Report as of FY2006 for 2002IA16G: "Relationship of Nitroso Compound Formation Potential to Drinking Source Water Quality and Organic Nitrogen Precursor Source Characteristics"

Publications

- Dissertations:
  - Assuoline, Jason, 2004, An Exploratory Study of the Formation of N-Nitrosodimethylamine (NDMA) in Chloraminated Natural Waters, MS Thesis, Dept. of Civil & Environmental Engineering, University of Iowa, Iowa City, Iowa.
- Other Publications:
  - Assuoline, Jason, Richard L. Valentine, Douglas J. Schnoebelen, Ashley Mordasky. An Exploratory Study of N-Nitrosodimethylamine (NDMA) Formation in Chloraminated Natural Waters, submitted to Environmental Science and Technology.
  - Chen, Zhuo and Richard L. Valentine, 2006. Mechanisms and Kinetics of NDMA Formation from Natural Organic Matter, submitted to Environmental Science and Technology.

Report Follows

Final Report

Relationship of Nitroso Compound Formation Potential (NCFP) to Drinking Source Water Quality and Organic Nitrogen Precursor Source Characteristics

PROBLEM AND RESEARCH OBJECTIVES

Recent research indicates that certain disinfection practices may result in the formation of significant amounts of N-nitrosodimethylamine (NDMA), and quite likely other nitroso compounds in drinking water. These compounds are believed formed when chlorine is added to water containing ammonia, and certain organic nitrogen compounds ("precursors"). Measurements in several drinking water distribution systems suggest that unprotected sources receiving point and non-point waste discharges are particularly susceptible to their formation, especially when chloramination is practiced.

The formation of NDMA and possibly other nitroso compounds in drinking water is an emerging concern because they are generally carcinogenic, mutagenic, and teratogenic (Loeppky et al., 1994; O'Neill et al., 1984). For example, the nitrosamine, N-nitrosodimethylamine, NDMA $(CH_3)_2NNO$) is a particularly potent carcinogen. Risk assessments from California's Office of Environmental Health Hazard Assessment (OEHHA) and US EPA identify lifetime de minimis (i.e., 10^{-6}) risk levels of cancer from NDMA exposures as 0.002 ppb (2 ng/L) and 0.0007 ppb, respectively. In February of 2002 the California Department of Health Services established an interim action level of 0.01 ppb (10 ng/L) in drinking water.

Many drinking water sources in the Midwest and other parts of the country are unprotected receiving point and non-point waste discharges. Municipal and industrial waste discharges, and those associated with agricultural practices, are potentially important sources of the organic nitrogen precursors required for the formation of nitroso compounds. These waters are correspondingly expected to be susceptible to nitroso compound formation from chloramination. This may limit the use of some water sources for drinking water or restrict treatment options that otherwise have desirable characteristics. Initial observations indicate that some consumers are being exposed to undesirable levels of NDMA. Organic nitrogen is therefore not a simple benign pollutant typically associated with nutrients as generally thought.

A need exists for an improved understanding of the nature and extent of this potential problem. Work is especially needed that relates nitroso compound formation potential to source water quality and origin of organic nitrogen precursors, watershed uses, and to biogeochemical processes that could influence the quantity and types of nitroso compounds potentially produced.

Based upon the ascertained research needs, the following specific objectives of this research study have been formulated with respect to the relationship of source water quality and the formation of NDMA.:

1. Characterize the NCFP in a variety of "susceptible" surface and groundwater drinking source waters,
2. Examine the relationship of NCFP to source water quality and land usage.
3 Conduct mechanistic studies to characterize precursors and the influence of potentially important physical, chemical and biological processes on the formation of NDMA.

CHARACTERIZATION OF NCFP IN SUSCEPTIBLE WATERS

The primary focus of the work performed to date has been the measurement of NDMA "Formation Potential" (NDMAFP) in natural water samples obtained from a variety of agriculturally impacted sources in Iowa. The sample locations along various rivers were selected because they were identified as points within watersheds categorized by the USGS as bodies of water impacted by agricultural waste discharges. The NDMAFP was determined through a series of laboratory assays which focused on the amendment of the surface water samples with the disinfectant monochloramine (NH_2Cl). The NDMAFP in river water samples was examined by season and in relation to other water quality variables such as nitrite, nitrate and organic nitrogen concentrations. Additional studies were conducted to delineate the potential importance of DMA as an identifiable NDMA precursor versus other unidentified nitrogenous substances.

An additional activity was an investigation of the influence of riverbank filtration (RBF) on the formation of NDMA after chloramination. RBF is a practice in which drinking water is withdrawn from shallow wells near a river. As such, the water is subjected to a variety of biogeochemical processes that influence its water quality. While RBF is effective at reducing the formation of many halogenated DBPs such as THMs and HAAs, the relationship between riverbank filtration and NDMA precursor removal is not known.

Source Waters. Surface waters were sampled monthly from April 2003 to February 2004 at four locations categorized by the USGS as being substantially impacted by agricultural runoff and waste discharges (Table 1). The relative agricultural impact at each sampling site was estimated based on historical data representing average nitrite+nitrate (NO_2+NO_3) data found on the USGS website (NAWQA website) for years 1996 to 2002.

Table 1 Summary table of USGS-NAWQA sampling locations used throughout the course of this study. Four liters of water were collected from each site near the beginning of each month in 1 liter amber bottles which were stored at 4°C until analyzed. The relative agricultural impact ranking has been assessed by average NO_2+NO_3 for each site.

ation umber	Station Name	Historical* NO_2+NO_3 in mg/L as N	Relative Agricultural Impact**
20680	S. Fork Iowa River NE of New Providence	9.19	1
65500	Iowa River near Rowan	7.05	2
49500	Wapsipinicon River near Tripoli	5.61	3
51210	Iowa River at Wapello	4.72	4

* Historical data represents the average NO_2+NO_3 values based on monthly measurements taken from 1996 to 2002.
** 1=highest, 4= lowest

In this study, the influence of riverbank filtration on NDMA formation potential of two typical Midwestern river supplies was examined. Both facilities use similar treatment processes within the plant however, minor differences in treatment process do exist. The IC treatment facility is located nearly 30 miles south of the CR plant in Southeastern Iowa. The IC plant is located on the Iowa River, where 2 well fields containing a total of 4 horizontal wells draw water through a previously pristine alluvial aquifer. The CR facility has three large well fields stretching along a meandering segment of the Cedar River where a combination of more than thirty vertical wells supplies water to the treatment facility. While this plant and its various wells have been operating for nearly 20 years, blending waters with a range of turbidity, organic carbon and other water quality characteristics, the IC facility came on line in 2003, during the course of this study.

Another difference between the two plants is that they use different chemical disinfectants. While both facilities originally planned to use chloramines, the IC plant, since it began using riverbank filtration, is able to rely solely on free chlorine to provide the required disinfectant dose while remaining within the guidelines of the Disinfectant/Disinfection By-Product Rule designated by the recent SDWA amendments. However, it should be noted that ammonia levels entering the plant are often substantial enough to lead to the incidental formation of monochloramine upon the addition of chlorine. This may have implications on NDMA occurrence at these facilities even in the absence of intentional chloramine usage.

Water samples were obtained from the raw river water and from monitoring wells located at several locations representing a span of hydraulic residence times. Water samples were also collected from several in the treatment plants. Table 2 summarizes the characteristics of two vertical wells which feed the 60 MGD CR treatment facility. Not all wells are operated continuously, yet in this study the same wells were sampled each time. The wells were selected because the water residence times differed greatly as estimated by the (USGS, 1995). The IC plant began full scale operation in October 2003

and therefore, sampling in November was one of the first times the wells were sampled after they had been in full service. The IC wells were situated about 50 feet from the banks of the Iowa River, and the horizontal sections of the collection wells extended from the wells, under the river. However, it was not feasible to estimate specific residence time within the aquifer since detailed hydraulic characterization for the new IC wells was not readily available for this study.

Table 2 Hydrogeologic characteristics for Seminole well field. Estimated travel time was calculated based on the distance from the well to the river and the approximate hydraulic conductivity initially measured at each specific well.

Sampling Well	Distance From River (ft)	Hydraulic Conductivity (ft/d)	Transmissivity (ft^2/d)	Specific Capacity (gpm/ft)	**Estimated Travel Time (d)**
Seminole 14	800	57.2	3,374	25.4	**14**
Seminole 17	63	192.7	11,177	73.1	**0.33**

Analytical Methods. The basis of the NDMA FP test has been described by Mitch and Sedlak, 2004. It is based upon addition of preformed monochloramine to water samples and a 7-day reaction time. The use of preformed monochloramine instead of the usual practice of in-situ formation by addition of free chlorine and followed by ammonia addition maximizes NDMA formation. Additional work (results not shown) indicated that NDMA formation was reduced significantly by pre-chlorination. While this suggests a strategy to reduce NDMA formation, it nonetheless creates an artifact difficult to control.

The first step in preparing the reactors was filtering the water samples through Millipore AP25 glass fiber filter designed to remove particles greater than 0.8-1.6 μm in size. Next, the filtered water was measured into the reactor jars so that the final volume of the solution containing sample water, buffer, and NH_2Cl would be 500 mL. Concentrated buffer solutions were used to create pH stability in the reactors throughout the incubation period. A 10 mM phosphate buffer was used for the lower pH 7 while 10 mM bicarbonate was added to maintain a pH near 8. These two pH levels were used in the agriculturally impacted surface water samples, however only the bicarbonate buffer was used for the riverbank filtration reactors. Blank samples for every site were amended with the appropriate buffer to form the same concentration as the reactors spiked with 1mM NH_2Cl. Duplicates were run when there was sufficient sample volume collected.

Concentrated monochloramine stock solution with a 0.1 Cl/N molar ratio was prepared fresh prior to each experiment by addition of reagent grade ammonia and hypochlorous acid to a pH 10 solution containing 10 mM bicarbonate. Dosages added to the reactors ranged from 0.05 mM to 1 mM. The NH_2Cl was measured in control samples on a daily basis in order to ensure that high levels were present throughout the

incubation period. NH_2Cl concentrations were determined by DPD-FAS titrimetric method (APHA, AWWA, and WEF; 1998).

Experiments were initiated by addition of the preformed monochloramine at a high dose of 1 mM, or 71 mg/L as Cl_2 was added to all agricultural watershed samples (approximately 20 times that of the typical residual allowed in drinking water distribution systems as dictated by the Stage 1 Disinfection/Disinfectant By-Product Rule. A much lower dosage of 0.05 mM was added to some of the riverbank filtration samples to mimic typical dosages used to maintain a substantial residual throughout a distribution system (approximately 4 mg/L as Cl_2).

All samples were incubated in the dark for 7 days (168 hours) at 20°C. Reducing light exposure to the samples as much as possible ensured that the quantity of NDMA formed would not be significantly affected by photodegradation. After the 7 day incubation period, the final pH was measured to ensure buffer stability and minimal pH variation throughout the assays. A solid/liquid extraction process was used to concentrate the NDMA formed into a small volume of methylene chloride for analysis (Luo and Clevenger, 2003 and Taguchi et al., 1994). An internal standard of d6-NDMA was added to each reactor to form a baseline concentration of 100 ng/L. This internal standard, in conjunction with calibration curves developed for each assay, facilitated the subsequent quantification of these experiments.

NDMA was measured with a Varian GC CP3800 coupled with a Saturn 2200 MS/MS detector. The column used is Varian gas chromatograph had a length of 30 m, film thickness of 0.25 μm and insider diameter of 0.25 mm. The general temperature ramping protocol for the GC started with a temperature of 35°C for 4 minutes. Next the temperature was increased to 140°C at a rate of 20°C/min. A secondary ramp elevated the temperature to 200°C at a rate of 50°C/min. This temperature was held for 9.55 minutes. The total time each sample was 20 minutes. The Saturn 2200 MS/MS detector was used under the following settings: m/z 81 for quantification of d6-NDMA and m/z 75 for NDMA.

Glassware used in the experiments was washed thoroughly with warm tap water, soaked in a nitric acid bath and then rinsed again with copious quantities of deionized (DI) water. After washing, the glassware was baked in a muffle furnace at 500°C for 1 hour. All solutions were prepared using DI water obtained from a Barnstead ROPure Infinity™/NANOPure Diamond™ system (Barnstead/Thermolyne Corp., Dubuque, IA). This treatment system produced water with a target resistivity of 18.2 mΩ-cm and [TOC] ≤ 3 ppb. All chemicals purchased and used in this study were ACS reagent grade and properly stored.

Principal Findings and Significance

NDMA Formation Potential in Watershed Samples. Figure 1 and Figure 2 are box and whisker plots showing the mean, quartile and extreme NDMA FP from July to February at each of the four locations sampled during this study. The extreme values at each site were fairly broad and ranged from 12.5 to 145.4 ng/L. Mean values for each site and at each pH value ranged from 45.6 to 92.9 ng/L. Despite significant fluctuations in the levels of NDMA formed in these samples, concentrations measured were consistently above the 10 ng/L California action level. This broad spectrum of measured NDMA in the reactors illustrates the role that fluctuations in water quality may play in the ultimate NDMA formation of a given water source. While avenues of this study are ongoing and some conclusions can be made from these results, seasonal trends were not apparent over this year. As aspects of this study continue based on these preliminary findings, seasonal trends may become more obvious.

Among the reactors tested in each sampling period, it should be noted that nearly all blank samples, those containing only sample water and buffer with no NH_2Cl, did not produce measurable levels of NDMA. This strongly suggests that background levels of NDMA in the source water for each sampling point was negligible throughout the course of the experiment and therefore NDMA formation was induced by the addition of NH_2Cl.

The relative agricultural impact of these watersheds was initially assessed based on total organic carbon (TOC), nitrite + nitrate (NO_2+NO_3) and organic nitrogen measurements performed by USGS scientists on historical samples. Relative agricultural impact for each sample location was based on the levels of these telltale water quality parameters as well as known agricultural operations in the area (see Table 1). The majority of historical data spans sample dates from 1996 until August, 2002. These parameters were not measured during this study, however agricultural practices in the areas have not significantly change since 2002. Statistical plots for the samples presented in Figures 1 and 2 suggest that there is no particular correlation between the relative agricultural impact on the watershed and NDMA formation because NDMA was consistently formed for all samples. A specific minimum threshold for these parameters influencing NDMA formation was not determined. Nonetheless, the fact that high levels of consistently quantifiable NDMA were formed suggests that these agricultural impact parameters play a role in the formation of NDMA when the samples are amended with NH_2Cl.

