parallel ozonation tests for the precursors in buffered ultrapure water with and without tBA resulted in greater molar yields when •OH were scavenged (Figure 4.7).

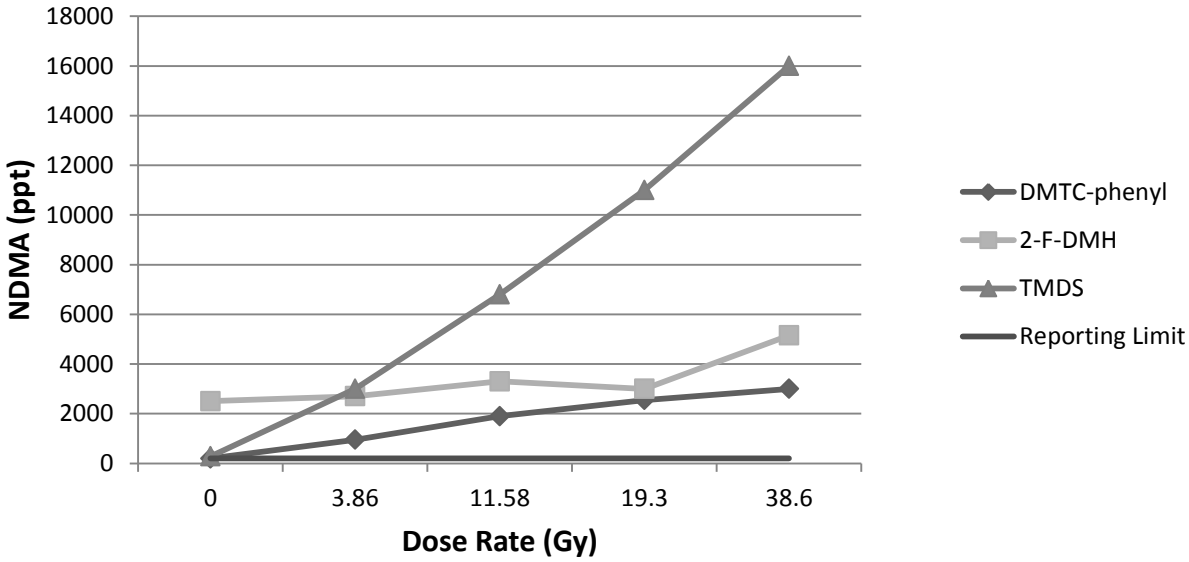


Figure 4.5: Formation of NDMA in buffered ultrapure water during radiolysis.

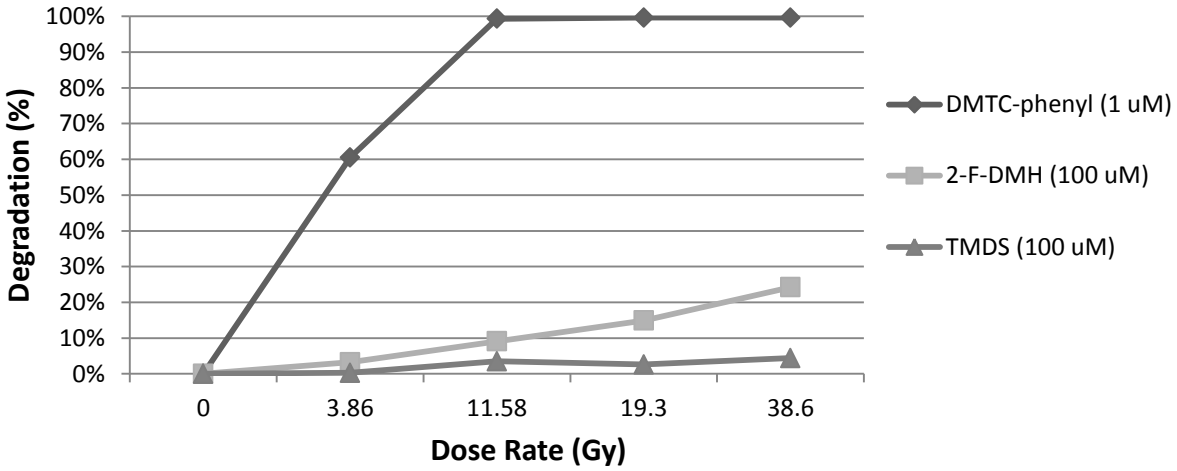


Figure 4.6: Degradation of NDMA precursors during radiolysis.

Table 4.3: Degradation of NDMA precursors and molar yields during radiolysis with and without tBA.

Precursor	Sample Description	Dose (Gy)	Conc. (µM)	% Degradation	Molar Yield (%)
DMTC-phenyl	No radiolysis	0	1.38 ± 0.020	N/A	3.0%
	Radiolysis Dose 1	3.9	0.55	61%	
	Radiolysis Dose 2	11.6	0.009	99%	
	Radiolysis Dose 3	19.3	< 0.005	> 99.6%	
	Radiolysis Dose 4	38.6	< 0.005	> 99.6%	
	No radiolysis + 100 mM tBA	0	1.24 ± 0.007	N/A	
	Radiolysis Dose 4 + 100 mM tBA	38.6	0.89 ± 0.023	35%	
2-F-DMH	No radiolysis	0	154 ± 1.7	N/A	0.2%
	Radiolysis Dose 1	3.9	149	3%	
	Radiolysis Dose 2	11.6	140	9%	
	Radiolysis Dose 3	19.3	131	15%	
	Radiolysis Dose 4	38.6	117 ± 2.1	24%	
	No radiolysis + 100 mM tBA	0	151 ± 2.1	N/A	
	Radiolysis Dose 4 + 100 mM tBA	38.6	114 ± 1.4	26%	
TMDS	No radiolysis	0	114 ± 1.7	N/A	4.3%
	Radiolysis Dose 1	3.9	114 ± 0.6	0.3%	
	Radiolysis Dose 2	11.6	110	3.5%	
	Radiolysis Dose 3	19.3	111	2.6%	
	Radiolysis Dose 4	38.6	109	4.4%	
	No radiolysis + 100 mM tBA	0	114 ± 1.4	N/A	
	Radiolysis Dose 4 + 100 mM tBA	38.6	114 ± 0.7	0.4%	

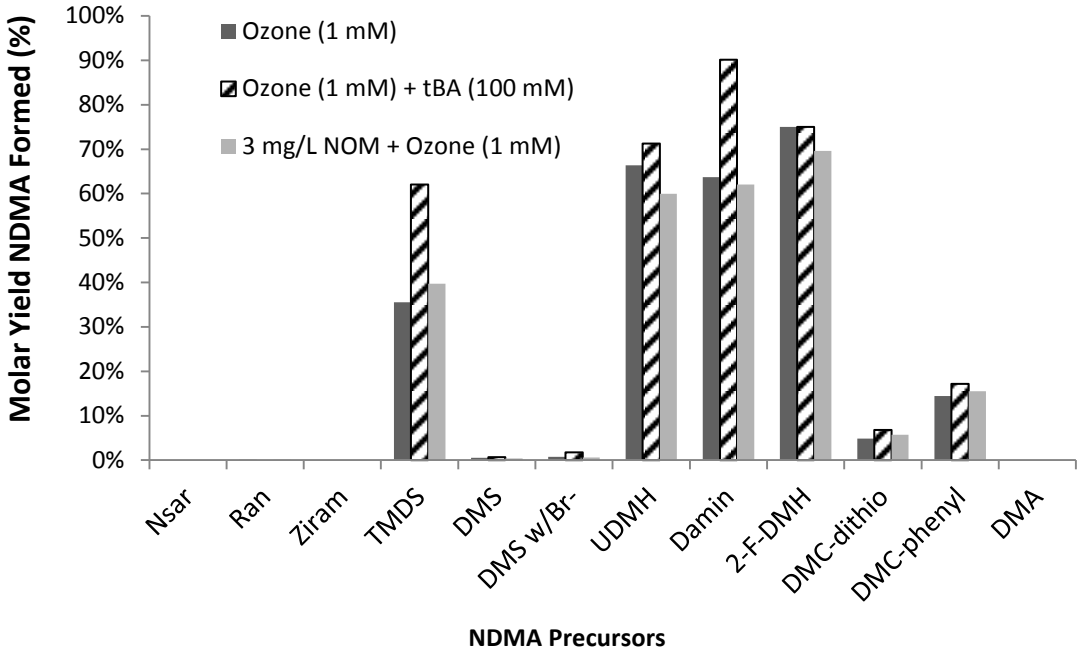


Figure 4.7: Comparison of NDMA formation after ozonation (O_3 = 1 mM) in buffered ultrapure water at pH 7 with and without tert-butyl alcohol (tBA) for scavenging hydroxyl radicals and buffered ultrapure water with 3 mg/L (organic carbon) Suwannee River fulvic acid as a source of natural organic matter (NOM).

4.4.6 Molar Yields in an Actual Secondary Wastewater Matrix

NDMA formation was examined in wastewater by dissolving each precursor compound individually in tertiary-treated wastewater effluent and reacting with a 10-fold molar excess of ozone using the same procedure as the buffered ultrapure water. The concentration of NDMA in the ozonated wastewater effluent (without any precursors added) was below the method reporting limit. NDMA formation was affected by the water matrix for a few compounds. It was anticipated that the ozone demand presented by the wastewater would decrease the ozone concentration available for reaction with the precursor compounds, and, therefore, lower NDMA molar conversion yields were expected. However, the opposite was observed. For four

compounds (UDMH, acetone-DMH, TMDS and DMSC), the NDMA molar conversion yield was significantly greater in the wastewater matrix compared to phosphate buffered ultrapure water (Figure 4.1). This trend was also seen by a group of researchers comparing NDMA formation by ozonation of two dyes in river water and ultrapure water matrices at pH 7 (Oya et al. 2008). They measured higher NDMA formation in the river water matrix that contained bromide and nitrite, but at a concentration too low to account for this increase. At this time, specific constituents in the wastewater responsible for the increased formation have not been determined. The presence of natural organic matter alone does not increase NDMA formation (Figure 4.7); however, metal ions, such as Cu^{2+}, may affect NDMA formation. It was demonstrated that Cu^{2+} ions, in the presence of dissolved oxygen, catalyzed the transformation of daminozide to succinic acid and UDMH (Huang and Stone 2003). The effect was increased in the presence of halide ions. Another explanation for the increased molar yields in wastewater is through •OH scavenging. Effluent organic matter in wastewater can scavenge •OH. As demonstrated in the previous section, •OH scavenging is associated with increased NDMA formation.

4.4.7 Practical Implications of the Research

As shown in this research, compounds with a general structure of $(H_3C)_2N$-N-R or $(H_3C)_2N$-L-N-R, where L is a good leaving group like $–SO_2$ or $–CO_2$, have a high likelihood of forming NDMA with ozonation. While previously reported NDMA precursors UDMH, DMS, TMDS and daminozide have been reported to occur in groundwater or are known products in use, the new precursors reported in this study were selected by structure only and have not been quantified in wastewater, surface water or groundwater.

According to the results of this study, the ozone dose for treating wastewater may strongly affect NDMA formation. Treatment plants operating at high ozone doses for color removal or chemical contaminant removal could experience much greater NDMA formation compared to treatment plants using low ozone doses for final disinfection. Alternatively, NDMA precursors may be removed through treatment steps, such as reverse osmosis, biological treatment, and oxidation, leading to less NDMA formation when ozonation is applied at the end of a treatment train. Consequently, one should consider both the dose and placement within the treatment train when determining an appropriate ozone application.

Bench-scale ozonation testing with ultrapure water may not demonstrate the full potential of the precursors to form NDMA. Wastewater constituents can increase NDMA formation, such as by bromide catalysis or hydroxyl radical quenching (von Gunten et al. 2010). Therefore, further study is needed to understand the influence of aqueous matrix components on NDMA formation and to develop possible mitigation strategies.

Chloramination may follow ozonation when a chlorine residual is necessary. The combined disinfection scheme could have varying results. If the source water contains mostly NDMA precursors that react with chloramine, then pre-ozonation may reduce NDMA formation potential (Pisarenko et al. 2012). However, if the source water contains NDMA precursors that react with ozone, then initial ozonation may form NDMA, as well as additional chloramination precursors via degradation products (i.e., from UDMH). Without an analytical method to quantify NDMA precursors for either oxidant, it is necessary to experimentally determine NDMA formation potential for each water matrix in order to determine the optimal disinfection strategy.

4.4 Conclusion

Experiments with known and potential NDMA precursors resulted in the following findings on NDMA formation by ozonation:

- Out of 9 compounds selected based on structural characteristics, six new compounds were identified as NDMA precursors. Two are hydrazones, two are semicarbazides, and two are carbamates.
- Bromide concentration was significant for NDMA formation in solutions of dimethylsulfamide (DMS), unsymmetrical dimethylhydrazine (UDMH) and acetone dimethylhydrazone. Other compounds showed no enhancing effect of bromide on NDMA formation.
- Although all the precursors tested contain a dimethylamine that reacts with chloramine to form NDMA, the reaction with ozone results in significantly higher NDMA formation. This group of precursors (with structures $(H_3C)_2N$-N-R or $(H_3C)_2N$-L-N-R) is distinctly different than other dimethylamine-containing compounds.
- Transformation products from the ozonation of UDMH may be NDMA chloramination precursors.
- Molecular ozone was confirmed as the main oxidant responsible for NDMA formation for the model precursors.
- Higher NDMA formation was observed in wastewater than ultrapure water for several precursors. Wastewater may contain constituents that promote NDMA formation.
- Hydroxyl radical scavenging and a greater ozone dose lead to increased NDMA formation for the model precursors, while the addition of hydrogen peroxide had no significant effect on NDMA formation.

CHAPTER 5

THE EFFECT OF PRE-CHLORINATION ON OZONE-REACTIVE NDMA PRECURSORS AND DISINFECTION BYPRODUCT FORMATION TRADE-OFFS

5.1 Abstract

Disinfection byproducts (DBPs), such as trihalomethanes (THMs), haloacetic acids (HAAs) and *N*-nitrosodimethylamine (NDMA), are formed by oxidant disinfectants such as chlorine, chloramine, and ozone. However, these same oxidants may be used to control formation of particular DBPs either separately or in combination. This study compared the formation and reduction of NDMA, THMs, and HAAs in treated wastewaters using seven disinfection treatment schemes. By investigating multiple combinations, including one not previously investigated (chlorination-ozonation-chloramination), NDMA formation by chloramination and ozonation was isolated and the effects on both chloramine- and ozone-reactive NDMA precursors were assessed. The top two treatment schemes for secondary wastewater effluent resulting in the lowest total DBP formation, after converting concentrations to an equivalent unit based on drinking water risk, were ozonation and ozonation-chloramination. Both treatment schemes exhibit several advantages for application in water reuse. Using secondary wastewater effluent spiked with model precursors, it was demonstrated that pre-chlorination can inactivate ozone-reactive NDMA precursors; this finding has not been previously reported. More research is needed to understand the oxidation products from this reaction, as well as to determine the minimum chlorine exposure needed to destroy these precursors.

5.2 Introduction

Limiting the formation of disinfection products (DBPs) is a constant challenge for water treatment utilities. Trihalomethanes (THMs) and haloacetic acids (HAAs) are regulated at 80 µg/L and 60 µg/L (USEPA 2014), respectively, and are mainly the result of chlorination, though they are also formed by chloramination, especially iodinated THMs (Krasner 2009; USEPA 2016a). As cities turn to alternative water supplies or explore water reuse options, there is an increased concern about DBP formation. *N*-nitrosodimethylamine (NDMA) is formed by chloramination and ozonation (Krasner et al. 2013). In general, the precursors are anthropogenic and associated with wastewater components not removed during treatment (Mitch et al. 2009), which makes NDMA a prime issue for water reuse. Examples of NDMA precursors in wastewater include pharmaceuticals (Shen and Andrews 2011), coagulation polymers, (Padhye et al. 2011), industrial chemicals (Kosaka et al. 2014b; Sedlak et al. 2005), dyes (Oya et al. 2008), and agricultural products (Schmidt and Brauch 2008).

NDMA is not yet regulated in drinking water by the United States Environmental Protection Agency (USEPA), but some U.S. states have declared thresholds (California: 10 ng/L notification level; Massachusetts: 10 ng/L regulatory limit) and other countries have set limits in drinking water (Canada: 40 ng/L, Australia: 100 ng/L) and recycled water (Australia: 10 ng/L) (CEPA 2014; Health Canada 2011; Massachusetts Energy and Environmental Affairs 2016; Water Research Australia 2013). NDMA has a higher toxicity than THMs or HAAs, as evidenced by a drinking water unit risk that is 1000 times greater (USEPA 2016b). One strategy to minimize NDMA formation is through oxidation of the precursors. Previous research has demonstrated that chlorine, ozone, chlorine dioxide, ferrate and permanganate deactivate NDMA precursors (Charrois and Hrudey 2007; Lee et al. 2007b; McCurry et al. 2015; Shah et al. 2012).

However, these studies have all focused on NDMA formation by chloramination, which means the outcomes are only known to apply to chloramine-reactive NDMA precursors. Ozone-reactive NDMA precursors, distinctly different from the other group, form NDMA in high yields upon ozonation, but form minimal NDMA upon chloramination, even at high concentrations of 140 mg/L as Cl_2 (Marti et al. 2015). Different disinfection treatment schemes may be needed to target ozone-reactive NDMA precursors. However, adjusting disinfection to control for one contaminant or group of precursors is ill-advised. Inactivation of pathogens and the formation of multiple DBPs should be considered in order to determine an optimal disinfection scheme.

This study investigates multiple disinfection treatment schemes for control of NDMA, THMs and HAAs. Many other DBPs exist, but these ones are of substantial concern for water reuse. A particular goal of this investigation was to determine if pre-chlorination was an effective strategy for mitigating ozone-derived NDMA formation. A second goal was to examine trade-offs in DBP formation quantitatively by converting the different DBP concentrations to an equivalent unit based on their drinking water risk factors.

5.3 Materials and Methods

5.3.1 Sample Collection

Secondary and tertiary effluent samples were collected prior to any oxidant addition from seven wastewater treatment plants in the U.S. and Australia. Grab samples were collected in pre-cleaned glass jugs or HDPE containers and transported to the lab in coolers with ice or shipped overnight with ice packs. Samples were held at 4 °C until use and processed in-country. Table 5.1 contains details on the wastewater treatment processes and water quality information for the treated wastewaters. Research was performed in the U.S. and in Australia.

5.3.2 Chemicals

Reagents were ACS grade or higher and all solutions were prepared using ultrapure water. Sodium hypochlorite (10-14 wt% free available chlorine; Sigma-Aldrich, St. Louis, MO) solutions were standardized each time using iodometric titration as described in section 3.5.6. Phosphate buffer solution (1 M) was prepared from equal molar amounts of KH_2PO_4 and Na_2HPO_4 (Fisher Scientific, Fair Lawn, NJ) and adjusted to pH 7. Borate buffer solution (0.4 M) was prepared by dissolving 24.732 g boric acid into 500 mL DI water and adjusting the pH to 6.6 using sodium hydroxide. Neat standards of seven NDMA precursors (daminozide, TMDS, 2-F-DMH, DMC-dithio, DMC-phenyl, DMTC-phenyl, DMSC) were individually dissolved in ultrapure water and/or acetonitrile (for solubility) as described in section 4.3.2 and then combined as a mixture (1 mM each).

Table 5.1: Wastewater treatment processes and water quality for tested wastewater effluents.

Sites	Secondary Treatment	Tertiary Treatment	TOC	pH	Bromide (µg/L)	NH_4^+-N (mg/L)	TN (mg/L)	NDMA (ng/L)
A	Nitrif. & partial Denitrif., AS (AE/AX)	N/A	7.63	7.2	311	DND	DND	5.9 ± 0.55
B	Nitrif. & Denitrif., Oxidation Ditches	N/A	6.37	7.6	138	1.9	3.9	< 3.0
C	Nitrif., Sequencing Batch Reactors	N/A	8.15	7.7	161	4.6	11	17.9
D	Nitrif., CAS	N/A	23	DND	DND	0.66	DND	220
E	Nitrif., CAS	Media filtration	5.5	DND	DND	0.03	DND	2.8
F	Nitrif., BNR (AE/AN)	N/A	9.5	DND	DND	0.05	DND	< 3.0

TOC = Total organic carbon; TN = Total nitrogen; Nitrif. = Nitrification; Dentrif. = Denitrification; AS = Activated Sludge; CAS = Conventional Activated Sludge; BNR = Biological Nutrient Removal; AE = Aerobic; AN = Anaerobic; AX = Anoxic; N/A = not applicable; DND = Did not determine

5.3.3 Disinfection Treatment Schemes

The seven treatment schemes tested in this study comprise individual and consecutive applications of chlorine, ozone and chloramine (Table 5.2). Free chlorine and ozone residuals were allowed to decay prior to chloramination, except for Sites A-C as discussed later.

Table 5.2: Disinfection treatment schemes used in DBP formation investigation.

Single		**Double**		**Triple**	
Oxidant	*Abbrev.*	*Oxidants*	*Abbrev.*	*Oxidants*	*Abbrev.*
Chlorine	Cl_2	Chlorine-Ozone	Cl_2-O_3	Chlorine-Ozone-Chloramine	Cl_2-O_3-CLM
Ozone	O_3	Ozone-Chloramine	O_3-CLM		
Chloramine	CLM	Chlorine-Chloramine	Cl_2-CLM		

5.3.4 Experimental Procedures

Chlorination

Samples were chlorinated (Cl_2) at room temperature (22-25 °C) above the breakpoint to achieve a free chlorine residual. The initial chlorine spike concentration was different for each wastewater and depended on the chlorine demand, which was mainly caused by ammonia. The free chlorine concentration was monitored for 24 hours or until no residual remained in order to generate a chlorine decay curve. Chlorine demand and decay curves are shown in Appendix B.

Ozonation

Bench-scale ozonation (O_3) was performed through the addition of ozone-saturated water to the sample. Ozonated water was generated using an oxygen-fed generator (model CFS-1A, Ozonia North America, Inc., Elmwood Park, NJ, USA) to diffuse ozone into cold ultrapure water

as described elsewhere (Wert et al. 2009). The concentration of the ozone stock solution was measured on a Hach DR5000 UV/Vis spectrophotometer at 600 nm using the indigo method (Rakness et al. 2010). The ozone stock solution was typically between 65 and 85 mg/L as O_3. An appropriate volume was dosed into samples to achieve the desired ozone to TOC ratio (O_3:TOC), taking dilution into account. Samples were sealed, mixed by inverting, and left at room temperature for one day to ensure ozone residual was zero before analyzing for NDMA.

Ozone exposure was determined through ozone decay curves, which were performed for the unaltered and pre-chlorinated wastewater. A one liter sample was spiked with ozone and the ozone concentration was measured periodically until no ozone residual remained. Concentrations were adjusted for dilution and plotted against time to generate the decay curve.

Chloramination

Chloramination (CLM) was performed using formation potential conditions (FP) for the preliminary experiments and uniform formation conditions (UFC) for the second set of experiments. Chloramine NDMA-FP was performed as described in section 4.3.2. Briefly, samples were spiked with preformed monochloramine at 2 mM (140 mg/L) as Cl_2 and stored at room temperature (22-25 °C) in the dark for ten days. UFC testing was completed following a procedure from Shah et al. (2012). A fresh monochloramine solution was prepared each time from sodium hypochlorite and ammonium chloride (Sigma-Aldrich, St. Louis, MO), as described in section 3.2.5. Samples were buffered (4 mM borate, pH 8), spiked at 5 mg/L as Cl_2, and kept at room temperature in the dark for three days. At the conclusion of the procedure, samples were checked for a minimum residual (1 mg/L as Cl_2) and then quenched with sodium thiosulfate.

5.3.5 Analytical Methods

General water quality parameters

Total organic carbon (as non-purgeable organic carbon or NPOC) was measured by 680°C combustion catalytic oxidation, and total nitrogen was measured by 720°C catalytic thermal decomposition with chemiluminescence detection (Shimadzu TOC-L with TN unit). Ammonium was measured using the salicylate method (Hach Method 10031, AmVer™ Salicylate Test 'N Tube™) and bromide by ion chromatography using a Dionex ICS3000. Free and total chlorine were measured using the DPD method and a handheld colorimeter (Hach Pocket Colorimeter™ II, Hach Methods 8021 and 8167).

NDMA analysis

NDMA quantification differed depending on the expected concentration and lab (U.S. or Australia). Australian samples used liquid-liquid extraction (LLE) and gas chromatography mass spectrometry (GC-MS) analysis with isotopic dilution (Linge et al. 2015). For LLE, a 50 mL sample spiked with d6-NDMA was adjusted to pH 8 with sodium hydrogen carbonate. Oven-dried (450 °C) sodium chloride (15 g) was added and the sample was mixed until all salt dissolved. The sample was extracted with 5 mL dichloromethane and dried through anhydrous magnesium sulfate. The extract was concentrated to ~200 µL in a heating block (40 °C) under a nitrogen stream and transferred to a GC microvial containing 50 µg/L of diphenylamine-d10 as the internal standard. NDMA was analyzed by GC-MS using an Agilent Technologies 7890A gas chromatograph coupled with a 5975C inert mass spectrometer operated in positive chemical ionization mode with ammonia as the reagent gas (flow = 0.5 mL/min). The limit of detection was 4 ng/L.

U.S. samples used solid phase extraction (SPE) and GC-MS analysis with isotopic dilution (Holady et al. 2012) for low concentrations (range: 2.5-1000 ng/L NDMA) and direct injection liquid chromatography tandem mass spectrometry (LC-MS/MS) for high concentrations (range:

25-3000 µg/L NDMA) (Marti et al. 2015). SPE was performed with 1 L samples using an AutoTrace workstation (Dionex Corporation). Samples were loaded at 15 mL/min onto prepacked coconut charcoal cartridges (Resprep 521, Restek) conditioned with dichloromethane, methanol and water. Cartridges were rinsed with water and dried with nitrogen gas prior to elution with dichloromethane. Residual water was removed with sodium sulfate cartridges (Sep-Pak Dry, Waters Corporation). Extracts were concentrated to 500 µL for a concentration factor of 1:2000. 2 µL of the final extract was injected into a CP-3800 gas chromatograph with autosampler (Varian) after column separation (DB 624, Agilent) under helium flow. The injector (Varian 1177) was operated splitless mode with a Siltek™ deactivated glass liner (Restek). The temperature gradually increased from 35 to 250 °C. Analysis was performed using a Varian 2200 ion trap mass spectrometer and multiple reaction monitoring in positive chemical ionization mode using methanol. The precursor and product ion pairs were: 75/47, 75/58, and 75/44. The method reporting limit (2.5 µg/L) was set at three times the method detection limit. LC-MS analysis for high NDMA concentrations was performed as described in section 4.3.2. Two transitions were monitored for NDMA (75/43 and 75/58) and d6-NDMA (81/46 and 81/64). The method reporting limit was 25 µg/L (0.34 µM).

THM and HAA analysis

Four trihalomethanes (bromodichloromethane, bromoform, chlorodibromomethane, chloroform) and five haloacetic acids (bromoacetic acid, dibromoacetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid) were measured using EPA methods 524.3 and 552.2, respectively. A Stratum PTC purge and trap concentrator with AQUATek 100 autosampler (Teledyne Tekmar) were used for THM extraction. THM analysis used a Thermo Scientific TRACE gas chromatograph with Electronic Pressure Control and a Split/Splitless injection port

coupled to a Thermo Scientific ISQ mass spectrometer. Samples were separated on a RTX-VMS GC column (Restek). HAA analysis used a Varian CP-3800 gas chromatograph with dual Electron Capture Detectors and a CTC Analytics CombiPal Autosampler. Samples were separated with a J&W DB-1701 GC column (Agilent) and spectra were quantified with Dionex/Thermo Chromeleon version 6.8 software. Results are reported for individual compounds and as total THMs and total HAAs.

5.3.6 Calculations

Oxidant exposure (Ct) for chlorine and ozone was determined by integrating concentration versus time for decay curves. The trapezoidal rule (Equation 3) was applied to the data in an Excel spreadsheet. The manually calculated values for each pair of points were summed to get the total exposure. Since the decay is initially fast and then slows, more measurements were taken in the first few minutes. Typical measurement times were 1, 2, 3, 5, 7, 10, 12, 15, 20, 30, 45, 60, 90, and 120 min for chlorine and 0.5, 0.75, 1, 1.5, 2, 3, 5, and 7 min for ozone. Data and calculations are shown in Appendix C.

Equation 3: Trapezoidal rule for calculating oxidant exposure from concentration and contact time.

$$Area = \int_{a}^{b} f_x dx = (b-a)\frac{f(a)+f(b)}{2}$$

a = time at point 1 f(a) = concentration at point 1

b = time at point 2 f(b) = concentration at point 2

NDMA, THM, and HAA concentrations were converted to an equivalent unit based on drinking water unit risk, which, to the author's knowledge, is a new approach for quantitative comparison. USEPA conducts carcinogen risk assessments to estimate a chemical's cancer potency for exposure in food, water and air (USEPA 1992). The drinking water unit risk is the risk associated with a drinking water concentration of 1 µg/L (e.g., 1 µg/L NDMA) and based on an average-sized adult (70 kg) who drinks 2 L of water per day. First, the drinking water unit risk values were averaged for THMs (n = 4) and HAAs (n = 2). Although there are five HAAs regulated under total haloacetic acids, only two have established drinking water unit risk values (Table 5.3). A risk ratio was calculated using NDMA as the reference since it has the highest toxicity. NDMA, THM and HAA concentrations were converted to ng/L and multiplied by this ratio.

