Iowa Water Center
Annual Technical Report
FY 2006

Introduction

The Iowa Water Center is a multi-campus and multi-organizational center focusing on research, teaching and outreach program activities. The Center's goal is to encourage and promote interdisciplinary, inter-institutional water research that can improve Iowa's water quality and provide adequate water supplies to meet both current and future needs of the state. The Iowa Water Center continues to build statewide linkages between universities and public and private sectors and to promote education, research, and information transfer on water resources and water quality issues in Iowa. The Center also plays a vital role in identifying critical water research needs and providing the funding or impetus needed to initiate research that cannot or is not being conducted through other means.

Research has repeatedly illustrated the value and necessity of quality water in this state. Iowa is one of the nations leading agricultural producers, if not the leader, with a vast majority of its land under row crop production. Non-point source degradation of water quality is well recognized as a leading cause of Iowa water quality impairment as well as being a major contributor to water quality problems beyond the state border. The water resources of this state will undergo substantial quality and quantity stress with the developing bioeconomy. Large amounts of water are being withdrawn from subsurface aquifers and discharged on the surface by ethanol processing plants. Lignocellulose conversion technology will likely result in increased water use, removal of crop residue from the land surface, increased applications of fertilizers, and accelerated rates of soil erosion and water runoff. The role the Iowa Water Center plays in addressing these challenges is large and needed by the state.

Research Program

Research priorities for the Iowa Water Center include: nutrient management, animal waste and water quality, sediments, subsurface drainage, and emerging water-related issues. There were three projects funded through the 104B program and two projects supported with 104G funding during this funding period. In addition to addressing critical water resource research needs in Iowa, these projects support graduate and undergraduate students participating in the research.

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

Basic Information

Title:	Relationship of Nitroso Compound Formation Potential to Drinking Source Water Quality and Organic Nitrogen Precursor Source Characteristics
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Congressional District:	IA 1st
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Principal Investigators:	Richard Louis Valentine

Publication

1. 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.
2. 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.
3. Chen, Zhuo and Richard L. Valentine, 2006. Mechanisms and Kinetics of NDMA Formation from Natural Organic Matter, submitted to Environmental Science and Technology.

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 mber	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	Hydraulic Conductivity	Transmissivity	Specific Capacity	**Estimated Travel Time**
	(ft)	(ft/d)	(ft^2/d)	(gpm/ft)	**(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$_2$Cl 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$_2$Cl. 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$_2$Cl was measured in control samples on a daily basis in order to ensure that high levels were present throughout the

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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 $20^{o}C$. 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 $35^{o}C$ for 4 minutes. Next the temperature was increased to $140^{o}C$ at a rate of $20^{o}C$/min. A secondary ramp elevated the temperature to $200^{o}C$ at a rate of $50^{o}C$/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 $500^{o}C$ 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] $\leq$ 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.
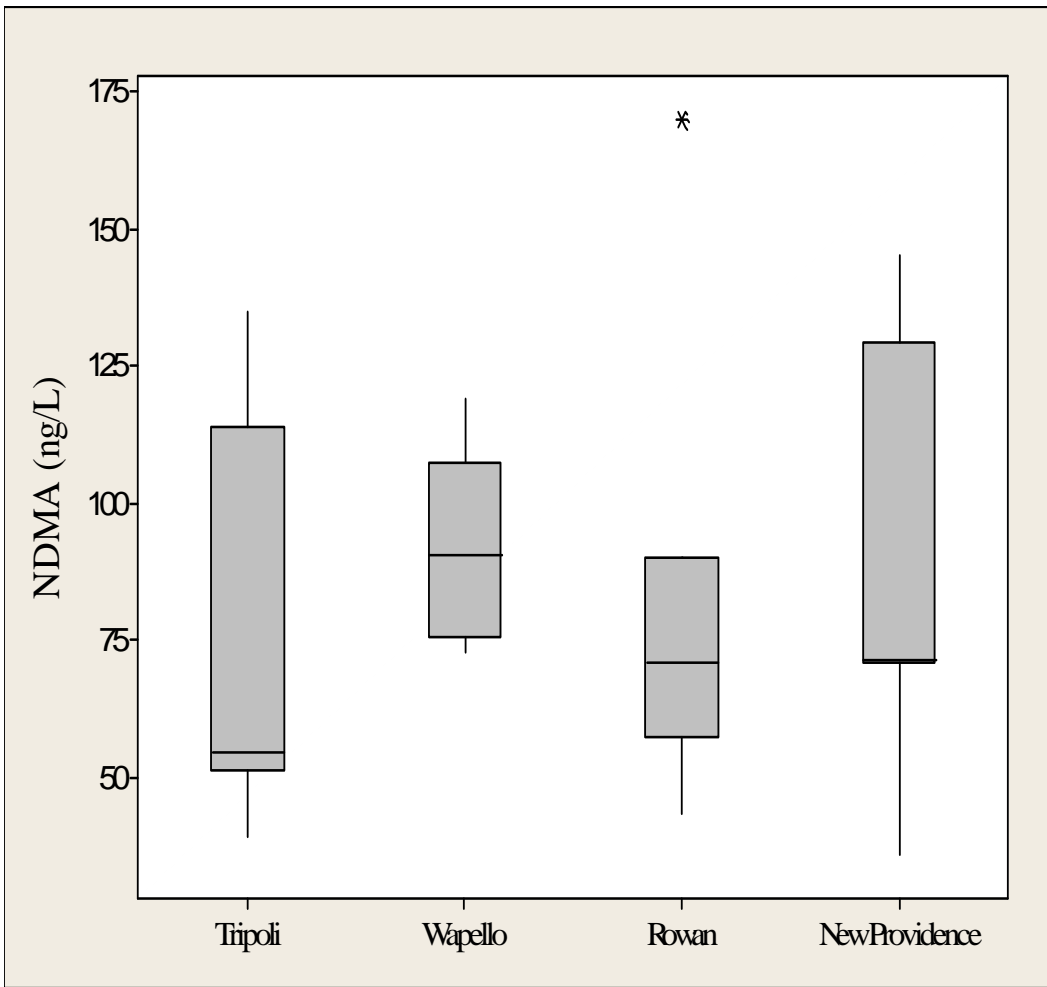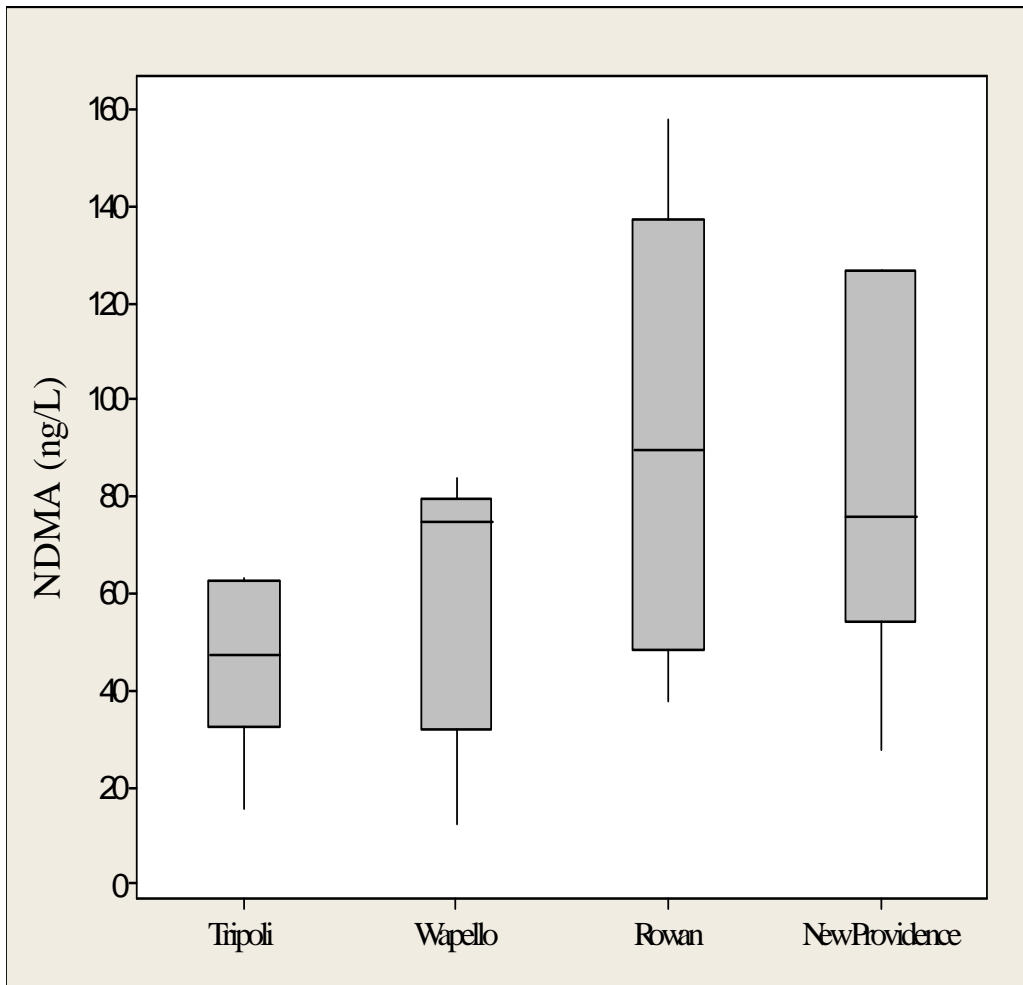
Figure 1.   Box plot representing NDMA formation potential at pH~8 for each site pooled over the course of this study. The extremities of the whiskers show minimum and maximum NDMA formation potential at each site while the boxes define the quartile values and the median value. The "*" represents the 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.
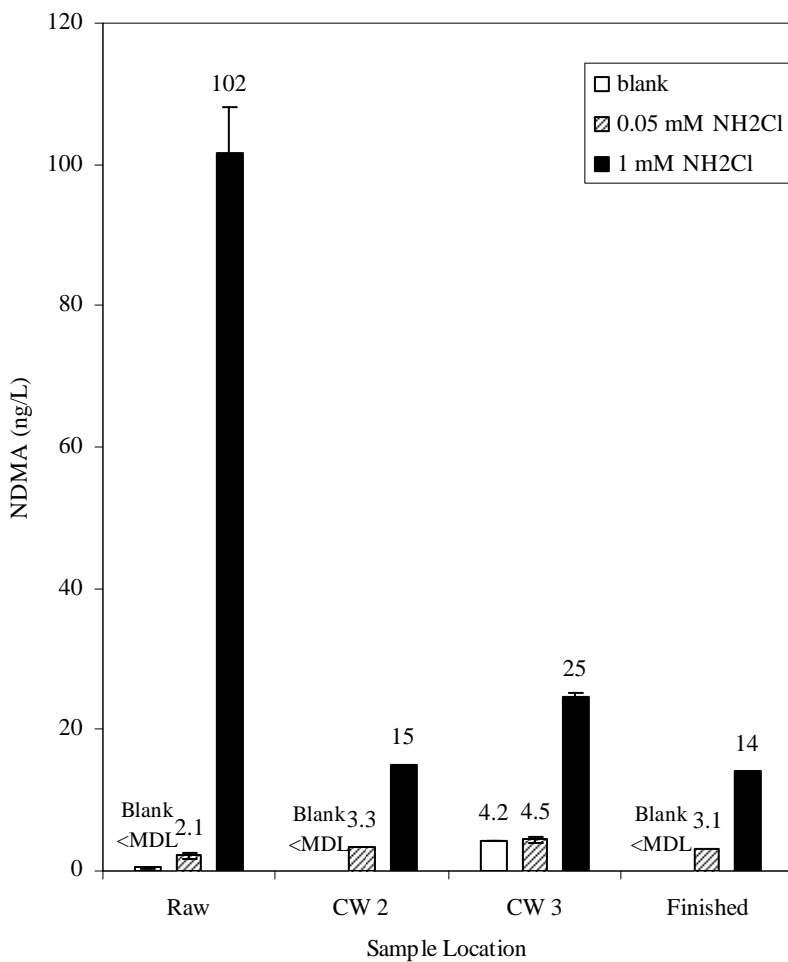

Figure 3. IC samples collected on 11-17-03. Monochloramine was added to the samples to produce a concentration in each reactor as indicated in the figure. Error bars are shown for reactors in which duplicates were run. All samples were incubated in the dark at 20°C for 7 days. The average pH of the bicarbonate buffered reactors was 8.27 ± 0.2.
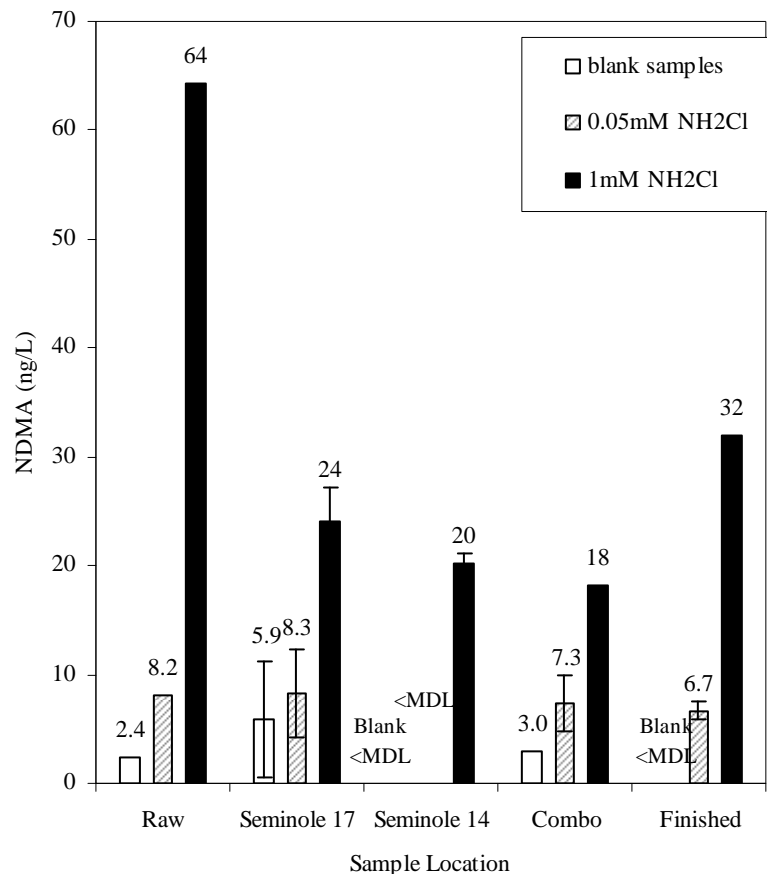
Figure 4.   Cedar Rapids samples collected on 9-29-03. Monochloramine was added
to the samples to produce a concentration in each reactor as indicated in the figure. Error
bars are shown for reactors in which duplicates were run. All samples were incubated in
the dark at 20oC for 7 days. The average 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.
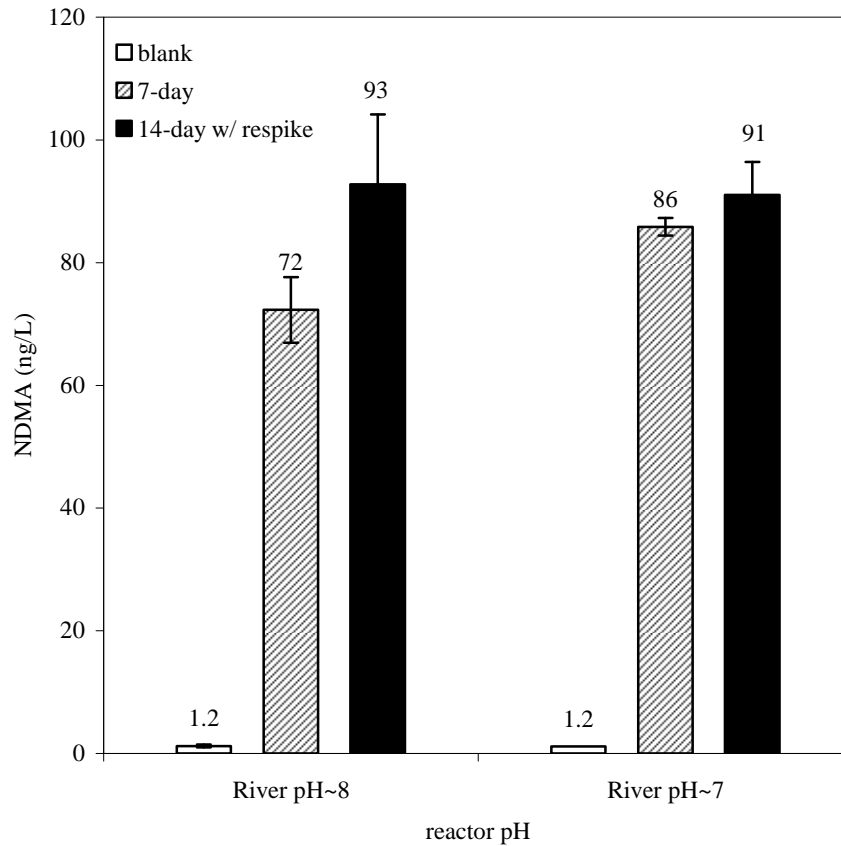
Figure 5.   Precursor limitation experiment performed on 3-17-04 with filtered Iowa
River water. All samples were buffered with either 10 mM bicarbonate or phosphate
buffers in order to maintain pH values around 8 and 7, respectively. All reactors were
incubated in the dark at 20oC

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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

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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.
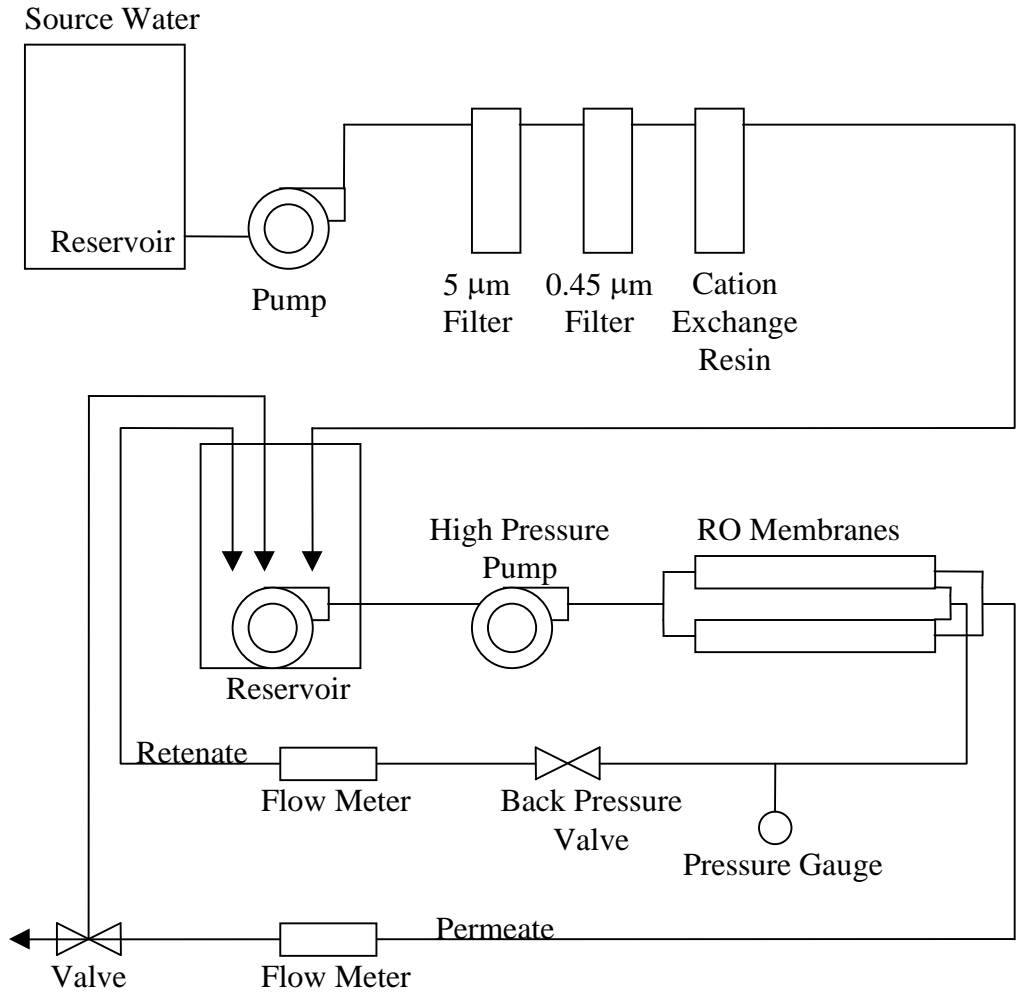
Source Water

