Photocatalytic Oxidation of N-Nitrosodimethylamine by UV-LED Light

Major Qualifying Project completed in partial fulfillment
Of the Bachelor of Science Degree at
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Submitted by:
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This report represents the work of two WPI undergraduate students submitted to the faculty as evidence of a degree requirement. This report is similar to the report submitted by Peishan Wang as the two students completed Chapters 1 - 5 of the project together.

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Abstract

The detection of harmful trace organics in drinking water is becoming an increasing concern as detection technologies become more accessible and widely available. N-nitrosodimethylamine (NDMA) is a byproduct of disinfection that is a suspected human carcinogen. Case studies of surface waters and drinking water distribution systems have found NDMA at concentrations high enough to cause an increased lifetime risk of cancer. NDMA levels may be regulated in the future, meaning that cost effective and efficient treatment is needed. This project focused on photocatalytic oxidation using a UV-LED lamp. The goal of this project was to study the degradation and removal rate of NDMA from water and to compare the removal achieved to results of treatment by a mercury UV lamp. Two concentrations of anatase phase titania photocatalyst, 800 mg/L and 1200 mg/L, were tested with results showing slightly better removal by the lower concentration. Analysis by Gas Chromatography (GC) and kinetics analysis techniques yielded evidence of effective removal at a near first-order behavior. The lamp comparison showed more efficient removal by the mercury lamp when normalized by power usage and reactor volume. As an addition to the project, the risk of NDMA in four major rivers was investigated.

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Chapter 1: Introduction

Wastewater and drinking water treatment are vital for the wellbeing of society and the environment. In the United States, drinking water treatment is regulated by the US Environmental Protection Agency (EPA) Safe Drinking Water Act (SDWA) and wastewater treatment is regulated by various regulations including NPDES and TMDL. With technological advancements, detection of unregulated contaminants is more attainable. One contaminant of increasing concern is N-Nitrosodimethylamine (NDMA), a probable carcinogen (US EPA, 2014b "Technical Factsheet-NDMA"). Prior to the 2000s, NDMA had been studied more in relation to industrial effluent sources than from domestic wastewater effluents but in the early 2000s, NDMA was linked to wastewater and drinking water facilities using chlorine and chloramines for disinfection.

NDMA belongs to a class of chemicals known as nitrosamines. Nitrosamines are organic compounds formed by the reaction of amines with nitrosating agents. The formation of NDMA and its effect on human health has been studied since the 1960s. A 1976 article in *Science* identified this class of chemicals as "suspects in urban cancer" (Shapley, 1976) and the compound was listed on the EPA Contaminant Candidate List 3 published in 2009 as a contaminant known to be present in public water systems with potential need for regulation under the SDWA. The US EPA correlated a concentration of 0.7 ng/L with lifetime cancer risk of 10^{-6} in 1993 (IRIS, 1993). California Department of Human Services initiated a notification limit of 10 ng/L in 2002 following drinking water investigations in the early 2000s (Sedlak & Kavanaugh, 2006).

Since the early 2000s when investigations began in California, assessments of NDMA in surface waters and drinking water distribution systems have been completed and results have shown contamination levels above the 0.7 ng/L risk factor. NDMA forms after disinfection treatment from several possible precursors including dimethylamine, dichloramine, and secondary and tertiary amines. Chlorination and chloramination in drinking water treatment processes lead to the production of an intermediate, unsymmetrical dimethylhydrazine (UDMH), which oxidizes to form NDMA. Results from the EPA 2013 Unregulated Contaminant Monitoring Rule 2 (UCMR 2) showed that NDMA was present above the 0.7 ng/L cancer risk factor in over one quarter of the facilities monitored (EPA, 2012 "UCMR 2 Occurrence Data Summary"). Studies of drinking water sources in Japan reported NDMA ranging from no detectable amount to around 4 ng/L (Asami et al., 2009; Van Huy et al. 2011) and a study of effluent wastewater in the United States reported concentrations of 7.6-400 ng/L (Schreiber et al., 2006). No documented cases of cancer have been directly linked to NDMA in drinking water, but cancer is a considerable concern for society with cancer rates predicted to increase by 70 percent over the next twenty years (Beaubien, 2014). An increased risk for bladder cancer has been linked to long term exposure to disinfection byproducts (CDC, 2012).

The removal of NDMA from drinking water is not yet required by federal regulations, but several methods have shown promise for removing it from industrial wastewater. Direct photolysis with ultraviolet (UV) light is the most common, but several physical methods have been shown to be effective including adsorption to coconut shell activated carbon. UV photolysis with advanced oxidation via hydrogen peroxide was shown by Sedlak et al. to slightly improve NDMA removal in comparison to direct UV photolysis, but at higher concentrations of H_2O_2, removal was lower due to competition between UV absorption of the H_2O_2 and NDMA (Sedlak et al., 2006). The energy usage of direct UV treatment and the cost of adsorption methods limit the desirability of established methods. Further research is needed to determine viable treatment alternatives for NDMA removal.

A form of advanced oxidation using titania (TiO_2) photocatalysts has been used to remove organic contaminants from water. The treatment mechanisms involve oxidation of organics by free radicals generated with exposure to UV light. An ultraviolet-light-emitting-diode (UV-LED) light source is proposed to be more economical than conventional mercury powered UV light sources. The UV-LED lamps last five times longer than mercury UV lamps, cost less, and do not require the disposal of mercury at the end of useful life (Steele, 2007). The lower cost of UV-LED lamps and the enhanced removal of NDMA using TiO_2 nanoparticle photocatalysts could prove ideal for drinking water and wastewater treatment facilities. The purpose of this project was to determine the NDMA removal of TiO_2 with UV-LED activation to provide evidence supporting the suitability of this method for conventional water treatment. Two concentrations of the anatase allotrope were tested to propose the ideal concentration of TiO_2 and to investigate possible limitations caused by TiO_2 in the system.

Chapter 2: Background

This chapter provides background information about the presence of N-Nitrosodimethylamine (NDMA) in drinking water sources and aquatic environments. Natural formation mechanisms and formation as a disinfection byproduct are given along with current detection methods, removal techniques, and regulations. This chapter describes the suspected impact of NDMA on the health of humans and the importance of finding more effective and economical treatment methods.

2.1 Formation

Industrial sources of NDMA include facilities producing hydrazine rocket fuel, tanneries, rubber, pesticide, and dye manufacturers, fish processing facilities, and foundries (EPA, 2014b “Technical Factsheet - NDMA). Historically, NDMA was used for the production of hydrazine rocket fuels in the mid-1970s and 80s (ATSDR 1997). Waste from these industrial sources have been linked with high NDMA in groundwater and surface waters. Understanding the formation of NDMA due to industrial activity gives insight into the formation mechanisms of NDMA in drinking water and wastewater.

NDMA is formed by two mechanisms: nitrosation and unsymmetrical dimethyhydrazine (UDMH) oxidation - further described in Figure 1 (Mitch et al., 2003). In nitrosation, nitrogenous organics and alkylamines react to form NDMA (Smith & Leoppky, 1967). Nitrosation occurs when a nitrosyl cation or dinitrogen trioxide (N_2O_3) is formed during acidification of nitrite in a two-step mechanism (Mitch et al., 2003).

$$HNO_2 + H^+ \leftrightarrow H_2O + NO^+ \quad (1)$$

$$NO^+ + (CH_3)_2NH \rightarrow (CH_3)_2N\text{-}N{=}O + H^+ \quad (2)$$

The rate of reaction is slow at neutral pH, reflected by a second-order rate constant of $1.5*10^{-5}\ M^{-2}*s^{-1}$ at pH similar to drinking water and wastewater treatment systems. Sedlak, D. et al. determined that the formation in treatment systems is likely due to the second mechanism that proceeds via the UDMH intermediate (Sedlak et al., 2006). A study by Gerecke and Sedlak in 2003 evaluated NDMA precursors and NDMA formation in natural systems. They found NDMA formation around 0.1 nM in tests simulating natural occurring NDMA precursors with the influence of typical wastewater effluent, suggesting that natural systems do not provide favorable conditions for the nitrosation mechanism (Gerecke et al., 2006). Once formed, NDMA is highly soluble at a solubility of 290 mg/m^3 at 20 C (Delleur, 2007).

Prior to the early 2000s, NDMA formation from chlorination was considered only to occur via nitrosation and the UDMH oxidation process was constrained to rocket fuel byproducts (Mitch et al., 2003). Its presence had been studied more in relation to industrial effluent sources than from wastewater treatment. In the early 2000s, investigations into the presence of NDMA in drinking water sources was spurred by the detection of extremely high levels of NDMA downstream from a rocket fuel plant in California. The California survey found “unexpected” NDMA in bodies of water that were not impacted by industrial effluents but did contain municipal wastewater effluents (CDPH, 2002).The Department of Homeland Security initiated a study in November 1999 to study the occurrence of NDMA as a disinfection byproduct. All samples from 32 surface water treatment plants demonstrated the presence of NDMA in all after treatment with chloramines, chlorine, or ozone/chlorine. Chloramine treatment was associated with highest NDMA concentration in effluents of water recycling facilities. In addition to the chloramine and chlorine association with NDMA, ion exchange treatment systems also were linked to NDMA formation.

Two studies in 2002 called attention to UDMH as an intermediate in both drinking water and wastewater treatment and drinking water facilities that use chlorination (Mitch & Sedlak, 2002; CDPH, 2002). Figure 1 shows the pathway of UDMH formation and oxidation to form NDMA with dimethylamine as the key precursor. After formation of UDMH, it is rapidly oxidized at near neutral pH, forming NDMA. Competing reactions at near neutral pH like that in the effluent of a wastewater treatment effluent decrease the rate dependence on nitrite and dimethylamine to form NDMA. Any chlorination reaction that produces UDMH also produces NDMA, and previous studies showed that UDMH is formed in a reaction between monochloramine and trimethylamine or dimethylamine. In this mechanism, the slow rate of formation of UDMH limits the rate of formation of NDMA over several days.

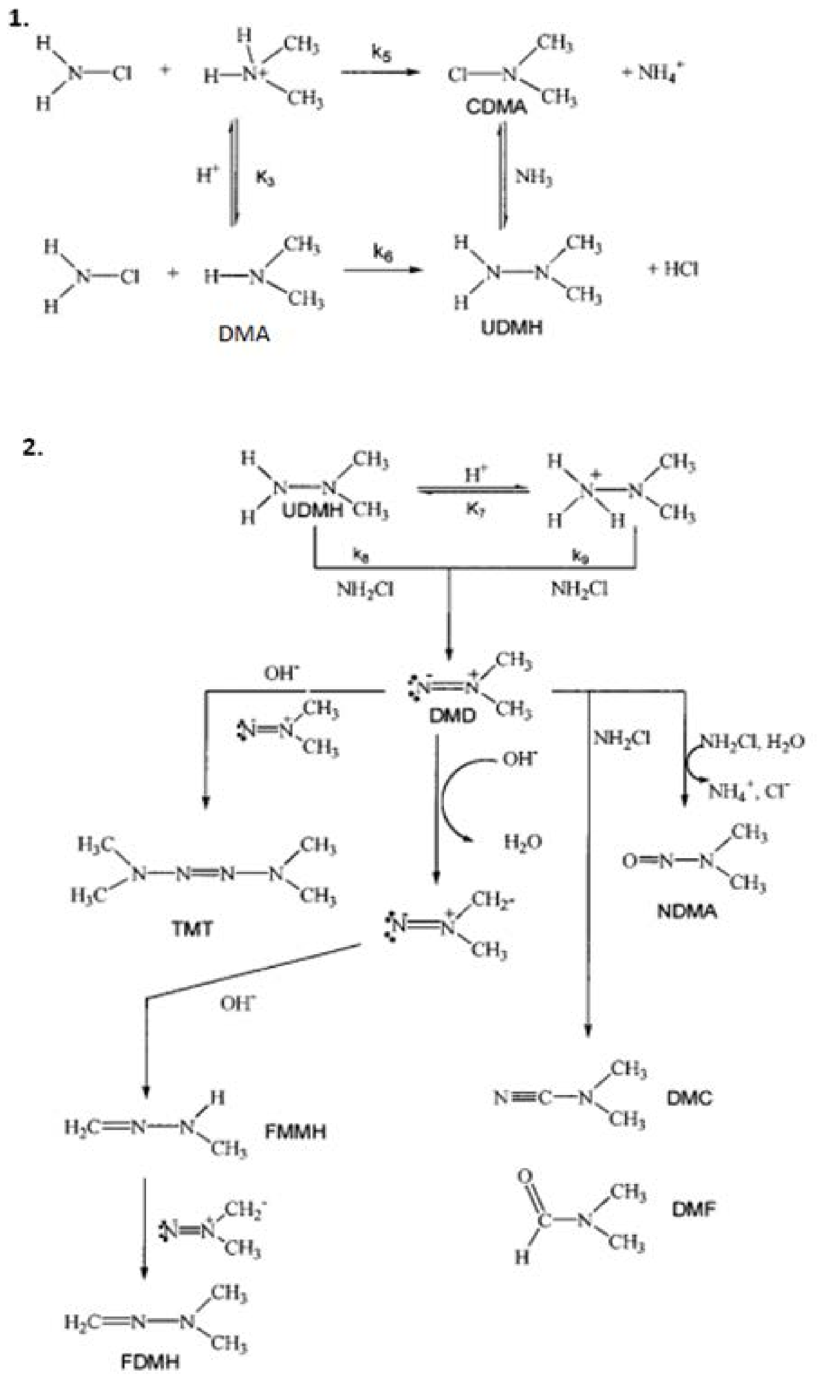


Figure 1 NDMA formation by UDMH pathway: 1. UDMH formation, 2. UDMH oxidation (Mitch & Sedlak, 2002, p. 589)

Anion exchange resins have been linked to the formation of NDMA and NDMA precursors. Commonly used as home-use water treatment systems for contaminated wells, anion exchange resins are used to remove anionic contaminants like nitrates, sulfate, and selenate, and perchlorate (Wagenet, et al., 1995; Kemper et al., 2009). The resins are polymer matrices laced with quaternary amines that facilitate ion exchange with anionic contaminants (Flowers, 2013, p. 7365). A study conducted in the late 1970s found NDMA released when deionized water was passed through resin columns of type 1, trimethylamine (TMA), or type 2, dimethylethanolamine (DMEA), strong-base resins (Fiddler, et al., 1977; Gough et al. 1977). This study found an average of 20 ng/L NDMA formed. A batch test by Najm and Trussel in 2001 using type 1 and 2 resins with chlorine present and 3 hour contact time found NDMA up to 60 ng/L (as cited in Kemper et al., 2009, p.466). However, this contact time was unrealistic for typical treatment. Kemper et al. tested the same type 1 and type 2 resins in batch reactor and column reactor systems with contact time typical of treatment plants (<15 min.) to find nitrosamine formation of 300 ng/L for type 1 resins and 300-700 ng/L for type 2 resins. Type 1 resins produced 4000 ng/L during the normal cycle with initial high levels of 16000 ng/L due to manufacturing residuals from new resins. Type 2 resins steadily produced NDMA precursors at 1500-3500 ng/L (Kemper et al., 2009, p.468).

2.2 NDMA Precursors

Organic nitrogen precursors for NDMA formation are measured as an evaluation of NDMA potential (Mitch, 2003; Sedlak & Kavanaugh, 2006). Dimethylamine is a NDMA precursor present in wastewater. It is excreted by humans at average 40 mg daily per person (Mitch & Sedlak, 2002). Dimethylamine was measured by Sedlak et al. by adding dichloramine to a sample, waiting 5 days, and then measuring NDMA formed. Sampling at conventional contact stabilization wastewater treatment facilities in a study by Sedlak et al. showed a removal of NDMA precursors of 65-75 percent, but even with this removal, NDMA was formed after chloramination and exceeded California detection limit of 10 ng/L (Sedlak & Kavanaugh, 2006, p. xx). In secondary wastewater, organic amines in humic material with nitrogen-containing functional groups can also act as precursors for NDMA formation (Mitch & Sedlak, 2002, p.594). Methods for reducing NDMA precursors have been suggested by Mitch et al., such as removing ammonia prior to adding chlorine, reducing formation of dichloramine and dimethylamine (DMA). If nitrification is conducted before the addition of free chlorine, the NDMA precursors will be lower.

Since dimethylamine and nitrogenous organics are not likely to be present in drinking water and secondary wastewater. Mitch & Sedlak suggested other precursors for NDMA formation such as other secondary and tertiary amines after alkyl groups are removed by oxidation (Mitch & Sedlak, 2002).

2.3 Detection

Several methods are currently used for NDMA detection including gas chromatography, mass spectroscopy and then high resolution electron impact mass spectroscopy followed by low resolution ionization, liquid-liquid extraction, and solid phase extraction using Ambersorb absorbent material (Sedlak, 2006). Chemical ionization with tandem mass spectrometry is most commonly used.

The US EPA has published several methods (EPA, 2014) for measuring NDMA in drinking water (Method 521) and wastewater (Methods 607 and 1625). The Ontario Drinking Water Quality Standards (ODWQS) Accepted Drinking Water Testing Methods published in 2008 also gives three methods for detecting NDMA (MOE, 2008):

- EPA and MOE Method 521: Solid Phase Extraction (SPE) and capillary column gas chromatography (GC) with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (MS)
- EPA Method 607: Methylene chloride extraction, GC and nitrogen-phosphorous detector
- EPA Method 1625: isotope dilution, GC and MS
- MOE Method E3291: Gas Chromatography-High Resolution Mass Spectrometry (GC-HRMS) by adsorption to Ambersorb 572 followed by elution into an organic solvent
- MOE Method E3388: GC-HRMS with addition of dn-N-nitrosodi-n-propylamine as an internal standard

According the US EPA in its 2012 *Guidelines for Water Reuse*, recent improvements in analytical capabilities have led to the increased detection of NDMA in water. However, methods of detection have been available for decades: a research study published in 1974 studying NDMA in treated lake sewage and lakewater used thin-layer and gas chromatography, ultraviolet and infrared spectrometry, and combined gas chromatography-mass spectrometry (Ayanaba, 1974, p.83).

2.4 Occurrence in Drinking Water, Wastewater Treatment Effluents, and Surface Waters

Increased monitoring of for NDMA in drinking water and drinking water sources can be attributed to its inclusion on the Contaminant Candidate List (CCL), first appearing in 2002 and included in the CCL4 draft released on February 4, 2015 (Drinking Water Contaminant Candidate List 4-Draft, 2015). Studies of NDMA in wastewater, surface waters, and influents and effluents of drinking water treatment systems have found detectable amounts of NDMA. A report by Sedlak et al. included a summary shown in Figure 2 of NDMA in surface water, recycled water, and secondary effluents from wastewater treatment systems (Sedlak, 2006). All values are predicted to produce risk higher than the EPA 10^{-6} lifetime cancer risk level.

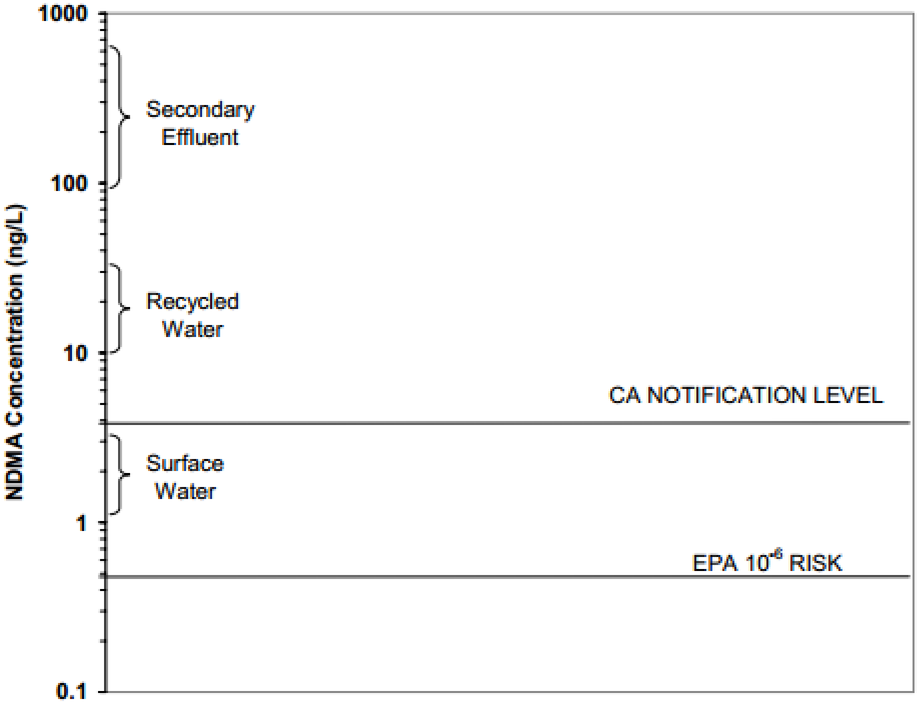


Figure 2 Typical distribution of NDMA concentration in surface waters impacted by wastewater (Sedlak, 2006, p.7)

Despite separation of wastewater effluents from drinking water sources, Sedlak states that indirect potable water reuse increases the potential for wastewater treatment effluents to contact drinking water sources. Treated wastewater effluent is used in applications such as irrigation, groundwater recharging, and industrial uses. The US EPA expects wastewater reuse to become more popular in the US as advancements are made in wastewater treatment technologies (US EPA, 2012). In 2012 the US EPA published *Guidelines for Water Reuse* to address the impact of intentional wastewater reuse on human health and the environment. Disinfection of treated wastewater is required, but no residual chlorine is required. The EPA acknowledges the presence of NDMA as a carcinogen present in water reuse applications at levels higher than human health protection limits. The topic is defined as critically requiring further investigation and action (EPA, 2012, p.224).