Table 5.3: Drinking water unit risk values for NDMA, THMs, and HAAs and ratio used to convert values.

Compound		**Drinking water unit risk (µg/L)***	**Average drinking water unit risk (µg/L)**	**Ratio**
NDMA		1.4 E-3	1.4 E-3	1.0
THMs	Chloroform	1.7 E-7	1.15 E-6	0.00082
	Bromodichloromethane	1.8 E-6		
	Dibromochloromethane	2.4 E-6		
	Bromoform	2.3 E-7		
HAAs	Dichloroacetic acid	1.4 E-6	1.7 E-6	0.0012
	Trichloroacetic acid	2.0 E-6		
	Monochloroacetic acid	N/A		
	Bromoacetic acid	N/A		
	Dibromoacetic acid	N/A		

*Sources: USEPA 2016b; Office of Environmental Health Hazard Assessment (OEHHA) 2007

5.4 Results and Discussion

5.4.1 Preliminary Results and Free Chlorine Complications

Preliminary testing was completed for sites A-C in Australia. The chosen sites differed in secondary treatment type and level of treatment. NDMA ranged from < 4 to 17.9 ng/L in the unaltered wastewater (i.e., not oxidized), with the lowest concentration for site B (nitrification and denitrification) and the highest concentration for site C (nitrification only). Although studies have examined NDMA and NDMA precursor removal after various levels of secondary treatment, there is no clear correlation between the amount of NDMA formed and level of nitrification or denitrification (Krauss et al. 2009; Yoon et al. 2011). If a minimum level of treatment is met, NDMA and NDMA precursors may be removed through biodegradation, even in non-nitrifying wastewater treatment plants (Krauss et al. 2009). In some cases, more intense secondary treatment has resulted in lower NDMA formation. For example, a pilot plant with a membrane bioreactor was operated at two different sludge retention times (SRTs). NDMA formation with ozone (O_3:TOC = 0.2) was significantly lower at SRT = 18.8 days (< 5 mg/L NDMA) as compared to SRT = 2.4 days (25 mg/L NDMA) (Gerrity et al. 2015). NDMA precursor removal, as measured by chloramination formation potential, also does not differ among biological treatment process types (Sedlak et al. 2005; Yoon et al. 2011), but specific precursors do show greater removal at higher SRT (Wang et al. 2014). It would seem that individual NDMA precursors are affected by treatment conditions, but this is not generalizable to the mixture of precursors found in wastewater. In this research, since NDMA formation could not be correlated to secondary treatment level, quantitative comparisons were restricted to changes in NDMA formation observed for wastewaters individually and not compared among the different wastewaters.

All three sites showed the same general trends for NDMA formation after oxidant addition. These experiments involved six oxidation treatment schemes (Cl_2, O_3, CLM, Cl_2-O_3, O_3-CLM, Cl_2-O_3-CLM) at two O_3:TOC ratios (0.1, 0.5) and only NDMA was quantified. Chlorination did not increase NDMA above the concentration in the unaltered wastewater; however, NDMA did increase with ozonation, and the formation was greater at the higher ozone dose (Figure 5.1). Significant concentrations of chloramine-reactive precursors were present in all three locations based on the formation potential results (298-703 ng/L NDMA). Implementing ozonation or chlorination before chloramination led to a substantial reduction in chloramine NDMA formation potential (NDMA-FP) (Figure 5.2). The greatest reduction was for chlorination-ozonation-chloramination at O_3:TOC = 0.5, which corresponded to decreases in NDMA of 95%, 98% and 94% for sites A, B and C, respectively. Many other studies have shown that pre-oxidation with ozone, chlorine, and chlorine dioxide decreases NDMA-FP in drinking waters and wastewaters (Lee et al. 2007a; McCurry et al. 2015; Pisarenko et al. 2012; Shah et al. 2012; Sharif et al. 2012; Selbes et al. 2014). However, no other studies have examined combined pre-oxidation with chlorine and ozone before post-chloramination. This option may be a valuable strategy for wastewaters containing both chloramine- and ozone-reactive NDMA precursors, as discussed later.

Further analysis of the results obtained in this preliminary experiment is not advised because of complications with free chlorine. Samples were chlorinated to achieve a free chlorine exposure of 113-166 mg·min/L, which is a sufficient dose for 3-log removal of *Giardia lamblia* at pH 6.5-7.5 and 10 °C at 3 mg/L as Cl_2 (USEPA 1999) and comparable to another study (Shah et al. 2011). The treated wastewaters had varying concentrations of ammonia and enough chlorine (20-45 mg/L as Cl_2) was added to exceed the breakpoint and achieve a free chlorine

residual (2-4 mg/L as Cl_2 at one minute after dosing). A free chlorine residual was present when the sample was ozonated, which caused two problems. First, ozone reacts with free chlorine (Haag and Hoigné 1984). Even 2 mg/L as Cl_2 is enough to substantially increase ozone decay (Wert and Lew 2008), and this reduces the expected ozone exposure (Ct). On the other hand, chlorination changes the water quality and can reduce ozone demand, which would increase the impact of ozonation. There is no clear way to isolate the effects; therefore, results for ozonation and chlorination-ozonation at the same O_3:TOC ratios cannot be directly compared for any given wastewater. The second issue is that free chlorine interferes with the indigo method used to measure ozone concentration (Bader and Hoigné 1982). Free chlorine has the same effect as ozone on the indigo dye, which makes it appear that the ozone residual is higher and lasts longer. Consequently, ozone decay curves will overestimate the ozone concentration over time and the calculated ozone exposure will not be accurate. Due to the problems associated with the free chlorine residual, subsequent experiments were conducted by allowing the free chlorine residual to decay completely.

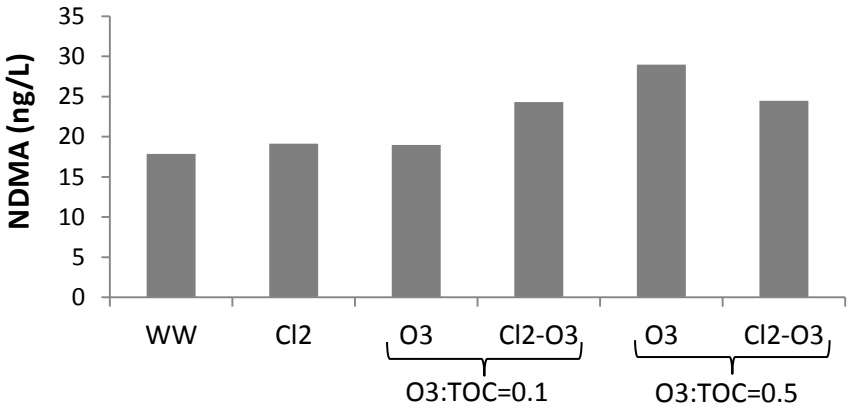


Figure 5.1: NDMA concentration for site C after chlorination and ozonation at two O_3:TOC ratios. Similar results were obtained for sites A and B (Appendix B).

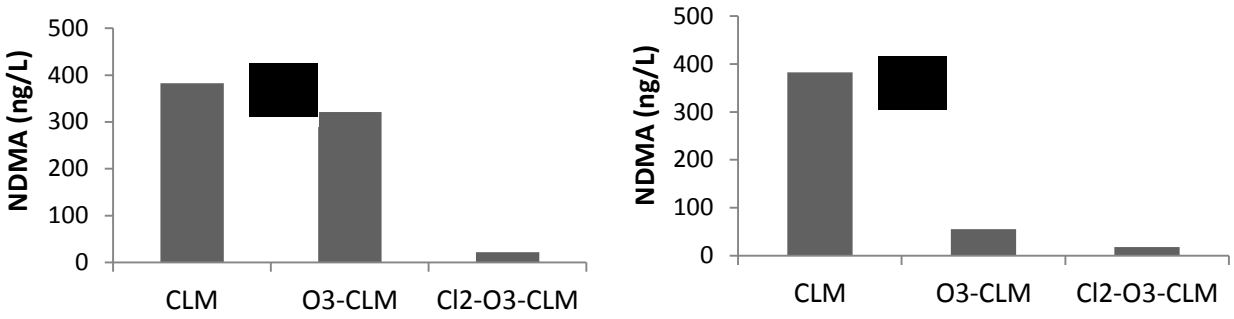


Figure 5.2: Reduction in NDMA formation potential for site A with a) O_3:TOC = 0.1 and b) O_3:TOC = 0.5. Similar results were obtained for sites B and C (Appendix B).

5.4.2 Effect of Pre-chlorination on Chloramine-derived NDMA Formation

Wastewaters were chlorinated at free chlorine exposures of 102, 70 and 275 mg·min/L for Sites D, E, and F, respectively (Appendix C). As expected, pre-chlorination reduced NDMA formation for post-chloramination, as seen by the low NDMA concentrations for Cl_2-CLM compared to CLM (Figure 5.3). Note that the high NDMA concentrations for Site D (Figure 5.3a) are mainly the result of NDMA in the unaltered wastewater rather than NDMA formed by disinfection. The maximum NDMA formation for Site D was a 20% increase over the unaltered wastewater and not far above analytical variability, making interpretation on NDMA formation difficult for this location. NDMA decreased by 30 ng/L (71%) and 176 ng/L (73%) with pre-chlorination at Sites E and F, respectively. This matches results from previous studies, as mentioned earlier.

Although NDMA formation decreased with pre-chlorination, THMs and HAAs were formed. Chlorination increased THMs by 200 µg/L for Site D, 60 µg/L for Site E, and 59 µg/L for Site F. In comparison, post-chloramination (5 mg/L as Cl_2 for three days) only increased THMs slightly (D: 4-25 µg/L; E: 2-20 µg/L; F: 0-6 µg/L). Multiple factors affect THM formation with

chlorination in water or wastewater, such as fast- or slow-reacting precursors, pH, temperature, chlorine dose and other ions exhibiting a chlorine demand (Gallard and von Gunten 2002). Therefore, the variation in THM formation at Sites D-F cannot simply be explained by the different chlorine exposures. Chlorination also increased HAA concentrations by 38 µg/L for Site D, 23 µg/L for Site E, and 32 µg/L for Site F. Post-chloramination resulted in a similar increase in HAA formation (D: 12-13 µg/L; E: 9-18 µg/L; F: 13-29 µg/L) compared to chlorination.

5.4.3 Effect of Ozonation on Chloramine-derived NDMA Formation

Wastewaters were ozonated at a consistent ozone to TOC ratio in order to achieve similar treatment efficacy across different samples (Gerrity et al. 2014; Lee et al. 2013). The chosen ratio (0.8) represents an ozone dose that is typical for trace organic contaminant removal (Zeng and Mitch 2015). Ozone exposures were 0.2, 1.7, and 3.0 mg·min/L for non-chlorinated samples and 0.4, 6.5, and 11.4 mg·min/L for chlorinated samples at Sites D, E, and F, respectively (Appendix C).

As expected, ozonation reduced NDMA formation for post-chloramination. NDMA decreased by 27 ng/L (64%) and 165 ng/L (69%) with ozonation at Sites E and F, respectively. The decrease in NDMA formation was essentially the same for chlorination and ozonation. Although higher ozone doses generally lead to greater NDMA precursor removal, the relationship is not linear (Lee et al. 2007a; Pisarenko et al. 2012; Shah et al. 2012). It is possible that a lower ozone dose could have achieved a similar reduction in NDMA formation for post-chloramination.

While ozonation alone did not cause THM formation or affect THM formation with post-chloramination, it did result in direct NDMA formation above the concentration in the unaltered

wastewater. NDMA increased by ~10 ng/L (~5-fold) and ~60 ng/L (~20-fold) with ozonation at Sites E and F, respectively. NDMA concentrations for O_3 and O_3-CLM were very similar with slightly higher levels for O_3-CLM. The percent differences were D: 4% (10 ng/L); E: 12% (1.5 ng/L) and F: 21% (13 ng/L). This suggests that ozone destroyed nearly all the chloramine-reactive NDMA precursors, and the resulting NDMA concentration can be attributed mainly to ozone-reactive NDMA precursors.

As with THMs, ozone did not directly form HAAs above the levels in the unaltered wastewater. However, it seemed to promote HAA formation with post-chloramination (D: 1-10 μg/L; E: 4-8 μg/L; F: 3-22 μg/L). While a trend is apparent, these values represent single trials for only three wastewaters and may not be statistically significant. An increase in chlorinated HAAs after ozonation was also observed for *Cyclotella* algae, though this study involved HAA formation potential with chlorine and not chloramines (Plummer and Edzwald 2001). Most studies report decreased HAAs for chlorination or chloramination with pre-ozonation (Hua and Hoigné and Bader 1988; Jacangelo et al. 1989; Miltner et al. 1992; Reckhow 2007), but HAA formation may also occur (Hartmann 2002; Singer 1999).

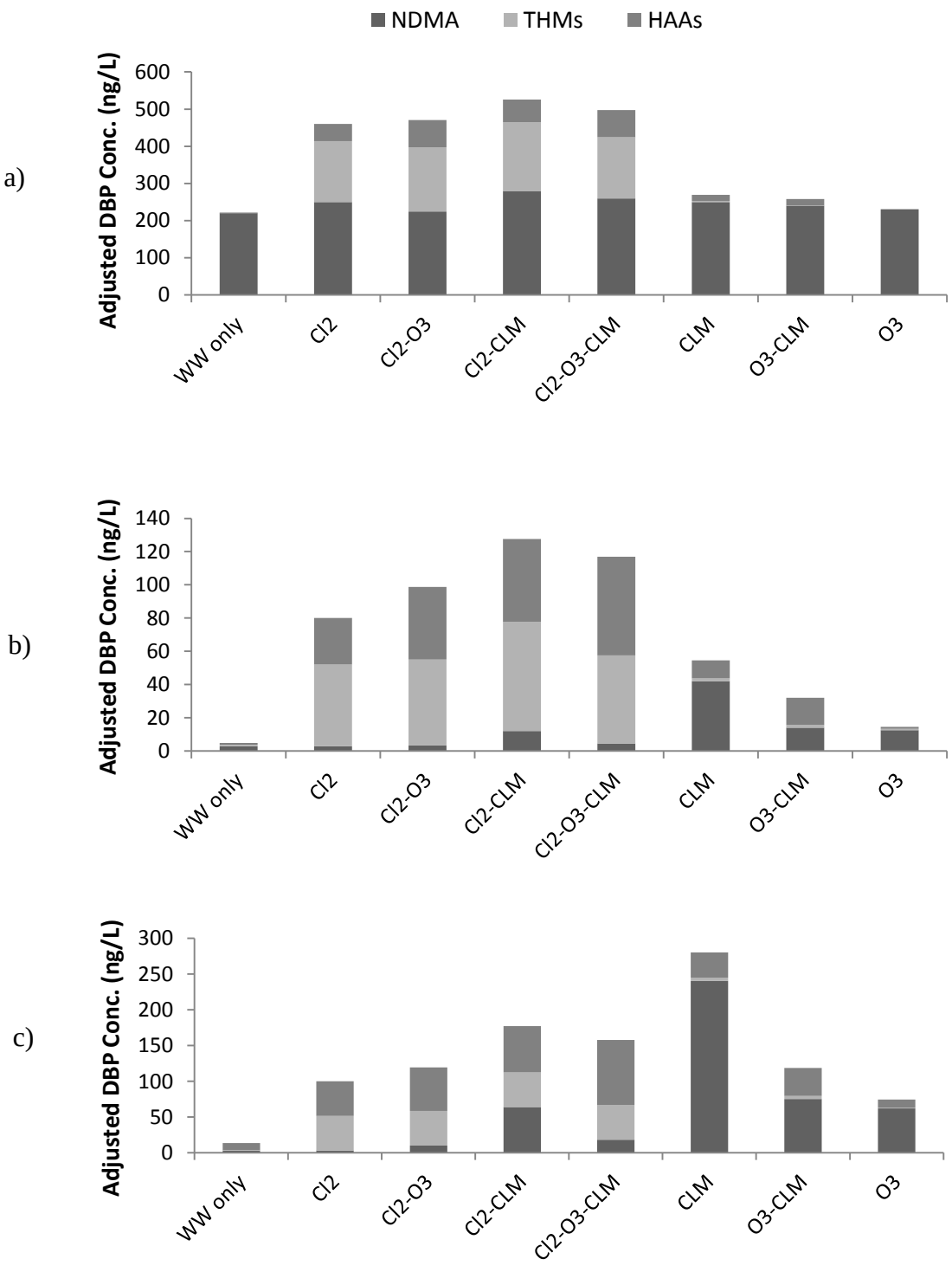


Figure 5.3: Measured NDMA and adjusted THM, HAA concentrations after disinfection treatment schemes for a) Site D, b) Site E and c) Site F. Error bars are standard deviations for duplicate samples.

5.4.4 Effect of Pre-chlorination on Ozone-derived NDMA Formation

This study provides evidence that pre-chlorination resulted in decreased NDMA formation with post-ozonation of treated wastewaters. Compared to ozonation alone (O_3), chlorination-ozonation (Cl_2-O_3) led to NDMA concentration reductions of 8 ng/L (75%) and 52 ng/L (84%) for Sites E and F, respectively. However, caution is needed when evaluating these results. Although the samples received the same ozone dose, the ozone exposure was not equal. As a nonselective oxidant, chlorine reacts with a wide variety of organic and inorganic compounds (Faust and Aly 1998). This means that pre-chlorination alters the water quality and reduces ozone demand. Consequently, the ozone exposure was higher for the pre-chlorinated samples (see previous section). Assuming that the ozone-reactive NDMA precursors were unchanged by chlorination, then higher NDMA formation would be expected due to the higher ozone Ct. The decreased NDMA formation signals that chlorination rendered the ozone-reactive precursors inactive, at least to the extent that they no longer form NDMA upon ozonation. The 75% and 84% reductions in NDMA concentration may actually underestimate the effect of pre-chlorination. Matching ozone exposures for the O_3 and Cl_2-O_3 treatments would be needed to determine this. To the author's knowledge, this is the first study that demonstrates pre-chlorination as a method for destroying ozone-reactive NDMA precursors.

In contrast to NDMA reduction, chlorination-ozonation increased THM and HAA concentrations. Compared to ozonation alone, chlorination-ozonation caused increases of 210 ng/L, 62 ng/L, and 58 ng/L for THMs and 60 ng/L, 35 ng/L, and 40 ng/L for HAAs at Sites D, E, and F, respectively. Since concentrations of THMs and HAAs were the same for the ozonated sample as the unaltered wastewater, these increases are entirely due to chlorination.

5.4.5 *Effect of Pre-chlorination on Ozone-reactive NDMA Precursors and Insight on the Oxidation Products Formed*

For additional confirmation that chlorination destroys ozone-reactive NDMA precursors, a parallel test was completed where a mixture of known ozone-reactive NDMA precursors was spiked into a batch of wastewater from Site F. Precursors (daminozide, TMDS, DMC-phenyl, DMTC-phenyl, 2-F-DMH) with an average NDMA molar yield of 38% were spiked at high concentrations (mixture = 500 µg/L) for ease in analyzing the results by direct injection LC-MS/MS (i.e., no concentration step). Only ozonation (O_3) and ozonation-chloramination (O_3-CLM) treatments resulted in NDMA formation above the method reporting limit (MRL), and the concentrations were nearly the same at 172 ± 5.7 and 178 µg/L (Figure 5.4). This was very close to the expected concentration (190 µg/L) based on the average NDMA molar yield for the mixture. No detectable formation with chloramination was expected since the precursors are known to have very low molar yields (< 2.5%) with chloramines (Marti et al. 2015). Accordingly, the observed NDMA formation for the two samples can be attributed to ozonation alone. Pre-chlorination was extremely effective; NDMA formation for ozone-reactive precursors was reduced by over 150 µg/L (> 86%) to below the MRL (25 µg/L).

Information on the oxidation products of NDMA precursors is limited, especially for ozone-reactive NDMA precursors. A recent study by Wang et al. (2015) looked at oxidation products of doxylamine and ranitidine, which are chloramine-reactive NDMA precursors. Oxidation products were determined for chlorine, chlorine dioxide, ozone, and potassium permanganate using LC-MS/MS. Oxygen transfer to the dimethylamine under ozonation and N-dealkylation of the dimethylamine under chlorination explains why doxylamine oxidation products do not form NDMA upon subsequent chloramination (Wang et al. 2015). Similar reactions formed oxidation

products for ranitidine, which result in decreased NDMA formation with chloramination. It is possible that chlorination causes dealkylation for ozone-reactive NDMA precursors, too. In general, ozone-reactive NDMA precursors differ from chloramine-reactive NDMA precursors in that the tertiary amine is bonded to another nitrogen atom, rather than a carbon atom. One recent study investigated a variety of amine compounds, including UDMH and DMS, as formaldehyde precursors during chlorination. Although mechanisms were not offered, these two precursors had 90% and 24% formation molar yields for formaldehyde, and it was hypothesized that the chlorine attacked the primary amine sites (Kosaka et al. 2014a). It is possible that formaldehyde is one of the chlorination products for ozone-reactive NDMA precursors, but many of these compounds have secondary and tertiary amines rather than primary amines. Further investigation is warranted in order to understand the chlorination products of ozone-reactive NDMA precursors.

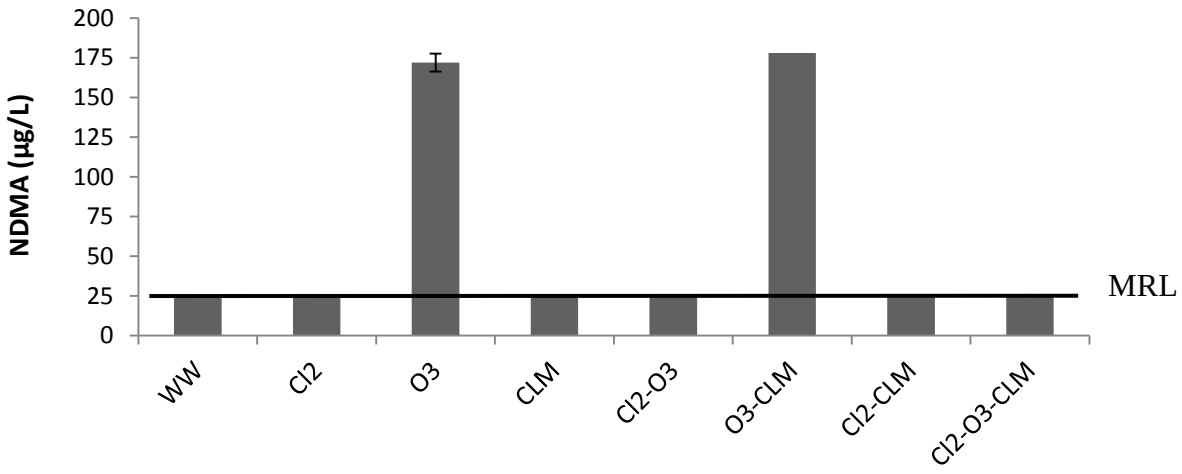


Figure 5.4: NDMA formation after disinfection treatment schemes for Site F wastewater spiked with ozone-reactive NDMA precursors. Error bar is the standard deviation (n = 2). The horizontal line is the method reporting limit (MRL).

5.4.6 Trade-offs in Disinfection Byproduct Formation

Although Site D has unusual results (i.e., high NDMA concentrations in the unaltered wastewater effluent), there were clear trends at all three sites in DBP formation and reduction by the different oxidants. Chlorination increased both THMs and HAAs, while chloramination increased HAAs and caused a slight increase in THMs. Ozonation had no impact on formation or reduction of THMs or HAAs. Ozonation and chloramination formed NDMA, but pre-chlorination reduced NDMA formation for both oxidants. Although ozonation caused direct NDMA formation, it also reduced NDMA formation in the case of post-chloramination. Based on the regulated maximum contaminant levels (MCLs) for THMs and HAAs in the U.S. (80 µg/L, 60 µg/L), chlorination resulted in THM and HAA exceedances in all cases for Site D and with Cl_2-CLM for Site E. When ozone or chloramines were used as the initial oxidants, neither MCL was exceeded for all three sites. For various NDMA guidelines (10, 40, and 100 ng/L), Site D was above the highest level in all cases because of the background concentration in the wastewater. Site E was always below the 40 ng/L Canadian guideline and below the 10 ng/L U.S. guidelines with Cl_2, Cl_2-O_3 and Cl_2-O_3-CLM treatments. Cl_2 and Cl_2-O_3 treatments at Site F met the 10 ng/L NDMA guideline, while Cl_2-O_3-CLM treatment achieved the 40 ng/L guideline. Only CLM formed NDMA above the 100 ng/L guideline at Site F.

In order to understand the combined effects and the overall outcomes, the tested disinfection treatment schemes were analyzed for trade-offs in DBP formation. First, concentrations were converted to a common unit (ng/L). Then, using NDMA as the reference, THM and HAA concentrations were multiplied by the calculated risk ratio (Table 5.3). Measured and converted values for the DBPs are shown in Table 5.4. For Site D, there was a shift in DBP composition from > 90% NDMA in the unaltered and ozonated wastewater to 52-54% NDMA when

chlorination was involved. Sites E and F had a very low sum of DBPs in the unaltered wastewater, but the shifts were the same: NDMA was a larger fraction when the first treatment step was ozonation or chloramination, and the composition was mainly THMs and HAAs when chlorination was used.

For all three sites, ozonation alone resulted in the lowest sum of DBPs compared to the unaltered wastewater. Previous studies comparing disinfection treatments also determined that ozone was more effective than chlorine, chlorine dioxide, or ultraviolet light (McCurry et al. 2015; Shah et al. 2011). Other disinfection combinations that resulted in low total DBP formation were O_3-CLM and CLM, although CLM without pre-oxidation resulted in high NDMA formation at Site F. While Cl_2-O_3 was very effective in reducing NDMA formation, increased THM and HAA formation lead to poorer performance at Sites D and E. At Site F, Cl_2-O_3 and Cl_2 performed at the same level as O_3-CLM. This site appears to have lower THM and HAA precursors than the other locations, which brings to attention that optimal disinfection treatment schemes depend on the characteristics of the particular wastewater being treated. A single treatment scheme will not be superior in all situations. In general, Cl_2-CLM and Cl_2-O_3-CLM formed the highest total of DBPs in this study. O_3-CLM provides the same benefit as Cl_2-CLM (i.e., pre-oxidation of chloramine-reactive NDMA precursors), but without additional THM and HAA formation.

Despite the poor performance for the three-step disinfection scheme (Cl_2-O_3-CLM), certain water reuse situations may benefit from this process. First, if a treated wastewater contains a high concentration of ozone-reactive NDMA precursors, which were not removed by upstream treatment processes, pre-chlorination would destroy those precursors. Optimization would be needed to balance the destruction of ozone-reactive NDMA precursors and limit the formation of

THMs and HAAs. Other methods for precursor removal, such as adsorption, membranes or reverse osmosis, would have a much higher cost. Second, ozonation would destroy any remaining chloramine-reactive NDMA precursors, as well as providing the added advantages of (1) an advanced oxidation process (i.e., formation of hydroxyl radicals) for oxidation of a wide variety of trace organic contaminants, even at a Ct < 1 mg·min/L (Dickenson et al. 2009; Gerrity and Snyder 2011; Wert et al. 2009) and (2) additional disinfection against chlorine-resistant pathogens. The third step, chloramination, would provide the necessary disinfectant residual with a low likelihood for NDMA formation and lower THM/HAA formation than chlorination.

Table 5.4: Comparison of NDMA, THM and HAA concentrations due to different disinfection treatments.

		NDMA	Total THMs		Total HAAs		Σ DBPs		Breakdown of DBPs			*DBP formation		
		Measured	Measured	Converted	Measured	Converted			NDMA	THMs	HAAs	NDMA	THMs	HAAs
Site	**Treatment**	ng/L	µg/L	ng/L	µg/L	ng/L	ng/L	*Rank*	%	%	%	ng/L	ng/L	ng/L
D	WW	220	< 0.5	< 0.4	< 1	< 1	222		99.1%	0.2%	0.5%			
	Cl_2	250	200	164	38	46	460	*4*	54.3%	35.7%	10.0%	30	163	45
	Cl_2-O_3	225 (3.1%)	210 (0.0%)	173	60 (1.2%)	73	471	*5*	47.7%	36.7%	15.5%	5	172	72
	Cl_2-CLM	280 (0.0%)	225 (3.1%)	185	50 (0.0%)	61	526	*7*	53.2%	35.2%	11.6%	60	184	60
	Cl_2-O_3-CLM	260	200	164	60	73	497	*6*	52.3%	33.0%	14.7%	40	163	72
	CLM	250	4	3	13	16	269	*3*	92.9%	1.1%	5.9%	30	2	15
	O_3-CLM	240	1	0.8	14	17	258	*2*	93.0%	0.3%	6.6%	20	0	16
	O_3	230	< 0.5	< 0.4	< 1	< 1	232	*1*	99.1%	0.2%	0.4%	10	0	0
E	WW	< 2.8	1	1	< 1	< 1	5		N/A	N/A	N/A			
	Cl_2	< 2.8	60	49	23	28	80	*4*	3.8%	61.3%	35.0%	0	48	27
	Cl_2-O_3	4	63	52	36	44	100	*5*	4.0%	52.0%	44.0%	1	51	43
	Cl_2-CLM	15	80	66	41	50	131	*7*	11.5%	50.4%	38.2%	12	65	49
	Cl_2-O_3-CLM	5.0 (1.4%)	65 (0.0%)	53	49 (0.0%)	60	118	*6*	4.2%	44.9%	50.8%	2	52	59
	CLM	42	2	2	9	11	55	*3*	76.3%	3.6%	20.0%	19	1	10
	O_3-CLM	15 (4.8%)	2 (0.0%)	2	14 (0.0%)	16	33	*2*	45.5%	6.1%	48.5%	12	1	15
	O_3	12	1	0.8	< 1	< 1	14	*1*	85.7%	5.7%	7.1%	9	0	0
F	WW	< 3.0	1	1	8	10	14		21.4%	7.1%	71.4%			
	Cl_2	< 3.0	59	48	40	49	100	*2*	3.0%	48.0%	49.0%	0	48	39
	Cl_2-O_3	10	59	48	50	61	119	*3*	8.4%	40.3%	51.3%	7	48	51
	Cl_2-CLM	64	59	48	53	64	176	*6*	36.4%	27.3%	36.4%	61	48	55
	Cl_2-O_3-CLM	18	59	48	75	91	157	*5*	11.5%	30.6%	58.0%	15	48	81
	CLM	240	6	5	29	35	280	*7*	85.7%	1.8%	12.5%	237	4	26
	O_3-CLM	75 (3.7%)	6 (0.0%)	5	32 (0.0%)	39	119	*3*	63.0%	4.2%	32.8%	72	4	29
	O_3	62 (2.3%)	1 (0.0%)	1	10 (0.0%)	12	75	*1*	82.7%	1.3%	16.0%	59	0	2

*Formation is relative to concentration in unaltered wastewater

N/A = not applicable (concentrations too low); CV% is shown in parentheses for duplicate samples

5.4.7 Implications for Water Reuse

Each disinfectant, chlorine, ozone and chloramine, forms specific DBPs, but also provides control against other DBPs. These points are summarized in Table 5.5. Additionally, the table indicates what challenges, as well as advantages, the treatment schemes pose for water reuse situations, which are discussed below.