Reservoir

Pump

5 μm
Filter

0.45 μm
Filter

Cation
Exchange
Resin

High Pressure
Pump

RO Membranes

Reservoir

Retenate

Flow Meter

Back Pressure
Valve

Pressure Gauge

Permeate

Valve

Flow Meter

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.
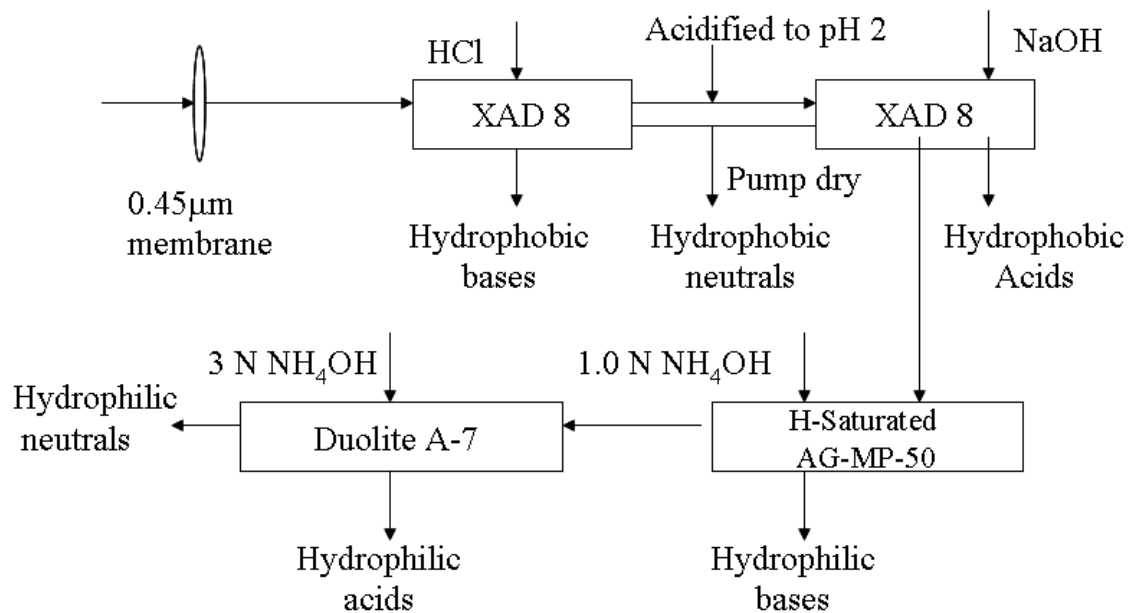

Figure 7.   Schematic for fractionation of NOM (Leenheer, 1981)

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 $500^{o}C$ 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^oC. 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^oC for 4 minutes. Next the temperature was increased to 140^oC at a rate of 20^oC/min. A secondary ramp elevated the temperature to 200^oC 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.
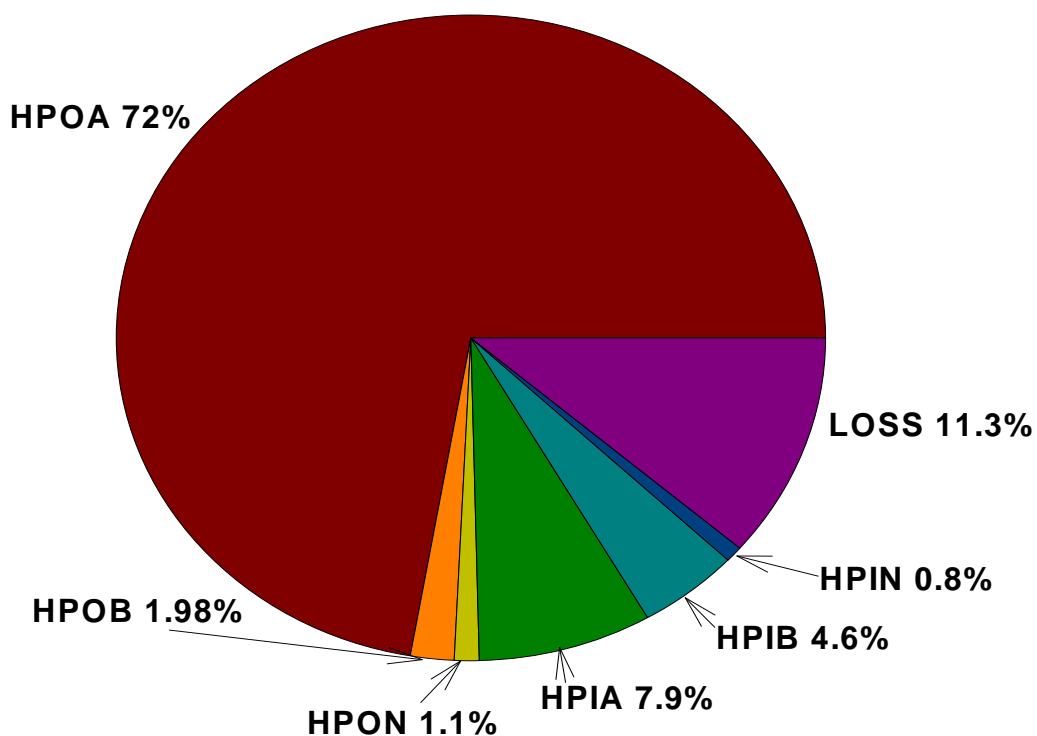
Figure 8.   DOC recovery of NOM fractionation (IRW NOM, fractionation using procedure proposed by Leenheer, 1981)

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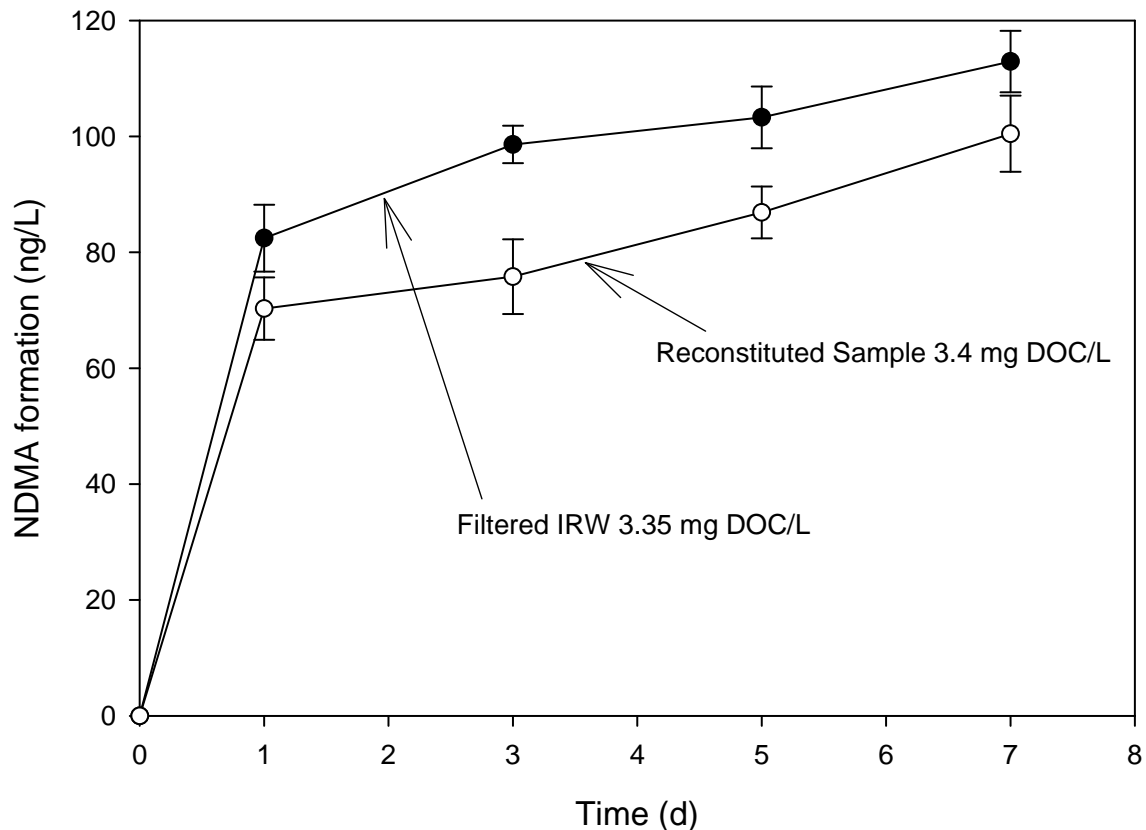
Figure 9.   Preservation of NDMA formation potential in RO concentrate water
$(1mM\ NH_2Cl,\ pH = 7.0,\ T = 20ºC)$

        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.
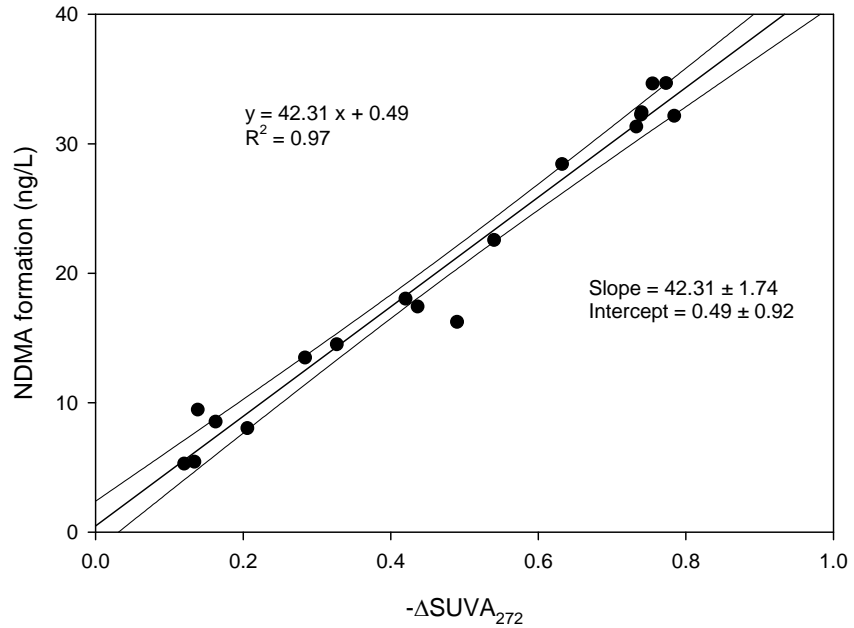

Figure 10.   Relationship between specific UV absorbance change of NOM and NDMA formation in the reaction of NOM with monochloramine (pH 7.0, T = 20ºC, IRWC NOM TOC = 3.5 mg/L, [NH2Cl]0 = 0.05 mM, slope and intercept are shown with their 95% confidence intervals)

Interestingly, the SUVA value of each NOM fraction did not show any correlation with NDMA formation potential, while the ΔSUVA$_{272}$ 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).
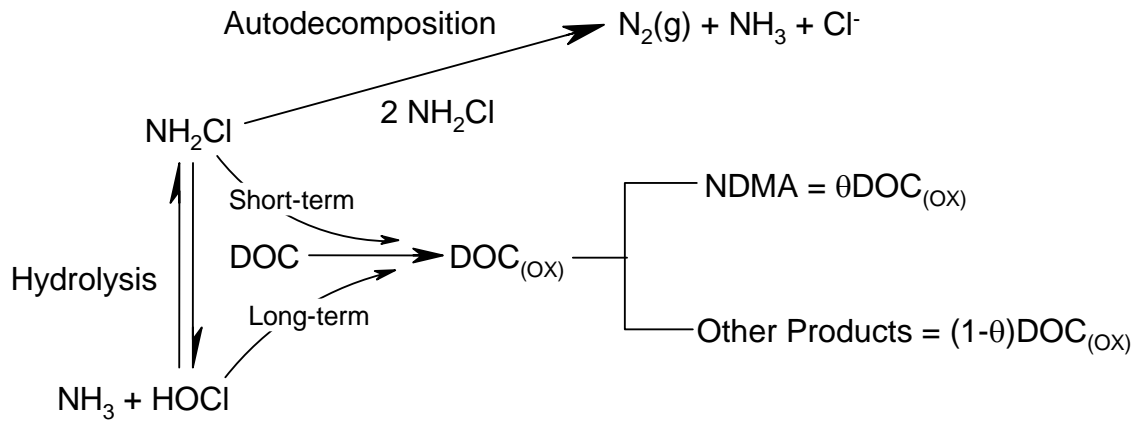
Mechanisms and Kinetics of NDMA Formation by Reaction of NOM with Monochloramine.

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.

$$\text{Autodecomposition} \longrightarrow N_2(g) + NH_3 + Cl^-$$

$$NH_2Cl \qquad 2\ NH_2Cl$$

$$\text{Short-term}$$

$$\text{Hydrolysis} \qquad DOC \longrightarrow DOC_{(OX)} \qquad NDMA = \theta DOC_{(OX)}$$

$$\text{Long-term}$$

$$NH_3 + HOCl \qquad \text{Other Products} = (1-\theta)DOC_{(OX)}$$

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^{TM} (Scientist, 1995). Scientist^{TM} 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	$\times10^3$	$1.21\times10^4\pm4.30$	10^3	$1.12\times10^4\pm6.60\times$	10^3	$1.43\times10^4\pm3.07\times$
S_1		0.011 ± 0.003		0.009 ± 0.003		0.015 ± 0.006
k_2	$\times10^4$	$5.92\times10^5\pm1.87$	10^4	$4.88\times10^5\pm1.72\times$	10^4	$6.01\times10^5\pm6.30\times$
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
θ_{NDMA}		$2.85\times10^{-5}\pm5.17\times10^{-6}$		$1.67\times10^{-5}\pm4.10\times10^{-6}$		$3.23\times10^{-5}\pm2.19\times10^{-6}$

[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.
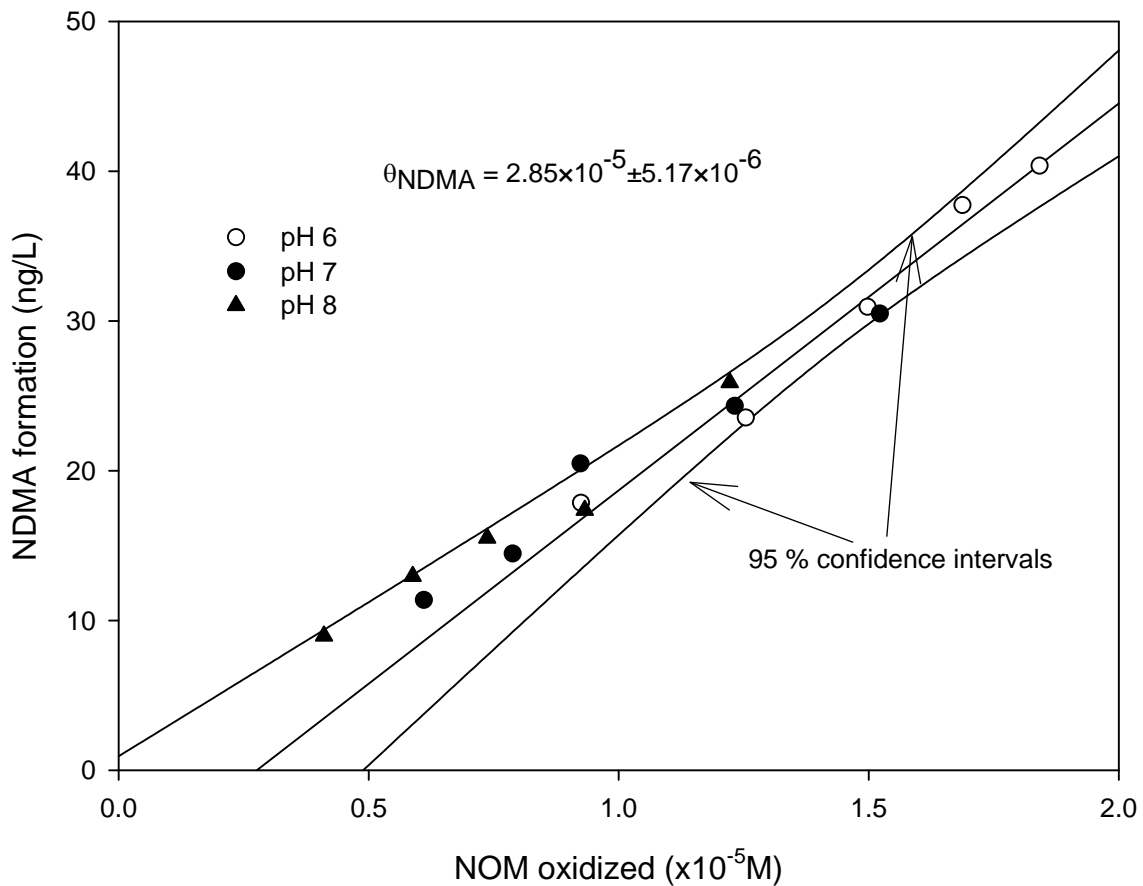

