EFFECT OF PREFORMED CHLORAMINES AND CHLORINE TO AMMONIA RATIO ON THE FORMATION OF N-NITROSODIMETHYLAMINE (NDMA) IN TRWD EAST TEXAS RAW WATER DELIVERY SYSTEM

by

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Abstract

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Tarrant Regional Water District (TRWD) pumps untreated raw water from Richland Chambers and Cedar Creek reservoirs in East Texas to provide water to several customer cities including Arlington and Fort Worth. TRWD adds chloramines to the pipeline to combat biofilm growth, that reduces pipeline capacity and increases pumping costs, and to control zebra mussels, that clog intake structure screens and the pump wet wells. However, addition of chloramines leads to the formation of N-nitrosodimethylamine (NDMA), a potent carcinogen, by reaction of chloramines with nitrogenous organic precursors possibly present in the raw water. NDMA formation presents a challenge to TRWD because potential regulation of NDMA and other nitrosamines will force TRWD and other utilities alike to seek treatment options. Because post treatment removal of NDMA is ineffective and expensive, the best strategy is to optimize conditions to minimize NDMA formation and to eliminate nitrogenous NDMA precursors in the system. This research examines the effect of preformed chloramines and chlorine to ammonia mass ratio on NDMA formation in the District's current and future pipelines.

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Chapter 1

Introduction and Objectives

1.1 Introduction

Richland Chambers and Cedar Creek reservoirs are major sources of water supply and storage for Tarrant Regional Water District (TRWD) to meet its increasing demand. TRWD pumps untreated raw water approximately 78 miles from Richland Chambers and Cedar Creek reservoirs in separate pipelines to several customer cities including Fort Worth, Arlington, Mansfield, and Waxahachie. Pipeline network is shown on Figure 1.1.

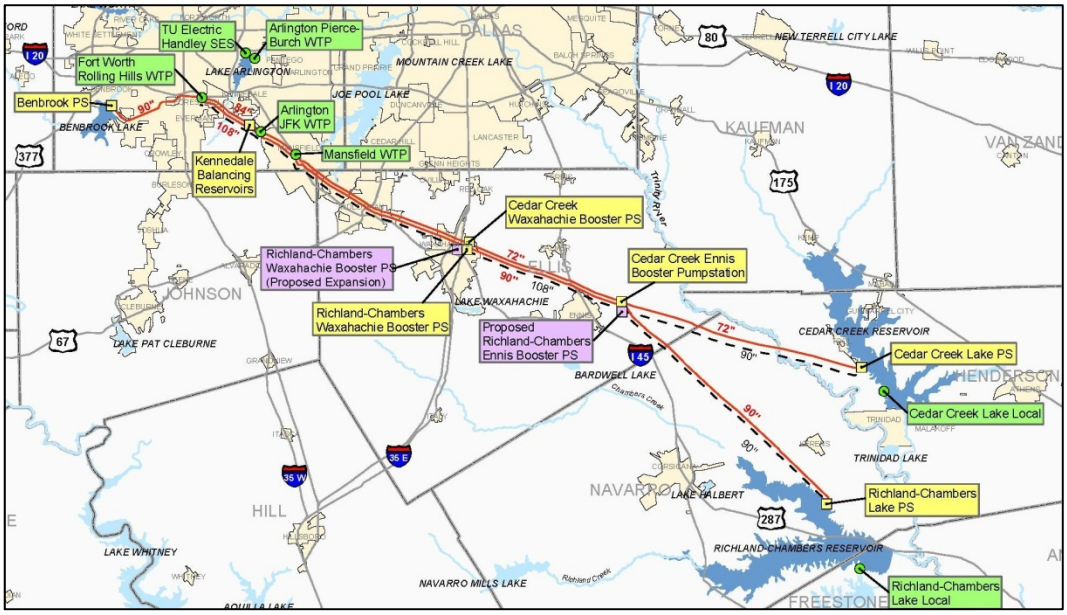

Figure 1.1: Richland Chambers and Cedar Creek Pipeline Network

Biofilm growth in the pipeline reduces pipeline capacity and increases pumping costs due to increased friction factor. Biofilm growth also leads to increased internal concrete corrosion due to depressed pH. In addition, zebra mussels present a potential future challenge because they clog intake structure screens and the pump wet wells resulting in reduced capacity, damage to the pumps, and increased maintenance

expenditure. To combat all three problems, TRWD feeds chloramines at the Richland Chambers and Cedar Creek Lake Pump Stations typically from March through November of each year when biofilm growth is at its peak. TRWD aims to maintain a minimum chloramine residual of at least 0.5 mg/L to achieve the goal (TRWD, 2014).

Since the enactment of the Disinfection Byproducts Rule (DBPR) to control THMs and HAAs, more water utilities have switched to using chloramination for secondary disinfection instead of chlorination. However, addition of chloramines leads to the formation of N-nitrosodimethylamine (NDMA) in the presence of amine precursors (Mitch et al., 2003). NDMA has the chemical formula $C_2H_6N_2O$ and Molar mass of 74.08 g/mol. NDMA consists of two methyl groups and nitroso functional group attached to nitrogen atom. Structural formula of NDMA is shown on Figure 1.2.

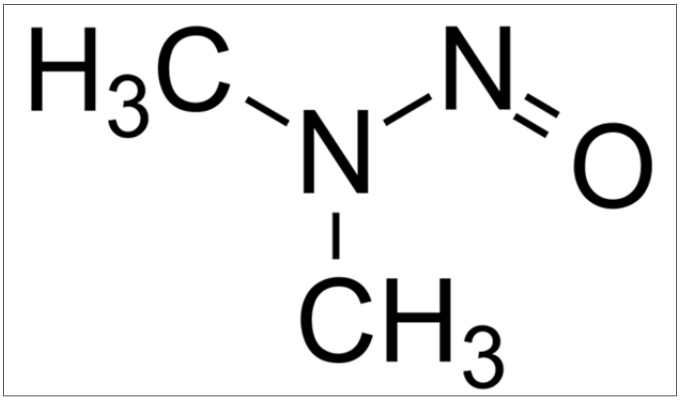

Figure 1.2: NDMA Structural Formula

A few research papers by various researchers have documented the prevalence of NDMA in natural source waters or finished treated waters. These values are shown in the following Table 1.1.

Table 1.1: Comparison of NDMA Concentration in Source and Finished Waters from Different Studies

Country	Source Water	Finished Water	Researcher
China	6.4 - 13.9 ng/L (From wastewater effluent contamination)	4.6 - 20.5 ng/L (Chlorination)	(Wang et al., 2011)
China	0.12 - 21.6 ng/L (From wastewater effluent contamination)	0.7 - 8.8 ng/L (Chlorination, chloramination)	(Luo et al., 2012)
Spain	0.6 - 2.1 ng/L (Pesticides contamination)	1.4 – 7.8 ng/L (Preoxidation/ chlorination)	(Jurado-Sanchez et al., 2012)
USA	Not Reported	less than 10 ng/L (Chlorination)	(Mitch and Sedlak, 2002)
Canada	Not Reported	was less than 5 ng/L to more than 9 ng/L (Disinfection scheme not specified)	(Mitch et al., 2003)

NDMA is classified as Group 2A probably carcinogenic to humans by the International Agency for Research on Cancer (IARC) (Selin, 2011). The Environmental Protection Agency (EPA) classifies NDMA as a Category B2 probable human carcinogen (Selin, 2011). It is formed by the reaction of chloramines with organic amine groups and other nitrogenous organic precursors possibly present in the raw water. According to USEPA data, NDMA occurrence in chloraminated systems is 34.4% (Rosenfeldt et al., 2011).

NDMA is included in the Contaminants Candidates List 3 (CCL3) and in the draft Contaminants Candidates List 4 (CCL4) for drinking water. CCL is a list of contaminants that are not subject to any established drinking water regulations, but are candidates for such regulation under the Safe Drinking Water Act due to their health effects and occurrence data (EPA, 2015). In addition, NDMA was added to EPA's Unregulated Contaminant Monitoring Rule 2 (UCMR 2) on January 4, 2007, which required the monitoring of 25 contaminants including NDMA from January 2008 through December 2010. EPA, the States, laboratories and public water systems (PWSs) have participated in UCMR 2 (EPA, 2013).

These actions by EPA make NDMA a candidate for potential regulation under the Safe Drinking Water Act (Hebert et al., 2010). Accordingly, NDMA formation would present a challenge to water utilities since potential regulation of NDMA and other nitrosamines could force water utilities to seek other alternatives.

1.2 Objectives

One objective of this research is to document the occurrence and formation potential of NDMA in TRWD's current and future pipelines transferring raw water from Richland Chambers Lake, Cedar Creek Lake, and Lake Palestine under the current operating conditions. The second objective is to investigate factors affecting NDMA formation in the system including pH, chlorine contact time, temperature, residence time in the distribution system, concentration of free chlorine, order of reagents addition, preformed chloramines, rapidity of mixing, and chlorine to ammonia ratio. The research focuses on investigating the effect of preformed chloramines and chlorine to ammonia mass ratio (Cl_2/N) on NDMA formation and to find the ratio that will minimize formation of NDMA in the system.

Chapter 2

Literature Review

2.1 NDMA Guidance Levels

Since NDMA is still in the monitoring stage, a maximum contaminant level (MCL) has not been established for drinking water (Mitch et al., 2003). There is no national or worldwide consensus on actionable limits or maximum contaminant level for NDMA. Various regulatory agencies have established different monitoring levels depending on risk assessment, which depends on the risk level, choice of animal study, extrapolation from animal studies, low-dose extrapolation, interspecies extrapolations, and risk threshold (Selin, 2011). Considering that risk levels established by regulatory agencies varies from 1 in 100,000 to 1 in 1,000,000 cancer risk and the differences in risk assessment methodologies, it is not surprising that guidance levels vary by several orders of magnitude (Selin, 2011). Guidance levels are shown in Table 2.1.

Table 2.1: Established NDMA Guidance Levels

Agency	Cancer Risk Level	Limit Designation	Limit
US Department of Health and Human Services (Krauss et al., 2009)	1 in 1,000,000	Cancer Risk Level	0.7 ng/l
Netherlands (Krauss et al., 2009)	*	Action Level	10 ng/l
Germany (Krauss et al., 2009)	*	Action Level	10 ng/l
U.S. EPA (Mitch et al., 2003)	Increased lifetime cancer risk of 1026	Cleanup Level	0.7 ng/L
Ontario Ministry of the Environment and Energy (Mitch et al., 2003)	*	Maximum Acceptable Concentration	9 ng/L
California Water Resources Control Board (CSWRCB, 2014)	1 in 1,000,000	Risk Level	3 ng/L
		Notification Level	10 ng/l
		Response Level	300 ng/l
World Health Organization (WHO, 2008)	*	Maximum Level	100 ng/L
Japan Ministry of Health, Labor and Welfare (Kitamoto et al.)	*	Target Value	100 ng/L
State of Massachusetts (MDEP, 2004)	1 in 1,000,000	practical quantitation limit	10 ng/l
Health Canada (Selin, 2011)	*	maximum acceptable concentration	40 ng/l
United Kingdom (Selin, 2011)	*	Tier 1- Risk Assessment	Any concentration
		Tier 2- Monitoring	>1 ng/l
		Tier 3- Action	>10 ng/l
		Tier 4- Urgent	>200 ng/l

*Not reported

2.2 NDMA Formation

2.2.1 Chloramines Chemistry

Monochloramine is more stable than free chlorine, so its disinfection ability to prevent biofilm growth and zebra mussel attachment is long-lasting (Snoeyink and

Jenkins, 1980). However, NDMA is formed as disinfection by product as a result of chloramination of raw water in the presence of amine precursors.

Chlorine is typically added to the water in the form of either chlorine gas or sodium hypochlorite (NaOCl). NaOCl dissociates to sodium and hypochlorite ions. The hypochlorite ion then reacts with water to yield hypochlorous acid (HOCl) and hydroxide ion (OH^-) (Snoeyink and Jenkins, 1980):

$$NaOCl \rightarrow Na^+ + OCl^-$$

$$OCl^- + H_2O \leftrightarrow HOCl + OH^-$$

Alternatively, when chlorine gas is added to water, it undergoes oxidation and reduction in water to form hypochlorous (HOCL) acid, hydrogen ion, and chlorine ion in accordance with the following disproportionation reaction:

$$Cl_{2(aq)} + H_2O \leftrightarrow H^+ + Cl^- + HOCl$$

When ammonia (NH_3) is added to the chlorinated water, either inorganic monochloramine, dichloramine, or trichloramine will form depending on the pH of the water, chlorine to ammonia ratio, and contact time. The competing reactions are summarized by the follows equations (Lindeburg, 2006):

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

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

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

Chloramines can be preformed in stock chloramine feed tank where ammonia solution is mixed with hypochlorite solution at a target Cl_2/N molar ratio before being added to water stream. The solution has to be buffered to maintain a pH above 8.5 to prevent or minimize disproportionation of monochloramine to dichloramine. Because monochloramine solutions degrade with time and are difficult to preserve, the use of

preformed chloramines is not common (Padhye, 2010; Cerda, 2005). Alternatively, monochloramine can be formed continuously by reaction of hypochlorous acid with ammonia in the recirculation line in the disinfection process (Krauss et al., 2009). In addition, it has been shown that NDMA can still form when using chlorination instead of chloramination if the raw water contains amine species such as ammonia, and dimethylamine DMA (Mhlongo et al., 2009).

2.2.2 NDMA Organic Amine Precursors

Formation of NDMA involves reaction of organic amine precursors with chloramines. Dimethylamine (DMA) and tertiary amines with dimethylamine functional groups are believed to be the most significant organic nitrogen precursors for NDMA formation (Mitch et al., 2003). However, dimethylamine concentrations are generally less than 0.1 µg/L in natural waters unpolluted by wastewater discharge and waters not receiving agricultural runoff. In addition, it has been concluded that the yield of NDMA from chloramination of DMA is only 0.6% (Gerecke and Sedlak, 2003). These observations lead to the conclusion that dimethylamine (DMA) concentrations alone cannot account for NDMA formation during chloramination. Accordingly, other organic nitrogen precursors are probably important in explaining NDMA concentration in finished treated water (Mitch et al., 2003). Some researchers speculate that raw water obtained from reuse of municipal wastewater effluent may contain significant amounts of dimethylamine leading to NDMA formation upon chlorination (Mitch et al., 2003). In contrast, it was found that concentrations of dimethylamine in source water samples ranged between 0.0 µg/L and 3.9 µg/L, which indicates that surface water was polluted with wastewater effluent especially when taking into account that dimethylamine concentration in surface water in Germany was found to range from 0.0 to 0.55 µg/L. It was also shown that NDMA can be formed from chloramination of its dimethylamine

precursor (Wang et al., 2011). Presence of DMA in surface waters could be attributed to discharges from chemical and pharmaceutical industries (Wang et al., 2011).

2.2.3 Other Possible NDMA Precursors

Although the full range of NDMA nitrogenous and other compounds that can act as precursors has not been identified, several sources of possible precursors have been identified. It has been suggested that dissolved organic nitrogen (DON) in natural waters could lead to the formation of NDMA through conversion of organic compounds into nitroso compounds containing the R-NO functional group in a process known as nitrosation (Mhlongo et al., 2009). However, Gerecke and Sedlak reported that total DON in natural waters ranging from 1 to 100 μM can serve as precursors. DON in samples collected accounted for less than 0.005% of NDMA formed after chloramination (Gerecke and Sedlak, 2003).