Membranes and reverse osmosis are frequently used in advanced water treatment, especially if wastewater reuse is intended. Membrane biofouling is a major operational issue and frequently managed by chemical oxidants (Guo et al. 2012). Chlorine can be very damaging for polyamide and other membranes (Lau et al. 2012; Simon et al. 2009). Membrane degradation may still occur with chloramines, but they are much more resistant to chloramines than chlorine (Cran et al. 2011; da Silva et al. 2006). Ozone has been shown to decrease membrane fouling (Stanford et al. 2011; Van Geluwe et al. 2011). Therefore, ozone, and to a lesser extent chloramines, would be preferential pre-treatments for membranes.

A disinfectant residual is necessary during distribution. While ozone provides substantial trace organic oxidation and generates hydroxyl radicals, as mentioned previously, it has no benefit in terms of residual disinfection in distribution systems. Long chlorination contact times lead to increased THMs and HAAs (Hrudey and Charrois 2012). Chloramines are preferable since THM formation is low and it is more stable in distribution systems than chlorine (Valentine 1998). Pre-oxidation with ozone would minimize NDMA formation with chloramine-reactive precursors. Advanced water treatment plants frequently receive treated wastewater from another facility and that facility may use a chemical oxidant prior to releasing the treated wastewater. In this case, the agencies may need to collaborate and reevaluate the disinfection treatment scheme

used by the wastewater treatment facility in order to integrate the treatment processes and meet both parties' needs.

The advantages of ozone clearly stand out for water reuse and DBP control. A special water reuse situation, where the treated water contains a significant concentration of ozone-reactive NDMA precursors, could be controlled with pre-chlorination and careful optimization to limit THM and HAA formation or removal of THMs and HAAs with activated carbon. Further research is required to determine the lowest possible chlorine exposure needed to reduce NDMA formation from ozone-reactive precursors. In addition, it would be sensible to conduct toxicity testing to get a better picture of total DBPs for the disinfection treatment schemes.

Table 5.5: Summary of disinfection byproduct formation and control and advantages for water reuse situations with different treatment schemes

Treatment scheme	DBP Formation			DBP Control			Water Reuse Scenario
	NDMA	THM	HAA	NDMA	THM	HAA	
Cl_2		–	–	+			– Harmful to membranes + Reduces membrane biofouling
O_3	–			+	+	+	+ TOrC oxidation, AOP + Reduces organic membrane fouling + Bulk organic transformation
CLM	–		–		+		+ Reduces membrane biofouling
Cl_2-O_3		–	–	+			+ TOrC oxidation, AOP + Reduces organic membrane fouling
O_3-CLM	–			+	+		+ TOrC oxidation, AOP + Reduces organic membrane fouling + CLM residual without NDMA formation
Cl_2-CLM		–	–	+			+ Reduces membrane biofouling + CLM residual without NDMA formation
Cl_2-O_3-CLM		–	–	+			+ Additional disinfection credits + TOrC oxidation, AOP + Reduces organic membrane fouling + Reduces membrane biofouling + CLM residual without NDMA formation

– (negative sign) = disadvantage / DBP formation; + (positive sign) = advantage / DBP control; TOrC = trace organic contaminant; AOP = advanced oxidation process; MF = microfiltration; RO = reverse osmosis

5.5 Conclusion

This study examined the formation and reduction of NDMA, THMs, and HAAs, with seven disinfection treatment schemes. As seen in previous work, ozone was very effective at minimizing formation of the targeted DBPs. The top two treatment schemes resulting in the lowest total DBP formation were ozonation and ozonation-chloramination. Both of these treatment schemes also provide several advantages for application in water reuse situations. Evidence from this work indicates that pre-chlorination destroys ozone-reactive NDMA precursors, though the mechanism is not yet known. More research is needed to understand the oxidation products from this reaction, as well as the minimum chlorine exposure needed to destroy these precursors.

CHAPTER 6

THE IMPACTS OF BIOFILTRATION ON NDMA PRECURSOR REMOVAL AND DISINFECTION BYPRODUCT FORMATION

6.1 Abstract

Removal of *N*-Nitrosodimethylamine (NDMA) precursors during non-optimized biofiltration of tertiary-treated wastewater was investigated. NDMA precursor removal for four compounds (ranitidine, daminozide, 1,1,1',1'-tetramethyl-4,4'-(methylene-di-p-phenylene)disemicarbazide (TMDS) and 2-furaldehyde dimethylhydrazone (2-F-DMH)) and disinfection byproduct (DBP) formation potentials (trihalomethanes, haloacetic acids) were assessed before and after biofiltration in a pilot biofiltration unit with three anthracite-containing columns operated at different contact times (5, 10, 20 minutes). Precursor removal varied (ranitidine: 6-7%; daminozide: 74-85%; 2-F-DMH: 15-26%; TMDS: 11-24%) and was correlated to dissolved oxygen concentration for 2-F-DMH and TMDS. Contact time significantly affected removal for TMDS. Although some sorption to the media occurred, biodegradation and sorption to biofilm are likely the main mechanisms for precursor removal. Trihalomethane and haloacetic acid formation potentials were marginally decreased with non-optimized biofiltration.

6.2 Introduction

Reducing the formation of disinfection byproducts (DBPs) is a continual challenge for drinking water treatment. The US Environmental Protection Agency regulates two groups of DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs), and allows for maximum concentrations of 80 μg/L and 60 μg/L, respectively (USEPA 2014b). THMs and HAAs are principally formed when water is disinfected with chlorine (Singer 1999).

N-Nitrosodimethylamine (NDMA), a DBP and probable human carcinogen, is one of many substances under review for regulation under the Safe Drinking Water Act and may be regulated in drinking water in the near future (USEPA 2014a; USEPA 2014c). NDMA formation is a concern not only in drinking water, but also in water reuse applications (Fujioka et al. 2012; Gerrity and Snyder 2011; Joss et al. 2011; Sonntag and von Gunten 2012).

Biofiltration is an option for eliminating DBP precursors, such as those that result in NDMA, THM and HAA formation. Compared to chemical oxidation processes, biodegradation typically leads to greater mineralization of compounds (van Agteren et al. 1998). Full-scale biological activated carbon (BAC) filters have been shown to reduce NDMA chloramine formation potential (NDMA-FP) by more than 80% (Farre et al. 2011). Biofiltration media type impacts removal and BAC generally results in greater removal compared to sand or anthracite (Reaume et al. 2015; Reungoat et al. 2011). Because many organic compounds are adsorbed to activated carbon within the filter, the bacteria have more time to biodegrade the compounds, resulting in greater removal when activated carbon is used as the media instead of sand or anthracite. As alluded to earlier, the amount of time that the contaminant interacts with the media and the biofilm, known as empty bed contact time (EBCT), is another important parameter and can significantly affect removal in biofilters (Halle et al. 2015).

Biodegradation of several chloramine-reactive NDMA precursors (dimethylamine, ranitidine, trimethylamine, dimethylformamide, *N*-dimethyldithiocarbamate, dimethylaminobenzene, doxylamine) in activated sludge systems has been studied (Jelic et al. 2011; Radjenovic et al. 2007; Wang and Li 2015), but there is limited information on removal during biofiltration of treated wastewater effluent. Reungoat and collaborators tracked removal of doxylamine, erythromycin, roxithromycin, tramadol, and ranitidine from wastewater after BAC treatment.

Removal was variable and attributed to both biodegradation and sorption (Reungoat et al. 2010; Reungoat et al. 2011). To the best of the author's knowledge, no studies have specifically focused on removal of ozone-reactive NDMA precursors by biofiltration.

The goal of this research was to investigate the removal of specific NDMA precursors from treated wastewater effluent during biofiltration. Several knowledge gaps exist, including: the process responsible for precursor removal (e.g. sorption to media, sorption to biofilm, biodegradation), the impact of EBCT, and the extent of removal for specific NDMA precursors in a non-optimized biofilter. Additionally, THM and HAA formation potential was measured in order to determine if biofiltration could provide simultaneous removal of NDMA, THM, and HAA precursors.

6.3 Materials and Methods

6.3.1 Biofiltration Unit Design and Operation

Biofiltration columns, located at a wastewater treatment facility, were constructed with glass columns (Ace Glass, Vineland, NJ) of different lengths (45, 60, 120 cm) with threaded nylon adapters at each end and glass beads and packing support at the outlet. Columns were filled with ANSI/NSF 61 certified anthracite (effective size 1.35-1.45 mm; uniformity coefficient < 1.40) and covered with aluminum foil to block out light. The three columns had the same flow rate (100 mL/min) and different amounts of media, which corresponded to empty bed contact times (EBCTs) of 5, 10, and 20 minutes. EBCT is the average time the water stays in contact with the media and was calculated by dividing the volume of the media in the column by the wastewater flow rate through the column. Hydraulic loading rate was calculated as flow rate divided by the surface area of the column. Biofiltration column design parameters are shown in Tables 6.1 and

6.2. Figure 6.1 shows the experimental setup for the biofiltration columns. Prior to starting the NDMA removal experiments, the columns were acclimated to tertiary-treated wastewater in alternating cycles of recirculating batch mode and flow-through mode for 11 weeks as part of a related experiment. Before commencing the NDMA precursor removal test (i.e., preparation phase), the columns were run in flow-through mode for 10 days, which corresponds to about 720 EBCTs. Biofilm growth was visible on the anthracite and confirmed through solid-phase measurement of adenosine triphosphate (ATP).

Columns were operated continually during the preparation phase and test period, with the exception of one day during the preparation phase when the feedwater tank ran dry. No backwashing occurred. Instead, between the 10-day preparation phase and 14-day test period, the columns were shaken to fluidize the media and detached particulates were flushed off the top layer of the media. During the preparation phase, columns received the same feedwater and a single influent sample was collected for all columns from the feedwater tank. During the test period, the feedwater (tertiary-treated wastewater) was spiked with a mixture of NDMA precursors. The wastewater and NDMA precursor mixture were pumped into a 125 gallon high density polyethylene (HDPE) tank for blending. Sampling ports were added to each feed line instead of assuming a homogeneous mixture in the tank. Peristaltic pumps (Cole Palmer, Masterflex with Easy Load Pump Head) were used to maintain a constant flow of 100 mL/min to the columns. The residence time in the feed lines was less than five minutes, and the residence time in the tank was 18-24 hours. Biodegradation or sorption may have occurred in the feed lines or tank; however, the residence time between the sample ports and the columns was short (influent: < 20 s; effluent: < 5 s). As a result, measured removals were the result of the biofiltration rather than any biodegradation or sorption occurring within the feedwater system.

The performance of the system was monitored daily by total organic carbon (TOC), chemical oxygen demand (COD), and dissolved oxygen (DO). DO was not regulated and varied depending on the concentration in the feedwater. ATP was measured at the start and end of the test period. Ambient temperature within the pilot plant likely varied, but the wastewater temperature remained reasonably consistent in the range of 22-25 °C. Column influent and effluent samples were analyzed daily for individual precursors and total nitrogen (TN). NDMA, THMs and HAAs were analyzed on three days (4, 11, 14) during the test period and once during the preparation phase.

All connecting tubing was periodically replaced due to biofilm growth. New ¼ inch inner diameter Tygon tubing was used for the feedwater lines at the start of the test period and these were replaced on day 11 of the test period because biofilm was sloughing off the tubing interior and accumulating at the top of the columns. Biofilm also clogged the waste lines and those were replaced during the test period, but this had no impact on precursor removal. Biofilm in the feedwater lines may have increased precursor removal; however, the tubing lengths were similar for the columns, so all columns should have been affected equally.

Table 6.1: Parameters used in the design of the biofiltration columns.

Parameter	**Value**	**Value**
Column Inner Diameter	5 cm	0.164 ft
Column Area	09.63 cm^2	0.021 ft^2
Hydraulic Loading Rate	5.0 mL/min·cm^2	1.2 gpm/ft^2
D/d ratio (Column diameter to media diameter)	34-37	34-37
Flow Rate	100 mL/min	0.026 gpm

Table 6.2: Empty bed contact times and media parameters for the biofiltration columns.

Column	EBCT	Media Height	Media Volume
1	5 min	25 cm	0.49 L
2	10 min	50 cm	0.98 L
3	20 min	100 cm	1.96 L

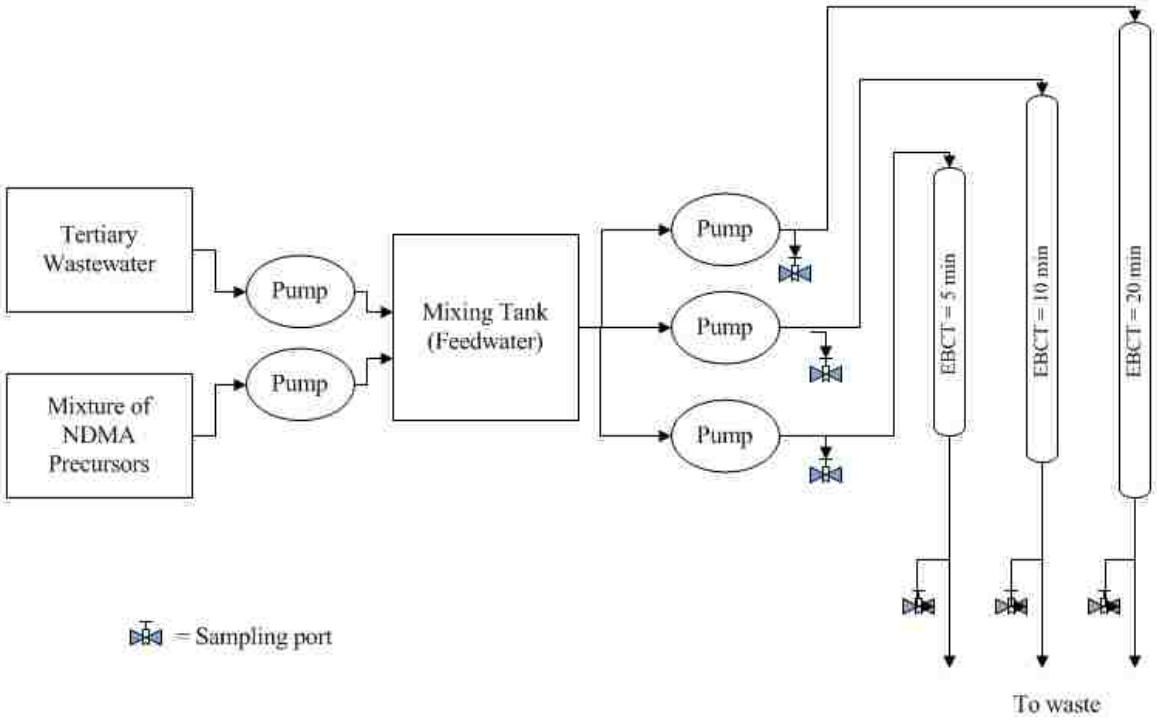


Figure 6.1: Schematic of the biofiltration columns setup used to investigate disinfection byproduct precursor removal.

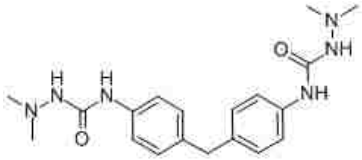
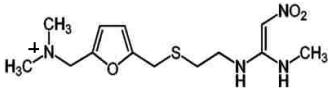
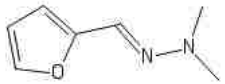
6.3.2 Preparation of NDMA Precursors Mixture

Compounds to be added to the treated wastewater effluent were selected based on known potential to form NDMA with ozone or chloramines, purchase availability, and capability for liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis. Only one of the selected compounds, ranitidine, has been detected in U.S. wastewaters (Kolpin et al. 2002) and was present in the feedwater (0.0065 μM or 2.0 μg/L). Individual stock solutions of four NDMA precursors were prepared from neat standards (

Table 6.3): 2-furaldehyde 2,2-dimethylhydrazone (2-F-DMH) (Alfa Aesar, Lancashire, United Kingdom); ranitidine hydrochloride (Sigma, St. Louis, MO); 1,1,1',1'-tetramethyl-4,4'-(methylenedi-p-phenylene)disemicarbazide (TMDS) (TCI America, Portland, OR); and daminozide (Fluka, Steinheim, Germany). Stock solutions were prepared at 1 mM. TMDS was prepared in 50/50 acetonitrile/water because of its low solubility in water. After dilution in the wastewater, acetonitrile concentration was < 42 mg/L, which is well below the toxicity that would inhibit the growth of aerobic heterotrophs, methanogens and other bacteria (Blum and Speece 1991; Kahru et al. 1996). All other precursor stock solutions were made with ultrapure water.

Batches of the NDMA precursor mixture were generated daily. First, equal aliquots of the stock solutions were mixed together and diluted by approximately 300-fold with tap water. This diluted mixture was then pumped into the 125 gallon HDPE tank and mixed with the tertiary wastewater at a ratio of about 30:1. A precursor concentration of 0.1 μM was targeted in the feedwater in order to have an initial concentration within the LC-MS/MS analytical range and without the need to concentrate the sample.

Table 6.3: Molecular weights, pK_a, charge and sorption, partition and soil coefficients for the tested NDMA precursors.

Precursor	Structure	Use	Molecular Weight (g/mol)	Sorption coefficient, K_d (L/kg)	Partition coefficient, Log K_{ow}, pH 7	Soil Sorption coefficient, Log K_{oc}	pK_a	Charge of compound at pH 7
TMDS		Yellow inhibitor and light stabilizer for polyamide resins	368.48	N/A	1.61[b]	N/A	1.6[a]	Neutral
Ranitidine		Histamine-2 blocker for treating and preventing stomach ulcers	314.4	420[d] 50[g]	-1.2[b] 0.27[e]	3.13[g]	7.9[a] 8.2[e]	Positive
Daminozide		Plant growth regulator	160.17	N/A	-3.81[b] -1.50[f]	0.903[c]	1.50[a] 4.68[f]	Neutral
2-F-DMH		Synthesis building block	138.17	N/A	0.63[b]	N/A	1.11[a]	Neutral

[a] Predicted with MarvinSketch (ChemAxon 2016b); [b] Predicted with MarvinJS (ChemAxon 2016a); [c] Calculated from Kenaga 1980; [d] Vasiliadou et al. 2013; [e] Hernando et al. 2007; [f] Tomlin 1997; [g] Predicted from Barron et al. 2009; N/A = not available

6.3.3 Sample Collection, Preservation and Storage

Influent and effluent samples were collected from sampling ports before and after the biofilter columns. To nullify any issue with feedwater non-homogeneity, effluent samples were collected after influent samples at times corresponding to the EBCT. Sampling lines were purged for several minutes into a waste vessel prior to filling sample containers. Collection occurred at different times on sampling dates and some of the change in daily TOC and COD may be attributed to diurnal variation in the feedwater.

Samples were brought to the lab, stored at 4 °C until analyses were performed within the time frames given below. Ozonation and chloramination testing, described in the next section, occurred on the same day as sample collection. All samples for NDMA analysis were preserved with sodium thiosulfate (80 mg/L) and sodium azide (1 g/L). The 7-day THM/HAA formation potential (THM/HAA-FP) procedure was initiated the day after collection. After the test was complete, THM and HAA samples were preserved with 30 µL of 10% sodium thiosulfate and 6 mg of ammonium chloride, respectively. NDMA, THM and HAA analysis occurred within 14 days. NDMA precursors were analyzed within 7 days.

6.3.4 Experimental Procedures

Collected samples underwent ozonation formation potential (O_3-FP), chloramination at uniform formation conditions (CLM-UFC), and THM/HAA-FP testing. O_3-FP was performed through the addition of ozone-saturated water to the sample. Ozonated water was generated using an oxygen-fed generator (model CFS-1A, Ozonia North America, Inc., Elmwood Park, NJ, USA) to diffuse ozone into cold ultrapure water as described elsewhere (Wert et al. 2009). The concentration of the ozone stock solution was measured with a Hach DR5000 UV/Vis spectrophotometer at 600 nm using a modified indigo method (Rakness et al. 2010). The ozone

stock solution was typically between 65 and 85 mg O_3/L. An appropriate volume was dosed into samples to achieve the desired ozone to TOC ratio (O_3:TOC = 0.8), taking dilution into account. Samples were capped, mixed by inverting, and left at room temperature for one day to ensure ozone residual was zero before opening the bottles.

CLM-UFC testing was completed following an established procedure (Shah et al. 2012). A fresh monochloramine solution was prepared for each analysis from sodium hypochlorite and ammonium chloride (Sigma-Aldrich, St. Louis, MO). Samples were buffered (4 mM borate, pH 8), spiked at 5 mg/L as Cl_2, and kept at room temperature in the dark for three days. At the conclusion of the procedure, samples were checked for a minimum residual (1 mg/L as Cl_2) and then quenched with sodium thiosulfate.

THM/HAA-FP testing involved determining an initial chlorine demand, spiking multiple samples with chlorine, and choosing the sample with an appropriate residual. First, a 60 mL sample was dosed at 100 mg/L as Cl_2 with 10 mM phosphate buffer at pH 7. After leaving the sample for 24 hours at room temperature and in the dark, the chlorine residual was measured using the DPD method and the chlorine demand was calculated as the difference between the original concentration (100 mg/L as Cl_2) and the chlorine residual. Next, a series of samples (n = 6) were buffered and dosed with chlorine (ranging from 15-60 mg/L as Cl_2 depending on the chlorine demand) and kept in the dark at room temperature. After 7 days, the chlorine residual was measured and the sample that fell in the range of 3-5 mg/L as Cl_2 was used for analysis.

6.3.5 Testing for Adsorption of the Precursors to Anthracite

Sorption of the precursors to anthracite was determined in order to establish which mechanisms (i.e., sorption to media, sorption to biofilm, biodegradation) were responsible for precursor removal. Batch adsorption tests were performed using 125 mL borosilicate glass serum

bottles and fresh anthracite media. The anthracite and bottles were sterilized by autoclaving (20 min at 250 °C). Anthracite was weighed (0.1, 0.2, 0.3, 0.4, 0.5, and 2.0 g) and added to the glass bottles, along with 100 mL of the precursor-spiked wastewater. The bottles were sealed with a rubber septum and crimped closed with an aluminum ring (Wheaton, Vernon Hills, IL) before being attached to a rotating shaker and mixed constantly at 20 rpm for 24 or 48 hours. The following control samples were included: blank (deionized water with 2.0 g anthracite), control (precursor-spiked wastewater and no anthracite), and negative control (wastewater without precursors and 2.0 g anthracite). After the desired contact time, bottles were opened and samples were filtered through a pre-rinsed syringe filter (Whatman 0.7 μM GF/F with GMF) to remove suspended anthracite particles. The filtrate was analyzed for the individual precursors.

6.3.6 Analytical Methods

Biofiltration performance parameters

DO, TOC and COD were measured daily, and TN was measured twice weekly. DO was measured by luminescence using a portable probe (Hach sensION+ DO6). The probe was calibrated once with water-saturated air at the start of the biofiltration study. The probe reading was confirmed (0.5 mg O_2/L) on one occasion with the Hach dissolved oxygen method (Method 8166) that utilizes the Indigo Carmine method, AccuVac ampules, and a Hach DR 6000 spectrophotometer. TOC samples were acidified to pH < 3 with hydrochloric acid and analyzed using a Shimadzu TOC-V (Shimadzu Scientific Instruments, Carlsbad, CA). Samples were acidified within a few hours of collection and stored at 4 °C for up to 48 hours before analysis. Calibration standards (0-20 mg C/L) were prepared from a 1000 mg C/L glucose stock solution and a 100 mg C/L working stock solution. The stock solution was replaced every two months, and calibration standards were prepared fresh for every analysis. Blanks were prepared by

acidifying deionized water with HCl to pH < 3. One standard was analyzed after every 6-8 samples as a calibration check. COD was measured using Hach low range (3-150 mg/L) COD digestion vials by the reactor digestion method (Method 8000) with dichromate. A 2 mL sample was added the vial and digested in a DRB 200 reactor for 120 minutes at 150 °C. Absorbance was measured at 420 nm for the cooled samples using a Hach DR 5000 spectrophotometer. The instrument was zeroed for each analysis with a blank prepared from deionized water. TN was measured using the low range Persulfate Digestion Test 'N Tube™ Method (Hach Method 10071) and analyzed using a Hach DR 5000 spectrophotometer. The instrument was zeroed with a blank prepared from deionized water and treated (i.e., digested) in the same manner as the sample.

N-Nitrosodimethylamine

Samples were preserved with sodium thiosulfate (80 mg/L) and sodium azide (1 g/L) upon collection. One liter samples underwent automated solid phase extraction with a Dionex Autotrace 280 workstation (Thermo Scientific) by the Southern Nevada Water Authority Laboratory (Holady et al. 2012). Conditioned activated charcoal cartridges were used and extracts were eluted with dichloromethane and dried under nitrogen to 1 mL. Water was removed with sodium sulfate DryDisks and the final concentration factor was 1:1000. Extracts were injected (2 µL) in splitless mode through a 30 m x 0.32 mm ID x 1.4 µm DB624 column with helium flow and into the GC-MS (Agilent 7000C). Parent (m/z = 75) and product ions (m/z = 47, 44, 58) were monitored, and the reporting limit (2.5 µg/L) was set at three to five times the calculated method detection limit.

Trihalomethanes

THMs were quantified using EPA method 524.3 by the Southern Nevada Water Authority Water Quality Chemistry Laboratory. Four THMs (bromoform, bromodichloromethane, chloroform, chlorodibromomethane) were measured. A Stratum PTC purge and trap concentrator with an AQUATek 100 autosampler (Teledyne Tekmar) was used for THM extraction of a headspace-free 40 mL sample. THM analysis used a Thermo Scientific TRACE gas chromatograph with Electronic Pressure Control and a Split/Splitless injection port coupled to a Thermo Scientific ISQ mass spectrometer. Samples were separated on a RTX-VMS GC column (Restek).

Haloacetic acids

HAAs were quantified using EPA method 552.2 by the Southern Nevada Water Authority Water Quality Chemistry Laboratory. Five haloacetic acids (bromoacetic acid, dibromoacetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid) were measured from a headspace-free 60 mL sample. HAA analysis used a Varian CP-3800 gas chromatograph with dual Electron Capture Detectors and a CTC Analytics CombiPal Autosampler. Samples were separated with a J&W DB-1701 GC column (Agilent), and spectra were quantified with Dionex/Thermo Chromeleon version 6.8 software.

Adenosine Triphosphate

ATP was analyzed using a Deposit and Surface Analysis test kit (LuminUltra Technologies Ltd), which is designed for measuring ATP in biofilm and on biological filter media. The test uses firefly luciferase enzyme to produce light in the presence of ATP, and the light is measured in a luminometer as Relative Light Units (RLU). Calibration was performed with 100 µL of UltraCheck 1. Luminase enzyme was rehydrated and tested to ensure a reading of > 5,000 RLU.

Media samples were gently rinsed with ultrapure water to remove unattached growth and dried by vacuum filtration. 1 g of media was transferred to 5 mL of UltraLyse 7 for extraction. After vigorous mixing for 30 seconds and at least five minutes sitting in the extraction solution, the sample was diluted by transferring 1 mL to a 9 mL UltraLute Dilution Tube. Then 100 µL of the diluted sample was mixed with 100 µL of rehydrated luminase enzyme in an assay tube, swirled, and measured in the luminometer (PhotonMaster^{TM} Luminometer, LuminUltra). LuminCalc software was used to calculate the total ATP (pg tATP/g sample) from the measured RLU value.