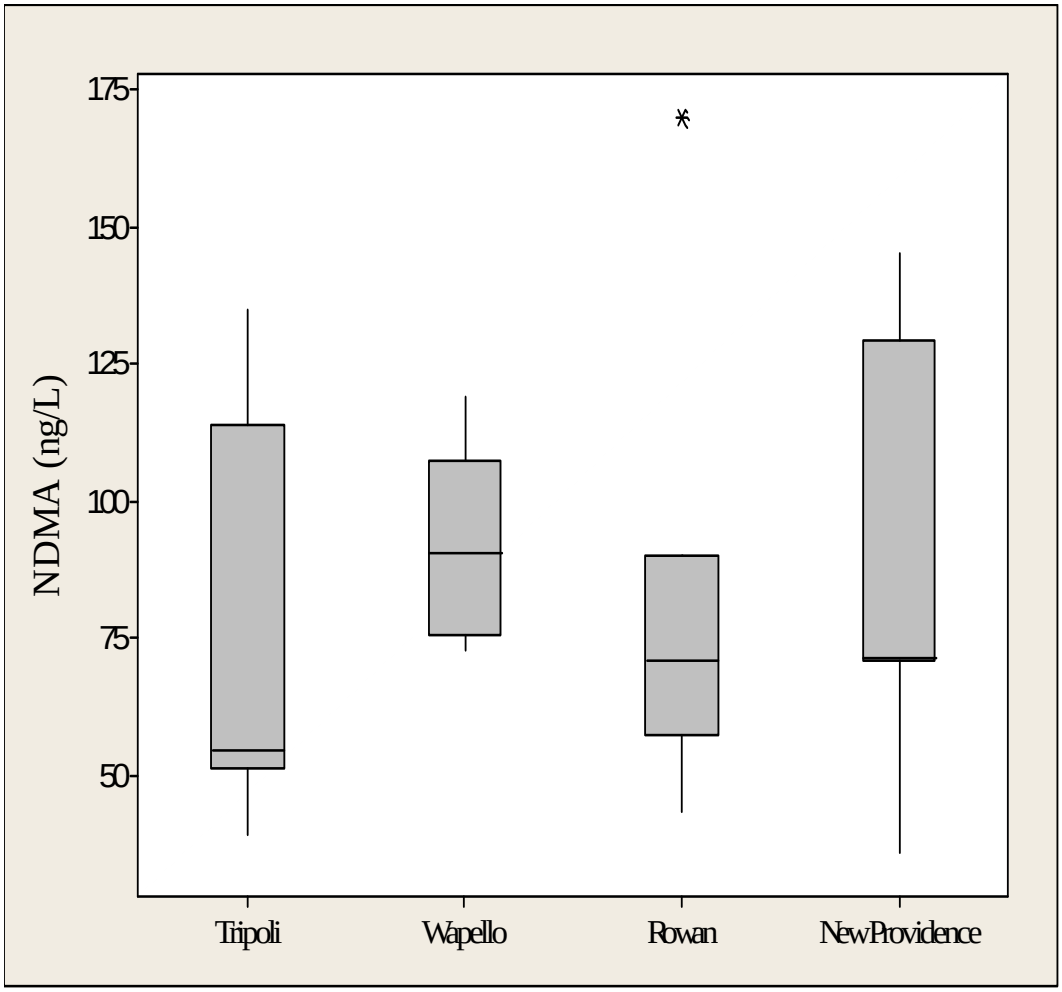

Figure 1. Box plot representing NDMA formation potential at pH~8 for each site pooled over the course of this study. The extremities of the whiskers show minimum and maximum NDMA formation potential at each site while the boxes define the quartile values and the median value. The "*" represents the outlier NDMA value measured in one the Rowan sample months.

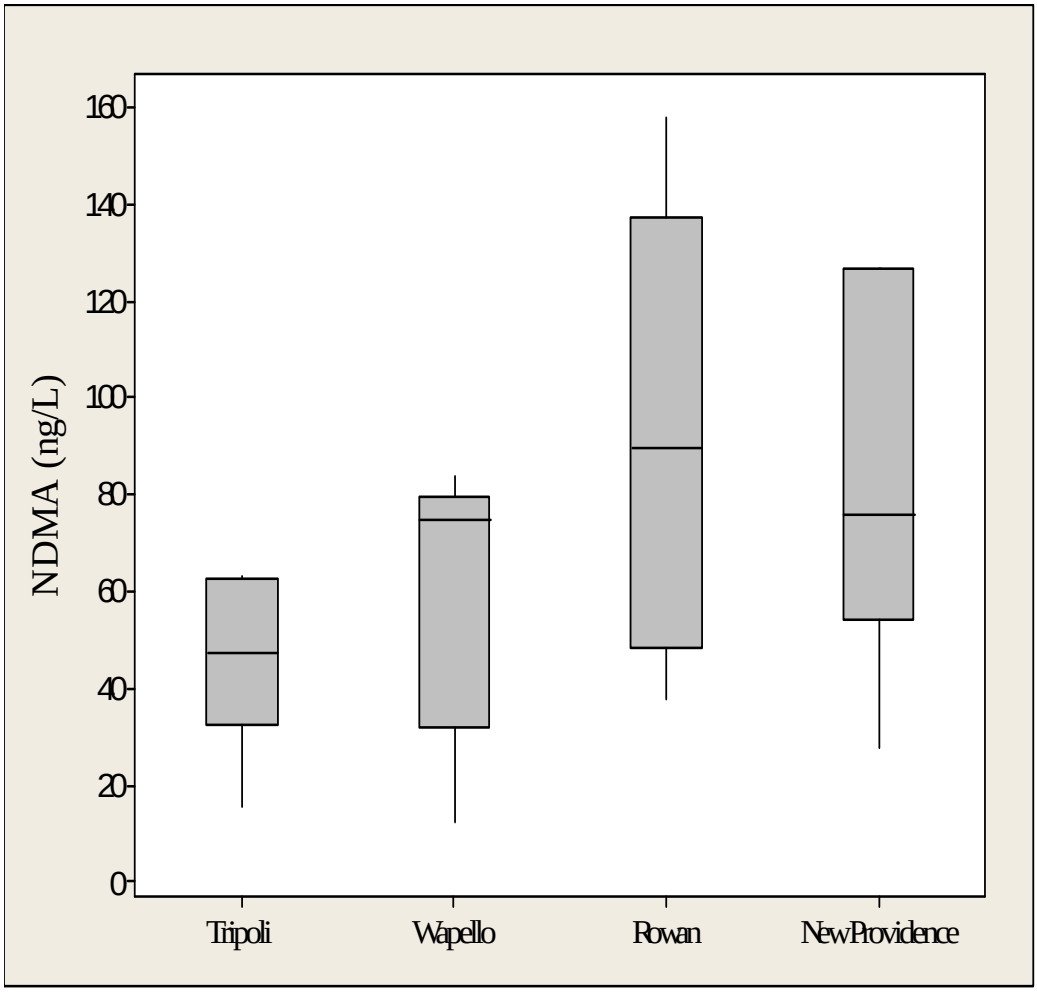

Figure 2. Box plot representing NDMA formation potential at pH~7 for each site pooled over the course of this study. The extremities of the whiskers show minimum and maximum NDMA formation potential at each site while the boxes define the quartile values and the median value.

Riverbank Filtration. The riverbank filtration samples shown in this section exhibit results from watersheds which are not directly influenced by agricultural practices, but can nonetheless have high levels of TOC, NO_2+NO_3 and NH_3 due to the migration of these parameters throughout surface waters in the state of Iowa. This can be seen in the levels of NDMA formed in the raw water (original surface water source for each facility) samples, which remained within the range previously observed in the samples defined as directly impacted by agricultural practices. Results from the samples collected from various locations at each of the two treatment facilities are shown in Figures 3 and 4.

Representative plots are presented (Figures 3 and 4) to show NDMA formation trends observed in several sampling events. In these graphs it can be seen that NDMA formation was significantly reduced by riverbank filtration at both the IC and CR locations when the high dose of 1 mM monochloramine was added. The NDMA levels dropped from 102 ng/L to 15 ng/L and 64 ng/L to 24 ng/L between the raw river water

and the well samples. Interestingly, further conventional treatment did not appear to influence the NDMA FP at the higher NH_2Cl dose.

In contrast, neither riverbank filtration nor conventional treatment had a significant impact on NDMA formation when it was measured using the more practically significant monochloramine dose of 0.05 mM. Under these lower monochloramine dosage levels, NH_2Cl exhaustion maybe occurring before the precursor reservoir in each sample is consumed.

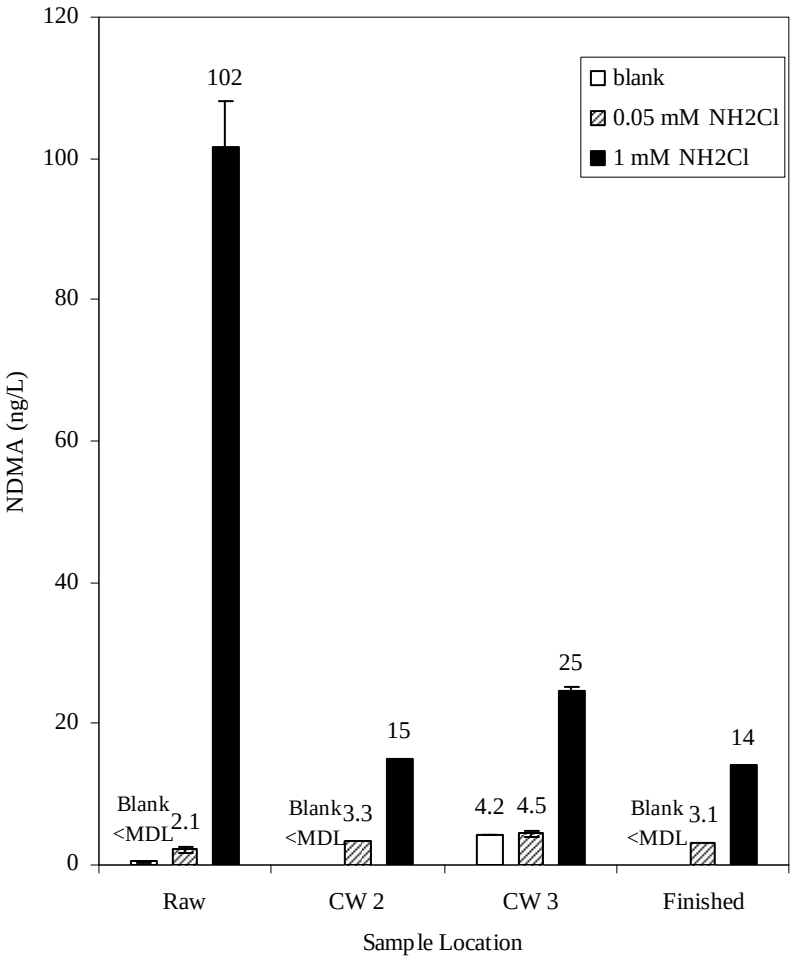

Figure 3. IC samples collected on 11-17-03. Monochloramine was added to the samples to produce a concentration in each reactor as indicated in the figure. Error bars are shown for reactors in which duplicates were run. All samples were incubated in the dark at 20°C for 7 days. The average pH of the bicarbonate buffered reactors was 8.27 ± 0.2.

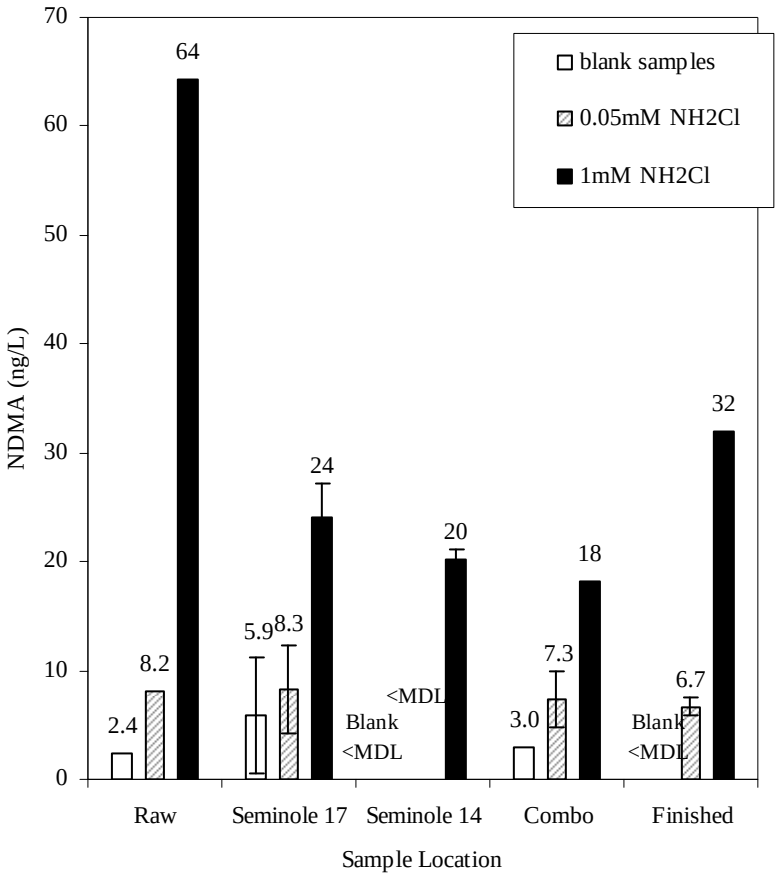

Figure 4. Cedar Rapids samples collected on 9-29-03. Monochloramine was added to the samples to produce a concentration in each reactor as indicated in the figure. Error bars are shown for reactors in which duplicates were run. All samples were incubated in the dark at 20oC for 7 days. The average pH of the bicarbonate buffered reactors was 8.20 ± 0.15.

Mechanistic Studies: Role of DMA . As little direct correlation was observed between NDMA FP and the agricultural indicator parameters, additional mechanistic studies were conducted to determine the role of DMA as a potential precursor of NDMA formation. DMA is a known NDMA precursor and a substance generally ubiquitous in water (Mitch and Sedlak, 2003). DMA was measured in samples obtained from four

locations shown in Table 3, ranging from approximately 170 to 650 ng/L supporting the notion that it could be an important precursor.

In order to determine the NDMA formed from observed levels of DMA, a controlled experiment was conducted to show how much NDMA could potentially be attributed to typical DMA levels measured in the water samples. DI water was spiked with 200 and 650 ng/L of DMA and preformed NH_2Cl was dosed as in other parts of this study. The levels of NDMA formed were then compared with what was measured in the natural samples.