Observation of higher concentration of DMA in finished water samples than source water samples suggested that carbon-nitrogen (C-N) bond-bearing compounds may be transformed to DMA during the treatment process (Wang et al., 2011). Dissolved organic carbon (DOC) in surface water could lead to NDMA formation upon chloramination in the treatment process (Mhlongo et al., 2009). The specific reactions are not fully understood. Coefficient of determination (r^2=0.41) between the NDMA precursors and the DOC content was calculated which suggest that DOC possibly plays a role in the formation of NDMA (Gerecke and Sedlak, 2003). Similarly, other research concluded that decreasing total organic carbon (TOC) concentration in raw water by filtration and activated carbon adsorption generally decreased NDMA concentration in finished water (Luo et al., 2012). In addition, NDMA concentrations were compared with high organic matter content (TOC=9-20 mg/L) and low organic matter content (TOC 2-5 mg/L), and it

was found that NDMA concentration was correlated to organic matter content (Jurado-Sanchez et al., 2012).

In the flocculation process in water treatment, high molecular weight cationic polymers containing the DMA moiety, like polyelectrolytes, can function as NDMA precursors (Gerecke and Sedlak, 2003). This can explain the increased NDMA concentration at the exit of the treatment process although NDMA and precursors' concentration were low in the source water. Charrois and Hrudey observed that NDMA concentrations varied partially in response to changes in organic polymer poly-diallyldimethylammonium chloride (poly-DADMAC) dosing in addition to source water quality conditions (Charrois and Hrudey, 2007).

In experiments to characterize the dissolved precursors, it has been noticed that precursors in lake water samples were retained in solid phase extraction resin, and it has been suggested that NDMA precursors were associated with humic substances and high molecular weight polymers (Gerecke and Sedlak, 2003).

In lakes, NDMA precursors observed in the epilmnion are possibly a result of photo-transformation of organic matter, sources originating in local streams discharging to the reservoirs, and atmospheric deposition of precursors. The correlation between algae bloom and NDMA precursor concentrations was quite weak (Gerecke and Sedlak, 2003).

Other probably important sources of organic nitrogen precursors are biofilms and microbes inside pipe deposits in distribution systems. Formation of NDMA and other nitrosamines can be biologically catalyzed by the presence of biofilm and microbes, which are rich in organic matter. (Valentine, 2000). Furthermore, biodegradation of proteins, amino acids, and other organic matter compounds can lead to DMA formation through biologically mediated pathways (Wang et al., 2011).

2.2.4 Formation Pathway

It was shown that the use of monochloramine increased NDMA formation which led to the belief that the NDMA formation pathway is through formation of unsymmetrical dimethylhydrazine (UDMH) intermediate that is formed from the reaction of monochloramine with DMA. UDMH is then instantaneously oxidized to form NDMA and other products (Mhlongo et al., 2009). This pathway is depicted in Figure 2.1.

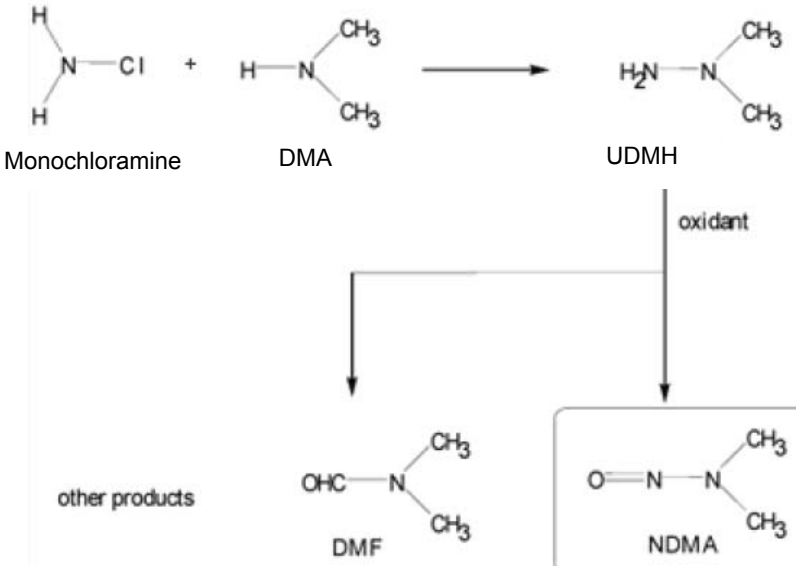

Figure 2.1: NDMA Formation Pathway from Reaction of DMA with Monochloramine, adopted from Mhlongo at al. (2009)

Although the rate of formation of dimethylhydrazine (UDMH) intermediate from monochloramine is slower than the rate of formation from dichloramine, it was believed that monochloramine contributed a significant amount because it is the predominant chloramine species under pH values typically present in treatment conditions (Vikesland et al., 2001). However, this formation pathway did not clearly explain how the NH_2 moiety in UDMH converts to the NO moiety in NDMA (Padhye, 2010). In addition, it was

observed that when 0.8 mequiv/L of hypochlorite, monochloramine and dichloramine were added separately to secondary municipal wastewater effluent samples containing 2.4 mM ammonia at pH 6.9, dichloramine formed two orders of magnitude more NDMA than monochloramine over a 3 hours period. This indicated that dichloramine is more important in explaining NDMA formation than monochloramine (Schreiber and Mitch, 2005).

Observation of the significant NDMA formation from dichloramine rather than from monochloramine led to an alternative NDMA formation pathway. It was suggested that NDMA is formed at circumneutral pH (6.5 - 7.5) when dichloramine reacts with dimethylamine (DMA) resulting in chlorinated unsymmetrical dimethylhydrazine (UDMH-Cl), which when oxidized by dissolved oxygen will form NDMA as shown in Figure 2.2 (Mitch et al., 2003).

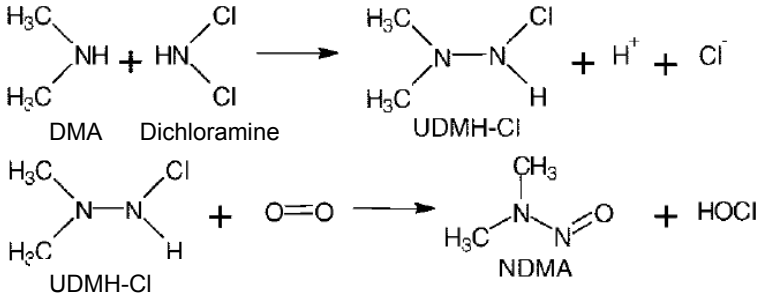

Figure 2.2: NDMA Formation Pathway from Reaction of DMA with Dichloramine, adopted from Mitch and Walse (2008)

NDMA was not observed when ammonia was chlorinated in the absence of amine or when hydrogen peroxide was added to a mixture of ammonia and dimethylamine. Therefore, chlorine, rather than a general oxidant, is necessary for NDMA formation. Chlorinated dimethylamine (CDMA) can react with ammonia to form UDMH, but at a slower rate (Mitch and Sedlak, 2002).

In addition, 0.19 mM preformed monochloramine and 0.19 mM dichloramine were added to separate samples containing 1.3 μM DMA and 1.3 μM Chlorinated DMA (CDMA) at pH 6.9. Dichloramine/ DMA combination resulted in an order of magnitude more NDMA than monochloramine/ DMA combination over 8 hours. In addition, DMA reactions with either monochloramine or dichloramine always resulted in higher NDMA concentrations than CDMA with monochloramine or dichloramine. The lowest NDMA formation was insignificant and resulted from reaction of monochloramine with CDMA (Schreiber and Mitch, 2005). This further demonstrates the importance of dichloramine in NDMA formation.

It was found that trichloramine is not essential for NDMA formation due to rapid formation of CDMA which inhibits NDMA formation (Schreiber and Mitch, 2005).

Choi and Valantine suggest an alternative NDMA formation pathway through hypochlorous acid (HOCl) catalyzed reaction between DMA and nitrite. The reaction between HOCl and nitrite results in dinitrogen tetroxide (N_2O_4) intermediate, which is the nitrosating agent. It was speculated that NDMA forms from the reaction of N_2O_4 with DMA. NDMA formation was enhanced by the addition of 0.1 mM hypochlorous acid to 0.1 mM DMA with increasing nitrite concentration (0.0 – 1.0 Mm) in the absence of ammonia as ammonia inhibits the reaction (Choi and Valentine, 2003). It was shown that this NDMA formation pathway through nirtosation contributes more to total NDMA formation than the pathway involving UDMH intermediate. Furthermore, it was shown that this mechanism formation is much faster resulting in NDMA formation within 1 hour in comparison to the slow chloramine induced NDMA formation in over 24 hours at pH 7 (Choi and Valentine, 2003). However, since reactions were conducted in conditions unlikely to be present at treatment plants, this formation pathway is not considered a major NDMA formation pathway in drinking water treatment.

2.3 Factors Affecting NDMA Formation

NDMA formation is a complicated process that is influenced by many variables, some of which are controllable in the treatment process. Formation depends on the pH, chlorine contact time, temperature, residence time in the distribution system, concentration of free chlorine, order of reagents addition, preformed chloramines, rapidity of mixing, and chlorine to ammonia ratio.

2.3.1 pH

pH of the water affects NDMA rate of formation with a maximum rate between pH 7 and 8. Some other studies showed that the maximum rate of formation occurs at pH between 5.5 and 7.4 (Mitch et al., 2003). In water treatment process, the water pH is typically between 6 and 9, which leads to maximum NDMA formation (Mitch and Sedlak, 2002). It was also shown that NDMA concentration varied with pH. At pH 8, the highest NDMA formation was observed (Kim and Clevenger, 2007).

0.8 mequiv/L of hypochlorite, monochloramine, and dichloramine were added to separate wastewater effluent samples at pH 5.5 and pH 6.9. All samples generated more NDMA at pH 6.9 than pH 5.5 in a 3 hours period. When the same reagents were added to different samples at pH 5.5 for 3 hours, the differences in NDMA formation were insignificant but were two orders of magnitude lower than NDMA formation at pH 6.9 over 3 hours. In addition, adding 0.29 mM OCl^- , 10μM DMA, and 0.34 mM NH_4Cl in deionized water in different orders at pH 5.1, 6.9, 8.8 showed that NDMA formation has increased with increasing pH (Schreiber and Mitch, 2005).

2.3.2 Chlorine Contact Time

Two hours of 2 mg/L free-chlorine contact time prior to ammonia application was partially attributed to 16.0±3.5 ng/L NDMA concentrations than no free-chlorine contact time that resulted in 51.0±8.3 ng/L NDMA concentration (Charrois and Hrudey, 2007).

Bench scale testing of 2 hour free-chlorine contact time before chloramination resulted in up to 93% reduction of NDMA in partially treated water before secondary disinfection (Charrois and Hrudey, 2007).

2.3.3 Chloramine Reaction Time

When 0.8 mequiv/L hypochlorite was added to a sample containing 2.4 mM ammonia from wastewater effluent, NDMA formation was two orders of magnitude after 3 hours than in 30 minutes at pH 6.9. Similarly, when 0.8 mequiv/L of monochloramine and dichloramine were added to separate samples of wastewater effluent containing 2.4 mM ammonia at pH 6.9, monochloramine generated one order of magnitude more NDMA in 3 hours than in 30 minutes while dichloramine formed two orders of magnitude more NDMA in 3 hours than 30 minutes (Schreiber and Mitch, 2005).

2.3.4 Temperature

The effect of water temperature was studied in three seasons (summer 28°±3°C, fall 17°±3°C, and winter 9°±3°C) on nitrosamines concentration. It was found that higher nitrosamines concentrations were partially associated with lower water temperatures. In addition, it was observed that the mean concentration of nitrosamines was approximately 3 times higher in winter and 2 times higher in fall than in summer. Apparently, the lower water temperature decreased the effectiveness of potassium permanganate (KMnO4), which was used in preoxidation step, to oxidize organic precursors. In addition, fall and winter months were associated with high rainfall leading to increased precursors concentration in influent raw water (Jurado-Sanchez et al., 2012).

2.3.5 Residence Time in Distribution System

It was observed that as the distance from the treatment plant increased in the distribution system, the concentration of NDMA also increased due to increased residence time and presence of free chlorine residual and organic nitrogen containing

compounds (Mhlongo et al., 2009; Charrois and Hrudey, 2007; Luo et al., 2012). The overall rate of NDMA formation is extremely slow which indicates that NDMA will continue to form over a period of days, and concentration of NDMA in the distribution system will continue to increase (Mitch et al., 2003). Even when using monochloramine, 12 µg/L of NDMA was formed after 24 hours from the reaction of 0.1mM DMA and 0.1mM preformed monochloramine. NDMA formation continued beyond 40 hours reaching 18 µg/L (Choi and Valentine, 2002).

2.3.6 Concentration of Free Chlorine

Speciation of chloramines changes with the concentration of hypochlorite stock solution used. Dichloramine formation has increased by 50% when using higher concentration of hypochlorite stock solutions from 14.4 mM to 144.0 mM) at pH 6.9 (Schreiber and Mitch, 2005). Increased dichloramine concentration leads to increased NDMA formation.

2.3.7 Order of Reagents Addition

Experiments in deionized water investigating the effect of order of reagents addition showed that adding 0.29 mM OCl^- to samples containing 10µM DMA before adding 0.34 mM NH_4Cl resulted in one order of magnitude less NDMA than when 0.34 mM NH_4Cl was added to samples containing 10µM DMA before adding 0.29 mM OCl^-. NDMA formation was less because the reaction resulted in completely chlorinated DMA and monochloramine formation, which don't react with each other due to their electrophilicity (Schreiber and Mitch, 2005).

2.3.8 Preformed Chloramines

Adding 0.29 mM OCl^- to a well-mixed solution of 0.34 mM NH_4Cl then adding the mixture to samples containing 10µM DMA resulted in approximately the same NDMA formation as when 0.34 mM NH_4Cl was added to a well-mixed solution of 0.29 mM OCl^-

then adding the mixture to samples containing 10μM DMA. Both reactions resulted in higher NDMA formation than reactions involving direction addition of ammonium chloride and hypochlorite to DMA samples due to the reaction between inorganic chloramines and unchlorinated DMA. Reactions involving adding ammonium chloride and hypochlorite to DMA samples resulted in lower NDMA formation due to formation of chlorinated DMA that limited concentration of dichloramine that can form. All experiments were conducted with 0.85 Cl_2/N molar ratio (Schreiber and Mitch, 2005). It was observed that increasing pre-formed monochloramine concentration also increased NDMA formation (Choi and Valentine, 2002).

2.3.9 Rapidity of Mixing

Rapidity of Mixing influences chloramine speciation because it results in different Cl_2/N molar ratio at the point of reagent addition prior to mixing from that after mixing. Adding NH_4Cl to a well-mixed solution of OCl^- results in Cl_2/N molar ratio<1.0 at the point of reagent addition before complete mixing, which favors NH_2Cl formation that hinders NDMA formation. In comparison, Adding OCl^- to a well-mixed solution of NH_4Cl results in Cl_2/N molar ratio>1.0 at the point of reagent addition before complete mixing, which favors $NHCl_2$ formation that enhances NDMA formation (Schreiber and Mitch, 2005). These experiments imply that the mixing in reaction tanks has to be instantaneous to guarantee the desired Cl_2/N ratio.

