2018 Project Abstract
For the Period Ending June 30, 2023

PROJECT TITLE: Improving Drinking Water for Minnesotans through Pollution Prevention
PROJECT MANAGER: Raymond M. Hozalski, William A. Arnold
AFFILIATION: University of Minnesota
MAILING ADDRESS: 500 Pillsbury Drive SE
CITY/STATE/ZIP: Minneapolis, MN 55455
PHONE: (612) 626-9650
E-MAIL: hozalski@umn.edu
WEBSITE: http://www.cege.umn.edu/directory/faculty-directory/hozalski.html
FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2, Subd. 04f as extended by M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 18

APPROPRIATION AMOUNT: $345,000
AMOUNT SPENT: $337,534
AMOUNT REMAINING: $7,466

Sound bite of Project Outcomes and Results

This project comprehensively studied the spatio-temporal occurrence of N-nitrosodimethylamine (NDMA, a potent carcinogen) precursors in the Crow River watershed as well as treatment approaches for NDMA precursor removal. The project results will aid in evaluation and mitigation of potential risks from NDMA formation during disinfection of drinking water with chloramines.

Overall Project Outcome and Results

NDMA, a contaminant of emerging concern in drinking water supplies, is notorious both for its potent carcinogenicity and toxicity and for its formation in drinking water following the addition of chloramines for disinfection. From a preliminary sampling campaign, the Crow River was found to be a major contributor of NDMA precursors to the Upper Mississippi River, the drinking water supply for the Twin Cities.

To protect the public from potential exposure to NDMA, spatial and temporal variations of NDMA precursors were investigated by collecting water samples from two tributaries and the main stem of the Crow River from 2020 to 2022. A non-targeted analysis approach using mass spectrometry was developed to identify NDMA precursors. Experiments evaluated the effectiveness of pre-oxidation with ozone, free chlorine, or both on removal of NDMA precursors.

NDMA precursor concentrations in raw (untreated) water exhibited seasonal variation, with resulting NDMA concentrations ranging from 7.5 to 109 ng/L. Lime-softening treatment typically increased NDMA formation during disinfection with chloramines by reducing the concentration of natural organic matter (NOM). NOM competes with the precursors for the chloramines. Animal operations and municipal wastewater discharges were identified as potential sources of NDMA precursors. A fluorescence analysis of water samples revealed a correlation between NDMA precursor levels and the protein-like fraction of NOM. Specific NDMA precursors identified in the Crow River include pharmaceutical compounds (e.g., tramadol, metformin, and venlafaxine) and 3-cyclohexyl-1,1-dimethylurea. NDMA formation could be controlled via treatment of water using ozone at doses as low as 1 mg/L or free chlorine.

This project offered valuable insights to water treatment plant operations and policy makers by providing important information about the sources of NDMA precursors into surface waters and how precursor levels vary

with seasons. Additionally, the project findings provide water utilities with potential strategies for mitigating NDMA formation when precursors are present.

Project Results Use and Dissemination

To date, this project has produced two peer-reviewed journal articles (Noe et al. 2023, Li et al. 2023 (accepted)), one journal article is in review, and there one more journal article will be submitted soon. The research has been directly communicated to scientists at the Minnesota Department of Health. The findings of this project were presented at several conferences, including the annual conference of the Minnesota Section of the American Water Works Association, the National Meeting of the American Chemical Society, and the Association of Environmental Engineering and Science Professors conference. Results are also summarized in a master's thesis (Eric Noe) and doctoral dissertation (Jiaqi Li), which are available in the UMN Digital Conservancy.

Environment and Natural Resources Trust Fund (ENRTF)
M.L. 2019 Final Work Plan

Date of Report: August 15, 2022
Final report

Date of Work Plan Approval: June 24, 2019

Project Completion Date: June 30, 2023

PROJECT TITLE: Improving Drinking Water for Minnesotans through Pollution Prevention

Project Manager: Raymond M. Hozalski

Organization: University of Minnesota

Mailing Address: 500 Pillsbury Drive SE

City/State/Zip Code: Minneapolis, MN 55455

Telephone Number: (612) 626-9650

Email Address: hozalski@umn.edu

Web Address: http://www.cege.umn.edu/directory/faculty-directory/hozalski.html

---

Location: Statewide

Total ENRTF Project Budget:	**ENRTF Appropriation:**	**$345,000**
	Amount Spent:	**$337,534**
	Balance:	**$7,466**

M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2, Subd. 04f as extended by M.L. 2022, Chp. 94, Sec. 2, Subd. 19 (c.1) [to June 30, 2023]

Appropriation Language: $345,000 the first year is from the trust fund to the Board of Regents of the University of Minnesota to reduce exposure of Minnesotans to a toxic, cancer-causing chemical by identifying key pollutant precursor sources in the upper Mississippi River watershed and assessing options to reduce the formation of this chemical during drinking water treatment.

M.L. 2022 - Sec. 2. ENVIRONMENT AND NATURAL RESOURCES TRUST FUND; EXTENSIONS. [to June 30, 2023]

PROJECT TITLE: Improving Drinking Water for Minnesotans through Pollution Prevention

I. PROJECT STATEMENT:

The upper Mississippi River, the water supply for ~1 million Minnesota residents, is under constant assault by a variety of chemical and microbiological contaminants. A contaminant of emerging concern in Twin Cities drinking water supplies is the **highly toxic** and **potent cancer-causing chemical N-nitrosodimethylamine (NDMA)**. NDMA itself is not present in the river water but the chemical is formed by the reaction of so-called 'precursors' in the water with chloramines, a form of chlorine added to the water for disinfection. Although NDMA currently is not a regulated contaminant, many states are considering regulations and California has established a notification level of 10 ng/L (10 parts-per-trillion). Initial testing has shown high levels of precursors in Upper Mississippi River water, with the potential to form more than 50 ng/L of NDMA. A preliminary sampling campaign completed with the aid of St. Paul Regional Water Services personnel has identified the Crow River as a major contributor to NDMA precursor levels in the Upper Mississippi, but the sources of these precursors to the Crow River are not known. NDMA precursors are associated with municipal wastewater discharges and include some industrial chemicals and pharmaceutical compounds such as ranitidine, a medicine used to treat acid reflux. Another potential source in the Crow River watershed is animal waste from agricultural operations. To protect drinking water consumers from NDMA and other toxic nitrosamines, it is critical to first identify and then curb the main sources of precursors. **The main impact of the proposed project is to reduce exposure of Minnesotans to the toxic chemical NDMA by recommending pollution prevention strategies to the MN Pollution Control Agency (MPCA) and the MN Department of Health (MDH) and treatment options to water utilities.** This will be done by:

- Assessing seasonal variability in NDMA precursor levels in the Upper Mississippi and Crow Rivers;
- Identifying the major sources of NDMA precursors to the Crow by sampling along the length of the river from the confluence and working upstream along the North and South Forks as well as Buffalo Creek; and
- Investigating options to reduce NDMA formation during water treatment.