The NDMA measured in relation to DMA addition is shown in Table 3. These results indicate that DMA could account for only approximately 3-6% of the NDMA FP in the collected water samples. These relative yields are slightly higher, yet relatively consistent with the findings of Mitch and Sedlak (2004) who observed that the DMA present in their water samples could only account for approximately 0.6% of the NDMA FP (Mitch and Sedlak, 2003). Our results indicate that DMA does contribute to NDMA formation but that it cannot account for most of the NDMA formed. Therefore, other more important precursors must be present in these surface waters.

Table 3. Results of NDMA formation and DMA analysis for samples collected July, 2003 in relation not specific DMA addition to DI water. The % NDMA attributed to DMA concentrations in the water is based on the NDMA formed in the DI samples assuming no other NDMA precursors were present in the DI water.

Site	NDMA ng/L	DMA ng/L	% NDMA from DMA
DI water pH~8	4.5	200.0	100%
DI water pH~8	7.0	650.0	100%
New Providence	129.6	196.3	3%
Rowan	77.5	170.6	6%
Wapello	90.4	174.0	5%
Tripoli	114.0	651.2	6%

NDMA Precursor Exhaustion Study. Determining the class of likely precursors (e.g., agricultural indicators or DMA) was previously discussed as part of this study, however regardless of what the NDMA forming precursors are, it was relevant to conduct additional studies to determine the extent of precursor exhaustion based on the experimental methods used. The kinetics of NH_2Cl autodecomposition as delineated by Valentine and Jafvert at various pH values was used to calculate the concentration-time (C*t) curve for each assay. C*t values were used to assess whether the observed disappearance of NH_2Cl over the course of each assay was due to reaction with precursor material in the samples or autodecomposition. Subsequent experiments measured NH_2Cl decay in DI water and Iowa River water under varying Cl/N ratios at the pH values relevant in this study. From these studies monochloramine decay kinetics were measured and used to normalize NDMA formation potential to the calculated C*t for each reactor.

An experiment to fully exhaust all NDMA precursors in the water samples was conducted to measure the NDMA formation after 7 and 14 days. Iowa River water was collected from the University of Iowa water treatment plant and filtered through the same 1.6 μm glass fiber filters used in other experiments. Batch reactors were comprised of roughly 500 ml of water, 1 mM NH_2Cl and either 10 mM phosphate or bicarbonate buffers in order to maintain a pH values around 7 and 8, respectively. Blank samples were not dosed with preformed NH_2ClAs in other experiments, measurements of NH_2Cl concentrations were measured on a daily basis for each reactor over the 7 day and 14 day reaction periods. Precursor exhaustion was therefore tested by comparing the amount of NDMA that could be formed by a second dosage of NH_2Cl, readjusting to the initial 1 mM NH_2Cl concentration, followed by 7 more days of incubation.

Based on the precursor exhaustion experiment performed, the majority of NDMA was formed within the first 7 days of the experiment. As shown in Figure 5, appreciable levels (between 5 and 21 ng/L) of NDMA are additionally formed after a subsequent respike of NH_2Cl which readjusted the concentration to 1 mM. Also, Table 4 shows the results of normalized NDMA formation (NDMA/C*t) based on the precursor exhaustion experiment. Due to the fact that the ratio of NDMA to C*t is significantly reduced between the 7-day and 14-day reactors it can be surmised that the NDMA formation precursors initially present in the surface water samples were mostly consumed within the first 7 days. If this were not the case the second chloramine dosage would form similar amounts of NDMA as the first dosage and the NDMA/C*t values would be closer.

This experiment was performed in order to provide a quantitative basis for past and future experiments involving the formation of NDMA in natural waters in conjunction with NH_2Cl decay. From the data measured, the Valentine Chloramine Stability coefficient for each reactor was measured and compared to theoretical calculations based on the average pH, initial and final NH_2Cl concentrations as well as the equilibrium coefficients associated with each buffer used. The normalization of NDMA formation with C*t demonstrate how precursor limitation was experienced in all reactors dosed with 1 mM NH_2Cl. From this, the potential for various NDMA formation precursors can be suggested based on NH_2Cl demand.

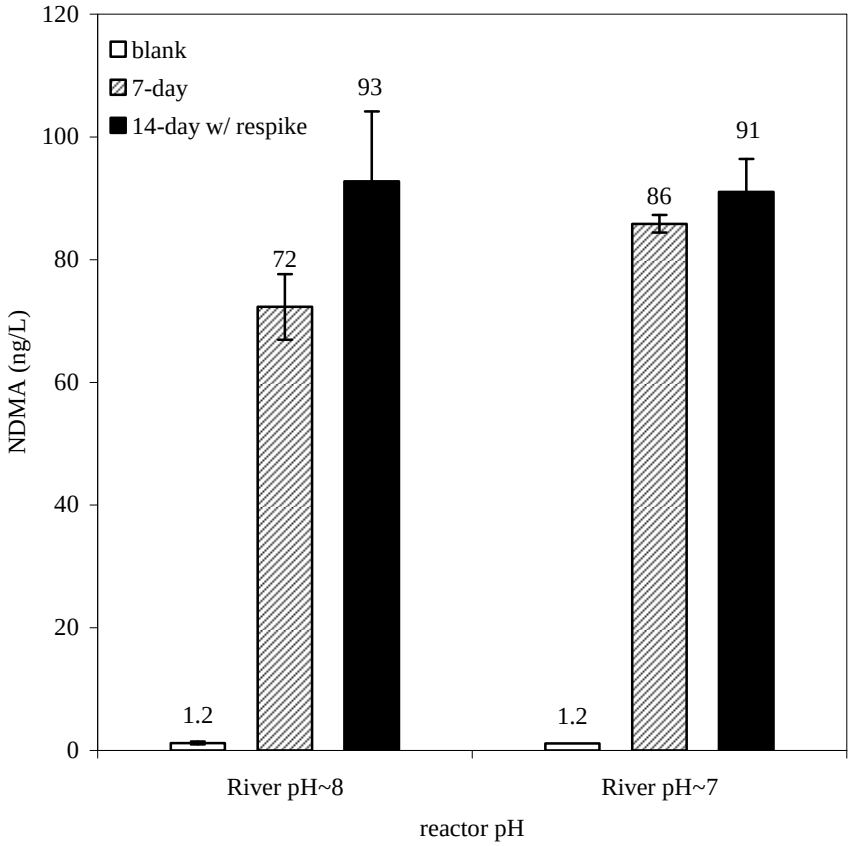

Figure 5. Precursor limitation experiment performed on 3-17-04 with filtered Iowa River water. All samples were buffered with either 10 mM bicarbonate or phosphate buffers in order to maintain pH values around 8 and 7, respectively. All reactors were incubated in the dark at 20oC

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Table 4. Summary table of C*t normalized NDMA formation (NDMA/C*t) in Iowa River water at various pH values. 7-day samples were dosed with 1 mM preformed NH2Cl and incubated in the dark at 20oC. The 14 day samples were amended with sufficient NH2Cl in order to readjust **the concentration to the original 1 mM.**

Sample	NDMA (ng/L)	C*t (mg Cl_2-h/L)	NDMA/C*t	%NDMA formed in 7 days
7-day @ pH~8	72.3	8632	8.4	--
14-day @ pH~8	92.8	21874	4.2	78
7-day @ pH~7	85.8	6134	14.0	--
14-day @ pH~7	91.0	21431	4.2	94

Summary and Conclusions

Results from this exploratory study demonstrate that a significant NDMA formation potential exists in the agriculturally impacted surface waters sampled. Measurements of NDMA formation potential in two typical Iowa drinking water sources and treatment facilities further suggest that chloramination practices may need to be assessed based on potential NDMA formation in the distribution system. Maximum NDMA formation values were based upon monochloramine dosages approximately 20 times that typically used in drinking water disinfection. NDMA was also formed at quantifiable levels when samples were dosed with monochloramine at concentrations typically used in drinking water treatment. The maximum NDMA FP for samples amended with the higher concentrations of monochloramine is typically in a range that can exceed 100 ng/L which is 10 times higher than that generally considered acceptable by any regulatory or health risk standards.

No statistical evidence was obtained that showed a significant difference in NDMA FP between the four agriculturally impacted watersheds over the course of this study when data was pooled over all the sampling periods. Seasonal trends for predicting variations in formation potential were distinguishable over the course of this preliminary study. Additionally, NDMA FP did not conclusively correlate with nitrate, organic nitrogen, or total organic carbon at any location. The determination of these statistical correlations was limited by the sample size available for each parameter over the course of the study as well as the relatively short time period available for data collection and analysis.

Dimethylamine was measured in selected agriculturally impacted watershed samples as an established NDMA forming precursor. Experiments conducted in this study corroborated other research which suggests that DMA is not the sole NDMA precursor present in surface waters. Results from this study revealed that the DMA content measured could account for only a relatively insignificant amount (approximately 3-6%) of the NDMA FP suggesting that the presence of other precursors also existed in the samples.

The influence of riverbank filtration (RBF) on NDMA formation was studied at both low (0.05 mM) and high (0.5 or 1.0 mM) monochloramine dosage. NDMA formation was generally greater at the higher monochloramine dosages but this trend was not always the case. The high monochloramine 7-day NDMA formation potential in the raw water was approximately 100 ng/L in IC and between 40 and 60 ng/L in CR. Riverbank filtration generally reduced the NDMAFP in IC water by 90 % and between 30% and 80% in CR water, for the higher monochloramine dosage.

Significant amounts of NDMA were also formed by the addition of 0.05 mM monochloramine when measured against the 0.7 ng/L EPA 10^{-6} cancer risk level. Raw water dosed with 0.05 mM NH_2Cl produced NDMA values of approximately 10 ng/L in IC water and 20 ng/L in CR water. Interestingly, neither RBF nor conventional surface water treatment techniques seemed to have a significant effect on reducing NDMA formation potential at the lower monochloramine dosage.

The study of NDMA formation from two sequential dosages of 1 mM NH_2Cl and two 7-day incubation periods support the hypothesis that most of the precursors present are exhausted after the first dosage and incubation period and the NDMA FP increased by only 5-10% after the second dosage. This may explain why NDMA FP did not correlate linearly with the concentration-time (C*t) values as it would if the precursor concentration were not reduced with monochloramine dosage. This may also explain why the NDMA FP was approximately the same at pH 7 and 8. While differences were observed in the NDMA FP between nominal pH values of 8 and 7, they were generally within approximately 10%. This may be attributable to near exhaustion of the NDMA precursors in both cases not necessarily reflective of identical formation kinetics.

From this research further work should be done to investigate precursors originally present in typical agriculturally impacted surface waters as well as additional compounds which may be introduced as a result of riverbank filtration and conventional drinking water treatment. Anthropogenic chemicals introduced in urban and agricultural watershed areas may both lead the augmentation of NDMA formation potential in source waters. The classification of NDMA formation potential should be recommended as part of future source water quality evaluations in newly designed treatment facilities located in potentially high risk areas. As a result of preliminary source assessments, alternative and or additional treatment strategies may be needed in order to reduce the risk of exposure to NDMA. Although this may increase the overall cost of treatment for a particular community, research presented here and in other studies demonstrates the importance of chronic NDMA exposure and the importance it plays in drinking water treatment.

NDMA FORMATION MECHANISMS AND STUDIES

Mechanistic studies of NDMA formation in drinking source water obtained from rivers previously examined for their NDMA FP (i.e. ag impacted) as well as one pristine source. As such the findings presented are excerpted wholly from the Ph.D. dissertation of Dr. Zhuo Chen (August 2006, University of Iowa). The work reported here can be divided into three focus areas:

1. Characterization of NDMA formation from selected humic fractions of isolated riverine NOM. NOM was fractionated into 6 humic fractions and the NDMAFP of each was determined. A comparison was made of the contribution of each fraction to the observed NDMAFP of the whole water sample.

2. Characterization of the reaction mechanism and kinetics of NDMA formation from reaction of monochloramine with natural organic matter. The approach was to postulate a reaction mechanism, conduct experiments in which water quality such as pH and chloramines dosages were varied, and then compare measured with predicted NDMA concentrations.

3. Examination of the influence of chemical and photochemical oxidation on NDMA formation. The water was subjected to various chemical oxidants that reacted with NOM as well as simulated sunlight to photo-oxidize some NOM. The influence on NDMA formation was also examined for relationships to changes in the UV spectra.

Source Waters and the Collection, Concentration, and Fractionation of NOM

Natural organic matter sources

This study utilized both concentrated natural organic matter (NOM) and whole natural water samples from two typical agriculturally impacted river sources, a pristine "colored water" wetland, and drinking water obtained from several utilities.

Whole water and NOM concentrates were obtained from the Iowa River (IRW) and from Valentine Pond in the Keweenaw Peninsula of Upper Michigan (UPW). While the first source is from a river highly impacted by agricultural practices that result in significant additions of inorganic and organic nitrogen, the later is located in a largely uninhabited and pristine area. Therefore comparisons are expected to yield valuable information on possible human/animal sources of NDMA precursors. Additional whole water samples were collected from the Cedar River (CRW) and from a surface water source for a drinking water utility in the State of Ohio provided by Malcolm Pirnie Company (MPW).

Concentration of NOM by reverse osmosis (RO)

NOM was concentrated by reverse osmosis (Figure 6). The reverse osmosis system used in this study was a RealSoft PROS/2S reverse osmosis unit (Stone Mountain, GA). To prevent fouling of the membranes by organic and inorganic constituents, the raw water was filtered through a 5 μm prefilter, 0.45 μm filter, and then passed through Dowex Marathon C cation exchange resin (Dow Chemical, Midland, MI). The RO unit's permeate to retenate flow ratio were maintained at 1:7 ratio at 200 psi. Other researchers who used similar RO units for isolation of Suwannee River DOC, as well as other surface and groundwater DOC, recovered 90% of the NOM at a process rate of 150-180 L/h (Serkiz and Perdue, 1990; Sun et al., 1995). Kitis et al. (2001) showed that reverse osmosis isolation maintains the integrity and reactivity of the NOM with respect to chlorine demand and selected DBP formation. Figure 1 shows a simplified schematic of the pre-filtration and RO unit.

Iowa River water (IRW) sample was drawn directly from the river surface, [DOC] = 3.4 mg-C/L, and seven hundred liters of water was collected and concentrated in February, 2004. The Upper Peninsula of Michigan water (UPW) had a DOC concentration of 9.55 mg-C/L. 80 liters of UPW sample was processed in July, 2004.