2.4 Chlorine to Ammonia Mass Ratio Effect on NDMA Formation

In water treatment, Cl_2/N molar ratio <1 is typically used to provide excess ammonia to prevent breakpoint chlorination in poor mixing conditions and to maximize generation of monochloramine for prolonged disinfection duration (Schreiber and Mitch, 2005). However, presence of free ammonia is problematic since it can lead to biological

nitrification in the distribution system. To limit ammonia, relatively high Cl_2/N ratios are used, but this practice will decrease stability of monochloramine. While lower Cl_2/N ratios lead to a more stable monochloramine, they also provide conditions for nitrification. Accordingly, the effect of Cl_2/N is not clear (Vikesland et al., 2001). Adding to the complexity, Cl_2/N ratio seems to affect speciation of chloramines which has an effect on NDMA formation.

At Cl_2/N molar ratios <1.0, NH_2Cl is the predominant species with some $NHCl_2$ in the absence of free chlorine. At Cl_2/N molar ratios between 1.0 and 1.5, $NHCl_2$ is the predominant species with some NH_2Cl in the absence of free chlorine. At Cl_2/N molar ratios > 1.5, NCl_3 predominates with free chlorine (Schreiber and Mitch, 2005). At Cl_2/N molar ratios>2.0, NDMA formation was insignificant due to destruction of chloramines leaving only free chlorine (Schreiber and Mitch, 2005).

The maximum NDMA concentration was observed to occur just below the theoretical 1:1 (Cl_2/N molar ratio), which is the molar ratio that results in maximum monochloramine formation (Charrois and Hrudey, 2007).

When increasing Cl_2/N molar ratio from 0.1–0.7 at a fixed monochloramine and DMA concentrations at 0.1mM over 24 hour reaction period, NDMA concentration slightly increased. It should be noted that decomposition of monochloramine occurred over this time period (less than 30%) at pH 7. The rate of decomposition of monochloramine tends to increase with increasing Cl_2/N ratio (Choi and Valentine, 2002). This probably leads to higher NDMA formation due to the formation of dichloramine through monochloramine disproportionation reaction.

Kim and Clevenger studied the relationship between NDMA formation and monochloramine concentration by varying monochloramine concentration from 0.001 to 5mM to obtain the NDMA yields at different molar ratios of (monochloramine/ DMA) at pH

8. They found that as the monochloramine concentration increased, NDMA formation also increased (Kim and Clevenger, 2007).

Breakpoint chlorination experiments showed that when 8.0 mequiv/L OCl^-, NH_2Cl, $NHCl_2$ were added to separate wastewater effluent samples containing 2.4 mM ammonia at pH 6.9, $NHCl_2$ formed the most NDMA followed by NH_2Cl, which in turn formed more than an order of magnitude NDMA than OCl^- (Schreiber and Mitch, 2005).

If ammonia is present in the surface water from agricultural runoff, NDMA will form even when chlorination is used for disinfection. In addition, if ammonia is present, lower Cl_2/N will be the result if chloramine is generated at the target Cl_2/N. Accordingly, testing the raw water for presence of ammonia before recommending Cl_2/N ratio and before deciding between chlorination or chloramination is recommended.

Since temperature and organic contents in raw water distribution systems are not easily controlled, it is concluded that preformed chloramines and Cl_2/N ratio are probably important in influencing NDMA formation. These factors are easily controlled in the treatment process. It is hypothesized that by maximizing the monochloramine formation and minimizing dichloramine formation by controlling conditions, formation of NDMA can be minimized. In addition, effect of utilizing preformed chloramines versus direct addition of hypochlorous acid and ammonium chloride on NDMA formation will be investigated.

Chapter 3

Research

3.1 Experimental Procedure

Samples were collected from Lake Palestine, Richland Chambers Lake, and Cedar Creek Lake. Upon collection, samples were dechlorinated with sodium thiosulfate ($Na_2S_2O_3$) to prevent in situ NDMA formation. Samples were preserved in the refrigerator until sample preparation and analysis. Samples from each lake were divided into two groups to test for effect of preformed chloramine versus direction addition of ammonia and chlorine on NDMA formation. Furthermore, the preformation and direct addition sets were further divided into two subgroups, one with 4:1 Cl_2/N mass ratio and the other with 5:1 Cl_2/N mass ratio, to test for the effect of varying Cl_2/N mass ratio on NDMA formation.

For all test conditions, 5% sodium hypochlorite (NaOCl) and 10% ammonium chloride (NH_4Cl) by mass were used. The target chloramine concentration was 4 mg/L in 2.65 L sample jar. The sample jars were placed on automatic shakers for either 30 minutes or 48 hours before being quenched with sodium thiosulfate. Samples were analyzed for NDMA concentration afterwards.

Preformed chloramines were prepared at 2mM because at higher concentrations monochloramine decay accelerates. Due to high hypochlorite concentration, which accelerates monochloramine decay, pH of water samples was adjusted to 8.3 to ensure that monochloramine decay is minimized. In addition, chloramine formation time effect on NDMA formation was tested at 2 minutes and 35 seconds formation times. These formation times were chosen to simulate actual formation time in the pipeline from the point of formation to point of reagents addition in the pipeline. 35 seconds formation time was the shortest time achievable due to time limitation to obtain a sample and analyze for residual chloramine reading.

3.1.1 Lake Palestine Water Samples

Lake Palestine water samples were collected directly from the lake in November 2014. To examine the effect of preformed chloramines with varying Cl_2/N mass ratio on NDMA concentration, preformed chloramines were prepared at 2 mM with either 5:1 or 4:1 Cl_2/N mass ratio at pH 8.3 in lake water samples. Ammonia NH_3-N, in the form of ammonium chloride NH_4Cl, was added first to 253 mL pH adjusted lake water and mixed for 5-10 seconds. Chlorine, in the form of sodium hypochlorite NaOCl, was added second and mixed for 5-10 seconds. The solution was allowed to react for 2 minutes before being added to 2.65L lake water sample jars.

To examine the effect of direct addition of ammonia and chlorine with either 5:1 or 4:1 Cl_2/N mass ratio on NDMA formation at pH 8.3, ammonia NH_3-N, in the form of ammonium chloride NH_4Cl, was added first to lake samples and mixed for 5-10 seconds. Then, chlorine, in the form of sodium hypochlorite NaOCl, was added second and mixed for 5-10 seconds.

A third experiment was conducted to examine the effect of longer chlorine reaction time before ammonia addition on NDMA concentration with direct addition at 5:1 Cl_2/N mass ratio at pH 8.3. For the first set, ammonia NH_3-N, in the form of ammonium chloride NH_4Cl, was added first to lake samples and mixed for 5-10 seconds. Then, chlorine, in the form of sodium hypochlorite NaOCl, was added second and mixed for 5-10 seconds. This set is identified by the scheme: (NH_3+Cl_2). For the second set, chlorine, in the form of sodium hypochlorite NaOCl, was added first and mixed for 5-10 seconds then allowed to react for 2 minutes. Ammonia NH_3-N, in the form of ammonium chloride NH_4Cl, was added second to lake samples and mixed for 5-10 seconds. This set is identified by the scheme: (Cl_2+NH_3).

3.1.2 Richland Chambers Lake Water Samples

Richland Chambers Lake water samples were collected from a tap on the recirculation line that feeds chemicals to the pipeline. The line was flushed for extended time before collecting the samples in order to obtain a representative lake water samples. The samples were collected in January 2015. To examine the effect of preformed chloramine solution with varying Cl_2/N mass ratio on NDMA concentration, preformed chloramines were prepared at 2 mM with either 5:1 or 4:1 Cl_2/N mass ratio at pH 8.3 before being added to lake water samples. Ammonia NH_3-N, in the form of ammonium chloride NH_4Cl, was added first to 253 mL pH adjusted lake water and mixed for 5-10 seconds. Chlorine, in the form of sodium hypochlorite NaOCl, was added second and mixed for 5-10 seconds. The solution was allowed to react for 2 minutes before being added to 2.65L lake water sample jars.

To examine the effect of direct addition of ammonia and chlorine with either 5:1 or 4:1 Cl_2/N mass ratio on NDMA formation at pH 8.3, ammonia NH_3-N, in the form of ammonium chloride NH_4Cl, was added first to lake samples and mixed for 5-10 seconds. Then, chlorine, in the form of sodium hypochlorite NaOCl, was added second and mixed for 5-10 seconds.

A third experiment was conducted to examine the effect of chloramine formation time at 4:1 Cl_2/N mass ratio on NDMA concentration with preformed chloramine at pH 8.3. For both sets, ammonia NH_3-N, in the form of ammonium chloride NH_4Cl, was added first to lake samples and mixed for 5-10 seconds. Then, chlorine, in the form of sodium hypochlorite NaOCl, was added second and mixed for 5-10 seconds. Then, one set was allowed to react for 2 minutes while the second set was allowed to react for only 35 seconds before being added to different lake water samples.

3.1.3 Cedar Creek Lake Water Samples

Cedar Creek Lake water samples were collected directly from the lake in March 2015. To examine the effect of preformed chloramines with varying Cl_2/N mass ratio on NDMA concentration, preformed chloramines were prepared at 2 mM with either 5:1 or 4:1 Cl_2/N mass ratio at pH 8.3 before being added to lake water samples. Ammonia NH_3-N, in the form of ammonium chloride NH_4Cl, was added first to 253 mL pH adjusted lake water and mixed for 5-10 seconds. Chlorine, in the form of sodium hypochlorite NaOCl, was added second and mixed for 5-10 seconds. The solution was allowed to react for 2 minutes before being added to 2.65L lake water sample jars.

To examine the effect of direct addition of ammonia and chlorine with either 5:1 or 4:1 Cl_2/N mass ratio on NDMA formation at pH 8.3, ammonia NH_3-N, in the form of ammonium chloride NH_4Cl, was added first to lake samples and mixed for 5-10 seconds. Then, chlorine, in the form of sodium hypochlorite NaOCl, was added second and mixed for 5-10 seconds.

A third experiment was conducted to examine the effect of chloramine formation time at 5:1 and 4:1Cl_2/N mass ratios on NDMA concentration with preformed chloramines at pH 8.3. Two sets were prepared. One set was with 5:1Cl_2/N mass ratio while the other was with 4:1 Cl_2/N mass ratio. For both sets, preformed chloramine was prepared by adding ammonia NH_3-N, in the form of ammonium chloride NH_4Cl, to 253 mL pH adjusted lake water and mixed for 5-10 seconds. Then, chlorine, in the form of sodium hypochlorite NaOCl, was added and mixed for 5-10 seconds. Then, one set was allowed to react for 2 minutes while the second set was allowed to react for only 35 seconds before being added to different lake water samples.

The experimental tables showing experiments details for each lake sample are shown in Appendix A – Laboratory Experiments Data Sheets.

3.2 Samples Extraction and Analysis Procedure

The standard procedure used for NDMA extraction, as well as for other nitrosamines, is EPA Method 521 - Determination of Nitrosamines in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (MS/MS) (Munch and Bassett, 2004). The Lowest Concentration Minimum Reporting Level (LCMRL) for NDMA is 1.6 ng/L. The procedure involves extracting 500 ml samples through solid phase extraction cartridge using vacuum, samples elution with methylene chloride, drying the samples by passing through drying columns, concentrating the samples under a gentle stream of nitrogen, and analysis of samples by gas chromatography with tandem mass spectrometry system (GC/MS/MS) operated in the chemical ionization mode.

3.2.1 Required Material and Appurtenances

Table 3.1 summarizes the materials and appurtenances used for NDMA extraction and analysis.

Table 3.1: Material and Appurtenances used for NDMA Extraction and Analysis

1. 0.5-L Sample containers - Wheaton glass bottles fitted with PTFE lined polypropylene screw caps	

Table 3.1—*Continued*

2. Autosampler vials with PTFE faced septa	
3. Syringes - 50 µL, 1.0 mL	
4. Analytical balance - 0.0001 accuracy	
5. Extraction cartridges - 6-mL polypropylene tubes	
6. Drying columns – Pre-packed with 5 to 7 grams of anhydrous sodium sulfate	

Table 3.1—*Continued*

7. 15 mL Conical centrifuge tubes	
8. 1 mL Volumetric flasks	
9. Solid Phase Extraction (SPE) Apparatus: a. Vacuum extract manifold b. Sample delivery tubes c. Vacuum system	

Table 3.1—*Continued*

10. Gas Chromatograph/ Mass Spectrometer/ Data System (GC/MS/MS/DS) - Shimadzu GCMS-TQ8030 with Capillary Gas Chromatography Column 
11. Reagents and solvents: a. Methanol (CH_3OH, CAS# 67-56-1) b. Methylene chloride (CH_2Cl_2, CAS# 75-09-2) c. Ultrapure reagent water d. Anhydrous sodium sulfate (Na_2SO_4, CAS# 7757-82-6) e. Sodium thiosulfate ($Na_2S_2O_3$, CAS# 7772-98-7)

3.2.2 Sample Collection, Preservation, and Storage

1. For dechlorination and to minimize in situ NDMA formation at the time of collection, 45 mg sodium thiosulfate was added for 500-mL sample. Sample bottles were swirled until all sodium thiosulfate was dissolved.
2. All samples were iced during transport to not exceed 10°C. Samples stored in the lab were held at or below 6°C until extraction.
3. Samples were extracted within 14 days of collection.
4. The standard EPA 521 procedure states that sample extracts may be stored for up to 28 days after sample extraction, when stored in amber vials at -15 °C or less, and protected from light.

3.2.3 Sample Preparation

1. An aliquot of the water surrogate analyte, prepared from primary dilution standard solution, was added to all samples and mixed by swirling the samples. In this experiment, 50.0 µL of a 2.0 µg/mL water (NDMA-d6) surrogate analyte was added to a 500-mL sample resulting in a concentration of 200 ng/L.

3.2.4 Cartridge Conditioning

1. The SPE cartridge was filled with approximately 3 mL methylene chloride. The vacuum was turned on, and the solvent was pulled through aspirating completely.
2. Step 1 was repeated once.
3. The SPE cartridge was filled with approximately 3 mL methanol. The vacuum was turned on, and the solvent was pulled through aspirating completely.
4. Step 3 was repeated once.
5. The SPE cartridge was filled with approximately 3 mL methanol and eluted with vacuum to just above the top frit. The cartridge was not allowed to go dry at the end.
6. From this point forward, the cartridge was not allowed to go dry to the end of the conditioning step.
7. Step 5 was repeated once.
8. The cartridge was filled with approximately 3 mL ultrapure water. The vacuum was turned on, and the water was pulled through to just above the top frit.
9. Step 7 was repeated five times without allowing the cartridge to go dry in between washes or at the end.

3.2.5 Sample Extraction

1. A transfer tube was attached from each sample bottle to each cartridge, and the vacuum was turned on to about 10psi. The individual valves on the extraction manifold were adjusted so that the approximate flow rate was 5-6 mL/min.
2. After all of the sample has passed through each SPE cartridge, all valves on the manifold were fully opened, and air was drawn through the cartridges for 10 minutes at full vacuum. The vacuum was then turned off and released.

3.2.6 Cartridge Elution

1. The extraction manifold top was lifted.
2. A rack with collection tubes was inserted into the extraction tank to collect the extracts as they are eluted from the cartridges.
3. Each cartridge was filled with methylene chloride. Enough of the solvent was pulled into the cartridge at low vacuum to soak the sorbent.
4. The vacuum was turned off, and the system was vented.
5. The sorbent was allowed to soak in methylene chloride for approximately 1 minute. Low vacuum was then applied, and the methylene chloride was pulled through the cartridge in a drop wise fashion into the collection tube.
6. Methylene chloride was continued to be added to the cartridge as it was being drawn through until the volume of extract was about 12 or 13 mL as determined by the markings on the side of the centrifuge collection tube.
7. It was ensured that all samples had the same volume approximately.