This research project will benefit Minnesotans by providing critically important information for policy makers regarding which waste streams to target to reduce inputs of NDMA precursors to surface waters and for water utilities regarding potential treatment strategies for reducing NDMA formation when precursors are present.

II. OVERALL PROJECT STATUS UPDATES:

AMENDMENT REQUEST August 9, 2019

We are requesting that funding for a post-doc in the amount of $3,704.22 (salary + fringe) be shifted from graduate student support to post-doctoral researcher. The post-doctoral researcher is needed to train the graduate student to work on the project. The training concerns collecting water samples along the Crow and Mississippi Rivers and how to perform jar tests that simulate the local water treatment systems, two critical aspects of the project.

Amendment Approved by LCCMR **9/22/2019**

First Update March 1, 2020

A solid-phase extraction liquid chromatography-mass spectrometry (SPE-LC/MS) method to determine NDMA concentration was developed and tested in the laboratory. Six water samples were collected on July 18, 2019 from the North Fork of the Crow River, South Fork of the Crow River, and main stem of the Crow River and analyzed for NDMA precursors before and after lime softening. An investigation of industrial, agricultural and other activities in the Crow River watershed and associated chemical uses was done through online searching.

Second Update September 1, 2020

From July to November, a monthly sampling campaign was conducted in the North Fork of the Crow River, South Fork of the Crow River, the mainstem of the Crow River, and in the Mississippi River both upstream and downstream of the confluence with the Crow. Each campaign consists of a total of twelve sampling locations. Sixty water samples were collected during the 5 sampling events and subsequently processed in the laboratory. Water samples collected in August, September, and October have been analyzed for NDMA precursors before and after lime softening. We indirectly analyze for NDMA precursor levels by dosing the water samples with chloramines to simulate the disinfection practice of the local water treatment plants, incubating for 3 days to allow the NDMA to form, then analyzing for NDMA. Because each sample was analyzed twice (i.e., duplicate analyses), a total of 132 samples have been analyzed for NDMA after the incubation period using the SPE-LC/MS method developed previously. Analysis of the samples collected in July and November is ongoing.

Third Update March 1, 2021

From December 2020 to February 2021, the sampling campaign described above continued. Because of ice cover at some locations, we were unable to collect water at all 12 locations. In total, 24 water samples were collected and analyzed for NDMA precursors before and after lime softening during the three sampling events. Duplicate water samples were incubated for three days after dosing monochloramine to simulate the disinfection process in a water treatment plant. In this step, NDMA precursors in the water samples react with the chloramines and are transformed into NDMA. NDMA concentration was analyzed using the SPE-LC/MS method developed previously. From July 2020 to Feb 2021, a total of 264 samples were analyzed. During each sampling event, water samples before and after lime softening as well as chloraminated samples were stored in a freezer for future non-targeted analysis work in an attempt to identify NDMA precursors. We are working with the mass spectrometry facility in the UMN chemistry department on non-target analysis. Pre-oxidation of NDMA precursors with ozone or an ozone/advanced oxidation process prior to chloramination might destroy NDMA precursors and thus serve as an effective strategy to limit NDMA formation. Pre-oxidation experiments via ozone are currently being designed and will begin in March 2021.

AMENDMENT REQUEST August 24, 2021

We are requesting a 12-month no-cost extension to June 30, 2023. The reason for the request is delays resulting from the COVID-19 pandemic. Everything has proven to be more challenging since the pandemic began, from obtaining research supplies, to assembling crews for sampling, to accessing core facilities for our analyses, etc. The additional time would allow us to complete the study as close to as originally planned as possible.

Amendment approved June 30, 2022 (see below)

Fourth Update September 1, 2021

The monthly sampling campaign in the Crow river and its tributaries continued from March 2021 to August 2021. Besides the twelve locations described in the previous updates, we also collected samples from the headwaters of the North Fork and South Fork of the Crow river to further investigate spatial variation in NDMA precursor levels in the watershed. A total of 89 samples were collected and analyzed for NDMA precursors before and after lime softening. NDMA precursors were processed by simulated disinfection processes described previously. NDMA in the samples were then concentrated by solid phase extraction (SPE) using activated carbon cartridges, then analyzed via UHPLC-MS/MS. In total, 392 samples were analyzed by the SPE-LC-MS/MS method. The method development for non-targeted NDMA precursor identification is ongoing. Currently, we are working on developing a sample preparation method for extracting a variety of NDMA precursors from water samples with a suitable concentration factor that will permit detection on our analytical instrumentation. Finally, we have initiated experiments to determine if ozone, a common water treatment chemical, can be used to destroy NDMA precursor via chemical oxidation. Specifically, initial bench-scale experiments are being performed to measure ozone decay rates in raw and lime softened water samples obtained from the Saint Paul Regional Water Services water treatment facility. The ozone decay rate varies with

the water temperature and ozone dose applied. The ozone decay rate is important because the longer the ozone stay around in the water, the more effectively NDMA precursors can be degraded.

Fifth Update March 1, 2022
The method for non-targeted NDMA precursor identification has been further developed. The recovery efficiency of the mix-bed cartridges for NDMA precursor extraction was determined using samples collected over time at selected locations. Beginning in January 2022, water samples were collected from the Upstream Crow River sampling location every Monday for six consecutive weeks to identify NDMA precursors in the Crow River. The collected samples will be processed for both NDMA determination by the SPE-LC-MS/MS method described before and precursor identification by the SPE-LC-QTOF-MS method we developed. In addition, bench-scale experiments were performed to investigate the effect of chemical oxidation of NDMA precursors with ozone or an ozone/advanced oxidation process prior to chloramination to destroy NDMA precursors and thus limit NDMA formation. Experiments were conducted on water samples collected during the summer of 2021 from the Saint Paul Regional Water Services (SPRWS) water treatment facility. In total, 63 chemical oxidation experiments were conducted, exploring a range of treatment conditions by varying oxidant dose and water temperature. Compared to NDMA concentrations of samples prior to chemical oxidation treatment (8.5 to 26.3 ng/L), all pre-oxidation treatments reduced NDMA formation to low levels (< 4 ng/L). Pre-oxidation experiments are currently being repeated with water samples collected from SPRWS during the winter of 2022.