Figure 12.   Linear relationship between NDMA formation and NOM oxidation and determination of   NDMA with its 95% confidence intervals (IRW concentrate DOC = 3.4 mg/L, [NH2Cl]0 = 0.05 mM, I = 8 mM)
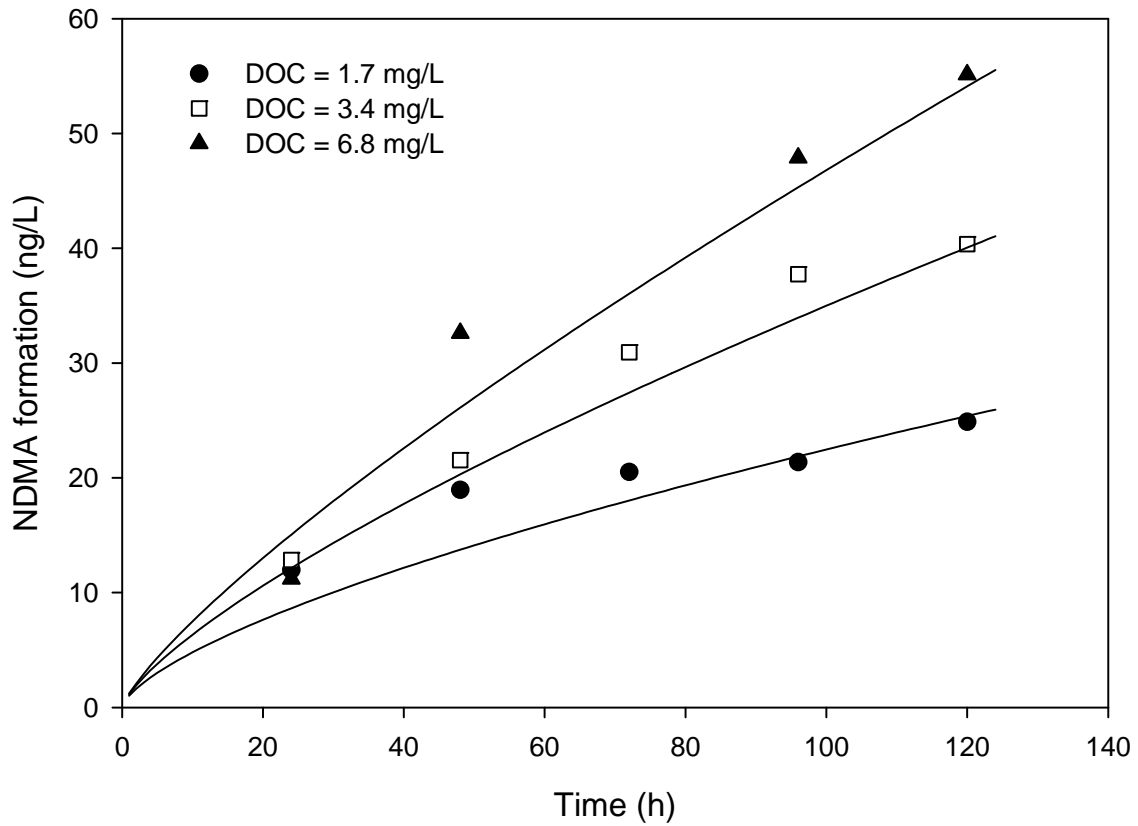
Figure 13. Model prediction of NDMA formation at various DOC levels from the reactions between monochloramine and NOM (IRW concentrate, pH = 7.0, [NH2Cl]0 = 0.05 mM, I = 8 mM, line represents model prediction)
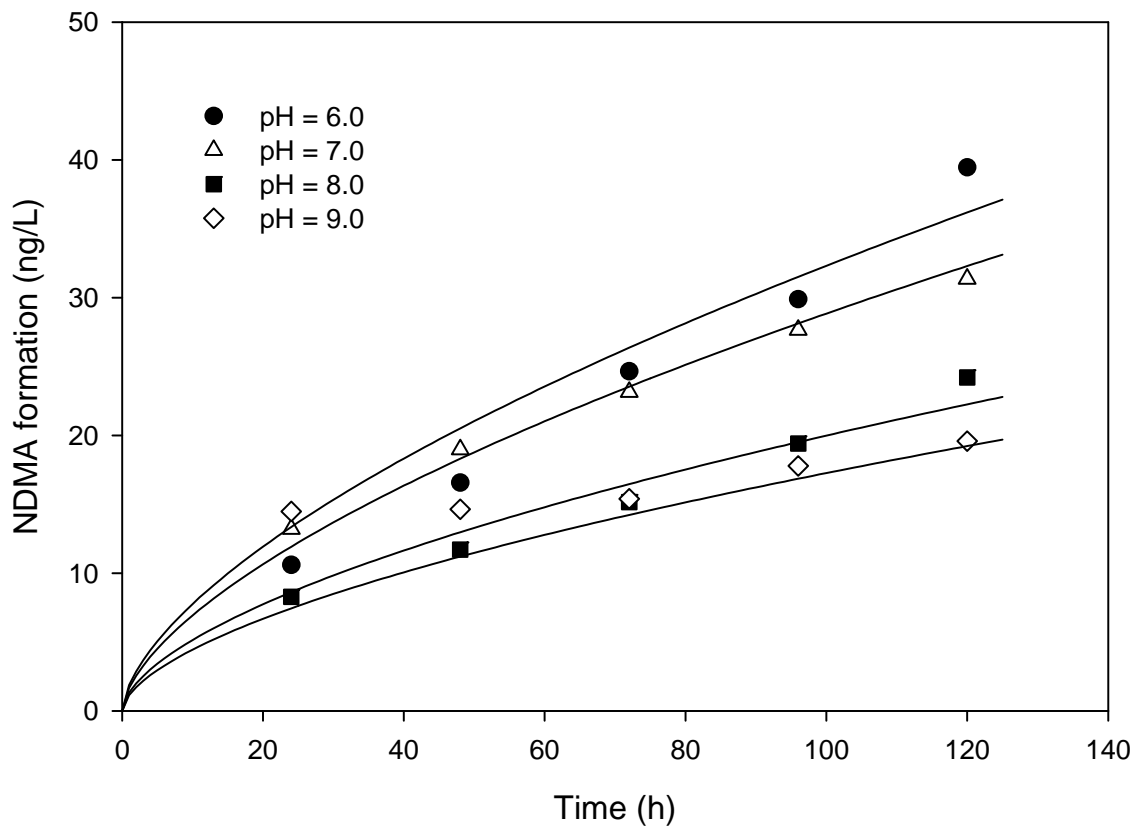
Figure 14   Model prediction of NDMA formation at various pH values from the reactions between monochloramine and NOM (IRW concentrate DOC = 3.4 mg/L, [NH2Cl]0 = 0.05 mM, I = 8 mM, line represents model prediction)
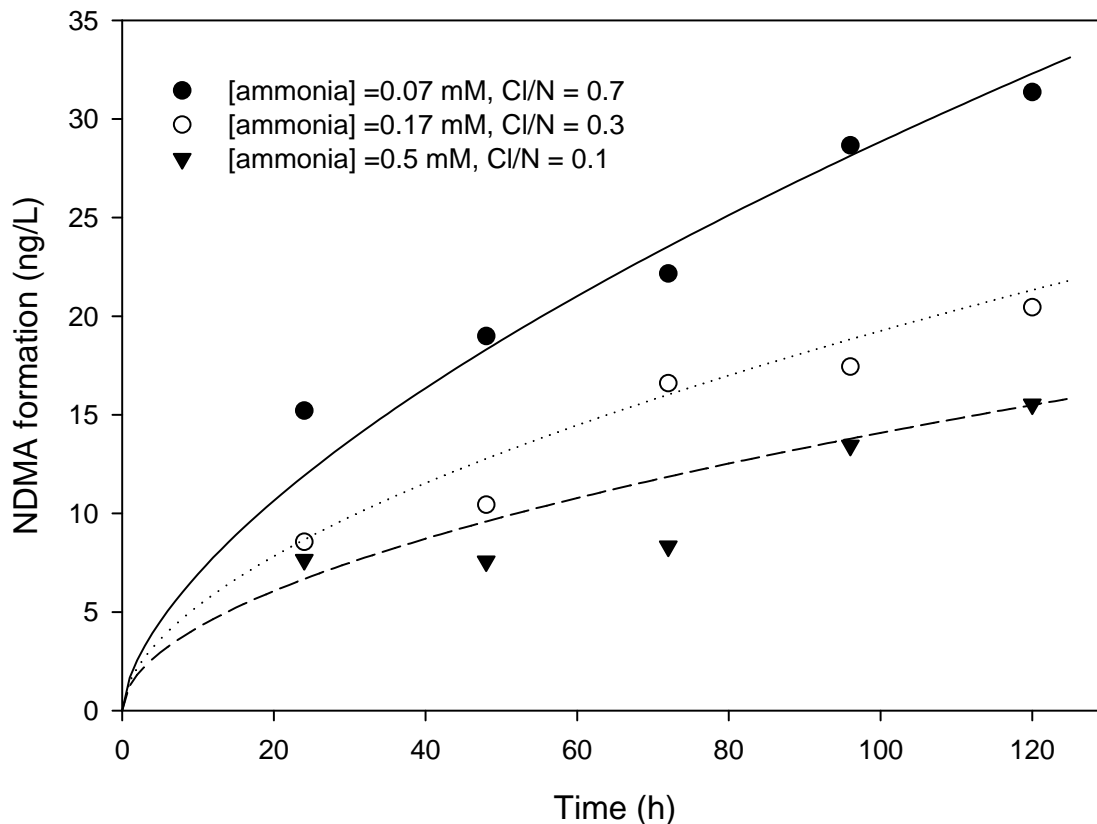
Figure 15.   Effect of ammonia on NDMA formation (IRW NOM DOC = 3.4 mg/L, pH = 7.0, $[NH2Cl]_0 = 0.05$ mM, I = 8 mM, line represents model results)

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).
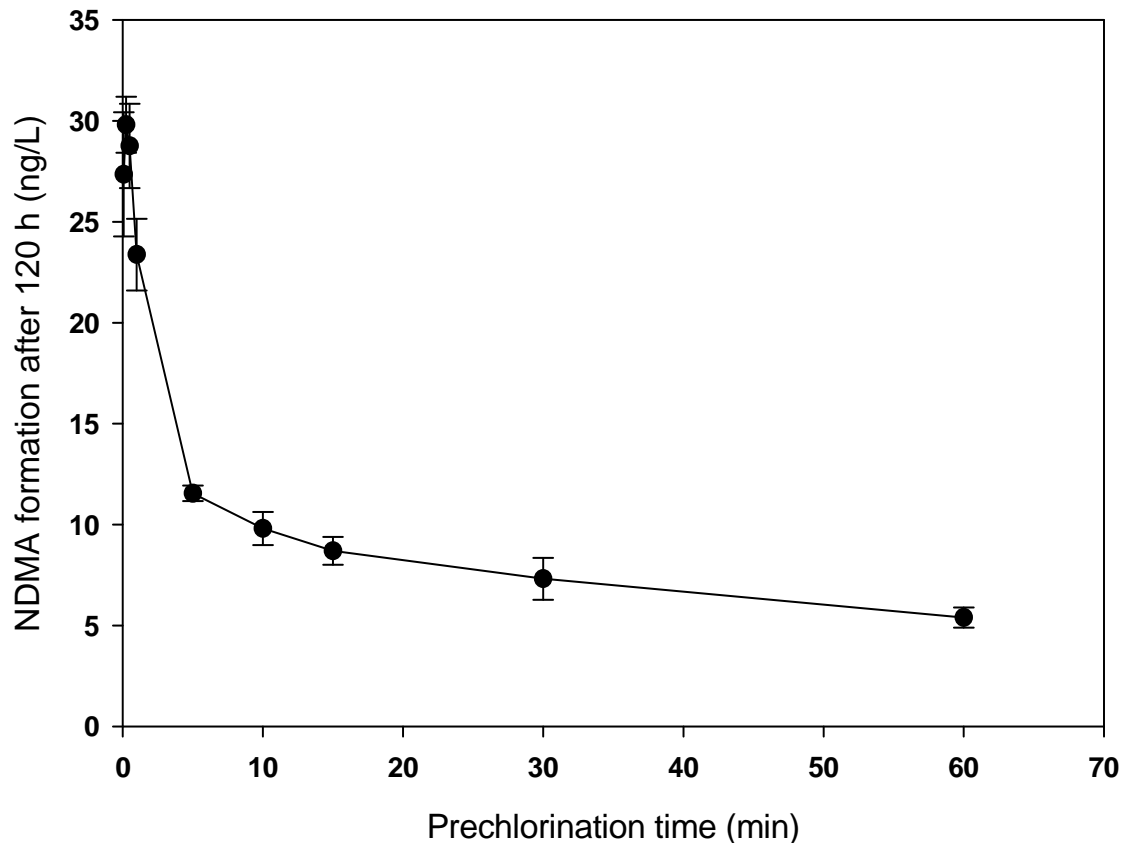

Figure 16   Effect of pre-chlorination time on NDMA formation (IRW NOM DOC = 3.4 mg/L, pH = 7.0±0.2, Cl2 = 0.08 mM, Cl/N = 0.7)
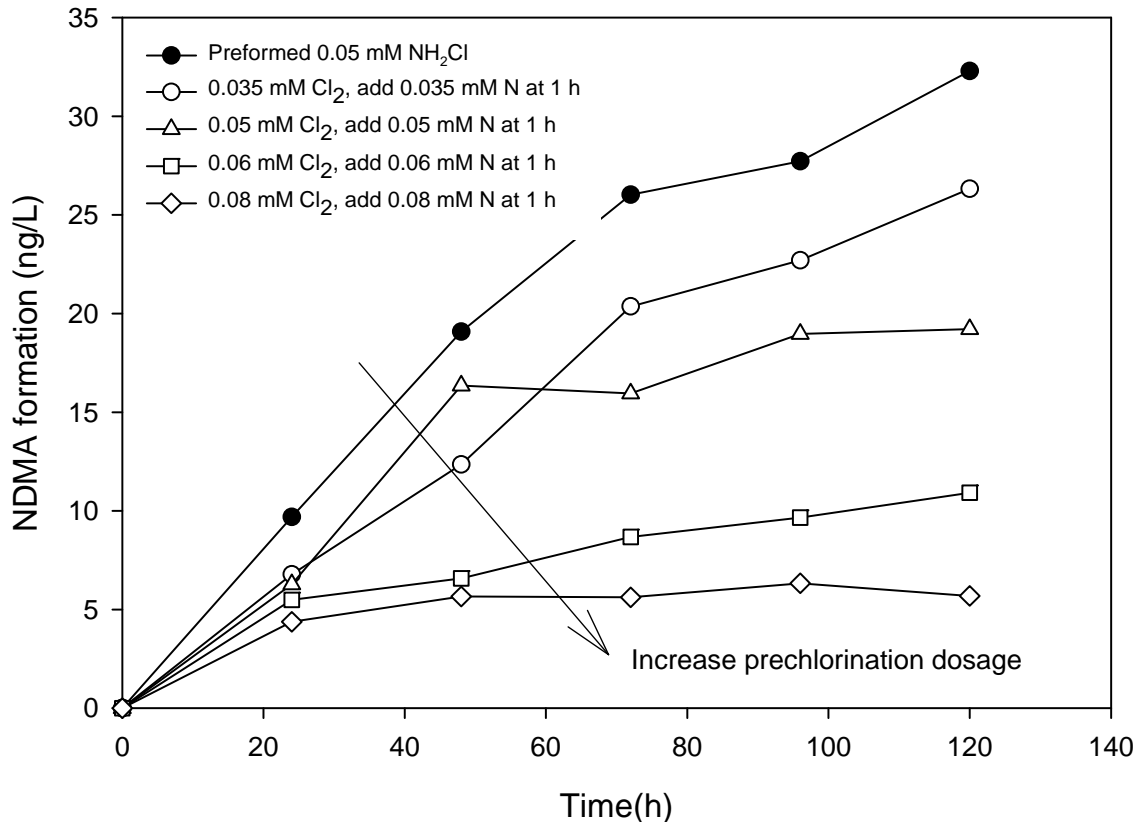
Figure 17.   Effect of pre-chlorination dose on NDMA formation (IRW NOM DOC = 3.4 mg/L, 4 mM NaHCO3, pH = 7.0, pre-chlorination time = 1 h, Cl/N = 0.7)

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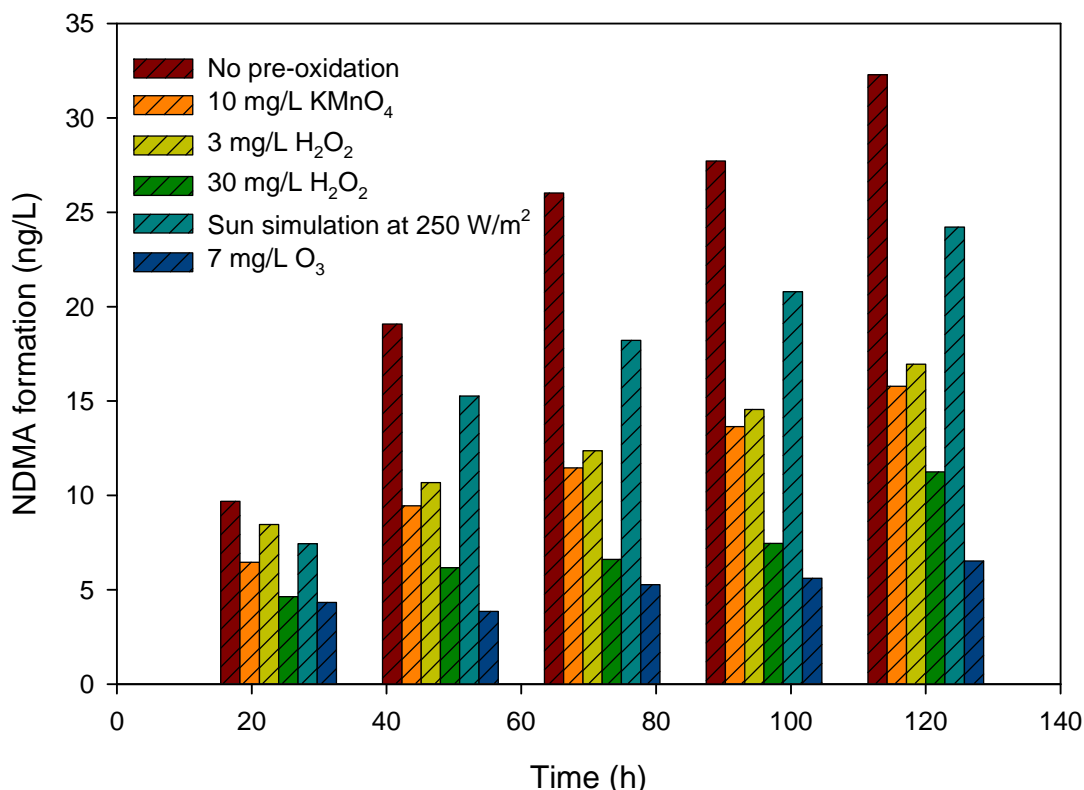
Figure 18   Effect of pre-oxidation on NDMA formation during post-chloramination (IRW NOM, DOC = 3.4 mg/L, pH = 7.0±0.2, pre-oxidation time = 1 h, [NH2Cl]0 = 0.05 mM)

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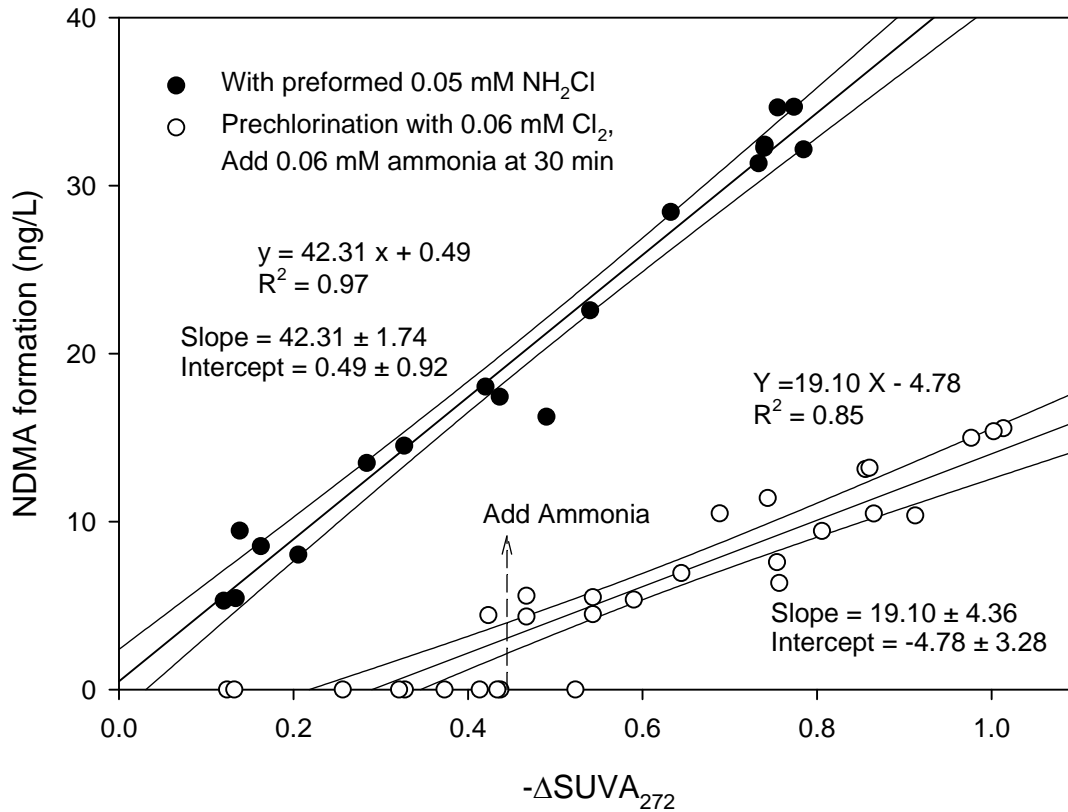
Figure 19. Relationship between SUVA272 and NDMA formation (IRW NOM DOC = 3.4 mg/L, Cl2 dosage = 0.06 mM, pre-chlorination time = 0.5 h, pre-formed [NH2Cl]0 = 0.05 mM, slopes and intercepts are shown with their 95% confidence intervals)