3.2.7 Drying Column

1. Small amounts of residual water from the sample container and the SPE cartridge often formed an immiscible layer with the extract.

2. 7 grams of anhydrous sodium sulfate were added to each drying column. Compacting the sodium sulfate in the tube was avoided to allow the extract to pass freely and to avoid clogging the drying column.
3. To eliminate residual water, the extract was passed through the drying column. The drying column was initially packed with approximately 5 to 7 grams of anhydrous sodium sulfate, and is pre-wetted with a small volume of methylene chloride prior to passing the extract through it.
4. The dried extract was collected in a clean centrifuge tube. After passing the extract through the drying tube, the sodium sulfate was washed with at least 3 mL methylene chloride, and the solvent wash was collected in the same collection tube.
5. It was ensured that all samples had the same volume approximately.

3.2.8 Sample Concentration

1. Ultrapure water was added to the manifold tank to keep samples at room temperature and to prevent freezing while passing nitrogen. The extract was concentrated in a water bath near room temperature (20 to 25 °C) under a gentle stream of nitrogen.
2. All the valves in the delivery system were opened. The main nitrogen discharge valve on the nitrogen cylinder was opened very slowly to avoid sudden blows of the nitrogen and instantaneous volatilization of the aliquots resulting in loss of analyte.
3. Concentration with nitrogen was continued until the sample volume was 6 mL.
4. Pressure from nitrogen cylinder was increased a little to concentrate the extract from 6 ml to approximately 0.7-0.8 mL.

5. It was recommended that the extract not be concentrated to less than 0.6 mL as this may result in loss of analytes.
6. As each sample reached 0.7-0.8 mL, the nitrogen line was removed and the main cylinder valves slightly dialed down to avoid increasing the pressure at other samples.
7. After all samples reached 0.7-0.8 mL, 1 ml of methylene chloride was added with syringe to each conical centrifuge.
8. Conical Centrifuges were capped with their individual caps.
9. The centrifuges were rinsed slowly by rotating horizontally to cover inner surface of the centrifuge. It was ensured that methylene chloride was not touching the cap to avoid sample loss due to adhesion.
10. The extract was carefully transferred to 1 ml volumetric flask. The flask was capped. This step was finished for all samples.
11. Water was removed from the tank by opening vacuum valve.
12. The volumetric flasks were placed in the rack and inserted in extraction tank. The extract was concentrated in the 1 ml volumetric flask with nitrogen till it is approximately 0.9 mL.
13. 50 µL of 2 µg/mL N-nitroso-di-n-propylamine-d14 (NDPA- d14) internal standard was injected to each extract.
14. The final volume was adjusted to 1.0 mL with methylene chloride.

3.2.9 Analysis with GC/MS/MS

1. Shimadzu's GCMS-TQ8030 was used with chemical ionization (CI) and AOC-5000 Plus auto-sampler. The capillary column was Rxi – 5Sil MS (30m x 0.25mm inner diameter x 0.5µ film thickness) with 5m guard column. The injector temperature was maintained at 200 °C. The mode of operation was splitless (0.7

min, 50:1 split). The flow velocity was maintained at 50 cm/s. The oven temperature was programmed with initial temperature of 35°C for 2 min, and increased to 170 °C at 15 °C/min and held for 2 min. Electron energy was 16eV for softer ionization to increase precursor response. NDMA retention time was at 4.62 min.

2. The instrument was operated in chemical ionization (CI) and MS/MS mode.
3. The manifold temperature and trap temperatures were raised according to the manufacturer's recommendations.
4. An aliquote of the sample extract was analyzed with the GC/MS/MS system.
5. The software accompanying the instrument was used to identify peaks in predetermined retention time window for NDMA.
6. The ion abundance of NDMA was examined by examining the chromatograph.
7. The NDMA product ion spectrum was compared to the reference spectrum in the previously created data base from the calibration step.
8. Concentrations were calculated by measuring the product ion or mass-to-charge ratios (m/z) of NDMA and the isotopic surrogate NDMA-d6. For NDMA, m/z=74:048 and for NDMA- d6 (m/z=80:086).
9. The analyte and surrogate concentrations were calculated, and the final analyte concentrations were adjusted to reflect the actual sample volume determined. This use of surrogate to calculate final concentrations accounts for the uncertainty in extraction efficiency between samples.

   Part of a chromatograph illustrating the peaks for NDMA and other couple nitrosamines is shown in Figure 3.1.

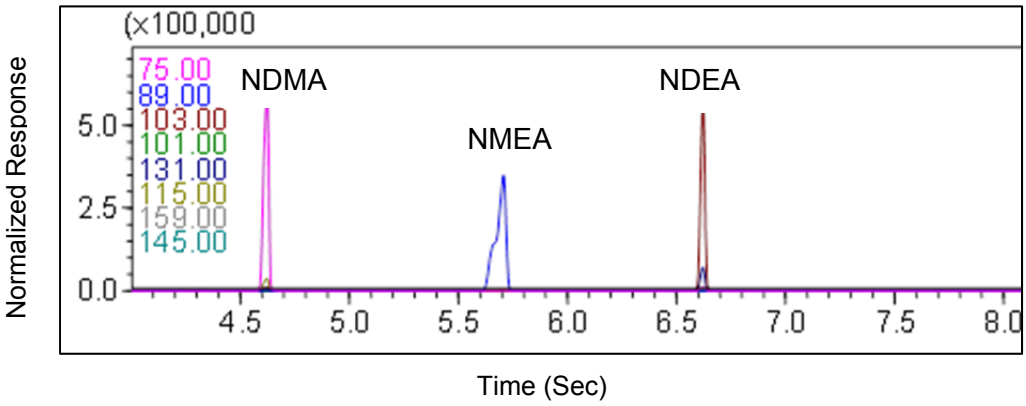

Figure 3.1: Chromatograph for Standard Solution

3.3 Quality Control

For quality control (QC), each extraction batch included laboratory reagent blank, Laboratory fortified blank, laboratory fortified sample matrix, and laboratory fortified sample matrix duplicate (Munch and Bassett, 2004).

Laboratory reagent blank (LRB) is prepared by adding dechlorination agent, surrogate, and internal standard solutions to Milli-Q water. LRB is used to check for background system contamination. It assesses whether interferences from SPE extraction media or reagents prevent identification and quantification of the analytes by producing peaks.

Laboratory fortified blank (LFB) is prepared by adding dechlorination agent, surrogate, internal standard, and known concentration of NDMA analyte to Milli-Q water and is analyzes exactly like a sample. LFB is used to assess whether the procedure is in control and whether measurements are accurate and precise.

Laboratory fortified sample matrix (LFSM) is prepared by adding dechlorination agent, surrogate, internal standard, and known concentration of NDMA analyte to field

sample and is analyzes exactly like a sample. LFSM is used to assess whether the sample matrix contributes bias to the analytical results.

Laboratory fortified sample matrix duplicate (LFSMD) is prepared and analyzed exactly as LFSM. LFSMD is used to assess method precision when the target analyte concentration is low.

3.4 Deviations and Modification to Standard Procedure

A few modifications to the standard EPA Method 521 procedure for Nitrosamines extraction were made throughout the course of this research to improve the recovery of the analyte and to improve the quality of samples before analysis. These modifications included:

1. The standard procedure recommends adjusting the vacuum, so that the approximate flow rate is 10 mL/min. It was found that adjusting the vacuum for uniform flow rate across all cartridges was difficult because the packing of individual cartridges was not uniform. Accordingly, the pressure drop across individual cartridges varied, which resulted in varying extraction times. Alternatively, it was found that adjusting the individual valves on the extraction manifold was more practical to achieve the desired approximate flow rate for each sample.
2. The standard procedure recommends that the flow rate should be approximately 10 mL/min. However, Cheng et al. examined the effect of flow rate on NDMA recovery. It was found that the recovery of NDMA (76.4 ± 5%) was significantly higher at the lowest tested flow rate of 5 mL/min (Cheng et al., 2006). For this research, similar results were observed. The flow rate was varied from 50 minutes (10 mL/ min) to 3 hours (2.7 mL/min). Extraction times longer

than 1.5 hours (5-6 mL/min) did not yield better recoveries. It was decided that the best flow rate to adopt was 5-6 mL/ min.

3. It was noted that small amounts of water often accumulated in the conical centrifuges after the elution procedure regardless of the amount of vacuum applied and length of drying time at the end of the extraction step. By experiment, it was found that adding approximately 7 grams of anhydrous sodium sulfate to each drying column, in addition to the amount of anhydrous sodium sulfate already present in the column, eliminated water from all samples. Accordingly, this step was incorporated into the standard procedure.

3.5 Calibration Curves

Initial calibration is necessary before analyzing any samples. Calibration standard solutions are used to calibrate the instrument response with respect to analyte concentration and to establish the Minimum Reporting Level (MRL) for the procedure. The standard solutions were prepared from stock standard solutions. NDMA standard solutions were prepared in two concentration groups; lower concentration group and higher concentration group. The lower concentration group included NDMA standard solutions at 0.5, 1.0, 5.0, 20.0, and 50.0 ng/L concentrations in ultrapure water produced from Milli-Q system. The higher concentration group included NDMA standard solutions at 50.0, 100.0, 250.0, 500.0, 750.0, and 1000.0 ng/L concentrations in ultrapure water produced from Milli-Q system. Laboratory Fortified Blanks (LFB) with different standard solutions were prepared and extracted in accordance with the steps outlined in section 3.2 Samples Extraction and Analysis Procedure including injection of 50.0 µL of a 2.0 µg/mL water (NDMA-d6) surrogate analyte and 50 µL of 2 µg/mL (NDPA- d14) internal standard.

To test linearity of the calibration curve for lower standard concentrations, concentrations of NDMA ranging from 0.5 to 50.0 ng/L were analyzed. Similarly, concentrations from 50.0 to1000.0 ng/L were analyzed to establish calibration curve for higher standard concentration. Calibration curves were constructed by calculating the ratio of peak area of the quantitation ion for the reference standard to that of the internal standard (NDPA-d14).

In Figure 3.2, the calibration curve for NDMA with low standard concentrations over the range 0.5 to 50.0 ng/L is shown. A very good linearity is obtained with an R^2= 0.989. The calibration curve for NDMA with high standard concentrations over the range 50.0 to 1000.0 ng/L is shown in Figure 3.3. A very good linearity is obtained with an R^2= 0.981. The calibration curves were used to calculate NDMA concentration in lake water samples.

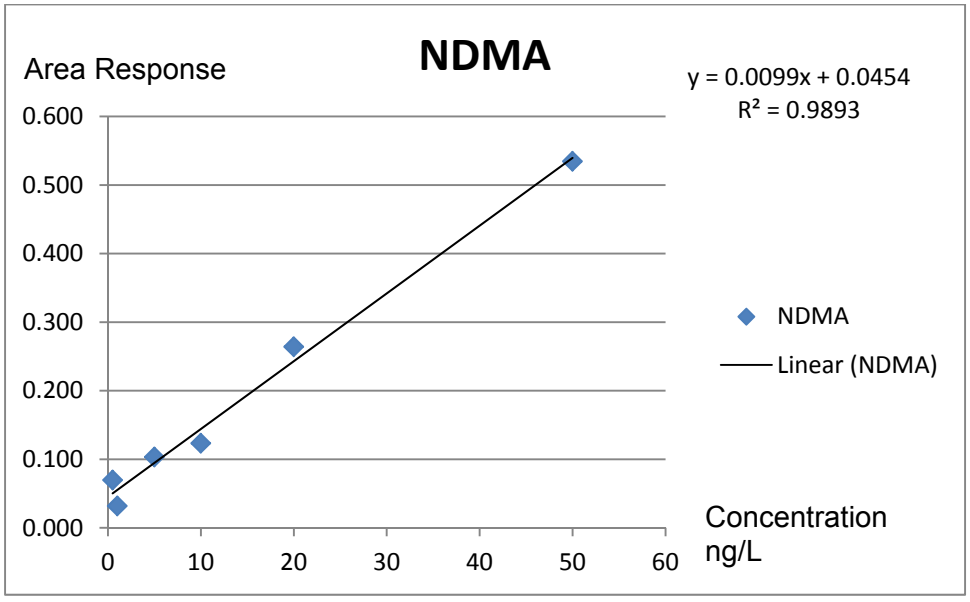

Figure 3.2: NDMA Calibration Curve, Low Standard Concentrations (0.5-50.0 ng/L)

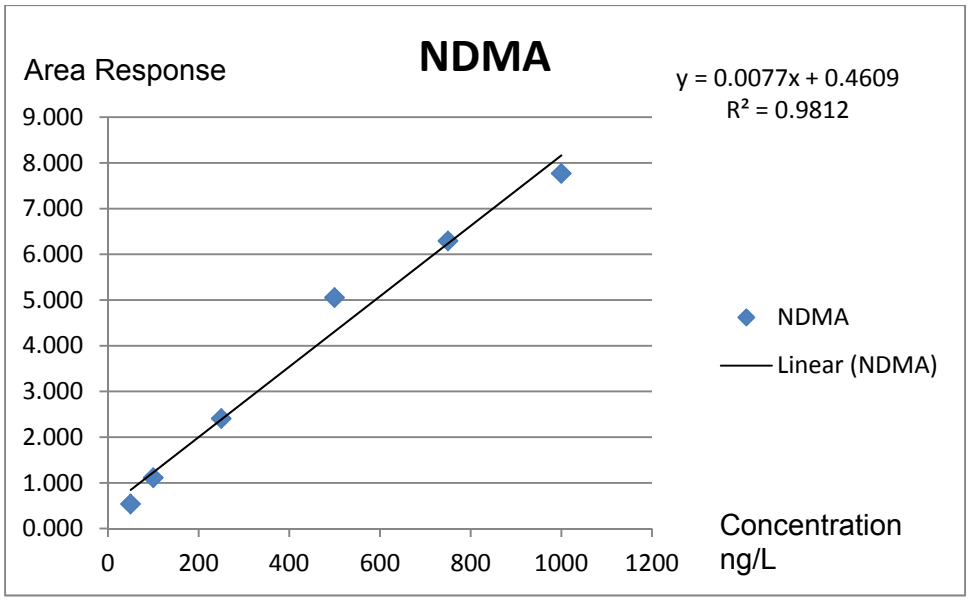

Figure 3.3: NDMA Calibration Curve, High Standard Concentrations (50.0-1000.0 ng/L)

Chapter 4

Results and Discussion

For all test conditions, the target chloramine concentration was 4 mg/L in 2.65 L sample jar. Preformed chloramines were prepared at 2mM. The sample jars were placed on automatic shakers for either 30 minutes or 48 hours before being quenched with sodium thiosulfate. Samples were analyzed for NDMA concentration afterwards.

4.1 Lake Palestine Results

Experiments were conducted on Lake Palestine water samples to examine the effect of preformed chloramines with either 5:1 or 4:1 Cl_2/N mass ratio on NDMA concentration. Preformed chloramines were prepared at 2 mM with either 5:1 or 4:1 Cl_2/N mass ratio at pH 8.3 before being added to lake water samples.

In addition, to examine the effect of direct addition of ammonia and chlorine with either 5:1 or 4:1 Cl_2/N mass ratio on NDMA formation at pH 8.3, ammonium chloride NH_4Cl was added first to lake samples. Then, sodium hypochlorite NaOCl was added second.

The average recovery of internal standard surrogate for all samples was 87% with a range between 69% and 137%. These values are a slight deviation from the acceptable recovery values set by EPA Method 521 of 70-130% of the true value.

Measured NDMA concentrations for each test condition described above for Lake Palestine water samples are shown on Figure 4.1. Each test was a unique set of conditions to obtain initial results.