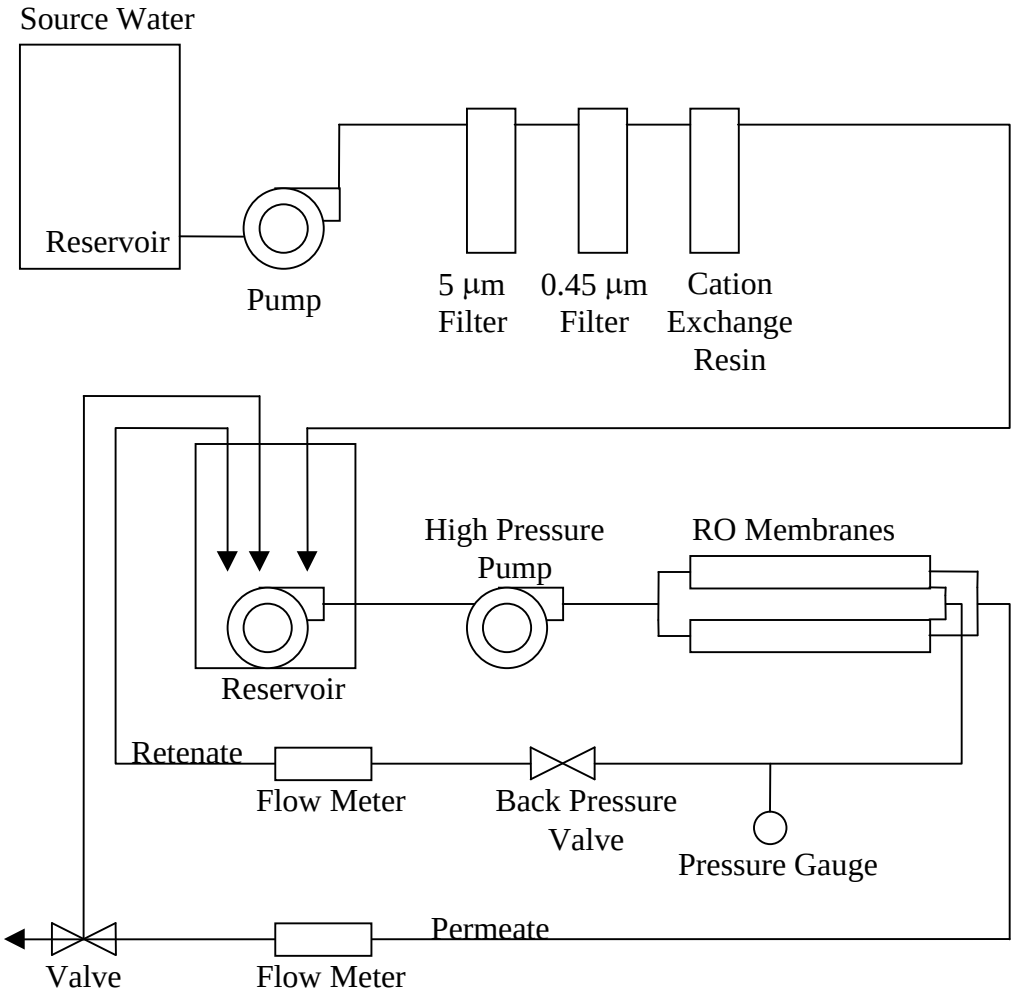


Figure 6. Schematic of pre-filtration and reverse osmosis unit used to filter and concentrate NOM from source waters

Fractionation of NOM

In this study, the original NOM fractionation method proposed by Leenheer (1981) was adopted with slight modification to separate Iowa River water (IRW) NOM into two categories: hydrophobic and hydrophilic portions. Each portion was also further fractionated into acidic, basic and neutral fractions by selective elution procedures (Figure 7).

Specifically, the collected IRW NOM concentrate was passed through 0.45 μm membrane before being pumped into a XAD-8 column at 30 bed volumes/h. At saturation, hydrophobic base was eluted with back flush of 0.25 bed volumes of 0.1 N HCl followed by 1.5 bed volumes of 0.01 N HCl. Effluent from the 1st XAD-8 resin was acidified to pH 2.0 with HCl and pumped onto 2nd XAD-8 column at 30 bed volumes/h. After rinsing the column with 1 bed volume of 0.01 N HCl, hydrophobic acid was eluted with back flush of 0.25 bed volume of 0.1 N NaOH, followed by 1.5 bed volume of DI water. Pump both the XAD-8 resin columns dry and hydrophobic neutral fraction was obtained by Soxhlet extracting the resins with methanol. After freeze drying, the hydrophobic neutral was dissolved back into water. Effluent from the 2nd XAD-8 was pumped through H-saturated AG-MP-50 cation exchange resin and hydrophilic-base was forward eluted with 1.0 N NH_4OH. Then the effluent was pumped through Duolite A-7 anion exchange resin and hydrophilic acid was obtained by back flush with 3 N NH_4OH. Only hydrophilic neutral was left in the effluent. All fractions were concentrated into small volumes by rotovapping below 40 °C.

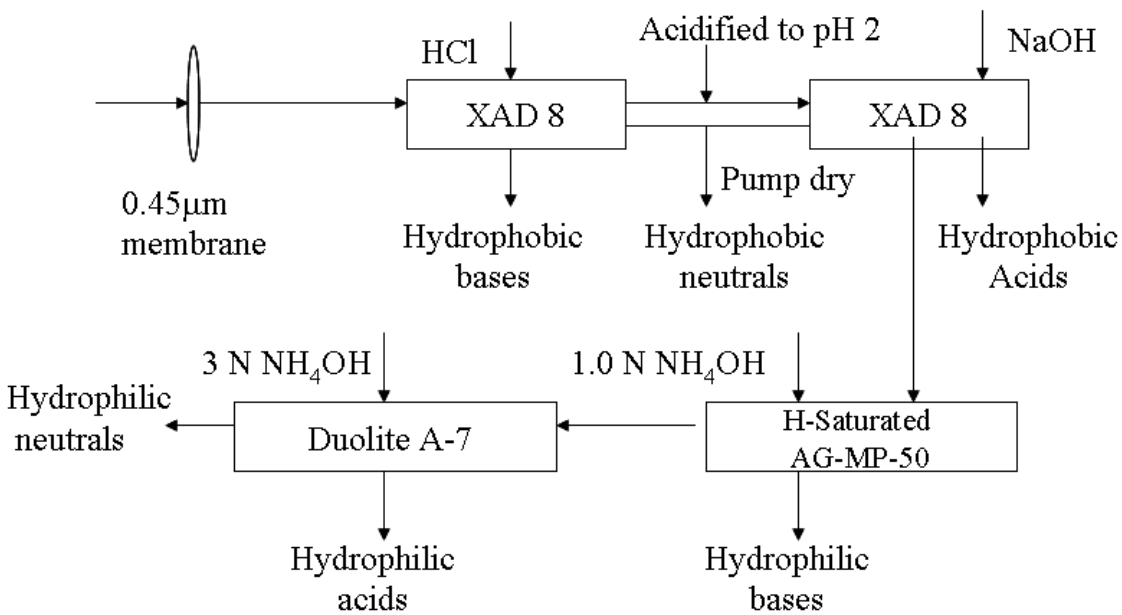


Figure 7. Schematic for fractionation of NOM (Leenheer, 1981)

Characterization of NOM

DOC measurements, UV spectroscopy, and fluorescence spectroscopy were used to characterize NOM. Dissolved organic carbon (DOC) was measured using a Shimadzu TOC 5000 (Shimadzu Scientific, Columbia, MD) and standardized according to Standard Method 505A (APHA et al., 1992). The detection limits using the platinum catalyst combustion was determined to be 0.25 mg-C/L. UV absorbance and spectral characteristics of the natural organic mater were obtained with a Shimadzu UV1601 dual beam spectrophotometer. Fluorescence spectra were obtained using Perkin-Elmer LS55 Luminescence Spectrometer. Excitation-emission matrix (EEM) spectra were collected with subsequent scanning emission spectra from 290 nm to 600 nm at 10 nm increments by varying the excitation wavelength from 200 nm to 400 nm at 10 nm increments.

Reactors and Experimental Approach

Glassware used in the experiments was washed thoroughly with warm tap water, soaked in a nitric acid bath and then rinsed again with copious quantities of deionized (DI) water. After washing, the glassware was baked in a muffle furnace at 500°C for 1 hour. All solutions were prepared using DI water obtained from a Barnstead ROPure Infinity™/NANOPure Diamond™ system (Barnstead/Thermolyne Corp., Dubuque, IA). This treatment system produced water with a target resistivity of 18.2 mΩ-cm and [TOC] ≤ 3 ppb. All chemicals purchased and used in this study were ACS reagent grade and properly stored.

The basis of the NDMA FP test has been described by Mitch and Sedlak, 2004. It is based upon addition of preformed monochloramine to water samples and a 7-day reaction time. The use of preformed monochloramine instead of the usual practice of in-situ formation by addition of free chlorine and followed by ammonia addition maximizes NDMA formation. Additional work (results not shown) indicated that NDMA formation was reduced significantly by pre-chlorination. While this suggests a strategy to reduce NDMA formation, it nonetheless creates an artifact difficult to control.

The first step in preparing the reactors was filtering the water samples through Millipore AP25 glass fiber filter designed to remove particles greater than 0.8-1.6 μm in size. Next, the filtered water was measured into the reactor jars so that the final volume of the solution containing sample water, buffer, and NH_2Cl would be 500 mL. Concentrated buffer solutions were used to create pH stability in the reactors throughout the incubation period. A 10 mM phosphate buffer was used for the lower pH 7 while 10 mM bicarbonate was added to maintain a pH near 8. These two pH levels were used in the agriculturally impacted surface water samples, however only the bicarbonate buffer was used for the riverbank filtration reactors. Blank samples for every site were amended with the appropriate buffer to form the same concentration as the reactors spiked with 1mM NH_2Cl. Duplicates were run when there was sufficient sample volume collected.

Concentrated monochloramine stock solution with a 0.1 Cl/N molar ratio was prepared fresh prior to each experiment by addition of reagent grade ammonia and hypochlorous acid to a pH 10 solution containing 10 mM bicarbonate. Dosages added to the reactors ranged from 0.05 mM to 1 mM. The NH_2Cl was measured in control

samples on a daily basis in order to ensure that high levels were present throughout the incubation period. NH_2Cl concentrations were determined by DPD-FAS titrimetric method (APHA, AWWA, and WEF; 1998).

Experiments examining the kinetics of NDMA formation and the role of various humic fractions were initiated by addition of the preformed monochloramine at a high dose of 1 mM, or 71 mg/L as Cl_2 was added to all agricultural watershed samples (approximately 20 times that of the typical residual allowed in drinking water distribution systems as dictated by the Stage 1 Disinfection/Disinfectant By-Product Rule. A much lower dosage of 0.05 mM was added to some of the riverbank filtration samples to mimic typical dosages used to maintain a substantial residual throughout a distribution system (approximately 4 mg/L as Cl_2).

All samples were incubated in the dark for 7 days (168 hours) at 20°C. Reducing light exposure to the samples as much as possible ensured that the quantity of NDMA formed would not be significantly affected by photodegradation. After the 7 day incubation period, the final pH was measured to ensure buffer stability and minimal pH variation throughout the assays. A solid/liquid extraction process was used to concentrate the NDMA formed into a small volume of methylene chloride for analysis (Luo and Clevenger, 2003 and Taguchi et al., 1994). An internal standard of d6-NDMA was added to each reactor to form a baseline concentration of 100 ng/L. This internal standard, in conjunction with calibration curves developed for each assay, facilitated the subsequent quantification of these experiments.

All experiments examining the role of prechlorination/preoxidation were conducted in batch reactors (one-liter capacity clear Pyrex bottles with PTFE screw caps). The pre-chlorination studies involved adding 0.03-0.08 mM free chlorine for a prescribed contact time (15 sec~1 h) followed by addition of ammonia at a Cl/N molar ratio of 1:1. Chemical pre-oxidants used included O_3, H_2O_2, and $KMnO_4$. The dosages of H_2O_2 were 3 mg/L and 30 mg/L, while the dosage of $KMnO_4$ was fixed at 10 mg/L. Ozone was formed freshly in distilled water at 12 mg/L using an ozonator (Model ss-150, Pillar Technologies, Hartland, WI) and added to the tested NOM solutions at O_3/DOC weight ratio of 2:1. A Suntest CPS+ sun light simulator (Atlas Electric Devices Co., Chicago, IL) was used for simulated solar irradiation at a constant irradiance of 250 W/m^2 to investigate the influence of photochemical oxidation. Quartz tubes were used for the irradiation and the irradiation time was fixed at 1 h. Following a pre-oxidant contact time of 1 h, preformed monochloramine was added (0.05 mM). The post-chloramination reaction time following the pre-chlorination and pre-oxidation step was allowed to extend for 24 to 120 hours. NDMA concentration was measured periodically and compared to that obtained in control experiments without pre-chlorination or pre-oxidation.

Analytical

Monochloramine was measured by DPD-FAS titration. NDMA was measured with a Varian GC CP3800 coupled with a Saturn 2200 MS/MS detector. The column used is Varian gas chromatograph had a length of 30 m, film thickness of 0.25 μm and insider diameter of 0.25 mm. The general temperature ramping protocol for the GC started with a temperature of 35°C for 4 minutes. Next the temperature was increased to 140°C at a rate of 20°C/min. A secondary ramp elevated the temperature to 200°C at a

rate of 50°C/min. This temperature was held for 9.55 minutes. The total time each sample was 20 minutes. The Saturn 2200 MS/MS detector was used under the following settings: m/z 81 for quantification of d6-NDMA and m/z 75 for NDMA.

Principal Findings and Significance

Precursor Studies of the Formation of NDMA from Selected Humic Fractions

NDMA formation potential tests (Mitch et al., 2003) were conducted using both whole Iowa River water, and reconstituted river water prepared using RO concentrate to replicate the whole water DOC concentration of 3.4 mg C/L. RO concentrated Iowa River NOM (IRW NOM) was further fractionated into six operationally-defined fractions using the standard procedure proposed by Leenheer (1981).. Figure 8 is a pie chart showing DOC recovery of each fraction. Figure 3 clearly shows that hydrophobic acids (HPOA), which usually contain both humic acids and fulvic acids, is the major contributor of total DOC in the tested river water (72 %). Hydrophobic bases (HPOB) and hydrophobic neutrals (HPON) contributed 1.98 % and 1.1 %, respectively. Hydrophilic fractions generally make up a smaller fraction of DOC than that due to hydrophobic fractions, which is shown here. Hydrophilic acids (HPIA) contributed 7.9 %, while hydrophilic bases (HPIB) and hydrophilic neutrals (HPIN) contributed 4.6 % and 0.8 %, respectively, of the total DOC. A relatively small, 11 % loss in total DOC was realized, probably due to the washing and elution of columns and evaporation during the Roto-vapping procedure.