NDMA Precursors

Individual precursors were analyzed by direct injection (10 µL) with LC-MS/MS. Precursors were monitored for one or two mass transitions (Table 6.4). A Luna C18(2) column (Phenomenex) was used for separation with the LC system (Agilent 1100 LC with binary pump and CTC PAL autosampler). The mobile phases 0.1% formic acid (A) and methanol (B) were run at 0.8 mL/min on a gradient starting at 10% B for 5 min, increased linearly over 5 min to 90% B at 10 min, held until 15 minutes, and returned to 10% B over 3 min. The mass spectrometer (API 4000 triple quad, Applied Biosystems) was operated via multiple reaction-monitoring in positive-ion electrospray ionization (ESI+) mode with a source temperature of 500 °C. An external calibration with 7 points for each precursor was used. R^2 values of 0.995 or better were observed for all compounds. One standard was analyzed every 6-8 samples as a calibration check. Reporting limits were set at greater than five times the signal to noise ratio and were based on the instrument detection limit (n = 12) for individual precursors.

Table 6.4: Parameters for LC-MS/MS analysis of NDMA precursors.

Precursor	Analytical Range (µM)	Transition	Confirmation Transition	Retention Time
TMDS	0.0025 – 0.125	371.2 / 285.2		12.6
Daminozide	0.0075 – 0.20	161.0 / 143.1		2.84
2-F-DMH	0.005 – 0.25	139.0 / 96.1		11.68
Ranitidine	0.0005 – 0.10	315.3 / 176.2	315.3 / 130.1	8.75

6.3.7 Calculations and Statistical Analyses

NDMA precursor removal was calculated based on the concentrations in the influent and effluent according to Equation 4. In this regard, removal represents the loss of the parent compound and does not indicate complete mineralization.

Equation 4: Calculation of NDMA precursor removal during biofiltration using precursor concentrations in column influent (C_{inf}) and effluent (C_{eff}).

$$\frac{C_{inf} - C_{eff}}{C_{\text{inf}}} x\ 100 = \%\ removal$$

Statistical analyses were completed in Excel using the Analysis Toolpak add-in. Significant removal was determined through a one-tailed paired t-test for column influent and column effluent concentrations. ATP measurements at the start and end of the test period were analyzed with a t-test to determine if the means were significantly different. One-way analysis of variance (ANOVA) was used to determine statistically significant differences ($\alpha = 0.05$) among the three columns for TOC, COD and precursor removal. Correlation between precursor removal and DO was examined by regression.

6.4 Results and Discussion

6.4.1 Biofiltration Performance

Water quality data for the tertiary-treated wastewater are presented in Table 6.5. The carbon:nitrogen:phosphorus (C:N:P) ratio is substantially important to interpreting the results of this research. A generally accepted chemical formula for biomass is $C_5H_7O_2NP_{0.074}$ (Droste 1997), which corresponds to a C:N:P mass ratio of 100:23:4. The tertiary-treated wastewater had a C:N:P mass ratio of 100:165:1.3. Clearly, nitrogen is in excess and this is due to the presence of a significant amount of nitrate because the wastewater treatment plant does not have a denitrification process step. Phosphorus was one-third of the recommended ratio, which indicates it is a limiting element for bacterial growth. This wastewater treatment facility is required to achieve very low phosphorus concentrations and applies biological phosphorus removal (BPR) for this purpose. The low phosphorus concentration likely limited biofilm growth, which, in turn, affected organic carbon and DBP removal.

Performance was monitored daily by TOC, COD and DO. During the preparation phase, TOC removal was more consistent and at a higher percentage than COD removal across all EBCTs (Table 6.6). Among the columns, TOC and COD removal were highest for column 2, but the removals were not significantly different from columns 1 and 3, as determined by one-way ANOVA (TOC: $p = 0.099$; COD: $p = 0.227$). Notably, column 2 had the lowest observed ATP concentration, but it is not possible to determine the statistical significance of this measurement because only a single analysis was performed. Notwithstanding, previous studies have observed that the amount of biomass does not accurately predict organic carbon and DBP removal, especially when biomass is only measured at the top of a biofilter (Urfer et al. 1997). Biofiltration performance was more variable during the 14-day test period (Table 6.7). The

increase in TOC and COD concentrations in the test period compared to the preparation phase (Figure 6.2) can be attributed to the acetonitrile used to dissolve one of the NDMA precursors, rather than the carbon contribution of the precursors themselves (~0.08 mg C/L). The inconsistent TOC and COD concentrations in the influent are most likely due to uneven mixing of the precursor mixture and wastewater within the feedwater tank. Increased biofilm growth over time in the feedwater lines may also affect influent TOC and COD by providing extra removal ahead of the sample collection ports. Average COD removal increased linearly with greater contact time (R^2 = 1.000) while average TOC removal was relatively unchanged for the three columns; however, in neither case were the removals for the three columns statistically significantly different as determined by one-way ANOVA (TOC: p = 0.739; COD: p = 0.117). TOC and COD removals were also not significantly different between the preparation phase and test period for any column (Student's t-test, $p > 0.08$)

TOC removal was low compared to other biofiltration studies involving treated wastewater where removal was > 40% (Farre et al. 2011; Reaume et al. 2015; Reungoat et al. 2011). However, TOC removal in this study, under the limiting phosphorus condition, is comparable to biofiltration for drinking water where TOC removals were 6-26% for sand and mixed-media (anthracite, sand, garnet) biofilters (LeChevallier et al. 1992; Zearley and Summers 2012).

Dissolved oxygen concentration was lower during the test period (0.54 ± 0.20 mg/L) compared to the preparation phase (1.62 ± 0.63 mg/L), except for two days when the wastewater was aerated due to another pilot plant experiment. DO decreased ~0.6 mg/L across each column during the preparation phase, but only ~0.1 mg/L across each column during the test period, indicating there was limited aerobic activity during the test period. At the end, all columns had similar ATP concentrations for biofilm removed from the top of the column, and the mean ATP

concentrations at the start and end of the test period were not significantly different (Student's t-test, $p = 0.595$). Although the microbial community composition was not determined, there was likely a mixture of aerobic and anaerobic bacteria in the biofilter as a result of varying DO concentration and the likely presence of pockets of aerobic and anaerobic micro-environments (Hu and Wang 2005). Micro-environments can be the result of a DO gradient stemming from DO loss across the height of the media or caused by extracellular polymeric substances produced by microorganisms (Chenu 1993; Wingender et al. 2012).

It is probable that higher phosphorus concentration in the effluent would promote greater TOC and COD removal by biofiltration. Phosphorus addition was shown to increase biofilter performance and bacteria growth for drinking water, groundwater and surface water systems (Lauderdale et al. 2012; Lehtola et al. 2002; Li et al. 2010; Nishijima et al. 1997; Sang et al. 2003), and the wastewater used in this research has a phosphorus concentration comparable to those waters. If biofiltration were to be added to this facility, phosphorus removal could be reduced during secondary BPR treatment to allow for sufficient phosphorus concentration in the effluent, which would facilitate bacteria growth and promote biofiltration.

Table 6.5: Water quality data and formation potential concentrations for the tertiary-treated wastewater during the preparation phase.

Parameter	**Avg. Value**	**Unit**	**Parameter**	**Conc.**		**Unit**
				Column 3 Influent	Column 3 Effluent	
TOC	6.91 ± 0.43	mg C/L	THM-FP	0.34	0.28	mg/L
COD	20.8 ± 2.9	mg/L	HAA-FP	0.37	0.29	mg/L
DO	1.62 ± 0.63	mg O_2/L	NDMA	< 2.5	< 2.5	ng/L
pH	6.93 ± 0.04		CLM-UFC	280	290	ng/L NDMA
Ammonium	< 0.05	mg/L as N	O_3-FP	20.5 ± 0.71	15	ng/L NDMA
Total Nitrogen	11.4 ± 1.1	mg/L as N				
Temp.	23.7 ± 0.7	° C				
Total Phosphorus	0.087 ± 0.008	mg PO_4^{3-}/L				

Table 6.6: Average TOC and COD influent and effluent concentrations and removal for biofiltration columns during the preparation phase.

	Column 1 EBCT = 5 min	**Column 2** EBCT = 10 min	**Column 3** EBCT = 20 min	**All Columns** Avg. all EBCTs
tATP (pg/g)	$5.17x10^6$	$2.61x10^6$	$3.52x10^6$	$3.77x10^6$
Avg. TOC influent (mg C/L)	-	-	-	6.89 ± 0.41 CV = 5.9%
Avg. TOC effluent (mg C/L)	6.44 ± 0.43 CV = 6.6%	6.08 ± 0.23 CV = 3.8%	7.03 ± 2.53 CV = 36.0%	6.52 ± 1.49 CV = 22.8%
Avg. TOC removal (%)	6.3% ± 0.065 CV = 104%	11.6% ± 0.039 CV = 33.4%	9.3% ± 0.042 CV = 45.4%	9.1% ± 0.053 CV = 58.9%
Avg. COD influent (mg O_2/L)	-	-	-	20.8 ± 2.9 CV = 14.4%
Avg. COD effluent (mg O_2/L)	19.3 ± 2.7 CV = 13.7%	18.5 ± 2.9 CV = 15.5%	20.2 ± 4.0 CV = 20.0%	19.4 ± 3.2 CV = 16.6%
Avg. COD removal (%)	5.6% ± 0.055 CV = 98.0%	10.9% ± 0.046 CV = 42.1%	5.8% ± 0.100 CV = 172%	7.6% ± 0.072 CV = 94.6%

- = not measured; CV = coefficient of variation; TOC = total organic carbon; COD = chemical oxygen demand; EBCT = empty bed contact time; tATP = total adenosine triphosphate

Table 6.7: Average TOC and COD influent and effluent concentrations and removal for biofiltration columns during the test period.

	Column 1 EBCT = 5 min	**Column 2** EBCT = 10 min	**Column 3** EBCT = 20 min	**All Columns** Avg. all EBCTs
Final tATP (pg/g)	$3.32x10^6$	$3.48x10^6$	$3.08x10^6$	$3.29x10^6$
Avg. TOC influent (mg C/L)	12.4 ± 4.7 CV = 37.7%	12.7 ± 5.0 CV = 39.1%	12.3 ± 4.9 CV = 39.8%	12.7 ± 4.7 CV = 36.8%
Avg. TOC effluent (mg C/L)	12.1 ± 4.4 CV = 35.8%	12.1 ± 4.5 CV = 36.8%	11.9 ± 4.8 CV = 40.4%	12.0 ± 4.4 CV = 36.7%
Avg. TOC removal (%)	7.3% ± 0.053 CV = 72.1%	9.5% ± 0.043 CV = 45.6%	8.5% ± 0.105 CV = 124%	8.4% ± 0.071 CV = 84%
Avg. COD influent (mg O_2/L)	32.3 ± 11.9 CV = 36.9%	34.1 ± 12.1 CV = 35.4%	33.6 ± 10.9 CV = 32.6%	34.3 ± 11.8 CV = 34.4%
Avg. COD effluent (mg O_2/L)	33.0 ± 11.6 CV = 35.0%	33.6 ± 10.7 CV = 31.7%	31.2 ± 12.9 CV = 41.1%	32.6 ± 11.5 CV = 35.2 %
Avg. COD removal (%)	3.5% ± 0.160 CV = 461%	7.3% ± 0.079 CV = 108%	14.8% ± 0.160 CV = 108%	8.5% ± 0.143 CV = 167%

CV = coefficient of variation; TOC = total organic carbon; COD = chemical oxygen demand; EBCT = empty bed contact time; tATP = total adenosine triphosphate

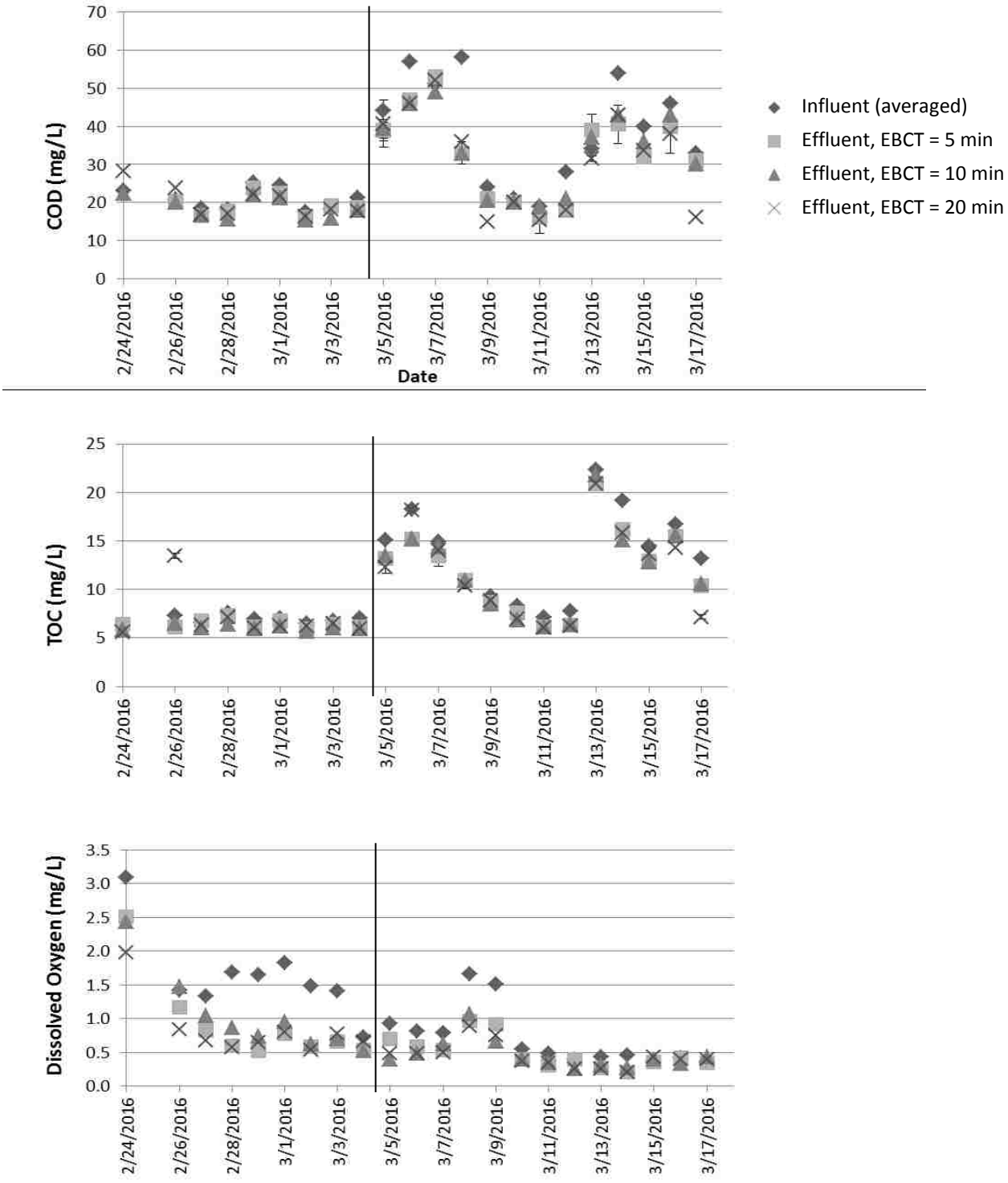


Figure 6.2: Daily TOC, COD and DO measurements for biofiltration column influent (average) and effluent. The vertical line denotes the change from the preparation phase to the test period. Error bars are one standard deviation (n = 2).

6.4.2 Sorption of Precursors to Media

Although anthracite is considered a non-adsorptive media for organics (Urfer et al. 1997), some adsorption can occur. A batch test for adsorption was completed using sterile, fresh anthracite and the same precursor-spiked wastewater as the biofiltration columns. Based on the hydraulic loading rate for the columns and the column area, the amount of wastewater passing through the media in 24 and 48 hours was calculated (48 hours shown):

$$Amount\ of\ WW = hydraulic\ loading\ rate\ \left(\frac{gpm}{ft^2}\right) x\ column\ area\ (ft^2)\ x\ time\ (\text{min})$$

$$Amount\ of\ WW = \frac{1.2\ gpm}{ft^2} x\ 0.021\ ft^2\ x\ 2880\ \text{min} = 72.57\ \text{gal WW}$$

Next, the media volume for each column was converted to mass using density (column 3 shown):

$$Mass\ of\ media = Volume\ (L)\ x\ density\ (\frac{kg}{L})$$

$$Mass\ of\ media = 1.963\ L\ x\ 1.4\frac{kg}{L} =\ 2.75\ kg$$

Finally, the ratio of wastewater to media was determined:

$$\frac{Volume\ of\ WW}{Mass\ of\ media} = \frac{gal\ WW}{kg\ media}\ x\ \frac{3.785\ L}{gal}\ x\frac{1000\ mL}{L}\ x\ \frac{kg}{1000\ g} = \frac{mL\ WW}{g\ media}$$

$$\frac{Volume\ of\ WW}{Mass\ of\ media} = \frac{72.57\ gal}{2.75\ kg}\ x\ \frac{3.785\ L}{gal}\ x\frac{1000\ mL}{L}\ x\ \frac{kg}{1000\ g} = \frac{99.88\ mL}{1\ g} \sim \frac{100\ mL}{1\ g}$$

A constant volume of 100 mL wastewater was used for the batch sorption test, and the amount of anthracite varied from 0.1 to 2.0 g. Given the possible combinations of time (24, 48 h) and media volumes (0.491, 0.982, 1.963 L), the range for the wastewater:media ratio was 100 mL:0.25 g and 100 mL:2.0 g. Therefore, the batch test can approximate maximum sorption in any column for 48 hours.

TMDS, 2-F-DMH and ranitidine all had a negative linear correlation with good fit (R^2 > 0.90) (Figure 6.3). Daminozide was below the method reporting limit (MRL) in all samples, including the control, which suggests it was degraded within the feedwater tank. The slopes for TMDS and ranitidine were nearly the same, indicating similar adsorption rate, although TMDS was below the MRL for 2.0 g anthracite. Very little change in concentration was observed for 2-F-DMH, meaning it does not adsorb strongly to the media. Partition coefficients (K_{ow}) at pH 7 were estimated (

Table 6.3) using MarvinSketch, which correlates K_{ow} with atomic hydrophobicities (Viswanadhan et al. 1989). Of the studied precursors, daminozide has the lowest K_{ow} and would be expected to remain in the aqueous phase as opposed to adsorbing to the media. The predicted K_{ow} for TMDS suggests some preference for adsorption; this matches the observed results. However, the similar adsorption observed for ranitidine does not fit well with the predicted and measured K_{ow} values, which indicate lower adsorption than TMDS. Anthracite typically has a negative charge in near-neutral water due to an isoelectric point in the range of 4.5 to 6 (Wen and Sun 1977). At pH 6.9, which is the pH of the tertiary-treated wastewater used in the study, ranitidine can have a positive charge (pKa = 7.9-8.2), and this could account for additional attraction to the media. Another point of consideration is that the batch test was performed with fresh anthracite and maximum adsorption capacity. The columns were in operation for more than 10 weeks before the test period and may have lost some adsorption capacity during that time. Overall, adsorption to the media is predicted to result in only partial removal of TMDS and ranitidine.

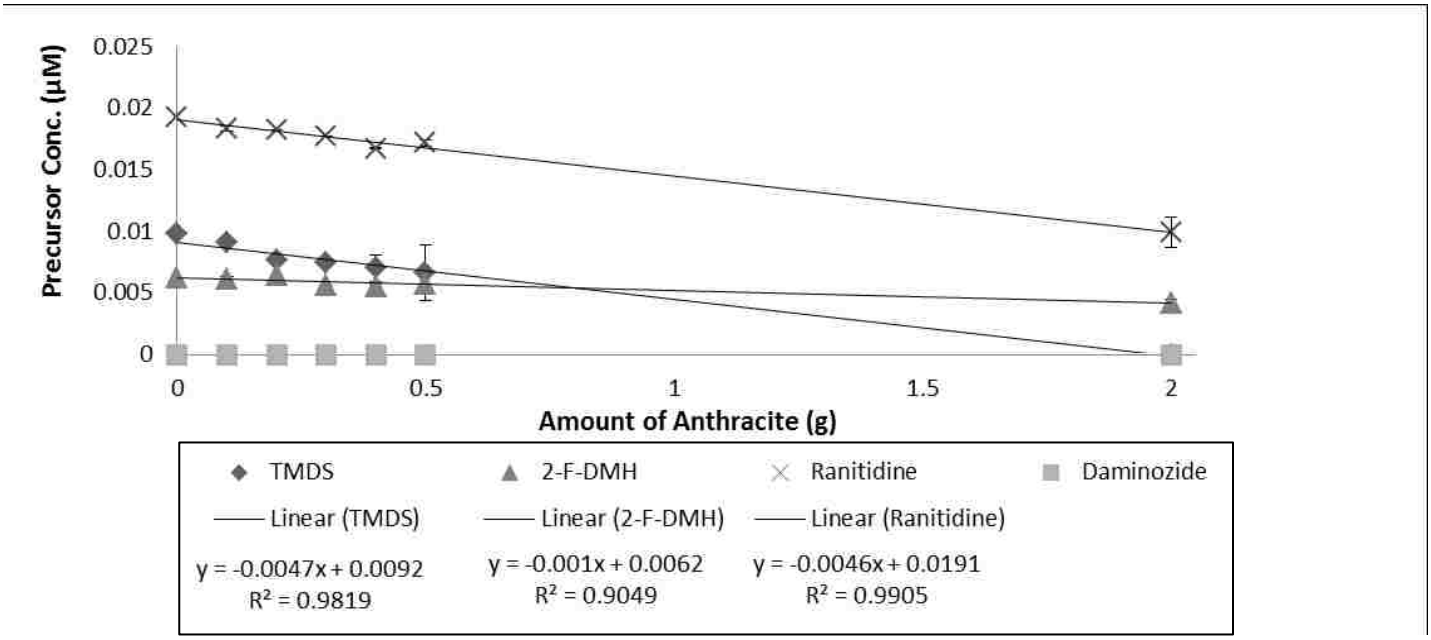


Figure 6.3: Batch sorption results and linear regressions for NDMA precursors in tertiary-treated wastewater at pH 6.9 after 24 hours in contact with fresh anthracite.

6.4.3 Precursor Removal

Removal varied depending on the precursor (Table 6.8). The average removals (all columns) during the test period were: TMDS 16.2%, 2-F-DMH 20.8%, daminozide 80.2%, and ranitidine 6.7%. Removal could be attributed to one or more of the following: biodegradation (not necessarily complete mineralization), adsorption to the media, and sorption to biofilm. Daminozide exhibited high removal. In soil, daminozide has a half-life of three to four days (Dannals et al. 1974). Since adsorption is unlikely based on its K_{ow}, biodegradation is deemed to be the main removal mechanism for this compound and this conclusion correlates well with the fast biodegradation reported by Dannals et al. The EAWAG-BBD predicted biodegradation pathway shows transformation to succinic acid as a possible reaction (EAWAG 2016). Although daminozide is not expected to be found in wastewater effluent, owing to its restricted use on

ornamental plants in greenhouses, there may be unknown NDMA precursors that share a similar structure to daminozide (i.e., hydrazide coupled to carbonyl). Therefore, the findings for daminozide removal are still applicable for predicting NDMA precursor removal with biofiltration.

TMDS and 2-F-DMH both exhibited low removal. TMDS is a semicarbazide, a class of compounds which frequently appear in patents for use as stabilizers and anti-yellowing agents (Hennessy and Selling 1993; Kawaguchi 1991). Although no biodegradation studies for TMDS exist to the author's knowledge, this compound and similar semicarbazides are poorly removed during conventional wastewater treatment and are found in wastewater-impacted surface waters (Kosaka et al. 2014). As a result, the low removal during biofiltration was anticipated, especially in light of the phosphorus-limited wastewater. Other unknown semicarbazide NDMA precursors would be expected to share a similar fate under the same biofiltration conditions. 2-F-DMH is a dimethylhydrazone coupled to furan and sold as a building block for chemical synthesis. There are no biodegradation studies available for this compound. As with TMDS, 2-F-DMH removal may have been restricted by the low phosphorus concentration.

Ranitidine exhibited very low removal during biofiltration. Ranitidine is poorly removed during activated sludge treatment, and its concentrations in wastewater sludge are low (Khan and Ongerth 2002; Radjenovic et al. 2007). Some wastewater treatment plants demonstrate high removal (60-80%) for ranitidine (Jelic et al. 2011), but this is due to chlorination or ozonation, which are both effective at destroying the compound (Reungoat et al. 2010; Wang et al. 2015). Biological treatments, such as activated sludge, dissolved air flotation or biological activated carbon, typically have < 40% removals (Radjenovic et al. 2007; Reungoat et al. 2010). Bergheim and colleagues examined ranitidine biodegradation and determined that it is not readily

biodegradable except in aerobic conditions with high nutrient availability (Bergheim et al. 2012). Vasiliadou et al. (2013) investigated ranitidine removal in a suspended growth bioreactor. Significant removal of ranitidine was observed for sorption (K_d = 420 L/kg) to living or dead biomass, and there was negligible biodegradation. When ranitidine was mixed with other pharamaceuticals in the bioreactor, there was a significant decrease in sorption (K_d = 150 L/kg). This suggests that ranitidine removal by sorption may be much lower in real scenarios as compared to laboratory tests (Vasiliadou et al. 2013). The low ranitidine removal observed in this biofiltration study cannot be attributed to a specific mechanism, and many factors may be involved, including: low DO, low phosphorus, and acclimation.

High coefficients of variation for removal (76-147%) were obtained, except for daminozide (17%). This could be due to variability in DO (discussed later), the lack of an acclimation period or operation parameters like temperature and initial concentration. Temperature is known to have a considerable impact on removal (Halle et al. 2015), but there was little variation in temperature over the 14-day test period. Initial concentration has been shown to affect removal, with greater removal for higher initial concentrations (Halle et al. 2015). However, this difference in removal was observed at a ten-fold increase for high and low initial concentrations, which is much higher than the difference in initial concentration found in this study (CV = 41-73%). No statistical correlation between removal and influent concentration was observed ($R^2 < 0.10$). On the other hand, all of the precursors were spiked at low µg/L levels (13-36 µg/L); this is a high concentration compared to many trace organics. It is possible that removal would decrease if the precursors were present at sub-µg/L concentrations, which are more typical of trace organics in wastewater.

Although not specifically investigated, all tested precursors were removed by chlorination. Effluent from the biofiltration columns, as well as a precursor-spiked feedwater flow equalization line that bypassed the columns, were collected in a 200 gallon HDPE container and sodium hypochlorite was added to achieve > 2 mg/L as Cl_2. Samples from the HDPE container were collected (Days 4, 14) and analyzed for NDMA precursors. On both occasions, daminozide, 2-F-DMH, TMDS, and ranitidine were all below the reporting limit.

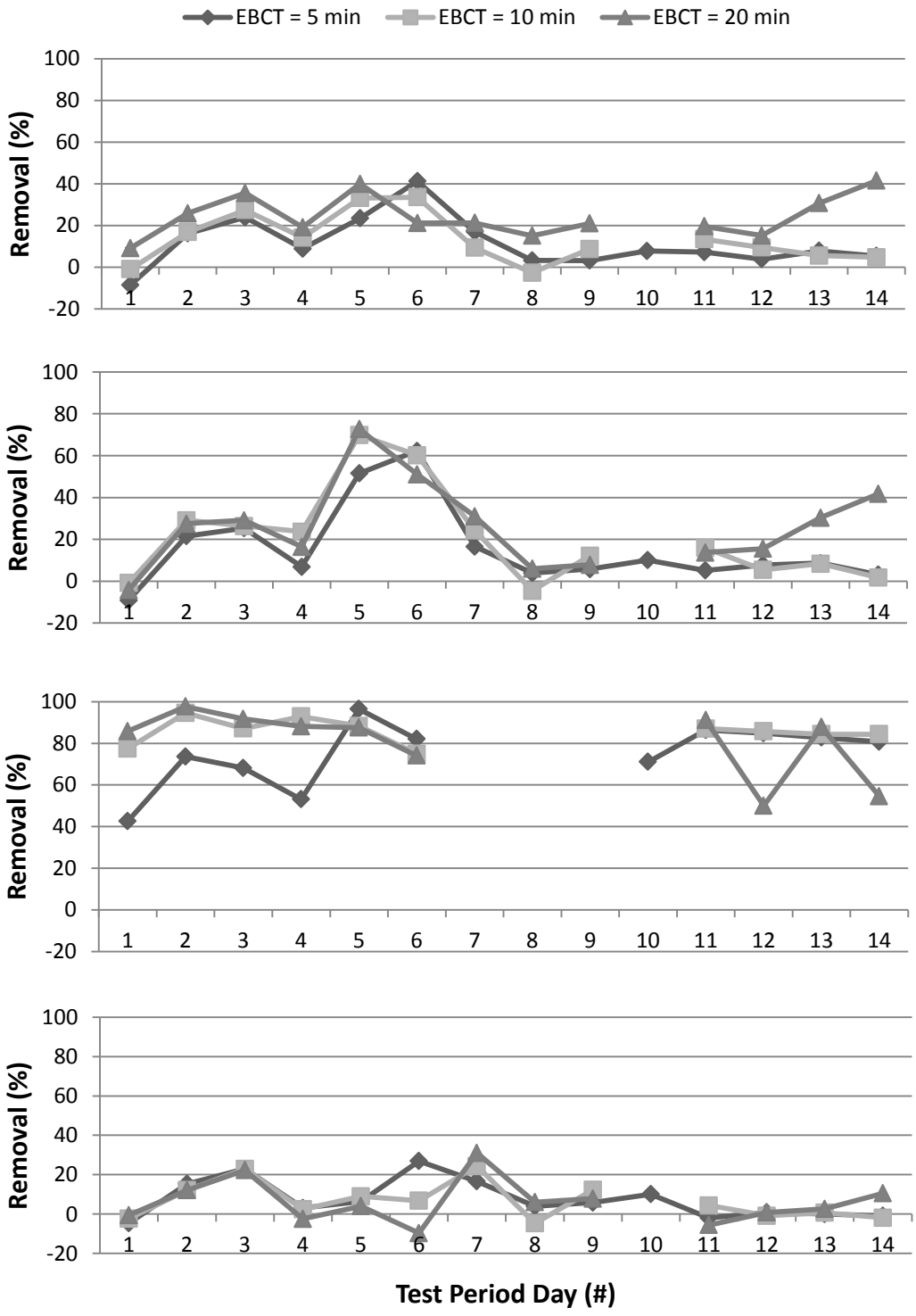


Figure 6.4: Precursor removal after biofiltration during the 14-day test period for (a) TMDS, (b) 2-F-DMH, (c) daminozide and (d) ranitidine. Missing data are for results that were below the reporting limit.