Unplanned wastewater reuse occurs in conditions of dry weather in inland areas. A 1980 study predicted 7.7 million people in the US were using utilities with at least 50% reused wastewater (Swayne, et al., 1980). Wastewater effluent discharged to surface waters can become part of drinking water treatment facility influents (Sedlak et al., 2006). The EPA *Guidelines* references the SDWA national standards for drinking water quality protection, stating that human health will be protected through Maximum Contaminant Limits (MCLs). Unfortunately, at this time NDMA does not have a MCL. The presence of NDMA in the environment has been documented, however, and an evaluation of several published studies follow.

2.4.1 Case Studies

The distribution systems studied in the 2002 California survey previously introduced had an average of 2.4 ng/L and within the distribution systems the chloramine treated streams had the highest concentration of NDMA at 3.0 ng/L (CDPH, 2002). Ozone/chlorination had an average concentration in the distribution system of 1.8 ng/L, and chlorination averaged 1.2 ng/L in distribution systems.

In the California survey, the effluent and distribution samples had measurable amounts of NDMA and in most cases, the concentration increased from influent to distribution (CDPH, 2002). Results were not consistent for every facility using the same type of disinfection. Multiple NDMA formation mechanisms and rates were suspected to occur, depending on the water quality and conditions. Correlations were found between higher levels of NDMA and longer retention times in the distribution system, the presence of cationic polymers, and the use of chloramines. Increased awareness of cancer-causing chemicals in drinking water led to the 2005 EPA Stage 2 Disinfectants and Disinfection Byproducts Rule for monitoring of chlorination byproducts trihalomethane (THM), haloacetic acids (HAA), chlorite, and bromate (2006). According to Schreiber, et al., the rule has led facilities to switch from chlorine treatment systems to chloramine systems (Schreiber & Mitch, 2006). The EPA estimated that 75,000 facilities would be affected by the rule, but only a small portion would require treatment changes (EPA, 2006). The Schreiber researchers reported NDMA in effluent from municipal wastewater treatment plants in the US between the range of 7.6 - 410 ng/L (Schreiber & Mitch, 2006).

The most common source of drinking water, surface waters, may be impacted by NDMA concentrations by wastewater effluents. In a nationwide survey of NDMA in raw water and treated water in Japan found NDMA in 15 of 31 raw water samples (Asami, 2009). NDMA concentrations in raw river water studied throughout Japan were higher in more populated areas. A study by Zhang et al. found significant levels of NDMA in all sample locations of the Huangpu River in China (Zhang et al., 2014). The work by Zhang et al. included a literature review referencing past reports of NDMA measured in surface waters around the world. Table 1 shows the data gathered. Municipal wastewater treatment effluents measured in the United States had the highest levels of NDMA documented in literature. NDMA precursors in the Buyokcekmece watershed in Turkey had high NDMA formation potential (NDMA-FP).

Table 1 Documented NDMA data in literature (originally compiled by Zhang et al., 2014)

Location	NDMA Concentration, ng/L	Reference
Drinking water sources: Raw waters and treated waters in Japan	ND-4.3	Asami et al., 2009
Groundwater and river water in Tokyo, Japan	Groundwater: <0.5-5.2 NDMA; 4 - 84 ng-NDMA eq./L River water: < 0.5-3.4 NDMA; 11 - 185 ng-NDMA eq./L	Van Huy et al., 2011
Municipal wastewater effluents, USA	7.6-400	Schreiber and Mitch, 2006
Lake water in Istanbul: Buyokcekmece watershed, Turkey	Measured NDMA formation potential at range: <2 to 1648 ng/L	Aydin et al., 2012
Two chloraminating water treatment facilities in Alberta, Canada from 2003-2005	2-180	Charrois et al., 2004
Inlets of 12 DWTPs in Beijing, China	ND-13.9	Wang et al., 2011
Shallow groundwater, river water, and wastewater in the Jialu River Basin, China	31.7 +/- 49.5	Ma et al., 2012

Drinking water and wastewater are impacted by the presence of NDMA. These two types of facilities have differing treatment processes and influents. Wastewater facilities treating carbonaceous and nitrogenous containing sources and also using chlorine disinfection, and have been associated with high concentrations of NDMA in effluents (Sedlak et al., 2005). Another study by Sedlak et al. for the Water Reuse Foundation measured average concentrations greater than 400 ng/L in wastewater treatment facilities with industrial influences ranging from <2 to 18% by volume (Sedlak et al., 2006). The study identified facilities reusing wastewater effluents treated with chlorine as most susceptible to high NDMA formation. In addition to the effect on surface waters, aquifers recharged with treated wastewater are affected by persistent NDMA. Concentration of precursors in underground aquifers may be lower than surface waters due to underground degradation. Van Huy et al. tested groundwater samples and found levels of NDMA similar to surface waters sampled but a concentration of NDMA precursors that was lower than river water samples. They suggested that the precursors can be removed during infiltration via biodegradation, adsorption, or volatilization (Van Huy, 2011, p.3369). The persistence of NDMA in groundwater is further described in Section 2.5.

2.5 Fate in the Environment

The presence of NDMA in wastewater effluents to surface waters and its formation at near-neutral pH (Ayanaba, 1976) support the concern for the need to control NDMA and NDMA precursors in water discharged from wastewater treatment facilities. NDMA is semi-volatile and soluble in water at 25 C (EPA, 2014). It has a solubility of 290 mg/m^3 at 20 C and a Henry's Law coefficient of $2.6*10^{-4}$ atm/M at 20 C (Delleur, 2007). In surface waters and air it degrades by UV photolysis. Biotransformation and volatilization are the main degradation mechanisms in the underground vadose zone above the water table (Zhou et al., 2009). Despite UV photolysis by natural light, the rate of degradation in surface waters is slow enough to allow detection. This is reflected by measurable amounts of NDMA in rivers and lakes in Japan and China (Asami, 2009; Ma, 2012; Van Huy, 2011).

Persistence of NDMA in groundwater is demonstrated by its presence in groundwater wells in the vicinity of rocket fuel production plants and its presence in California wells recharged with wastewater. However, the persistence of NDMA underground may be dependent on the microorganisms present. A study of NDMA attenuation in a groundwater treatment system found evidence that both aerobic and anaerobic degradation by native microorganisms significantly reduced NDMA and prevented migration from the aquifer being treated (Gunnison et al., 2000). The study also concluded that NDMA adsorption to site soils was negligible.

2.6 Effects on Human Health

Nitrosamines have been identified to cause cancer in mammals, and are particularly damaging to the liver and gastric systems (US Dept. of Health, 2011). In recent years, the currently unregulated presence of nitrosamines in drinking water has been of increasing concern. The recent CCL4 draft released by the EPA in February 2015 lists NDMA as a contaminant candidate, stating its presence from industrial residuals and its potential to form as a disinfection byproduct (Drinking Water Contaminant Candidate List 4-Draft, 2015). The presence in drinking water is a health concern. NDMA has a drinking water risk factor two to three orders of magnitude higher than currently regulated halogenated DBPs (Charrois & Hrudey, 2007). The historical focus on halogenated DBPs is largely due to the ease of detection and their abundance in drinking water, but improved detection limits have facilitated the measurement of other contaminants as well. Charrois & Hrudey state the need to focus on the significance of health risks associated with these small yet impactful levels of contaminants (p.104). They state that while small, an increased risk for bladder cancer and reproductive problems has been linked to drinking water chlorinated DBPs like NDMA. This small increased risk could translate to a significant number of cases in the large population of consumers exposed to disinfected drinking water.

While unregulated in drinking water, NDMA is a chemical hazard with associated safety documents like MSDS and entry in the NIOSH Pocket Guide to Chemical Hazards. NIOSH lists inhalation, skin absorption, and ingestion as routes of exposure with symptoms such as nausea, headache, fever, and decreased liver, kidney, and pulmonary function (CDC, 2014). The recommended personal protective equipment include preventing skin and eye contact. The toxicological profile from the Agency for Toxic Substances & Disease Registry (ATSDR) was created in 1989 and was last updated in 2011. It states that NDMA is a likely carcinogen to humans based on laboratory tests on animals with human exposure through food containing NDMA, cosmetic products, rubber materials, and occupational exposure associated with tanneries, rubber manufacturing, and laboratory work (ATSDR, 2011).

The EPA publishes the Integrated Risk Information System (IRIS) database to share information about the health risks of chemicals. Table 2 shows the risk factors published in 1993. The risk factor for drinking water concentration providing the increased risk of cancer of 1 in 10,000 is 70 ng/L. According to IRIS, the Oral Slope Factor, or proportion of the population affected by an *excess* (less than 1 in 100 risk level) lifetime cancer risk when exposed to a lifetime exposure of 1 milligram per kilogram of body weight per day is 51 per mg per kg/day (IRIS, 1993).

Table 2 IRIS drinking water concentration providing cancer risk (IRIS, 1993)

Cancer Risk Level	NDMA Concentration, ng/L
1 in 10,000	70
1 in 100,000	7
1 in 1,000,000	0.7
Oral Slope Factor	51 mg/kg/day

In the case studies listed in Table 1 of this paper, nearly all upper bounds of the reported ranges are in excess of the 1 in 10,000 cancer risk level of and nearly all lower bounds of reported ranges exceed the 1 in 1,000,000 risk level (Zhang et al., 2014). The average NDMA measured in distribution systems in the California drinking water study exceeded the 1 in 1,000,000 risk level (CDPH, 2002). A study by Charrois et al. found that four of the 11 public drinking water distribution systems that treated with chloramines had concentrations nearly meeting the 1 in 10,000 risk level with an average of 50 ng/L and a median of 66 ng/L (2007).

2.7 Current Regulations and Safety Limits

The Safe Drinking Water Act (SDWA) does not currently regulate NDMA in drinking water. The presence of NDMA in drinking water, its potential risks, and need for regulations to address the issue were first acknowledged by the EPA in the 2009 CCL 2 (EPA, 2009). The miscibility with water and carcinogenic effects lead to concern, especially with increased detection capabilities and more testing targeting NDMA in drinking water. In its 2012 *Guidelines for Water Reuse*, the EPA defines lack of regulations as a critical issue (EPA, 2012). By now, NDMA has shown up in a number of US regulations and reports such as the Unregulated Contaminant Monitoring Regulation Rule 2 (UCMR 2). However, the documents include limited information. There is no federal maximum contaminant level (MCL) for NDMA (EPA, 2014). As previously mentioned, the CCL4 draft contains NDMA in its list of contaminants. Its presence on this list and the last two CCL publications shows the importance of investigating and developing regulations for NDMA in drinking water.

Establishing a notification level and response level is a method for protecting public health from contaminants that do not yet have maximum contaminant levels (MCL). Public outreach is required when a contaminant reaches the notification level and the drinking water source should be taken out of service when the response level is reached (CDPH, 2010). In 2007, the UCMR 2 was published, setting a notification level of 7 ng/L for NDMA (EPA, 2013). The rule required selected public water systems (PWs) to monitor NDMA and 24 other contaminants over a period from January 2008 to December 2010. The method for detection of NDMA was EPA 521 and the selected PWs included all PWs serving more than 100,000 people and 480 representative PWs serving 10,000 people or less. Data is publicly available. Of the 1198 PWs that analyzed for NDMA, 324 had NDMA measured above the reporting limit. The average level of NDMA reported by was 9 ng/L and the maximum detected was 630 ng/L (EPA, 2013). The median detection was 4 ng/L. Aside from the UCMR2 monitoring, the state of California requires monitoring for NDMA for recycled water projects with indirect potable reuse (CDPH, 2010).

In addition to the US investigations, Canada and the European Union are also actively contributing to determine the acceptable limits of NDMA in drinking water (Selin, 2011). In 2010, the Canadian Environmental Protection Agency proposed a maximum acceptable NDMA concentration in drinking water to be 40 ng/L in 2010 (Health Canada, 2010; as cited by Selin, 2011, p. 8). While federal research is ongoing in the US, individual states are developing their own regulations, California has done the most research on these nitrosamines and established a Public Health Goal limit in 2006 for NDMA in drinking water at 3 ng/L associated with *de minimis* cancer risk.

Table 3 Nitrosamine concentrations in drinking water (California Environmental Protection Agency, 2013)

Nitrosamine	**10^{-6} Risk Level (ng/L)**	**Notification Level (ng/L)**	**Response Level (ng/L)**
N-Nitrosodiethylamine (NDEA)	1	10	100
N-Nitrosodimethylamine (NDMA)	3	10	300
N-Nitrosodi-n-propylamine (NDPA)	5	10	500
N-Nitrosodi-n-butylamine (NDBA)	3	--	--
N-Nitrosomethylethylamine (NMEA)	1.5	--	--
N-Nitrosomorpholine	5	--	--
N-Nitrosopiperidine (NPIP)	3.5	--	--
N-Nitrosopyrrolidine (NPYR)	15	--	--

As shown above in Table 3, the most recent updates from the California Environmental Protection Agency toward drinking water issues mainly focus on Nitrosamines were made on December 29th, 2013 with notification and response levels for concentrations of several kinds of nitrosamines. A concerning observation is that the literature review conducted for this paper found that most case studies of distribution systems and surface water bodies (listed in Table 3 and discussed in section 2.4.1 of this report) measured NDMA concentrations above notification levels and response levels set by the US and Canada.

The Massachusetts Government published its analytical NDMA concentration on the government website in May 2014. The current MA regulatory limit is 10 ng/L which is the level detectable by most analytical laboratories (Energy and Environmental Affairs, 2004). However, these safety limits suggested by different states are only providing reference and guidelines to local governing agencies and consumers according to California Environmental Protection Agency. Scientists are still working on the accurate and official limit of NDMA and such nitrosamines. It might take several years to finally determine the MCL for NDMA in drinking water (MA EEA, 2004).

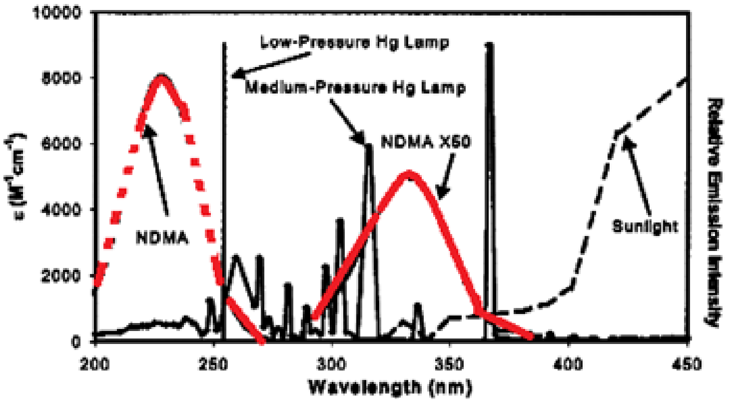
2.8 NDMA Treatment

Methods to remove NDMA are being developed and improved as time goes on. Several treatment methods are already being used by industrial wastewater treatment plants including UV treatment primarily and adsorption to physical media. Emerging methods like UV advanced oxidation and resin adsorption have potential for future use but currently require additional research before they can be implemented on a large scale. Biodegradation may also be effective for removing NDMA.

2.8.1 Ultraviolet Treatment

Photolysis by ultraviolet light (UV) radiation has been found to be an effective technique for NDMA removal from water (Mitch et al., 2003). Organic nitrogen, an important NDMA precursor, can be treated via photolysis which is a chemical process to break molecules down to smaller units by light absorption. At NDMA concentrations below 1 mg/L, the photolysis reaction order is first order (Bolton, 2001 as referenced by Sedlak et al., 2006, p. 68).

Currently, there are two major UV treatment methods: low pressure UV lamp output and medium pressure UV lamp output. By comparing NDMA absorption spectrum with the output wavelengths of the two types of UV lamps as shown in Figure 3, low pressure UV lamp spectrums are a perfect match with the first peak of NDMA at the range of 225-250 nm. Medium pressure Hg lamps match well with the second NDMA absorbance peak at 300-350 nm.



<u>NDMA Absorbance Peaks</u>
225-250 nm
300-350 nm

Figure 3: UV lamp and NDMA absorbance wavelengths (Mitch et al., 2003, p.397)

A typical Low-Pressure Hg Lamp would provide UV light at a wavelength within the first absorbance peak to cleave the N-N bond. As shown in Figure 4 below, the medium pressure UV lamp, as shown in the spectra, produces UV light with a range of wavelengths between 200 nm and 270, also matching with NDMA spectra. According to researchers comparing the low and medium pressure lamps, photolysis with low pressure UV lamps has been found to achieve higher removal rates and is more cost effective than medium pressure UV lamps (Sedlak et al., 2005).

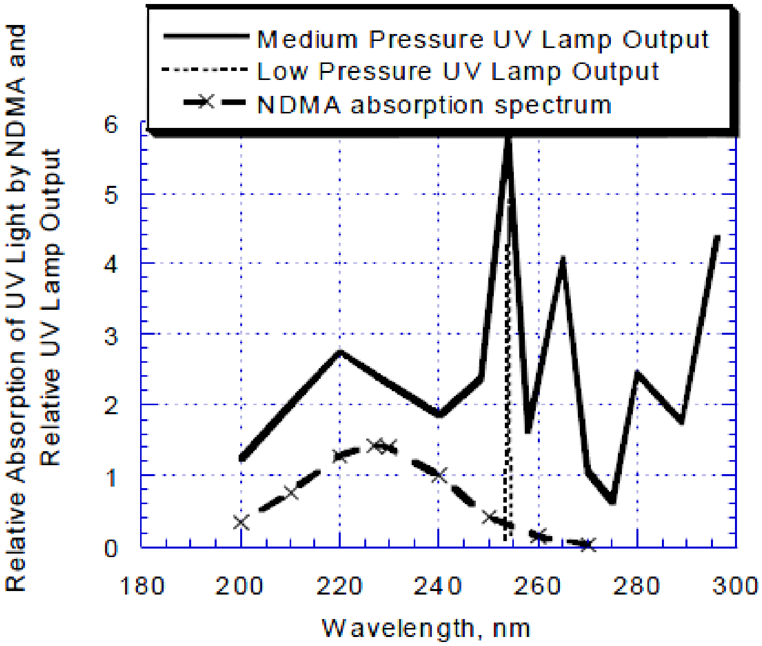


Figure 4: Absorption spectra of NDMA with low/medium pressure UV lamp output (Whitley Burchett & Associates, 2000 as referenced by Sedlak et al., 2006, p. 60)

The UV light could cleave the N-N bond, with the remaining NO fragment could then be oxidized to nitrite, nitrate, and dimethylamine. UV light removes both NDMA and its precursor, dimethylamine. This removes NDMA and also inhibits further formation of NDMA. The mechanism is illustrated in Figure 5 below.

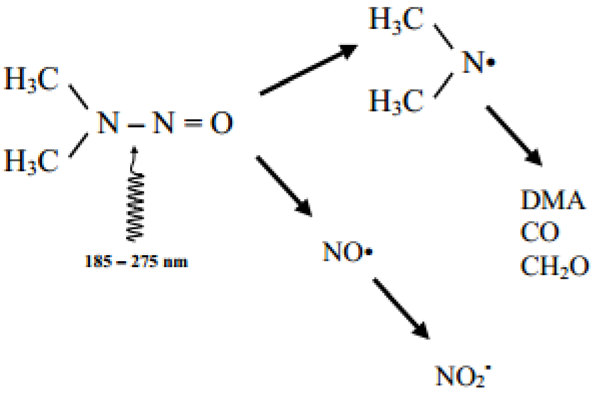


Figure 5: UV-Photolysis reaction mechanism (Chow, 1973; Hanst and Spence, 1977; as cited by Sedlak et al., 2006, p. 59)

Building from the establishment of UV treatment for NDMA removal, a more advanced method of combining UV after microfiltration (MF) and reverse osmosis (RO) has also been found to remove NDMA and NDMA precursors sufficiently. Results are obtained by comparing the sample composition of NDMA and NDMA precursors before and after each step from Orange County Water District (OCWD) in California (Plumlee et al., 2007). MF, as a pretreatment step prior to RO, could help removing suspended solids and organic carbon instead of actually removing NDMA and its precursors. Through the RO step, NDMA such low molecular weight organics is hard for removal, only achieving a removal rate of 50%. However, NDMA precursors could be removed by selecting RO membranes according to their different functions, which could achieve as high as 98% (Sedlak et al., 2006). Finally, the effluent from RO treatment is sent through UV treatment. The sample collected from OCWD greatly reduced its NDMA concentration to meet the state's NDMA regulation levels. Therefore, with a basis of UV treatment, trained step of MF-RO-UV could be another effective treatment method if regardless of the cost.