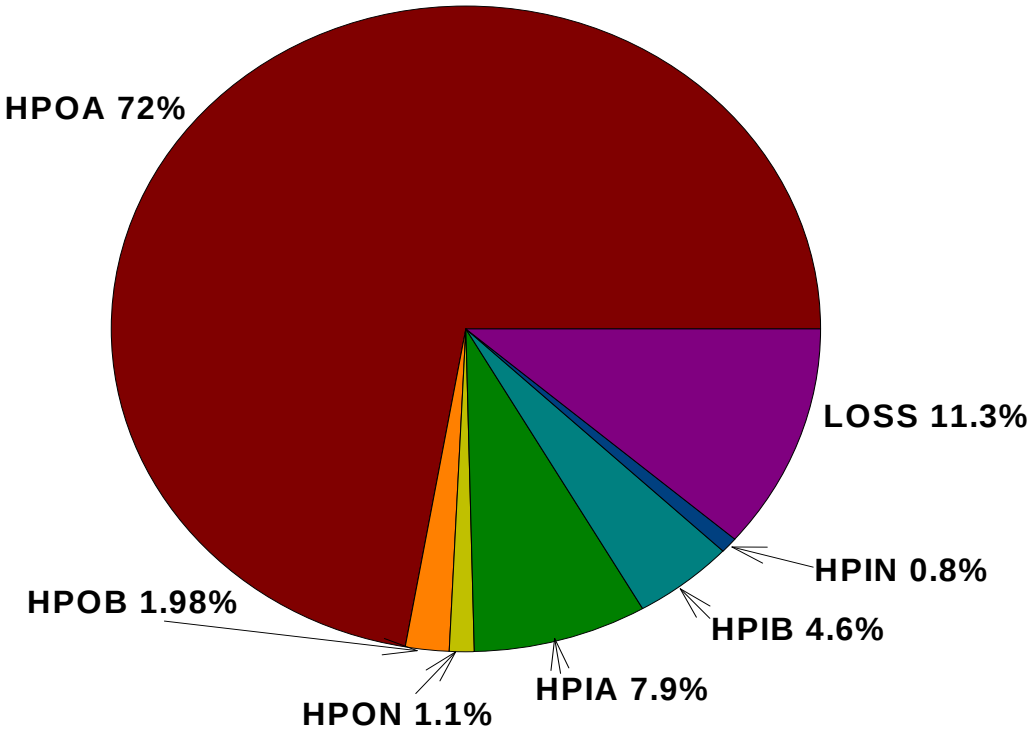


Figure 8. DOC recovery of NOM fractionation (IRW NOM, fractionation using procedure proposed by Leenheer, 1981)

Figure 9 shows the NDMA formation potential in the original unprocessed whole water sample as a function of time. NDMA formation steadily increased with time attaining a value of 112 ng/L at the end of the 7-day test period. In comparison, approximately 100 ng/L of NDMA was formed in laboratory prepared water containing RO concentrate at the same DOC concentration as the unprocessed water. In addition, the concentration-time profiles were similar. This nearly 90% recovery of NDMA formation potential indicated that the RO concentration method that was used produced concentrated NOM from natural water with excellent preservation in reactivity. In other words, most NDMA precursors were captured and concentrated during this RO concentration procedure.

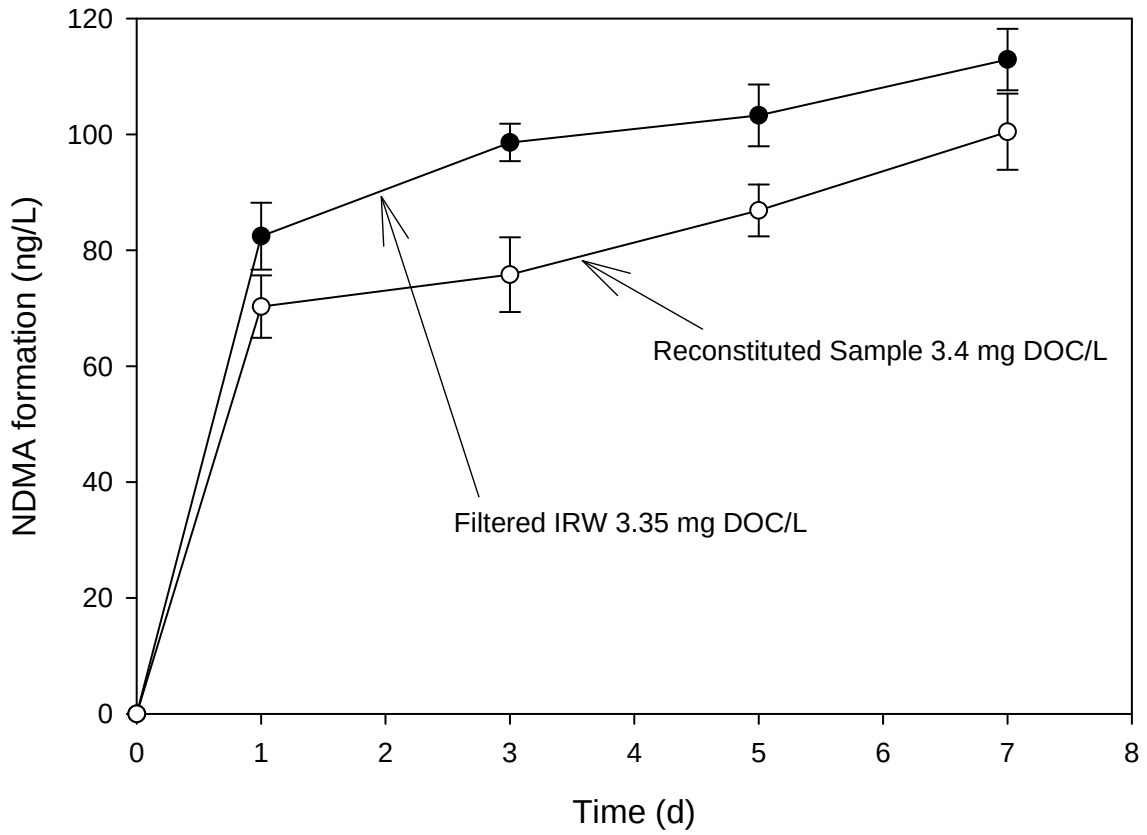


Figure 9. Preservation of NDMA formation potential in RO concentrate water (1mM NH_2Cl, pH = 7.0, T = 20ºC)

The NDMA formation potential of each humic fraction was also determined. Table 1 tabulates the NDMA formation potential normalized to carbon content (nanograms of NDMA formed per milligram of DOC). For example, 77.5 nanograms of NDMA was formed from every milligram of carbon in the hydrophilic bases (HPIB) fraction. Obviously HPIB showed the highest NDMA formation potential compared to other NOM fractions. Two trends are evident from the data. First, hydrophilic fractions tend to form more NDMA than hydrophobic fractions. Second, basic fractions tend to have a larger NDMA formation potential than acid fractions. This may be due to the higher nitrogen content in the polar hydrophilic and basic fractions (Croue et al., 1999).

Table 5 summarizes the expected contribution of all fractions to the NDMA formation potential measured in the whole water. In this table, the NDMA formation potential was calculated as normalized to the DOC concentration found in original river water (3.4 mg/L). After fractionation, based on the DOC percentage contribution of each fraction (figure 4.4) and the NDMA formation potential test results of each fraction (table 4.6), the predicted NDMA FP from the sum of the six fractions is determined to be approximately 95 ng/L. This can be compared to the 112 ng/L in the original Iowa River water, which indicates excellent recovery of NDMA formation potential in both the RO water and in the humic fractions.

Table 5 List of NDMA formation potential of fractionated NOM fractions

Fractions	DOC contribution	NDMA FP* (ng/(mg DOC))	Total NDMA FP contribution
HPOA	72.00 %	27.47	71 %
HPOB	1.98 %	31.43	2.2 %
HPON	1.10 %	22.44	0.9 %
HPIA	7.90 %	43.50	12.3 %
HPIB	4.60 %	77.50	12.8 %
HPIN	0.80 %	25.76	0.7 %

FP*: Formation potential

Table 6 3.4 mg/L DOC equivalent NDMA formation potential

Samples	NDMA formation potential (ng/L)
Original river water	112
RO water	100
Sum of fractions	95

Relationship of changes in SUVA to NDMA formation

Aromatic moieties in NOM have been shown to affect UV absorbance spectrum of NOM (Chen et al., 2000; Vogt et al., 2004). The SUVA value at 254 nm and 272 nm are especially considered as good indicators of the aromaticity and reactivity of NOM. However, the relationship between the SUVA value of each NOM fraction and their individual NDMA formation potential indicated that the initial SUVA value of NOM is not a comprehensive index for NDMA formation potential. It certainly represents the aromaticity of NOM, but apparently not the functional groups that are responsible for NDMA formation.

Additional experiments were conducted to investigate the relationship between changes in the $SUVA_{272}$ value and the amount of NDMA formed in chloraminated water. This was done using reconstituted IRW NOM at the DOC level of 3.4 mg/L and dosed with 0.05 mM preformed NH_2Cl. Periodically, the monochloramine residual was quenched by addition of excess ascorbic acid and both NDMA concentration and $SUVA_{272}$ value were determined.

The formation of NDMA was found to correlate quantitatively with the change of $SUVA_{272}$ occurring during the course of the reaction. Figure 10 shows a linear

relationship between the reduction of $SUVA_{272}$ and the formation of NDMA, suggesting the possibility of tracking NDMA formation by measuring changes in SUVA.

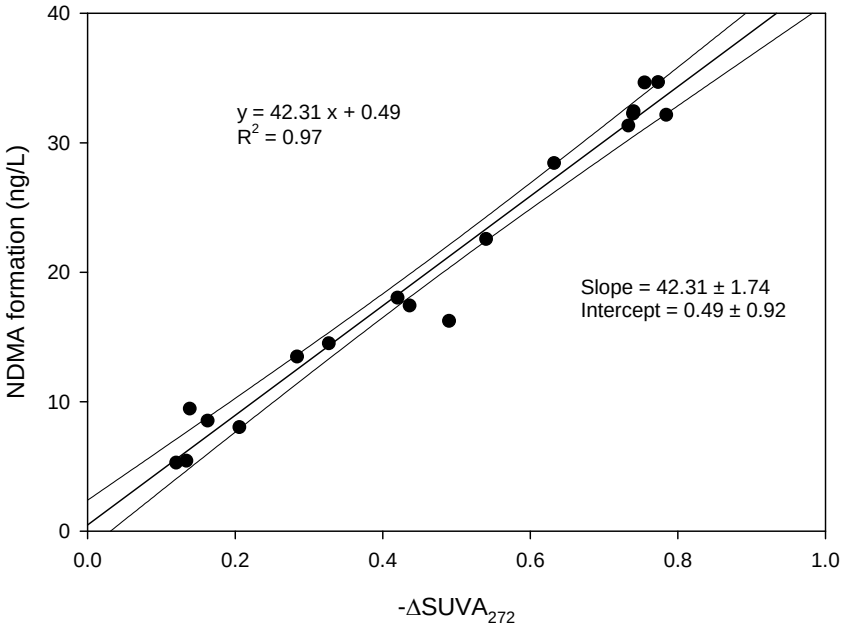


Figure 10. Relationship between specific UV absorbance change of NOM and NDMA formation in the reaction of NOM with monochloramine (pH 7.0, T = 20ºC, IRWC NOM TOC = 3.5 mg/L, [NH2Cl]0 = 0.05 mM, slope and intercept are shown with their 95% confidence intervals)

Interestingly, the SUVA value of each NOM fraction did not show any correlation with NDMA formation potential, while the $\Delta SUVA_{272}$ demonstrated a strong linear relationship with NDMA formation. As discussed earlier, SUVA has been extensively used as indicator of the reactivity of NOM with disinfectants (Westerhoff et al., 2004). Some studies directly used SUVA values as a predictor for the formation of halogenated DBP precursors (Korshin et al., 1997; Kitis et al., 2001). Duirk (2003) also demonstrated that $SUVA_{254}$ value could be used as a surrogating index for the reactivity of NOM with monochloramine. Nevertheless, the work reported here seems contradictory in that NDMA formation did not correlate with the SUVA value of the humic fractions, while the change in SUVA did correlate. This is probably attributable to structural differences in various humic fractions that lead to differences in precursor content. SUVA might be a good predictor of NDMA formation potential if all water sources had the same distribution of each humic fraction, and presumably the same distribution of potential NDMA precursors. Processes such as oxidation or removal of NOM that causes a reduction in SUVA may govern the rate of NDMA formation. But the SUVA changes from treatment that removes NOM would only be good predictor of NDMA reduction if all fractions were removed to the same percent (Croue et al., 1999; Allpike, et al., 2005).

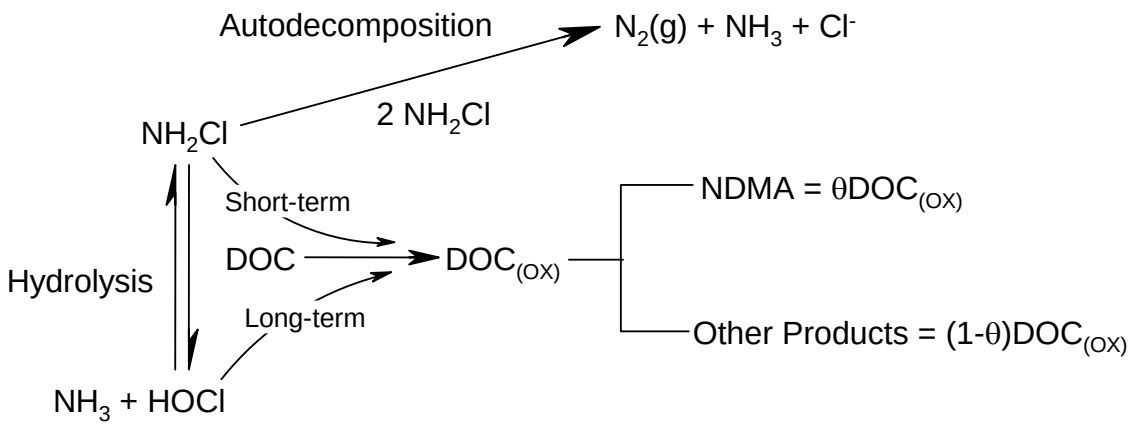
Mechanisms and Kinetics of NDMA Formation by Reaction of NOM with Monochloramine.