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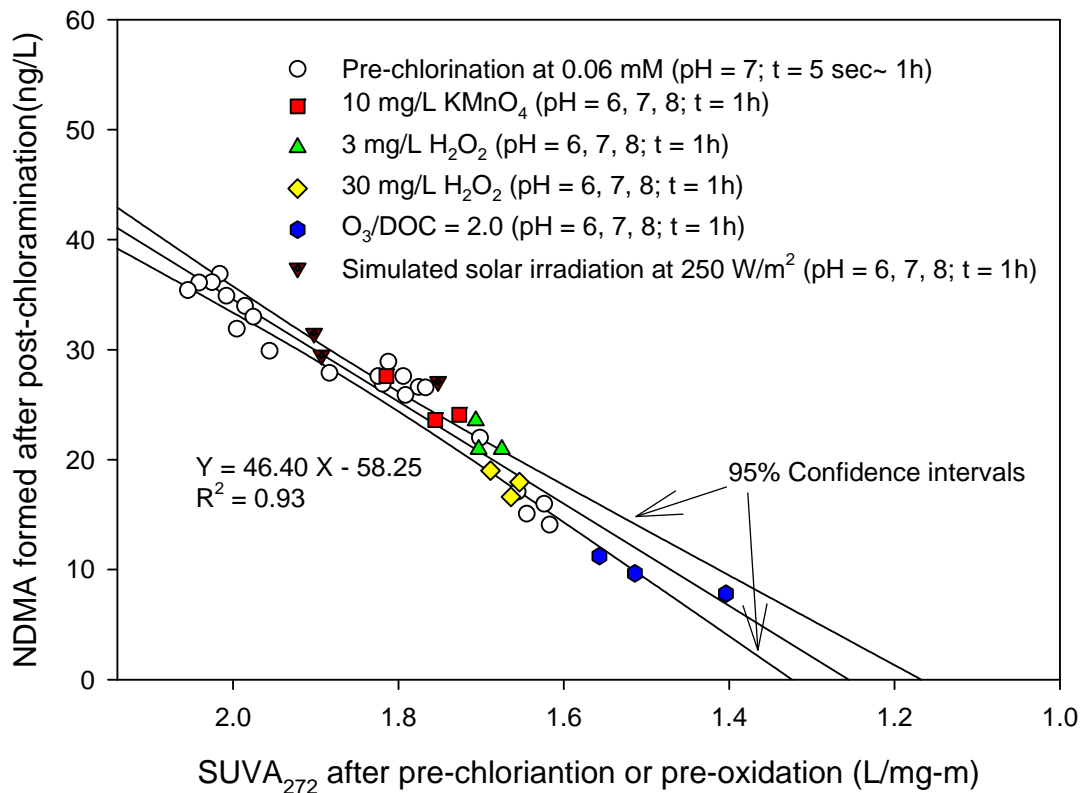
Figure 15 Correlation between the change in SUVA272 and NDMA formation (IRW NOM DOC = 3.4 mg/L, pH = 6~8, pre-oxidation time = 5 sec~1h, chloramine contact time = 120 hours, [NH2Cl]0 = 0.05 mM)

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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An Integrated Immunological-GIS Approach for Bio-monitoring of Ecological Impacts of Swine Manure Pollutants in Streams

Basic Information

Title:	An Integrated Immunological-GIS Approach for Bio-monitoring of Ecological Impacts of Swine Manure Pollutants in Streams
Project Number:	2002IA25G
Start Date:	9/15/2002
End Date:	9/14/2006
Funding Source:	104G
Congressional District:	Iowa 3rd
Research Category:	Water Quality
Focus Category:	Methods, Non Point Pollution, Agriculture
Descriptors:	water quality, fish, immunology, GIS, swine manure, non-point source pollution
Principal Investigators:	James A. Roth, Bruce Willard Menzel, Dusan Palic, Clay Lynn Pierce

Publication

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2. Palic, D., C.B. Andreasen, D.E. Frank, B.W. Menzel, and J.A. Roth. (2005). Gradient separation and cytochemical characterization of neutrophils from kidney of fathead minnow (Pimephales promelas Rafinesque, 1820). Fish and Shellfish Immunology 18(3), 263-267.
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An Integrated Immunological-GIS Approach for Bio-monitoring of Ecological Impacts of Swine Manure Pollutants in Streams

James A. Roth, Dušan Palić, Bruce W. Menzel, Clay L. Pierce

Problem and Research Objectives

Thirty years after enactment of the Clean Water Act, 40% of our nation's rivers, lakes, and coastal waters are still considered unfit for fishing, swimming, drinking or aquatic life. The U.S. EPA identified agricultural operations as the primary cause of non-point source pollution in the nation's impaired rivers and lakes. At least 10% of the nation's impaired river miles are affected by pollution from livestock operations. In portions of the Midwest, confinement livestock operations are a particular problem in this regard. Cases of massive deaths of aquatic organisms, often referred to as fish kills, are an extreme manifestation of the ecological impact of fecal contamination. Typically, they result from high concentrations of toxic ammonia contained in the manure or from depletion of dissolved oxygen in the water caused by decomposition of the pollutant. Chronic effects of manure pollution are poorly known, because of the difficulty of measuring them and placing them in ecological context. Moreover, low-level delivery of fecal pollutants can portend larger catastrophic inputs, for example, when a gradually leaking storage lagoon eventually bursts or an erosive, manure-fertilized crop field receives heavy rainfall.

State and federal agencies engaged in reducing non-point source water pollution are interested in obtaining new technologies for identifying, measuring and anticipating pollution occurrence. Clearly, development of tools that could integrate biological and environmental information to produce site-specific predictive models for guiding pollution-prevention management practices is highly desirable. The proposed research would develop a novel tool that integrates molecular biological and ecological approaches to quantitatively evaluate environmental impacts of swine manure pollutants. Although the technique will be developed with specific reference to Midwestern waters, it will be more broadly applicable, both geographically and with reference to other forms of pollution that engender immune responses in animals. Thus, we believe that the technique has potential to be widely adopted by state and federal environmental management agencies.

The research conducted under this grant reflects the need for integrated, multidisciplinary approaches to deal with complex environmental issues. It combines physiological laboratory techniques, computer modeling of agricultural landscapes and non-point source pollution pathways, and field-based ecological analyses to create a new and integrated approach for evaluating impacts of livestock fecal contamination on Midwestern streams.

The research relates to two major priorities of the NIWR National Competitive Grants Program.

A) It complements work by the USGS related to non-point source pollution, contributing to development of integrated watershed decision support tools for assessing organics and microorganisms transport and fate, along with their effects on aquatic systems.

B) It promises development of a new water quality sensor technology that will be based on integrated methodologies and will provide results that are readily accessible through the Internet.

This research is predicated on the hypothesis that low levels of swine liquid manure slurry and anaerobic lagoon liquid released to open water cause changes in immunological response in fish and increase fish susceptibility to infection.

The initial objectives, therefore, are: 1) to evaluate this hypothesis through a series of laboratory immunological assays applied to the test organism, the fathead minnow (*Pimephales promelas*); and 2) to identify one or more assays for use as a bio-monitoring technique to detect ecological impact of manure pollution in nature. A subsequent task involves use of digital environmental databases that are maintained and managed by the USGS BRD Iowa Cooperative Fish and Wildlife Research Unit at Iowa State University. The objective is 3) to characterize a number of Iowa watersheds and stream systems according to their potential susceptibility to hog manure pollution and to use this information to design a water quality and fish sampling regime. Finally, fish communities at selected stream sites will be analyzed through developed GIS tools to 4) quantitatively measure ecological impact of manure pollution on the streams, and 5) to evaluate the utility of this approach as a biomonitoring tool for environmental protection agencies.

Methodology

The fathead minnow is a native Iowa species, abundant and ubiquitous in small streams. Thus, it is a good choice as a representative of fish communities exposed to low level concentrations of swine manure pollutants released into Iowa waters. Moreover, it is commonly used as a standard bioassay organism in toxicological analyses, so there is substantial knowledge on its tolerance to a wide array of environmental physical conditions and pollutants. Additionally, colonies are easily established and maintained in the laboratory. Fathead minnows used for the experiment were raised in a controlled environment, without previous exposure to swine manure.

The immune response was determined by activity of phagocytic cells, through several forms of measurement. Evidence from limited research involving fish suggested that assays measuring respiratory burst and degranulation are useful for determining phagocytic function in fish, and the procedure also seems to hold promise as a bio-indicator for fish health.

Geographic Information Systems (GIS) technologies provide a tool to enter, store, manipulate and integrate geo-referenced data on, for example, landscape features, water

quality, and aquatic organisms. The project applied GIS technology and landscape modeling to calculate possible swine pollutant flow path patterns in Iowa watersheds having large hog confinements and in those where liquid manure fertilizer is applied on crop fields. Using this approach, we estimated temporal and spatial distribution of manure loads and concentrations that reach receiving waters. This provided the basis for determination of actual conditions of water quality and fish communities at stream sites selected to represent a range of calculated manure pollutant loadings. Ecological impact of the pollution was evaluated by the developed immunological assays performed on wild-caught fathead minnows and on collected data on water chemistry and fish community structure using avaialbel data from Iowa Department of Natural Reosurces. Statistical comparisons are ongoing between the calculated and measured evidence for the pollutant to determine the accuracy and reliability of the GIS-immunological approach in actual practice. As a further check on the procedure, Index of Biotic Integrity (IBI) values determined by Iowa Department of Natural resources in their stream monitorning program is used. The IBI is a commonly used bioindicator of stream environmental quality. It serves as a summary measure of biotic community response to pollution and other forms of habitat degradation. It is being used routinely for long-term environmental monitoring programs in Iowa and other Midwestern states. This design, therefore, allowed for comparisons between this established coarse-scale environmental indicator and the experimental fine-scale immunological indicator.

Principal Findings and Significance for Period from 03/2005 to 09/2006

The effects of acute and chronic stress on the fathead minnow neutrophil function *in vitro* and *in vivo* were determined. Fathead minnows exposed to acute and chronic stress conditions had significantly reduced degranulation, demonstrating that the degranulation assay can be used to measure both acute and chronic stress effects on neutrophil function in this species. This step demonstrated the capability of the assay to measure reduction in neutrophil function. Scientific background and baseline data for use of fathead minnow neutrophil function in future research and aquatic ecosystem evaluation was provided. Fathead minnows are shown to be a useful model to investigate neutrophil degranulation in fish exposed to different environmental conditions. Experiments characterizing effects of sublethal manure exposure on innate immune function in fathead minnows are underway and the data analysis is ongoing.

The spatial distribution of manure on fields has been investigated in the context of aquatic ecosystem health. The inter-relatedness of disposal facilities, management plans, field location, rate of manure application, and stream network were investigated using spatial analysis over different data sets. The GIS model was developed to identify stream sections that have high likelihood to encounter potential hazards for stream biota. Furthermore, analysis of watershed scale flow path was performed for the State of Iowa and evaluation of high and low risk sampling points and comparison with fish kills and population assessment data from Iowa Department of Natural Resources is ongoing.

Fig. 1. Spatial distribution of A: Animal waste control facilities with operating permits in Iowa (red), Manure Management Plans for Animal Feeding (green); and B: Fish kills (red), in The State of Iowa.
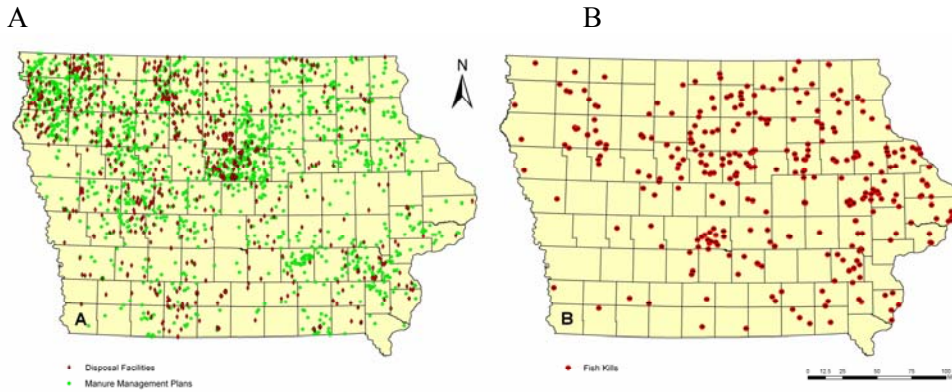

Fig. 2. Digitized fields used for manure disposal. Green: Agriculture Disposal facilities; Red: Manure Management Plans; Yellow: field boundaries. (Hamilton County)

Fig. 3. Predicted flow of manure after field application. Quantity of manure is expressed as intensity of color (dark red = more). Gray areas indicate potential critical points in streams (blue). (Hamilton County)

Figure 2.   Figure 3.

Fig. 4. Three possible scenarios for manure flow based on differences in land cover. Dark green: forest (A); Light green: grassland (B); Tan: row crops (C). Quantity of manure is expressed as the intensity of color (dark red = more). Black arrows indicate the distance of manure flow in streams (blue). (Hamilton County)
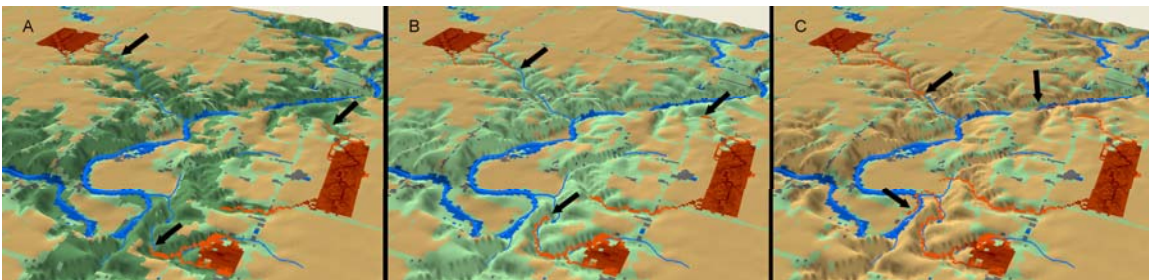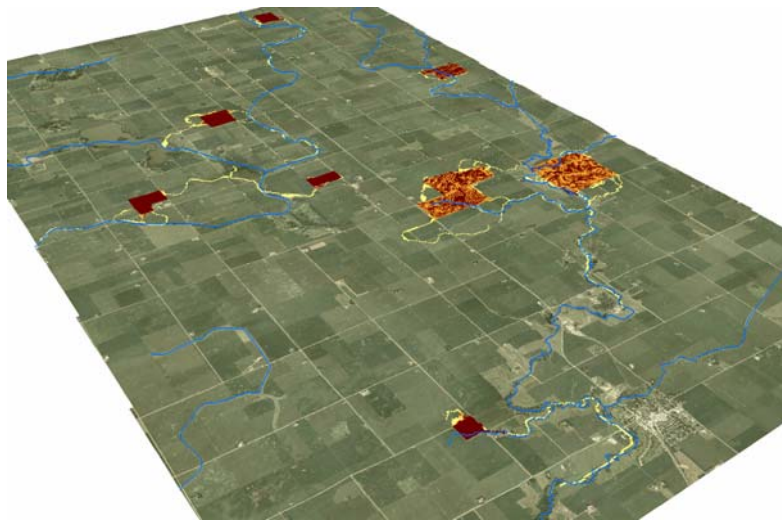
Fig. 5. Example of county (watershed) scale flow path anlysis with identification of critical points of potential manure inflow in public and private waterways. This flow path anaysis is used on state-wide scale to investigate potential correlation of manure exposure, fish kills, and fish community structure (IBI).

Using spatial distribution of AGDs, MMPs, and fish kills, the areas with potential environmental concern were identified in northeast and northwest Iowa (Fig 1.). Based on data accessibility, Hamilton County was selected for detailed study. Conversion of vector to raster datasets, calculations of manure flow path, and setting the threshold level were performed in ArcGIS for different field situation scenarios. The manure flow from three different fields was calculated and critical points in stream were identified (Figs 2-4.). The critical points were determined based on the presence of the manure in stream sections above the threshold level. The difference in land cover has a significant effect on the flow path length and quantity of manure reaching streams ($P<0.01$). The flow of manure through forested areas is the shortest and through row crop is the longest (Fig 4.). The anal;ysis was repeated for total of 12 counties, including Emmet county (Fig 5.).

Based on preliminary analysis of available datasets, we suggest that the TauDEM flow path analysis and the developed geospatial model have potential to be used as a tool to determine stream sections with increased probability of critical impairment due to manure contamination. A fully developed tool could assist in the selection of stream sampling points relevant to ecosystem health assessment and reduce the cost of field surveys. Changes in land cover can be modeled to help management decisions, improve spatial distribution of animal facilities, and predict possible outcomes of restoration efforts.

In summary, work performed from 03/2005 to 09/2006 clearly demonstrated that:

1. Neutrophil functional assays show potential for use in studying effects of immunomodulatory compounds, as well as effects of environmental stress on fish physiology, providing us with new tools to be used in the assessment of aquatic ecosystem health.

2. The TauDEM flow path analysis and the developed geospatial model have potential to be used as a tool to determine stream sections with increased probability of critical impairment due to manure contamination. A fully developed tool will assist in the selection of stream sampling points relevant to ecosystem health assessment and reduce the cost of field surveys.
3. Changes in land cover can be modeled to help management decisions, improve spatial distribution of animal facilities, and predict possible outcomes of restoration efforts.

Improving water quality in Iowa rivers: cost-benefit analysis of adopting new conservation practices and changing agricultural land use

Basic Information

Title:	Improving water quality in Iowa rivers: cost-benefit analysis of adopting new conservation practices and changing agricultural land use
Project Number:	2005IA79B
Start Date:	3/1/2005
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	IA 4
Research Category:	Water Quality
Focus Category:	Water Quality, Conservation, Agriculture
Descriptors:	
Principal Investigators:	Catherine L. Kling, Hongli Feng, Philip W. Gassman, Lyubov A. Kurkalova, Silvia Secchi

Publication

From CARD, PI: Cathy Kling
June 2007 (for report period March 1 2006—February 28, 2007)

Problem and Research Objectives

The objective of this project was to assess water quality improvements and costs of alternative policy scenarios for the state of Iowa. The water quality measures of interest were nitrogen, phosphorus, and sediment. Our study fully assessed different conservation policies in the state by modeling adequately the spatial heterogeneity of land characteristics and the interactions between land use decisions at the micro level and watershed dynamics. Nonpoint source pollution due to agricultural activities is a vital issue for the State. It is difficult to overstate the importance of these issues to the environment and land managers, given the importance of agriculture in Iowa, and the large number of impaired waters in the state. This project provided a first assessment of the overall impact on in-stream water quality of large scale conservation policies that included several practices simultaneously. The results from our project would be particularly valuable for effective, science-based water quality management in the state of Iowa.