2.8.2 Physical Methods

The primary method for removing NDMA by physical methods is adsorption. Physical treatment methods involving volatilization are impractical due to the physical properties of NDMA. Pure NDMA has a relatively high vapor pressure of 2.7 mm Hg (approximately 360 Pa) at room temperature and a relatively low Henry's Law constant of about 2×10^{-6} atm*m^3/mol at room temperature, meaning it will generally remain in solution with water at atmospheric pressure (as cited by Mitch et al., 2003, p.396). Adsorption was used to at a remediation project at the rocket-fuel impacted groundwater at Rocky Mountain Arsenal in Denver, CO (Fleming et al., 1996). At first, the existing granular activated carbon media targeting other contaminants was assessed for NDMA removal with poor removal observed. Further adsorption media were tested in bench scale and column tests using coconut activated carbon and carbonaceous resin, particularly Ambersorb(R) 572. These were much more effective than coal GAC. The study concluded that the existing granular-activated carbon groundwater treatment system at the Rocky

Mountain Arsenal site could be modified to effectively remove NDMA rather than constructing a new system for NDMA removal.

The possibility for adsorption of the NDMA by aquifer soils was determined insignificant by a further study at Rocky Mountain Arsenal. This testing was initiated when NDMA was observed to decrease from 200 ng/L to no measured amount in an area down-gradient of the GAC treatment effluent (Gunnison et al., 2000, p.181). The researchers concluded that biodegradation was the main mechanism in the underground NDMA removal and soil adsorption and determined that biodegradation had a significant impact while adsorption by soils was insignificant.

Physical removal by adsorption to zeolites is possible but limited; one study found around 17 mg/g removal by zeolite (as cited by Xiaodong et al., 2009). Xiaodong et al. tested surface altered activated carbons and found adsorption capacity of 25 mg/g from water. The most effective activated carbon was AC-3 that has a pore size of 0.46 nm, closely fitting the NDMA molecular dimension of 0.45 nm.

2.8.3 Biodegradation

The rate of NDMA biodegradation and its effectiveness have great variability in different natural environments. Biodegradation pathways are unpredictable since NDMA in natural environments occurs at low concentrations (Fournier et al., 2009). However, a study by Fournier et al. showed that *Rhodococcus ruber* ENV425 was effective at removing NDMA from µg/L concentrations to levels below 2 ng/L. The study by Gunnison et al. concluded that *Pseudomonas sp.* in both anaerobic and aerobic conditions could be associated with NDMA degradation of 30-60% following first-order kinetics (Gunnison et al., 2000). This biological treatment was applied to NDMA contamination in the 50 to 500 microgram/kg range over 30 days (p.196). They identified the potential to encourage underground biological activity by adding nutrients to an aquifer over a scheduled time frame while carefully monitoring to avoid excessive growth.

2.8.4 Future Treatment Technologies

More research is needed to discover effective techniques which could have better performance and lower cost. UV Advanced Oxidation and resin adsorption might be two potential methods. Yet, no published test results could support this idea. All in all, there is still a long way to go to improve NDMA treatment methods. To improve water quality and further protect human health, more research should be done with developing corresponding regulations and treatments.

2.9 Titania Photocatalyst

A form of UV Advanced Oxidation uses the ability of TiO_2 to produce radicals under UV light. Titania, also known as titanium dioxide with a formula of TiO_2, is a commonly occurring mineral. Among all allotropes of TiO_2, rutile and anatase are the most dominant and stable forms. Because of their chemical stability, non-toxicity, and abundance in nature, TiO_2 has been used in a wide range of applications, such as in paints, plastics and paper. Recently, more studies and researches on TiO_2 as photocatalyst for organic pollutants decomposition have been investigated, especially on chemical stability, structure, and energy to rutile and anatase. When excited - typically by UV light, TiO_2 produces hydroxyl radicals that attack the adsorbed molecules on the TiO_2 surface. This follows the general reactions below (Carp, Huisman, and Reller, 2004):

$$TiO_2 + hv \rightarrow h_{VB}^{+} + h_{CB}^{-}$$

$$h_{VB}^{+} + H_2O \rightarrow \cdot OH + H^{+}$$

Rutile, which contains 93% TiO_2, is titania's primary modification. With a body-centered tetragonal structure as shown in Figure 6, it is the most stable form and could achieve the highest refractive indices to visible and infrared wavelengths up to 4.5 μm ("Rutile," 2014).

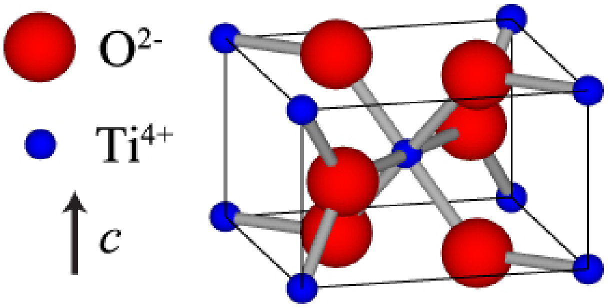


Figure 6: Unit cell of rutile TiO2 (Gunnlaugsson et al., 2014)

Anatase is often found as small, isolated, and sharply developed crystals. With the structure shown in Figure 7, even though it has the same overall tetrahedral structure, anatase has a bond angles of 82°9' comparing to the angles of rutile at 56°52 ½ '.

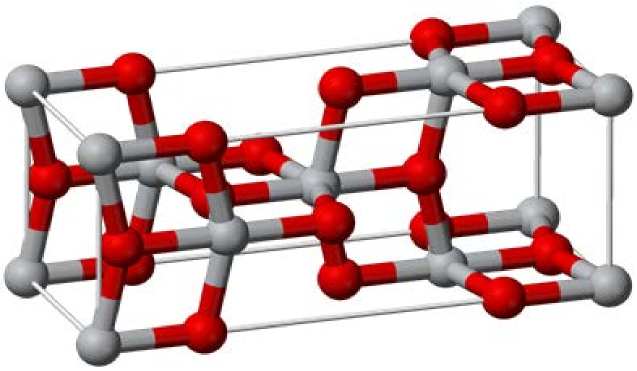


Figure 7: Structure of anatase (Crystal Structure of Anatase)

Whether rutile or anatase is the better photocatalyst is a constant debate topic. A study by Matsumura et al. concluded that anatase has a lower activity for water oxidation than rutile but has a comparatively high activity for oxidation of low concentrations of reactive compounds (Ohno et al., 2002). On the other hand, there are other studies suggesting that anatase was more active than rutile. Experiments on bulk transport effects of excitons of the two polymorphs to the high-quality epitaxial TiO_2 film surfaces have been conducted (Luttrell et al., 2014). The film surface increased up to about 5 nm activated by anatase, while increased up to about 2.5 nm activated by rutile. The experimental results showed that anatase carrying a charge could have better surface interactions with NDMA. Unfortunately, there is no agreement on the better choice for photocatalysis.

With the uncertain distinction between rutile and anatase, a mixed-phased TiO_2 nanoparticles with the two main polymorphs has been tested. Results from the experiment showed that a third intermediate phase could be created through the reaction. Comparing to the pure phases, particles of this third phase intermediate were arranged in a certain way in the tetrahedral which would help with charge transfer, trapping, and even reaction (Li et al., 2008).

Chapter 3: Methodology

The laboratory procedure was conducted in a 4-month period (October, 2014 - January, 2015). Safety was a high priority, and precautions were taken to protect lab workers. This chapter describes the procedures that were followed.

3.1 Sample Preparation

Stock solutions of NDMA were prepared twice during the four month laboratory work session using a standard NDMA solution provided by Supelco (ampoule of 100 mg analytical standard). The exact NDMA stock solution concentration were concluded in Table 4. A stock solution was prepared in a glass 40 mL vial using 0.10 mL pure NDMA and adding 28.5 mL of purified water. Pure NDMA (0.1 mL) was dispensed from the ampoule of analytical standard NDMA provided by Sigma-Aldrich (100 mg ampule), and water was measured by weight with an analytical balance. The ampoule was measured before and after the NDMA was withdrawn to determine the exact amount present in stock solution. The vial of stock solution was covered in aluminum foil and stored in a refrigerator at 4 C.

Table 4: NDMA stock solution concentration

Stock Solution	NDMA Stock Solution Concentration
1: For 2014 Nov-Dec uses	3509 mg/L
2: For 2015 Jan-Mar uses	3337 mg/L

3.2 GC Measurement Procedure and Standard Curve

The gas chromatograph (Agilent 6980N with Combi Pal, CTC Analytics) in the WPI Water Lab in Kaven Hall was used to determine the concentration of NDMA in water samples. A headspace Solid Phase Microextraction technique with Gas Chromatography and Flame Ionization Detector was used (HS-SPME-GC) with chlorobenzene internal standard (CHROMASOLV for HPLC, Sigma Aldrich, 99.9%). The method was developed by Jose Alvarez Corena, a graduate student at WPI conducted a previous study of NDMA removal using the same instrument. Specific settings are detailed in Appendix A. Sample vials (20 mL) containing 4 g NaCl (Fisher, ACS Crystalline, 99.8%) were filled with 10 mL of sample, spiked with 0.05 mL of 10 mg/L chlorobenzene solution, shaken for 30 seconds to mix thoroughly, and measured by GC from lowest to highest concentration (concentration was assumed to decrease over treatment time). Based on previous experience by Alvarez Corena, the chromatogram peaks were expected at 21 minutes for chlorobenzene and 18 minutes for NDMA. The standard curve was generated by plotting the NDMA peak area divided by the chlorobenzene peak area versus the known concentration of NDMA.

The standard curve was generated using four samples of known NDMA concentrations: 4 mg/L, 1 mg/L, 0.5 mg/L, and 0.10 mg/L. The first sample with the concentration of 4 mg/L was made from 0.1 mL of the stock solution and 88 ml of purified water. The rest of the solutions at lower concentrations were made by sequentially diluting the previous more concentrated solution. After mixing each standard solution in parafilm covered beakers for 15 minutes, 10 mL of the solution was transferred to 20 mL GC vial using a 10 mL autopipette. Dilutions used are shown in Table 5. A 50 mL glass pipette was used to measure the initial water to an accuracy of 1 mL and subsequent water additions were added using 10 mL micropipettes.

Table 5: Matrix for calibration standard solutions

Standard Solution Concentration	Amount of solutions at various concentration	Amount of water needed
4 mg/L	0.10 mL of stock solution (3509 mg/L)	88 mL
1 mg/L	10 mL of 4 mg/L solution	30 mL
0.5 mg/L	20 mL of 1 mg/L solution	20 mL
0.10 mg/L	5 mL of 0.5 mg/L solution	20 mL

3.3 UV-LED TiO_2 Treatment Procedure

The experiment was carried out in three main steps: preparation of samples and initial measurements, mixing TiO_2 without UV treatment, and UV-LED treatment.

3.3.1 Preparation

Before each trial with the UV-LED reactor, 600 mL of 4 mg/L solution was prepared by adding 600 mL of purified water to a 1000 mL beaker using a volumetric flask, and then adding 0.38 mL of stock solution with a micropipette (0.719 mL for stock solution 2). The solution was covered with parafilm and placed on a magnetic stir plate and allowed to stir for at least 15 minutes prior to conducting UV/TiO_2 treatment.

Prior to conducting each trial using the UV-LED lamp, 10 mL of the untreated 4 mg/L NDMA solution was analyzed in order to ensure the NDMA starting concentration and stability with storage time. This was to provide a baseline for NDMA concentration prior to UV-LED/titania treatment and to verify that the GC system was working properly according to the standard curve.

3.3.2 Titania Photocatalyst Activity

Anatase (99.9+% pure, 10-25 nm) provided by Aerodyne Research, Inc., Billerica, MA was tested with the UV-LED treatment to determine the best concentration for the NDMA removal effect.

A previous MQP tested the concentration of ciprofloxacin (CIP) using the same photocatalyst (Fogarty, 2013). The concentration of CIP decreased slightly immediately after adding the TiO_2. This decrease was suspected to be due to surface adsorption onto the TiO_2.In order to determine whether

NDMA may be adsorbed by the TiO_2 surface, prior to each UV-LED photolysis treatment session, TiO_2 was added to the prepared 4 mg/L solution and allowed to mix for 20 minutes without the UV treatment. A sample was taken before and after the 20 minute mixing to determine if any removal was achieved. Samples were filtered using with an interchangeable hypodermic syringe equipped with syringe filters (Minisart RC15, Sartorious Stedim, RC membrane, 0.20 µm). GC analysis was carried out and concentration was determined using the standard curve.

3.3.3 UV-LED Lamp Treatment

Two anatase TiO_2 concentrations were tested at 1200 mg/L and 800 mg/L based on prior research finding 1000 mg/L TiO_2 to be optimum for photocatalytic oxidation (Gad-Allah, 2010; Fogarty, 2013; Alvarez Corena, 2014). An analytical balance (AB104-S Mettler Toledo) was used to weigh the appropriate amounts of TiO_2 with accuracy of ±0.001 g. The matrix below shows the amounts used in each setup.

Table 6: Trials for UV-LED anatase tests

Trial	NDMA initial Conentration	Anatase Concentration	Mass TiO_2
1, 2	4 mg/L	1200 mg/L	0.720 g
3, 4	4 mg/L	800 mg/L	0.480 g

Lamp Setup

An Ultraviolet- Light Emitting Diode (LED) lamp assembly supplied by Aerodyne Research (Nichia NC4U133A, 360 nm) was used to conduct UV LED experiments. The reactor is shown in Figure 8. The UV-LED reactor is a 1000 mL glass beaker with clamp-suspended quartz test tube containing the UV-LED lamp. The reactor was covered by a large cardboard box during treatment to protect lab workers from UV exposure. The adjustable power supply provided by Aerodyne Research was set at 14 Volts and 1.0 Amps, verified prior to each trial with a voltmeter.

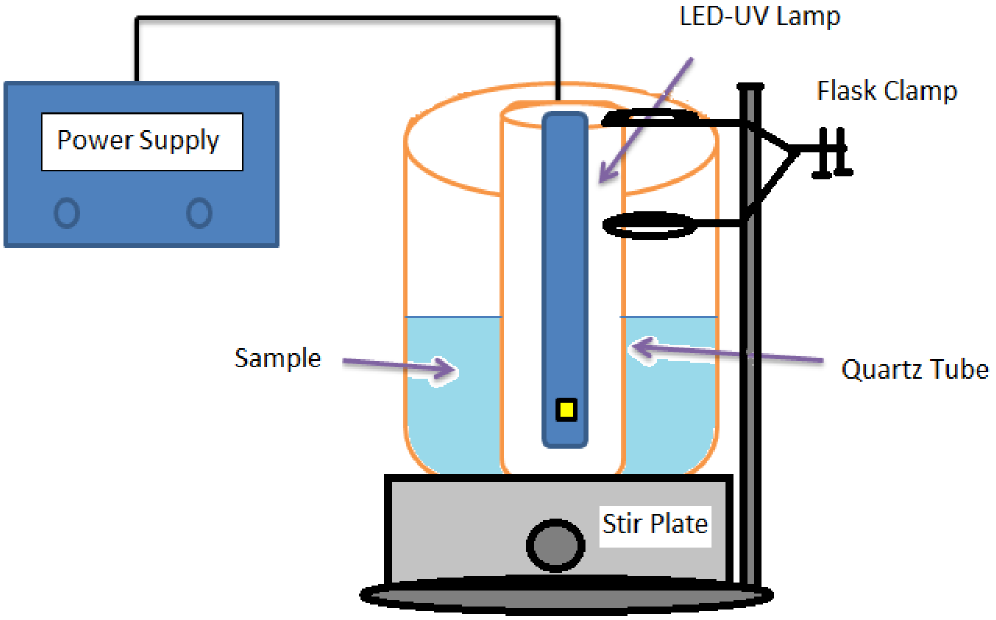


Figure 8: UV-LED reactor

Treatment Procedure

Prepared purified water (600 mL) containing 4 mg/L NDMA was added to the UV-LED batch reactor setup. After adding TiO_2, mixing for 20 minutes, and extracting an initial sample, samples (10 mL) were extracted by syringe filtration after 2, 5, 10, 12, 15, and 20 minutes of treatment time. For each extraction, the UV-LED lamp was shut off and the run-time was paused. The 10 mL samples were immediately transferred to GC vials containing sodium chloride, capped, and racked until the final sample was extracted. The lamp was turned back on and the run-time was resumed immediately after each extraction. Before the GC analysis, 50 microliters of 10 mg/L chlorobenzene was added to each vial and the vials were shaken for 30 seconds each. The GC analysis provided NDMA concentration using the standard curve previously generated.

3.4 Measurements of Energy Usage

The UV-LED lamp was operated for a 20 minute treatment period with the power supply connected to a Kill A Watt measurement device (P3 International) to track energy usage. A simulated reaction session was conducted using 600 mL of purified water in the 1000 mL reactor. Energy demand was recorded every five minutes. The amount of energy usage was determined from this data.

Chapter 4: Results and Discussion

Reactions were conducted in well-mixed batch reactor configuration with a 20 minute contact time to analyze the rate of removal of NDMA using UV-LED photolysis with anatase TiO_2. This section describes the removal achieved and the relevance of the data. Several limitations are also described.

4.1 Standard Curve

A standard curve was generated using the HS-SPME-GC analysis method with known concentrations of NDMA. Chlorobenzene was used as an internal standard. The calibration curve generated is shown in Figure 9 below.

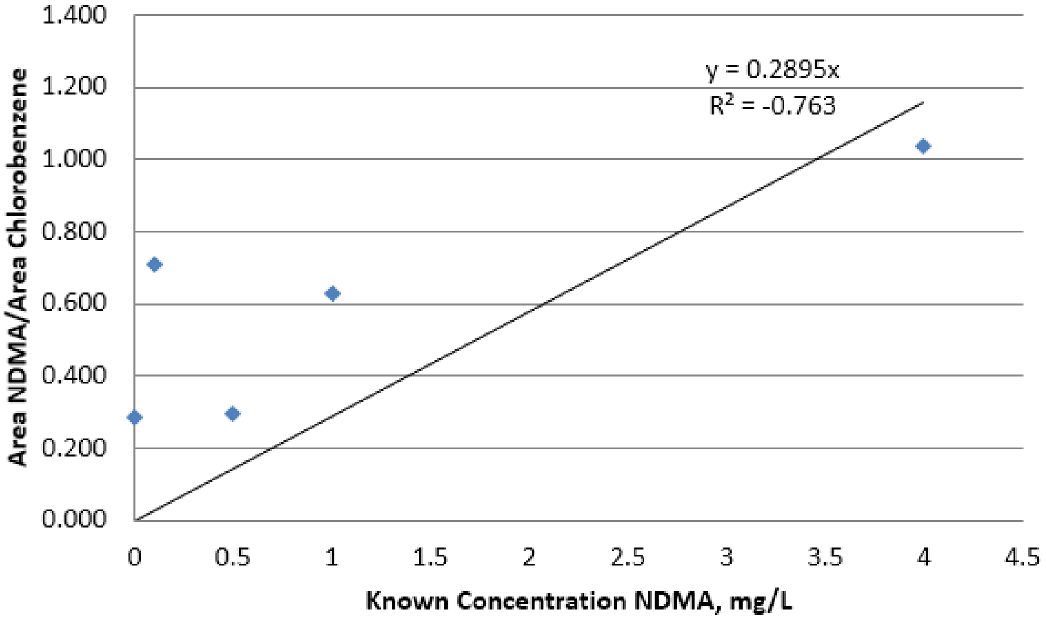


Figure 9: Standard curve to evaluate the concentration of NDMA from GC chromatogram

4.2 NDMA Degradation Results

Chromatogram results from GC analysis were analyzed by normalizing peak area of NDMA to the internal standard peak area. The standard curve linear equation was solved for the concentration of NDMA and the following equation was used:

$$[NDMA] = \frac{peak\ area\ of\ NDMA}{peak\ area\ of\ Chlorobenzene} * 3.454$$

Raw data are included in Appendix B.