6.4.4 Effect of Contact Time on Precursor Removal

Statistical analyses were performed to determine if removal across the column and if the effect of EBCT on removal were significant. The change in concentration between the column influent and effluent (i.e., removal) was statistically significant for daminozide, TMDS, and 2-F-DMH, but not ranitidine (Table 6.9). This is in agreement with the low removal observed for ranitidine. Removal increased as EBCT increased for TMDS and 2-F-DMH, but only TMDS was statistically significant as determined by one-way ANOVA. It should be noted that the high variability in the data makes it more challenging to achieve statistical significance. Different results might be found if biofiltration were performed for a longer period of time and more data were collected, leading to less variability and higher statistical power.

Contact time is known to heavily influence dissolved organic removal (Reungoat et al. 2011; Halle et al. 2015), but the relationship is not directly proportional (Urfer et al. 1997). As observed in this study, contact time influenced the removal of TMDS and 2-F-DMH, and both precursors have a good linear correlation ($R^2 > 0.95$). However, more than three data points are needed to verify if the fit is actually linear or better matched to a curve. TMDS and 2-F-DMH are not readily biodegradable, yet their removals are affected by contact time. Daminozide is highly biodegradable, even to the extent that it was periodically removed within the feedwater tank and feedwater lines before reaching the column influent sampling port. It is possible that the effect of EBCT was not observed for daminozide because the EBCTs were too long, resulting in high removal at all tested contact times.

Table 6.8: Average precursor influent and effluent concentrations and removal for biofiltration columns during the test period.

		Column 1 EBCT = 5 min	**Column 2** EBCT = 10 min	**Column 3** EBCT = 20 min	**All Columns** Avg. all EBCTs
TMDS	Influent Avg. (µM)	0.0561 ± 0.0377 CV = 67.4%	0.0558 ± 0.0363 CV = 65.1%	0.0540 ± 0.0343 CV = 63.5%	0.0486 ± 0.0347 CV = 71.5%
	Effluent Avg. (µM)	0.0501 ± 0.0361 CV = 71.9%	0.0492 ± 0.0362 CV = 73.5%	0.0431 ± 0.0334 CV = 77.5%	0.0475 ± 0.0345 CV = 72.7%
	Avg. Removal (%)	**11.5% ± 0.122** CV = 106%	**13.3% ± 0.118** CV = 88.4%	**24.3% ± 0.100** CV = 41.0%	**16.2% ± 0.124** 76.7%
2-F-DMH	Influent Avg. (µM)	0.0534 ± 0.0394 CV = 73.7%	0.0538 ± 0.0384 CV = 71.4%	0.0522 ± 0.0358 CV = 68.6%	0.0450 ± 0.0345 CV = 76.6%
	Effluent Avg. (µM)	0.0469 ± 0.0388 CV = 82.7%	0.0438 ± 0.0358 CV = 81.8%	0.0436 ± 0.0361 CV = 82.8%	0.0448 ± 0.0360 CV = 80.4%
	Avg. Removal (%)	**15.7% ± 0.195** CV = 124%	**21.0% ± 0.224** CV = 107%	**26.1% ± 0.206** CV = 79.1%	**20.8% ± 0.208** CV = 99.9%
Daminozide	Influent Avg. (µM)	0.0582 ± 0.0376 CV = 64.5%	0.0635 ± 0.0260 CV = 41.0%	0.0598 ± 0.0309 CV = 51.6%	0.0516 ± 0.0331 CV = 64.2%
	Effluent Avg. (µM)	0.0287 ± 0.0205 CV = 71.3%	0.0157 ± 0.0135 CV = 86.2%	0.0111 ± 0.0067 CV = 60.8%	0.0195 ± 0.0165 CV = 84.9%
	Avg. Removal (%)	**74.7% ± 0.156** CV = 20.8%	**85.7% ± 0.060** CV = 7.0%	**80.8% ± 0.162** CV = 20.1%	**80.2% ± 0.138** CV = 17.3%
Ranitidine	Influent Avg. (µM)	0.0996 ± 0.0589 CV = 59.1%	0.0997 ± 0.0573 CV = 57.4%	0.0971 ± 0.0561 CV = 57.8%	0.0988 ± 0.0575 CV = 58.2%
	Effluent Avg. (µM)	0.0936 ± 0.0581 CV = 62.0%	0.0931 ± 0.0592 CV = 63.5%	0.0917 ± 0.0586 CV = 63.9%	0.0928 ± 0.0571 CV = 61.5%
	Avg. Removal (%)	**7.45% ± 0.097** CV = 130%	**6.53% ± 0.093** 143%	**6.06% ± 0.111** 184%	**6.70% ± 0.098** CV = 147%

CV = coefficient of variation; EBCT = empty bed contact time

Table 6.9: Correlation and *p* values to determine statistical significance for the effect of empty bed contact time on removal, change in influent and effluent concentration, and the effect of dissolved oxygen (DO) on removal.

	ANOVA: EBCT		**Paired t-test (one-tailed): Influent / Effluent**	**Correlation: DO and Removal**
TMDS	$p = 0.013$ **Sig.** $F_{(2,39)} = 4.89$	EBCT = 5 min EBCT = 10 min EBCT = 20 min	**Sig.** $p = 0.008$ **Sig.** $p = 0.008$ **Sig.** $p < 0.001$	$R^2 = 0.483$ **$R^2 = 0.666$** $R^2 = 0.077$
2-F-DMH	$p = 0.441$ NS $F_{(2,39)} = 0.836$	EBCT = 5 min EBCT = 10 min EBCT = 20 min	**Sig.** $p = 0.010$ **Sig.** $p = 0.001$ **Sig.** $p < 0.001$	**$R^2 = 0.667$** **$R^2 = 0.792$** $R^2 = 0.410$
Daminozide	$p = 0.193$ NS $F_{(2,30)} = 1.74$	EBCT = 5 min EBCT = 10 min EBCT = 20 min	**Sig.** $p < 0.001$ **Sig.** $p < 0.001$ **Sig.** $p < 0.001$	$R^2 = 0.001$ $R^2 = 0.002$ $R^2 = 0.155$
Ranitidine	$p = 0.936$ NS $F_{(2,39)} = 0.066$	EBCT = 5 min EBCT = 10 min EBCT = 20 min	**Sig.** $p = 0.038$ NS $p = 0.320$ NS $p = 0.295$	$R^2 = 0.242$ $R^2 = 0.061$ $R^2 = 0.033$

Sig. = significant; NS = not significant
Bold text indicates significant results and strong correlations ($R^2 > 0.6$)

6.4.5 Correlation Between Precursor Removal and Dissolved Oxygen Concentration

The influence of initial dissolved oxygen concentration on removal was examined by regression analysis. An example correlation is shown in Figure 6.5. Other figures appear in Appendix D. There was a strong positive correlation for 2-F-DMH at EBCTs of 5 and 10 min and TMDS at 10 min, as well as a moderate positive correlation for 2-F-DMH at 20 min and TMDS at 5 min (Table 6.9). This suggests that 2-F-DMH and TMDS removal could increase if

DO were present at a higher concentration; however, this cannot be confirmed because information on biodegradability (aerobic or anaerobic) of the compounds is unavailable.

There was no apparent correlation between initial DO concentration and removal for daminozide and ranitidine. Daminozide may be highly biodegradable by bacteria that survive at low DO concentrations or daminozide may undergo anaerobic biodegradation. The limited ranitidine removal observed in this study may be due to sorption alone, which could explain why removal is not influenced by EBCT or DO concentration. It is also possible that no effects of EBCT or DO were noticed for ranitidine because the removal was too low (not significant at EBCT = 10, 20 min) to detect any effects.

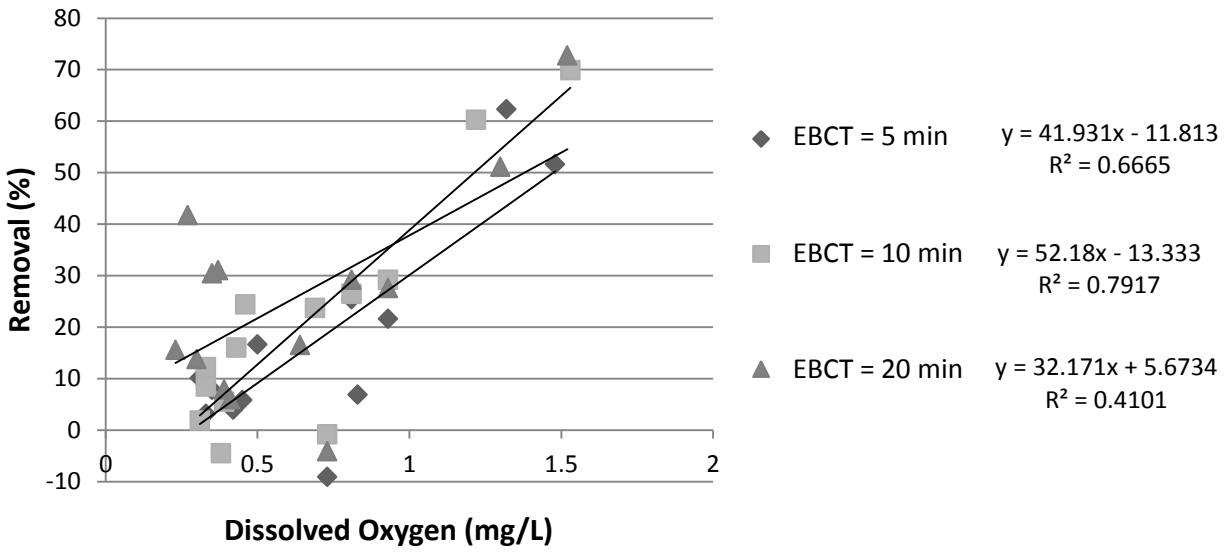


Figure 6.5: Correlation between initial dissolved oxygen concentration and removal at three empty bed contact times (EBCTs) for 2-F-DMH. Graphs for other precursors are found in Appendix D.

6.4.6 NDMA, THM and HAA Formation Potentials

Formation potentials for NDMA, THMs, and HAAs were measured in the column influent and effluent during the preparation phase and test period. In the preparation phase, NDMA was below the detection limit; however, formation potential tests revealed the presence of NDMA precursors (Table 6.5). Chloramine-reactive precursors generated an NDMA concentration that was 10-fold higher than ozone-reactive precursors. There was no removal of chloramine-reactive precursors across column 3, but there was a slight removal (26.8%) of ozone-reactive precursors. Results for the THM/HAA-FP test indicated the presence of a significant amount of precursors, though the reported values are not indicative of the concentrations that would form by application of a typical chlorine disinfection dose. The acclimated biofilters demonstrated some removal of THM and HAA precursors as shown by 21.6% and 17.6% decreases in THM-FP and HAA-FP, respectively. It should be noted that NDMA, THM and HAA formation potential results are for a single sample on one column during the preparation phase and variability during the ten days is unknown. Biomass growth, and accordingly removal, was likely inhibited by the low phosphorus concentration in the wastewater.

Ranitidine was measured in the tertiary-treated wastewater (0.0065 μM). Using a molar yield of 90% (Shen and Andrews 2011), it could account for 433 ng/L NDMA or > 100% of the CLM-UFC concentration, meaning this single precursor might account for all of the chloramine-derived NDMA formation potential. However, it is important to consider that molar yields are established during laboratory tests in a clean matrix and without interfering constituents. In the presence of other organics, the effective molar yield is probably lower, but ranitidine may be the main precursor responsible for NDMA formation with chloramines in the unspiked tertiary-treated wastewater.

Slight removal of the DBPs and their precursors was observed during the test period for column 3. Total THM formation potential across the column was unchanged on Day 4 and decreased by 5% on Day 11 (Figure 6.6). Total HAA formation potential showed similarly low removal of precursors; removal decreased by 3% and 4% on Day 4 and Day 11, respectively (Figure 6.7). Compared to the preparation phase, THM and HAA formation potential removal was lower. This can be attributed at least partially to lower initial DO during the test period (correlations: HAA-FP R^2 = 0.751; THM-FP R^2 = 0.743). NDMA was marginally removed during the test period (Day 4: 4 ng/L increase; Day 11: 11 ng/L decrease or 34%; Day 14: 3.5 ng/L decrease or 27%). NDMA was not detected in the feedwater prior to adding the precursors. This indicates that the precursor stock solutions have trace NDMA contamination, which has been observed previously (Marti et al. 2015), or that precursors were transformed within the feedwater tank. If transformation did occur, the yield was very low (maximum 0.006% assuming NDMA derived from a single precursor). Combined NDMA precursor removal was unsuccessfully measured through ozone and chloramine formation potential tests. The concentrations did not fall within the calibration ranges, and sample volumes were not sufficient for further extraction and analysis. Values were not determined for all samples (Table 6.10); nonetheless, it was observed that significant chloramine- and ozone-reactive NDMA precursors were present in the effluent after biofiltration. This agrees with the results for incomplete precursor removal.

Removal of NDMA, THM and HAA precursors through biofiltration has been shown previously. Farré et al. (2011) found that BAC reduced NDMA chloramine formation potential by > 85%, and several chloramine-reactive NDMA precursors (doxylamine, roxithromycin, tramadol, venlafaxine) were removed by more than 95% from a secondary wastewater effluent.

Removal was much lower in both cases for biological sand filtration, which indicates that sorption to activated carbon (especially for the positively charged compounds in question) may be a key removal mechanism. THM and HAA precursors were similarly removed at high levels (Farre et al. 2011). Another study using GAC-sand and anthracite-sand biofilters with raw drinking water demonstrated 6-17% and 12-19% reductions in THM and HAA precursors, respectively (Chaiket et al. 2002). These removals are similar to those observed in this study, and this is understandable given that this phosphorus-deficient wastewater is more comparable to the drinking water than a typical wastewater. Another key difference between the current research and reported biofiltration studies with wastewater was that ozone preceded biofiltration, so substantial dissolved oxygen and readily biodegradable soluble organics were present. Optimization of certain parameters, such as dissolved oxygen and phosphorus, could lead to increased removal for DBP precursors.

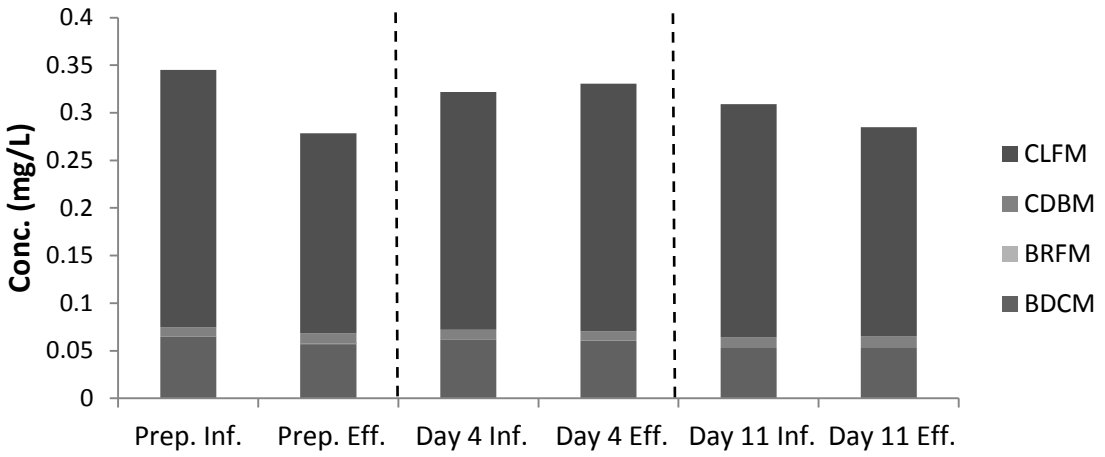


Figure 6.6: Trihalomethane formation potential results for column 3 influent and effluent during the preparation phase and test period. Results are shown for bromodichloromethane (BDCM), chlorodibromomethane (CDBM), chloroform (CLFM), and bromoform (BRFM).

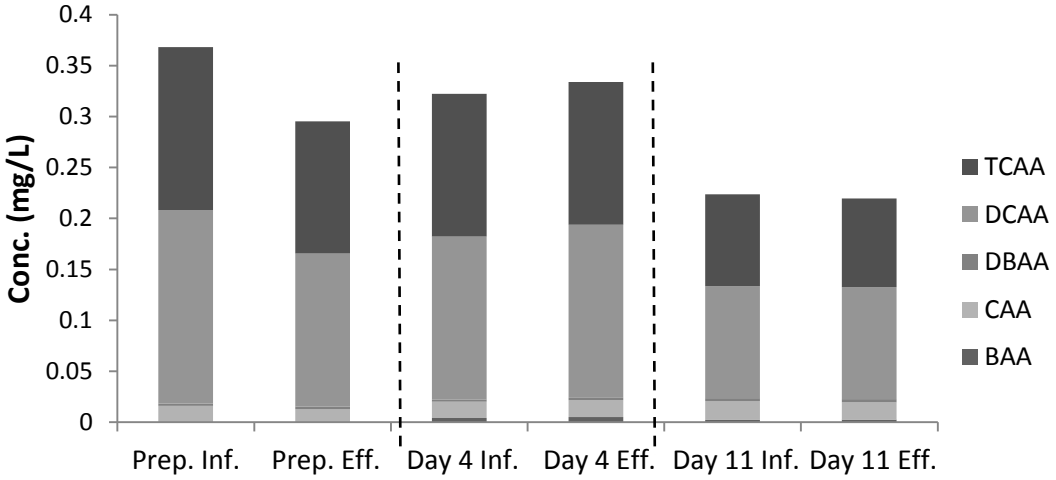


Figure 6.7: Haloacetic acid formation potential results for column 3 influent and effluent during the preparation phase and test period. Results are shown for bromoacetic acid (BAA), chloroacetic acid (CAA), dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA).

Table 6.10: Concentrations for NDMA and NDMA formation potential tests in column 3 influent and effluent on three days during the test period.

Analysis	Concentration (ng/L as NDMA)					
	Day 4		Day 11		Day 14	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
NDMA	43	47	32	21	13	9.45 ± 0.07
O_3-FP	< 25,000	> 2,500	< 25,000	> 2,500	< 25,000	> 2,500
CLM-UFC	< 25,000	860 ± 57	< 25,000	770	< 25,000	1100

Analyses: NDMA = NDMA present in the sample without any additional treatment; O_3-FP = NDMA analysis after ozonation; CLM-UFC = NDMA analysis after chloramination at uniform formation conditions.

6.4.7 Implications for Water Reuse

Biofiltration can be a useful treatment process for water reuse. In combination with pre-ozonation, biofiltration can remove substantial organic carbon and reduce many trace organics to below detection levels (Farre et al. 2011; Gerrity et al. 2011; Gerrity et al. 2014; Reaume et al. 2015; Reungoat et al. 2011; Reungoat et al. 2012). Ozone-BAC (O_3-BAC) is a promising treatment strategy for reducing NDMA formation and has been shown to remove more than 50% of precursors contributing to NDMA chloramine formation potential (Gerrity et al. 2014; Liao et al. 2015). One caveat for O_3-BAC is the presence of ozone-reactive NDMA precursors. In this case, an alternative option is pre-ozonation at a low ozone dose, followed by BAC and a second ozonation at a high ozone dose. An Australian water reclamation plant with this configuration has demonstrated minimal NDMA formation with pre-ozonation and high NDMA precursor removal (Farre et al. 2011). Another alternative would be to reverse the order to BAC-O_3 in order to remove the ozone-reactive precursors with biofiltration prior to ozonation. However, some of the benefits of the O_3-BAC would be lost. Ozonation increases the amount of

assimilable organic carbon, which is removed by BAC, and ozonation provides "free" dissolved oxygen for biofiltration. Bench-scale or pilot-scale testing would be necessary to determine if BAC-O_3 is more favorable despite the loss in benefits.

Optimization is necessary to removed targeted compounds. As discussed already, media, pH, nutrient availability, initial concentration of the contaminant, temperature, and dissolved oxygen all affect removal. For treatment plants that exhibit large seasonal changes (e.g., hot/cold temperatures, nutrient loads caused by fertilizer runoff), biofilters may require constant fine-tuning. Once parameters are optimized, then the challenge becomes maintaining the performance. Biofiltration appears to be reliable (i.e., performs well during normal operation) and robust (i.e., low likelihood of failure), but may be deficient in terms of resiliency (i.e., ability to recover from problems). Biofilters should be in operation continuously and cannot easily be stopped and restarted after prolonged shutdown (Jang et al. 2006).

6.5 Conclusion

This study provides information on NDMA precursor removal during non-optimized biofiltration with tertiary-treated wastewater. The compounds were chosen as model NDMA precursors in predicting removal during biofiltration and include three ozone-reactive NDMA precursors (daminozide – hydrazine, TMDS – semicarbazide, 2-F-DMH – hydrazone) and one chloramine-reactive precursor (ranitidine – dimethylamine). Aerobic biodegradation was restricted by low dissolved oxygen and phosphorus concentrations, which resulted in low TOC and COD removal and biofiltration performance was more comparable to drinking water biofilters than treated wastewater biofilters. The investigation resulted in the following findings:

- Precursor biodegradability varied and decreased in the order of daminozide >> 2-F-DMH ~ TMDS > ranitidine.
- A batch sorption test revealed no adsorption to fresh anthracite for 2-F-DMH and moderate adsorption for TMDS and ranitidine.
- Removal by biofiltration was correlated to initial dissolved oxygen concentration for 2-F-DMH and TMDS.
- TMDS removal increased with greater EBCT, but there was no significant difference with EBCT for the other precursors. The effects of contact time could not be observed because daminozide removal was too fast and ranitidine removal was too slow within the EBCTs investigated.
- Daminozide was highly biodegradable even in conditions with limited dissolved oxygen and phosphorus concentrations.
- 2-F-DMH may be removed by biodegradation and sorption to biofilm, since it did not adsorb to the anthracite.
- TMDS removal may be a combination of sorption to the media, biodegradation, and sorption to biofilm; however, the removal mechanisms cannot be confirmed.
- Ranitidine is poorly removed with anthracite biofiltration, but can be mitigated by other means (e.g., ozonation, photolysis).
- All four precursors were removed by chlorination above 2 mg/L as Cl_2.
- Biofiltration could likely provide simultaneous removal of NDMA, THM and HAA precursors; however, optimization is necessary to improve removal.

CHAPTER 7

CONCLUSIONS, IMPLICATIONS AND RECOMMENDATIONS

7.1 Conclusions

Three issues regarding *N*-nitrosodimethylamine (NDMA) formation and mitigation were addressed in this research. All three issues are relevant to the further treatment of wastewater effluents for reuse applications. In Issue One, model precursors for NDMA formation with ozone were identified and parameters affecting NDMA formation were investigated. It was hypothesized that hydrazones and carbamates with a dimethylamine component would react with ozone to form NDMA in the same manner as known NDMA precursors with hydrazine, semicarbazide and sulfamide moieties. The following findings and conclusions can be reported for the research in investigating Issue One:

1a) Hydrazones and carbamates were confirmed as ozone-reactive NDMA precursors. Two of each class were identified as model precursors.

1b) Bromide enhanced NDMA formation for three NDMA precursors: dimethylsulfamide (DMS), unsymmetrical dimethylhydrazine (UDMH) and acetone dimethylhydrazone. Other compounds were not affected by the presence of bromide.

1c) Ozone-reactive NDMA precursors are distinctly different from chloramine-reactive NDMA precursors. Ozone-reactive NDMA precursors have structures resembling $(H_3C)_2N\text{-}N\text{-}R$ or $(H_3C)_2N\text{-}L\text{-}N\text{-}R$, where L is a good leaving group (e.g., $–SO_2$, $–CO_2$), and they have low molar yields (< 3%) for NDMA formation with chloramines. Chloramine-reactive precursors have a tertiary or quaternary dimethylamine moiety and have low molar yields (< 0.1 %) for NDMA formation with ozone.

1d) Transformation products from the ozonation of UDMH and acetone dimethylhydrazone may be chloramine-reactive NDMA precursors.

1e) Molecular ozone was confirmed as the main oxidant species responsible for NDMA formation for the model precursors.

1f) Hydroxyl radical scavenging and a greater ozone dose led to increased NDMA formation for the model precursors.

1g) Higher NDMA formation was observed in treated wastewater compared to ultrapure water for several precursors. Treated wastewater may contain constituents that are not removed during treatment and can promote NDMA formation.

Overall, the results from this research add to the general understanding of how NDMA is formed. The investigation identified compounds that are ozone-reactive NDMA precursors and the results confirm that molecular ozone is necessary for NDMA formation for all the model precursors identified. However, the formation mechanisms are not necessarily the same because some precursors exhibit enhanced NDMA formation when bromide is present or hydroxyl radicals are removed.

Issue Two examined pre-chlorination as a mitigation strategy for NDMA formation. It was hypothesized that chlorine would react with ozone-reactive NDMA precursors and inactivate them so that subsequent ozonation will result in reduced NDMA formation. The following conclusions were drawn from the results obtained in investigating Issue Two:

2a) Out of the seven tested disinfection schemes for secondary wastewater effluent, the top two treatment schemes resulting in the lowest total disinfection byproduct (DBP) formation were ozonation and ozonation-chloramination. Treated wastewaters are highly variable and some wastewater characteristics (e.g. high ammonia, high ozone-

reactive NDMA precursor concentration) could result in a different optimal treatment scheme in order to achieve the lowest total amount of DBPs.

2b) Although the mechanism was not identified, there is strong evidence that pre-chlorination inactivates ozone-reactive NDMA precursors.

2c) Pre-chlorination was very effective in reducing NDMA formation for both chloramine- and ozone-reactive NDMA precursors, but it caused formation of trihalomethanes (THMs) and haloacetic acids (HAAs), resulting in concentrations that exceeded drinking water regulations. THM and HAA precursors can be reduced via pretreatment (i.e., enhanced coagulation), which would make pre-chlorination a more favorable option for inactivating NDMA precursors.

2d) Ozonation had no impact on the formation or reduction of THMs or HAAs.

2e) Ozonation caused direct NDMA formation, but it also reduced NDMA formation in the case of post-chloramination.

On the whole, it was shown that each disinfectant (i.e., chlorine, ozone or chloramine) forms specific DBPs, but also provides control against other DBP formation. Disinfection treatment schemes using ozone are very effective in mitigating NDMA, THM and HAA formation, as long as ozone-reactive NDMA precursors are not present. When those precursors are present, pre-chlorination can successfully reduce NDMA formation. Most importantly, optimal disinfection treatment schemes depend on the characteristics of the particular wastewater being treated. A single treatment scheme will not be superior in all situations.

Issue Three examined the removal of specific NDMA precursors through biofiltration using treated wastewater effluent as the aqueous matrix. It was hypothesized that daminozide and 2-furaldehyde dimethylhydrazone (2-F-DMH) would be well removed by biofiltration, while

ranitidine and 1,1,1',1'-Tetramethyl-4,4'-(methylenedi-p-phenylene)disemicarbazide (TMDS) would be poorly removed by biofiltration. The following conclusions were drawn from the results obtained in investigating Issue Three:

3a) Precursor biodegradability varied and decreased in the order of daminozide >> 2-F-DMH ~ TMDS > ranitidine.

3b) A batch sorption test revealed no adsorption to fresh anthracite for 2-F-DMH and moderate adsorption for TMDS and ranitidine.

3c) Removal by biofiltration was correlated to initial dissolved oxygen concentration for 2-F-DMH and TMDS.

3d) TMDS removal increased with greater EBCT, but there was no significant difference with EBCT for the other precursors. The effects of contact time could not be observed because daminozide removal was too fast and ranitidine removal was too slow within the EBCTs investigated.

3e) Daminozide was highly biodegradable even in conditions with limited dissolved oxygen and phosphorus concentrations.

3f) 2-F-DMH may be removed by biodegradation and sorption to biofilm, since it did not adsorb to the anthracite. TMDS removal may be a combination of sorption to the media, biodegradation, and sorption to biofilm; however, the removal mechanisms cannot be confirmed.

3g) Ranitidine is poorly removed by anthracite biofiltration, but can be mitigated by other means (e.g., ozonation, photolysis).

3h) All four precursors (daminozide, 2-F-DMH, TMDS, ranitidine) were removed by chlorination.

3i) Biofiltration could likely provide simultaneous removal of NDMA, THM and HAA precursors; however, optimization is necessary to improve removal.