Methodology

Micro-unit-based economic models and data on land use and conservation practices are combined with a watershed-based hydrological model (Soil and Water Assessment Tool, SWAT) to estimate the costs of obtaining water quality changes from the hypothetical placement of conservation practices. The main procedures involved in the project include: estimate the costs of conservation practices, identify the location of conservation practices, calculate the cost of alternative conservation policies, estimate the water quality consequences of the policies, and finally assess the cost and benefit of the policies.

The SWAT executions, including the input and output data, are managed with the interactive SWAT (i_SWAT) software (http:// www.public.iastate.edu/~elvis).

Principal Findings and Significance

During the first year of the project, we finished investigating the costs and benefits of improving water quality in Iowa under two policy objectives. In the first scenario we assessed the impact of a program designed to improve water quality in Iowa on carbon sequestration, and in the second scenario we calculated the water quality impact of a program aimed at maximizing carbon sequestration. Our results indicate that the amount of benefits depends on what indicators are used to measure water quality. Our results also suggest that the term "improving water quality" can mean different things for different people. This is because the responses of different water quality indicators to conservation efforts can be quite different. For more detailed analysis, please see Secchi et al. (2007, **Choices**).

In the second year of the project, we obtained additional funding from a coalition of organizations, namely the Iowa Farm Bureau, the Iowa Corn Growers' Association, the Iowa Soybean Association, and the Leopold Center for Sustainable Agriculture. As a result, we were able to do a much more thorough analysis of the research problem than otherwise possible. In particular, we were able to gather detailed cost data for major conservation practices used in Iowa. Equally importantly, we were able to set up and use an algorithm that optimized the set of conservation practices and their location in the landscape.

As a result of the augmented project, we gathered county-level data for some major conservation practices with regard to their costs and coverage. A database of county average cost is established for terraces, grass waterways, land retirement, sediment control basins, grade stabilization structures, filter strips, wetland restoration, riparian buffers, contour buffer strips, and nutrient management. We also obtained a state wide estimate of total costs for major conservation practices currently implemented in Iowa.

In the search for cost-effective conservation policies, we considered three different types of nutrient targets: reducing phosphorus loadings by 40%, reducing nitrate loadings by 25%, and a goal of reducing both phosphorus (by 40%) and nitrate (by 25%). The evolution algorithm was used to search for the least cost of reaching the targets. Focusing on nitrates exclusively without any regard to phosphorus levels led to an increase in total phosphorus loadings in 8 out of 13 watersheds. The total statewide gross cost of reducing nitrates was about $472 million annually. For the phosphorous target, the total gross cost was estimated to be almost $613 million a year. Implementing the phosphorous target would simultaneously result in a statewide reduction in nitrate loadings of over 31%. This means that meeting the target of a 40% reduction in phosphorous would also meet the target of a 25% reduction in nitrogen.

Our results indicated that conservation practices that are efficient for erosion and phosphorous control are not in general efficient for nitrogen control. In general, conservation practices that have been implemented on the ground tend to focus on erosion control. Based on this, our recommendation is that to reduce nitrogen pollution in the waterways, measures that directly target nitrogen might be necessary. This has implications for policies that are designed to alleviate the hypoxic problem in the Gulf of Mexico. Our results also indicate that the cost-effective measures are different across different watersheds. The message for stakeholders in the watersheds is that they should gain a good knowledge of their watersheds before adopting any control policies that have been proving to be promising in other watersheds. Finally, a clear result from our analysis is that targeting different pollutants will mean different land use options. Thus, the needs of stakeholders in the watersheds should be identified before any policy discussions take place. While our results indicate that targeting phosphorous would also achieve the nitrate goal in our scenarios, we think it is highly likely that this particular result will not hold as more practices are considered and a more thorough search is conducted through the genetic algorithm.

For the Raccoon watershed, where the calibration and validation of the SWAT is focused on for this project, we conducted an additional study to assess alternative targeting policies. We use SWAT, along with transfer coefficients, to assess alternative principles of allocating nutrient load reduction in the Raccoon River watershed in central Iowa. Delivery coefficients have long been used in economic analysis of policies that seek to address environmental problems like water pollution. However, the derivation and validity of delivery coefficients have not been examined carefully by empirical analyses. In this study, we derived estimates of delivery coefficients and then evaluated them as a bridge between complex water quality models and economic policies. Specifically, delivery coefficients were first derived from the simulation results of SWAT. Nutrient reduction responsibilities were then allocated to subwatersheds based on the delivery coefficients using four allocation principles. We found that the allocations achieved outcomes that differed from intended water quality targets by less than ten percent in most cases. For the least cost allocation with homogeneous cost, potential cost savings, relative to uniform allocation, were about the same magnitude as the divergence between outcomes and targets. However, cost savings significantly outweighed the deviation from water quality targets when cost was heterogeneous across the subwatersheds.

Sensors for CyberEngineering: Monitoring and Modeling the Iowa River for Nutrients and Sediments

Basic Information

Title:	Sensors for CyberEngineering: Monitoring and Modeling the Iowa River for Nutrients and Sediments
Project Number:	2005IA81B
Start Date:	3/1/2005
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Funding Source:	104B
Congressional District:	IA 1st
Research Category:	Water Quality
Focus Category:	Nutrients, Sediments, Water Quality
Descriptors:	
Principal Investigators:	Jerald L. Schnoor

Publication

Problem Statement and Research Objectives

The flux of nutrients and sediments into Iowa's lakes and rivers can have severe impacts on health of these systems, and the way which these resources are utilized. Delivery of nutrients such as nitrogen and phosphorus to water bodies via surface runoff can increase the total mass of those constituents in surface waters, creating eutrophic conditions. These conditions can spur the growth of harmful algal blooms which can lead to aesthetically unpleasing water. Consumption of dissolved oxygen by algal populations may inhibit the ability of an ecosystem to sustain fish populations. Nutrients and sediments are also transported downstream to the Gulf of Mexico causing large scale hypoxic episodes and harmful bloom events. Sensors used to track nutrients, sediments and other water quality parameters have traditionally been deployed in a passive manner; meaning that data is collected and analyzed after the fact. However, increasing capabilities in sensor technology, telemetry hardware, and cyberinfrastructure allow for the real-time integration of sensors and water quality models. This fusion of real-time water quality data with water quality models can potentially provide regulators with a tool to predict environmental events. This knowledge can be used to implement management actions to remedy deleterious events before they happen.

The aim of this research project was to construct an operational water quality node to provide near real-time measurements at an environmental observatory on Clear Creek, Iowa River Basin, near South Amana, Iowa. Specifically, the main goal of this project was to use sensors and wireless communications to gather high frequency data on water quality which is assimilated in modeling efforts. This required the purchase, assembly and configuration of hardware such as water quality sensors, dataloggers, power sources, and modems. Once these components were purchased, they were assembled and deployed at Clear Creek.

The ability to measure water quality parameters, transmit them in near real-time, down-load them into a data base, and model them in real-time represented an ambitious goal for a two-year project. This was made possible using cellular technology to transmit information to a database in the Environmental Engineering Laboratories at the University of Iowa. Although the information flow from the database to our water quality model has not yet been made permanent, preliminary model results have been generated. Results from this project have provided the first step to creating a fully functioning environmental observatory at Clear Creek which can be used to predict downstream water quality.

Method Development

System Components
Development of the water quality node required the assembly and configuration of several key pieces of hardware and cyberinfrastructure (Figure 1). This includes sensors, dataloggers, cellular telemetry hardware, and water quality models. To detect water quality constituents, we have purchased and configured water quality sensors. Data from

these units can be collected and transmitted to a database in the Environmental Engineering Laboratories at the University of Iowa using the remote data collection platforms purchased from Campbell Scientific.
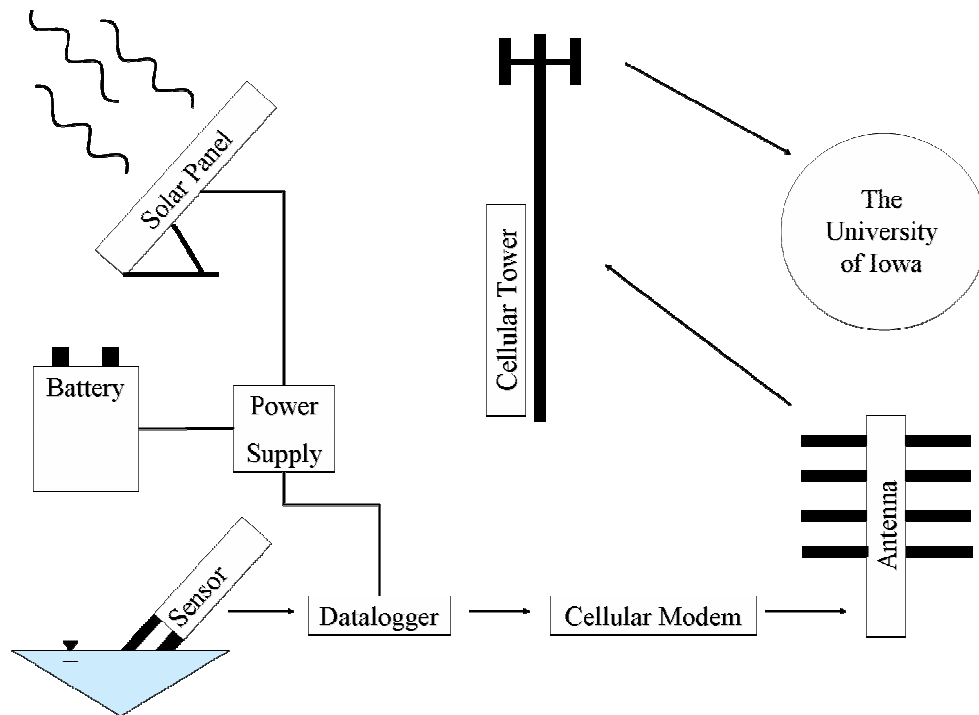

Figure 1. Schematic of the water quality node installed at the environmental observatory on Clear Creek.

Water quality measurements have been recorded and are currently monitored using two different models of water probes: the Hydrolab DS5X data sonde and the MicroLAB Nutrient Analyzer. The Hydrolab DS5X Water Quality Multiprobe (Hach, Loveland, Colorado) can measure chlorophyll *a*, conductivity, dissolved oxygen, pH, temperature and turbidity. It also contains a sweeper that removes biomass from several of the sensors. The MicroLAB Nutrient Analyzer (EnviroTech LLC, Chesapeake, VA) can be used to measure ammonia, nitrate, and phosphate.

Water quality measurements have been successfully downloaded and transferred using a remote data collection platform purchased from Campbell Scientific, Inc. The datalogger used in this system is the CR1000 Measurement and Control System (Campbell Scientific Inc., Logan, Utah). This unit receives and stores sensor measurements until they are uploaded into a database in the Environmental Engineering Laboratories. Measurements were transmitted from the remote data collection platform using cellular technology. Specifically, data was transferred through a Redwing 100 CMDA Modem (Airlink Communications, Hayward, California) and through the Verizon Cellular Network (Verizon, Elgin, Illinois) by way of a YA Series Yagi Directional Antenna (Radiall/Larsen Antenna Technologies, Vancouver, Washington). The cellular plan used was an America's Choice II for Business 450 Plan which includes 450 minutes.

The remote data collection platform and sensors were powered by a NP12 Rechargeable 12-Volt Lead Battery (Campbell Scientific Inc., Logan, Utah) and a BP SX20U Solar Cell (British Petroleum, London, United Kingdom) via a CH100 12 Volt Charger/Regulator (Campbell Scientific Inc., Logan, Utah). All components of the remote data collection platform except the antenna, solar panel and data sondes were enclosed in a RJ Series Junction Enclosure (Stahlin Non-Metallic Enclosures, Belding, Michigan, Model No. RJ1816HPL). The enclosure protected the components from rain and moisture. Locks were placed on the enclosure latches to discourage vandalism. Desiccant bags were placed in the enclosure to help remove moisture inside the Stahlin enclosure.

Water Quality Node Configuration
Before water quality data could be collected, transmitted and input into water quality models, hardware components of the water quality node were configured and integrated. Formatting of the Hydrolab DS5X data sondes was performed using software supplied by Hach. The MicroLAB Nutrient Sensors were assembled and supplied with the necessary reagents to take measurements. Finally, components in the remote data collection platform were wired and programmed to seamlessly collect and transmit water quality data in real-time.

Configuration of the Hydrolab DS5X data sondes was performed using the Hydras 3LT software supplied by Hach. Using this software, settings on the data sonde such as the internal clock, output configuration, and deployment settings were programmed. Calibration of the individual sensors was performed by connecting the Hydras 3LT software with a DS5X data sonde. This was done by selecting the calibration tab on the software and clicking a sub-tab for each individual sensor. The calibration cup for the data sondes was then filled with the required standard to a level which covered the sensor, and the value of the standard was entered into Hydras 3LT. Standards used include the following: 0.100 mS/cm Conductivity Standard Solution (Hydrolab cat. No. 013610HY), 1.1412 mS/cm Conductivity Standard Solution (Hydrolab cat. No. 013620HY), 100 NTU StablCal Turbidity Standard (Hydrolab cat no. 007308), 1000 NTU StablCal Turbidity Standard (Hydrolab cat no. 007309.), pH 7.00 buffer solution (Acros, New Jersey, USA, cat no. 61106-0040), and pH 10.00 buffer solution (Fisher Fair Lawn, New Jersey cat no. SB115-4). Between the calibration of the sensors to each solution, the calibration cup used to hold the standard was rinsed out three times with deionized water. A full description on this procedure can be found in the Hydrolab DS5X User Manual (Hach Company, 2005).

The MicroLAB Nutrient Sensors were configured and assembled to sense fluxes of ammonia, nitrate and phosphorus. The first step in assembling these sensors was to construct the chemical reagent bag system. Next, the required chemical reagents were created as per the instructions in the MicroLAB Operating Manual (EnviroTech LLC, 2006). The instruments were readied for operation by filling the reagent bags. The MicroLAB Nutrient Sensors can only be configured to measure the concentration of one nutrient at a time. This is due to the fact that the analysis for each nutrient requires a

unique set of chemical reagents and a detector specific for the specified nutrient. Currently these sensors are configured to measure for nitrate.

In addition to the configuration of the Hydrolab DS5X data sondes and the MicroLAB Nutrient Sensors, effort also went into the assembly and operation of the remote data collection platform. This platform was essential for the collection and near real-time transmission of water quality measurements, as well as supplying power to the data sondes. Configuration of the platform began with the CR1000 datalogger using the Loggernet 3.1.5 Software. This software was used to download water quality measurement schedules onto the datalogger. The Loggernet software itself was also programmed to download measurements collected at the water quality node to the database in the Environmental Engineering Laboratories at the University of Iowa. Configuration of the cellular modem was completed to link the Loggernet Software to with the datalogger in the field. This was performed using the Cellset program available for download from Campbell Scientific Website (Campbell Scientific, Inc, 2006). Cellset allowed the system ID number and telephone number to be programmed into the cellular modem. Further detail on the full configuration of the remote data collection platform can be found in the 2005 Annual Report.

Water Quality Models
The ability to predict deleterious water quality events required the use of models. Models selected for this project include the BASINS (Better Assessment Science Integrating Point and Nonpoint Sources), the Watershed Analysis Risk Management Framework (WARMF) and the QUAL2K Stream and Water Quality Model. Before conducting analyses using these models, basic knowledge about the operation of these models was required.

BASINS is a model used to perform watershed and water quality-based studies which enable the integration of point and nonpoint source analysis for a variety of pollutants. This model was developed by the USEPA to assist state regulatory agencies in identifying and analyzing water quality issues. BASINS is driven by a graphical user interface which combines environmental data, fate and transport models, and geographical information systems (GIS) to facilitate the development of watershed management alternatives. BASINS includes an automatic delineation tool which breaks a watershed into smaller hydrologically connected subwatersheds. The delineated watershed can then be imported into a model of choice. For this project the HUC 8 watershed of the Lower Iowa River watershed, of which the Clear Creek is located in the north-central section, was delineated.

BASINS provides several tools which were used to download data for the Lower Iowa River HUC 8 from several sources including USGS, EPA, and local-sources. Data downloaded includes the Digital Elevation Model (DEM), National Hydrography Dataset (NHD), and the National Landcover Database (NLCD) for the Lower Iowa River HUC 8. Once all necessary data was extracted the automatic delineation tool was used to divide the Lower Iowa River watershed into multiple subwatersheds. The subwatershed that defined the Clear Creek watershed was then selected as the focus area. The delineated

Clear Creek digital watershed was then imported into both the QUAL2K and WARMF models. Figure 2 shows the BASINS delineation of the Clear Creek watershed.
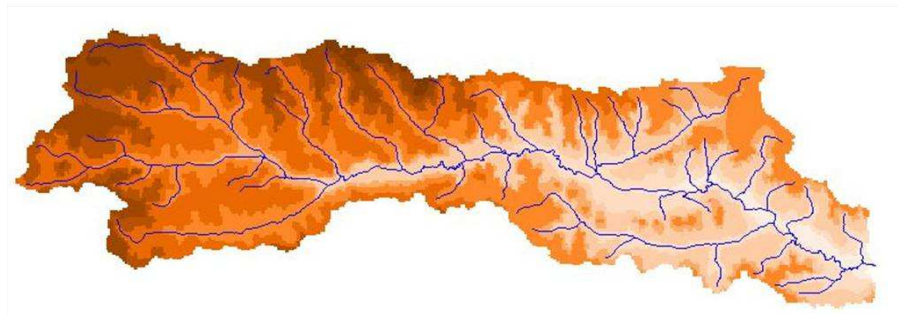

Figure 2. BASINS delineation of the Clear Creek watershed.

The ability to predict water quality throughout Clear Creek in real-time required the integration of real-time water quality data into a model. Several different water quality models were analyzed to determine their compatibility with the project goals. We originally planned to integrate the AVSWAT Model with data streaming from the water quality node. However, AVSWAT was found to be too cumbersome for this application. Specifically, the model requires too much spatially detailed information and requires a significant amount of time to run each simulation. An alternative model we have chosen to develop is the QUAL2K Stream Water Quality Model.

The QUAL2K model is a one-dimensional model (longitudinal direction) based on assumptions that the channel is well mixed in the vertical and lateral directions. It has the ability to simulate a system comprised of a main branch and several tributaries. All hydraulics are simulated as steady state with non-uniform flow. The model can capture diurnal variations in certain water quality parameters (like pH, dissolved oxygen, and carbon dioxide), and the heat budget is determined on a diel time scale. This allows the integration of highly resolved water quality data which the Hydrolab DS5X data sondes collect.

To set up the model, data from several resources were used. Output from the BASINS model was used to transform the physical creek network into the digital model. This output included information such as the location of branching tributaries and the length of those tributaries. Diurnal water quality data collected from the water quality node were input into the model as initial conditions for model trials. Constituents modeled by QUAL2K are shown in Table 1 (Chapra et al., 2006). Hydraulic data input into the QUAL2K Model was estimated using data from the USGS stream gage located in Coralville, IA (USGS, 2007). Although further work is needed to better define non-point source inputs into the creek, preliminary trials runs of the QUAL2K have modeled water quality constituents throughout the main stem of Clear Creek and its tributaries.