4.2.1 Concentration over Time

Resulting concentrations for each sample time were plotted to illustrate the NDMA degradation. Figure 10 and Figure 11 below show the results for the two concentrations tested.

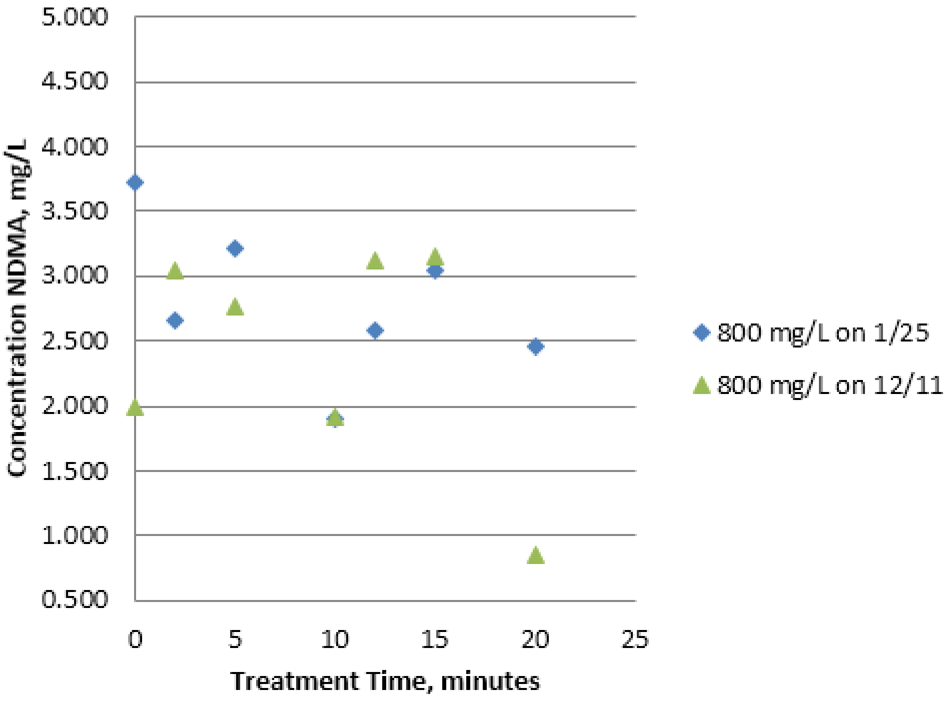


Figure 10: NDMA Concentration degradation by UV-LED and 800 mg/L anatase

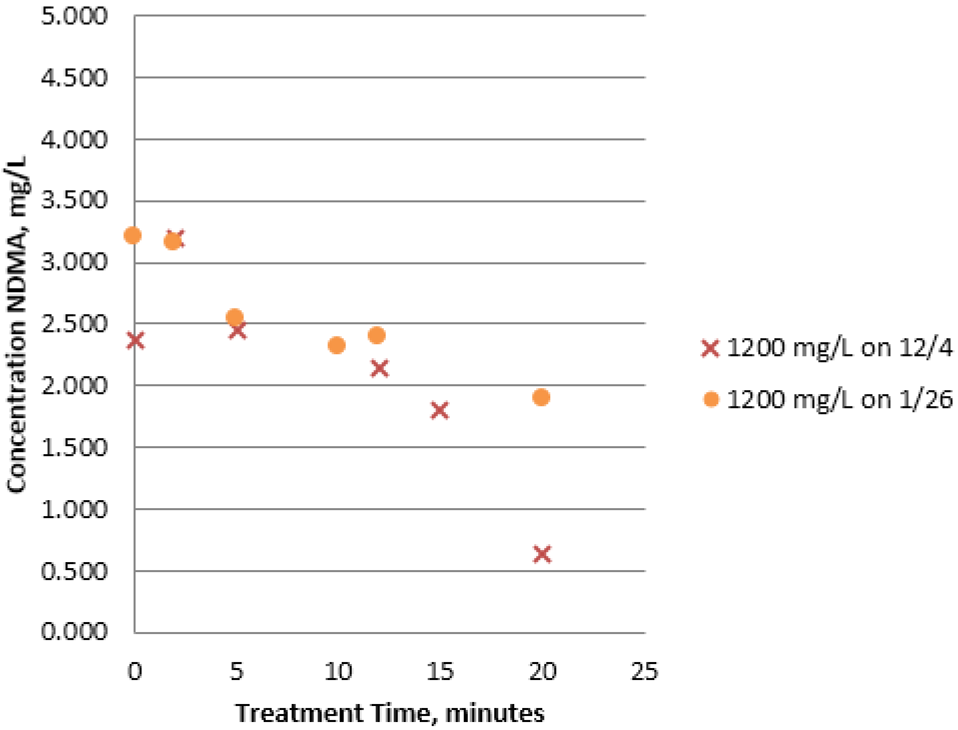


Figure 11: NDMA Concentration degradation by UV-LED and 1200 mg/L anatase

As shown in the figures above, the concentration of NDMA generally followed a decreasing trend. The scattered points at the beginning of the treatment and the increasing NDMA concentration along the treatment time could due to the detection variability of the sensitive GC instrument. According to the final concentration after the 20 minutes of treatment, UV-LED with anatase at 1200 mg/L had a greater removal compared to 800 mg/L anatase.

4.2.2 Removal Effectiveness

The final amount of NDMA removed after treatment was calculated for each trial. As shown in Table 7, neither of the concentrations had consistently higher percent removal.

Table 7: NDMA removal by UV-LED and anatase

Date	TiO_2 (mg/L)	Removal, %
1/25	800	51
12/11	800	76
1/26	1200	49
12/4	1200	79

4.3 Kinetics Analysis

The general reaction of activated titania hydroxyl radicals with NDMA is shown below:

$$\mathrm{OH\cdot + NDMA} \xrightarrow{\text{UV light}} \text{products}$$

Based on the data gathered for concentration measured over time, the kinetics of the reaction was analyzed by two techniques:

1. Rate analysis to determine reaction order and rate constant using POLYMATH 6.20 software (Sacham et al., 2006) method developed in the text Essentials of Chemical Reaction Engineering (Fogler, 2011).
2. First order linear plotting method to determine rate constant.

For each method, a model curve of concentration over time was developed. The resulting curves were plotted on a graph for comparison with the experimental data points.

4.3.1 Software Method for Exact Reaction Order

The rate of reaction can be modeled as the following differential equation where *k* is a constant of proportionality called the rate constant and *a* is the reaction order with respect to the reactant NDMA.

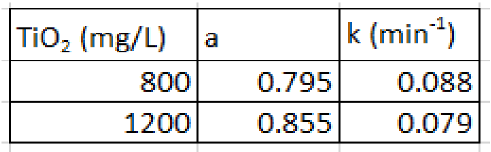
$$r = \frac{dx}{dt} = -kC_{NDMA}{}^{a}$$

After integration, this equation was solved for time, t as follows. This equation was used as the Model equation in POLYMATH and experimental data points were entered for measured sample concentrations over time (Fogler, 2011).

$$t = \frac{1}{k} * \frac{C_{NDMA,0}{}^{(1-a)} - C_{NDMA}{}^{1-a}}{1-a}$$

After nonlinear regression, values for rate constant and reaction order were determined with 95% confidence. Results are shown in Table 8.

Table 8: Reaction order and rate constant from POLYMATH analysis



TiO_2 (mg/L)	a	k (min^{-1})
800	0.795	0.088
1200	0.855	0.079

The concentration profiles for each concentration of anatase were developed from the integrated rate equation using the values for *a* and *k*. These profiles were plotted on the graph of raw data. Results are shown in Section 4.3.3 following. Based on the reaction rate order calculated in the POLYMATH software, the order could be considered close to one, even though the two *a* values are not exactly equal to one. This allowed use of the first order reaction assumption as an additional method of analysis.

4.3.2 First Order Assumption Method

The rate was determined from analysis of NDMA concentrations measured over time. Based on a first order rate expression, the system was represented by the following:

$$r = -k[OH\cdot][NDMA]$$

An assumption was made that the constant UV activation of TiO_2 yielded a steady concentration of hydroxyl radicals over time, allowing the concentration of hydroxyl radicals to be constant. A new rate constant, K, could be developed by grouping hydroxyl radical concentration and current rate constant, k, as follows.

$$K = k * [OH\cdot]$$

Since the sample concentrations are analyzed over time, the rate expression was expanded further:

$$\frac{\Delta[\mathrm{NDMA}]}{\Delta \mathrm{t}} = -\mathrm{K}[\mathrm{NDMA}]$$

After integration, the relation has a linear form as follows:

$$\ln{[NDMA]_t} = -Kt + \ln{[NDMA]_0}$$

The data for concentration of NDMA measured at specific treatment times was graphed over time. The slope of the line of best fit for each data set was the first order rate constant for the system.

Using raw data from Appendix B, plots for the first-order reaction are shown in Figure 12 and 13. From the slope of regression lines, the rate constants of anatase at 800 mg/L and 1200 mg/L were calculated at 0.069 min^{-1} and 0.053 min^{-1} respectively. These values were used in the equation for NDMA concentration and plotted along with the raw data and results from the software analysis shown in Section 4.3.3. In support of the findings in the software method, the rate constant, *k* , of anatase at 800 mg/L is higher, meaning a higher removal rate was achieved.

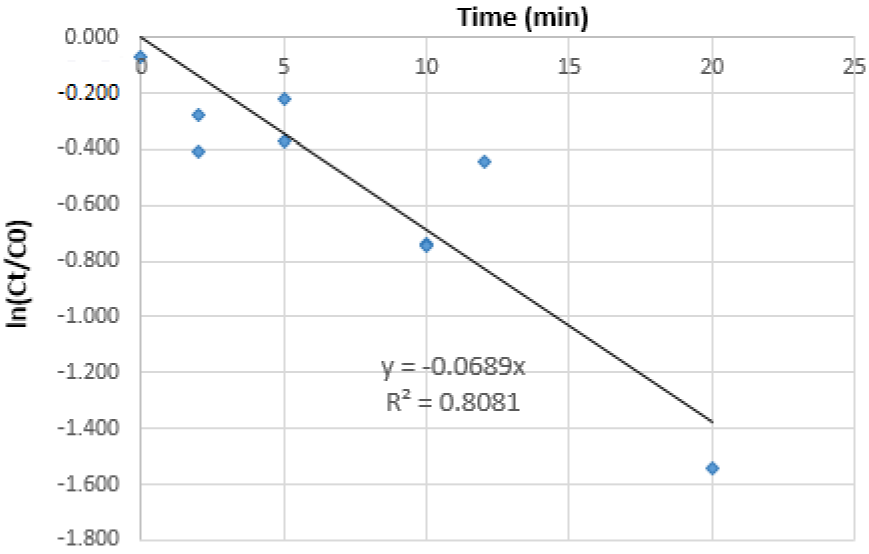


Figure 12: Rate constant by first-order assumption for 800 mg/L anatase

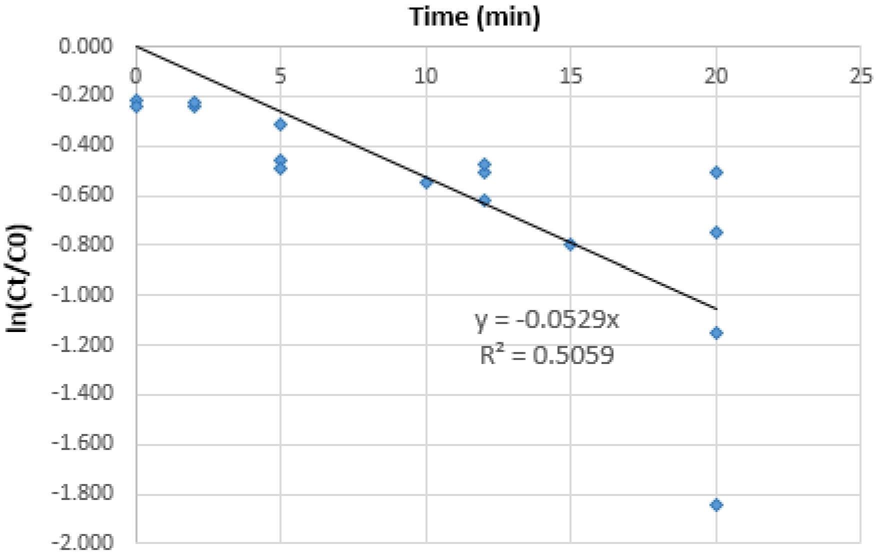


Figure 13: Rate constant by first-order assumption for 1200 mg/L anatase

4.3.3 Kinetics Results

The concentration of NDMA measured over time was plotted alongside the rate expressions determined by the software analysis and the first order assumption method. Equations for concentration are shown below.

Software Method:

$$[NDMA]_t = -(k * (1-a) * t - [NDMA]_0{}^{1-a})^{\frac{1}{(1-a)}}$$

First-order Assumption Method:

$$[NDMA]_t = [NDMA]_0 * e^{-kt}$$

For both curves, 4 mg/L was used as the initial concentration of NDMA. The results are shown in Figure 14 and Figure 15 below. Curves of two methods have similar behavior, thus validating the first order simplification. An area where data differs particularly is the y-intercept. The actual measured initial concentration was not exactly 4 mg/L due to a small amount of initial NDMA reduction caused by adsorption to TiO_2 without a light source (further described in Section 4.4). An initial concentration of 4 mg/L was used in the plots below to show total removal achieved.

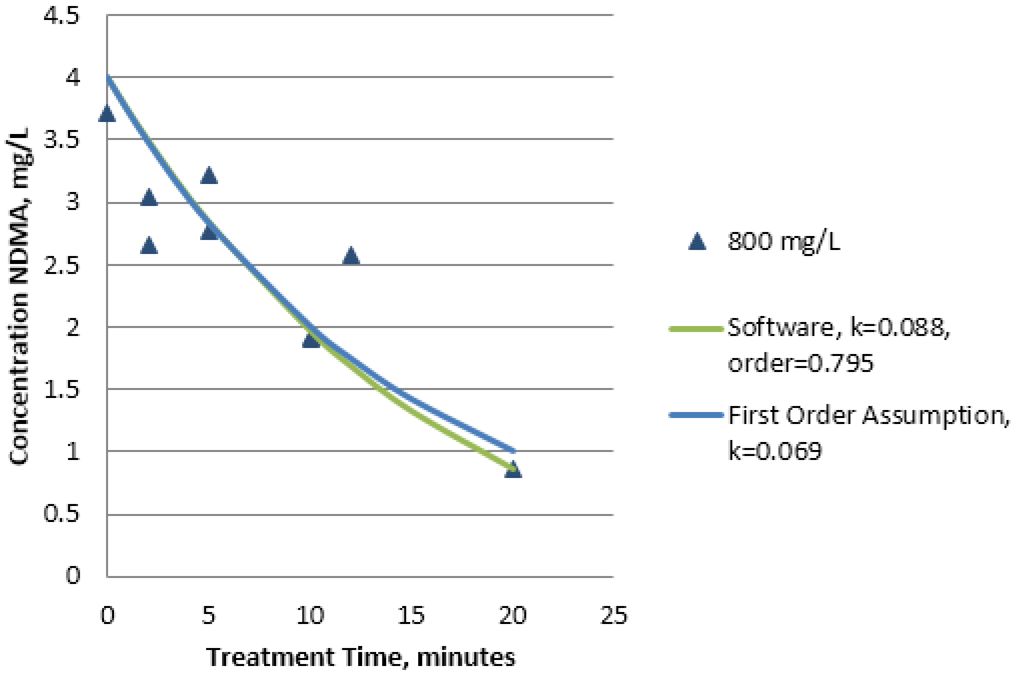


Figure 14: Kinetics results for 800 mg/L anatase

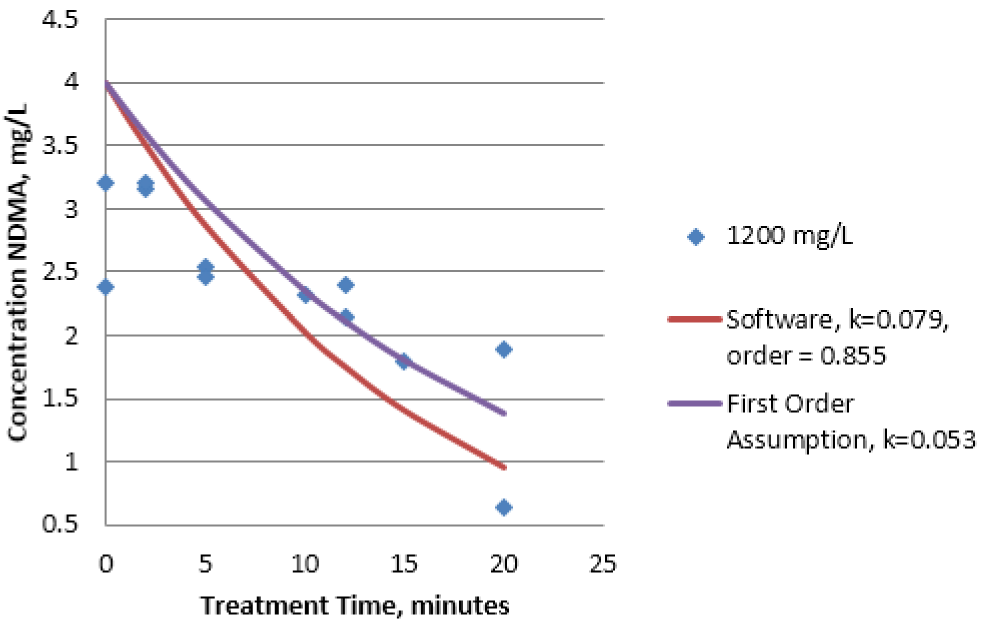


Figure 15: Kinetics results for 1200 mg/L anatase

Both methods yielded fair representations of the data. An exact fit for true behavior is not achievable due to scatter in original raw data (see Error Analysis, Section 4.4). Anatase at 800 mg/L had a slightly higher rate constant than anatase at 1200 mg/L, suggesting better removal achieved by the lower concentration. This may be due to higher concentrations of titania interfering with UV photolysis. Chun et al. found that at excessive doses, unfavorable light scattering can occur and penetration of light into the solution is reduced (as cited by Gaya et al., 2008, p.6). In comparison to Fogarty's analysis of CIP degradation using the same UV-LED lamp and TiO_2, an optimum concentration was determined around 1000 mg/L. Figure 16 shows supporting evidence that the rate constant associated with photolysis by TiO_2 started decreasing at concentrations above 1000 mg/L (Gad-Allah et al., 2011).

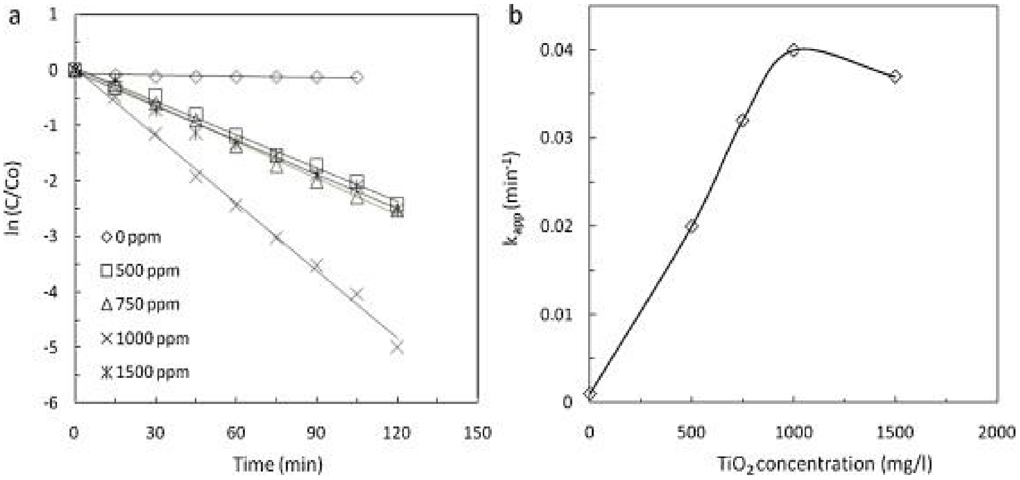


Figure 16: Effect of TiO2 concentration on CIP photodegradation, (a) pseudo-first order kinetics of the reaction and (b) change in rate constant with TiO2 concentration (Gad-Allah et al., 2011)

This previous determination for optimal concentration could help justify the reason larger rate constants were determined for the 800 mg/L TiO_2 over the 1200 mg/L. This project attempted to test Anatase at 1000 mg/L, but measurement errors did not provide useable data. Future researchers are encouraged to test Anatase at 1000 mg/L with UV-LED to determine if it is the optimal concentration.