7.2 Implications of Findings to Water Reuse

The results from this research have implications for water reuse, especially regarding advanced water treatment for potable reuse applications:

I-1) Ozone dose and placement of ozonation within the treatment train can strongly affect NDMA formation. Treatment plants operating at high ozone doses for color removal or chemical contaminant removal in early stages of treatment could experience much greater NDMA formation compared to treatment plants using low ozone doses for final disinfection. Source waters, whether surface water, groundwater or treated wastewater effluent, contain different amounts of NDMA precursors and the ozone dose needs to be optimized for individual treatment plants. Consequently, one should consider both the dose and location within the treatment train when determining an appropriate ozone application.

I-2) Ozone provides many benefits for advanced water treatment: (1) an advanced oxidation process that destroys a wide variety of trace organics, (2) effective disinfection at low exposures, (3) reduced membrane fouling without membrane degradation, (4) color and odor removal, and (5) reduced THM and HAA formation compared to chlorine or chloramines. When a disinfectant residual is required, chloramination can safely be applied after ozonation with minimal NDMA or THM formation. However, when substantial ozone-reactive NDMA precursors are present, pre-chlorination can be applied to prevent NDMA formation with ozone, as demonstrated in this research.

Chlorination will increase THMs and HAAs, but other methods for NDMA precursor removal, such as carbon adsorption, photolysis, membranes or reverse osmosis, might cost more. Enhanced coagulation prior to chlorination could remove THM and HAA precursors, making it possible to minimize THM, HAA, and NDMA formation, while attaining all the benefits of ozonation.

I-3) Advanced water treatment plants frequently receive treated wastewater from another facility and that facility may use a chemical oxidant prior to releasing the treated wastewater. In this case, the agencies may need to collaborate and reevaluate the disinfection treatment scheme used by the wastewater treatment facility in order to integrate the treatment processes and prevent NDMA and other DBP formation while still meeting both parties' needs.

I-4) Non-optimized biofiltration with anthracite provides limited removal of NDMA precursors. Optimized biofiltration using activated carbon instead of anthracite could provide greater NDMA precursor removal. While it is more common today to place ozone ahead of biofiltration, there could be an advantage to reversing the order; removal of NDMA precursors by biofiltration prior to ozonation may reduce NDMA formation.

7.3 Recommendations for Future Research

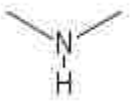
As a result of investigating these three issues for NDMA formation and mitigation, new possibilities for research projects and follow-up tasks were identified. The following recommendations are made for future research:

- Understanding increased NDMA formation in wastewater: Although hydroxyl radical quenching may be the cause of increased NDMA formation for precursors in a wastewater matrix, there is the potential for other wastewater constituents (besides bromide) to catalyze NDMA formation mechanisms. One possibility is the presence of metal ions, such as Cu^{2+}, which have been shown to assist in degradation of daminozide to UDMH (Huang and Stone 2003) and result in NDMA formation from UDMH (Mach and Baumgartner 1979). Another potential catalytic agent is iodide, which may act in the same manner as bromide. Although iodide concentrations may be low in drinking water or treated wastewater, iodide is used for point-of-use (POU) treatment by campers, military personnel and in developing countries (Smith et al. 2010); iodide is present at significant concentrations with POU and could pose a serious problem if it catalyzes NDMA formation.
- Mitigation of NDMA precursors with persulfate: A more recent advanced oxidation approach is the use of sulfate radicals generated from persulfate. Like hydroxyl radicals, sulfate radicals react with a wide variety of organic molecules. This advanced oxidation process could provide an alternative method for inactivating NDMA precursors and with reduced DBP formation compared to pre-chlorination (Xie et al. 2015).
- Chlorine oxidation products for ozone-reactive NDMA precursors: Pre-chlorination was shown to effectively inactivate ozone-reactive NDMA precursors, but the mechanism is not yet known. This could be accomplished by identifying oxidation products with liquid chromatography tandem mass spectrometry. One study already identified oxidation products for two chloramine-reactive NDMA precursors, doxylamine and ranitidine (Wang et al. 2015).

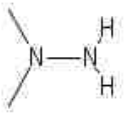
- Optimal chlorine exposure for eliminating ozone-reactive NDMA precursors: The current research used a single chlorine exposure to investigate reduction in NDMA formation. It would be valuable to determine the minimum chlorine exposure needed to inactivate ozone-reactive NDMA precursors. THM and HAA formation should be measured as well to establish if the regulated levels are exceeded.
- Toxicity of transformation products for NDMA precursors: Transformation products can be just as toxic as or more toxic than the parent compound, yet only the parent compound is typically measured. Quantifying the toxicity of oxidation products, in single and multi-step disinfection schemes, would afford a better understanding of whether or not inactivating NDMA precursors actually reduces the carcinogenic potential of the water.
- Optimization of biofiltration to remove NDMA precursors: NDMA precursor removal during biofiltration could be improved through optimization. For example, increased dissolved oxygen may enhance removal for some precursors. Other alternatives to consider are an upflow instead of downflow process and replacing anthracite with activated carbon or a mixed-media.
- Alternative pilot systems for NDMA mitigation: Biofiltration could be implemented ahead of ozonation to remove NDMA precursors. Alternatively, biofiltration could be inserted between ozonation steps to examine the effect on ozone-reactive NDMA precursors. A full-scale system utilizing this approach showed significant reduction in chloramine NDMA formation potential and THM/HAA reduction (Farre et al. 2011).

APPENDIX A STRUCTURES AND MOLAR YIELDS FOR NDMA PRECURSORS

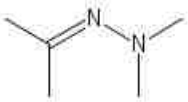
Table A.1: Structures of potential ozone-reactive NDMA precursors investigated in this dissertation (underlined) and other studies.



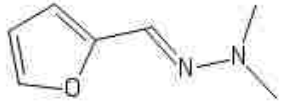
dimethylamine (DMA)



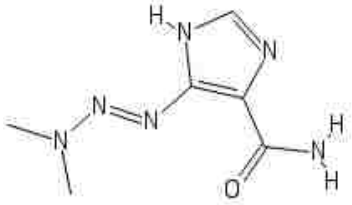
1,1-dimethylamine (UDMH)



acetone dimethylhydrazone (Acetone DMH)



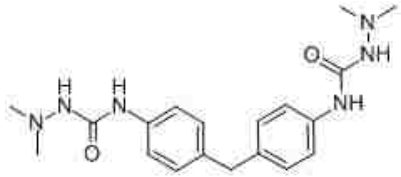
2-Furaldehyde 2,2-dimethylhydrazone (2-F-DMH)



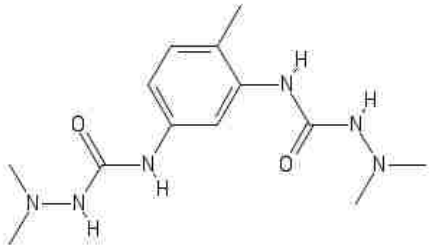
Dacarbazine

Daminozide

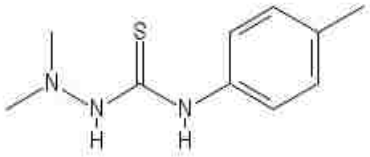
4,4′-hexamethylenebis (1,1-dimethylsemicarbazide) (HDMS)



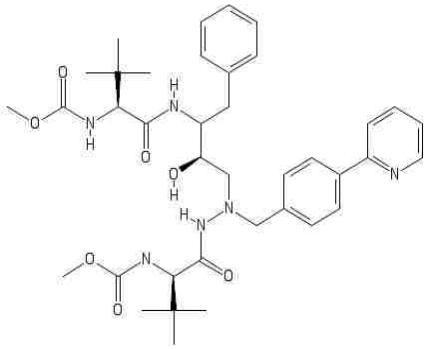
1,1,1’,1’-Tetramethyl-4,4’-(methylenedi-*p*-phenylene) disemicarbazide (TMDS)



N-1-(3-{[(2,2-dimethylhydrazino)carbonyl] amino}-4-methylphenyl)-2,2-dimethylhydrazine-1-carboxamide (DMSC)

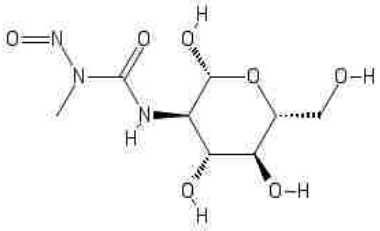


N-1-(4-methylphenyl)-2,2-dimethylhydrazine-1-carbothioamide (DMTC-phenyl)

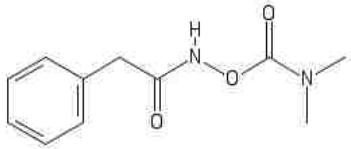


Atazanavir

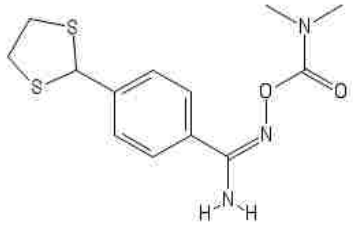
Cont. Table A.1: Structures of potential ozone-reactive NDMA precursors investigated in this dissertation (underlined) and other studies.



Streptozocin

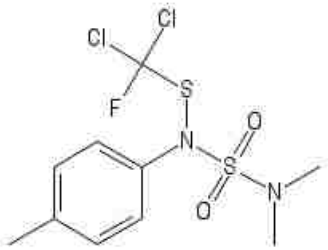


N-{[(dimethylamino)carbonyl]oxy}-2-phenylacetamide (DMC-phenyl)

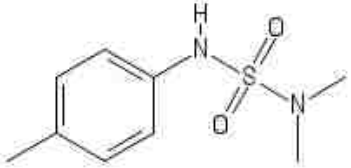


N'-{[(dimethylamino)carbonyl]oxy}-4-(1,3-dithiolan-2-yl)benzenecarboximidamide (DMC-dithio)

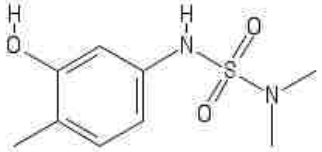
Dimethylsulfamide (DMS)



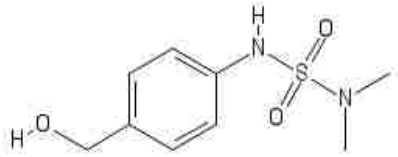
Tolylfluanid



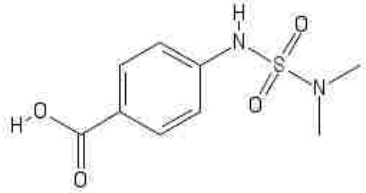
Dimethyl-*N'*-(4-methylphenyl)-sulfamide (DMST)



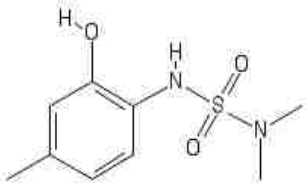
3-OH-DMST



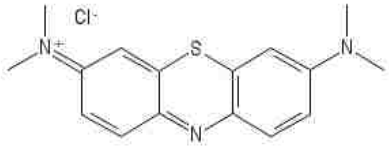
OH-methyl-DMST



COOH-DMST

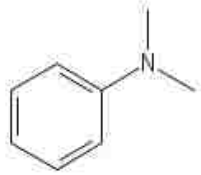


2-OH-DMST

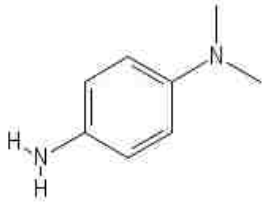


Methylene Blue

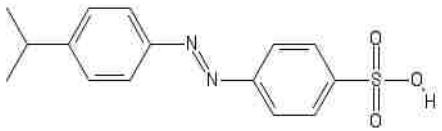
Cont. Table A.1: Structures of potential ozone-reactive NDMA precursors investigated in this dissertation (underlined) and other studies.



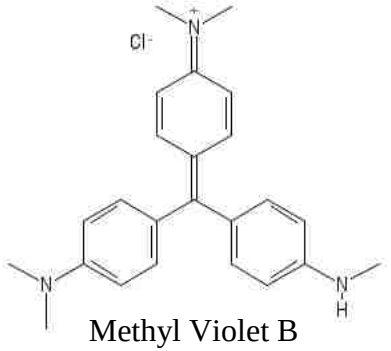
Dimethylaminobenzene (DMAB)



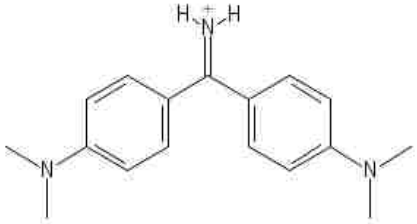
Dimethyl-*p*-phenilenediamine (DMPD)



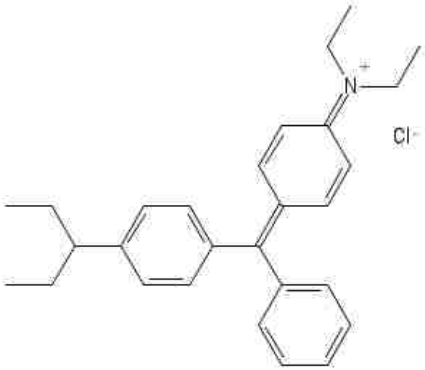
Methyl Orange



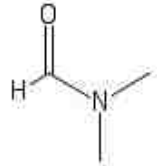
Methyl Violet B



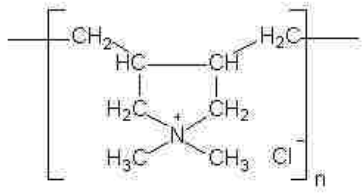
Auramine



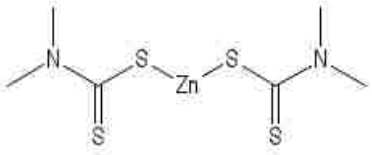
Brilliant Green



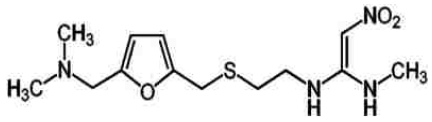
Dimethylformamide



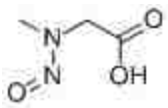
poly(diallyldimethyl-ammoniumchloride) polyDADMAC



Zinc dimethyldithiocarbamate (DMDTC or Ziram)



Ranitidine



N-nitrososarcosine

Table A.2: NDMA precursors and molar yields for NDMA formation with different oxidants in different water matrices.

Compound Name or Abbreviation	Molar Yield (%) Chloramination, ultrapure water [Br^-]	Molar Yield (%) Ozonation, ultrapure water	Molar Yield (%) Ozonation, ultrapure water + [Br^-]	Molar Yield (%) Ozonation, drinking water	Molar Yield (%) Ozonation, wastewater [Br^-]
Dimethylamine	7.5[a] < 1[g] 1.32[l]	< 0.3[a] < 0.4[d] 0.011[h]	< 0.3[a] [1250 ppb]	< 0.05[b]	< 0.3[a]
UDMH	< 0.3[a]	16[a]	34[a] [1250 ppb]	80[b]	54[a]
Acetone DMH	0.3[a]	22[a]	35[a] [1250 ppb]	--	53[a]
2-F-DMH	2.6[a]	61[a]	55[a] [1250 ppb]	--	66[a]
Dacarbazine	< 0.3[a]	< 0.3[a]	< 0.3[a] [1250 ppb]	< 0.05[b]	< 0.3[a]
Daminozide	0.5[a]	78[a]	69[a] [1250 ppb]	55[b]	83[a]
4,4-Hexamethylene bis(1,1-dimethyl semicarbazide), HDMS	N/A[c]	10[c]	--	--	--
TMDS	0.7[a] N/A[c]	23[a] 27[c]	19[a] [1250 ppb]	--	47[a]
DMSC	1.5[a]	64[a]	60[a] [1250 ppb]	--	90[a]
DMTC-phenyl	0.8[a]	12[a]	10[a] [1250 ppb]	--	14[a]
Atazanavir	< 0.3[a]	< 0.3[a]	< 0.3[a] [1250 ppb]	--	< 0.3[a]
Streptozocin	< 0.3[a]	< 0.3[a]	< 0.3[a] [1250 ppb]	--	< 0.3[a]
N-nitrososarcosine	< 0.3[a]	< 0.3[a]	< 0.3[a] [1250 ppb]	--	< 0.3[a]
Ranitidine	89.9[n]	$5x10^{-2}$ [a]	--	94.2[n]	--
DMC-phenyl	1.4[a]	15[a]	13[a] [1250 ppb]	--	14[a]
DMC-dithio	0.8[a]	3.8[a]	3[a] [1250 ppb]	--	2[a]
DMS	< 0.3[a] < 0.3[a] [250 ppb]	< 0.3[a]	20[a] [1250 ppb] 54[i] [15-20 ppb]	52[b]	< 0.3[a] 2.5[a] [250 ppb]
Tolylfluanid	--	--	--	9[b]	--
N,N-dimethyl-N'-p-tolylsulfamide, DMST	--	--	--	15[b]	--
3-OH-DMST	--	--	--	25[b]	--
OH-methyl-DMST	--	--	--	22[b]	--
COOH-DMST	--	--	--	18[b]	--
2-OH-DMST	--	--	--	27[b]	--

Cont. Table A.2: NDMA precursors and molar yields for NDMA formation with different oxidants in different water matrices.

Compound Name or Abbreviation	Molar Yield (%) Chloramination, ultrapure water [Br^-]	Molar Yield (%) Ozonation, ultrapure water	Molar Yield (%) Ozonation, ultrapure water + [Br^-]	Molar Yield (%) Ozonation, drinking water	Molar Yield (%) Ozonation, wastewater [Br^-]
Methylene blue	--	$8.3x10^{-3}$ [f]	--	--	--
N,N-dimethyl aminobenzene, DMAB	--	$6.4x10^{-3}$ [f]	--	--	--
N,N-dimethyl-p-phenylenediamine, DMPD	--	$4.3x10^{-2}$ [f]	--	--	--
Methyl orange	--	$7.2x10^{-3}$ [f]	--	--	--
Methyl violet B	--	$1.2x10^{-2}$ [f]	--	--	--
Auramine	--	$1.3x10^{-2}$ [f]	--	--	--
Brilliant green	--	$< 1.0x10^{-4}$ [f]	--	--	--
N,N-dimethylformamide	$6.3x10^{-2}$ [m]	$3.5x10^{-4}$ [f]	--	--	--
poly(diallyldimethylammoniumchloride), polyDADMAC	N/A[k]	N/A[j]	--	--	--
Dimethyldithio-carbamate, DMDTC	< 0.03[a] 0.008[e]	0.008[e]	--	--	--

[a]This dissertation, [b]Schmidt and Brauch 2008, [c]Kosaka et al. 2009, [d]Andrzejewski et al. 2008, [e]Padhye et al. 2013, [f]Oya et al. 2008, [g]Mitch et al. 2002, [h]Yang et al. 2009, [i]von Gunten et al. 2010, [j]Padhye et al. 2011, [k]Park et al. 2009, [l]Bond and Templeton 2011, [m]Mitch and Sedlak 2004; [n]Shen and Andrews 2011; --: not tested, N/A: molar yield not available

APPENDIX B

RAW DATA FOR NDMA FORMATION AND CHLORINE DEMAND CURVES FOR ISSUE TWO

This appendix contains raw data and graphs not presented in the main text for NDMA formation after chlorination, ozonation, and chloramination, as well as and chlorine demand curves, for six sites (A-F) featured in Chapter 5.

B.1. Raw Data

Table B.1: Nitrosamine concentrations for Site A after various disinfection treatment schemes.

Test	NDMA	NMEA	NDEA	NDPA	NDBA	NPIP	NPYR	NMOR	NDPhA
(MRL)	*(1)*	*(0.2)*	*(2.6)*	*(0.2)*	*(0.2)*	*(0.2)*	*(0.2)*	*(0.2)*	*(0.5)*
Blank	1.4	<MRL	<MRL	<MRL	0.7	<MRL	<MRL	0.2	1.4
WW	5.0	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	4.7	3.0
WW dup	5.7	<MRL	<MRL	2.2	<MRL	0.4	0.3	4.2	5.3
Cl2	5.3	0.21	<MRL	<MRL	9.0	<MRL	<MRL	<MRL	6.6
O3 0.1	6.6	0.94	<MRL	<MRL	<MRL	<MRL	<MRL	6.0	4.0
Cl2-O3 0.1	22.7	0.59	<MRL	<MRL	13.8	0.74	<MRL	<MRL	6.2
Cl2-O3 0.1 dup	26.6	0.56	<MRL	<MRL	11.8	0.44	<MRL	<MRL	7.7
O3 0.5	17.3	3.38	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	4.0
Cl2-O3 0.5	16.9	0.41	<MRL	<MRL	18.8	0.47	<MRL	13.8	6.7
CLM	339.4	1.39	<MRL	<MRL	9.2	<MRL	20.2	27.1	19.6
O3-CLM 0.1	284.3	2.20	<MRL	<MRL	14	<MRL	17.6	29.7	21.6
Cl2-O3-CLM 0.1	19.3	0.52	<MRL	<MRL	<MRL	<MRL	<MRL	47.6	13.1
O3-CLM 0.5	48.5	4.65	<MRL	<MRL	13.7	<MRL	7.1	32.1	13
Cl2-O3-CLM 0.5	16.2	0.45	<MRL	<MRL	16.5	<MRL	3.8	<MRL	8.8
Cl2-O3-CLM 0.5 dup	14.5	0.40	<MRL	<MRL	15.9	<MRL	3.1	<MRL	9.6

MRL = method reporting limit; NDMA = N-Nitrosodimethylamine; NDEA = N-Nitrosodiethylamine; NDPA = N-Nitrosodipropylamine; NDBA = N-Nitrosodibutylamine; NPIP = N-Nitrosopiperidine; NPYR = N-Nitrosopyrrolidine; NMOR = N-Nitrosomorpholine; NDPhA = N-Nitrosodiphenylamine

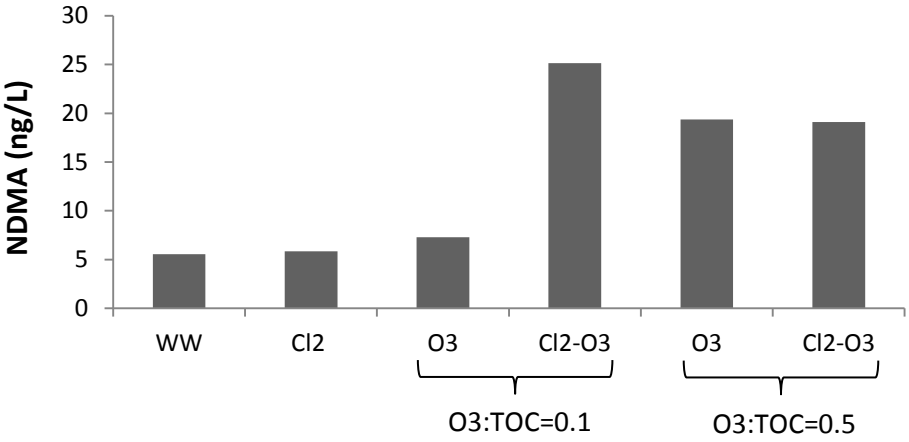


Figure B.1: NDMA concentration for site A after chlorination and ozonation at two O_3:TOC ratios.

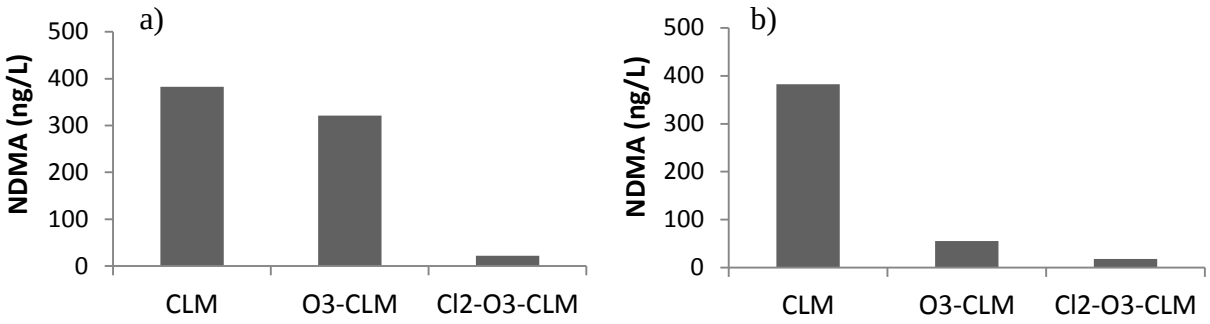


Figure B.2: Reduction in NDMA formation potential for site A with a) O_3:TOC = 0.1 and b) O_3:TOC = 0.5.

Table B.2: Nitrosamine concentrations for Site B after various disinfection treatment schemes.

Test	NDMA	NMEA	NDEA	NDPA	NDBA	NPIP	NPYR	NMOR	NDPhA
(MRL)	*(1)*	*(0.2)*	*(2.6)*	*(0.2)*	*(0.2)*	*(0.2)*	*(0.2)*	*(0.2)*	*(0.5)*
Blank	1.1	<MRL	2.7	<MRL	0.3	<MRL	<MRL	<MRL	2.5
WW	3.4	<MRL	<MRL	<MRL	9.5	<MRL	<MRL	<MRL	1.5
Cl2	5.1	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	6.5	1.5
Cl2 dup	4.1	<MRL	<MRL	<MRL	6.2	<MRL	<MRL	5.8	3.3
O3 0.1	6.0	<MRL	3.3	<MRL	8.2	<MRL	<MRL	2.5	1.6
Cl2-O3 0.1	19.5	<MRL	<MRL	<MRL	5.8	0.86	<MRL	5.5	3.4
O3 0.5	13.1	0.55	4.3	<MRL	5.3	0.42	0.8	12.4	1.7
Cl2-O3 0.5	29.3	0.26	4.0	<MRL	3.9	1.04	2.4	9.8	2.9
Cl2-O3 0.5 dup	27.7	0.28	3.2	<MRL	3.3	1.06	2.0	9.7	2.4
(MRL)	*(4)*	*(4)*	*(2)*	*(1)*	*(2)*	*(1)*	*(2)*	*(1.6)*	*(0.5)*
CLM	428.9	<MRL	3.1	<MRL	<MRL	2.62	12.4	5.3	N/A
O3-CLM 0.1	394.5	<MRL	5.0	<MRL	2.4	3.21	13.5	5.5	N/A
O3-CLM 0.1 dup	307.2	<MRL	3.2	<MRL	<MRL	3.16	11.4	5.8	N/A
Cl2-O3-CLM 0.1	24.1	<MRL	2.3	<MRL	2.3	2.18	4.7	8.3	N/A
O3-CLM 0.5	52.0	<MRL	3.3	<MRL	2.6	<MRL	3.1	6.1	N/A
Cl2-O3-CLM 0.5	28.2	<MRL	3.0	<MRL	4.5	<MRL	2.4	7.8	N/A
WW	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	N/A
Blank	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	N/A

N/A = not available; NDPhA degraded in GC and not quantifiable

MRL = method reporting limit; NDMA = N-Nitrosodimethylamine; NDEA = N-Nitrosodiethylamine; NDPA = N-Nitrosodipropylamine; NDBA = N-Nitrosodibutylamine; NPIP = N-Nitrosopiperidine; NPYR = N-Nitrosopyrrolidine; NMOR = N-Nitrosomorpholine; NDPhA = N-Nitrosodiphenylamine

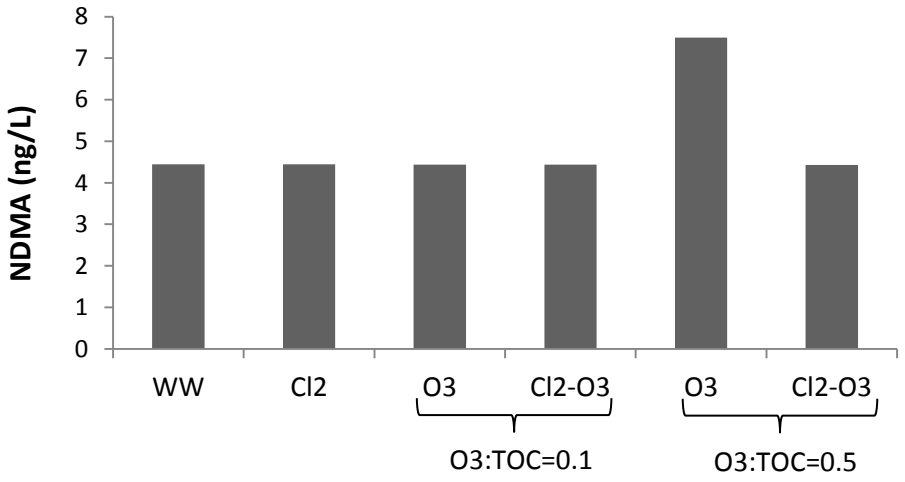


Figure B.3: NDMA concentration for site B after chlorination and ozonation at two O_3:TOC ratios.

b)

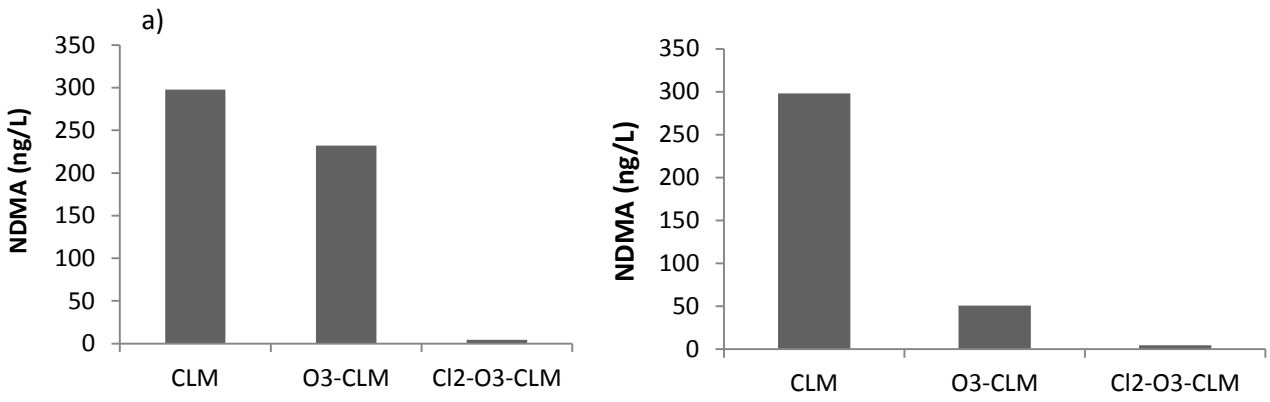


Figure B.4: Reduction in NDMA formation potential for site B with a) O_3:TOC = 0.1 and b) O_3:TOC = 0.5.