Table 1. Water quality parameters simulated in the QUAL2K model (from Chapra et al., 2006.).

Variable	Symbol	Units	Variable	Symbol	Units
Conductivity	s	µmhos	Inorganic phosphorus	p_i	µgP/L
Inorganic suspended solids	m_i	mgD/L	Total inorganic carbon	c_T	mole/L
Dissolved oxygen	o	mgO_2/L	Bottom algae biomass	a_b	mgA/m^2
Slowly reacting CBOD	c_s	mgO_2/L	Bottom algae nitrogen	IN_b	mgN/m^2
Fast reacting CBOD	c_f	mgO_2/L	Bottom algae phosphorus	IP_b	mgP/m^2
Organic nitrogen	n_o	µgN/L	Phytoplankton	a_p	µgA/L
Ammonia nitrogen	n_a	µgN/L	Detritus	m_o	mgD/L
Nitrate nitrogen	n_n	µgN/L	Pathogen	X	cfu/100 mL
Organic phosphorus	p_o	µgP/L	Alkalinity	Alk	$mgCaCO_3$/L

System Installation

Following the configuration of the sensors and remote data collection platforms, the water quality node was installed in the upper reaches of the Clear Creek catchment (Figure 3). The site selected for deployment was one which the Iowa Institute of Hydraulic Research (IIHR) had already developed with rain gauges, and a plot to study erosion processes. The existing partnership between the IIHR and the land owner made this an attractive site to install the water quality node. Highly erodable soil in the area also makes this site well qualified to study the "hot spots" and "hot moments" of nutrient and sediment delivery to Clear Creek.
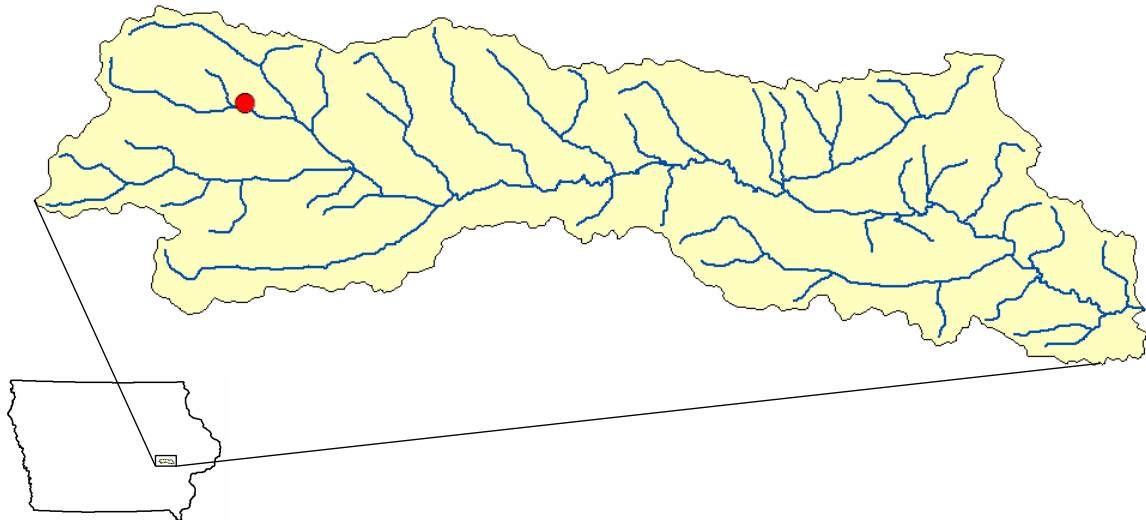

Figure 3. The University of Iowa water quality node (red dot) at the environmental observatory in the Clear Creek HUC 10 watershed.

The water quality node was installed in Clear Creek on March, 2006 (Figure 4). Both the solar panel and the remote data collection platform were each attached to their own set of two studded T-posts on the bank of the creek. The directional antenna was also attached to a studded T-post on the bank. An additional post was driven into the creek bed with a Hydrolab DS5X data sonde secured to it using a section of aircraft cable. Desiccant bags were placed in the enclosure for the remote data collection platform to reduce the humidity inside the enclosure. This was done to prevent any unnecessary damage that might occur due to moisture.

Figure 4. Water quality node installed in Clear Creek, Iowa.

Bi-Monthly Site Visits

Data sondes deployed at the water quality node are subject to biofouling; thus, bi-monthly site visits were performed to clean or replace a data sonde which showed a significant amount of biofouling. Although the data sondes were equipped with sweeper brushes, they did not remove all of the biofouling (Figure 5). Maintenance on the water quality node was also performed during bi-monthly site visits. This included the removal of debris from any of the T-posts, cleaning of the glass on the solar panel, and replacement of the desiccant in the remote data collection platform (if required).

Grab samples were also collected on site visits. This was done to validate measurements collected from the data sonde. Samples were taken from the middle part of the channel approximately half way below the surface of the water. These samples were then tested for dissolved oxygen, pH, and turbidity. Results were then compared to measurements taken by the data sondes. Measurements of dissolved oxygen, pH, specific conductivity, and temperature were also taken using a Hach Hydrolab Quanta G data sonde for further comparison.

Figure 5. Biofouling on the Hydrolab DS5X data sonde after a two week deployment.

Diurnal Study

Validation of trends seen in data from the summer of 2006 was performed during a diurnal study from 10:00 AM on August, 3rd to 12:00 PM on August 4th, 2006. During this time three Hydrolab DS5X data sondes were deployed and collected measurements once every twenty minutes. Grab samples and Hydrolab Quanta G measurements were also collected once every hour except at 3:00 AM and 5:00 AM on August 4th. Grab samples were analyzed for pH and turbidity and also for dissolved oxygen using a Hach HQ-10 portable dissolved oxygen meter. Variability between sensor measurements was assessed using data from this study. Before this study Hydrolab DS5X data sondes #1 and #2 were cleaned and calibrated. Hydrolab DS5X data sonde #3 had been deployed on seventeen days earlier to observe the effects of biofouling on sensor measurements.

Results and Discussion

The water quality node has allowed for measurement and collection of several water quality parameters for a large portion of the spring, summer and fall of 2006. These water quality parameters include dissolved oxygen, pH, specific conductivity, temperature, and turbidity. This data was collected using three Hydrolab DS5X data sondes, a Hydrolab Quanta G data sonde and grab samples. Three gaps in the data occurred during the deployment period. This was due operational error in deploying individual data sondes at those times. The water quality node was removed on September 12th, 2006 due low flows in Clear Creek and vandalism concerns from the onset of the fall hunting season.

Temperature

Temperature data collected in Clear Creek throughout the entire deployment is shown in Figure 6. This data shows a distinct seasonal trend as the water temperature generally increased during the warm summer months, and declined for the cooler periods in August

and September. The vertical "smearing" of the data points which occurs in Figure 6 can be attributed diurnal variations in the water temperature. Figure 7 shows a section of this data from July 20th to August 4th. Trends in this figure highlight the existence of multi-day phenomenon. For example, stable temperatures and during a frontal convective storm can be seen on July 25th through the 27th. The subsequent movement of a warm front through the study area from July 28th to July 31st can be seen by the increasing minimum and maximum daily temperatures. Daily fluctuations in water temperature were captured during the diurnal study (Figure 8). Water temperatures were shown to increasing during the day, and fall at night time, a process driven by the rising and setting of the sun. A lack of variability between data sonde measurements in the diurnal study indicates that temperature measurements taken by the DS5X data sondes are reliable and the effects of biofouling on temperature measurements are negligible.
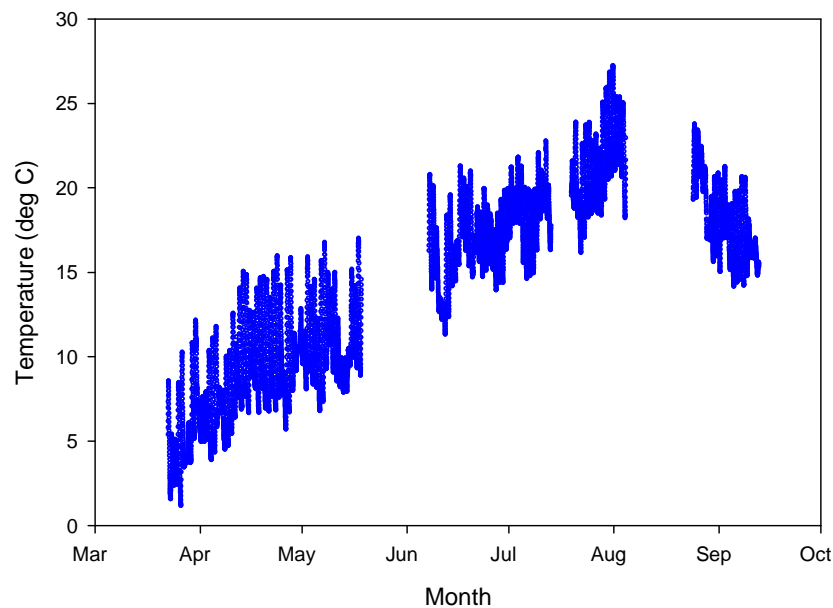

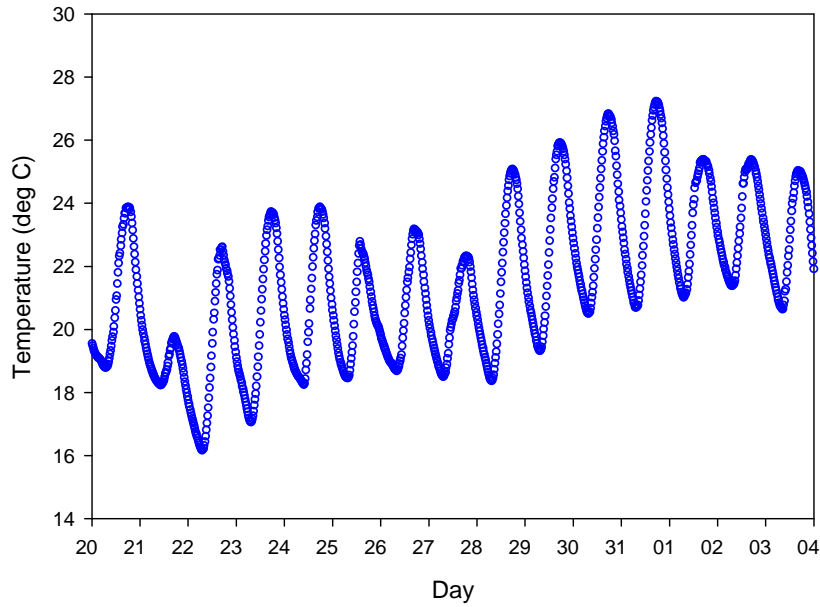**Figure 6. Seasonal variations in Clear Creek water temperature.**

Figure 7. Multi-day variations in Clear Creek water temperature from July 20th to August 4th.
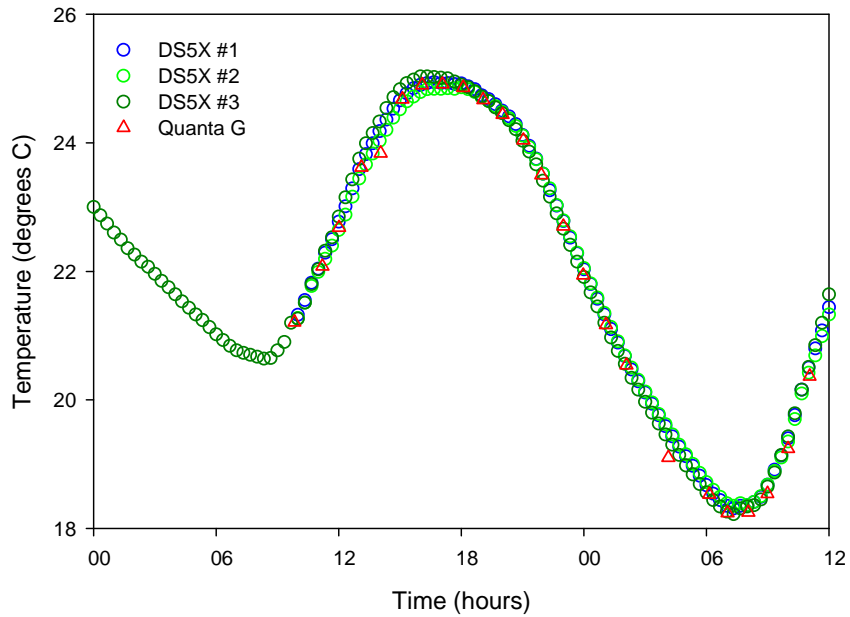
Figure 8. Temperature measurements from Clear Creek taken during the diurnal study.

pH

Measurements of pH were collected for a majority of the time from March to September, 2006. Data from the second half of April collected by two different DS5X data sondes is presented in Figure 9. This data shows the presence of a diurnal trend in pH. The data also shows some discontinuity between deployments of the two sensors. For example, on April 20th when DS5X #2 was replaced by DS5X #1, the pH measurements dropped from 8.3 to 7.7. A similar drop in pH measurement also occurred on April 27th. Possible

explanations for this phenomenon include calibration error, loss of calibration by the sensor, and biofouling.

Measurements collected during the diurnal study indicated the presence of a distinct daily cycle (Figure 10). In this cycle the pH increases during the daytime, and decreases during the nighttime. This trend is due to the consumption of carbon dioxide, a weak acid, via photosynthesis during the daytime (forward reaction, equation 1), and the creation of carbon dioxide at nighttime from the respiration by periphyton (back reaction, equation 1). Measurements taken by both DS5X data sondes, the Quanta G data sonde and grab samples during the diurnal study all show a low amount of variability between sensors throughout the daily cycle.

$$6\,CO_2 \; + 6\,H_2O \; + \text{sunlight} \; \leftarrow\rightarrow \; C_6H_{12}O_6 \;(\text{sugars}) \; + \; 6\,O_2 \qquad (\text{eq. 1})$$
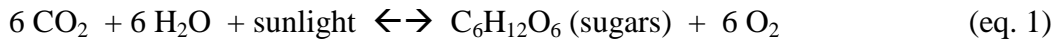
The diurnal trend in pH is also due to the role of dissolved carbon dioxide as a weak acid. When $CO_2(aq)$ increases during nighttime respiration, the pH decreases; and when $CO_2(aq)$ decreases during daytime photosynthesis due to uptake by algae, the pH increases. The first acidity constant (ionization) of carbonic acid can be used to illustrate the cause of the diurnal cycle of pH. As CO_2 (aq) is respired, it results in formation of a strong acid H^+ , which lowers the pH.

$$CO_2 \cdot H_2O \; \leftarrow\rightarrow H_2CO_3 \; \leftarrow\rightarrow \; H^+ \;(\text{strong acid}) + \; HCO_3^- \;(\text{weak base}) \qquad (\text{eq. 2})$$
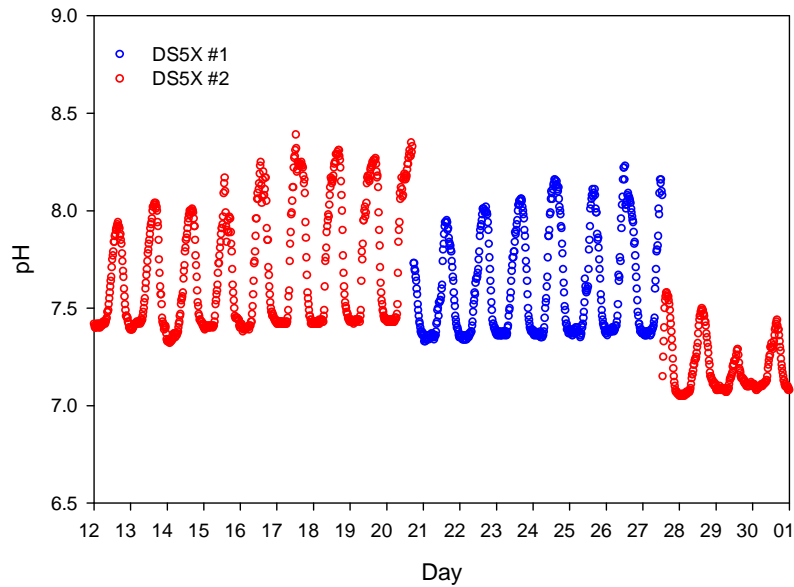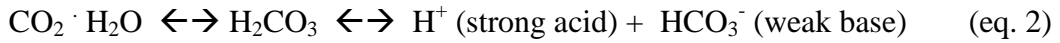

Figure 9. Clear Creek pH measurements from April 20th to May 1st, 2006.
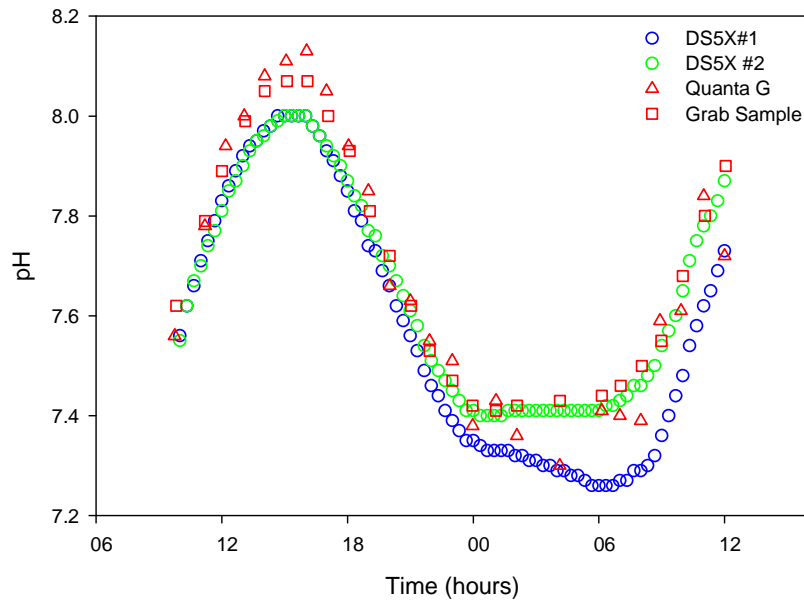
Figure 10. Clear Creek pH measurements during the diurnal study.

Dissolved Oxygen

Dissolved oxygen measurements collected during the entire summer are shown in Figure 11. The figure shows a decreasing trend from March to September. This may be due to the accumulation, death and decay of algal plant biomass in the creek. Increasing decay of this biomass would create an increasing oxygen demand, thus, reducing dissolved oxygen levels throughout the summer. Also shown on Figure 11 is the saturation concentration for dissolved oxygen which is based on temperature readings taken by the data sondes. A significant portion of the measurements were actually higher than the saturation values further indicating the presence of photosynthetic organisms. The diurnal trend of dissolved oxygen observed during the diurnal study is shown on Figure 12. This trend shows an increase of dissolved oxygen during the day which is again due to photosynthesis by periphyton (see eq. 1 above), and a decrease in dissolved oxygen concentration during the night time due to the respiration by phytoplankton. One point of particular interest in Figure 11 is the decrease of dissolved oxygen concentration below the EPA daily minimum of 5 mg/L for parts of July, August and September. This highlights the need of continuous sampling as traditional grab samples may have missed these critical events occurring largely during nighttime. The two events of low dissolved oxygen during March and April are actually due to sensor error and are not accurate measurements. Although the source of this error is unknown, it was remedied by reinstalling the drivers on the sensor.