4.3.4 Normalized Kinetics

From the first order assumption method, the rate constant values were normalized by the reactor volume and power usage. The normalized values yielded expressions in units of volume per kilowatt hour. The following equations show these steps. These values can be used to determine the resulting rate constant for a desired reactor volume and power supplied.

$$\frac{0.069}{min} * \frac{60\,min}{1\,hr} * 600ml * \frac{1\,m^3}{10^6 ml} * \frac{1}{56.8W * \frac{1\,KW}{10^3 W}} = \mathbf{0.044}\ (\frac{\boldsymbol{m^3}}{\boldsymbol{kw * h}})$$

$$\frac{0.053}{min} * \frac{60\,min}{1\,hr} * 600ml * \frac{1\,m^3}{10^6 ml} * \frac{1}{56.8W * \frac{1\,KW}{10^3 W}} = \mathbf{0.034}\ (\frac{\boldsymbol{m^3}}{\boldsymbol{kw * h}})$$

For anatase at 800 mg/L, a normalized rate constant of 0.044 m^3/kw*h was calculated. For anatase at 1200 mg/L, a normalized rate constant of 0.034 m^3/kw*h was calculated. It can be noted that the lower concentration provided a slightly higher rate constant. Possible reasons for this are described below.

4.3.5 Comparison to Mercury LED Kinetics

Kinetics results of the NDMA removal by a mercury-powered UV reactor developed by WPI graduate student, Jose Alvarez Corena, can be compared to the results from this experiment. The Ace Photochemical U.V. lamp (Lamp Cat. No. 7825-30) and power supply (115 V) were used with a 1 liter reactor (7861-255 reaction assembly, actual treatment capacity 40-50% of 1 liter total volume). Aeroxide ® P 25 TiO_2 was used at 1500 mg/L (CAS #: 13463-67-7). The first order rate constant of 0.46 min^{-1} was normalized by reaction volume of 500 mL and power consumption of 100 W was 0.138 m^3/kw*h.

$$\frac{0.46}{min} * \frac{60\ min}{1\ hr} * 500ml * \frac{1\ m^3}{10^6 ml} * \frac{1}{100W * \frac{1\ KW}{10^3 W}} = \mathbf{0.138}\ (\frac{\mathbf{m^3}}{\mathbf{kw * h}})$$

To directly compare the kinetics, this value was scaled to a reactor with the same volume and power consumption as the UV-LED configuration. A reactor volume of 600 mL and power of 56.8 W were applied in the following calculation to yield a rate constant of 0.218 min^{-1}.

$$0.138 \left(\frac{m^3}{kw * h}\right) * \frac{1}{600ml * \frac{1m^3}{10^6 ml}} * 56.8W * \frac{1kW}{10^3\ W} * \frac{1\ h}{60\ min} = \mathbf{0.218\ min^{-1}}$$

The rate constants achieved with a UV-LED lamp were used in the first order equation for concentration profile and plotted alongside the UV-LED lamp kinetics, shown in Figure 17 below.

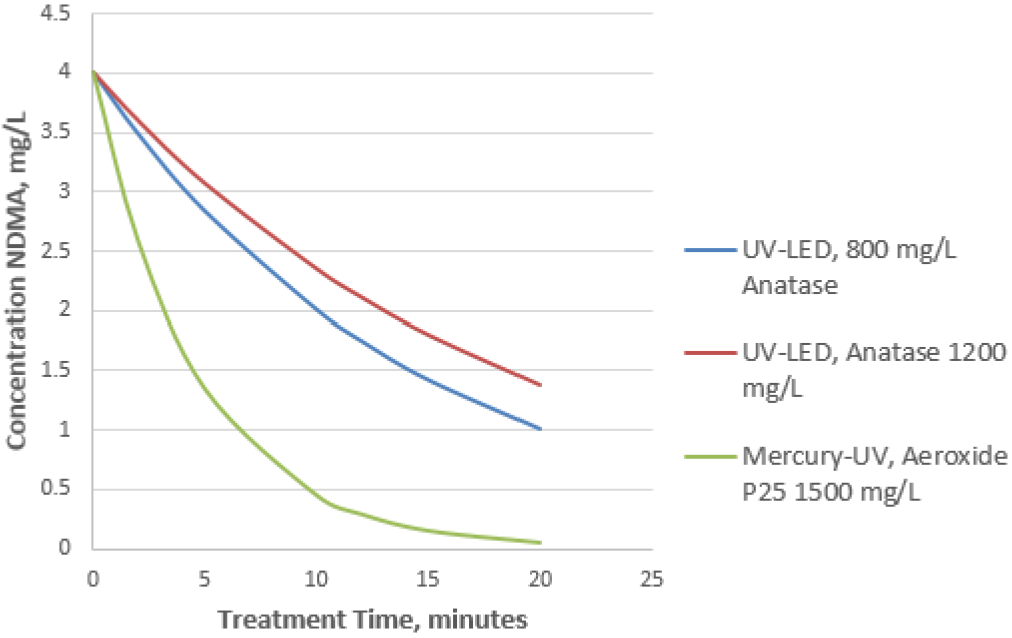


Figure 17: Lamp comparison for 600 mL batch reactor, 56.8 W

In comparison, the mercury UV lamp with Aeroxide ® P 25 at 1500 mg/L achieved a greater NDMA removal rate. However, this comparison is based on only two UV-LED lamp trials for each of the anatase concentrations. Further, the raw data shown in Figures 10 and 11 above were scattered, likely due to GC measurement variability and other laboratory factors described in Section 4.5 below. More data for the UV-LED lamp is needed in order to provide more certainty in kinetics results. Direct comparison is also limited by concentration and type of TiO_2 used.

A key difference between the mercury UV lamp and the LED/UV lamp is the amount of light emitted within the range of UV light. The mercury lamp provides a broader light emission spectrum. The mercury lamp used by Alvarez Corena only emits 4.64 W of its 100 W nominal wattage in the UV wavelength range (Ace Glass, “General Operating Instructions”), but nearly all of the Nichia UV-LED lamp wattage is emitted within UV range. Figure 18 shows the broad range of emission from a typical low pressure mercury UV lamp compared to high concentrations of pure UV light by UV-LED.

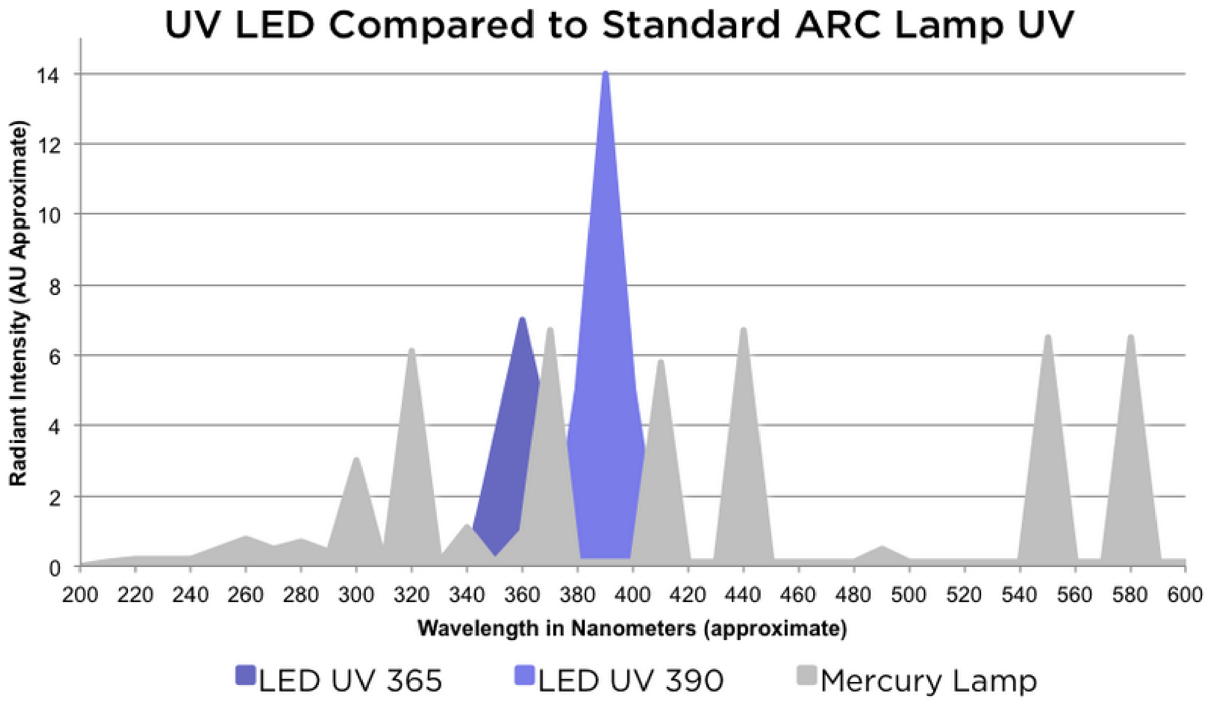


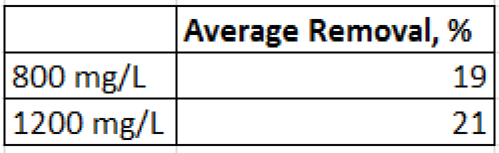
Figure 18: Lamp output for UV-LED compared to mercury UV lamp (AMS, 2015)

Due to the differences in lamp output, power supplied to the mercury lamp will be much higher to apply the equivalent amount of UV light. In addition to lower energy requirements, a UV-LED lamp also lasts longer, is less expensive, and does not require hazardous material disposal at the end of its useful life. Further testing of the NDMA removal achievable by UV-LED and TiO_2 could prove its superiority despite inferior kinetics.

4.4 Titania Adsorption Mechanism

In the previous laboratory study testing removal of CIP using the same anatase TiO_2 and UV-LED lamp, it was hypothesized that some removal by adsorption occurred immediately after addition of TiO_2 without UV activation (Fogarty, 2013, p.29). The amount of CIP removal was 30% by TiO_2 alone. To test this in relation to NDMA, initial concentration of NDMA was measured, TiO_2 was added, and then the reactor was mixed for 20 minutes prior to UV lamp treatment. A sample was taken after the 20 minute mixing period. For all trials, a decrease in NDMA occurred without UV treatment. Table 9 shows the percentage removal achieved by TiO_2 alone.

Table 9: Average NDMA removal with 20 minute TiO2 contact time



	Average Removal, %
800 mg/L	19
1200 mg/L	21

It can be reasoned that a significant decrease, around 20%, was achieved through adsorption alone. This could be explained by Thomas and Syres in a literature review and laboratory evaluation of adsorption of carboxylic acids, amino acids, alcohols, and other organic molecules to the surface of anatase and rutile TiO_2 (Thomas et al., 2012). Aliphatic amines were adsorbed by formation of a N-Ti bond in a study by Farfan-Arribas et al. (as cited by Thomas et al., 2012, p. 4215), finding that the desorption activation energy decreased in order of decreasing Lewis basicity. The NO- group in the CH_3CH_3-N-NO molecular structure of NDMA acts as a Lewis base in this case. Another site of adsorption of NDMA to TiO_2 could be cleavage of the N-N bond that has Lewis base character due to its lone pairs of electrons. A similar, but not identical, adsorption mechanism was observed by Li et al. in the cleavage of the N=N bond in nitroaromatics to form phenyl imide species (as cited by Thomas et al., 2012, p. 4215). Despite all of these proven adsorption mechanisms, adsorption still does not achieve an NDMA removal significant enough for its use alone. The amount of NDMA degradation was much greater with a light source, with an additional 30-60% degradation occurring during to UV-LED treatment. This follows the conclusions made by Fogarty for removal of CIP (Fogarty, 2013, p. 29).

4.5 Error Analysis

The experiment was designed to successfully test the NDMA removal effect under UV-LED treatment with TiO_2. However, there are still some factors involved through the experiments that contributed to errors in analysis of NDMA concentration. Firstly, the chlorobenzene stock solutions was a potential source of error. They were stored in amber glass bottles in 4℃ for the entirety of the laboratory work period. By storing it below room temperature, it was expected that it was not volatilized or degraded, although a fresh stock solution was mixed halfway through the 4 months of testing. Prior to use, this stock solution was mixed on a stir plate and then used to make a small amount of diluted solution for use as internalized standard. Due to low miscibility with water, the amount of mixing allowed could have contributed to some of the inconsistencies of GC measurements of the internalized standard peak.

Another problem with the GC measurement was residual NDMA on the GC fiber between samples. This became apparent when results showed an NDMA peak for a sample containing no NDMA. Even though the testing sequence was set from low concentration to high concentration, the residual was still apparent. To fix this problem, the temperature and run time for the GC method were increased and the method was tested with altering NDMA and blank vials to ensure zero NDMA residual. In the remaining analyses, a "blank test" was conducted prior to measuring samples from a full lamp trial. By ensuring zero NDMA detection before a full trial was analyzed, residual between runs was no longer a contributing error.

Finally, and most impactful, was degradation of the GC fiber. Since the fiber has a certain life cycle, changing was required approximately 4 times during the course of the 4 month lab testing period. It became apparent that the fiber needed to be changed when the chromatograms yielded low detection for chlorobenzene. Many data tests were thrown out due to GC measurement errors. In addition to low quality results before replacement, after replacement, each fiber seemed to have slightly different sensitivity and properties that led to differences between trial results, making it more difficult to compare all lamp trials for a certain concentration if they were conducted with two different GC fibers. This also made selecting a valid standard curve difficult and led to more thrown out data that did not fit. One other possible source of inconsistency was filtering TiO_2 from the solution. Especially at the higher concentration of TiO_2, some residual particles were contained in the GC samples, possibly leading to further NDMA degradation by adsorption mechanism inside the vial before GC measurement. This was assumed to be minor, however.

In addition to laboratory errors, much delay was caused by various GC analysis equipment failures like broken fibers, computer software errors, and running out of gas supply for the instrument. Future researchers are encouraged to thoroughly plan for an effective analysis process including plans for regular fiber replacement and inspections of the instrument prior to operation. Due to a final fatal error of the GC software, a control test could not be carried out to determine the removal of NDMA that could be associated with UV treatment alone.

Chapter 5: Conclusions and Recommendations

The degradation of NDMA achieved by UV-LED photolysis for both concentrations of anatase TiO_2 was significant. The 800 mg/L concentration showed greater removal. However, more data is required in order to fully determine the effectiveness. Due to the technical setbacks of Gas Chromatography, only two lamp trial runs were used for the final analysis. It is recommended to test the two concentrations, 1200 and 800 mg/L further, and also to test 1000 mg/L. The three other phases of TiO_2, rutile, antase/rutile, and Aeroxide® P25, could also be tested to determine the optimal form.

Based on an analysis of the exact rate order using the software method developed by Fogler, a first order rate assumption could be assumed. The first order rate constants developed for the system were compared to similar testing using TiO_2 with a mercury UV lamp. Results suggested that the mercury lamp could achieve better NDMA removal. However, considering the power usage of the UV-LED lamp, longer useful life, and direct UV wavelength emission, the UV-LED lamp could still be a viable option for NDMA removal.

Future laboratory research is recommended to gain more data points for better treatment efficiency analyses. A control test of UV treatment without TiO_2 is needed to better prove the superiority of the combined UV- TiO_2 method. Anatase at 1000 mg/L should be tested to verify the previous studies of optimal concentration for photolysis with TiO_2. Testing an identical procedure using a mercury powered lamp is recommended. The GC measurement variability should be addressed and planned for as much as possible. Scheduled fiber replacements are recommended with a new standard curve developed after each fiber replacement. Additionally, syringe filters with larger pore size such as 45 µm may improve sampling ease.

As detailed in Chapter 2, NDMA is a major concern for the health of all consumers. With drinking water regulations expected in the near future, this project and others like it are necessary to determine economical treatment methods for NDMA removal.

Chapter 6: To what extent will NDMA in wastewater effluents impact drinking water from major rivers in the US?

The goal of this chapter was to investigate the presence of NDMA in surface waters that are used as major municipal drinking water sources. An evaluation of the associated risk was also conducted. Occurrence of NDMA was estimated by drinking water disinfection methods, upstream wastewater influence, and data from several source water studies that measured NDMA or industrial impacts for source waters. The increased cancer risk associated with NDMA was estimated for each of the four reference locations. In conclusion, areas for further study were identified and the alternatives for preventing NDMA were discussed.

6.1 Sources of NDMA in the Environment

NDMA impacts the environment as a result of industrial and municipal wastewater applications. Underground, it may be naturally attenuated by biodegradation, and UV photolysis and volatilization are degradation methods in surface waters and air. In deep soils it is expected to break down in a few months, but in groundwater, adsorption to soils has been determined insignificant for reducing NDMA. Industrial sources can contribute significant concentrations of NDMA to the air, water, and soil. Groundwater recharge by water reuse utilities became a concern as an unanticipated result of a 1998 investigation of drinking water wells in Sacramento, California spurred by industrial contamination (Siddiqui et al., 2004). More difficult to detect and less-studied is the impact from its formation as a DBP in municipal wastewater plants. This paper focuses on the impact of NDMA from wastewater and water recharge applications rather than from industrial sources due to their universal presence and emerging concern.

6.1.1 Industrial Sources

As discussed in the Background chapter, industrial sources include rocket fuel byproducts, tanneries, rubber industries, dye manufacturers, fish processing facilities, and foundries (EPA, 2014d, “Technical Factsheet - NDMA). Its persistence at high levels in groundwater near rocket fuel sites, as high as 20,000 ng/L off site and 400,000 ng/L on site, suggests a large impact on the environment from this industrial source. Chloramination of wastewater containing nitrogenous organics has been found to form NDMA (Mitch & Sedlak, 2002). A study by Le Roux et al. tested the reactivity of anthropogenic nitrogen-containing compounds with monochloramine and found significant formation of nitrosamines including NDMA (Le Roux et al., 2011). The study identified wastewater containing tertiary amine herbicides (diuron, isoproturon, and trifluralin and pharmaceuticals (such as ranitidine) with NDMA formation. Industrial exposure to volatile nitrosamines in the “Ashland” process for core-making has been studied, but the level of NDMA present in foundries wastewater discharges or leachate from sludge waste has not been specifically identified (Ducos et al., 1988).

6.1.2 Water Reuse

Utilities using potable water reuse are of high concern regarding NDMA contamination (Sedlak et al., 2005; Mitch et al., 2003). Reused water can directly impact drinking water sources. California utilizes water reuse most extensively in the world (Sedlak et al., 2006). Figure 19 below shows the breakdown of California’s annual 19.5 m^3/s of reused water applications, accounting for 10% of its municipal wastewater effluent. With irrigation uses and groundwater replenishment uses accounting for 80% of the reused water applications, water from water reuse systems directly impacts the environment. Several water recycling plants have installed UV treatment systems after reverse osmosis treatment, however, the dose required is an order of magnitude higher than UV treatment for its typical use in wastewater disinfection. To reduce the cost, in a report for the WaterReuse Foundation, Sedlak et al. suggested methods of decreasing NDMA precursors in wastewater treatment processes instead of treating NDMA itself (Sedlak et al., 2006).

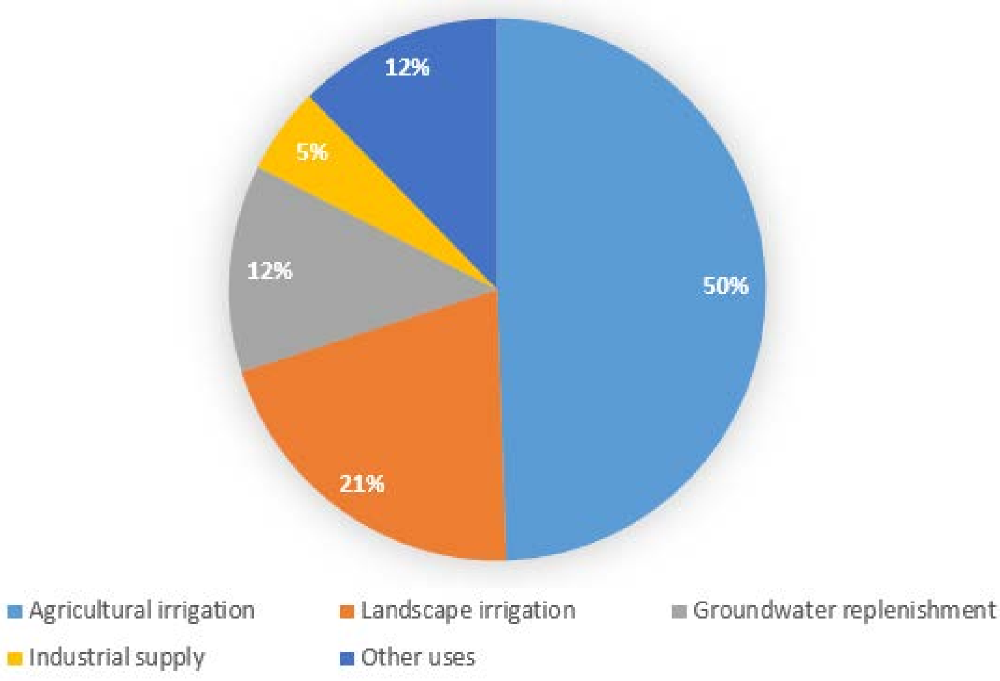


Figure 19: California water reuse applications (generated with data from Recycled Water Task Force, 2003)

Locations of groundwater recharge in relation to drinking water wells is important in identifying the potential level of NDMA in drinking water. NDMA degradation in groundwater is possible if proper microbes are present. A study of NDMA in a groundwater remediation system in Colorado showed that natural biodegradation by *Pseudomonas sp.*may occur in both aerobic and anaerobic conditions (Gunnison et al., 2000). The degradation over 30 days was 30-60% at a biological concentration in the range of 50-500 µg/kg. Another study found that the strain ENV425 can use NDMA as a primary nitrogen source and can degrade NDMA to ng/L concentrations from levels initially in the µg/L range (Fournier et al., 2009). *Rhodococcus ruber* was identified as a similar strain that could also potentially degrade NDMA. This study was a laboratory study and did not identify a treatment time for a natural system.