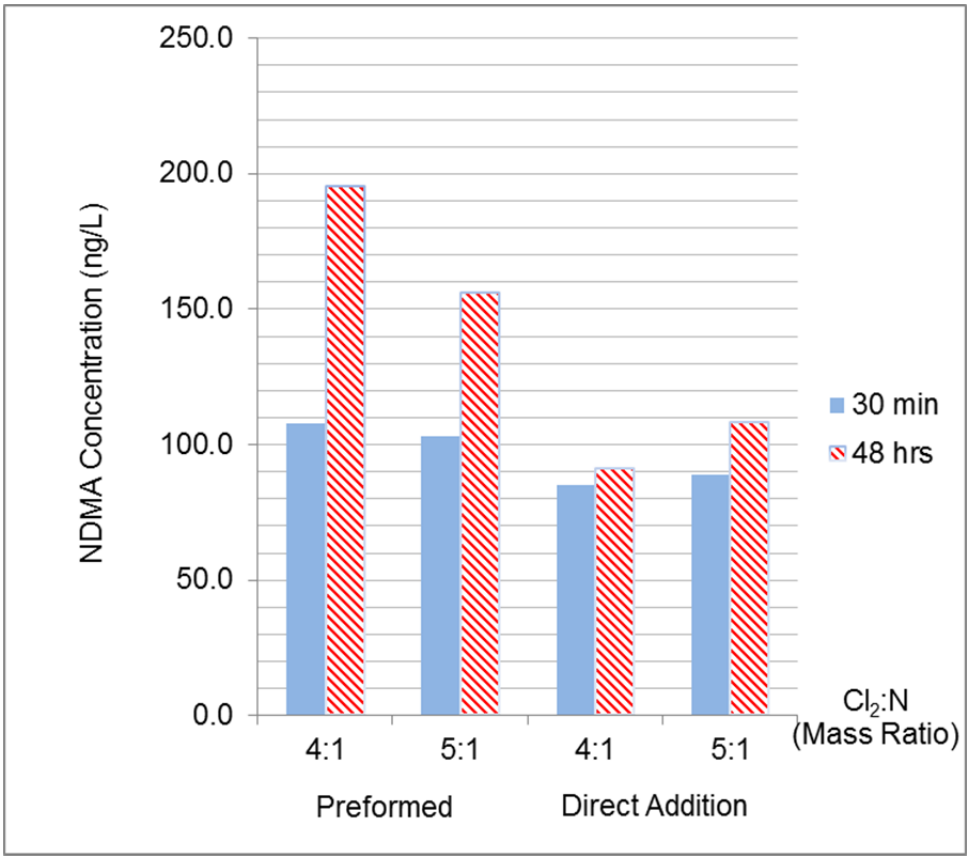

Figure 4.1: Effect of Preformed Chloramine, Direction Addition, and Cl_2/N Mass Ratio on NDMA Concentration, Lake Palestine

NDMA formation at 48 hours was between 7% and 81% more than NDMA formation at 30 minutes for all samples due to longer reaction time, which was expected based on the literature.

Preformed chloramines generated 21% and 53% more NDMA at 30 minutes and 48 hours respectively than direct addition at 4:1 Cl_2/N mass ratio. Similarly, preformed chloramines generated 14% and 31% more NDMA at 30 minutes and 48 hours respectively than direct addition at 5:1 Cl_2/N mass ratio.

In examining the results of Cl_2/N mass ratio on NDMA formation for preformed chloramines case, it was noted that at 30 minutes NDMA formation was slightly higher

(5%) at 4:1 Cl_2/N mass ratio than NDMA formation at 5:1mass ratio. Also, at 48 hours, NDMA formation was 20% higher at 4:1 Cl_2/N mass ratio than NDMA formation at 5:1 mass ratio. These results are contrary to what is expected, i.e., that lower Cl_2/N mass ratios would generate lower NDMA due to favored monochloramine formation. In contrast, for the direct addition case, at 30 minutes and 48 hours NDMA formation was 5% and 19% respectively less at 4:1 Cl_2/N mass ratio than at 5:1 mass ratio due to favored monochloramine formation at lower mass ratios. This result was expected based on literature. The results of the effect of Cl_2/N mass ratio on NDMA formation were inconclusive since 4:1 Cl_2/N mass ratio generated higher NDMA concentration in only 50% of Lake Palestine samples than 5:1 Cl_2/N mass ratio. 4:1 Cl_2/N mass ratio did not do better than 5:1 Cl_2/N mass ratio.

A third experiment was conducted to examine the effect of free chlorine reaction time of two minutes on NDMA concentration for the direct addition case at 5:1 Cl_2/N mass ratio at pH 8.3. Two sets were prepared. For the first set, ammonium chloride NH_4Cl was added first to lake samples. Then, sodium hypochlorite NaOCl, was added. This set was identified by the scheme: (NH_3+Cl_2). For the second set, sodium hypochlorite NaOCl was added first and was allowed to react for 2 minutes. Ammonium chloride NH_4Cl was added second to lake samples. This set was identified by the scheme: (Cl_2+NH_3).

The results of experiment to test the effect of two minutes free chlorine reaction time on NDMA concentration versus normal chloramination is shown on Figure 4.2.

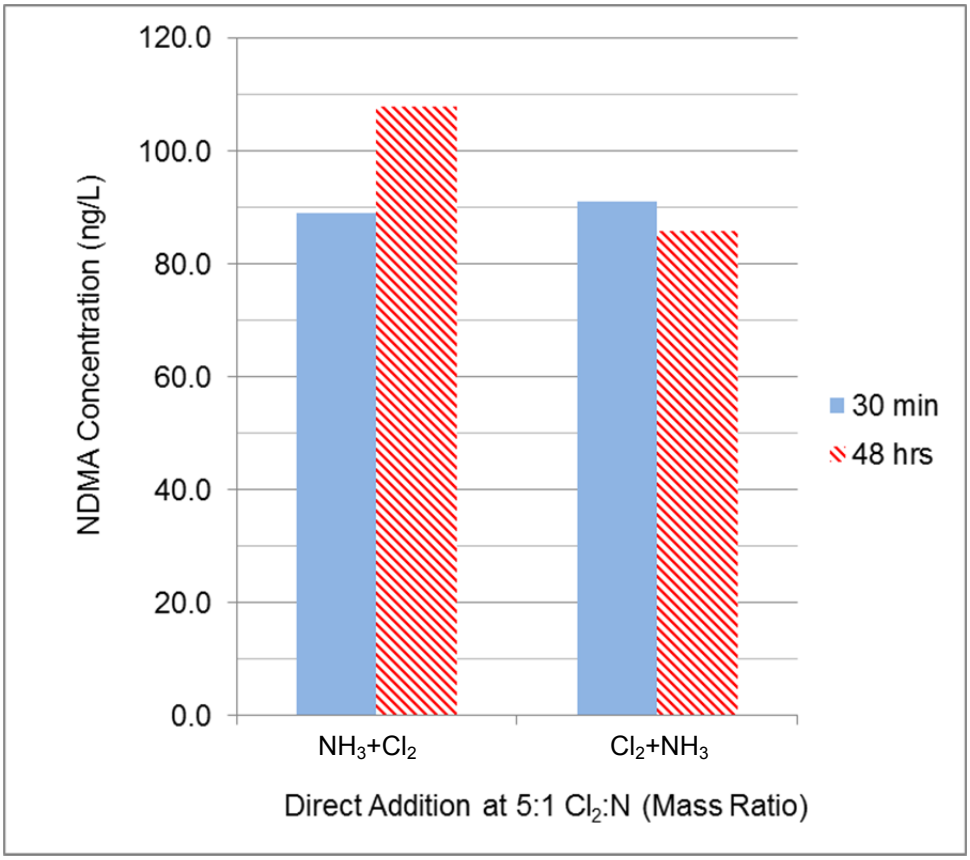

Figure 4.2: Effect of Two Minutes Free Chlorine Reaction Time on NDMA Concentration, Lake Palestine

While NDMA formation at 48 hours was higher than NDMA formation at 30 minutes for (NH_3+Cl_2) scheme, NDMA formation at 48 hours was 6% less than NDMA formation at 30 minutes for the (Cl_2+NH_3) scheme. This result was not expected based on the literature. It was expected that longer reaction times would results in more NDMA formation over time.

At 30 minutes, there was virtually no difference in NDMA formation whether ammonia or chlorine was added first. In fact, when ammonia was added first, NDMA formation was 2% less than NDMA formation when chlorine was added first. However, at 48 hours, adding chlorine first reduced NDMA formation by 20%. It should be noted that

the 48 hours NDMA concentration was less than the 30 minutes for the scheme (Cl_2+NH_3), which may be due to experiment error. The expected result that free chlorine would make a difference was not seen in all cases.

4.2 Richland Chambers Lake Results

Experiments were conducted on Richland Chambers Lake water samples to examine the effect of preformed chloramines with either 5:1 or 4:1 Cl_2/N mass ratio on NDMA concentration. Preformed chloramines were prepared at 2 mM with either 5:1 or 4:1 Cl_2/N mass ratio at pH 8.3 before being added to lake water samples.

In addition, to examine the effect of direct addition of ammonia and chlorine with either 5:1 or 4:1 Cl_2/N mass ratio on NDMA formation at pH 8.3, ammonium chloride NH_4Cl was added first to lake samples. Then, sodium hypochlorite NaOCl was added second.

The average recovery of internal standard surrogate for all samples was 99% with a range between 77% and 123%. These values are well within the acceptable recovery values set by EPA Method 521 of 70-130% of the true value.

Measured NDMA concentrations for each test condition described above for Richland Chambers Lake water samples are shown in Figure 4.3. Each test was a unique set of conditions to obtain initial results.

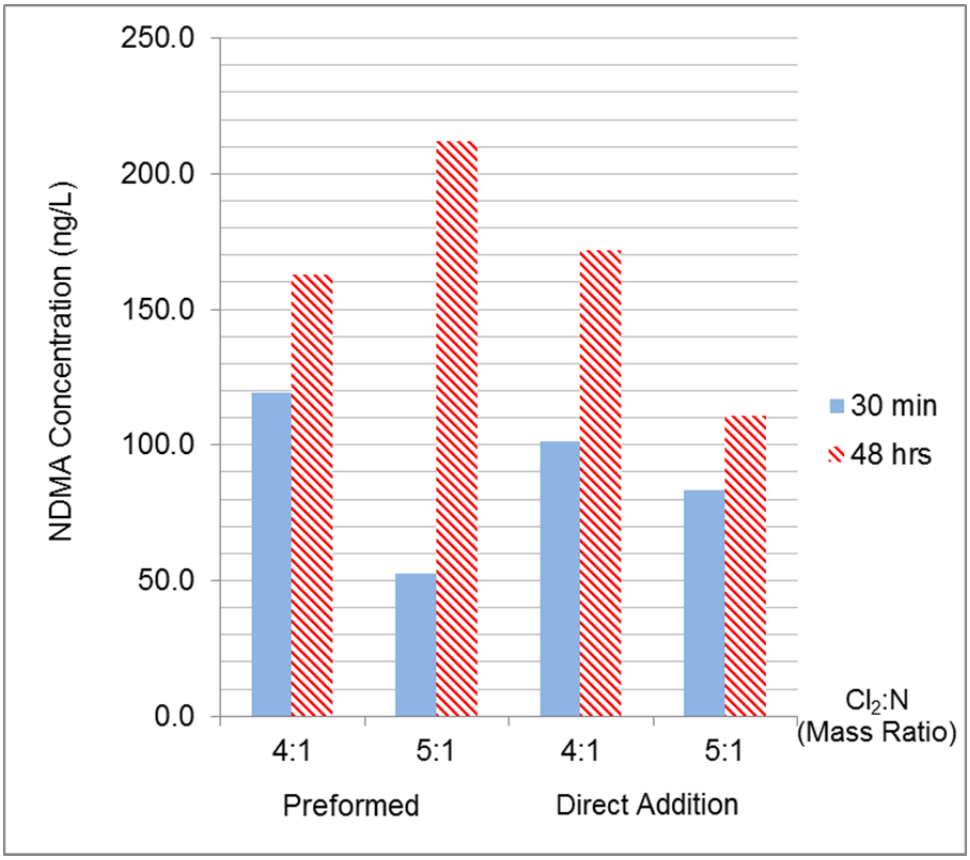

Figure 4.3: Effect of Preformed Chloramine, Direction Addition, and Cl_2/N Mass Ratio on NDMA Concentration, Richland Chambers Lake

NDMA formation at 48 hours was between 33% and 303% more than NDMA formation at 30 minutes for all samples due to longer reaction time, which was expected based on the literature.

Preformed chloramines generated 15% more NDMA at 30 minutes than direct addition at 4:1 Cl_2/N mass ratio, which was expected. Surprisingly however, at the same Cl_2/N mass ratio of 4:1, NDMA formation was 6% less at 48 hours for the preformed chloramine case than direct addition. This is contrary to the expectation that NDMA formation would be higher for the preformed chloramine case than direct addition. Similarly, at 5:1 Cl_2/N mass ratio, preformed chloramines generated 58% less NDMA

formation at 30 minutes than direction addition. However, at 48 hours, NDMA formation was 48% higher for preformed chloramines case than direct addition case, which was expected. Preformed chloramines did not consistently generate higher NDMA levels than direct addition. Preformed chloramines generated higher NDMA levels in only 50% of Richland Chambers samples than direct addition. Of particular interest is the data point for preformed chloramine at 5:1Cl_2/N mass ratio. This data point generated the lowest NDMA concentration of 52.6 ng/L at 30 minutes among all Richland Chamber lake samples. NDMA concentration was 37% lower than the next higher data point. Statistical analysis revealed that although this particular data point is furthest from the rest, it is not a significant outlier with 95% confidence.

In examining the results of Cl_2/N mass ratio on NDMA formation for preformed chloramines case, it was noted that NDMA formation at 30 minutes was 56% higher at 4:1 Cl_2/N mass ratio than at 5:1mass ratio. At 48 hours, NDMA formation was 30% lower at 4:1 Cl_2/N mass ratio than at 5:1mass ratio. These results are inconsistent. In contract, for the direct addition case, NDMA formation was 18% and 36% higher at both 30 minutes and 48 hours respectively at 4:1 Cl_2/N mass ratio than at 5:1 mass ratio. These results are more consistent but are contrary to what would be expected that lower mass ratios would generate lower NDMA due to favored monochloramine formation. The results of the effect of Cl_2/N mass ratio on NDMA formation were inconclusive but were more consistent for Richland Chambers than Lake Palestine. 4:1 Cl_2/N mass ratio generated higher NDMA concentration in 75% of Richland Chambers Lake samples than 5:1 Cl_2/N mass ratio. 4:1 Cl_2/N mass ratio did not do better than 5:1 Cl_2/N mass ratio.

A third experiment was conducted to examine the effect of chloramine formation time at 4:1 Cl_2/N mass ratio on NDMA concentration with preformed chloramines at pH 8.3. Two sets were prepared. For both sets, ammonium chloride NH_4Cl was added first to

lake samples. Then, sodium hypochlorite NaOCl was added second. Then, one set was allowed to react for 2 minutes while the second set was allowed to react for only 35 seconds before being added to different lake water samples. Figure 4.4 shows the results of chloramine formation time experiment on NDMA formation.