All measurements recorded by the DS5X data sondes and the Hydrolab HQ-10 Dissolved Oxygen Meter during the diurnal study showed only a small amount of variation. There was a distinct difference between measurements taken by these sensors and the Hydrolab Quanta G sensor as measurements from the Quanta G were consistently lower. This was also observed in data presented in the 2005 Annual Report. Effects from biofouling of the dissolved oxygen sensor appear to be minimal.
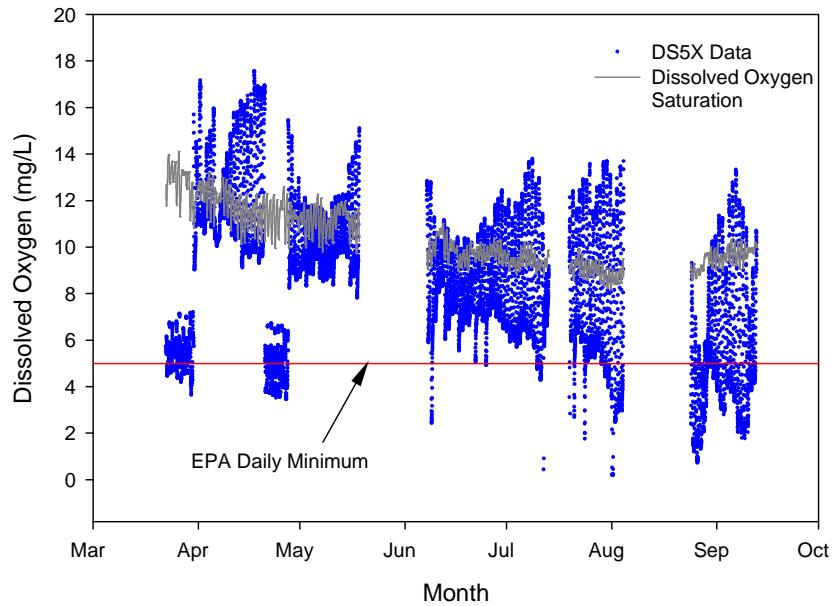
Figure 11. Dissolved oxygen measurements from Clear Creek during the summer of 2006.
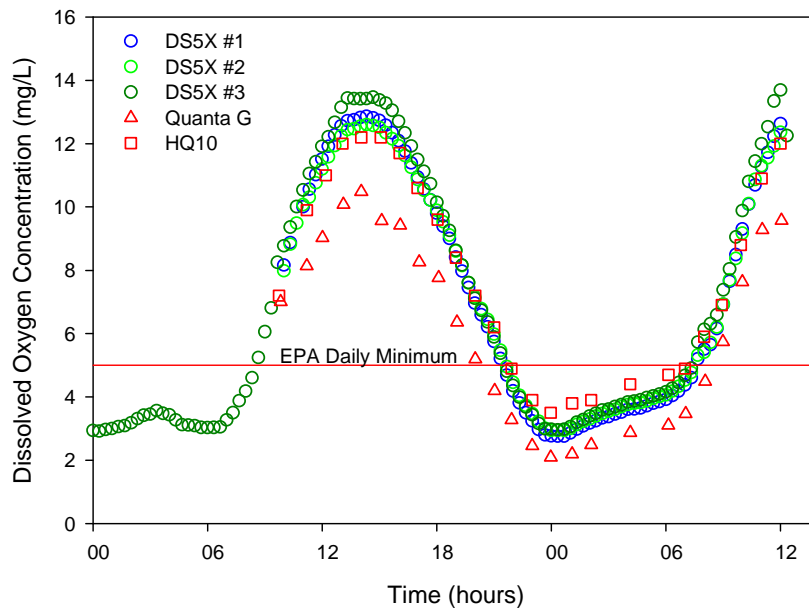
Figure 12. Dissolved oxygen measurements from Clear Creek during the diurnal study.

Turbidity

Figure 13 shows turbidity data from the summer of 2006. While most of the measurements were below 100 NTUs, there were a few events which reached the sensor's maximum limit of 3000 NTU. Some events with higher measurements (>100 NTU) are not believed to be representative of the actual water quality in the creek. This is supported by evidence shown in Figure 14. Data in this figure are from the continuous

deployment of one DS5X data sonde. Grab samples were collected and measured on March 30th and April 11th and are shown as red squares. The data sonde was calibrated and cleaned at the time of its installation on March 30th. During the April 11th site visit, the data sonde was observed to have significant amounts of biomass on it. The data sonde was cleaned and placed back into the creek without recalibration. The measurements taken before and after the cleaning of the data sonde were 299 NTU and 5.1 NTU respectively. The 5.1 NTU data sonde measurement corresponds well with the 4.3 NTU grab sample taken. Thus, it would be reasonable to conclude that the period of high turbidity measurements (>100 NTU) taken during the previous week were inaccurate due to biofouling of the turbidity sensor. Despite these problems with the turbidity sensors, measurements taken by the DS5X data sondes during the diurnal study seemed to indicate a minimal amount of variability (Figure 15). No measurement was recorded above 30 NTU which was consistent with the lack of particles observed in the water. Data points collected using the DS5X data sondes match values recorded from the grab samples. The lack of variability in measurements indicates that the effects of biofouling at this period of time were minimal.
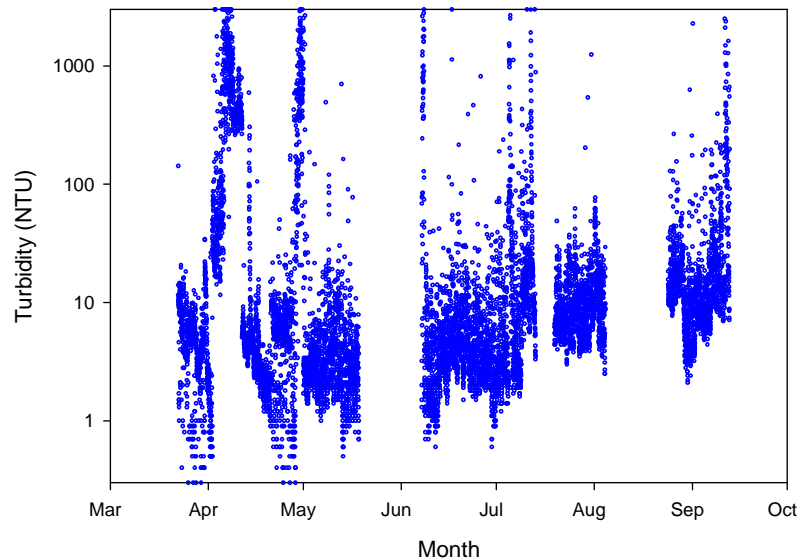
Figure 13. Clear Creek turbidity measurements during the summer of 2006.
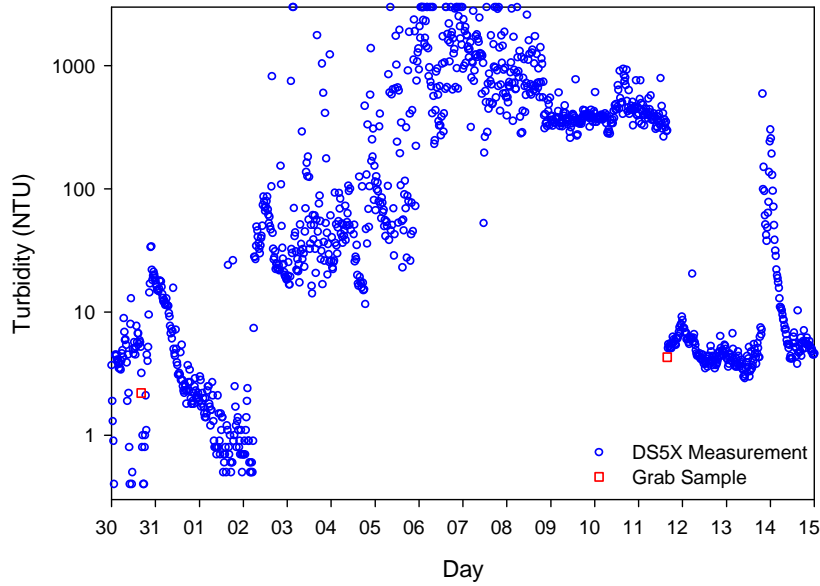
Figure 14. Clear Creek turbidity measurements taken between March 30th and April 15th.
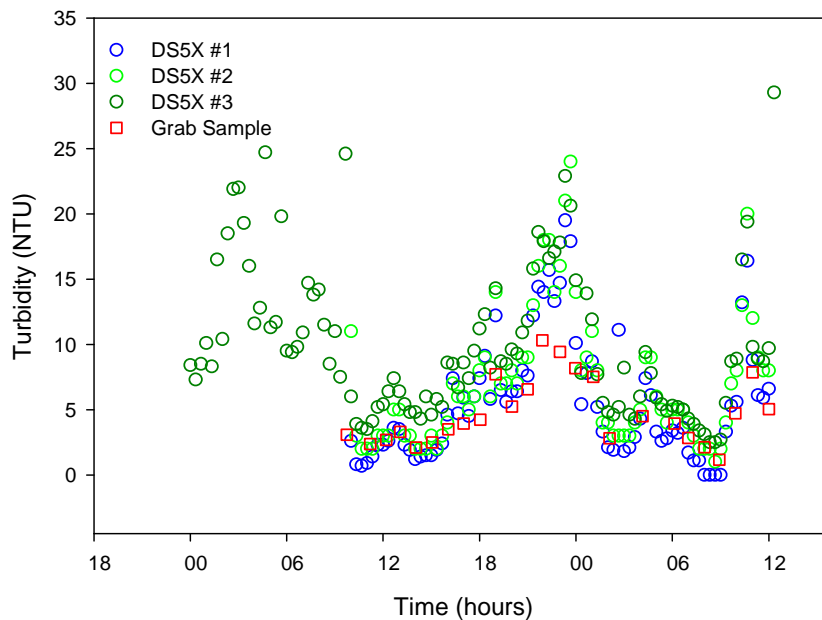
Figure 15. Clear Creek turbidity measurements taken during the diurnal study.

Specific Conductivity

Specific Conductivity measurements taken during the summer of 2006 are shown in Figure 16. Measurements stayed relatively constant throughout the entire summer with a few notable exceptions. The reason for the occurrence of the peaks is unknown and will be investigated the upcoming summer. Measurements taken from April 20th to April 27th appear to contain a bias compared to those collected before and after this period. These measurements were collected using a different data sonde. As a result, this bias may be due to an error when this data sonde was calibrated. A diurnal trend in specific conductivity can be seen in data collected during the diurnal study (Figure 17). This data

showed an increase in specific conductivity during the evening and a decrease in specific conductivity during the morning. The diurnal trend observed may be due to the dissolution and precipitation of calcium carbonate. Differences in the measurements between DS5X #3 and the Quanta G data may have again been due to calibration differences as the DS5X #3 data sonde was calibrated and deployed seventeen days prior to the Quanta G data sonde.

Figure 16. Specific conductivity measurements from Clear Creek during the summer of 2006.

Figure 17. Clear Creek specific conductivity measurements collected during the diurnal study.

System Analysis

The integrated use of sensors, communication hardware, and cyberinfrastructure is essential in the real-time transmission of environmental measurements. Analysis of our system is therefore necessary to determine what improvements can be made to enhance the performance of the water quality node. Figure 18 shows the potential d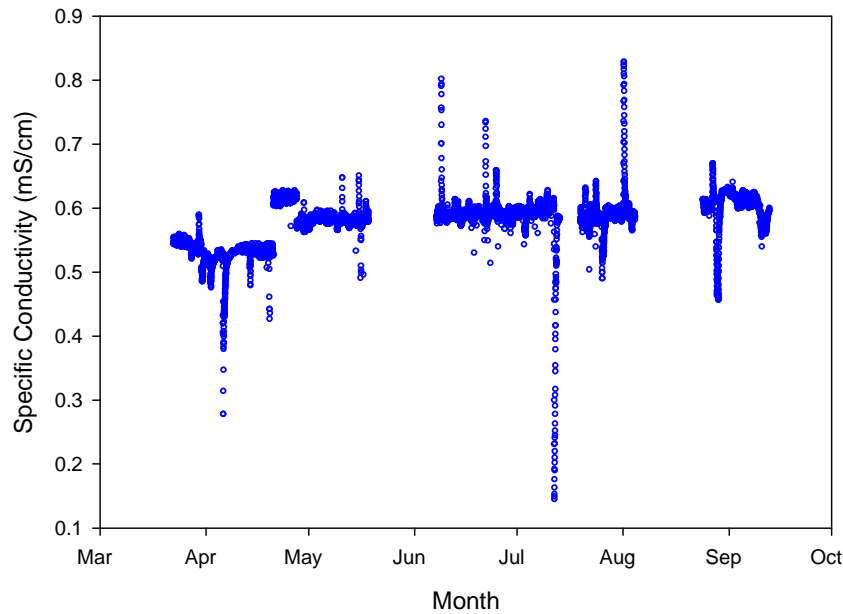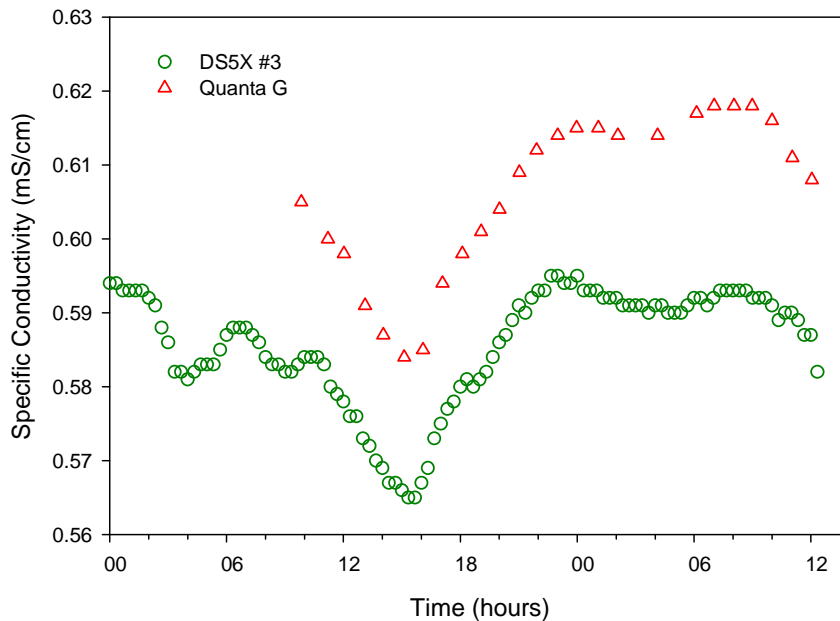ifference in the battery powering the remote data collection platform. This data illustrates the diurnal trend in potential difference in the battery as it is recharged during the daytime, and drawn down during the nighttime. Throughout the entire operation of the water quality node, the potential difference never dropped below twelve volts. This indicates that the powering system on the station is sufficient to meet current power requirements.
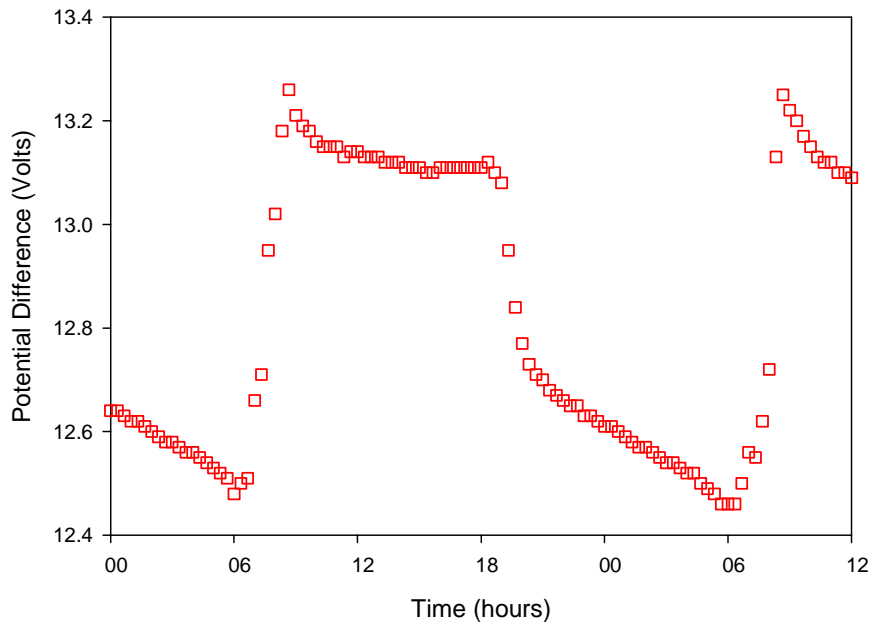
Figure 18. Potential difference in the remote data collection platform battery during the diurnal study.

This system has also been successful in transmitting near real-time water quality measurements to the database in the Environmental Engineering Laboratories. Measurements are downloaded into a database file and are readily accessible for analysis. Due to the remote location of the water quality node, communication with the cellular modem was difficult during poor weather. Although no data was lost during communication errors, data was not always downloaded in a timely manner. This can have implications if this system is used to make timely management decisions. A problem using cellular connections is that locations of individual stations are limited to where cellular coverage is provided by the carrier. Another problem with using cellular connections is that the number of minutes in the voice plan limits the frequency which data can be downloaded. In order to avoid charges for using too many minutes, communication with the water quality node can only occur once every hour. Thus, water quality measurements taken at a twenty minute interval can only be downloaded in a one hour time interval.

The CR1000 has allowed for the collection and transmission of water quality measurements, however, there are some disadvantages with using this datalogger. In order to update the frequency with which water quality measurements are collected, a new monitoring program must be manually programmed and sent to the datalogger. If real-time data is needed to make regulatory decisions on a large scale, the current water quality node would not be adequate. An automated process is needed to continually update dataloggers with the necessary frequency for data collection. This automated process should also be able to identify an event from the incoming data and increase the sampling frequency as needed, such as during a rain event.

Conclusions

Sensors, telemetry hardware, cyberinfrastructure, and models can be used to create real-time measurements and (eventually) predictions of water quality events. Funds from this grant were used to successfully create a water quality node to collect and process data in a real-time manner. This node is able to measure and transmit high temporal resolution data to a database in the Environmental Engineering Laboratories for input to the QUAL2K model. This high temporal resolution data has also shed light on the fundamental processes which are occurring in the watershed, as well as provided warning for violations of federal water quality standards. Experience with the maintenance of the water quality node has provided valuable experience by highlighting potential problems which may inhibit the large scale installation of these environmental observatories. Experiences from this project can be incorporated into future designs to create more robust system which seamlessly integrate real-time water quality data with model to forecast the health of Iowa's water.

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Impact of Swine Manure Application on Phosphorus, NO3-N, Bacteria, and Antibiotics Concentrations in Surface Runoff and Subsurface Drainage Water

Basic Information

Title:	Impact of Swine Manure Application on Phosphorus, NO3-N, Bacteria, and Antibiotics Concentrations in Surface Runoff and Subsurface Drainage Water
Project Number:	2006IA94B
Start Date:	3/1/2006
End Date:	2/29/2008
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Congressional District:	Iowa 3rd
Research Category:	Water Quality
Focus Category:	Nitrate Contamination, Nutrients, Water Quality
Descriptors:	
Principal Investigators:	Ramesh Kanwar, Allah Bakhsh, Matthew J. Helmers, Antonio P. P. Mallarino, John E. Sawyer

Publication

Problem Statement and Research Objectives

The agricultural sector, including animal production, has been identified as a leading source of water quality impairment in the nation's soil and water resources (USEPA, 1995). Over 56,000 km of rivers in the United States has been contaminated and 40% of these are unfit for fishing or swimming (USEPA/USDA, 1998). The non point source pollution originating from agricultural fields has not only contaminated the adjoining streams and lakes but also has left the far reaching effects such as the hypoxic zone in the Gulf of Mexico. Concentration of animals into larger production facilities is a cause for water quality concerns. When manure is misapplied (especially over applied) the quality of nearby waters can be compromised. Bacterial movement to surface and groundwater from manure applications is also of concern, however, and the same studies showed differences in bacterial numbers between treated and untreated plots from swine manure. More information is needed on the movement of N, P, bacteria and antibiotics associated with manure through soils and wetlands, and on the processes involved as the manure liquid moves through the soil water system on different landscapes. The proposed project will also bring very useful information for the state of Iowa to know the contribution of bacteria from liquid swine manure in contaminating surface and groundwater supplies.