Model development

The formation of NDMA is a relatively slow process generally occurring on a time scale of days (Mitch et al., 2003; Choi and Valentine, 2001), which is comparable to the time scale of monochloramine loss from autodecomposition (Vikesland et al., 2001) and from oxidation of NOM (Vikesland et al., 1998; Duirk et al., 2005). The monochloramine-NOM reaction model proposed by Duirk (2003) was used to describe these parallel processes to predict both the concentration of monochloramine and the amount of NOM oxidized with time. A schematic of the proposed model is shown in Figure 6.

Duirk et al. (2005) modified a description of monochloramine autodecomposition (Figure 11) by incorporating simple second-order kinetic description of NOM oxidation involving two types of reactive sites (reactions 11-12). Site type S_1 represents a comparatively small fraction of reactive dissolved organic carbon (DOC) that reacts very rapidly producing an “initial chloramine demand”. Site type S_2, comprising more than 90% of the reactive DOC, reacts quite slowly (over days) accounting for the most of the monochloramine loss typically observed over a five-day period. While the rate constants k_1 and k_2 are associated with these two types of reactive sites respectively, constant k_1 is simply set conveniently high so that the demand due to site type S_1 is accounted for rapidly, within an hour. The value of k_2 on the other hand is critical to predicting the slow loss of monochloramine with time. NOM oxidation is primarily attributed to reaction involving a direct reaction of DOC with HOCl that exists in minute amount in chloramine solutions, produced from such reaction as hydrolysis of monochloramine (reaction 2). Duirk et al. (2005) validated the model using several whole water sources, NOM

concentrates obtained by reverse osmosis, and fractionated humic isolates. The model could account for dependencies on pH, ammonia, DOC, and monochloramine concentrations. Results were consistent with the assumption that humic-type substances were the dominant reactive type of NOM.



Note: θ: a simple stoichiometric coefficient

DOC: dissolved organic carbon

$DOC_{(OX)}$: oxidized dissolved organic carbon

Figure 11. Model schematics of NDMA formation from reactions between NOM and monochloramine

This model was modified to account for NDMA formation by assuming that the rate of NDMA formation was proportional to the rate of NOM oxidation. This is similar to the approach recently taken to describe the formation of dichloroacetic acid from the oxidation of NOM (Duirk et al., 2002). A simple stoichiometric coefficient θ_{NDMA} was incorporated to linearly correlate the formation of NDMA with the oxidation of NOM. Other researchers have correlated the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) with free chlorine demand, presumably from the oxidation of NOM (Clark et al., 2001; Gang et al., 2002). This is equivalent to the assumption that ratio of NDMA formed to NOM oxidized is a constant θ_{NDMA} over the entire course of the reaction (Equation 1):

$$\frac{d[NDMA]}{dt} = \theta_{NDMA} \frac{d[DOC]_{OX}}{dt} \qquad \text{Equation 1}$$

The rate of NDMA formation can therefore be expressed as equation 2 in terms of model parameters and variables:

$$\frac{d[NDMA]}{dt} = \theta_{NDMA}\{k_1[NH_2Cl][DOC]\times S_1 + k_2[HOCl][DOC]\times S_2\} \qquad \text{Equation 2}$$

S_1 = DOC short-term reactive site fraction

S_2 = DOC long-term reactive site fraction

k_1, k_2 = reaction rate constants

θ_{NDMA} = stoichiometric coefficient

All constants characterizing monochloramine autodecomposition were obtained from literature (sources shown in table 7). Only k_1, S_1, k_2, S_2 and θ_{NDMA} were determined for this model as NOM source specific parameters. The model was expressed as a system of ordinary differential equations (ODEs), the whole set of which was solved using Scientist™ (Scientist, 1995). Scientist™ uses a modified Powell algorithm to minimize the unweighted sum of the squares of the residual error between the predicted and experimentally determined values to estimate the model parameters.

The comprehensive reaction model differentiates monochloramine loss into two pathways: auto-decomposition and oxidation of NOM. The initial modeling activity required determining the parameters that characterize monochloramine loss independently of the value of θ_{NDMA}, which is only used to predict NDMA formation. The final estimated model parameters for each particular NOM source, obtained by averaging parameter estimates for all data sets for the same NOM source, are listed in table 7. The model estimation of NOM reactive sites are consistent with the total reactive sites determined by free chlorine titration methodology. This shows that titrating the NOM with free chlorine serves as a good independent method to determine reactive site fractions.

Table 7. Model estimated parameters with their 95% confidence intervals for tested NOM sources including IRW, UPW and CRW NOM

Sources		IRW[1]	UPW[2]	CRW[3]
	k_1	$1.21\times10^{4}\pm4.30\times10^{3}$	$1.12\times10^{4}\pm6.60\times10^{3}$	$1.43\times10^{4}\pm3.07\times10^{3}$
	S_1	0.011±0.003	0.009±0.003	0.015±0.006
	k_2	$5.92\times10^{5}\pm1.87\times10^{4}$	$4.88\times10^{5}\pm1.72\times10^{4}$	$6.01\times10^{5}\pm6.30\times10^{4}$
	S_2	0.53±0.04	0.48±0.04	0.62±0.05
	S_1+S_2	0.54±0.04	0.57±0.04	0.63±0.06
	S_T[4]	0.59	0.45	0.65
NDMA	θ_{ND}	$2.85\times10^{-5}\pm5.17\times10^{-6}$	$1.67\times10^{-5}\pm4.10\times10^{-6}$	$3.23\times10^{-5}\pm2.19\times10^{-6}$

[1]: IRW: Iowa River water, n = 10

[2]: UPW: Valentine Pond water in Upper Peninsular of Michigan, n = 7

[3]: CRW: Cedar River water, n = 4

[4]: Total reactive sites determined by free chlorine titration

NDMA formation

With the establishment of the model's capability to describe monochloramine loss in the presence of NOM (data not shown), the model was used to calculate the amount of NOM oxidized (in terms of equivalent amounts of monochloramine) as a function of reaction conditions and time. Figure 12 shows a linear relationship between NDMA formed and NOM oxidized for IRW water. A similar relationship was found for the other two source waters. This linear relationship is consistent with the assumption that the rate of NDMA formation is given by equation 5.1 and that the value of θ_{NDMA} is a source specific constant that is independent of pH and hence the rate of NOM oxidation.

Figure 13 compares measured and predicted NDMA formation from IRW at DOC concentrations of 1.7 to 6.8 mg/L, which are in the typical DOC range representative of many water supplies (Roth and Ozment, 1998). A higher concentration of DOC resulted in higher NDMA formation. During the early stage of the reaction course, the model appears to slightly underestimate NDMA production at low DOC levels and slightly overestimate it at high DOC levels. But overall, the model predicted NDMA formation quite well. Figure 14 shows the influence of pH from 6.0 to 9.0 on NDMA formation. A good match between experimental data and model prediction is again indicated. The effect of free ammonia on NDMA formation was also investigated using a fixed initial monochloramine concentration and chlorine to ammonia molar ratios ranging from 0.1 to 0.7 (Figure 15. Results show that increasing ammonia reduces the rate of NDMA

formation, consistent with the expected influence of ammonia on the rate of NOM oxidation.

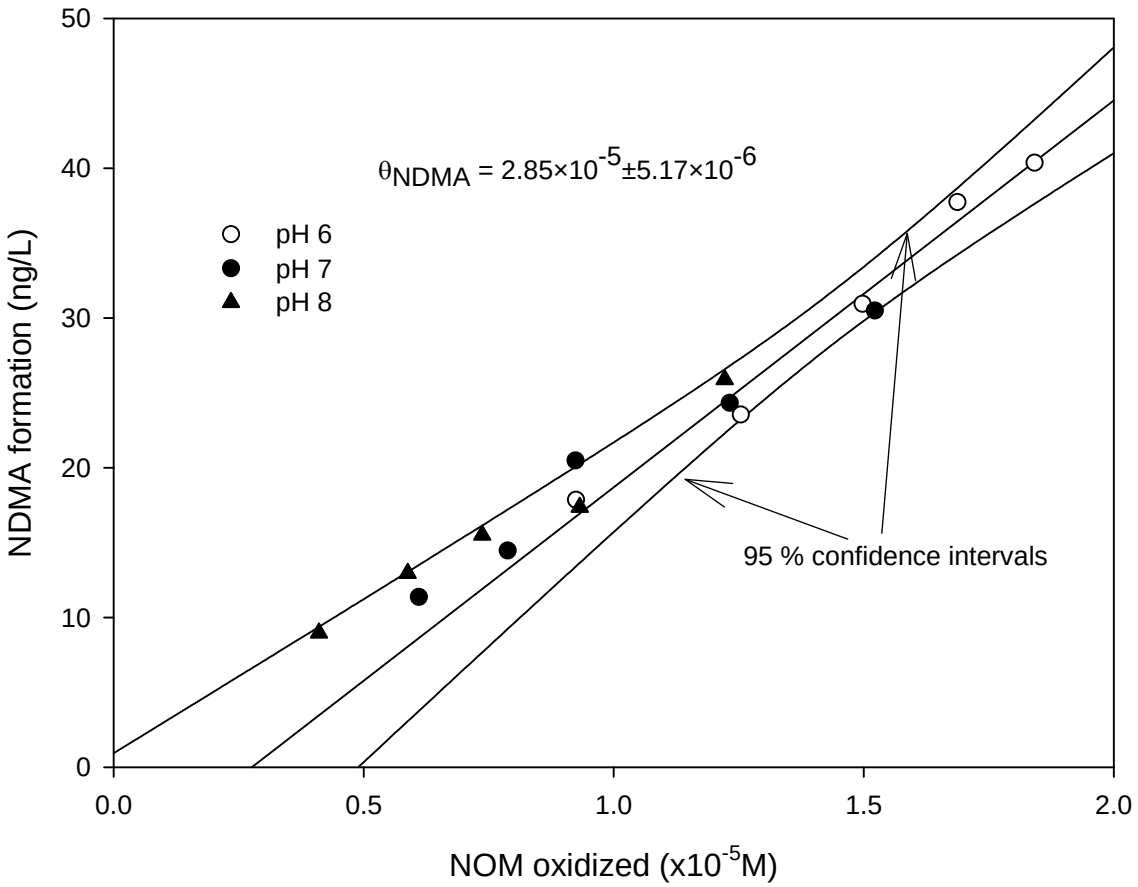


Figure 12. Linear relationship between NDMA formation and NOM oxidation and determination of NDMA with its 95% confidence intervals (IRW concentrate DOC = 3.4 mg/L, [NH2Cl]0 = 0.05 mM, I = 8 mM)

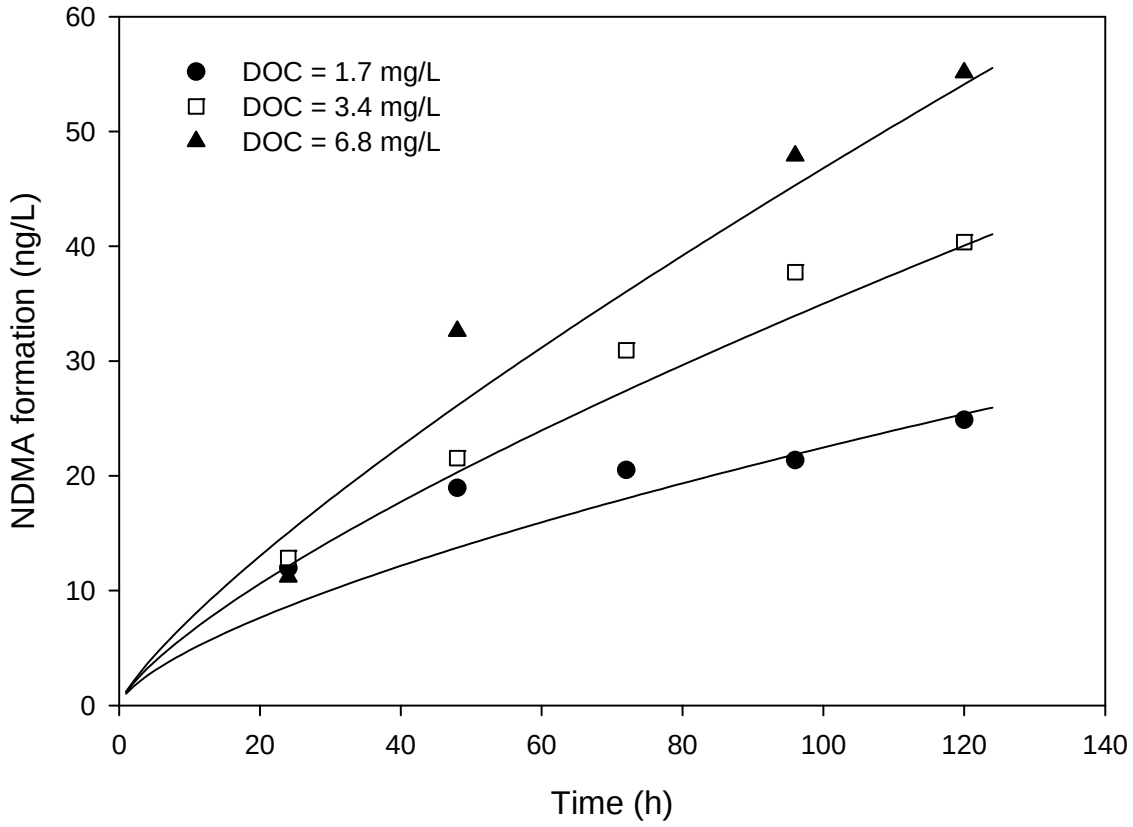


Figure 13. Model prediction of NDMA formation at various DOC levels from the reactions between monochloramine and NOM (IRW concentrate, pH = 7.0, [NH2Cl]0 = 0.05 mM, I = 8 mM,line represents model prediction)