Table B.3: Nitrosamine concentrations for Site C after various disinfection treatment schemes.

Test	**NDMA**	**NMEA**	**NDEA**	**NDPA**	**NDBA**	**NPIP**	**NPYR**	**NMOR**	**NDPhA**
(MRL)	*(4)*	*(4)*	*(2.5)*	*(1)*	*(2)*	*(1)*	*(2)*	*(1.6)*	
Blank	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	N/A
WW	16.1	<MRL	4.6	<MRL	<MRL	<MRL	<MRL	143.6	N/A
Cl2	17.2	<MRL	3.6	<MRL	<MRL	<MRL	<MRL	129.6	N/A
O3 0.1	17.0	<MRL	3.6	<MRL	<MRL	<MRL	<MRL	129.5	N/A
O3 0.1 dup	17.0	<MRL	3.7	<MRL	<MRL	<MRL	<MRL	132.8	N/A
Cl2-O3 0.1	21.8	<MRL	5.8	<MRL	3.7	<MRL	<MRL	126.1	N/A
O3 0.5	25.7	<MRL	2.7	<MRL	<MRL	<MRL	<MRL	109.7	N/A
Cl2-O3 0.5	21.8	<MRL	9.1	<MRL	3.9	<MRL	<MRL	113.5	N/A
CLM	630.3	5.31	15.1	<MRL	<MRL	9.57	58.8	198.2	N/A
O3-CLM 0.1	499.3	4.90	12.0	<MRL	<MRL	7.51	57.2	171.7	N/A
Cl2-O3-CLM 0.1	41.8	<MRL	4.9	<MRL	<MRL	<MRL	<MRL	177.6	N/A
Cl2-O3-CLM 0.1 dup	36.6	<MRL	5.8	<MRL	2.1	<MRL	<MRL	181.2	N/A
O3-CLM 0.5	232.4	<MRL	8.7	<MRL	<MRL	4.02	26.1	164.1	N/A
O3-CLM 0.5 dup	177.6	<MRL	8.1	<MRL	<MRL	5.37	23.1	164.5	N/A
Cl2-O3-CLM 0.5	35.8	<MRL	4.9	<MRL	4.2	<MRL	<MRL	158.4	N/A

N/A = not available; NDPhA degraded in GC and not quantifiable

MRL = method reporting limit; NDMA = N-Nitrosodimethylamine; NDEA = N-Nitrosodiethylamine; NDPA = N-Nitrosodipropylamine; NDBA = N-Nitrosodibutylamine; NPIP = N-Nitrosopiperidine; NPYR = N-Nitrosopyrrolidine; NMOR = N-Nitrosomorpholine; NDPhA = N-Nitrosodiphenylamine

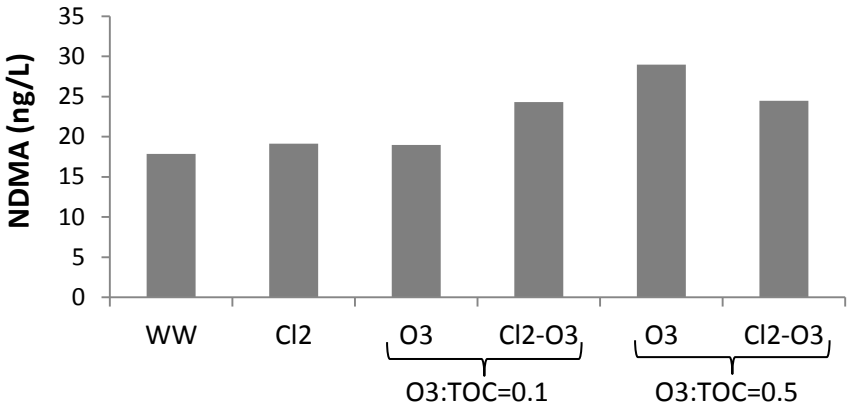


Figure B.5: NDMA concentration for site C after chlorination and ozonation at two O_3:TOC ratios.

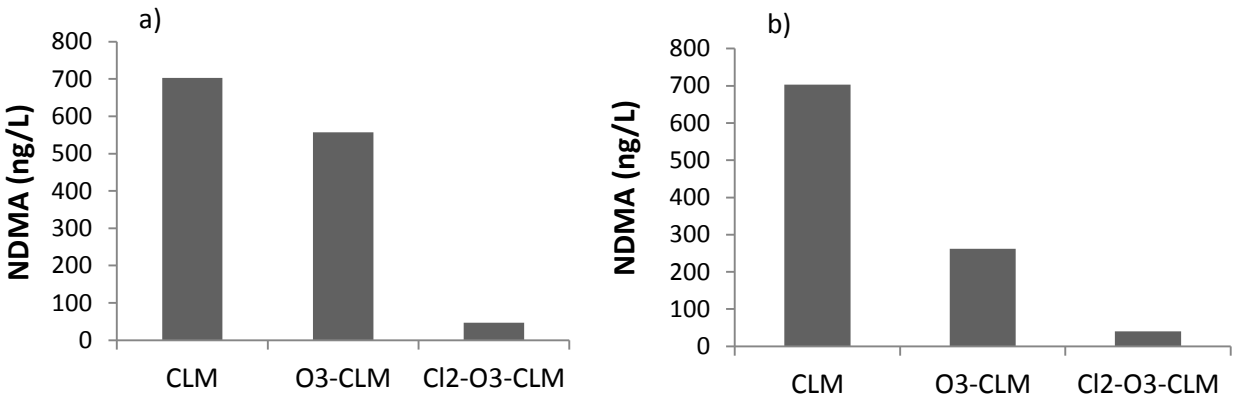


Figure B.6: Reduction in NDMA formation potential for site C with a) O_3:TOC = 0.1 and b) O_3:TOC = 0.5.

B.2. Chlorine Demand Data and Graphs

Table B.4: Free and total chlorine measured during chlorine demand test for Site A.

Chlorine Spike (mL)	Free Chlorine (mg/L as Cl_2)	Total Chlorine (mg/L as Cl_2)	Total Chlorine Added (mg/L as Cl_2)
0.25	0.15	0.95	5
0.38	0.34	1.44	7.5
0.50	0.37	1.80	10
0.75	1.25	2.20	15
1.00	2.1	2.40	20

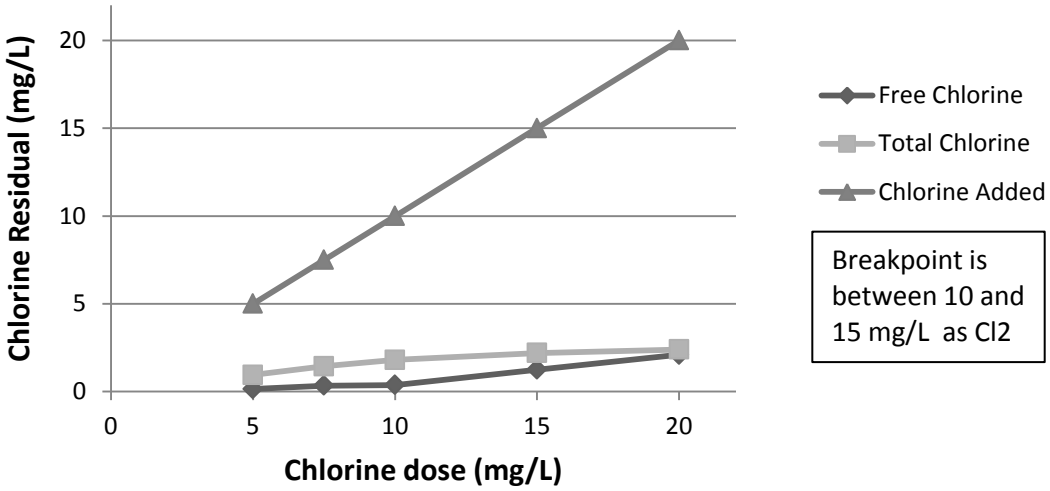


Figure B.7: Chlorine demand curve for Site A.

Table B.5: Free and total chlorine measured during chlorine demand test for Site B.

Chlorine Spike (mL)	Free Chlorine (mg/L as Cl_2)	Total Chlorine (mg/L as Cl_2)	Total Chlorine Added (mg/L as Cl_2)
0.15	0.18	4.14	5
0.23	0.18	6.50	7.5
0.30	0.16	8.40	10
0.45	1.98	8.50	15
0.60	5.88	9.20	20
0.75	11.1	12.7	25
0.90	15.8	17.5	30

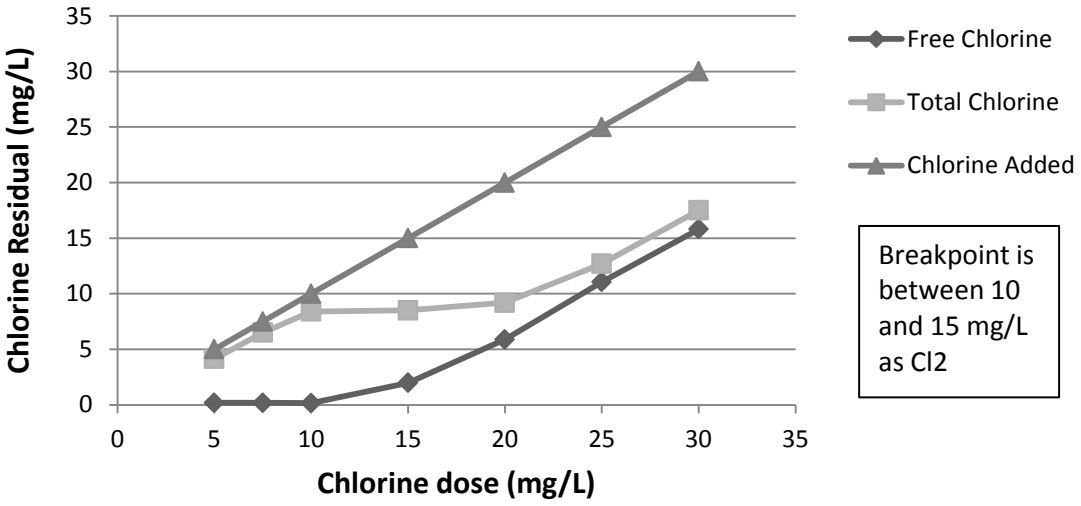


Figure B.8: Chlorine demand curve for Site B.

Table B.6: Free and total chlorine measured during chlorine demand test for Site C.

Chlorine Spike (mL)	Free Chlorine (mg/L as Cl_2)	Total Chlorine (mg/L as Cl_2)	Total Chlorine Added (mg/L as Cl_2)
0.025	0.14	4.05	5
0.038	0.29	6.93	7.5
0.050	0.39	8.73	10
0.075	0.47	13.7	15
0.100	0.77	20.2	20
0.125	0.89	23.2	25
0.138	0.91	23.8	27.5
0.150	0.81	22.6	30
0.175	0.57	18.0	35
0.188	3.0	14.4	37.5
0.200	0.36	9.00	40
0.225	3.0	5.80	45
0.250	7.0	12.0	50
0.275	10.9	15.6	55

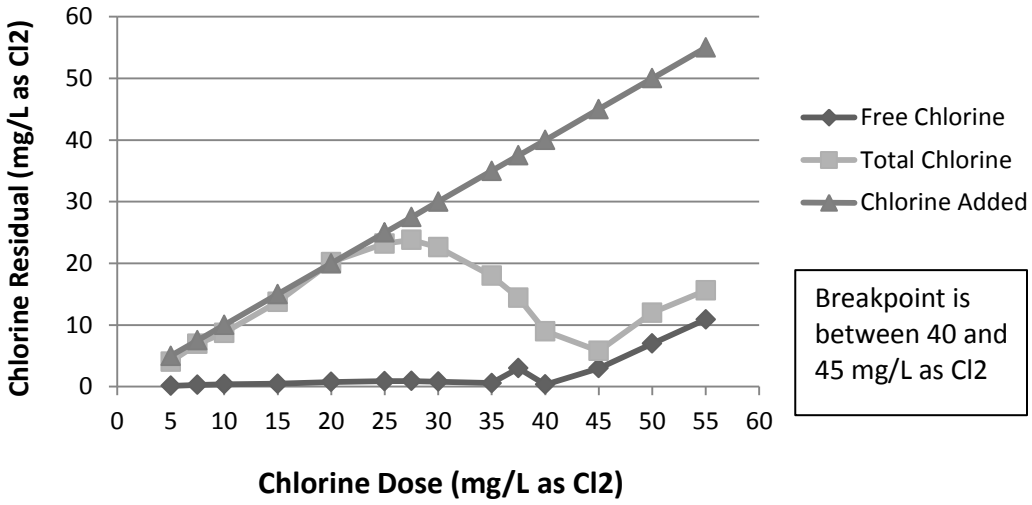


Figure B.9: Chlorine demand curve for Site C.

Table B.7: Free and total chlorine measured during chlorine demand test for Site D.

Chlorine Spike (mL)	Free Chlorine (mg/L as Cl_2)	Total Chlorine (mg/L as Cl_2)	Total Chlorine Added (mg/L as Cl_2)
0.12	0.29	1.59	3
0.16	0.20	1.96	4
0.20	0.25	2.48	5
1.24	0.20	2.86	6
0.28	0.35	3.44	7
0.32	0.33	3.88	8
0.36	0.49	4.68	9
0.40	0.36	4.96	10
0.44	0.71	5.42	11
0.48	0.74	6.00	12
0.52	0.87	6.16	13
0.56	0.87	6.00	14
0.60	1.12	6.96	15
0.64	1.19	7.32	16
0.68	0.99	6.95	17
0.72	1.20	7.05	18
0.76	1.42	7.30	19
0.80	1.95	7.60	20
0.84	1.84	7.95	21
0.88	2.38	9.00	22
0.92	2.56	9.55	23
0.96	3.46	10.35	24
1.00	3.64	9.25	25

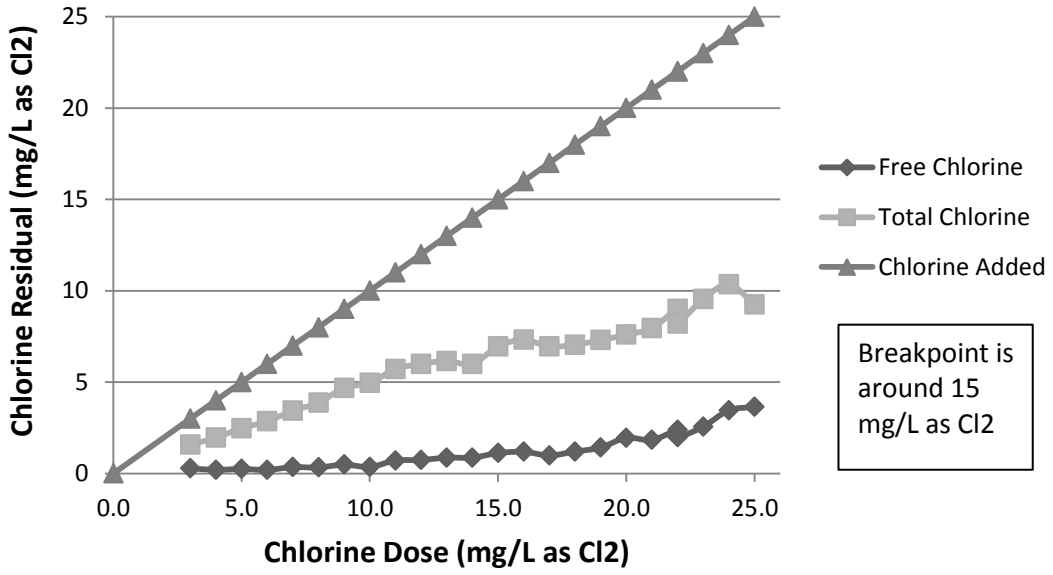


Figure B.10: Chlorine demand curve for Site D.

Table B.8: Free and total chlorine measured during chlorine demand test for Site E.

Chlorine Spike (mL)	Free Chlorine (mg/L as Cl_2)	Total Chlorine (mg/L as Cl_2)	Total Chlorine Added (mg/L as Cl_2)
0.05	0.07	0.22	1
0.10	0.07	0.48	2
0.15	1.40	1.85	3
0.20	2.30	2.75	4
0.25	2.80	3.05	5
0.30	3.80	4.10	6
0.35	4.80	5.35	7
0.40	5.55	6.25	8

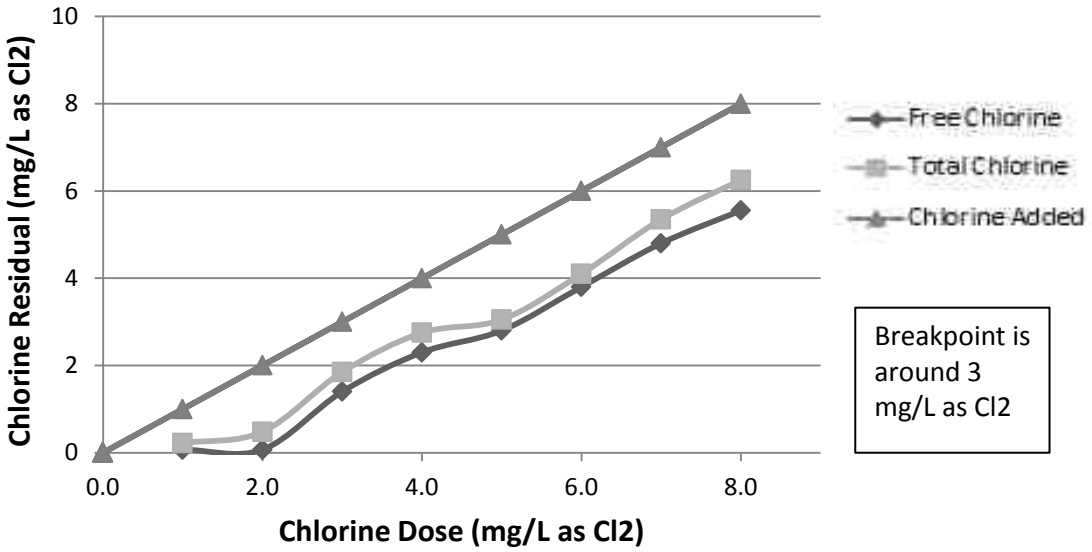


Figure B.11: Chlorine demand curve for Site E.

Table B.9: Free and total chlorine measured during chlorine demand test for Site F.

Chlorine Spike (mL)	Free Chlorine (mg/L as Cl_2)	Total Chlorine (mg/L as Cl_2)	Total Chlorine Added (mg/L as Cl_2)
0.04	0.36	0.36	1.5
0.08	0.91	0.93	3.1
0.12	1.56	1.70	4.6
0.16	2.78	2.86	6.2
0.20	4.75	4.90	7.7
0.40	11.3	11.4	15.4

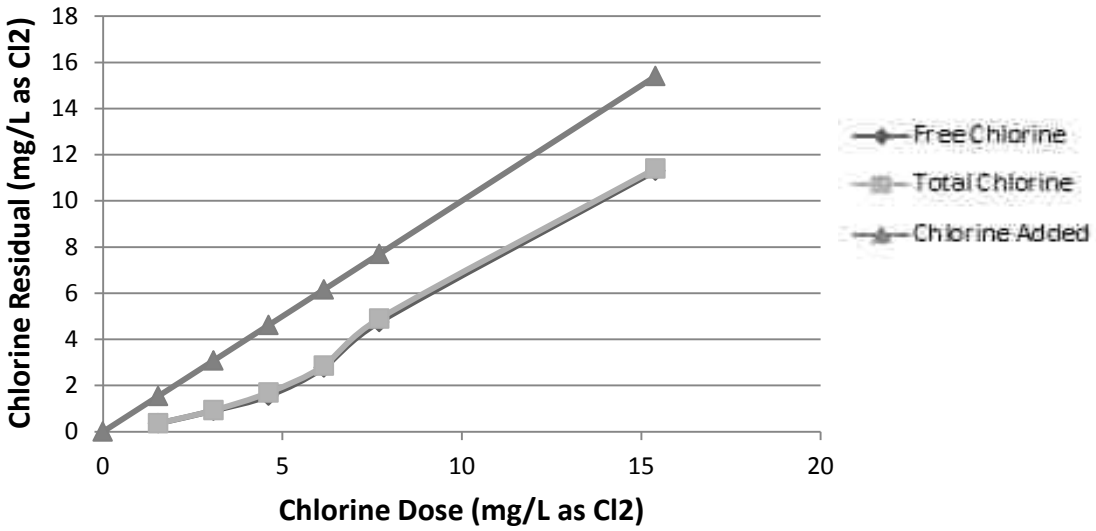


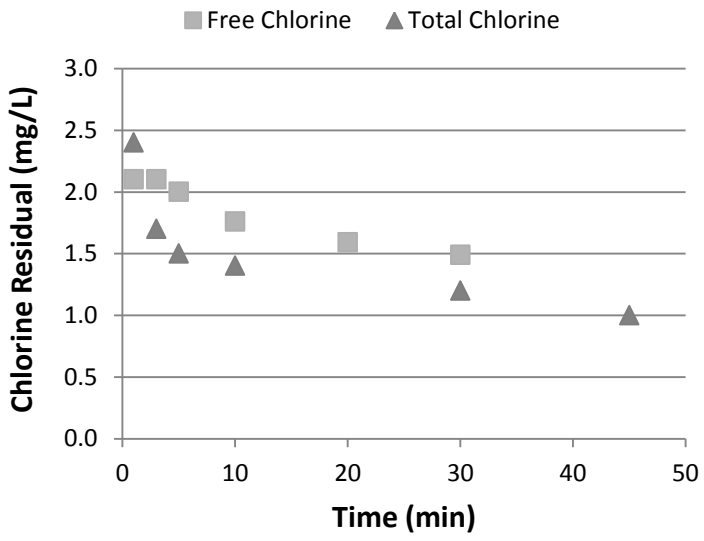
Figure B.12: Chlorine demand curve for Site F.

APPENDIX C

CHLORINE AND OZONE DECAY CURVES AND EXPOSURE CALCULATIONS FOR ISSUE TWO

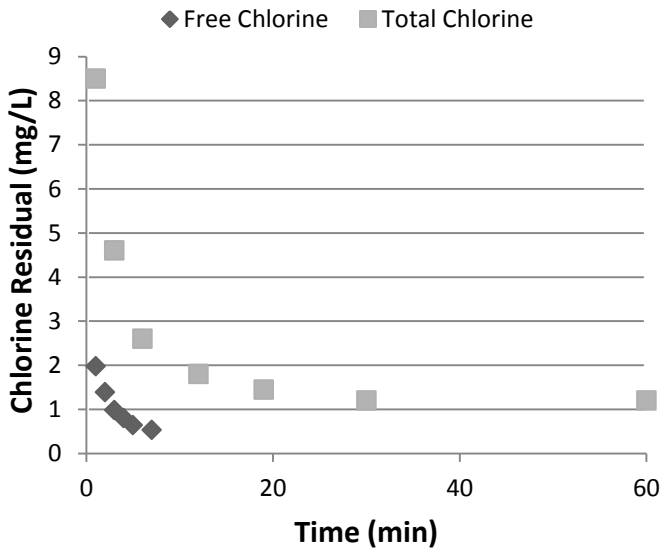
This appendix contains raw data, graphs of decay curves, and calculations of oxidant exposure using the trapezoidal rule for chlorination and ozonation of treated wastewater from six sites (A-F) featured in Chapter 5.

C.1. Chlorine Decay Curves and Free Chlorine Exposure



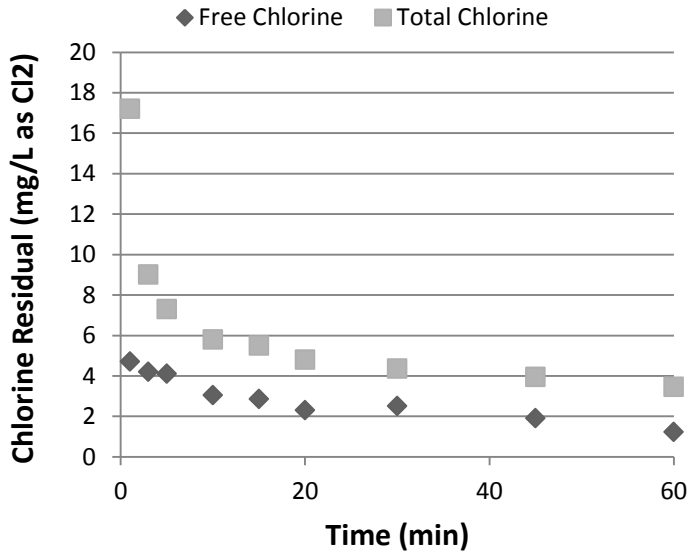
Free Chlorine Exposure		
X (min)	Y (mg/L)	Trap. Rule
0	20	11.2
1	2.4	4.10
3	1.7	3.20
5	1.5	7.25
10	1.4	26.0
30	1.2	16.5
45	1	114.8
180	0.7	
Total	mg·min/L	183.0

Figure C.1: Chlorine decay curve and calculation of free chlorine exposure for Site A at an initial concentration of 20 mg/L as chlorine.



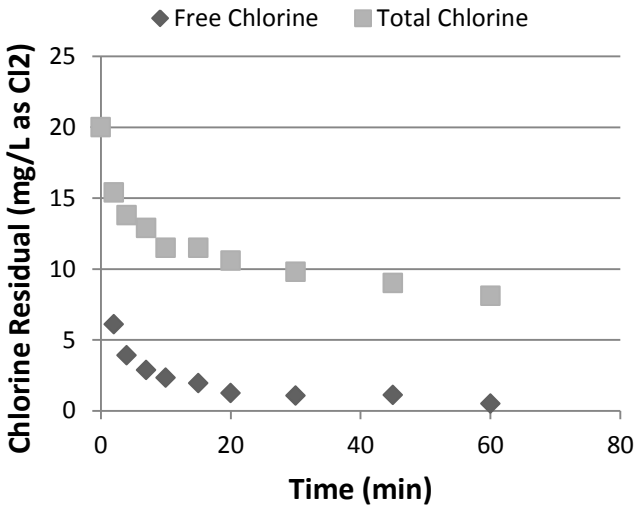
Free Chlorine Exposure		
X (min)	Y (mg/L)	Trap. Rule
0	15	8.49
1	1.98	1.69
2	1.39	1.19
3	0.98	0.89
4	0.8	0.72
5	0.64	1.17
7	0.53	1.55
10	0.5	2.45
15	0.48	2.33
20	0.45	4.35
30	0.42	4.10
40	0.4	3.90
50	0.38	3.65
60	0.35	
Total	mg·min/L	36.5

Figure C.2: Chlorine decay curve and calculation of free chlorine exposure for Site B at an initial concentration of 15 mg/L as chlorine.



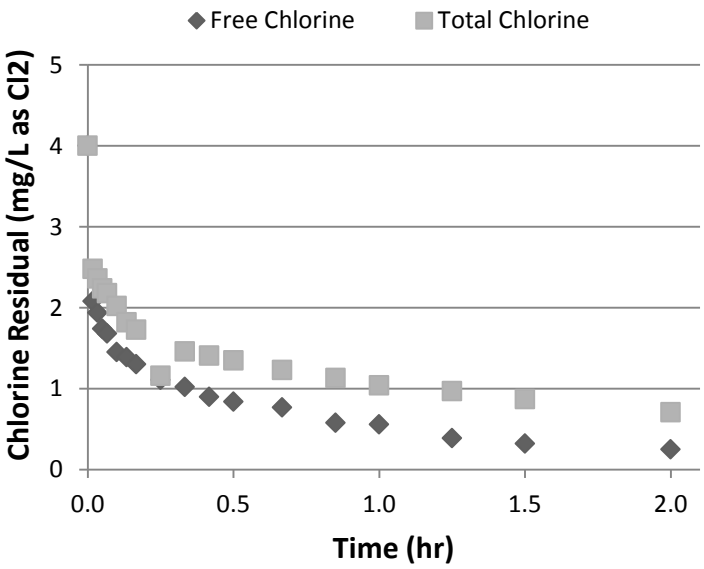
Free Chlorine Exposure		
X (min)	Y (mg/L)	Trap. Rule
0	45	24.9
1	4.7	8.90
3	4.2	8.30
5	4.1	17.9
10	3.05	14.8
15	2.85	12.9
20	2.3	24.0
30	2.5	33.0
45	1.9	23.4
60	1.22	
Total	mg·min/L	168.0

Figure C.3: Chlorine decay curve and calculation of free chlorine exposure for Site C at an initial concentration of 45 mg/L as chlorine.