Update as of June 30, 2022

Project extended to June 30, 2023 by LCCMR 6/30/22 as a result of M.L. 2022, Chp.94, Sec. 2, Subd. 19, legislative extension criteria being met.

Sixth Update as of September 1, 2022
The samples collected from Jan to March in 2022 were processed for NDMA formation potential using the SPE-LC-MS/MS method and the mass spectrometry data has been analyzed. To continuously monitor seasonal dynamics and year-to-year difference of NDMA precursors in Crow river region, a sampling campaign was conducted in May 2022. The NDMA precursor level of these sample could indicate NDMA precursor concentrations at the spring season in 2022. The data processing and analysis work about non-targeted identification of NDMA precursors in winter Crow River samples is ongoing. Moreover, the bench-scale oxidation experiments described in the last update were repeated using winter samples collected from Saint Paul Regional Water Services (SPRWS) water treatment facility to investigate the seasonal effect on the precursor removal efficiency by various oxidants. In addition, river samples collected from Crow River were treated with ozone to explore the effectiveness of ozone in reducing NDMA precursors specific in Crow River.

Seventh Update as of March 1, 2023
Sampling campaigns were conducted in the fall of 2022 and winter of 2023 to continue to assess the seasonal variability and annual differences of NDMA precursors in the Crow river region. For fall 2022, filtered raw and lime-softened samples were prepared following our previous protocol, and the NDMA formation using the uniform formation conditions test was determined. The samples collected in winter 2023 are being processed. As for the non-targeted analysis of NDMA precursors in the Crow River, a list of candidates was discovered, and several were identified and confirmed by MS/MS analysis. More identification work via MS/MS analysis to confirm the identities of the compounds is ongoing. This work will help identify which chemicals and human activities may be responsible for discharging NDMA precursors into the watershed. Moreover, the effectiveness of different oxidation practices on a known NDMA precursor, ranitidine, was examined, including 1 mg/L ozone, 2 mg/L ozone, 5 mg/L ozone, 5 mg/L free chlorine, and 2mg/L ozone + 5 mg/L free chlorine.

AMENDMENT REQUEST March 1, 2023
We are requesting that funds be shifted from the Analytical Services and Travel allocations to Laboratory Supplies and Personnel. Analytical services would decrease from $20,000 total to $15,010 and Travel from

$15,000 to $5,900. Laboratory Supplies would increase from $33,000 to $35,325 and Personnel would increase from $272,000 to $283,764. These changes are being requested to reflect differences between budgeted costs and actual expenditures.

Amendment Approved by LCCMR 5/16/2023

AMENDMENT REQUEST as of June 30, 2023
We request four budget adjustments to reflect final accounting of the project:

- Increase personnel by 11,764 from 272,000 to 283,764
- Increase laboratory supplies by 2,538 from 33,000 to 35,538
- Decrease travel by 9,523 from 15,000 to 5,477
- Decrease publication by 4,779 from 5,000 to 221

Amendment Approved by LCCMR 1/15/2024

Final Report as of June 30, 2023 (to be submitted before August 15, 2023)

NDMA, a contaminant of emerging concern in drinking water supplies, is notorious both for its potent carcinogenicity and toxicity and for its formation in drinking water following the addition of chloramines for disinfection. From a preliminary sampling campaign, the Crow River was found to be a major contributor of NDMA precursors to the Upper Mississippi River, the drinking water supply for the Twin Cities.

To protect the public from potential exposure to NDMA, spatial and temporal variations of NDMA precursors were investigated by collecting water samples from two tributaries and the main stem of the Crow River from 2020 to 2022. A non-targeted analysis approach using mass spectrometry was developed to identify NDMA precursors. Experiments evaluated the effectiveness of pre-oxidation with ozone, free chlorine, or both on removal of NDMA precursors.

NDMA precursor concentrations in raw (untreated) water exhibited seasonal variation, with resulting NDMA concentrations ranging from 7.5 to 109 ng/L. Lime-softening treatment typically increased NDMA formation during disinfection with chloramines by reducing the concentration of natural organic matter (NOM). NOM competes with the precursors for the chloramines. Animal operations and municipal wastewater discharges were identified as potential sources of NDMA precursors. A fluorescence analysis of water samples revealed a correlation between NDMA precursor levels and the protein-like fraction of NOM. Specific NDMA precursors identified in the Crow River include pharmaceutical compounds (e.g., tramadol, metformin, and venlafaxine) and 3-cyclohexyl-1,1-dimethylurea. NDMA formation could be controlled via treatment of water using ozone at doses as low as 1 mg/L or free chlorine.

This project offered valuable insights to water treatment plant operations and policy makers by providing important information about the sources of NDMA precursors into surface waters and how precursor levels vary with seasons. Additionally, the project findings provide water utilities with potential strategies for mitigating NDMA formation when precursors are present.

III. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Assess seasonal variability in the quantities of NDMA precursors in the Crow River and in the Mississippi River both upstream and downstream of the Crow.

Description: Known NDMA precursors include nitrogen-containing organic compounds with specific structures called secondary and tertiary amines. Such precursors are often associated with municipal wastewater discharges, but the main sources to the Crow River are not known and may include human waste, animal waste,

or both. Additional work is needed to assess seasonal variability in precursor levels in the Crow River and the Upper Mississippi River. We will collect water from 3 sampling locations on at least 4 sampling dates from the summer of 2019 through summer of 2020. As duplicate samples will be collected from each location on every sampling date, this results in a total of at least 24 water samples. Water samples will be collected from the middle of the river just below the surface. All water samples will be lime softened using a jar test apparatus to mimic the treatment that occurs in the two Twin Cities treatment facilities. We have discovered through previous work that lime softening is critical for 'activating' the precursors. After lime softening, the samples will be analyzed for NDMA precursor levels (formation potential test) as well as for organic amine concentrations. Finally, the samples will be analyzed for selected known NDMA precursor chemicals in an attempt to identify the dominant precursors and possible sources (e.g., human waste, animal waste, industrial activities).