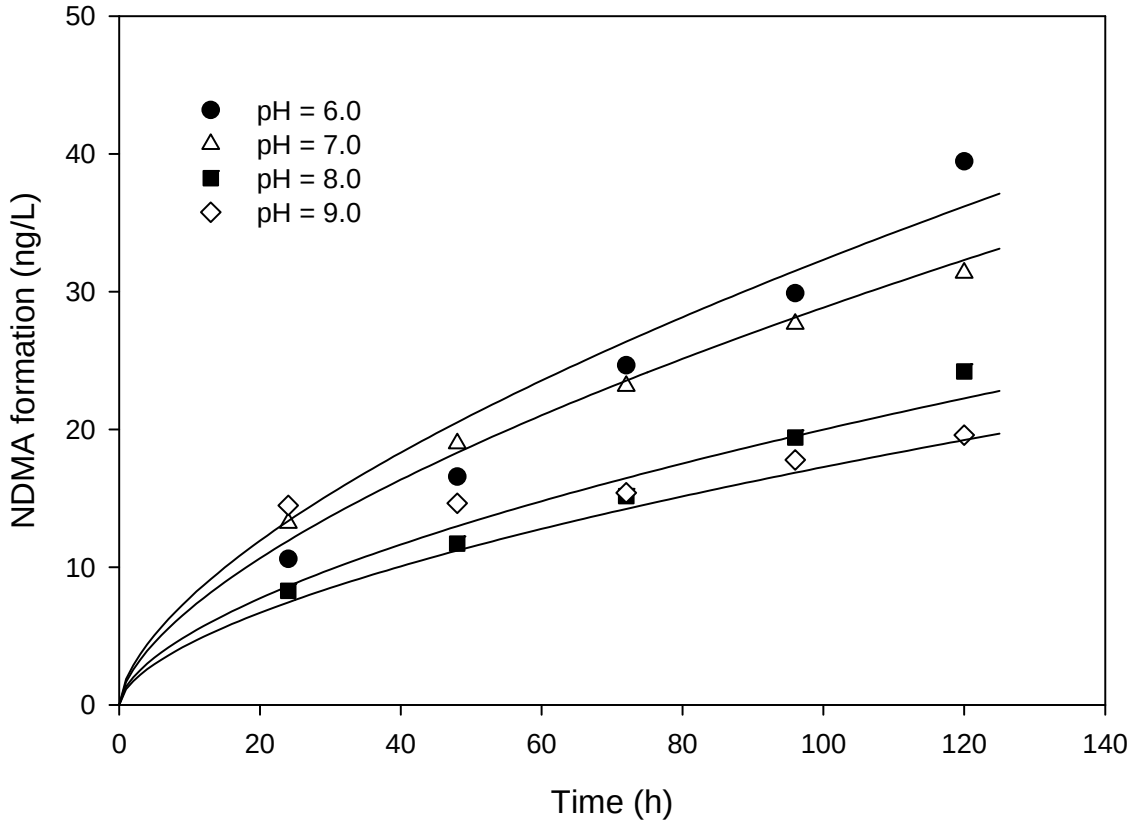


Figure 14 Model prediction of NDMA formation at various pH values from the reactions between monochloramine and NOM (IRW concentrate DOC = 3.4 mg/L, [NH2Cl]0 = 0.05 mM, I = 8 mM, line represents model prediction)

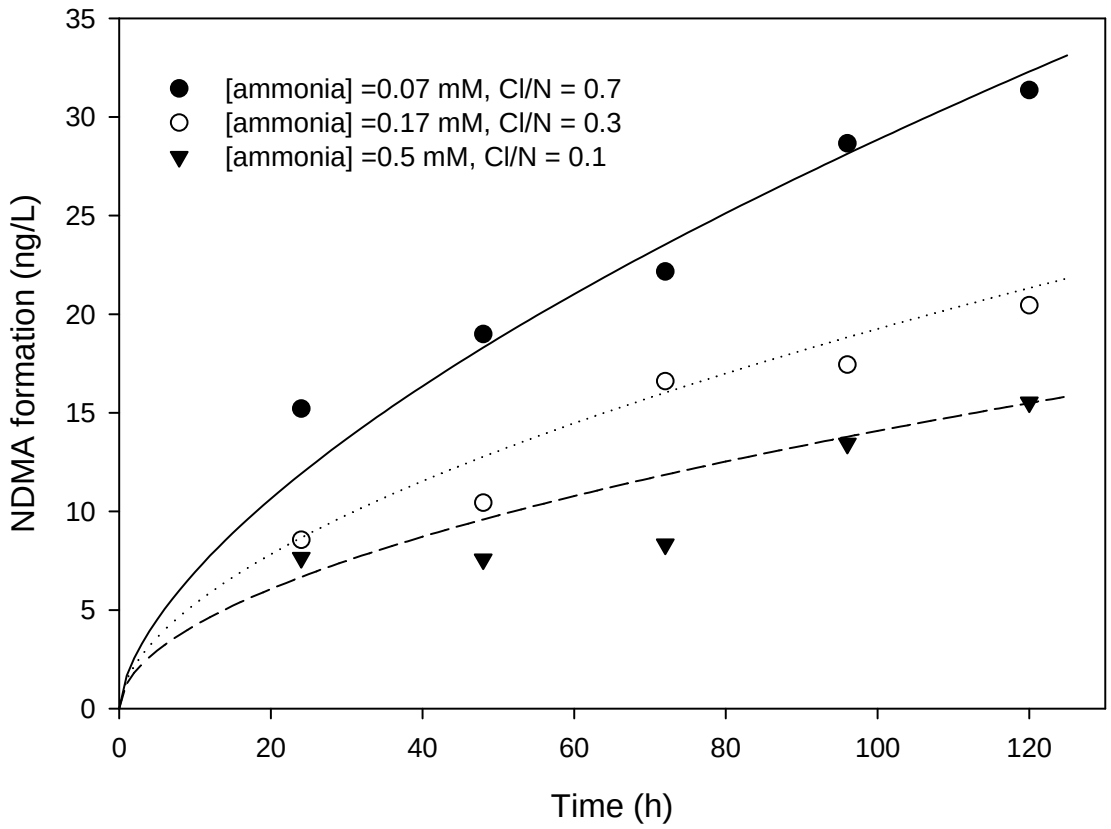


Figure 15. Effect of ammonia on NDMA formation (IRW NOM DOC = 3.4 mg/L, pH = 7.0, $[NH2Cl]_0$ = 0.05 mM, I = 8 mM, line represents model results)

Comparison of model parameters

Comparing the estimated model parameters for tested three NOM sources, all the rate constants as well as the site fraction values were remarkably similar, within a factor of 25% of each other (table 3), indicating very similar NOM oxidation characteristics among tested NOM sources. The value of θ_{NDMA} however, varied by a factor of two, ranging from a high of 3.23×10^{-5} for source CRW NOM to a low value of 1.67×10^{-5} for water contain UPW NOM. While the values for CRW and IRW derived NOM were statistically similar, the value of θ_{NDMA} for UPW NOM was significantly smaller. This difference presumably reflects differences in the nature of the NDMA precursors. Perhaps this difference is the indicative of differences in NOM characteristics, or conversely the presence of other types of precursors, possibly associated with agricultural discharges into the two rivers.

Influence of Chemical and Photochemical Oxidation on NDMA Formation

Influence of pre-chlorination on NDMA formation

NDMA formation decreased with the application of free chlorine prior to the addition of ammonia to produce chloramines. For example, the amount of NDMA formed after 120 hours in chloramine containing water was reduced by 50% by a free chlorine dosage of 0.08 mM and 10 minutes of contact time prior to chloramination. Increasing the pre-chlorination contact time also resulted in a further reduction in NDMA formation (Figure 16). It should be pointed out that the free chlorine demand was comparable in these studies so that the total initial monochloramine concentration was comparable in all experiments. Therefore the reduction in NDMA formation caused by pre-chlorination cannot be attributed to a lower initial chloramine concentration. NDMA formation also decreased with increasing chlorine dosage at a fixed free chlorine contact time (Figure 17). This finding is the opposite of that observed for the influence of pre-chlorination on the formation of many halogenated DBPs (Eldib and Ali, 1995).

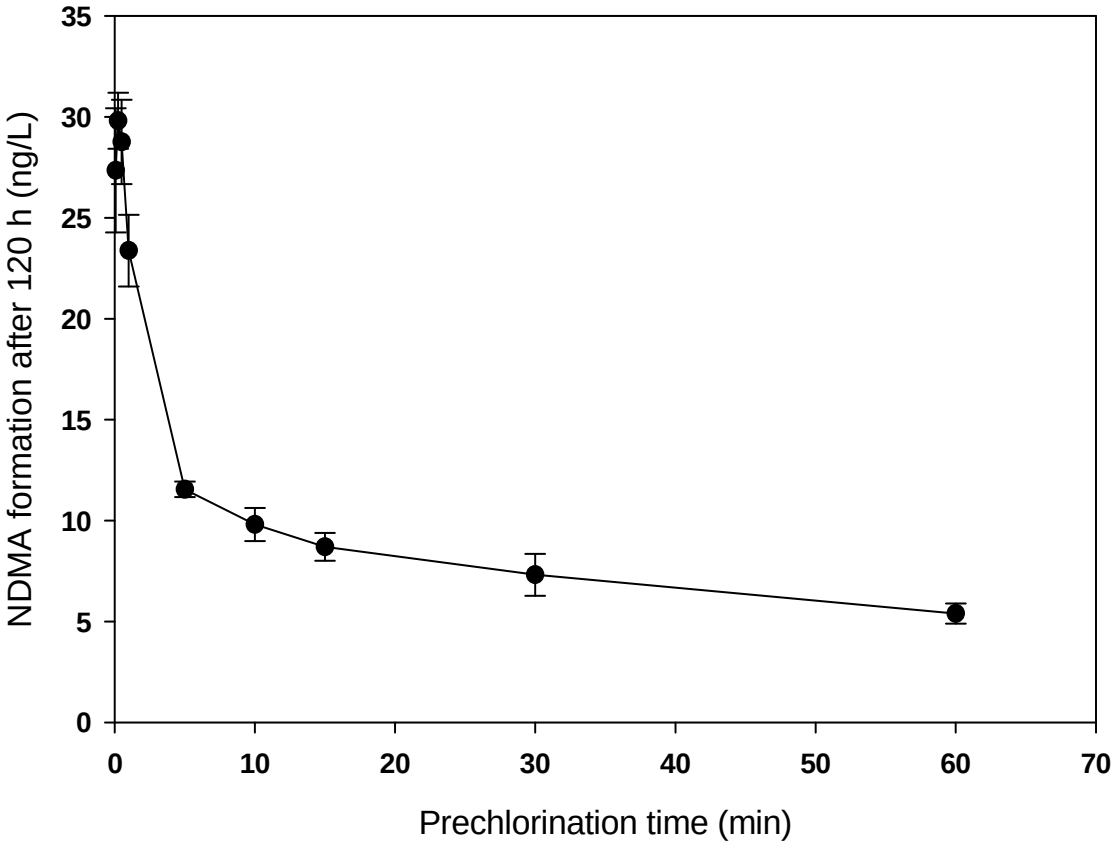


Figure 16 Effect of pre-chlorination time on NDMA formation (IRW NOM DOC = 3.4 mg/L, pH = 7.0±0.2, Cl2 = 0.08 mM, Cl/N = 0.7)

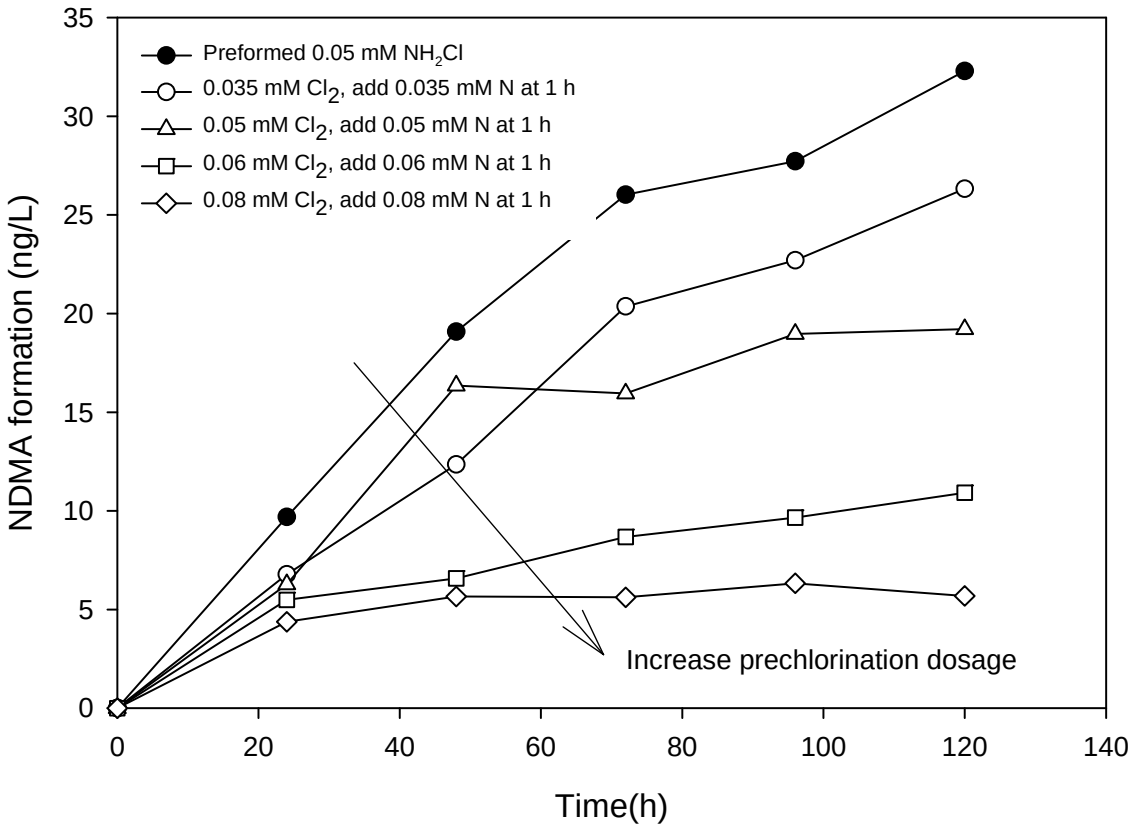


Figure 17. Effect of pre-chlorination dose on NDMA formation (IRW NOM DOC = 3.4 mg/L, 4 mM NaHCO3, pH = 7.0, pre-chlorination time = 1 h, Cl/N = 0.7)

A similar trend of decreasing NDMA concentration with pre-chlorination was obtained using the whole surface water for a drinking water utility in the State of Ohio provided by Malcolm Pirnie Company (Data not shown). After 108 minutes of pre-chlorination, NDMA formation after 5 days contact with chloramine was reduced approximately 50 %. Increasing pre-chlorination time to 345 minutes resulted in only a moderate further decrease in NDMA formation indicating a rapidly decreasing effect of time.