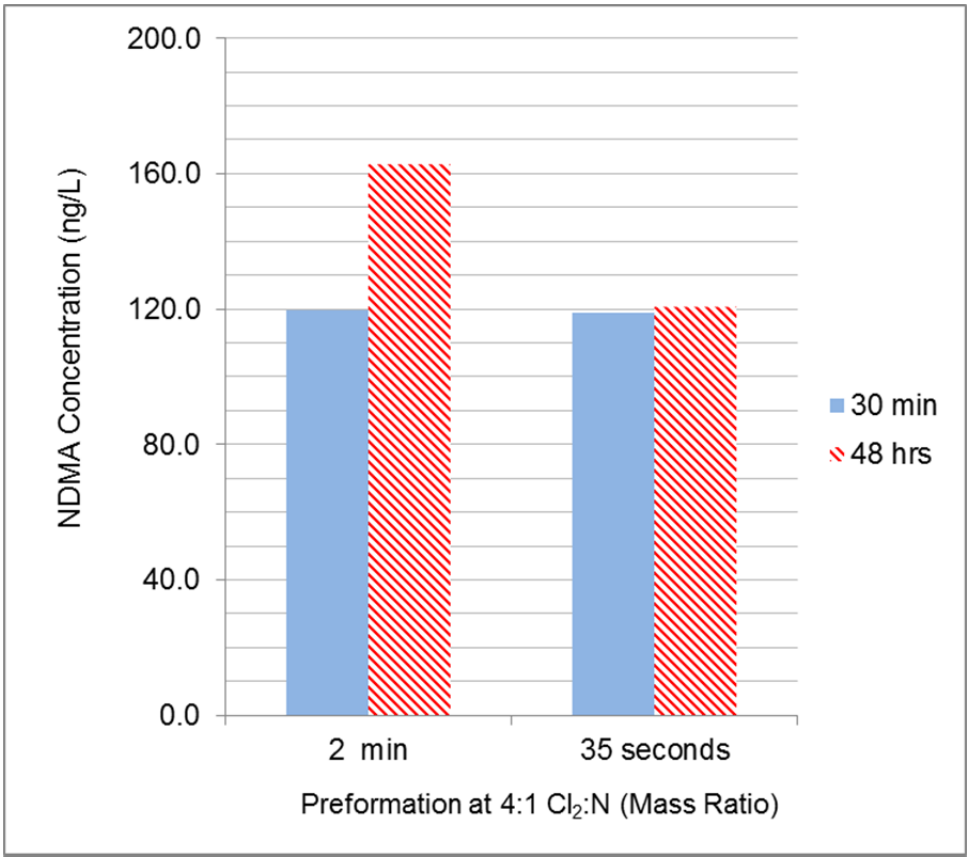

Figure 4.4: Effect of Chloramine Formation Time on NDMA Formation for Preformed Chloramines, Richland Chambers Lake

For preformed chloramine at 4:1 Cl_2/N mass ratio, there was no difference in NDMA formation at 30 minutes after either 35 seconds or 2 minutes formation time. However, NDMA formation at 48 hours after 2 minutes of formation time was 26% more than NDMA formation after 35 seconds of formation time. This is contrary to what would be expected that longer formation time would reduce NDMA formation.

4.3 Cedar Creek Lake Results

Experiments were conducted on Cedar Creek Lake water samples to examine the effect of preformed chloramines with either 5:1 or 4:1 Cl_2/N mass ratio on NDMA concentration. Preformed chloramines were prepared at 2 mM with either 5:1 or 4:1 Cl_2/N mass ratio at pH 8.3 before being added to lake water samples. Ammonium chloride NH_4Cl was added first. Sodium hypochlorite NaOCl was added second.

In addition, to examine the effect of direct addition of ammonia and chlorine with either 5:1 or 4:1 Cl_2/N mass ratio on NDMA formation at pH 8.3, ammonium chloride NH_4Cl was added first to lake samples. Then, sodium hypochlorite NaOCl was added second.

The average recovery of internal standard surrogate for all samples was 88% with a range between 69% and 104%. These values are within the acceptable recovery values set by EPA Method 521 of 70-130% of the true value.

Measured NDMA concentrations for each test condition described above for Cedar Creek Lake water samples are shown on Figure 4.5. Each test was a unique set of conditions to obtain initial results.

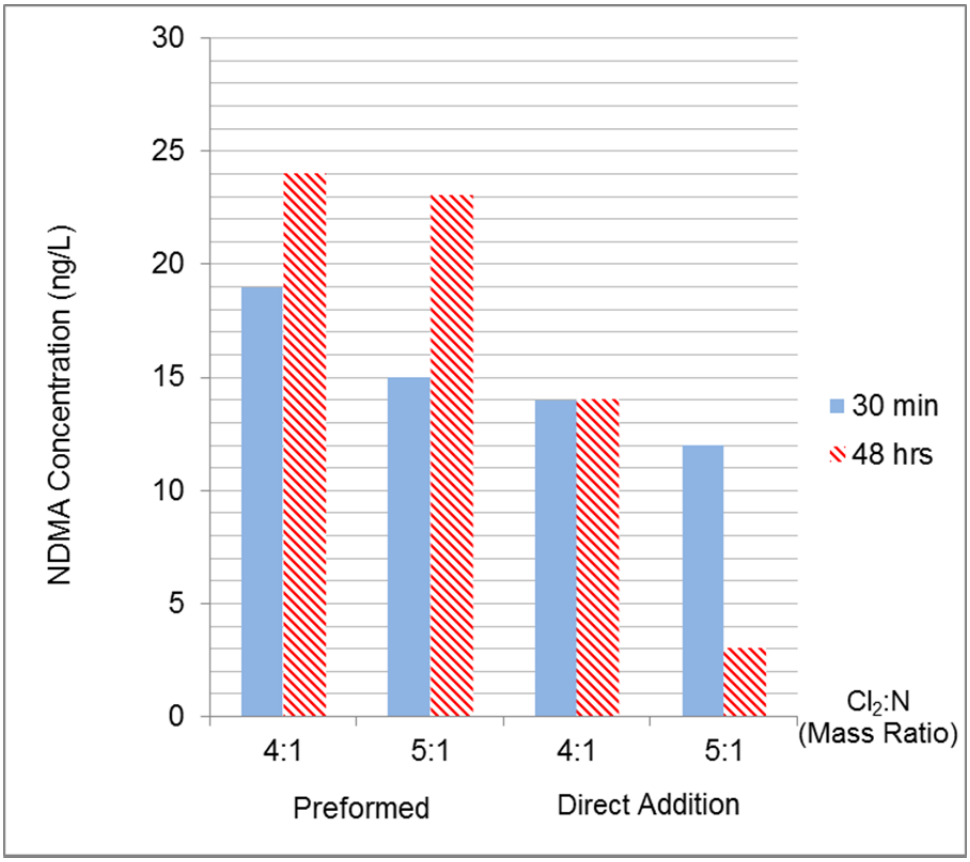

Figure 4.5: Effect of Preformed Chloramine, Direction Addition, and Cl_2/N Mass Ratio on NDMA Concentration, Cedar Creek Lake

For the preformed chloramines case, NDMA formation at 48 hours was between 26% and 53% more than NDMA formation at 30 minutes for 50% of the samples due to longer reaction time, which was expected based on the literature. However, one sample generated 75% less NDMA at 48 hours than at 30 minutes at 5:1 Cl_2/N mass ratio for direct addition case, while another sample showed no difference in NDMA formation between 30 minutes and 48 hours case at 4:1 Cl_2/N mass ratio for direct addition. These results were not expected, which could be the result of experimental error.

At 4:1 Cl_2/N mass ratio, preformed chloramines generated 26% and 42% more NDMA at 30 minutes and 48 hours respectively than direct addition. Similarly, at 5:1

Cl_2/N mass ratio, NDMA formation was 20% and 87% more at 30 minutes and 48 hours respectively than direct addition. These results were expected. Preformed chloramines consistently generated higher NDMA levels than direct addition for Cedar Creek Lake water samples. Of particular interest is the data point for direct addition at 5:1Cl_2/N mass ratio. This data point generated the lowest NDMA concentration of only 3.0 ng/L at 48 hours among all Cedar Creek lake samples combined. NDMA concentration was 75% lower than the next higher data point. Statistical analysis revealed that although this particular data point is furthest from the rest, it is not a significant outlier with 95% confidence.

In examining the results of Cl_2/N mass ratio on NDMA formation for preformed chloramines case, it was noted that NDMA formation at 30 minutes was 21% higher at 4:1 Cl_2/N mass ratio than at 5:1mass ratio. At 48 hours, NDMA formation was 4% higher at 4:1 Cl_2/N mass ratio than at 5:1mass ratio. In addition, for the direct addition case, NDMA formation was 14% and 79% higher at both 30 minutes and 48 hours respectively at 4:1 Cl_2/N mass ratio than at 5:1 mass ratio. These results are very consistent and show that lower Cl_2/N mass ratio of 4:1 tend to increase NDMA formation at 30 minutes and 48 hours. However, these results are contrary to what would be expected that lower Cl_2/N mass ratios would generate less NDMA due to favored monochloramine formation. 4:1 Cl_2/N mass ratio did not do better than 5:1 Cl_2/N mass ratio.

A third experiment was conducted to examine the effect of chloramine formation time at 5:1 and 4:1Cl_2/N mass ratio on NDMA concentration with preformed chloramines at pH 8.3. Two sets were prepared. One set was with 5:1 Cl_2/N mass ratio while the other was with 4:1 Cl_2/N mass ratio. For both sets, preformed chloramine was prepared by adding ammonium chloride NH_4Cl to 253 mL pH adjusted lake water. Then, sodium hypochlorite NaOCl was added. Afterwards, each set was divided into two subsets. One

set was allowed to react for 2 minutes while the second set was allowed to react for only 35 seconds before being added to different lake water samples.

The results of experiment to examine the effect of chloramine formation time with varying mass ratios are shown on Figure 4.6.

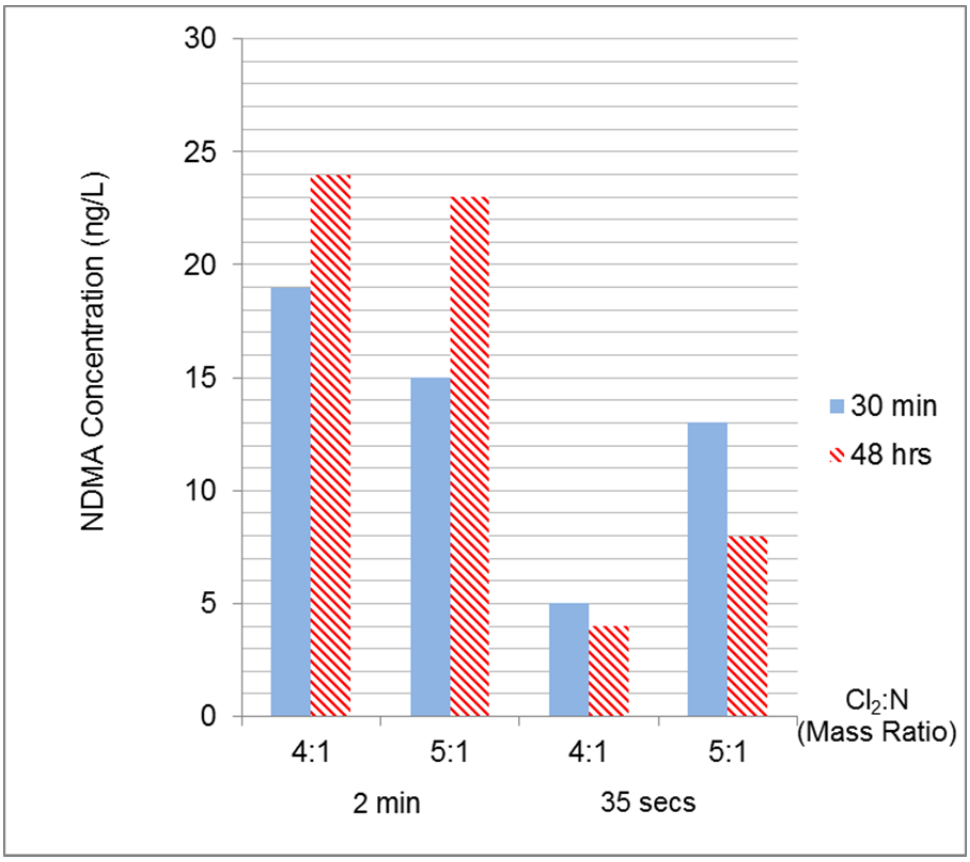

Figure 4.6: Effect of Chloramine Formation Time on NDMA Formation for Preformed Chloramines, Cedar Creek Lake

For preformed chloramine at 4:1 Cl_2/N mass ratio, 2 minutes of formation time resulted in 74% and 83% higher NDMA formation at 30 minutes and 48 hours respectively than 35 seconds of formation time. Similarly, at 5:1 Cl_2/N mass ratio, 2 minutes of formation time resulted in 13% and 65% higher NDMA formation at 30

minutes and 48 hours respectively than 35 seconds of formation time. Similar results were obtained from experiments on Richland Chambers Lake water samples.

4.4 Discussion and Comparison of Results

Based on a review of the literature, it is expected that NDMA continues to form and increases over a period of days (Mitch et al., 2003). In this study, NDMA concentration after 48 hours was generally higher than NDMA concentration after 30 minutes of adding reagents at both 5:1 and 4:1 Cl_2/N mass ratios for both preformed chloramine cases and direct addition cases. In 11 of the 16 samples analyzed (69%) for the different scenarios, the NDMA concentration was between 2% and 303% higher at 48 hours than 30 minutes. It is surprising that in some samples the 48 hours NDMA concentration was actually lower than the 30 minutes NDMA concentration, which was not expected. Possible explanations of these results are sampling or experimental errors during the extraction, elution, or an incorrect final sample injection volume due to errors with the autosampler.

In comparing the effect of preformed chloramines to direct addition of ammonia and chlorine on NDMA formation, preformed chloramines generated between 14% and 26% more NDMA than direct addition at 30 minutes in 83% of all lakes samples at 5:1 and 4:1 Cl_2/N mass ratios. Similarly, preformed chloramines generated between 31% and 87% more NDMA than direct addition at 48 hours in 83% of all lakes samples at 5:1 and 4:1 Cl_2/N mass ratios. The result that preformed chloramines formed more NDMA than direct addition can possibly be explained by addition of ammonia in quantities more than precursors present in the water samples. The abundance of ammonia favors chloramine formation, and subsequently leads to reaction between inorganic chloramines and unchlorinated DMA. Essentially, DMA, an electrophile, will react with chloramines to form

unsymmetrical dimethylhydrazine intermediate. In comparison, direction addition reactions involving applying ammonium chloride first to water samples generated lower NDMA concentration possibly because ammonium chloride and DMA are both electrophiles and will be in competition for free chlorine. This competition results in reduction of NDMA formation due to formation of chlorinated DMA and chloramines, which don't react with each other.

Initial results from chlorine reaction time before ammonia application for direct addition case indicated that a 2 minutes free chlorine reaction time prior to ammonia addition would reduce NDMA by 20% in water samples at 48 hours. It was surprising that there was no difference in NDMA concentration at 30 minutes. It is believed that adding chlorine first would oxidize some of the precursors present in the water and would also form chlorinated DMA, which does not react with ammonium chloride when added. Subsequently, NDMA formation will be reduced. The effect of free chlorine addition on NDMA formation was not as high as expected.