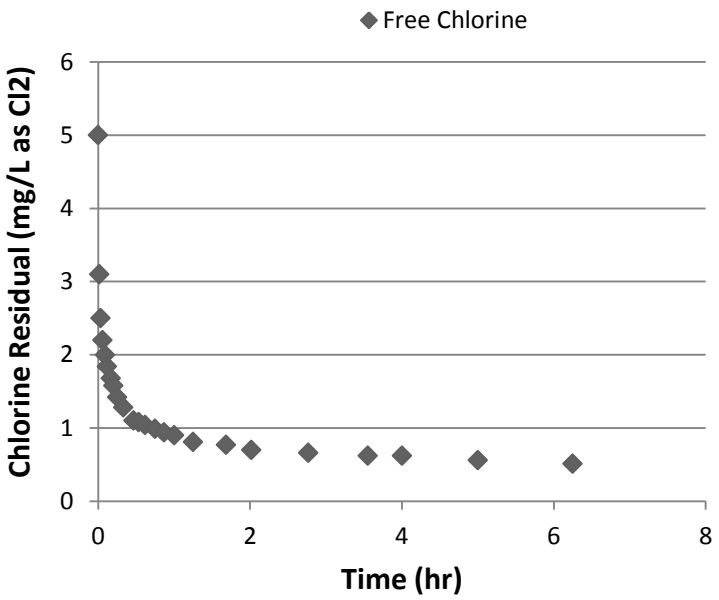
Free Chlorine Exposure		
X (min)	Y (mg/L)	Trap. Rule
0	20	26.1
2	6.1	10.0
4	3.9	10.1
7	2.86	7.77
10	2.32	10.7
15	1.94	7.95
20	1.24	11.6
30	1.07	16.3
45	1.1	12.1
60	0.51	15.3
120	0	
Total	mg·min/L	127.8

Figure C.4: Chlorine decay curve and calculation of free chlorine exposure for Site D at an initial concentration of 20 mg/L as chlorine.



Free Chlorine Exposure		
X (min)	Y (mg/L)	Trap. Rule
0	4	3.06
1	2.2	2.05
2	1.9	1.82
3	1.74	2.55
4	3.36	4.86
6	1.5	4.65
9	1.6	4.26
12	1.24	3.54
15	1.12	3.21
18	1.02	3.08
21	1.03	3.78
25	0.86	4.25
30	0.84	3.06
34	0.69	4.02
40	0.65	5.90
50	0.53	18.6
120	0	
Total	mg·min/L	69.6

Figure C.5: Chlorine decay curve and calculation of free chlorine exposure for Site E at an initial concentration of 4 mg/L as chlorine.



Free Chlorine Exposure		
X (min)	Y (mg/L)	Trap. Rule
0	5	4.05
1	3.1	2.80
2	2.5	3.53
4	2.2	4.20
6	2	2.88
7	1.84	5.28
10	1.68	3.26
12	1.58	4.50
15	1.42	6.75
20	1.28	9.52
28	1.1	4.36
32	1.08	5.30
37	1.04	8.12
45	0.99	6.76
52	0.94	7.36
60	0.9	12.8
75	0.81	20.5
101	0.77	14.7
121	0.7	30.6
166	0.66	30.1
213	0.62	16.7
240	0.62	35.4
300	0.56	40.1
375	0.51	
Total	mg·min/L	275.6

Figure C.6: Chlorine decay curve and calculation of free chlorine exposure for Site F at an initial concentration of 5 mg/L as chlorine.

C.2. Ozone Decay Curves and Ozone Exposure

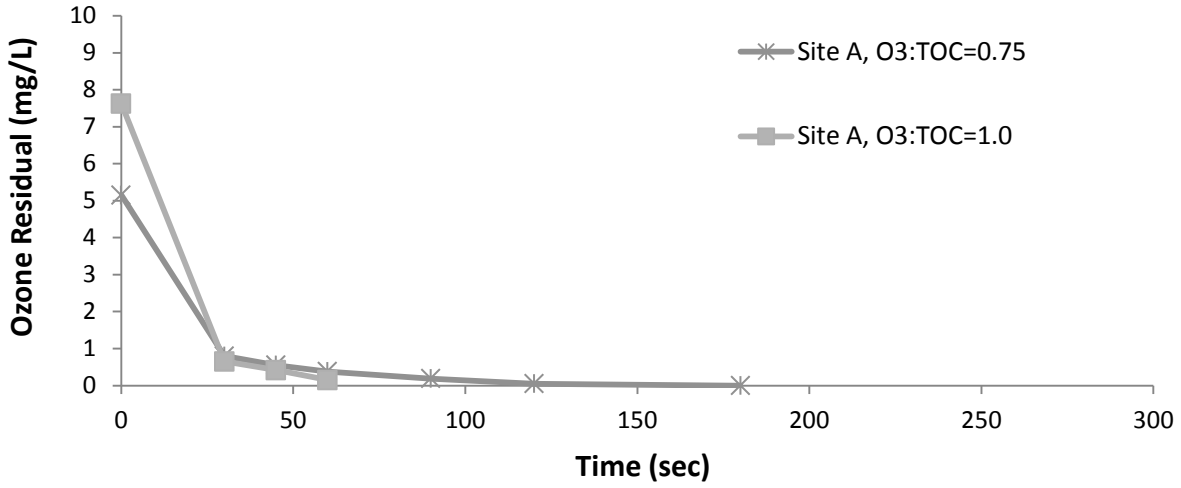


Figure C.7: Ozone decay curve for Site A at O_3:TOC ratios of 1.0 and 0.75.

Table C.1: Calculation of ozone exposure for Site A at O_3:TOC ratios of 1.0 and 0.75.

Site A, O_3:TOC=1.0			Site A, O_3:TOC=0.75		
X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule
0	7.63	124.2	0	5.152	89.3
30	0.65	8.03	30	0.8	10.1
45	0.42	4.28	45	0.55	6.98
60	0.15		60	0.38	8.55
90			90	0.19	3.60
120			120	0.05	1.50
180			180	0	
Total	mg*sec/L	136.5	Total	mg*sec/L	120.0
Total	mg*min/L	2.3	Total	mg*min/L	2.0

Note: Ozone exposures for O_3:TOC ratios of 0.5 and 0.1 were not calculated because the ozone residual was zero before the 30 second measurement.

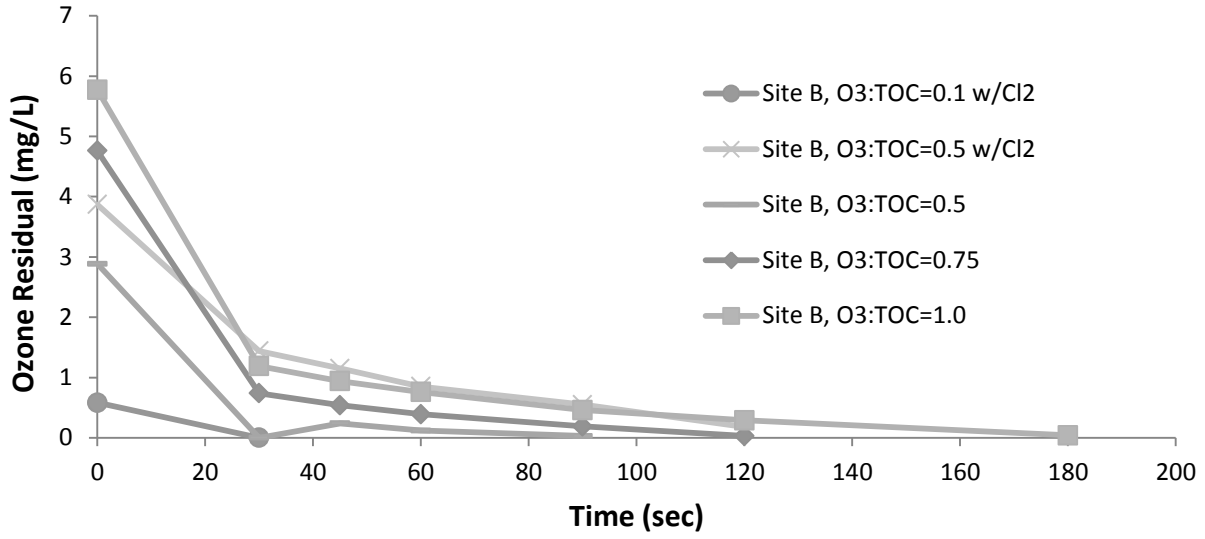


Figure C.8: Ozone decay curve for Site B at O_3:TOC ratios of 0.1, 0.5,0.75 and 1.0.

Table C.2: Calculation of ozone exposure for Site B at O_3:TOC ratios of 0.5, 0.75, and 1.0.

Site B, O_3:TOC=1.0			Site B, O_3:TOC=0.75			Site B, O_3:TOC=0.50		
X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule
0	5.775	104.5	0	4.763	82.5	0	2.886	43.3
30	1.19	16.0	30	0.74	9.60	30	0	1.80
45	0.94	12.8	45	0.54	6.98	45	0.24	2.70
60	0.76	18.3	60	0.39	8.70	60	0.12	2.25
90	0.46	11.3	90	0.19	3.30	90	0.03	
120	0.29	9.90	120	0.03		120		
180	0.04		180			180		
Total	mg*sec/L	172.7	Total	mg*sec/L	111.1	Total	mg*sec/L	50.0
Total	mg*min/L	2.9	Total	mg*min/L	1.85	Total	mg*min/L	0.8

Table C.3: Calculation of ozone exposure for Site B at O_3:TOC ratios of 0.1 and 0.5 for pre-chlorinated wastewater.

Site B, O_3:TOC=0.5 w/Cl_2			Site B, O_3:TOC=0.1 w/Cl_2		
X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule
0	3.872	79.7	0	0.583	8.75
30	1.44	19.4	30	0	
45	1.15	15.0	45		
60	0.85	21.0	60		
90	0.55	11.0	90		
120	0.18		120		
Total	mg*sec/L	146.1	Total	mg*sec/L	8.75
Total	mg*min/L	2.4	Total	mg*min/L	0.15

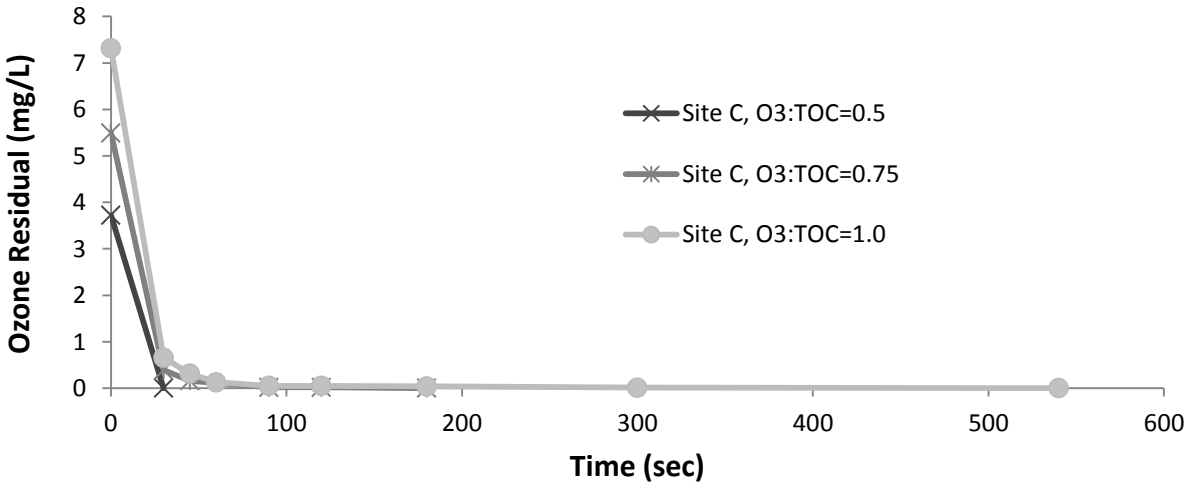


Figure C.9: Ozone decay curve for Site C at O_3:TOC ratios of 0.1, 0.5,0.75 and 1.0.

Table C.4: Calculation of ozone exposure for Site C at O_3:TOC ratios of 0.5, 0.75, and 1.0.

Site C, O_3:TOC=1.0			Site C, O_3:TOC=0.75			Site C, O_3:TOC=0.50		
X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule
0	7.316	119.6	0	5.491	88.2	0	3.72	55.8
30	0.66	7.28	30	0.39	0.16	30	0	
45	0.31	3.30	45	0.55	12.9	45		
60	0.13	2.70	60	0.02	0.02	60		
90	0.05	1.50	90	0.02	0.02	90		
120	0.05	2.70	120	0		120		
180	0.04	3.00	180			180		
300	0.01	1.20						
540	0							
Total	mg*sec/L	141.3	Total	mg*sec/L	101.2	Total	mg*sec/L	55.8
Total	mg*min/L	2.35	Total	mg*min/L	1.69	Total	mg*min/L	0.93

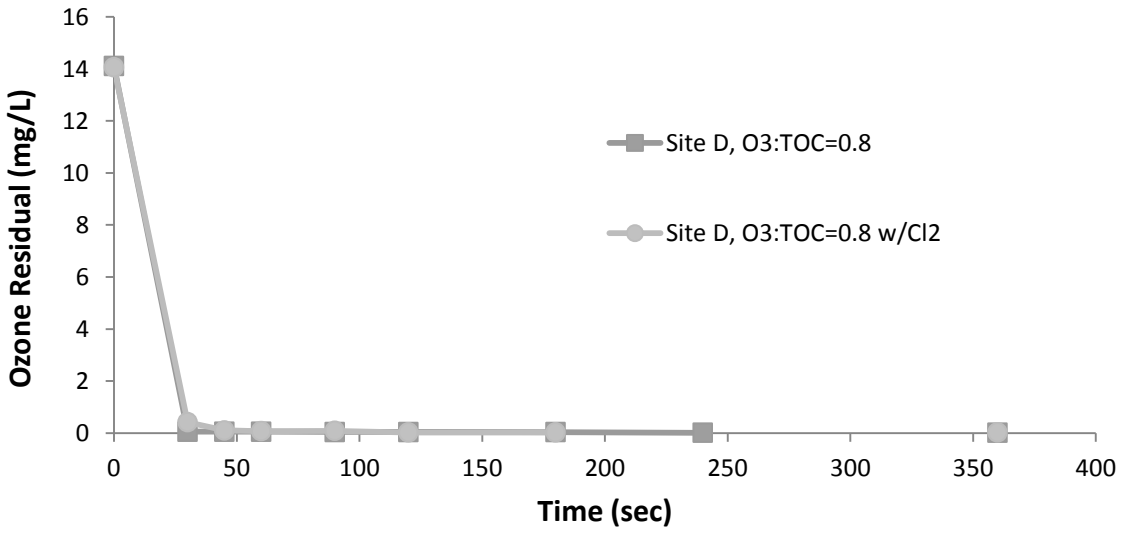


Figure C.10: Ozone decay curve for Site D at O_3:TOC=0.8 for pre-chlorinated and unaltered wastewater.

Table C.5: Calculation of ozone exposure for Site D at O_3:TOC=0.8 for pre-chlorinated and unaltered wastewater.

Site D, O_3:TOC=0.8			Site D, O_3:TOC=0.8 w/Cl_2		
X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule
0	0	0.90	0	0.000	6.30
30	0.06	0.90	30	0.42	3.98
45	0.06	0.90	45	0.11	1.43
60	0.06	1.65	60	0.08	2.55
90	0.05	1.50	90	0.09	1.80
120	0.05	2.70	120	0.03	1.80
180	0.04	1.80	180	0.03	5.40
240	0.02	2.40	360	0.03	
360	0.02				
Total	mg*sec/L	12.8	Total	mg*sec/L	23.2
Total	mg*min/L	0.2	Total	mg*min/L	0.39

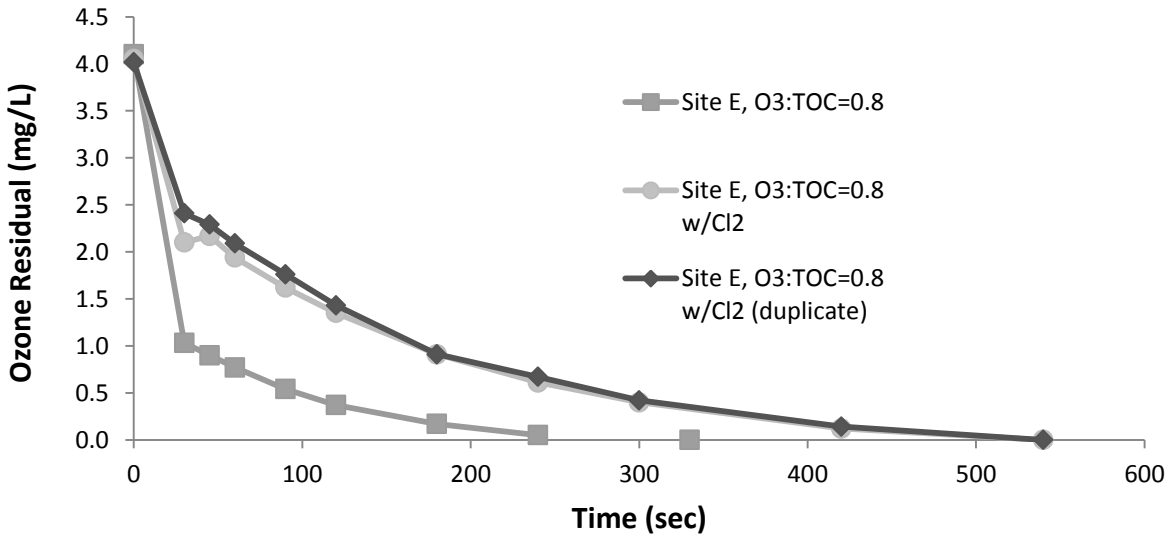


Figure C.11: Ozone decay curve for Site E at O_3:TOC=0.8 for pre-chlorinated and unaltered wastewater.

Table C.6: Calculation of ozone exposure for Site E at O_3:TOC=0.8 for pre-chlorinated and unaltered wastewater.

Site E, O_3:TOC=0.8			Site E, O_3:TOC=0.8 w/Cl_2			Site E, O_3:TOC=0.8 w/Cl_2 (duplicate)		
X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule
0	0.000	15.5	0	0.000	31.5	0	0.000	36.2
30	1.03	14.5	30	2.1	32.0	30	2.41	35.3
45	0.9	12.5	45	2.17	30.8	45	2.29	32.9
60	0.77	19.7	60	1.94	53.4	60	2.09	57.8
90	0.54	13.7	90	1.62	44.6	90	1.76	47.9
120	0.37	16.2	120	1.35	67.8	120	1.43	70.2
180	0.17	6.60	180	0.91	45.6	180	0.91	47.4
240	0.05	2.25	240	0.61	30.3	240	0.67	32.7
330	0		300	0.4	31.2	300	0.42	33.6
			420	0.12	7.20	420	0.14	8.40
			540	0		540	0	
Total	mg*sec/L	100.8	Total	mg*sec/L	374.4	Total	mg*sec/L	402.2
Total	mg*min/L	1.7	Total	mg*min/L	6.2	Total	mg*min/L	6.7

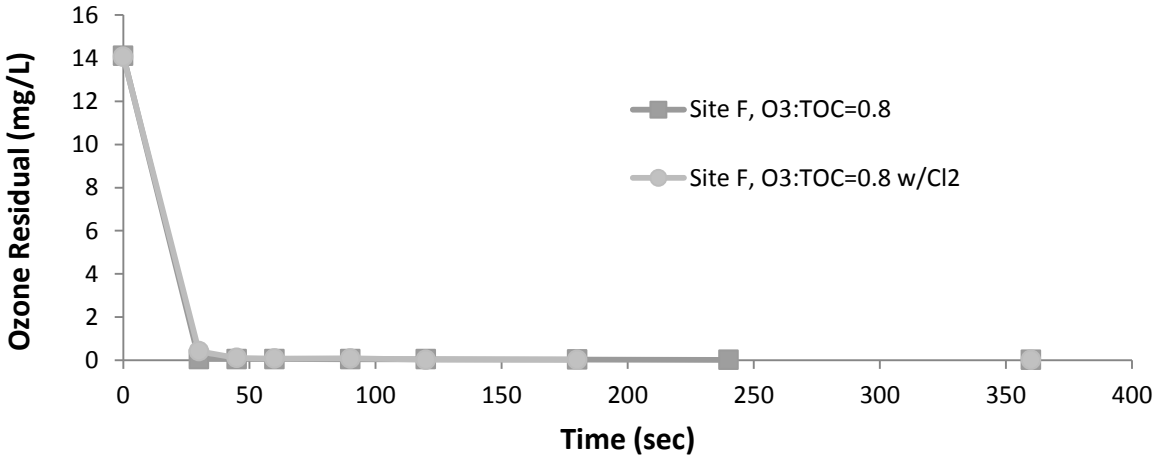


Figure C.12: Ozone decay curve for Site F at O_3:TOC=0.8 for pre-chlorinated and unaltered wastewater.

Table C.7: Calculation of ozone exposure for Site F at O_3:TOC=0.8 for pre-chlorinated and unaltered wastewater.

Site F, O_3:TOC=0.8			Site F, O_3:TOC=0.8 (Duplicate)			Site F, O_3:TOC=0.8 w/Cl_2		
X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule	X (min)	Y (mg/L)	Trap. Rule
0	0	27.3	0	0	30.0	0	0	54.6
30	1.82	25.9	30	2	27.4	30	3.64	54.0
45	1.63	22.4	45	1.65	22.5	45	3.56	50.0
60	1.35	33.9	60	1.35	35.0	60	3.1	86.1
90	0.91	22.4	90	0.98	24.3	90	2.64	73.1
120	0.58	24.3	120	0.64	29.1	120	2.23	114.6
180	0.23	8.70	180	0.33	14.7	180	1.59	82.8
240	0.06	3.60	240	0.16	7.65	240	1.17	58.8
360	0		330	0.01		300	0.79	38.1
						360	0.48	42.6
						480	0.23	14.9
						570	0.1	7.20
						660	0.06	4.05
						750	0.03	4.50
						900	0.03	
Total	mg*sec/L	168.4	Total	mg*sec/L	190.6	Total	mg*sec/L	685.2
Total	mg*min/L	2.8	Total	mg*min/L	3.2	Total	mg*min/L	11.4

APPENDIX D

CORRELATIONS BETWEEN BIOFILTRATION REMOVAL AND DISSOLVED OXYGEN FOR ISSUE THREE

This appendix contains graphs of correlations between NDMA precursor removal and dissolved oxygen concentration during biofiltration.

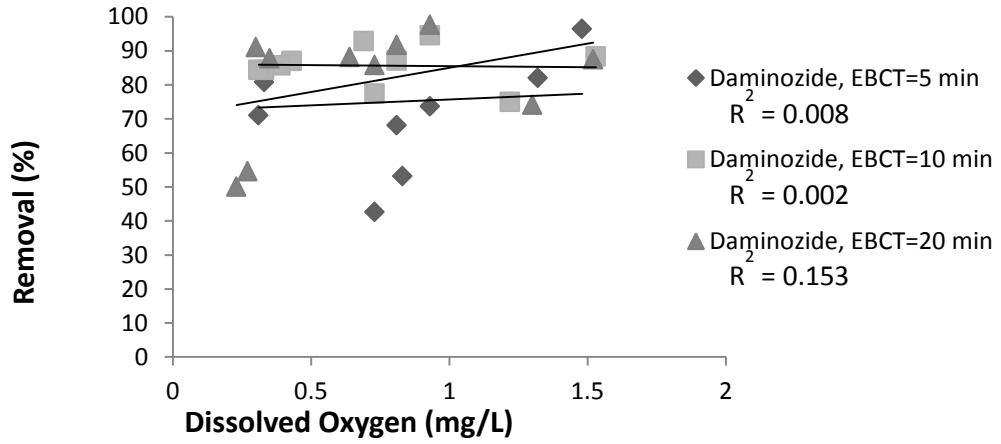


Figure D.1: Correlation regression between dissolved oxygen concentration and daminozide removal.

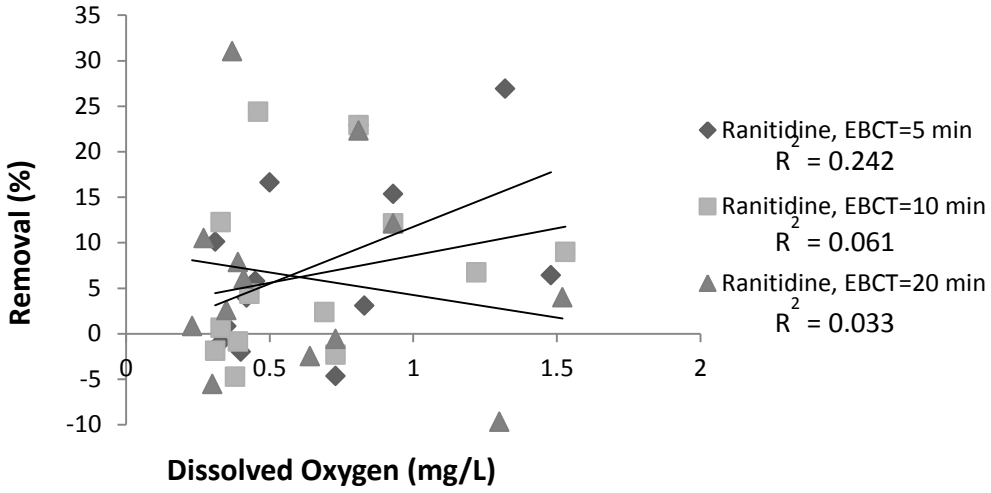


Figure D.2: Correlation regression between dissolved oxygen concentration and ranitidine removal.

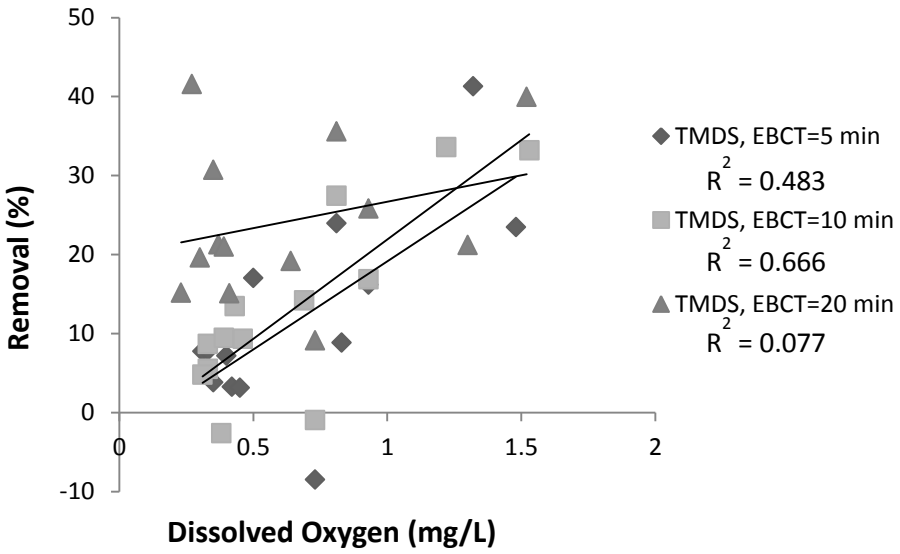


Figure D.3: Correlation regression between dissolved oxygen concentration and TMDS removal.

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CURRICULUM VITAE

The Graduate College
University of Nevada, Las Vegas

Erica Jean Marti

Communication:

Las Vegas, NV
Email address: echemie@gmail.com

Education:

Bachelor of Science in Chemistry, 2004
University of Illinois at Urbana-Champaign

Master of Education in Curriculum and Instruction, 2007
University of Nevada, Las Vegas

Master of Science in Engineering, 2012
University of Nevada, Las Vegas

Awards and Honors:

- Nevada Regents' Scholar Award, 2016 ($5,000)
- Young Scientist at the Lindau Nobel Laureate Meeting, June 2015: Selected as one of 55 U.S. graduate students to attend the 65th Annual Lindau Meeting in Lindau, Germany
- President's UNLV Foundation Graduate Research Fellowship, 2015 ($25,000)
- American Water Works Association: Dave Caldwell Scholarship, 2015 ($10,000)
- Society of Women Engineers: Ada I. Pressman Memorial Scholarship, 2015 ($5,000)
- UNLV: Gilman & Bartlett Engineering Scholarship, 2015 ($4,000)
- National Science Foundation, East Asia & Pacific Summer Institute, 2014 Australia Fellow: Conducted research in Perth, Australia; Principal Investigator (Award #1415103)
- Society of Women Engineers: Chrysler Foundation Scholarship, 2014 ($2,500)
- Society of Women Engineers: Claire Luce Booth Scholarship, 2012 ($20,000)

Publications:

Marti, E.J. and Batista, J.R. *Impact of Sludge Handling Processes and Secondary Treatment Types on Estrogen Concentration in Wastewater Sludge*. Science of the Total Environment 470–471 (2014) 1056–1067. DOI: 10.1016/j.scitotenv.2013.10.070

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Dissertation Examination Committee:

Chair Person, Jacimaria R. Batista, Ph.D.
Committee Member, Eric R.V. Dickenson, Ph.D.
Committee Member, Daniel Gerrity, Ph.D.
Committee Member, David E. James, Ph.D.
Graduate College Representative, MaryKay Orgill, Ph.D.