ACTIVITY 1 ENRTF Budget: $ 112,724

Outcome	Completion Date
1. *Collect water samples from the Crow River and Mississippi River upstream and downstream of the Crow at least 4 times over a one-year period.*	August 31, 2020
2. *Analyze the river water samples for NDMA precursor levels using the uniform formation conditions (UFC) test.*	September 31, 2020
3. *Analyze the river water samples for total organic amine levels and specific known precursor compounds (e.g., ranitidine, selected antibiotics).*	December 31, 2020

First Update March 1, 2020

A SPE-LC/MS method to determine NDMA concentration was developed and verified. The limit of quantification (LOD) is 5 ng/L with at least 70% recovery efficiency for NDMA in spiked river water samples after method optimization. These LOD and recovery values are deemed sufficient for our study. Duplicate water samples were collected from three locations on July 18, 2019. Each of these six water samples was split with approximately half of the sample analyzed for NDMA precursors directly and the other half subjected to lime softening prior to precursor analysis to simulate how water is treated in Minneapolis, St. Paul, and St. Cloud. NDMA precursor testing was done using the uniform formation conditions (UFC) method. The UFC test is a standard test that was developed to simulate typical or average disinfection conditions used at water treatment plants. Use of such standardized test conditions, rather than conditions specific to a given water treatment facility, allows us to compare results for all facilities and sites in our investigation and to compare our results with those from other studies done elsewhere. The average NDMA concentrations in North fork of the Crow River, South fork of the Crow River, and the Crow River samples were 22.6, 17.4, and 22.7 ng/L, respectively. After lime softening, NDMA concentrations increased substantially to averages of 101, 57.2, and 60.8 ng/L, respectively. There were substantial differences between the duplicate softened samples suggesting that we need to refine our lime softening methods in terms of lime dosing and pH control.

Second Update September 1, 2020

Monthly sampling campaigns from July to November were conducted at twelve locations. The samples were processed and analyzed using the SPE-LC/MS method. Each sample was split into two parts: half of the sample was analyzed for NDMA formation directly and the other half was first lime softened and then analyzed for NDMA formation. Both lime-softened and raw subsamples were analyzed in duplicate. For the months of August, September, and October, the average NDMA precursor concentrations in the North Fork of the Crow river were 29.58, 18.47 and 20.33 ng/L, respectively. In the South Fork of the Crow river, the concentrations were consistently lower at 16.48, 15.67, and 16.57 ng/L, respectively, and in the mainstem of the Crow river, concentrations were 26.97, 28.44 and 15.44 ng/L, respectively. After lime softening treatment, NDMA concentrations increased by an average of 18.31%, 17.34% and 64.19% for samples collected in August, September, and October, respectively. Although there currently are no Federal or State of Minnesota regulations concerning NDMA, these NDMA concentrations are of concern because they all exceed the State of California's 10 ng/L notification level for NDMA in drinking water. No major or obvious seasonal trends are

apparent from the limited data we have available thus far. A full year or more of data will be needed to identify any seasonality in NDMA precursor concentrations.

Third Update March 1, 2021

Monthly sampling campaigns were carried out from December 2020 to February 2021 at twelve sites. Because the river surface was completely frozen at several sites, we only collected seven samples in January and five samples in February. The monthly raw and lime softened water samples were analyzed for NDMA precursor concentration using the SPE-LC/MS method. The average NDMA precursor concentrations in the Crow River watershed including the mainstem and its two tributaries were 121, 22, 17.4, 17, 32.5, 40.2, 61.8, 109 ng/L from July 2020 to Feb 2021. The NDMA precursor concentration plummeted from July to August in 2020. After this, there was a gradual increase in NDMA precursor concentration from August 2020 to February 2021. After lime-softening treatment, the average NDMA precursor concentrations in the samples collected from the Crow River watershed were 57.2, 26.1, 18.6, 26.3, 64, 53.4, 812, 330 ng/L from July 2020 to Feb 2021. For most of the water samples, lime softening treatment "activated" the NDMA precursors and substantially increased NDMA formation. For example, in January and February the NDMA precursors concentration after lime softening were extremely high. These NDMA concentrations are of concern because they all exceeded, and in some cases far exceeded the State of California's 10 ng/L notification level for NDMA in drinking water. It is important to note, however, that the chloramination step was always done at room temperature (~ 20 °C) with preformed chloramines according to UFC test conditions. It is likely that the NDMA formation in the local water systems would be much lower for two main reasons, one is the much lower water temperatures (3-5 °C) during chloramination at the water treatment plants and another is the use of a short free chlorine contact time prior to adding ammonia to form chloramines. Colder water is expected to result in slower NDMA formation rates (i.e., slower kinetics) and free chlorine can destroy precursors in a similar, albeit much less effective, manner as ozone. For the March sampling event, we will evaluate the effect of temperature by comparing NDMA formation from chloramination at room temperature with chloramination at ~ 5°C.

Fourth Update September 1, 2021

Monthly sampling campaigns were carried out from March 2021 to Aug 2021 in the Crow river. Raw and lime softened samples were chloraminated via Uniform Formation Condition test, which enables NDMA precursors to be transformed into NDMA. From March 2021 to July 2021, there was a gradual increase in NDMA precursor concentration. For the five months, the average NDMA precursor concentrations in the Crow River including the mainstem and its two tributaries were 14.2, 20.6, 17.0, 7.1, and 15.8 ng/L, respectively. We found above-average precursor concentrations in the headwater of North fork Crow river, which were up to 40, 35, 12.5, and 21 ng/L from April to July 2021. Compared to the high NDMA precursors (> 100 ng/L) found in the Crow River in July 2020, concentrations of precursors were much lower in July this year. We propose that the decrease in precursor concentrations may have resulted from this the exceedingly low discharge, which was about seven times lower than the discharge last year based on data from the Minnesota Department of Natural Resources Cooperative Gauge system. After lime softening, the average NDMA precursor concentrations in the water samples collected from the Crow River were 22.4, 34.2, 25.0, 9.7, 14.8 ng/L from March 2021 to July 2021. Except samples collected in July 2021, lime softening treatment generally "activated" the NDMA precursors and increased NDMA formation, but not as substantially as lime softening did for samples collected in Jan and Feb 2021.

Fifth Update March 1, 2022

Sampling campaigns were conducted bimonthly from August 2021 to Dec 2021 to monitor NDMA precursor concentrations throughout the Crow river watershed. Raw water and lime-softened samples were chloraminated via the uniform formation condition test and the resulting NDMA concentrations were analyzed by the SPE LC-MS/MS method. In August, October, and December, the average NDMA precursor concentrations in the Crow River watershed were 27.82 ng/L, 28.77 ng/L, and 15.74 ng/L, respectively. With lime softening treatment, the average NDMA precursor concentrations were 28.90 ng/L, 8.34 ng/L, 18.43 ng/L, respectively. Thus, lime softening treatment did not significantly affect NDMA formation for these three sampling dates. The

average NDMA precursor concentration in the raw samples collected in Dec 2020 was 40.2 ng/L, which is much higher than for December 2021. Samples collected in Jan and Feb 2022 have been processed and will be analyzed in March and compared with results from last year.