Experiments on preformed chloramine formation time consistently showed that chloramine formation time of 2 minutes generated between 0% and 74% more NDMA than 35 seconds formation time at 30 minutes at 4:1 Cl_2/N mass ratio. At 48 hours, chloramine formation time of 2 minutes generated between 26% and 83% more NDMA than 35 seconds formation time also at 4:1 Cl_2/N mass ratio. Similarly, for preformed chloramine at 5:1 Cl_2/N mass ratio, NDMA concentration was 13% and 65% higher for 2 minutes than 35 seconds reaction times at 30 minutes and 48 hours respectively. A possible explanation of higher NDMA formation at 2 minutes reaction time is that at shorter reaction times, chloramine formation is not complete with free chlorine and ammonia still present in the solution. When added to water samples, precursors and ammonia will compete for free chlorine, which leads to lower NDMA formation. The

NDMA formation was consistently higher at 4:1Cl_2/N mass ratio than at 5:1 Cl_2/N mass ratio. One possible explanation that excess ammonia present at the lower Cl_2/N mass ratio of 4:1 may contribute to formation of other nitrogenous organic compounds that can act as NDMA precursors, which leads to higher NDMA formation at the lower Cl_2/N mass ratio.

Although the effect of Cl_2/N mass ratios on NDMA formation was not consistent among all lakes samples, lower Cl_2/N mass ratio generally resulted in higher NDMA formation. Comparison of all lakes NDMA formation at 30 minutes for all experiment scenarios is shown on Figure 4.7.

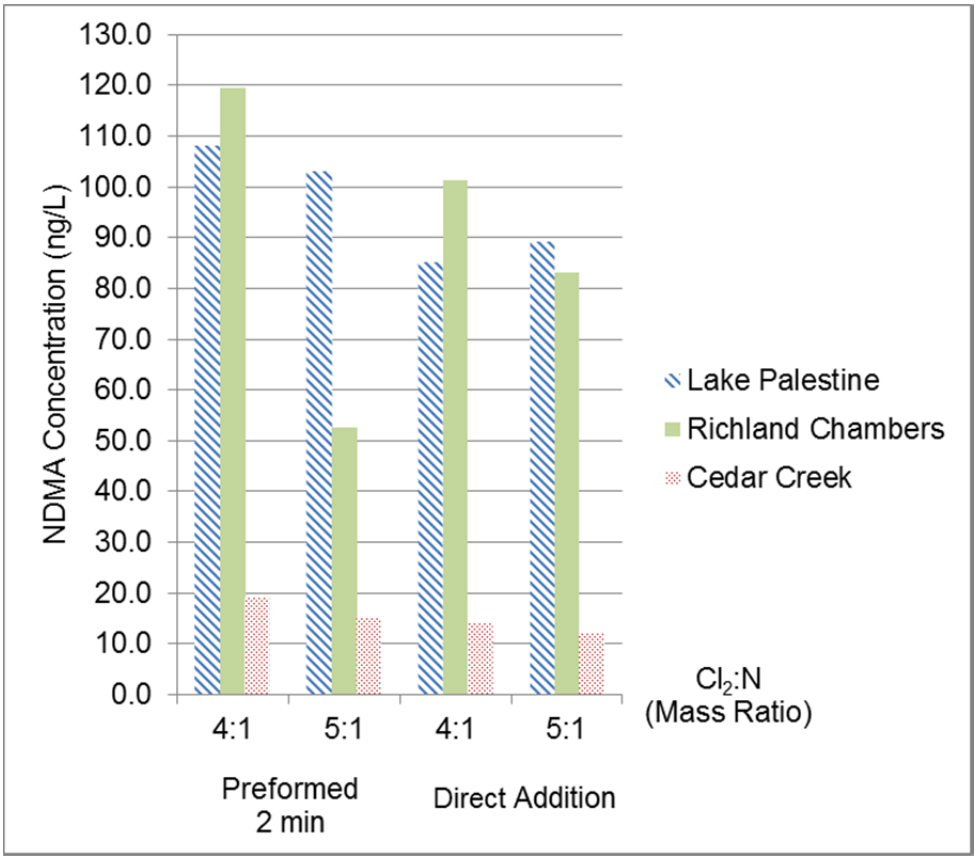

Figure 4.7: All Lakes Results Comparison at 30 Minutes

At 4:1 Cl_2/N mass ratio, preformed chloramine generated between 5% and 56% more NDMA than 5:1 Cl_2/N mass ratio at 30 minutes. Similarly, for direct addition cases, NDMA formation was between 5% less and 18% more at 4:1 than 5:1 Cl_2/N mass ratio at 30 minutes. However, examining the results collectively at 30 minutes reveals that 4:1 Cl_2/N mass ratio generally generated higher NDMA formation than 5:1 Cl_2/N mass ratio in 83% of all samples analyzed for preformed and direct addition cases. Accordingly, 4:1 Cl_2/N mass ratio did not seem to reduce NDMA formation.

At 30 minutes, Lake Palestine and Richland Chambers Lake formed the highest NDMA concentration 50% of the time each, while Cedar Creek Lake formed the least NDMA concentration 100% of the time among all lake samples for the different test conditions. These results lead to the belief that water quality of the leaks may play a role in NDMA formation. Given the water quality of Lake Palestine and Richland Chambers Lake, it may be reasonable to expect that NDMA formation will probably be consistently higher in these lakes than Cedar Creek Lake. Nonetheless, Richland Chambers Lake water samples were collected from a tap on the recirculation line that feeds chemicals to the pipeline. The line was flushed for extended time before collecting the samples in order to obtain a representative lake water samples. The flushing time may not have been sufficient to remove stagnant water in the recirculation line. Some of the stagnant water, with probably higher nitrogenous precursors, may have been collected in the samples, which led to higher NDMA concentrations. In addition, one data point for Richland Chambers Lake is suspiciously lower than other data points for the same lake. The inconsistent data point may have been the result of experimental error.

Comparison of all lakes NDMA formation at 48 hours for all experiment scenarios is shown on Figure 4.8.

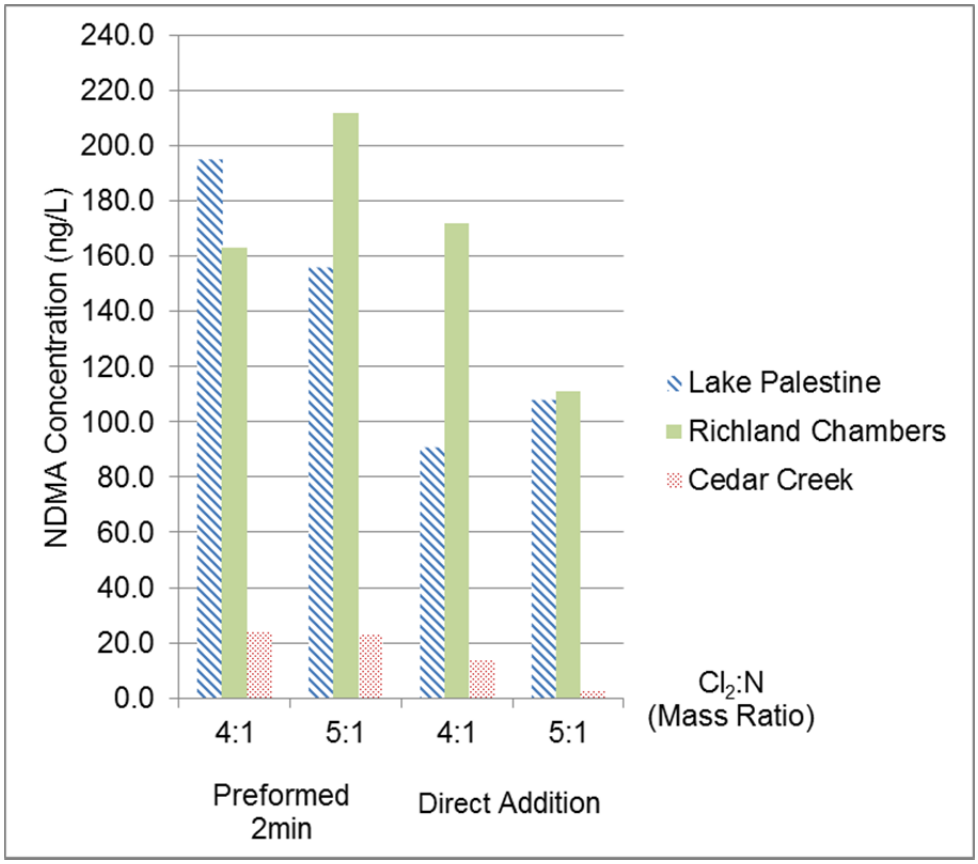

Figure 4.8: All Lakes Results Comparison at 48 Hours

At 4:1 Cl_2/N mass ratio, preformed chloramine generated between 30% less and 20% more NDMA than 5:1 Cl_2/N mass ratio at 48 hours. Similarly, for direct addition cases, NDMA formation was between 19% less and 79% more at 4:1 than 5:1 Cl_2/N mass ratio at 48 hours. However, examining the results collectively at 48 hours reveals that 4:1 Cl_2/N mass ratio generally generated higher NDMA formation than 5:1 Cl_2/N mass ratio in 67% of all samples analyzed for preformed and direct addition cases. Accordingly, 4:1 Cl_2/N mass ratio did not seem to reduce NDMA formation.

At 48 hours, Lake Palestine formed the highest NDMA concentration 25% of the time, while Richland Chambers formed the highest NDMA concentration 75% of the time. In contract, Cedar Creek Lake consistently formed the lowest NDMA concentration 100%

of the time among all lake samples for the different test conditions. These results lead to the belief that water quality of the lakes plays an important role in NDMA formation. Although it was expected that NDMA concentration would be higher in the raw water samples probably due to the occurrence of precursors, it was not expected that NDMA levels would be significantly different from levels in similar surface water sources. It is highly unlikely that the lakes receive unknown discharge from nearby wastewater treatment plan effluent leading to increased occurrence of precursors. However, the lakes may receive agricultural runoff loaded with nitrogenous fertilizers and pesticides that can act as NDMA precursors. The source of the elevated levels of NDMA in the samples should be further investigated. Furthermore, lake samples were collected between November 2014 and March 2015, which may affect NDMA formation due to temperature and rain runoff that may be loaded with amine precursors from fertilizers and pesticides.

Higher concentrations from Richland Chambers and Cedar Creek Lakes samples in laboratory experiments are not consistent with previously obtained values from the field samples for Richland Chambers and Cedar Creek pipelines taps at Waxahachie pump station. Field values were in the twenties ng/L range for NDMA concentration. The higher NDMA concentration values in the laboratory experiments are probably the result of contamination or experimental procedure errors.

An interesting problem was encountered with ultrapure water obtained from the Millipore system. Ultrapure water was obtained from Millipore apparatus which had a filter, two deionizing columns, and activated carbon column. The water was passed through a larger deionizing column to reduce the load on the Millipore deionizing column. It was discovered that this method of generating ultrapure water actually resulted in very high concentrations of NDMA in the laboratory fortified blanks and led to the replacement of the system with new system. A series of activated carbon/ reverse osmosis system

was placed before the Millipore system to remove chlorine before the deionizing column. A possible explanation of the increased NDMA concentration is that the activated carbon will absorb NDMA from the water until the activated carbon is saturated. Upon saturation, the activated carbon cannot absorb NDMA anymore, and the concentration of NDMA in the system will continue to increase. This problem demonstrates the importance of laboratory fortified blank to detect any background system contamination in samples analysis procedure.

Chapter 5

Conclusions and Recommendations

It was shown that NDMA concentration continues to increase with time after the initial addition of chloramine. The NDMA concentration after 48 hours was generally higher than the NDMA concentration after 30 minutes of reaction at both 5:1 and 4:1 Cl_2/N mass ratios. This trend was seen for both preformed chloramine cases and direct addition cases.

Addition of preformed chloramines with 2 minutes formation time consistently generated more NDMA than direct addition of reagents at both 5:1 and 4:1 Cl_2/N mass ratios investigated. These results were expected based on the literature. A potential reason preformed chloramines generated more NDMA than direct addition is that in preformed chloramine formation the ratio of ammonia to precursors is greater than in direct addition, which favors chloramine formation over the reaction of free chlorine with the precursors. Upon chloramine formation, NDMA will be formed as a result of the reaction between precursors and chloramines. The direct addition of ammonia and chlorine results in lower NDMA formation possibly due to competition between ammonia and dimethylamine (DMA)/ precursors for free chlorine. Free chlorine addition would result in chlorinated precursors and chloramine formation. This leads to lower NDMA formation due to the competing reactions.

Results on the effect of Cl_2/N mass ratio on NDMA formation were not conclusive although, overall, lower Cl_2/N mass ratio generated higher NDMA in 75% of the samples analyzed. The NDMA formation was consistently higher at 4:1 Cl_2/N mass ratio than at 5:1 Cl_2/N mass ratio for both preformed chloramines and direct addition cases at 30 minutes and 48 hours. It was surprising that 4:1 Cl_2/N mass ratio did not reduce NDMA formation. One possible explanation that excess ammonia present at the lower Cl_2/N

mass ratio of 4:1 may contribute to formation of other nitrogenous organic compounds that can act as NDMA precursors, which leads to higher NDMA formation at the lower Cl_2/N mass ratio.

Based on the results of the chloramine formation time experiments, it appears that a 2 minute chloramine formation time consistently generated more NDMA than a 35 second formation time at 30 minutes and 48 hours for both 5:1 and 4:1 Cl_2/N mass ratios. Also, NDMA formation was consistently higher at 4:1 Cl_2/N mass ratio than at 5:1 Cl_2/N mass ratio possibly due to the same reason discussed previously. No experiments were conducted on the effect of chloramine formation time on NDMA formation for the direct addition case. These experiments should be conducted, and the results should be compared with the results of this study. In addition, other chloramine formation times should be investigated to obtain the optimum formation time that would result in the minimum NDMA formation.

Research was conducted for free chlorine reaction time of 2 minutes before ammonia application. Free chlorine reaction time before application of ammonia is marginally effective in reducing NDMA formation in raw water systems. In addition, free chlorine was less effective at 30 minutes than 48 hours. The overall effect is less than expected. It is speculated that that adding chlorine first would oxidize some of the precursors present in the water leading to reduced NDMA formation.

Preformed chloramines formation time of 2 minutes appears to increase NDMA formation more than 35 seconds formation time for both 5:1 and 4:1 Cl_2/N mass ratios at 30 minutes and 48 hours. This is counter intuitive. It is speculated that at shorter reaction times, chloramine formation is not complete with free chlorine and ammonia still present in the solution. When added to water samples, unreacted free chlorine will oxidize

available precursors and chlorinate possibly available DMA and lead to lower NDMA formation.

Experiments should be conducted in duplicates or triplicates to ensure repeatability of the results, which ensures that clear patterns are established and correlations are easily discerned.

Appendix A

Laboratory Experiments Data Sheets

Date: Saturday 6/21/2014

Time In: 9:30 AM

Time Out: 4:30 PM

Procedure: NDMA Standard Solutions

Sample	Description	2 µg/mL Surrogate (µL)	Standard	Extraction Time		
				Start	End	Duration
1	MilliQ Water	50 ml of 2 µg/ml	Blank	12:29	2:15	106 min
2	MilliQ Water	50 ml of 2 µg/ml	1 ml of 0.5ng/ml	12:29	3:10	161 min
3	MilliQ Water	50 ml of 2 µg/ml	1 ml of 0.5ng/ml	12:29	2:20	111 min
4	MilliQ Water	50 ml of 2 µg/ml	1 ml of 1.0ng/ml	12:29	2:25	116 min
5	MilliQ Water	50 ml of 2 µg/ml	1 ml of 1.0ng/ml	12:29	2:15	106 min
6	MilliQ Water	50 ml of 2 µg/ml	1 ml of 5.0ng/ml	12:29	2:15	106 min
7	MilliQ Water	50 ml of 2 µg/ml	1 ml of 20.0ng/ml	12:29	2:40	131 min
8	MilliQ Water	50 ml of 2 µg/ml	1 ml of 50.0ng/ml	12:29	2:40	131 min

Notes:

- Surrogate in water preparation date: 6/8/2014
- Standards in water: 0.5, 1.0, 5.0, 20.0 prepared on 6/19/2014
- Standard 50.0ng/ml in water prepared 6/8/2014
- Drying with sodium sulfate columns was skipped to be consistent with previous
- Elution time was 41 mins to complete.
- SPE cartridges were dried by passing air for 10 minutes at full vacuum.
- Most samples had water that was removed with syringe.