Animal production systems, especially swine and poultry, in Iowa have changed significantly in recent years. Iowa is #1 swine producing state in the country. Today's animal production systems are becoming larger, and the public is concerned about the impacts of animal production facilities on surface and groundwater quality. Of particular concern are surface runoff losses of antibiotics, pathogens, nitrogen (N) in the forms of NH_4-N, NO_3-N, and organic-N, and phosphorus (P) as PO_4-P and organic-P, and leaching losses of NO_3-N, PO_4-P, antibiotics and bacteria into subsurface drainage water. Presence of pathogens and antibiotics in water bodies can be major sources of health related concerns. Antibiotics are commonly used as feed additive in animal production. Most of the antibiotics fed to animals are excreted in urine or manure. Once excreted, these antibiotics can enter surface and/or ground waters through non-point source pollution from manure-applied lands.

Determining the water quality effects of applying liquid swine manure to croplands will help us determine whether swine manure is a viable source of plant nutrient without polluting Iowa's water sources from two major water quality deterioration nutrients, N and P. If manure-born bacteria and manure containing antibiotics are moving through the soil profile into subsurface drainage water and to the deeper groundwater, manure application rates and methods may need further adjustments to minimize water quality deterioration from pathogens and other bacteria from swine manure. If the bacteria detected in the water quality tests are not from manure, further research may be needed to understand these processes better. Understanding the processes that are occurring in the soil-water system after the application of manure will help engineers and scientists design better, more efficient, and less polluting landscape treatment systems for managing excessive animal manure from large livestock production facilities. We expect to develop and recommend appropriate manure and nutrient management practices to producers to reduce the water contamination potential from manure applications and enhance the use of swine manure as an alternative to the use of inorganic fertilizers for sustainable agriculture. Not much data is available on the presence of antibiotics in water bodies. This study

will attempt to create a new/additional data set on the presence of nutrients, pathogens and antibiotics in surface and subsurface drainage waters for public use from controlled manure management systems.

This research will be conducted on 36, 0.4 ha (1 acre) experimental plots at the Iowa State University Northeast Research Center near Nashua, Iowa. The overall objective of this project is to investigate the impact of swine manure on water quality and understand the soil microbial and chemical processes occurring within the soil profile of swine manure receiving croplands. The secondary objective is to evaluate different nutrient management systems and implement the best systems on Iowa's landscape so that effluents from watersheds can be discharges to Iowa's water bodies safely. Rather than answering the question "what's happening?" the proposed project will also answer the question "why is it happening in the proposed treatment system?"
Specific objectives of this proposal are:

   i)   to determine the impact of recommended rates of swine manure, based on N and P uptake requirements of crops on water quality,
   ii)   to study long-term effects of over-application of swine manure on nitrogen, phosphorus, and bacteria leaching to shallow groundwater, and
   iii)   to study the effects of spring and fall injection methods of swine manure application on crop yields, and nitrogen, phosphorus, bacteria and antibiotics concentrations in surface runoff and shallow groundwater.

Methods
The field experiments for this proposed study were conducted at the Iowa State University's Northeast Research Center near Nashua, Iowa. The soils at the site include Floyd loam (fine-loamy, mixed, mesic Aquic Hapludolls), Kenyon loam (fine-loamy, mixed, mesic Typic Hapludolls), and Readlyn loam (fine-loamy, mixed, mesic Aquic Hapludolls) (Kanwar et al., 1997). These soils have a seasonally high water table and benefit from a subsurface drainage system. Subsurface drains at this site were installed in 1979 at 1.2-m depth and with 28.5-m spacing. The site has 36 plots, 0.4-ha (58.5 m x 67 m) in size with fully documented tillage and cropping records for the past 25 years. Each plot has an independent drainage sump with flow meter for measuring subsurface drain flows and collecting composite water samples for chemical and bacteria analysis. Drainage water sampling frequency averaged three times a week if subsurface drains were flowing. Subsurface drain water samples were collected and refrigerated until chemical analyses were made. More details on subsurface drainage system and water quality monitoring program at this site are given by Kanwar et al. (1999).

The field experiments conducted at the site can be divided into three phases. The *First phase* of research experiments were conducted from 1990 to 1992 where effects of four tillage systems of chisel plow (CP), moldboard plow (MB), ridge tillage (RT) and no-tillage (NT) systems on subsurface drain water quality were investigated. In addition, during the first phase, three cropping systems of continuous corn, corn-soybean and soybean-corn with N-application rate of 202 kg-N ha^{-1} for continuous corn, and 168 kg-N ha^{-1} for rotated corn were applied in a randomized complete block design and results of the first phase of the study are reported by Kanwar et al. (1997). In the fall of 1992, new experiments were implemented at this site as part of the *second phase* of the study which lasted from 1993 to 1998. In the second phase of this study, tillage systems were reduced to two (chisel and no-till) and nine N-management treatments were studies averaging N-application rates of 110 and 156 kg-N ha^{-1} with single pre-

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plant and late spring soil test based N-application to rotated corn plots, respectively. The average N-application rates from swine manure for continuous corn and rotated corn plots in the second phase were 160 and 136 kg-N ha^{-1}, respectively. The results of the second phase of the study were reported by Kanwar et al. (2005), and Bakhsh et al. (2004, 2005). ***The third phase*** of research experiments at this site began in the fall of 1999 with a six year plan of work to evaluate six different nutrient management systems using swine manure as a primary source of plant nutrients. In the third phase of the study, continuous corn production system was eliminated and more N-management treatments, using swine manure, were implemented with average N-application rate of 168 kg-N ha^{-1} (or 150 lb-N/ac) either fertilized with UAN or liquid swine manure. Table 1 gives experimental treatments established for the six year (2000-2006) study currently being conducted at the Nashua research site.

Table 1. Experimental treatments for the Nashua site for the manure management study.

Treat- ment No.	# of plots per tre- atment	Application timings and source of N	Crop	Tillage	Application method	Application rate, kg/ha	
						N-based rate	P-based rate
1	3	Spring (UAN)	Corn	CP	Incorporated	168	As needed*
	3	-	Soybean	CP	-	-	As needed
2	3	Fall (manure)	Corn	CP	Inject	168	-
	3	-	Soybean	CP	-	-	As needed
3	3	Fall (manure)	Corn	CP	Inject	168(manure+UAN)	-
	3	-	Soybean	CP	-	-	As needed
4	3	Fall (manure)	Corn	CP	Inject	168(manure+UAN)	P-based (corn uptake)**
	3	Fall (Manure)	Soybean	CP	Inject	200 (soybean removed)	P-based (soybean uptake)***
5	3	Fall (UAN)	Corn	CP	LCD***	168	
	3	-	Soybean	CP	-	-	- As needed
6	3	Spring	Corn	NT	Inject	168	
	3	-	Soybean	NT	-	-	- As needed

*As needed: application rate of P from fertilizer based on soil P test to meet P-uptake of corn
** P-based: application rate of P from swine manure on the basis of P removal by corn
*** P-based: application rate of P from swine manure on the basis of P removal by soybean
*** LCD: Localized compaction and doming applicator

In the third phase of this study (2000 to 2006), we are evaluating the effects of six different nutrient management treatments on subsurface water quality. Treatments 1 and 2 compare the effects of N application rates of 168 kg-N ha^{-1} (or 150 lb-N/ac) from liquid UAN fertilizer and swine manure on water quality. Treatments 3 and 4 include manure application rates based on P needs for both corn and soybean (with supplemental application of N from UAN if needed to meet corn N-uptake needs). Treatment 5 include N-application rate of 168 kg-N ha^{-1} (or 150 lb-N/ac) from UAN-fertilizer to corn using Localized Compaction and Doming (LCD) applicator for improved N-uptake and reduced NO_3-N leaching. Treatment 6 include spring application of liquid swine manure at application rates of 168 kg-N ha^{-1} (or 150 lb-N/ac) for no-till system using a new applicator designed for no-tillage conditions. Each treatment is replicated three times in a corn-soybean rotation. Soil and water samples from this study are analyzed for NO_3-N, PO_4-P, and bacteria to determine the impacts of proposed six treatments on soil and water quality. The major outcome of this research will be to determine the impact of manure applications to croplands, based on N and P uptake needs of crops, on water quality. Beginning 2004, selected surface runoff and subsurface drain water samples from major rainwater events in May and June are being analyzed for antibiotics in objective (ii) in addition to NO_3-N, phosphorus (P) as phosphate-phosphorus (PO_4-P) and bacteria. For bacteria, we are analyzing for total E. coli and fecal coliform bacteria.

For measuring antibiotics in surface runoff and subsurface drain water, this study deals with assessing the effect of land application of antibiotic laced swine manure on antibiotic losses in surface runoff and tile drainage water. Two antibiotics studied are chlortetracycline and tylosin. Preliminary data from last year showed very little transport of chlortetracycline and tylosin through Nashua soils into tile drainage water. This year we found only couple of detects of these two antibiotics. Another study at the University of Minnesota has shown that about 0.07% of the applied tylosin was transported as dissolved tylosin in surface runoff. Laboratory studies have shown that these two antibiotics are tightly adsorbed by soils and most of the manure-applied antibiotics are remaining in place where they are applied. One more year of data on antibiotics will give us a better understanding on the transport or leaching of these compounds to surface runoff or groundwater.

Progress Report March 1, 2006 to February 28, 2007
In this ongoing research study at the Northeast Research Farm near Nashua, Iowa, we are evaluating the effects of six different nutrient management treatments on subsurface water quality. Table 1 lists the experimental treatments, nitrogen application rates for each of the six treatments, and total average manure N and P applied. We collected soil and water samples from this study from about April 2006 to November 2006 and were sent to the laboratory for analyzing for NO_3-N, PO_4-P, and bacteria to determine the impacts of the six treatments on soil and water quality. Till today only water samples were analyzed for NO_3-N and the results are reported in Table 3. The water samples are being analyzed for PO_4-P, and bacteria and these analyses will be completed by April/May 2007. Once these samples are analyzed, we would be able to complete our results for a total of six years and draw final conclusions of this study. In addition, we have completed the data on crop yields which is given in Table 4. For simplicity and for better understanding of the local review team, we have reproduced the data in tables 2, 3, and 4 in English units rather than in metric system. Between March 1 2007 and August 1 2007 we plan to analyze all the lab data collected in 2006 and prepare summaries for the six year data set of this study and write the completion report of this study.

Table 1. Experimental treatments at the Nashua water quality research site

Application timings and source of N	Crop	Application rate, lb/ac	
		N based rate	P based rate
System 1. Spring UAN 150 lb N/ac	Corn	150	60
	Soybean	-	44
System 2. Fall manure150 lb N/ac	Corn	150	-
	Soybean	-	-
System 3. Fall P based manure/UAN 150 lb N/ac	Corn	150	60**
	Soybean	-	44
System 4. Fall manure 150 lb N/ac	Corn	150	-
(Plots receive manure both years)	Soybean	200	-
System 5. UAN w/LCD 150 lb N/ac (Side dress)	Corn	150	60
	Soybean	-	44
System 6. Spring manure 150 lb N/ac (No-till)	Corn	150	-
	Soybean	-	-

*As needed: application rate of P from fertilizer based on soil P test needed to meet P-uptake of corn

**P-based: application rate of P from swine manure on the basis of P removal by corn

***LCD: Localized compaction and doming applicator

Tables 3 and 4 summarize experimental data for the years 2000 through 2006. Table 3 gives yearly average NO_3-N concentrations and yearly average total NO_3-N losses with tile water. Treatment 4, where swine manure was applied every year to corn as well as soybeans resulted in the highest six year (2000-2006) average NO_3-N concentrations in tile water of 39.8 mg/l and 36.6 mg/l for corn and soybean plots, respectively indicating an effect of continuous applications of swine manure for six years. Treatment 6, with spring application of manure to corn plots only resulted in the lowest overall average NO_3-N concentrations of 16.2 mg/l and 12.4 mg/l in the tile water from corn and soybean plots, respectively. These results show that NO_3-N leaching to groundwater under manure applications can be managed under proper N application rates and timings. Table 4 shows that treatment # 4, with fall manure application to corn, resulted in highest six year average corn yield of 185 bushels/acre, and average soybean yield of 59 bushels/acre.

Table 2. Effects of experimental treatments on average NO_3-N concentrations and losses with tile drain water.

NO3-N Conc. in tile water, mg/l	2001		2002		2003		2004		2005		2006		2001-2006	
Experimental Treatments	CS	SC	CS	SC	CS	SC	CS	SC	CS	SC	CS	SC	CS	SC
1. Spring UAN 150 lb N/ac	14.2	18.8	11.4	18.8	21.7	18.2	30.2	18.6	19.2	16.4	13.9	12.5	18.4	17.2
2. Fall manure 150 lb N/ac	24.9	15.8	16.9	19.3	26.8	16.1	36.5	20.0	26.1	14.0	19.7	16.2	25.1	16.9
3. Fall P based manure150 lb N/ac	16.9	12.7	8.8	16.1	21.6	16.3	33.1	20.4	24.7	15.8	17.4	15.2	20.4	16.1
4. Fall manure 150 lb N/ac	25.9	31.5	31.8	20.7	29.4	44.6	70.4	50.1	40.8	43.2	40.5	29.6	39.8	36.6
5. UAN w/LCD 150 lb N/ac	12.6	18.4	12.4	20.3	19.4	20.5	19.6	22.1	20.6	15.2	14.6	18.3	16.5	19.1
6. Spring manure 150 lb N/ac	12.4	8.3	9.6	9.3	18.1	11.1	23.1	18.8	21.6	10.8	12.5	15.9	16.2	12.4
NO_3-N Loss in tile water lb/ac	2001		2002		2003		2004		2005		2006		2001-2006	
Experimental Treatments	CS	SC	CS	SC	CS	SC	CS	SC	CS	SC	CS	SC	CS	SC
1. Spring UAN 150 lb N/ac	10.3	17.2	0.4	1.8	11.2	12	27.5	15.8	8.8	8.3	7.5	6.3	10.9	10.2
2. Fall manure 150 lb N/ac	19.4	28.3	6.4	2	15.3	21.3	50.1	19.4	14.0	21.1	21.2	8.9	21.1	16.8
3. Fall P based manure150 lb N/ac	15.4	11.2	0.1	1	14.8	6.4	16.1	28.7	19.4	9.2	10.5	11.0	12.7	11.3
4. Fall manure 150 lb N/ac	21.7	41.6	3.7	1.8	18.4	40.4	64.1	58.8	29.8	30.7	23.8	16.6	26.9	31.6
5. UAN w/LCD 150 lb N/ac	13.6	27.8	3	3.5	11.9	20.1	15.1	14.3	18.3	7.8	13.7	11.7	12.6	14.2
6. Spring manure 150 lb N/ac	20.8	17.2	4.6	6.2	21.3	15.7	17.2	32.3	25.4	14.2	12.3	17.9	16.9	17.3

Table 4. Corn and soybean yields for various N treatments

Grain yields in bu/ac for six years (2000-2006) as a function of the treatments											
	Point Inject 150 # N		Fall Manure 150 # N		Fall Manure P Based		Fall Manure Excessive P		LCD 150 # N		Spring Manure 150 # N	
Corn	**System 1**		**System 2**		**System 3**		**System 4**		**System 5**		**System 6**	
2000	164	bc	171	a	166	ab	153	d	161	c	159	d
2001	163	de	177	ab	173*	bc	181	a	159	e	169	cd
2002	192	ab	194	a	191	ab	194	a	189	b	192	ab
2003	156	bc	163	ab	164	ab	167	a	149	c	157	bc
2004	205	a	196	b	202	ab	203	a	205	a	185	c
2005	192	b	191	b	193	ab	198	a	190	b	193	ab
2006	197	ab	200	a	195	b	197	ab	198	ab	188	c
Avg	**181**	**ab**	**184**	**a**	**184**	**a**	**185**	**a**	**179**	**ab**	**177**	**b**
Soybean												
2000	55	c	58	b	58	b	71	a	58	b	54	c
2001	46	c	51	b	43	e	56	a	46	cd	44	de
2002	54	c	56	b	57	b	59	a	54	c	53	c
2003	31	a	29	c	29	abc	28	c	30	ab	28	c
2004	60	a	59	a	59	ab	56	bc	59	a	56	c
2005	66	c	69	b	65	cd	74	a	64	d	69	b
2006	62	b	62	b	65	a	65	a	62	b	63	ab
Avg	**53**	**b**	**55**	**ab**	**54**	**b**	**59**	**a**	**53**	**b**	**52**	**b**

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Information Transfer Program

While the Iowa Water Center maintains a strong research component, disseminating information to water resource professionals, policy-makers and the public is a priority. With a renewed emphasis on information-transfer and outreach, the Center is developing itself as a clearinghouse for research information.

This year the Iowa Water Center sponsored a team-building poster symposium where three different academic institutions presented 48 posters addressing water-related research in Iowa. The goal of the poster symposium was to provide opportunity for scientists to interact with each other and learn each others research interests for possible future collaborations. The symposium was well attended and participants encouraged the Center to sponsor similar events in the future.

In addition, the Iowa Water Center webpage was redesigned this year. The website includes information about the Iowa Water Center as well as news about Center activities. It also serves as a link to a variety of other state and national water-related events, opportunities, and information. A Resources section has been added to include an Expert Directory, Fact Sheets, and a bibliography of Iowa related water research publications which the Center is in the process of developing.

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	1	8	0	0	9
Masters	2	2	0	0	4
Ph.D.	2	2	0	0	4
Post-Doc.	1	0	0	0	1
Total	6	12	0	0	18

Notable Awards and Achievements

Kanwar, R.S. 2006. Invited by the World Bank and Global Environment Facility to write an environmental policy paper on water quality monitoring of international waters and presented this paper at the World Bank Regional Conference in Moldova, October 3-6, 2006.

Kanwar, R.S. 2006. Appointed Workshop Coordinator by the USDA-FAS for the US-India Workshop on Water Management held in New Delhi, India on September 20-22, 2006.

Kling, C.L. 2006. Conservation Practices in Iowa: Historical Investments, Water Quality, and Gaps. the Iowa Farm Bureau, the Iowa Corn Growers' Association, the Iowa Soybean Association, and the Leopold Center for Sustainable Agriculture, 2006. (An externally funded research which was partly built on the project)

Kling, C.L. 2006. Allocating Nutrient Load Reduction across a Watershed: Implications of Different Principles. Selected paper presented at 2006 Annual Meeting of American Agricultural Economics Association in Long Beach, CA, July 23-26, 2006.

Schnoor, J.L. 2006. Awarding of the 1st, 2nd, and 3rd year of the CLEANER Project Office to UIUC (Barbara Minsker, PI) in which Dr. Schnoor serves as the Co-Director.

Schnoor, J.L. 2006. Awarding of the third year for the WATERS Network Project Office in which Dr. Schnoor is a Co-Director.

Publications from Prior Projects

None