Update as of June 30, 2022
Project extended to June 30, 2023 by LCCMR 6/30/22 as a result of M.L. 2022, Chp.94, Sec. 2, Subd. 19, legislative extension criteria being met.

Sixth Update as of September 1, 2022
We have sampled throughout the Crow River watershed once per month for about 1.5 years to assess how NDMA precursor concentrations change over space and time. To more intensively assess temporal variability, river water samples were collected weekly from the Upstream Crow River Site from late Jan to March for six consecutive weeks. The river water samples were processed according to the procedure mentioned in the previous update to prepare the raw water and lime-softened water for subsequent NDMA formation potential testing. The NDMA formation potential was measured using the uniform formation conditions (UFC) protocol with the resulting NDMA analyzed using the SPE-LC/MS/MS method we developed. The NDMA concentrations in raw water samples collected in the first, second, fourth, fifth and sixth weeks were 14.3, 16.9, 42.4, 54.0, and 35.7 ng/L respectively. The NDMA precursor concentration tripled from the first week to the fourth week and then declined, suggesting that variability in NDMA loading to the Crow River over the short term can be important. NDMA concentrations in lime softened samples were 19.6, 13.3, 36.6, 55.5, and 31.26 ng/L from the first week to the sixth week (week 3 excluded). Unlike last year when a dramatic increase in NDMA precursors was observed after lime softening for winter samples, NDMA precursor concentrations were essentially unaffected by lime softening during this sampling campaign.

In addition to this intensive temporal investigation, another sampling campaign was conducted throughout the Crow River watershed in May 2022. A total of 10 sampling sites were selected. Relatively low concentrations of NDMA precursors (i.e., average concentration of 9.85 ng/L) were observed in raw water samples collected from three sites in the South Fork of the Crow River. After lime softening treatment, NDMA precursor concentrations increased slightly to an average of 15.98 ng/L. The average NDMA precursor concentration in samples collected from the North Fork of the Crow River was 27.79 ng/L before lime softening and 51.51 ng/L after lime softening. For samples collected in the main stem of the Crow River, average precursor concentrations of 19.71 and 27.35 ng/L were detected before and after lime-softening treatment, respectively. Thus, lime softening increased NDMA formation potential more significantly for samples collected from the North Fork of the Crow River and the main stem of the Crow River.

Seventh Update as of March 1, 2023
The river water samples collected in the Fall of 2022 were processed to prepare the filtered raw water and lime-softened samples. The NDMA formation potential was measured via the uniform formation conditions (UFC) protocol. The NDMA concentration was determined using the SPE-LC/MS/MS method we developed previously. The mean NDMA formation was 17 ± 6.1 ng/L in raw water samples and 34.6 ± 11 ng/L in lime-softened water samples. Among all locations, a water sample collected in the headwaters of the North Fork of the Crow River had the highest NDMA formation (26 ± 1.2 ng/L) among raw water samples, followed by the main stem of the Crow River (22 ± 0.2 ng/L). The sample collected from the Mississippi River had the lowest NDMA formation among raw samples (6.4 ng/L). The percent increase in NDMA formation after lime softening treatment ranged from 0.41% to 238%, with a mean of 114.7%. In summary, the headwaters of the North Fork of the Crow River and the main stem of the Crow River are abundant in NDMA precursors and lime softening typically increases NDMA formation.

Final Report as of June 30, 2023 (to be submitted before August 15, 2023)

The Crow River, a tributary of the Mississippi River in Minnesota, was sampled approximately monthly from 2020 to 2022. Samples were collected from twelve locations along the North Fork of the Crow River, the South

Fork of the Crow River, and the main stem of Crow River, and occasionally from three locations in the headwaters regions of the North and South Forks. Each of these water samples was split with approximately half of the sample analyzed for NDMA precursors directly and the other half subjected to lime softening prior to precursor analysis to explore the effect of softening treatment on NDMA formation. It is important to note that the concentration of NDMA precursors was assessed using uniform formation conditions (UFC) testing, an experimental protocol that mimics average chloramination conditions used by U.S. water utilities (room temperature, dose of 5 mg Cl_2/L of preformed monochloramine, 3-day incubation time). Important water quality parameters including dissolved organic carbon (DOC), dissolved nitrogen (DN), ammonia, nitrate, and nitrite were also quantified from July 2020 to June 2021.

Average NDMA precursor concentrations in the Crow River determined via UFC testing varied over time from 7.5 ± 4.4 ng/L in June 2021 to 109.4 ± 14.0 ng/L in Jan 2021. Lime-softening treatment, where lime was added together with alum and ferric chloride, typically resulted in an increase in NDMA formation using the UFC protocol, which was attributed to the removal of natural organic matter as indicated by the DOC concentration. $NDMA_{UFC}$ concentrations positively correlated with DN when excluding the spring snowmelt period and negatively correlated with DOC concentration. Concentrated animal feeding operations (CAFOs) and municipal wastewater discharges are likely the major sources of NDMA precursors in the Crow River based on a combined analysis of the spatial variations of $NDMA_{UFC}$ and the geographical distribution of anthropogenic activities in the Crow River watershed. Cropland appeared to be a less important contributor of NDMA precursors.

ACTIVITY 2: Identify NDMA precursor sources by sampling along the length of the Crow River during the season where precursor levels are highest as determined from Activity 1.

Description: Initially, a background investigation will be performed to identify likely NDMA precursor chemicals used in the Crow River watersheds. Internet searches will be performed to identify industrial, agricultural, and other pertinent activities in the Crow River region and the types of chemicals used in these activities. We will also contact representatives at the MPCA, MDH, and USGS who would have knowledge on chemical usage and occurrence in the Crow and Mississippi Rivers. We will collect samples at roughly ten-mile intervals working upstream along the Crow, North and South Forks of the Crow, and Buffalo Creek to identify where precursor levels increase significantly. Subsequent trips will involve sampling with increasing spatial resolution in river reaches with large precursor increases to hone in on specific sources. Sampling and testing of specific waste streams will be used to confirm precursor sources. We will take approximately 10 trips and collect 10 water samples per trip for a total of approximately 100 samples. Water samples will be collected from the middle of the river just below the surface. All water samples will be lime softened using a jar test apparatus to mimic the treatment that occurs in the two Twin Cities treatment facilities. After lime softening, the samples will be analyzed for NDMA precursor levels (formation potential test) as well as for organic amine concentrations. Finally, the samples will be analyzed for selected known NDMA precursor chemicals in an attempt to identify the dominant precursors and possible sources (e.g., human waste, animal waste, industrial activities).