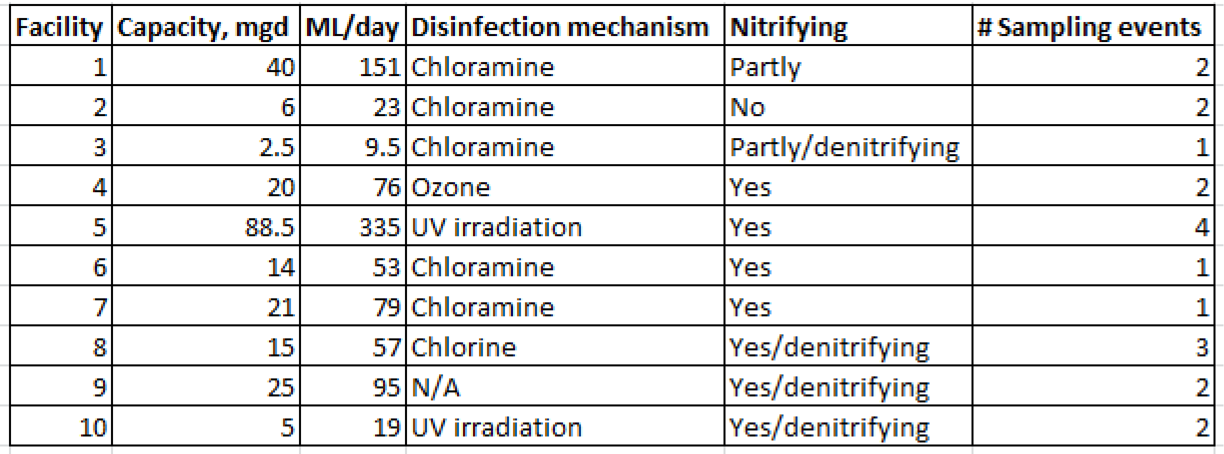
Arizona, Florida, Virginia, Colorado, South Carolina, and Texas also use indirect water reuse (Sedlak et al., 2006). The impact of NDMA in water reuse applications in these states can be considered similar to California and requires further assessment outside of this study.

6.1.3 Influence of Wastewater Discharge on Trace Organics in Water Bodies

Water discharged from municipal WWTPs can contribute NDMA to lakes in measurable amounts and can also make up a significant amount of river flow. In 1980 it was estimated that during low river flow conditions, 7.7 million people in the United States are served by utilities that use up to 50% wastewater (Swayne et. al., 1980). With the current elevated concern surrounding trace organics such as pharmaceuticals and DBPs, an increasing number of studies have been completed in recent years to expand knowledge of impacts on natural systems and human health.

Due to the large number of possible trace organics in wastewater, a practical method for determining their presence in water bodies is through indicator compounds, or compounds with an occurrence at least five times higher than their detection limit that can indicate the presence of other compounds with similar chemical structure and degradation characteristics. A study by Dickenson et al. reported on the impact of trace organic chemicals in municipal wastewater effluents on receiving streams (Dickenson et al., 2011). Ten full scale conventional wastewater treatment facilities, shown in Table 10, were sampled to determine the trace organics discharged to rivers. The locations of these sites were not disclosed. Shallow streams and those with low retention times (<17 hours) were most impacted. Results from monitoring at the ten facilities led to the identification of 52 indicator compounds with a common occurrence around five times higher than their detection limits.

Table 10: WWTPs monitored (Dickenson et al., 2011, p.1201).



Facility	Capacity, mgd	ML/day	Disinfection mechanism	Nitrifying	# Sampling events
1	40	151	Chloramine	Partly	2
2	6	23	Chloramine	No	2
3	2.5	9.5	Chloramine	Partly/denitrifying	1
4	20	76	Ozone	Yes	2
5	88.5	335	UV irradiation	Yes	4
6	14	53	Chloramine	Yes	1
7	21	79	Chloramine	Yes	1
8	15	57	Chlorine	Yes/denitrifying	3
9	25	95	N/A	Yes/denitrifying	2
10	5	19	UV irradiation	Yes/denitrifying	2

After identifying the indicator compounds, Dickenson et al. calculated the detection ratio (DR) developed by Sedlak et al. (2004). The DR is a quantification of the ability to measure the change in concentration of a compound if it is initially close to the detection limit. The concentration of the compound is considered relative to the limit of quantification (LOQ) as the following:

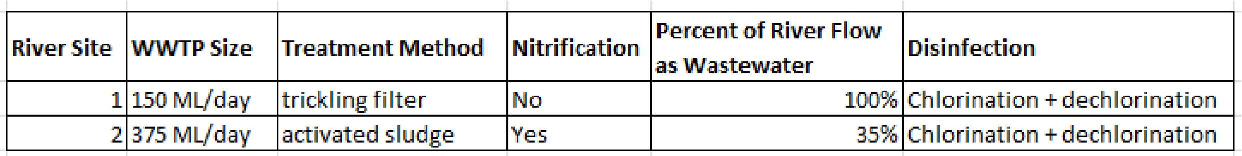
$$DR = \frac{[Concentration]_{median}}{LOQ}$$

The study used data gathered by Sedlak et al. for the assessment of NDMA in treated wastewater in samples from seven municipal wastewater treatment plant effluents between August 2002 and April 2004 (Sedlak et al., 2005). All seven plants used conventional activated sludge and chlorination for disinfection. NDMA had a median DR of 19, meaning that the median concentration was 19 times higher than the 2 ng/L detection limit specified in the GC/MS-MS method developed by Mitch et al. ((Mitch et al., 2003, as cited in Dickenson et al., Appendix). Of the other indicator compounds identified, Acetaminophen, Bisphenol A, Gemfibrozil, Meprobamate, and Sulfamethoxazole had the highest DR values. The presence of these indicator compounds could provide evidence of NDMA present in the water body.

The type of disinfection used is also important in classifying the impact of NDMA in natural waters. Table 10 above shows that half of the facilities evaluated used chloramination and one used chlorine with the others using ozone or UV irradiation. Dickenson et al. cited previous studies focusing on the type of disinfection and formation of or removal of trace organics. Chloramination and UV irradiation have been associated with insignificant removal of trace organics (Drewes, 2008). Ozone can cause oxidation of some trace organics. Chlorine as hypochlorite (HOCl) reacts selectively with certain functional groups including ammonia. Chloramine (NH2Cl) is an intermediate in the UDMH formation pathway for NDMA (Mitch & Sedlak, 2002).The presence of trace organics including NDMA can be estimated based on the presence of the easiest-to-measure indicator compounds and classification of the type of disinfection.

Natural attenuation mechanisms and the location of drinking water influents from rivers in relation to WWTP discharges is an important factor in determining the extent of NDMA risk. Dickenson et al. analyzed monitoring data gathered by Lin et al. in 2006 for trace organics in highly impacted receiving waters at two sites of the Santa Ana River in Southern California (Lin et. al., 2006). Table 11 below outlines the level of wastewater impact on the river sites.

Table 11: River assessments to evaluate natural attenuation mechanisms (Lin et al., 2006)



River Site	WWTP Size	Treatment Method	Nitrification	Percent of River Flow as Wastewater	Disinfection
1	150 ML/day	trickling filter	No	100%	Chlorination + dechlorination
2	375 ML/day	activated sludge	Yes	35%	Chlorination + dechlorination

Indicator compounds were measured in the two rivers at the WWTP discharge locations and at downstream locations. The indicator compounds were measurable recalcitrant, photolabile, and bioamenable compounds measured to identify any mechanism that could degrade other trace organic compounds. Among these, NDMA can be classified as photolabile by UV photolysis and potentially bioamenable if proper bacteria are present. Most of the compounds studied by Lin et al. were not naturally degraded in the distance traveled in any of the travel times tested (5, 6, 12, and 17 hours), but the photolabile indicators were degraded enough to make the mechanism plausible in site 1. This information is helpful to understand the potential for natural degradation of NDMA in rivers.

6.2 Estimating NDMA Impact in the U.S.

As referenced in the Background chapter, NDMA in surface waters and drinking water influents has been monitored in several studies, but these studies only represent a portion of the wastewater facilities in the US and abroad. To extrapolate the extent of impact, major wastewater treatment facilities were located and the type of disinfection was identified. Key water sources were identified by the serviced populations. In this section, the methodology is described and then the process is carried out.

6.2.1 Identifying Reference Rivers and Cities

Major rivers serving as drinking water sources in the United States were identified. Those with the most data available were chosen as reference rivers and major cities using the river as source water were identified. These reference rivers and cities, shown in black in Figure 20 below, include the Potomac River (Washington, D.C.), Delaware River and Shuyllkill River (Philadelphia), Mississippi River (Twin cities of Minneapolis and St. Paul, MN), Columbia River (Richland, WA).

Figure 20: Reference rivers and cities (edited from original map: Family Search, 2014).

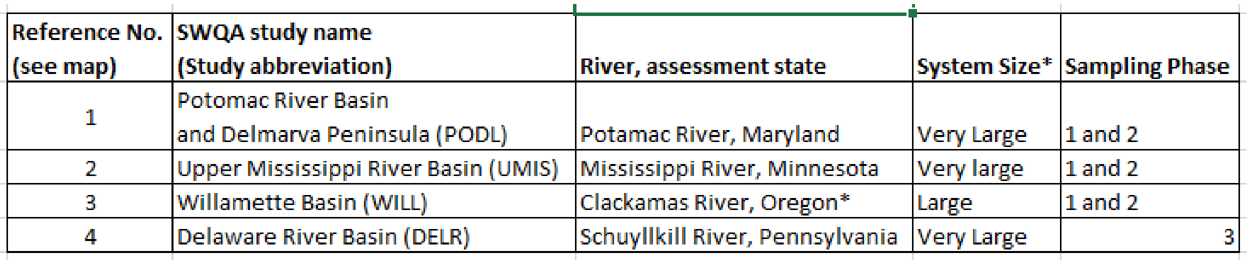
6.2.2 EPA Source Water Protection Data

The drinking water supplies for reference cities were studied in turn to analyze the water quality and impact of wastewater effluents that may suggest the presence of NDMA. A major data source was publicly available source water studies for municipal drinking water treatment plants (DWTPs) published by the EPA through the EPA Source Protection Project (EPA, 2000). Data from the UCMR for contaminants on the CCL and annual Consumer Confidence Reports (CCR) were also accessed from the EPA database.

6.2.3 USGS Study

Several reference rivers were monitored by the U.S. Geological Survey (USGS) in a study of anthropogenic organic compounds.Trace organics occurrence data was sourced from a study by U.S. Geological Survey (USGS) as part of the National Water-Quality Assessment (NAWQA) Source Water-Quality Assessments (SWQAs) Project focused on the source water quality in major rivers serving large community water systems (Carter et al., 2010). Samples were gathered from 2002-2010. Anthropogenic organic compounds were measured in source water from 448 community water system wells, and 21 surface water sites. Additionally, finished water samples were analyzed from 285 wells. After a preliminary sampling event of source waters analyzed for all 295 anthropogenic compounds (Phase 1 from 2002-05), a selection of sites from Phase 1 were further monitored by source and finished water samples analyzed for the most frequently occurring anthropogenic compounds (Phase 2 from 2002-05). Phase 3 (2006-10) measured source-water and finished water samples for all anthropogenic compounds. Data from Phases 1 and 3 can represent general occurrence trends and data from Phase 2 can be used to represent recurrence patterns and compare occurrence in surface waters to occurrence in finished waters. Figure 21 below shows the monitoring locations in the study with the three reference areas circled. The SWQAs representing the reference rivers are listed in Table 12 below.

Table 12: USGS study locations for three reference rivers



Reference No. (see map)	**SWQA study name (Study abbreviation)**	**River, assessment state**	**System Size***	**Sampling Phase**
1	Potomac River Basin and Delmarva Peninsula (PODL)	Potamac River, Maryland	Very Large	1 and 2
2	Upper Mississippi River Basin (UMIS)	Mississippi River, Minnesota	Very large	1 and 2
3	Willamette Basin (WILL)	Clackamas River, Oregon*	Large	1 and 2
4	Delaware River Basin (DELR)	Schuyllkill River, Pennsylvania	Very Large	3

*Clackamas river, OR is a sub-tributary of the Columbia River

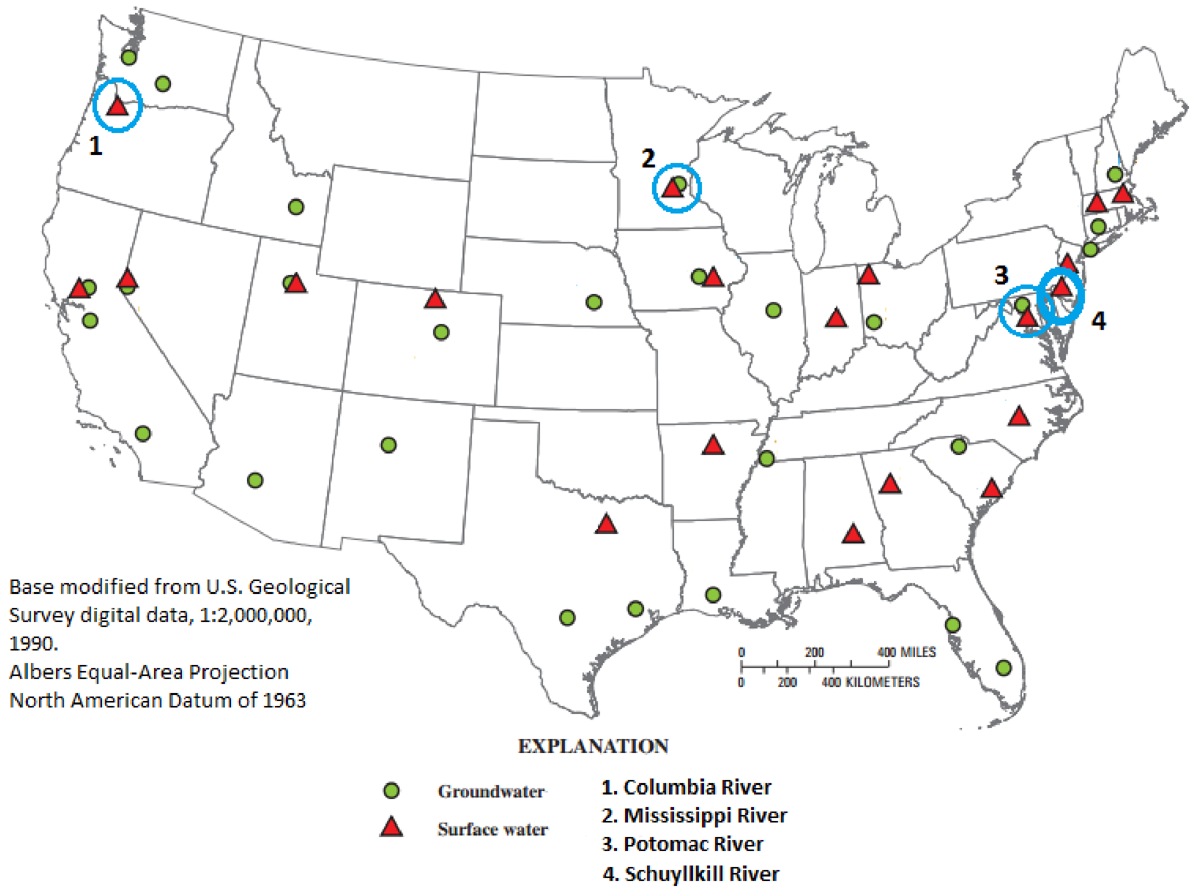


Figure 21: Location of Surface water and Groundwater monitoring locations (Carter, 2010, p.5)

According to the work by Drewes et al. to develop monitoring techniques for trace organics by measuring indicators and surrogates, “An indicator chemical compound is an individual chemical occurring at quantifiable level, which represents certain physicochemical and/or biodegradable characteristics of a family of trace organic constituents that are relevant to fate and transport, providing a conservative assessment” (as cited by the Committee on the Assessment of Water Reuse, 2012, p. 88). Therefore, measured amounts of compounds in water that have similar chemical characteristics and degradation mechanisms as NDMA can reasonably indicate the presence of NDMA. Three indicator compounds from the Dickenson study were monitored in the USGS report. The chemical structures of the three compounds and NDMA are shown in Table 13 below. Similarities include N-N bonds in atrazine and methyl groups in bisphenol A. Atrazine and NDMA are both degraded by microorganisms in the *Pseudomonas* genus (Gunnison, et al.; Udikovic et al., 2012). USGS results for bisphenol A were inconclusive and all samples for dichlorprop were below the detection limit, but atrazine was present at measurable levels for all samples. Table 14 below shows the atrazine and dichlorprop results for the three reference rivers.

The Potomac River had the highest level of atrazine, with a concentration about five times higher than the other rivers monitored. The presence of atrazine in all four finished waters could indicate the presence of other trace organic compounds with similar physical and chemical characteristics, including NDMA.

Table 13: Chemical characteristics of indicator compounds and NDMA (Merck Research Laboratories, 2001)

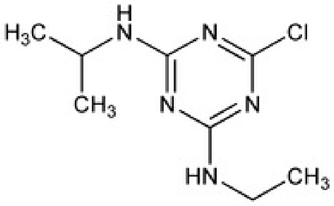
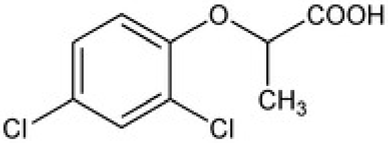
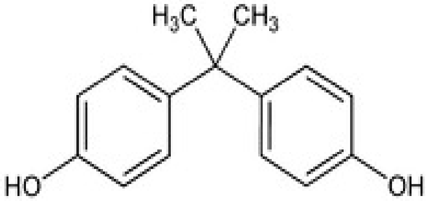
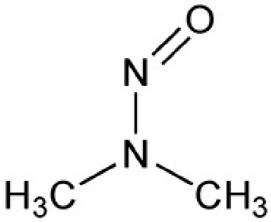
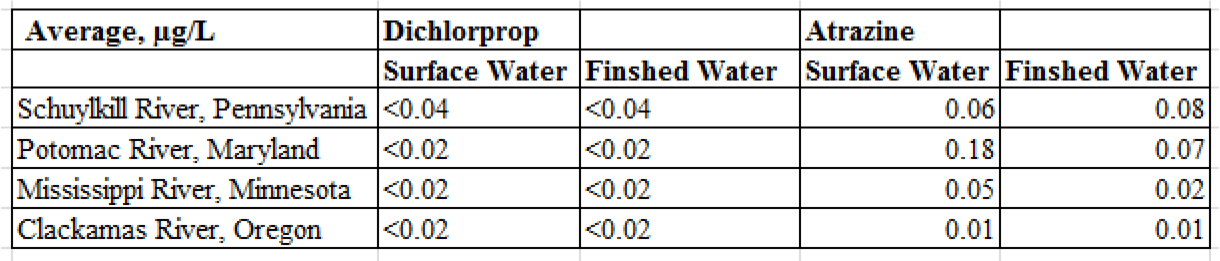
Compound	**Formula**	**Structure**	**Molar Mass**	**Solubility in Water at 25 C**	**Use**
Atrazine	$C_8H_{14}ClN_5$		215.7 g/mol	70 ppm	Selective herbicide
Dichlorprop	$C_9H_8Cl_2O_3$		235.1 g/mol	350 ppm	Selective herbicide
Bisphenol A	$C_{15}H_{16}O_2$		228.3 g/mol	Insoluble	Used in manufacturing of resins and polycarbonates. Fungicide.
NDMA	$C_2H_6N_2O$		74.1 g/mol	Very Soluble	Present in cured meat products; softener of copolymers; Byproduct of pesticide manufacturing plants (EPA, 2014d)

Table 14: Average concentration of dichlorprop and atrazine in surface water and finished water (Carter, 2010).