Influence of other pre-oxidants on NDMA formation

Figure 18 shows the effect of pre-oxidation on NDMA formation in water containing RO concentrated IRW NOM. Similar to the effect of pre-chlorination, water subjected to pre-oxidation produced significantly less NDMA during the subsequent contact period with preformed monochloramine. For example, the application of 10 mg/L $KMnO_4$ or 3 mg/L H_2O_2 reduced NDMA concentration by about 50% during the subsequent contact with monochloramine compared to that obtained without pre-oxidation. Increasing the concentration of pre-oxidant also resulted in a further decrease in the NDMA formation. The influence of both pre-chlorination and pre-oxidation on reducing NDMA formation suggests a common mode of action. It is hypothesized that this is due to the destruction of NDMA precursors.

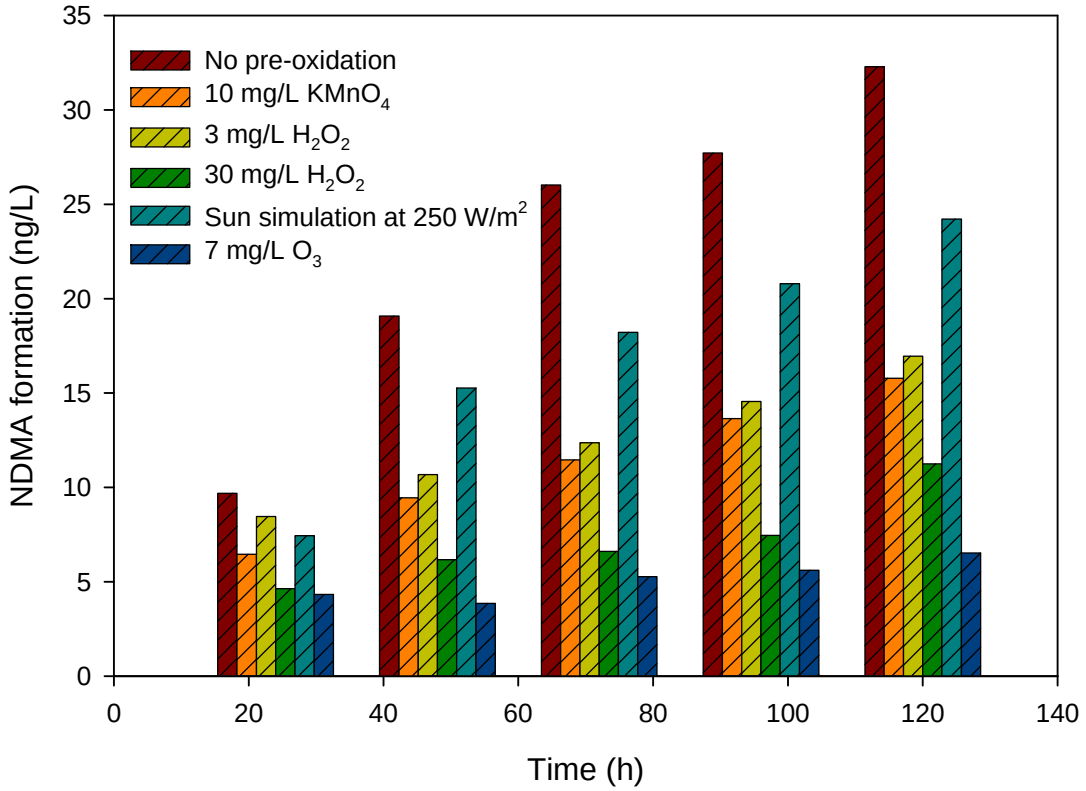


Figure 18 Effect of pre-oxidation on NDMA formation during post-chloramination (IRW NOM, DOC = 3.4 mg/L, pH = 7.0±0.2, pre-oxidation time = 1 h, [NH2Cl]0 = 0.05 mM)

Correlation of NDMA formation to changes in SUVA

NDMA formation in water not subjected to pre-chlorination or pre-oxidation was found to correlate linearly with the simultaneous decrease in $SUVA_{272}$ caused by the slow oxidation of NOM by monochloramine (Figure 19). This finding is similar to that obtained by Korshin et al. (1997) and Kitis et al. (2001) for the formation of total organic halogen (TOX) and haloacetic acids (HAAs). This strongly suggests that SUVA is also a good indicator of NDMA precursor content.

Interestingly, when water was first subjected to pre-chlorination, a decrease in NDMA formation is observed as expected, and the relationship between NDMA formation and the post-chloramination induced SUVA change was still linear but with a smaller slope. This may be attributable to the preferential destruction of a fraction of NOM that contributes more to the NDMA precursor content. This is consistent with the studies on NDMA precursors that indicates different NDMA formation potentials associated with different humic fractions.

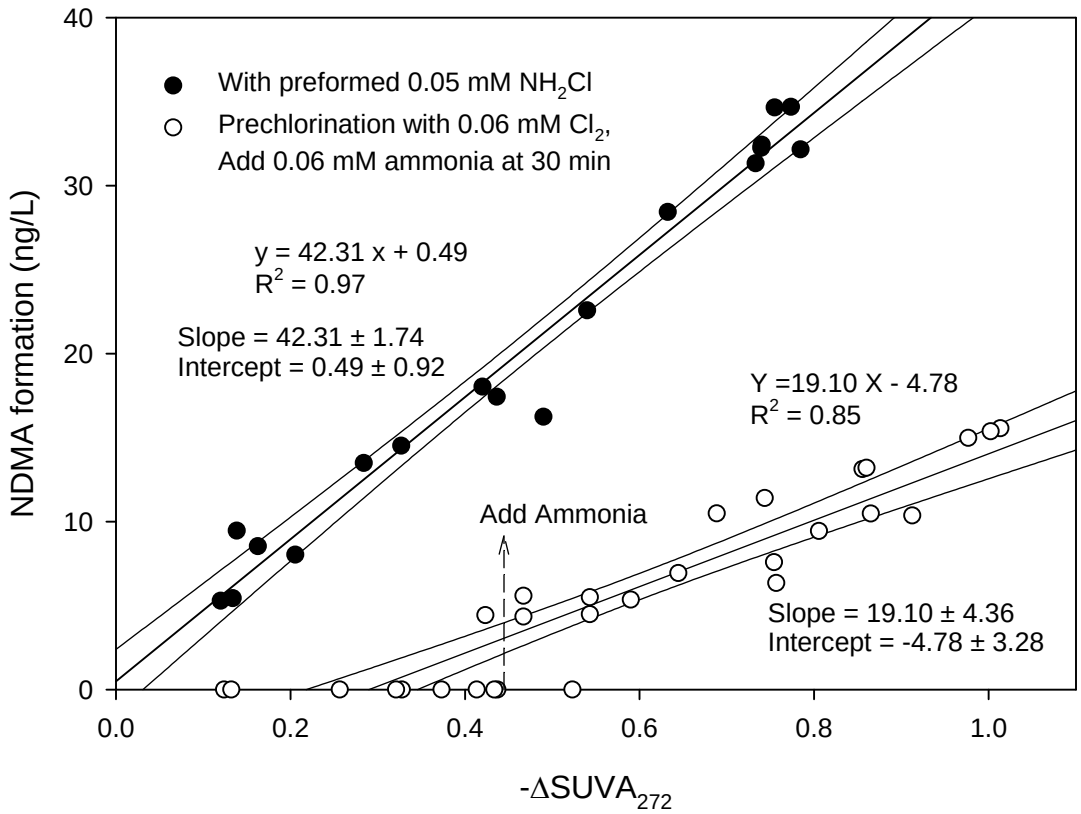


Figure 19. Relationship between SUVA272 and NDMA formation (IRW NOM DOC = 3.4 mg/L, Cl2 dosage = 0.06 mM, pre-chlorination time = 0.5 h, pre-formed [NH2Cl]0 = 0.05 mM, slopes and intercepts are shown with their 95% confidence intervals)

The amount of NDMA formed after 120 hours contact with chloramine in water was reduced by an amount proportional to the decrease in $SUVA_{272}$ caused by pre-chlorination or pre-oxidation (Figure 15). Quite unexpected is the observation that all pre-treatments have the same influence on reducing NDMA formation when normalized to the change in SUVA caused by pre-oxidation/pre-chlorination. This same relationship held even for a sunlight induced SUVA loss. Clearly a common mode of action is indicated which appears to be the destruction of precursors as indicated by a loss in SUVA. How this SUVA reduction is achieved does not influence the resulting loss in NDMA formation.

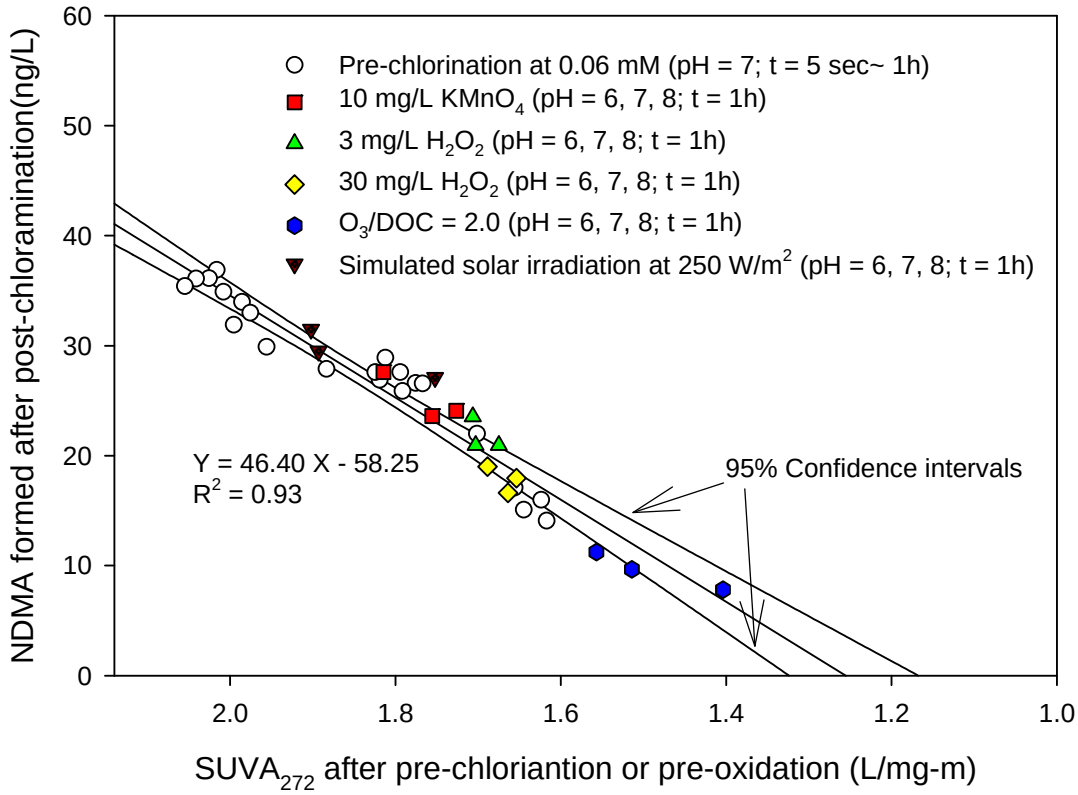


Figure 15 Correlation between the change in SUVA272 and NDMA formation (IRW NOM DOC = 3.4 mg/L, pH = 6~8, pre-oxidation time = 5 sec~1h, chloramine contact time = 120 hours, [NH2Cl]0 = 0.05 mM)

Summary and Conclusions

A primary purpose of this study was to investigate the mechanisms and kinetics of NDMA formation in natural water typical of that used as a drinking water source. Studies on the nature of the precursors showed that they are conserved when the NOM is concentrated by reverse osmosis (RO) and isolated into different humic fractions. Different humic fractions exhibited different NDMA formation potentials when normalized to carbon content. This indicates a fraction-dependent precursor content. Hydrophilic fractions were found to form more NDMA than hydrophobic fractions and basic fractions tend to form more NDMA than acid fractions. The dominant source of NDMA precursors in river water was determined to be the hydrophobic acid (HPOA) fraction of NOM because it is also the dominant fraction comprising NOM.

A reaction model incorporating monochloramine auto-decomposition, NOM oxidation, and NDMA formation using five water-specific parameters, provided validation for hypothesized reactions. Most important is the hypothesis that the rate of NDMA formation is linearly related to the rate of NOM oxidation and therefore NDMA formation can be described by a simple stoichiometric relationship between NOM

oxidized and NDMA formed. This is consistent with the linear relationship between the reduction in $SUVA_{272}$ that occurs with the oxidation of NOM and the formation of NDMA. Surprisingly, the five parameters that determine the rate of NOM oxidation and NDMA formation were very similar for samples obtained from a variety of sources, including a pristine source not impacted by agricultural practices or waste discharges. This implies that NDMA formation in the agriculturally impacted surface water sample is not likely to be governed by special agriculture-associated precursors. However, this finding may be a consequence of the particular season in which the river samples were taken.

Pre-chlorination and pre-oxidation was shown to be effective in reducing the potential of NOM to form NDMA from subsequent reactions in the presence of chloramines. Although the direct mechanism is not clear, NOM fluorescence spectra and UV absorbance changes indicate a loss of aromaticity upon oxidation, which appears indicative of a depletion or destruction of NDMA precursors. This also shows that free chlorine itself can play a dual role in influencing NDMA formation. The experimental and modeling work clearly shows that the oxidation of NOM by trace levels of free chlorine existing in the presence of monochloramine is required to produce NDMA presumably through the formation of precursors. But in high concentrations, typically associated with the practice of pre-chlorination, it destroys precursors.

The reduction in NDMA formed after 5 days in the presence of chloramines was found to be linearly correlated to the pre-oxidation and pre-chlorination induced reduction in $SUVA_{272}$. Quite unexpectedly, this relationship is independent of the nature of the oxidant. The reduction in NDMA formation with reduction in $SUVA_{272}$ caused by various oxidants including free chlorine, hydrogen peroxide, potassium permanganate, ozone, and simulated sunlight all fit on a single regression line. This suggests that the change in $SUVA_{272}$ could possibly be used as a parameter to predict changes in NDMA formation when pre-oxidation including pre-chlorination is practiced.

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