ACTIVITY 2 ENRTF Budget: $ 96,541

Outcome	Completion Date
1. *Collect river water and wastewater samples along the Crow River, North and South Forks of the Crow, and Buffalo Creek during the season with highest precursor levels.*	August 31, 2021
2. *Analyze the river and wastewater samples for NDMA precursor levels using UFC test.*	September 31, 2021
3. *Analyze the samples for total organic amine levels and specific known precursors (e.g., ranitidine, selected antibiotics).*	December 31, 2021

First Update March 1, 2020

An investigation of the distribution of animal feedlots, agricultural operations, and wastewater treatment plants in the Crow River watershed was done using internet searching. Antibiotics used for animal care and pesticides

used for agriculture were summarized and analyzed for their potential to form NDMA. A combined analysis on distribution of feedlots (cattle, turkey, chicken, cow, swine) and preliminary results concerning NDMA precursors in the Crow River indicates that some antibiotics used by the turkey and swine industries may be potential NDMA precursors. The herbicide diuron and other phenylurea compounds may serve as NDMA precursors because they potentially can release dimethylamine during lime softening treatment through a mechanism known as base-catalyzed hydrolysis. Dimethylamine is a well-known NDMA precursor compound. The results of NDMA precursor testing to date, including those from this study and from preliminary work in May and July of 2018, have shown that the North Fork of the Crow is consistently greater (30-50%) than the South Fork and that the Crow River is consistently greater than the Mississippi River just upstream of the confluence with the Crow. Additional sampling campaigns along the lengths of the North and South Forks of the Crow River will be performed this summer to determine "hot spots" where NDMA precursor concentrations increase suddenly suggesting nearby sources.

Second Update September 1, 2020

NDMA formation analysis of samples collected at different locations and times shows a generally high NDMA precursor concentration throughout the Crow River, indicating the sources of NDMA precursors are dispersed throughout the watershed and not concentrated in a few "hot spots". Even samples collected from the uppermost parts of the North and South Forks of the Crow river exhibited high NDMA precursor concentrations and the concentrations did not change much along the river. Sources of precursors could include antibiotics, pesticides, or other anthropogenic compounds used in the Crow River watershed. These compounds could be transported into the Crow River via surface runoff or via shallow groundwater. Lab experiments are underway to explore NDMA formation from selected antibiotics used in the turkey and swine industries, which are prevalent throughout the Crow River watershed. Antibiotics such as chlortetracycline may be susceptible to base-catalyzed hydrolysis, a chemical reaction that occurs during the high pH conditions of lime softening. Based-catalyzed hydrolysis of chlortetracycline can release dimethylamine, a known NDMA precursor. Therefore, water samples containing a selected antibiotic will be analyzed for NDMA formation before and after base-catalyzed hydrolysis to assess the risks posed by specific chemicals used in the watershed.

Third Update March 1, 2021

For each monthly sampling event, NDMA precursor concentrations in the samples collected throughout the Crow River Watershed and in the Mississippi River were typically high for all locations, which suggests that the sources of NDMA precursors are dispersed throughout the watershed and not concentrated in a few "hot spots". In an attempt to identify the important NDMA precursors in the Crow River, non-targeted analysis will be performed on selected raw water samples, lime softened samples, and disinfected (i.e., chloraminated) samples. Currently, we are developing a method for the non-targeted analysis which will use a new state-of-the-art QTOF mass spectrometer. We selected a few water samples with high NDMA precursor concentrations collected in October 2020 for initial testing. Samples were concentrated by a factor of ~15 using a vacufuge device and filtered in preparation for analysis by the QTOF instrument. The results are pending.

Fourth Update September 1, 2021

Sub-samples from the North Fork of the Crow River, mainstem of the Crow River and upstream Mississippi River were concentrated by a factor of 15 using a vacufuge device, and then analyzed by High-Performance Liquid Chromatography coupled with Quadrupole Time-of-Flight Mass Spectrometry (HPLC-QTOF-MS). The preliminary data showed that ranitidine, a known NDMA precursor, was found in the lime softened samples collected from the mainstem and the North Fork of the Crow River but was not found in the corresponding raw water for these locations. This may imply that lime softening could release bound ranitidine, making the compound more available for transformation to NDMA upon disinfection. We are also currently trying to improve the sample preparation method for a higher concentration factor and better precursor extraction efficiency. Mix-bed cartridges packed with five different sorbents targeted at extracting various micropollutants, and PPL cartridges that are efficient in extracting natural organic matter will be used to extract NDMA precursors and concentrate the samples by a factor of approximately 500. The solid phase extraction effluent will be collected, and its NDMA

precursor concentration will be measured to evaluate the extraction efficiency. Specifically, if the NDMA precursor concentrations in the effluent is much lower than what is absorbed by the cartridges, this would indicate a satisfactory extraction efficiency.

Fifth Update March 1, 2022

Water samples were collected from three sites in the Crow and Mississippi Rivers: Downstream North Fork of the Crow (DNF), Upstream Crow (UC), and Upstream Mississippi (UM) in August, October and December. The mix-bed cartridges containing five different sorbents were used to extract potential NDMA precursors from the water samples. Both raw and lime softened samples were loaded onto the mixed-bed cartridges. To assess the precursor extraction efficiency, the SPE effluents of each sample from the mix-bed cartridges were collected in vacuum flasks. The NDMA formation of the original water samples prior to cartridge loading (SPE influents) and the SPE effluents were determined. The NDMA formation for the original water sample represents the total amount of precursors and the NDMA formation of the SPE effluent represents the precursors not retained by the cartridge. Therefore, the precursor extraction efficiency or recovery is computed as:

SPE extraction efficiency = (SPE influent – SPE effluent)/SPE influent x 100%.