Date: Saturday 7/26/2014

Time In: 8:15 AM

Time Out: 6:15 PM

Procedure: NDMA Standard Solutions – High Concentration Set (Black Numbered Set)

Sample	Description	2 µg/mL Surrogate (µL)	Standard	Extraction Time		
				Start	End	Duration
1	MilliQ Water	50 ml of 2 µg/ml	1 ml of 50.0ng/ml	11:25AM	1:40	135 min
2	MilliQ Water	50 ml of 2 µg/ml	1 ml of 100.0ng/ml	11:25AM	1:03	98 min
3	MilliQ Water	50 ml of 2 µg/ml	1 ml of 250.0ng/ml	11:25AM	1:20	115 min
4	MilliQ Water	50 ml of 2 µg/ml	1 ml of 500.0ng/ml	11:25AM	1:25	120 min
5	MilliQ Water	50 ml of 2 µg/ml	1 ml of 750.0ng/ml	11:25AM	12:55	90 min
6	MilliQ Water	50 ml of 2 µg/ml	1 ml of 1000.0ng/ml	11:25AM	12:55	90 min
7	MilliQ Water	50 ml of 2 µg/ml	Blank	11:25AM	1:05	100 min
8	MilliQ Water	50 ml of 2 µg/ml	Blank	11:25AM	1:20	115 min
9	Tap Water	50 ml of 2 µg/ml	Blank	11:25AM	12:50	85 min

Notes:

- SPE Lot# C12A03W02
- Surrogate in water preparation date: 7/25/2014
- Standards in water preparation date: 7/25/2014
- 7g of Sodium Thiosulphate Anahydrous was added to each drying column to help eliminate

Water from extracted samples. No water was visible after passing the eluted samples

Through the drying columns although in some samples, the volume collected was less than

The original sample volume of 12-13ml.

- 2ml of Methylene Chloride were added to drying columns to elute any remaining NDMA.

Date: Saturday 7/26/2014

Time In: 8:15 AM

Time Out: 6:15 PM

Procedure: NDMA Standard Solutions – Low Concentration Set (Red Numbered Set)

Sample	Description	2 µg/mL Surrogate (µL)	Standard	Extraction Time		
				Start	End	Duration
1	MilliQ Water	50 ml of 2 µg/ml	1 ml of 0.5ng/ml	2:40PM	4:15	95 min
2	MilliQ Water	50 ml of 2 µg/ml	1 ml of 1.0ng/ml	2:40PM	4:25	105 min
3	MilliQ Water	50 ml of 2 µg/ml	1 ml of 5.0ng/ml	2:40PM	3:48	68 min
4	MilliQ Water	50 ml of 2 µg/ml	1 ml of 10.0ng/ml	2:40PM	4:18	98 min
5	MilliQ Water	50 ml of 2 µg/ml	1 ml of 20.0ng/ml	2:40PM	3:55	75 min
6	MilliQ Water	50 ml of 2 µg/ml	1 ml of 50.0ng/ml	2:40PM	4:05	85 min
7	MilliQ Water	50 ml of 2 µg/ml	Blank	2:40PM	5:00	140 min
8	MilliQ Water	50 ml of 2 µg/ml	Blank	2:40PM	4:30	110 min
9	Tap Water	50 ml of 2 µg/ml	Blank	2:40PM	4:00	80 min

Notes:

- SPE Lot# C12A03W02
- Surrogate in water preparation date: 7/25/2014
- Standards in water preparation date: 7/25/2014
- 7g of Sodium Thiosulphate Anahydrous was added to each drying column to help eliminate

Water from extracted samples. No water was visible after passing the eluted samples

Through the drying columns although in some samples, the volume collected was less than

The original sample volume of 12-13ml.

- 3ml of Methylene Chloride were added to drying columns to elute any remaining NDMA.
- Black color was noticed in samples 2, 4, 5, 6 at the start of elution step for only few drops

However, during the drying column step, the black matter was adsorbed to the sodium Sulphase and was eliminated from the extraction.

Date: Saturday 11/16/2014

Procedure: NDMA – Lake Palestine

Label No.	Sample	Description	2 µg/mL Surrogate (µL)	Spike/ Standard (1 ml)	1 µg/mL Internal Standard (µL)	Extraction Time		
						Start	End	Duration
1		Blank	50	-	50	11:00	12:45	1:48
2		1 ml 50ng/L	50	-	50	11:00	12:40	1:40
3		1 ml 50ng/L	50	1mL of 20ng/L	50	11:00	12:32	1:35
4	2		50	1mL of 20ng/L -	50	11:00	1:10	2:10
5	1		50	-	50	11:00	1:10	2:10
6	2		50	-	50	11:00	12:55	1:55
7	3		50	-	50	11:00	1:10	2:10
8	4		50	-	50	11:00	12:50	1:53
9	5		50	-	50	11:00	1:05	2:05
10	6		50	-	50	11:00	1:00	2:00
11	7		50		50	11:00	12:46	1:40
12	8		50		50	11:00	1:20	2:20
13	9		50		50	11:00	12:30	1:32
14	10		50		50	11:00	12:55	1:55

Saturday 11/16/2014 NDMA – Lake Palestine

			Step1	Step2	Step 3	Step 4	Step 5	Step 6	Step 7		
	Cl_2:N (Mass Ratio)	Sample volume	pH adjusted	Chemical addition	Mixing time	Chemical addition	Mixing time	Formation time	Target Concentration	Sample number corresponding to the previous page	
		mL		mg/L	sec	mg/L		min		30 min	48 hrs
Preformation at 2 mM	5:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2	4 mg/L in 2.65L	6	1
Preformation at 2 mM	4:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2	4 mg/L in 2.65L	7	2
Direct Addition	5:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	8	3
Direct Addition	4:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	9	4
				Chemical addition	Mixing time	Reaction time	Chemical addition	Mixing time	Volume of sample		
Direct Addition	5:1	-	8.3	Cl_2	5-10	2	NH_3-N	5-10	4 mg/L in 2.65L	10	5

Date: Sunday 1/25/2015

Procedure: NDMA – Richland Chambers (Batch 1) White Label

Label No.	Sample	Description	2 µg/mL Surrogate (µL)	Spike/ Standard (1 ml)	1 µg/mL Internal Standard (µL)	Extraction Time		
						Start	End	Duration
1		Blank	50	-	50	12:26	1:45	1:19
2		1 ml 50ng/L	50	-	50	12:26	1:40	1:14
3		1 ml 50ng/L	50	1mL of 20ng/L	50	12:26	1:43	1:17
4	2		50	1mL of 20ng/L -	50	12:26	2:40	2:14
5	1		50	-	50	12:26	2:30	2:04
6	2		50	-	50	12:26	2:05	1:39
7	3		50	-	50	12:26	1:49	1:23
8	4		50	-	50	12:26	2:11	1:45
9	5		50	-	50	12:26	1:46	1:20
10	6		50	-	50	12:26	2:00	1:34

Notes:

- 50 ng/L prepared 7/25/2014
- 20 ng/L prepared 7/25/2014
- Surrogate prepared unknown (yellow label)

Date: Sunday 1/25/2015

Procedure: NDMA – Richland Chambers (Batch 2) Red Label

Label No.	Sample	Description	2 µg/mL Surrogate (µL)	Spike/ Standard (1 ml)	1 µg/mL Internal Standard (µL)	Extraction Time		
						Start	End	Duration
1		Blank	50	-	50	1:47	3:00	1:13
2		1 ml 50ng/L	50	-	50	1:47	4:30	2:43
3		1 ml 50ng/L	50	1mL of 20ng/L	50	1:47	3:00	1:13
4	8		50	1mL of 20ng/L -	50	1:47	3:00	1:13
5	7		50	-	50	1:47	3:50	2:03
6	8		50	-	50	1:47	4:00	2:13
7	9		50	-	50	1:47	4:00	2:13
8	10		50	-	50	1:47	4:35	2:48
9	11		50	-	50	1:47	3:40	1:53
10	12		50	-	50	1:47	3:30	1:43

Sunday 1/25/2015 – Richland Chambers

			Step1	Step2	Step 3	Step 4	Step 5	Step 6	Step 7		
	Cl_2:N (Mass Ratio)	Sample volume	pH adjusted	Chemical addition	Mixing time	Chemical addition	Mixing time	Formation time	Target Concentration	Sample number corresponding to the previous page	
		mL		mg/L	sec	mg/L				30 min	48 hrs
Preformation at 2 mM	5:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2 min	4 mg/L in 2.65L	1	7
Preformation at 2 mM	4:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2 min	4 mg/L in 2.65L	2, 5	8, 11
Direct Addition	5:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	3	9
Direct Addition	4:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	4	10
Preformation at 2 mM	4:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	35 seconds	4 mg/L in 2.65L	6	12

Samples prepared 1/22/2015

Date: Saturday 03/14/2015

Procedure: NDMA – Cedar Creek (Batch 1-Red)

Label No.	Sample	Description	2 µg/mL Surrogate (µL)	Spike/ Standard (1 ml)	1 µg/mL Internal Standard (µL)	Extraction Time		
						Start	End	Duration
1		Blank	50	-	50	10:36	12:51	2:15
2		1 ml 50ng/L	50	-	50	10:36	12:40	2:04
3		1 ml 50ng/L	50	1mL of 20ng/L	50	10:36	12:09	1:33
4	2		50	1mL of 20ng/L -	50	10:36	1:09	2:33
5	1		50	-	50	10:36	12:45	2:09
6	2		50	-	50	10:36	12:47	2:11
7	3		50	-	50	10:36	12:40	2:04
8	4		50	-	50	10:36	12:30	1:54
9	5		50	-	50	10:36	12:30	1:54
10	6		50	-	50	10:36	1:15	2:39

Date: Saturday 03/14/2015

Procedure: NDMA – Cedar Creek (Batch 2-White)

Label No.	Sample	Description	2 µg/mL Surrogate (µL)	Spike/ Standard (1 ml)	1 µg/mL Internal Standard (µL)	Extraction Time		
						Start	End	Duration
1		Blank	50	-	50	12:15	1:40	1:25
2		1 ml 50ng/L	50	-	50	12:15	1:57	1:42
3		1 ml 50ng/L	50	1mL of 20ng/L	50	12:15	2:40	2:25
4	8		50	1mL of 20ng/L -	50	12:15	1:35	1:20
5	7		50	-	50	12:15	1:40	1:25
6	8		50	-	50	12:15	1:40	1:25
7	9		50	-	50	12:15	1:57	1:42
8	10		50	-	50	12:15	1:55	1:40
9	11		50	-	50	12:15	2:30	2:15
10	12		50	-	50	12:15	1:46	1:31

03/14/2015 NDMA – Cedar Creek

			Step1	Step2	Step 3	Step 4	Step 5	Step 6	Step 7		
	Cl_2:N (Mass Ratio)	Sample volume	pH adjusted	Chemical addition	Mixing time	Chemical addition	Mixing time	Formation time	Target Concentration	Sample number corresponding to the previous page	
		mL		mg/L	sec	mg/L				30 min	48 hrs
Preformation at 2 mM	5:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2 min	4 mg/L in 2.65L	1	7
Preformation at 2 mM	4:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2 min	4 mg/L in 2.65L	2	8
Direct Addition	5:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	3	9
Direct Addition	4:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	4	10
Preformation at 2 mM	5:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	35 seconds	4 mg/L in 2.65L	5	11
Preformation at 2 mM	4:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	35 seconds	4 mg/L in 2.65L	6	12

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Appendix B

Laboratory Experiments Results

NDMA: Lake Palestine

Average Internal Standard Recovery 87% (69% to 137%)

	Cl_2:N (Mass Ratio)	Sample volume	pH adjusted	Chemical addition	Mixing time	Chemical addition	Mixing time	Formation time	Target Concentration	NDMA Concentration (ng/L)	
		mL		mg/L	sec	mg/L		min		30 min	48 hrs
Preformation at 2 mM	5:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2	4 mg/L in 2.65L	103.0	156.0
Preformation at 2 mM	4:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2	4 mg/L in 2.65L	108.0	195.0
Direct Addition	5:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	89.0	108.0
Direct Addition	4:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	85.0	91.0

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				Chemical addition	Mixing time	Reaction time	Chemic-al addition	Mixing time	Volume of sample		
Direct Addition	5:1	-	8.3	Cl_2	5-10	2	NH_3-N	5-10	4 mg/L in 2.65L	91.0	86.0

NDMA – Richland Chambers

Average Internal Standard Recovery 99% (77% to 123%)

	Cl_2:N (Mass Ratio)	Sample volume	pH adjusted	Chemical addition	Mixing time	Chemical addition	Mixing time	Formation time	Target Concentration	NDMA Concentration (ng/L)	
		mL		mg/L	sec	mg/L				30 min	48 hrs
Preformation at 2 mM	5:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2 min	4 mg/L in 2.65L	52.6	212.0
Preformation at 2 mM	4:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2 min	4 mg/L in 2.65L	119.5	163.0
Direct Addition	5:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	83.2	111.0
Direct Addition	4:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	101.3	172.0
Preformation at 2 mM	4:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	35 seconds	4 mg/L in 2.65L	118.8	121.0

NDMA – Cedar Creek

Average Internal Standard Recovery 88% (69% to 104%)

	Cl_2:N (Mass Ratio)	Sample volume	pH adjusted	Chemical addition	Mixing time	Chemical addition	Mixing time	Formation time	Target Concentration	NDMA Concentration (ng/L)	
		mL		mg/L	sec	mg/L				30 min	48 hrs
Preformation at 2 mM	5:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2 min	4 mg/L in 2.65L	15.0	23.0
Preformation at 2 mM	4:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	2 min	4 mg/L in 2.65L	19.0	24.0
Direct Addition	5:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	12.0	3.0
Direct Addition	4:1	-	8.3	NH_3-N	5-10	Cl_2	5-10	-	4 mg/L in 2.65L	14.0	14.0
Preformation at 2 mM	5:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	35 seconds	4 mg/L in 2.65L	13.0	8.0
Preformation at 2 mM	4:1	253	8.3	NH_3-N	5-10	Cl_2	5-10	35 seconds	4 mg/L in 2.65L	5.0	4.0

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Biographical Information

Khidir Hamad is a professional engineer with 12 years of hands-on design experience in water/ wastewater engineering. He focuses on water distribution and wastewater collection system design including gravity sewers and force mains, storm drainage design and improvements, pump station design, site development, hydraulic/ hydrologic modeling, route studies, dam inspection and rehab, and project/ construction management. He has Bachelor of Science in Civil Engineering and a Master of Business Administration both from the University of Alabama at Birmingham. Khidir worked on projects for several clients in the DFW area including Dallas Water Utilities, DFW Airport, Town of Flower Mound, Tarrant Regional Water District, and Trinity River Authority. He is interested in research related to cost effective treatment methods for developing countries.