Average, µg/L	Dichlorprop		Atrazine	
	Surface Water	Finshed Water	Surface Water	Finshed Water
Schuylkill River, Pennsylvania	<0.04	<0.04	0.06	0.08
Potomac River, Maryland	<0.02	<0.02	0.18	0.07
Mississippi River, Minnesota	<0.02	<0.02	0.05	0.02
Clackamas River, Oregon	<0.02	<0.02	0.01	0.01

6.2.4 Case Studies

This section details the findings for each reference location based on EPA publications, USGS data, and research studies. The presence of NDMA is evaluated based on drinking water disinfection methods and the extent of pollution and wastewater influences.

6.2.4.1 Potomac River: Washington, D.C.

The District of Columbia Water and Sewer Authority websites describes the drinking water treatment methods and the source water (District of Columbia Water and Sewer Authority, 2015). The U.S. Army Corps of Engineers, Washington Aqueduct is responsible for the treatment facilities and distribution to over 600,000 residents. The intake to the treatment facility is on the Potomac River at the Great Falls and Little Falls intakes. After conventional coagulation, sedimentation, and filtration, the water is treated with free chlorine as primary disinfection followed by chloramination to remove the regulated DBPs. Based on the disinfection method, NDMA can be expected in drinking water supplied to residents.

The Potomac River Basin supplies water to more than 4 million consumers. The Interstate Commission on the Potomac River Basin (ICPRB) conducted a Source Water Assessment (SWA) in 2002, published findings, and created an action plan for the benefit of human health and the health of ecosystems (EPA, 2003). The major threats to the Potomac River that were identified include coliform bacteria from WWTP effluents and combined sewer overflows (CSO), petroleum spills from transportation corridors, and agricultural runoffs. Following previous studies of WWTP effluents, expected presence of NDMA in discharges to the Potomac River upstream of the D.C. drinking water uptake can be estimated. The 2002-2004 NDMA monitoring of WWTP effluents by Sedlak et al. found around 20-50 ng/L in wastewater discharges treating with chlorine (Sedlak et al., 2005).

Serving the D.C. area, the Blue Plains Advanced Wastewater Treatment Plant is one of the largest municipal wastewater treatment plants (MWTPs) in the world. Prior to discharge to the Potomac River at Outfall 001, water is disinfected by chlorination followed by dechlorination (District of Columbia Water and Sewer Authority, 2015). The discharge at Outfall 001 is permitted by NPDES Permit Number DC0021199 with a maximum flow rate of 225 MGD (Permit No. DC0021199, 2010). Since the discharge location is downstream from the Aqueduct for drinking water, this MWTP does not impact the drinking water quality for D.C. consumers, but it does impact downstream drinking water systems outlined in the

ICPRB SWA study including cities in Maryland, Virginia, and West Virginia (EPA, 2003). Whether or not NDMA formation is prevented by the dechlorination process is unknown, but the NDMA formation may depend on the time between chlorination and dechlorination (Charrois and Hrudey, 2007).

A map of the Potomac River showing the Blue Plains MWTP and downstream river path is shown in Figure 22 below. The map shows USGS water quality monitoring locations that were used to measure a 2/3 decrease in organic nitrogen levels between 1990 and 2007 following improvements to the Blue Plains WWTP (Lovett, 2010). This decrease suggests a large impact of the Blue Plains MWTP on downstream water quality in the Potomac River, including NDMA concentrations.

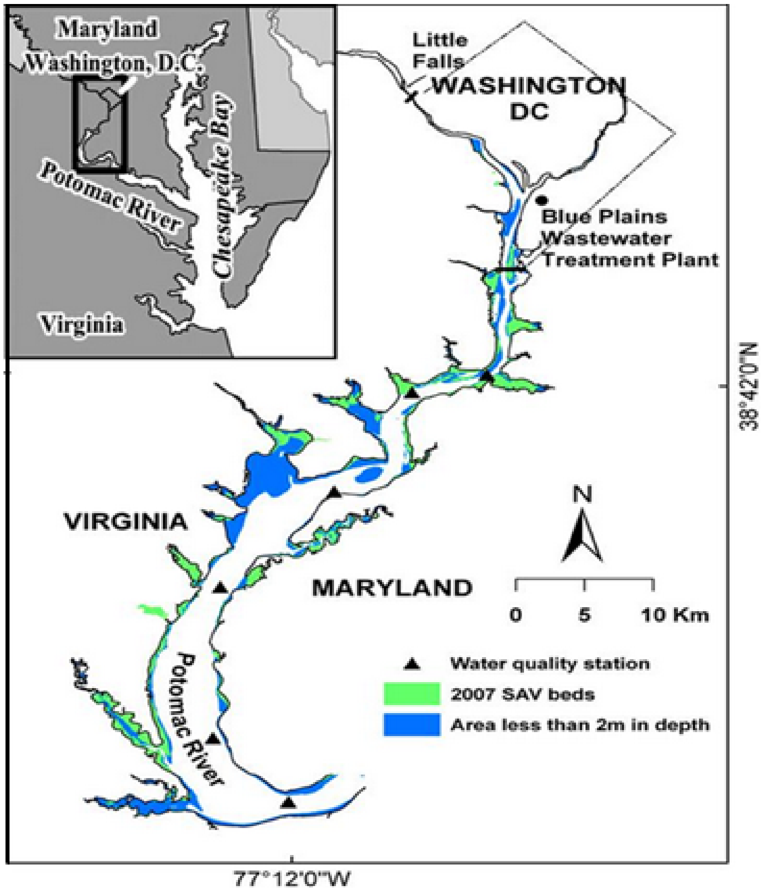


Figure 22: Potomac River (Lovett, 2010)

Under the UCMR 3, the D.C. Aqueduct monitored for the Emerging Contaminants of Concern that included hormones, metals, volatile organic compounds, and perfluorinated compounds. The UCMR3 data was not used for NDMA analysis due to limitations of correlating monitored organics to NDMA presence. Estrone was the only indicator compound outlined by the Dickenson study that was monitored, but it was not detected in the samples. The rubber manufacturing chemical 1,3-butadiene was measured in the UCMR 3 study. Since NDMA is also used in rubber manufacturing, the presence of this chemical could suggest the presence of industrial-sourced wastewater containing NDMA. This relationship is flawed, however. The two chemicals have dissimilar stabilities, with 1,3-butadiene volatile organic compound (VOC) and NDMA is stable at atmospheric conditions. It is possible that the VOC may be removed by volatilization in the D.C. water treatment while NDMA remains.

According to the USGS trace organics data, the Potomac River had the highest concentration of the indicator compound, atrazine in the USGS data. Following the theory developed in the study by Dickenson et al., the presence of this indicator compound at a measurable level suggests a significant influence of wastewater and runoff on the Potomac River. It is likely that other trace organics including NDMA are present in the surface water.

6.2.4.2 Delaware River, Shuyllkill River: Philadelphia, PA

The drinking water supply for the city of Philadelphia is the Delaware River and the Schuyllkill River. According to the Philadelphia Water Department website, the water system serves almost 2 million people and maintains a watershed protection program to protect the water quality (Philadelphia Water Department, 2015). The source water protection program includes best management practices (BMPs) for agricultural and stormwater runoff. Three plants supply water for Philadelphia, with two on the Schuyllkill River and one on the Delaware River. The intake for the Baxter Plant on the Delaware River is located at the plant along the Delaware River at State Road in Philadelphia. The City of Philadelphia website describes the treatment methods used for all three facilities (City of Philadelphia, 2015). Disinfection by the addition of sodium hypochlorite and final treatment by adding ammonia are used. These methods have been linked to the presence of NDMA in drinking water (Mitch et al., 2003; Charrois and Hrudey, 2007).

The Delaware River Baxter WTP supplies drinking water for around 750,000 people. Potential sources of pollution concern for the source water were identified in a SWA Public Summary by the Pennsylvania Department of Environmental Protection (PADEP, 2002). The high-concern sources of pollution were treated sewage from WTPs and CSOs between Camden, NJ and Trenton, NJ. Discharge and runoff from industrial facilities was given a moderate level of impact for water between Trenton and Camden. Figure 23 shows the 40-mile stretch of river designated as an area of concern. The Baxter facility is located 23 miles from Trenton, the upstream boundary (Google Maps, 2015).

The Schuylkill River supplies drinking water to the remaining 1.25 million customers of the Philadelphia water system (Philadelphia Water Department, 2015). The Schuylkill River is the largest tributary of the Delaware River and it merges with the Delaware about six miles from Camden. At times of low rainfall, the Shuylkill River has been found to consist of as much as 60% treated wastewater discharge. Monitoring data from the USGS for the Shuylkill River for indicator compounds showed a measurable amount of atrazine, even in finished water, suggesting that similar trace organics could also be present in the drinking water source for Philadelphia (Carter et al., 2010). No data was gathered for the Delaware River.

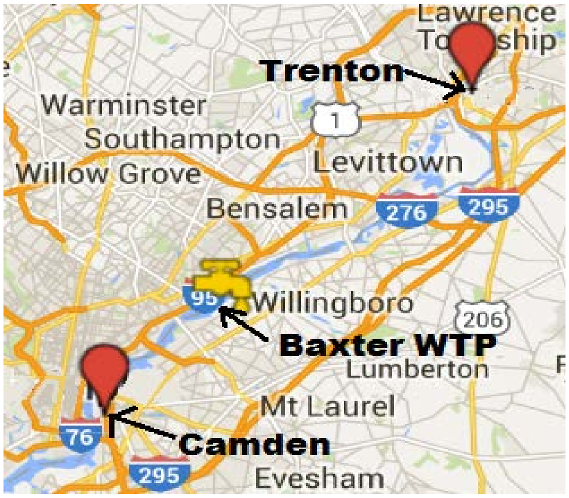


Figure 23: Baxter facility in concern area for source water protection (Google Maps, 2015)

6.2.4.3 Mississippi River: Minneapolis/St. Paul, MN

The Mississippi River supplies drinking water to 15 million people in the upper portion of the river basin from St. Cloud, MN to Cairo, IL (UMSWPP, 2013). It is the primary source of drinking water for St. Paul, MN and the only source for St. Cloud, MN and Minneapolis, MN. A source water protection program for the Upper Mississippi was initiated in 2009 to identify sources of pollution and areas of concern. Part of the project implementation was the development of an interactive map with locations of industrial permits, hazardous waste generators, above ground storage tanks, dumps, and priority outfalls for the stretch of the river between St. Cloud, MN and St. Paul, MN (UMSWPP, 2012). Figure 24 below shows the interactive map with the “priority outfalls” upstream of the drinking water uptakes for Minneapolis and St. Paul.

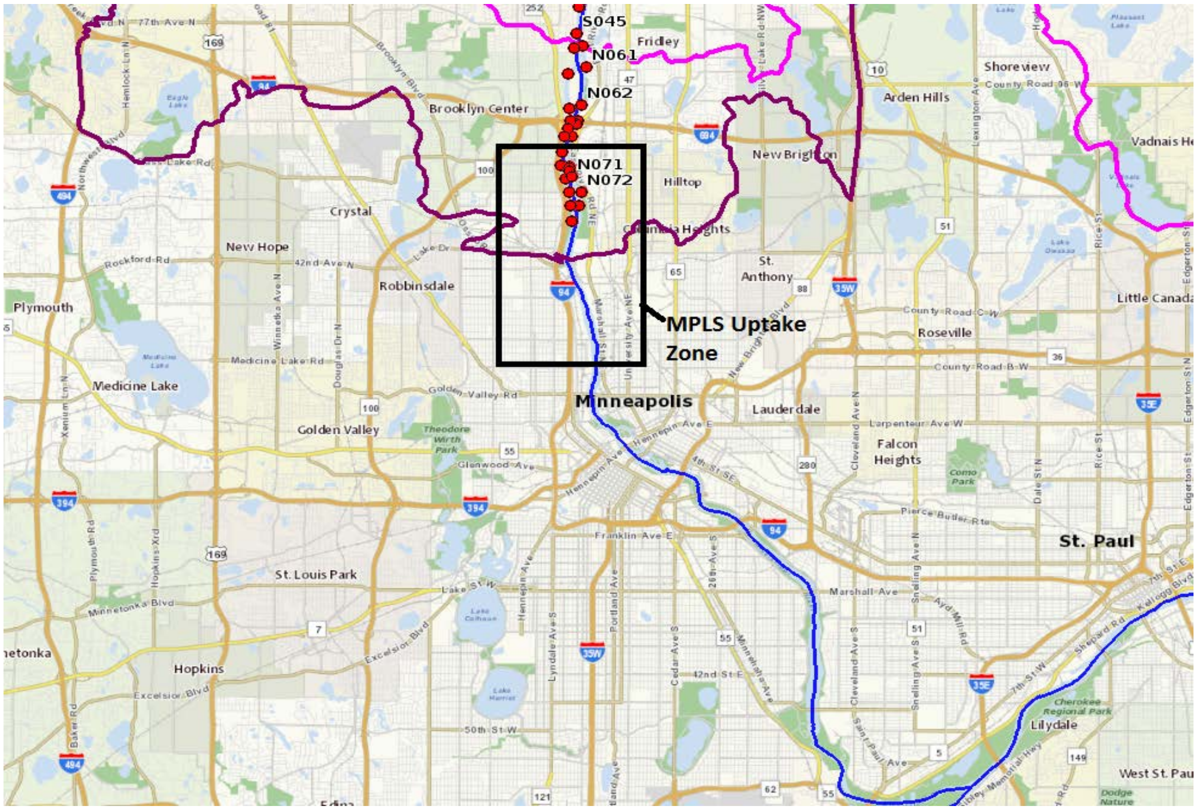
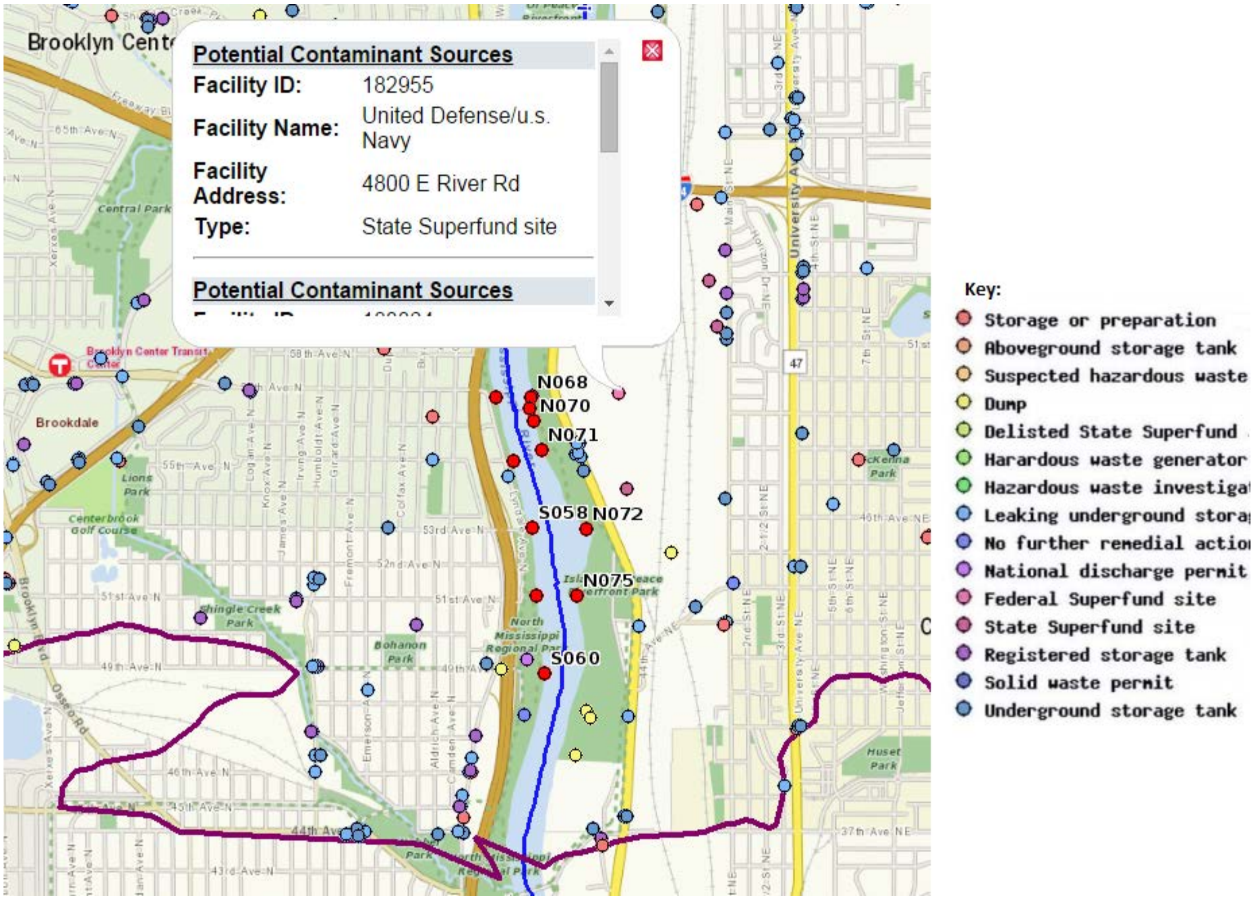


Figure 24: Mississippi River drinking water Minneapolis Uptake zone and Priority Outfalls marked in red (Flat Rock Geographics, 2014)

A major source of concern in relation to wastewater influence on the Minneapolis drinking water uptake is discharge from the remediation system at the Naval Industrial Reserve Ordnance Plant Superfund site, located 700 feet from the Mississippi River and about a mile upstream of the Minneapolis drinking water uptake (EPA, 2014c). The site was used to produce advanced weapons and was the source of organic solvents pollution, particularly trichloroethylene (TCE), in the Minneapolis drinking water. An investigation in 1988 found TCE flowing into the Mississippi River at concentrations up to 10,000 ppb -- 2,000 times higher than the MCL set by the EPA. The affected population of 529,000 was estimated to include the Minneapolis drinking water consumers and consumers of public drinking water from systems within 3 miles of the site.

A groundwater extraction and treatment system was installed and began operating in 1992, discharging treated wastewater to the Mississippi under permit. The extraction system has treated more than 4.3 billion gallons of groundwater since 1992, recovering more than 38,000 pounds of TCE. The presence of NDMA at detectable levels in treated water from the Superfund site is possible but unknown. NDMA is associated with rubber, plastics, and foundry waste and was likely present in waste from the NIROP site at moderate levels. Figure 25 below shows the Superfund location in the Minneapolis and St. Paul Surface Water Protection Priority Area. Numerous pollution sources are present in the Minneapolis and St. Paul Priority areas, and some are shown in the figure.



Potential Contaminant Sources

Facility ID: 182955

Facility Name: United Defense/u.s. Navy

Facility Address: 4800 E River Rd

Type: State Superfund site

Potential Contaminant Sources

Figure 25: Pollution sources and Superfund site near Minneapolis uptake

Monitoring for trace organics in the USGS study showed the indicator compound, atrazine, at measurable levels. The presence of atrazine and the influence of wastewater effluents combined with the chlorination of drinking water as disinfection suggests the presence of NDMA in Minneapolis and St. Paul drinking water at levels above the cancer risk level.

6.2.4.4 Colombia River: Richland, WA

The city of Richland, WA uses the Columbia River and five groundwater wells for drinking water serving a population of 45,500. The Columbia River supplies 24,000 GPD to The DWTP uses chlorination as a disinfection stage (City of Richland, 2013). The water is treated by UV treatment and chlorine is added to meet permit requirements for residual chlorine. The water quality report for Richland, WA describes the potential contaminants in the source water. Industrial, agricultural, and microbial influences are acknowledged. Groundwater plumes from the radioactive waste from the Hanford Nuclear Reservation cleanup site are being treated before they can reach the Columbia River (Washington Department of Ecology). On the Hanford site, 53 million gallons of radioactive and chemical waste were stored in 177 tanks between 1943 and 1986 with leaks currently experienced in 67 of the tanks (Price, “Hanford Nuclear Site”). NDMA has been documented in vapors from tank vents at the Hanford site (Savannah River National Laboratory, 2014). It is very likely that the wastewater from the Hanford site contains NDMA. Up to 28 million gallons of wastewater from the Hanford remediation site are treated per year and discharged to a state-approved disposal site in Area A on the Hanford site (US DOE, 2014). The presence of NDMA in groundwater from the disposal site is likely. As shown in Figure 26 below, the Hanford site is located near the Columbia River, and Area A is adjacent to the river.