For the samples collected from the Crow River (DNF and UC), the precursor extraction efficiencies on average were 81%, 46%, and 76% in August, October and December, respectively. For the Upstream Mississippi River samples, the extraction efficiencies were 40%, 11%, and 22% in August, October, and December, respectively. The mix-bed cartridge was more effective at recovering precursors from the Crow River samples (DNF and UC samples) than from the Upstream Mississippi River samples. This may be due to the different water matrices and the overall higher concentration of precursors in the Crow River. More importantly, the recoveries for the samples collected from the Crow River (46% ~ 81%) are sufficient for enriching precursors for non-target analysis. Therefore, solid phase extraction via mixed-bed cartridges coupled with LC-QTOF-MS analysis will be applied to identify NDMA precursors in the Crow River. Beginning in early January 2022, samples were collected from the Upstream Crow sampling site for six consecutive weeks to identify the precursors in the Crow river. Every week, the raw and lime softened samples were loaded onto mix-bed cartridge for non-target analysis to identify likely NDMA precursors. The same water samples before and after softening were also disinfected with chloramines and loaded onto mixed-bed cartridges. These post-disinfection extracts will allow us to examine changes in the chemical structures that occurred due to reaction with chloramines.

Update as of June 30, 2022
Project extended to June 30, 2023 by LCCMR 6/30/22 as a result of M.L. 2022, Chp.94, Sec. 2, Subd. 19, legislative extension criteria being met.

Sixth Update as of September 1, 2022
In winter 2021, water samples were collected from the Upstream Crow River Site for six consecutive weeks to prepare four kinds of samples for non-targeted analysis to attempt to identify NDMA precursors. Raw water samples and lime-softened samples were prepared using the procedure described in the previous update. Half of the raw water samples (2 L) and lime-softened samples were then chloraminated under uniform formation conditions, during which NDMA precursors should have reacted with chloramines to form NDMA. The four kinds of water samples including raw samples, lime-softened samples, raw-chloraminated samples, and lime-softened-chloraminated samples were processed and analyzed using the SPE-LC-QTOF-MS method developed previously. The LC-QTOF-MS method enables us to identify unknown precursor chemicals that may be contributing to NDMA formation. After detecting all compound features in the four types of samples, potential NDMA precursor compounds in raw and lime-softened samples were identified by the sample comparison method. Specifically, chemical features in raw samples were compared to those in the corresponding raw post-chloraminated samples in which the NDMA precursors should have reacted with chloramines. Thus, features that are abundant in raw samples but decrease or disappear in the corresponding post-chloraminated sample

were selected as potential NDMA precursors. The same approach was used to identify possible precursor compounds in the lime-softened samples. Currently, analysis and interpretation of the data from the non-targeted analysis work is ongoing.

Seventh Update as of March 1, 2023

As described previously, water samples were collected from the main stem of Crow River for six consecutive weeks in the winter of 2022-23. Each water sample was lime softened and/or chloraminated, resulting in four sample types: untreated or raw samples (R), lime-softened samples (LS), raw-chloraminated samples (R-UFC), and lime-softened-chloraminated (LS-UFC) samples. Thus, there were 24 samples (6 weeks, four sample types each week) in total, analyzed by the LC-QTOF-MS protocol. A total of 5500 unique features were detected in the raw, lime-softened, raw-UFC, and lime-softened-UFC samples. Features that were detected in at least 8 samples among the 24 samples were regarded as High Detection Frequency (HDF) features. Among all features, there were approximately 900 HDF features in total, among which 108 HDF features were substantially removed (at least 50% decrease) during the UFC test, indicating these compounds could be NDMA precursors.

A list of 35 candidate compounds was compiled, and we have confirmed the identities of ten of these compounds, including the anti-depressant desvenlafaxine and opioid analgesic o-desmethyltramadol (both are known NDMA precursors), and other pharmaceuticals, such as, gabapentin, metoprolol acid, alpha-hydroxy metoprolol, atenolol, mefenorex, 3-hydroxymorphinan, and the illicit substance cocaine. Ongoing work is focused on identifying the remaining candidate compounds. This will help us to assess if specific compounds and activities in the watershed are likely contributors to NDMA formation during water treatment.

Final Report as of June 30, 2023 (to be submitted before August 15, 2023)

Water samples were collected from the main stem of the Crow River for six consecutive weeks, at a time and location where high levels of NDMA precursors were expected. A multi-sorbent solid phase extraction (SPE) cartridge, packed with five different sorbents, was used to extract the potential NDMA precursors from water samples before and after chloramination. The basic idea was that nitrogen-containing compounds that were degraded during disinfection with chloramines were potential precursors. We then used liquid chromatography quadrupole time of flight mass spectrometry (LC-QTOF-MS) to analyze the chemicals extracted from the water samples. Features with a high detection frequency that showed significant degradation during chloramination were selected as candidates for identification via our a nontargeted analysis workflow that we developed.

NDMA precursors identified in the Crow River water samples included: tramadol, venlafaxine, metformin, 3-cyclohexyl-1,1-dimethylurea, amine oxide surfactants (myristamine oxide and lauramine oxide). In addition, precursors for other nitrosamines were also identified, including lidocaine (a commonly used local anesthetic), DEET (the most common active ingredient in insect repellents), tributylamine (industrial chemical), cocaine (narcotic), and trans-Nicotine-1-oxide (a derivative of nicotine). Some anthropogenic chemicals, that are not known N-nitrosamine precursors but were detected frequently in the Crow River were identified as well, including lamotrigine, carbamazepine, hydroxyatrazine, mefenorex, bupriopion, ciclopirox, fexofenadine, and irbesartan. The majority of the identified NDMA precursors can be attributed to municipal wastewater effluents, which emphasizes the significance of municipal wastewater or other human waste discharges (e.g., septic systems) as an important source of NDMA precursors to the Crow River.

ACTIVITY 3: Investigate the effects of chlorine and ozone concentration and exposure time on destruction of precursors.

Description: There is some evidence that pre-oxidation of the precursors with free chlorine or ozone prior to addition of chloramines reduces the subsequent formation of NDMA. We will investigate the effects of chlorine and ozone concentration and exposure time on destruction of precursors. Mississippi River water samples will be lime softened as describe above and then treated with either free chlorine or ozone over a range of typical concentrations and contact times and then subjected to UFC testing to determine NDMA precursor levels. The

results will be compared to those without free chlorine or ozone treatment to assess overall treatment effectiveness.

ACTIVITY 3 ENRTF Budget: $ 98,685

Outcome	Completion Date
1. *Collect Mississippi River water samples and pretreat using chlorine or ozone.*	April 30, 2022
2. *Analyze the river water samples before and after treatment for NDMA precursor levels using the UFC test.*	September 31, 2022

First Update March 1, 2020
No progress on this activity.