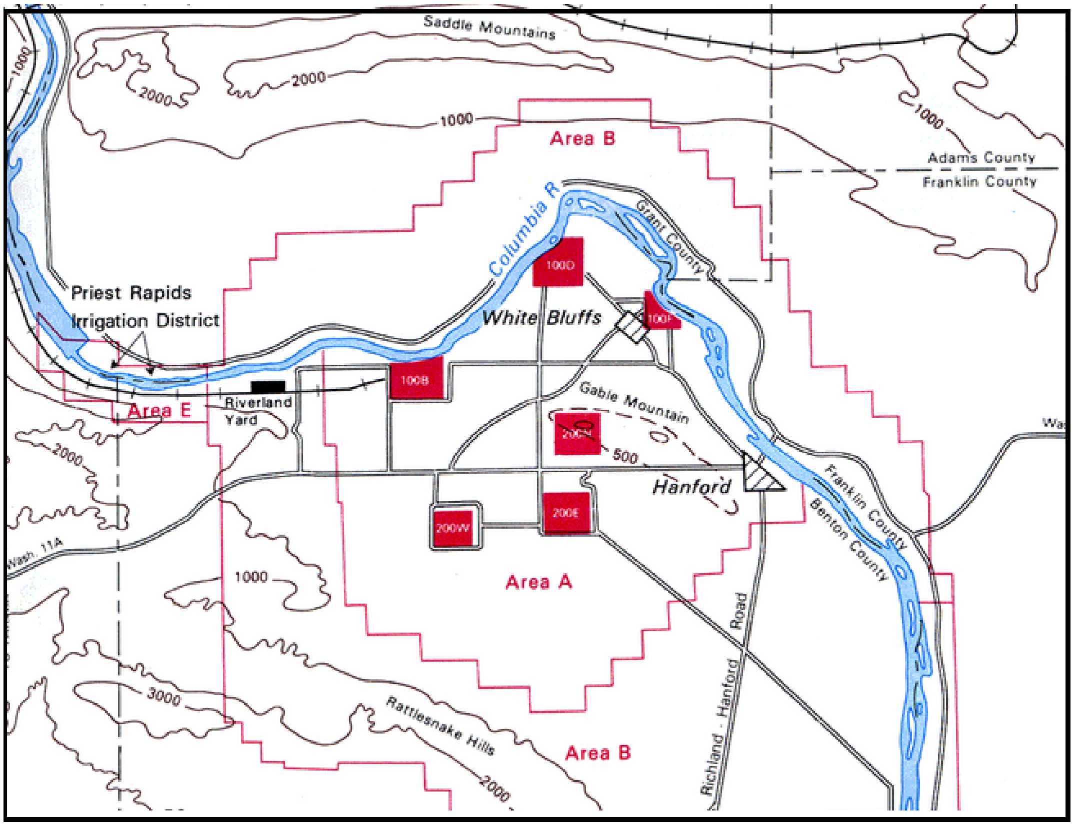


Figure 26: Hanford Site on the Columbia River (Atomic Archive, “Hanford Engineer Works 1943-195”)

The wastewater disposal area in relation to the city of Richland is shown in Figure X below. According to Google Maps, the elevation of Richland, WA is around 400 feet above sea level while the disposal site is around 1000 feet. Groundwater, likely containing NDMA, can flow from the wastewater disposal site can reach the Richland, WA drinking water supply. Additionally, evidence of detectable levels of atrazine in the Clackamas River downstream of Richland verifies the influence of agricultural wastewater (Carter, 2010). Since atrazine has similar biodegradation mechanisms to NDMA, it is likely that NDMA is also present in the Clackamas River. The Richland, WA wastewater treatment plant is a conventional activated sludge treatment system. It serves a population of 48,000 and has a 12 MGD capacity (City of Richland, “Wastewater”). Gaseous chlorine is used for disinfection prior to discharge to the Columbia River. Downstream drinking water supplies are potentially impacted by the Hanford and Richland wastewater. The city of Wilsonville, population 22,000, uses the Willamette River, a tributary of the Columbia River for drinking water. Figure 27 shows the location of Wilsonville in relation to Hanford and the Richland WWTP. Since Wilsonville is far from the Richland WWTP, NDMA from this source is likely not significant.

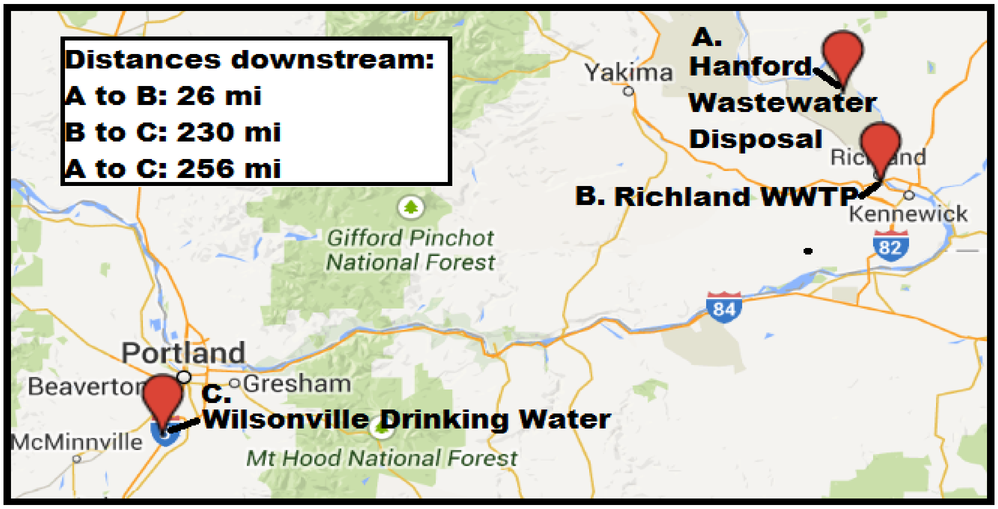


Figure 27: Low risk of contamination of Wilsonville drinking water from Richland and Hanford Wastewater (basemap: Google Maps, 2015)

6.3 Extent of the Problem

The Weibull model can be used to mathematically extrapolate the health risk associated with NDMA. This model is used by the US EPA, the California DPH, the Ontario Ministry, and the Regional Municipality of Waterloo (Ontario Ministry of the Environment, 1991). The method considers lifetime exposure and quantifies the slope of the dose response curve to represent cancer risk. Table 2 in the Background chapter shows the concentrations of NDMA associated with various cancer risk levels. The table is reprinted below for convenience.

Chapter 2, Table 2: IRIS drinking water concentration providing cancer risk (IRIS, 1993)

Cancer Risk Level	NDMA Concentration, ng/L
1 in 10,000	70
1 in 100,000	7
1 in 1,000,000	0.7
Oral Slope Factor	51 mg/kg/day

The health risk associated with exposure to nitrosamines in drinking water was studied by Hrudey et al. (2013). Exposure to NDMA was broken down into 3 main sources: endogenous synthesis, food, and drinking water. To develop a risk factor, the drinking water source and disinfection method were considered. The estimated exposure was developed based on UCMR2 data and per-capita consumption. Results showed the highest exposure associated with surface water sourced water disinfected by chloramination. The mean intakes estimated for an average adult consuming chlorinated or chloraminated surface water was 0.007 ng/kg/day and 0.06 ng/kg/day respectively. When compared to the other forms of NDMA exposure such as consumption of cured meats and formation in the body, drinking surface water treated with chlorination made up for 0.9% of the average daily dose based on the mean intake of water. Drinking surface water treated with choramination made up for 7.0% of the average daily dose. Based on the 95th percentile intake, the percent of average daily NDMA dose was about three times higher for both drinking water sources.When compared to the risk associated with chlorination, an eight-fold risk increase was concluded. The amount of exposure was calculated with two different intake values: the mean intake and the 95th percentile intake. The average daily NDMA dose was about three times higher for the 95th percentile intake for both drinking water sources.

The four reference drinking water sources had high potential for NDMA contamination. Since direct measurements of NDMA were not available, the estimated concentration of NDMA in the various water sources was approximated by the type of disinfection and the impact from upstream discharges. The study by Hrudey et al. identified an 8-fold increase in NDMA concentration for chloramination relative to chlorination; therefore the disinfection risk factor was determined by allowing a factor of 8 for chloraminated drinking water and a factor of 1 for chlorinated drinking water (2007). An estimated value of NDMA concentration based on the literature review carried out in the Hrudey study was assigned using 22 ng/L for chloramination and 3 ng/L for chlorination. The upstream risk was used to adjust the NDMA concentration by multiplying by 3 for high estimated upstream risk and 1.5 for moderate risk. These factors were used based on the assumption that the major rivers selected have some of the highest wastewater and industrial impacts in the US. Table 15 below shows the results for overall risk of each site, calculated on a scale of 1 to 3.

The cancer risk level was interpolated from the EPA cancer risk levels shown in Chapter 2, Table 2. The cancer risk for each population was determined and the estimated of cancer cases associated with NDMA in drinking water was found. The city of Philadelphia had the highest risk, with 43 cancer cases identified for the city.

Table 15: Cancer risk estimated for reference cities

Site	Disinfection Risk Estimated NDMA Concentration	Upstream Risk Factor	Estimated NDMA Concentration*, ng/L	Impacted Population	Interpolated Lifetime Cancer Risk	Cancer Cases
Washington, DC	Chloramination; High; 22 ng/L	WW, Agriculture, Transportation petroleum spills; Moderate	33	600,000	1 in 47,000	13
Philadelphia, PA	Chlorination+NH_3; High; 22 ng/L	WW, Agriculture, high industrial discharge; Moderate	33	2,000,000	1 in 47,000	43
Minneapolis, MN	Chlorination; Moderate; 3 ng/L	WW, industrial, treated water from Superfund site; High	9	590,000	1 in 97,000	6
Richland, WA	Chlorination; Moderate; 3 ng/L	WW, industrial, treated water from hazardous cleanup site; High	9	45,500	1 in 97,000	0.5

*Disinfection Risk Estimated NDMA Concentration based on work by Hrudey et al for NDMA concentration in drinking water by disinfection mechanism (2007).

**Estimated NDMA Concentration = disinfection risk concentration* upstream risk factor (moderate=1.5, high =3)

6.4 Conclusions

Since data was not available to confirm the actual NDMA concentration, the risk analysis was limited in precision and the cancer cases determined are loose projections. Future researchers are encouraged to gather NDMA occurrence data to confirm the levels actually present in the four locations. The highest priority should be placed on the Philadelphia water because of its large population size and the high potential to form NDMA by the chloramination disinfection method. The Minneapolis and

Richland drinking water facilities have intakes downstream from hazardous cleanup sites and should be investigated further to determine whether there is increased NDMA. The impact of low flow conditions and the average time each site experiences low flow conditions should also be determined. In addition to the reference locations studied in this report, sites of potable water reuse should be given high priority for NDMA investigations.

In the future, the EPA will likely regulate NDMA in finished drinking water to protect human health. Since drinking water is consumed by such large populations, a slight cancer risk such as 1 in 100,000, associated with 7 ng/L, translates to a perceptible cancer occurrence in a highly populated area. The risk for NDMA in drinking water can be greatly decreased by avoiding chloramination or adding minimal chlorine for secondary disinfection. On-site oxidant generation, also called anodic oxidation disinfection, is a secondary disinfection alternative method listed by the EPA as a small-scale compliance technology for secondary disinfection (EPA, 1998). The disinfectant solution is made by adding electric current to salt using an on-site generator, producing mostly free chlorine but also several other oxidants at lower concentrations. The treatment method is similar to chlorination, but it should be tested to determine its impact on NDMA formation.

The detection of NDMA requires GC analysis, but the levels of NDMA can be estimated without direct measurement by considering the type of disinfection and the upstream wastewater influence. Based on the limits set by the EPA in the future, facilities will need to conduct full analyses to determine their risk for NDMA and whether chlorination or chloramination is an acceptable disinfection method. From this study, it is unlikely that chloramination will be an acceptable technique. The alternatives for treatment facilities include advanced treatment for NDMA removal and changing disinfection method. A full cost-benefit analysis would be necessary for facilities to determine the best alternative for specific systems.

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Appendix

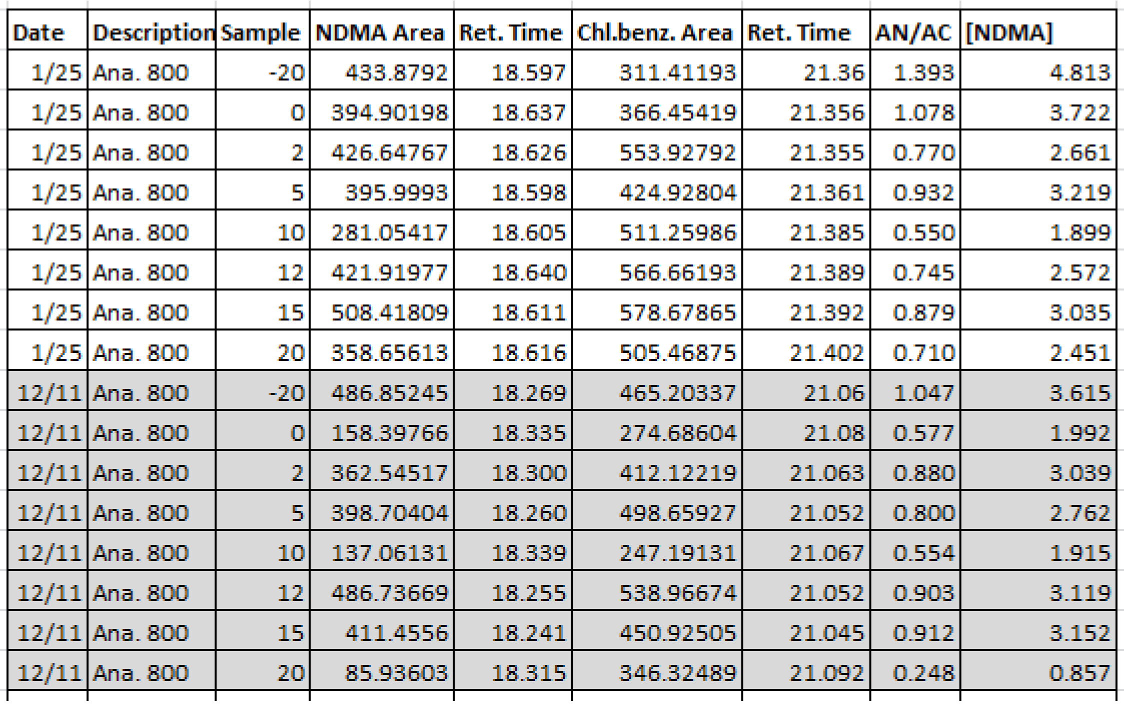
Appendix A: Gas Chromatography SPME Settings

Item	Parameters
Pre-incubation time	600 s
Incubation temperature	80 C
Pre-incubation agitator speed	400 rpm
Agitator on time	5s
Agitator off time	2s
Vial penetration	22 mm
Extraction time	1800 s
Desorb to	gc inj1
Injection penetration	54 mm
Desorption time	240 s
Post fib conditioning time	120 s
GC runtime	2700 s

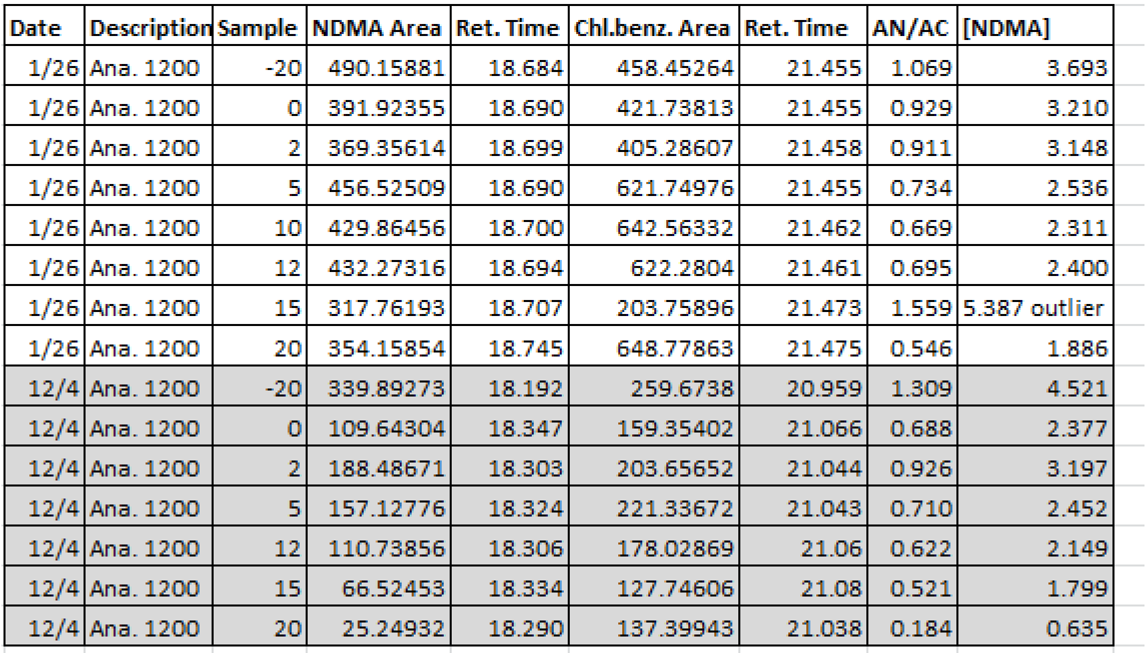
Each vial spiked with 50 µl of 10 mg/L of Chlorobenzene. (Alvarez Corena, 2014)

Add 4 g of NaCl to each vial.

Appendix B: Raw Data



Date	Description	Sample	NDMA Area	Ret. Time	Chl.benz. Area	Ret. Time	AN/AC	[NDMA]
1/25	Ana. 800	-20	433.8792	18.597	311.41193	21.36	1.393	4.813
1/25	Ana. 800	0	394.90198	18.637	366.45419	21.356	1.078	3.722
1/25	Ana. 800	2	426.64767	18.626	553.92792	21.355	0.770	2.661
1/25	Ana. 800	5	395.9993	18.598	424.92804	21.361	0.932	3.219
1/25	Ana. 800	10	281.05417	18.605	511.25986	21.385	0.550	1.899
1/25	Ana. 800	12	421.91977	18.640	566.66193	21.389	0.745	2.572
1/25	Ana. 800	15	508.41809	18.611	578.67865	21.392	0.879	3.035
1/25	Ana. 800	20	358.65613	18.616	505.46875	21.402	0.710	2.451
12/11	Ana. 800	-20	486.85245	18.269	465.20337	21.06	1.047	3.615
12/11	Ana. 800	0	158.39766	18.335	274.68604	21.08	0.577	1.992
12/11	Ana. 800	2	362.54517	18.300	412.12219	21.063	0.880	3.039
12/11	Ana. 800	5	398.70404	18.260	498.65927	21.052	0.800	2.762
12/11	Ana. 800	10	137.06131	18.339	247.19131	21.067	0.554	1.915
12/11	Ana. 800	12	486.73669	18.255	538.96674	21.052	0.903	3.119
12/11	Ana. 800	15	411.4556	18.241	450.92505	21.045	0.912	3.152
12/11	Ana. 800	20	85.93603	18.315	346.32489	21.092	0.248	0.857



Date	Description	Sample	NDMA Area	Ret. Time	Chl.benz. Area	Ret. Time	AN/AC	[NDMA]
1/26	Ana. 1200	-20	490.15881	18.684	458.45264	21.455	1.069	3.693
1/26	Ana. 1200	0	391.92355	18.690	421.73813	21.455	0.929	3.210
1/26	Ana. 1200	2	369.35614	18.699	405.28607	21.458	0.911	3.148
1/26	Ana. 1200	5	456.52509	18.690	621.74976	21.455	0.734	2.536
1/26	Ana. 1200	10	429.86456	18.700	642.56332	21.462	0.669	2.311
1/26	Ana. 1200	12	432.27316	18.694	622.2804	21.461	0.695	2.400
1/26	Ana. 1200	15	317.76193	18.707	203.75896	21.473	1.559	5.387 outlier
1/26	Ana. 1200	20	354.15854	18.745	648.77863	21.475	0.546	1.886
12/4	Ana. 1200	-20	339.89273	18.192	259.6738	20.959	1.309	4.521
12/4	Ana. 1200	0	109.64304	18.347	159.35402	21.066	0.688	2.377
12/4	Ana. 1200	2	188.48671	18.303	203.65652	21.044	0.926	3.197
12/4	Ana. 1200	5	157.12776	18.324	221.33672	21.043	0.710	2.452
12/4	Ana. 1200	12	110.73856	18.306	178.02869	21.06	0.622	2.149
12/4	Ana. 1200	15	66.52453	18.334	127.74606	21.08	0.521	1.799
12/4	Ana. 1200	20	25.24932	18.290	137.39943	21.038	0.184	0.635