Second Update September 1, 2020
No progress on this activity.

Third Update March 1, 2021
Experiments to test the effects of pre-oxidation with ozone on NDMA precursor levels are currently being set up in the laboratory. Raw and lime softened water samples from the Minneapolis and/or Saint Paul water treatment facilities will be subjected to varying doses of ozone, incubated until the ozone dissipates, and then chloraminated (UFC conditions) and subsequently analyzed for NDMA. Ozonation of the water samples will occur in 1-liter amber glass bottles. A laboratory-scale ozone generator will be used to create an ozone stock solution by bubbling ozone gas into chilled ultrapure water. Initially, we will assess how quickly the ozone decays or reacts in the water samples. An aliquot of the ozone stock solution will be added to the water sample and incubated for 10-15 minutes with periodic sampling to measure the aqueous ozone concentration using the indigo method. After these initial ozone decay experiments, the water samples will be dosed with ozone and incubated until the ozone dissipates and then tested for NDMA precursor concentration. Results will be compared with those from the samples before ozone was applied.

Fourth Update September 1, 2021
Initial bench-scale (i.e., batch) experiments to quantify ozone decay rates in water samples are currently being conducted. Different ozone doses (1, 2, and 5 mg/L) and water temperatures (5 and 20 degrees Celsius) are being investigated. Ozone coupled with hydrogen peroxide to promote hydroxyl radical formation will also be explored. Treatment with ozone and hydrogen peroxide is considered an advanced oxidation process (AOP), with hydroxyl radicals serving as potent oxidizers that can potentially enhance destruction of NDMA precursors and limit subsequent NDMA formation upon disinfection with chloramines. Hydroxyl radicals will be measured indirectly in parallel with the dissolved ozone measurements by introducing a probe compound called para-chlorobenzoic acid (pCBA). The concentration of probe compound over time is quantified via high-pressure liquid chromatography (HPLC). The decrease of the probe compound in relation to the measured ozone at a given time is used to calculate the hydroxyl radical concentration. After these initial ozone decay (and hydroxyl radical formation) experiments, we will ozone water samples and test NDMA formation and compare the results with those from samples that had not been subjected to ozone treatment.

Fifth Update March 1, 2022
Chemical oxidation experiments were conducted on water samples collected on July 19, 2021 from the Saint Paul Regional Water Services (SPRWS) treatment facility. These water samples consisted of raw water (i.e., before any treatment), lime softened water, and lime softened and recarbonated water (i.e., re-carb water). The oxidation treatments included ozone (1, 2, and 5 mg/L), ozone (2 mg/L) coupled with hydrogen peroxide (1 mg/L) which is termed an advanced oxidation process (AOP), and free chlorine (4.24 mg/L as Cl_2). The free chlorine treatment mimics the free chlorine exposure used at the full-scale SPRWS treatment facility.

Experiments were performed at two temperatures (5 and 20 ˚C) to represent the range of water temperatures experienced at the facility. The AOP process is termed “advanced oxidation” because the process promotes the formation of highly reactive hydroxyl radicals that are able to rapidly degrade a wide variety or organic chemicals found in water. The formation of these hydroxyl radicals was tracked using a probe compound. Water samples before and after chemical oxidation were then tested for NDMA formation. Without oxidation, raw, lime softened, and re-carb water formed NDMA concentrations of 8.5, 20.7, and 26.3 ng/L, respectively. Chemical oxidation with ozone or AOP decreased NDMA concentrations to similar levels (ranging from 1.9 to 4 ng/L) regardless of treatment conditions. Free chlorine treatment of re-carb water at both 5 and 20˚C was also effective, reducing NDMA concentrations from 26.3 ng/L to 2.1 and 1.4 ng/L, respectively. Analysis of hydroxyl radical formation indicated that more hydroxyl radicals were produced with increasing ozone doses for all water types. Finally, pre-oxidation experiments will be repeated on sample water collected from the Saint Paul water treatment facility on January 21, 2022 to investigate the impact of seasonal changes in water quality.

Update as of June 30, 2022
Project extended to June 30, 2023 by LCCMR 6/30/22 as a result of M.L. 2022, Chp.94, Sec. 2, Subd. 19, legislative extension criteria being met.

Sixth Update as of September 1, 2022
Batch oxidation experiments were performed over a range of oxidant concentrations and temperatures of 5 and 20°C using winter samples collected from the Saint Paul Regional Water Services (SPRWS) water treatment facility. Specifically, water samples were collected from three stages along the treatment train: raw influent, directly after lime-softening, and re-carbonated water post lime softening. Pre-oxidation was explored with three common oxidants over a range of dosage: ozone (1, 2, and 5 mg/L), free chlorine (4.24 mg/L as Cl2), and a combination of 2 mg/L ozone and 1 mg/L hydrogen peroxide. The treatment in which both ozone and hydrogen peroxide are used is termed an advanced oxidation process or AOP. NDMA precursor concentrations were determined before and after pre-oxidation using the uniform formation conditions test. NDMA precursor concentrations in the raw, lime softened, and re-carbonated samples collected in winter were 10.1 ng/L, 17 ng/L and 14 ng/L, respectively. All oxidation treatments applied to raw, lime-softened, and re-carbonated water effectively decreased the $NDMA_{UFC}$ concentrations to 1.1 ng/L to 4.6 ng/L, which were all below the Minnesota Department of Health’s (MDH) guidance value of 5 ng/L and the State of California’s notification level of 10 ng/L. Furthermore, the effectiveness of pre-oxidation at destroying NDMA precursors was also investigated using a water sample collected from the Crow River. $NDMA_{UFC}$ concentrations in raw and lime-softened Crow River samples were 33.7 ng/L and 36.5 ng/L, respectively. An ozone dose of 2 mg/L at 20°C was reasonably effective at destroying NDMA precursors in both raw and lime-softened Crow River water to 6.6 ng/L and 10.1 ng/L, respectively.

Seventh Update as of March 1, 2023
Ranitidine, a known NDMA precursor, was spiked into a sample of lime softened and recarbonated water (i.e., collected from the Saint Paul Regional Water Services water treatment facility in winter) to study the effectiveness of different pre-oxidation practices at destroying NDMA precursors when present at high concentrations. The water samples spiked with 1200 ng/L ranitidine and then pre-oxidized by dosing ozone (1 to 5 mg/L), 5 mg/L free chlorine, or 2 mg/L ozone followed by 5 mg/L free chlorine. Prior to oxidation, the ranitidine spike increased the average NDMA concentration in recarbonated water from 14 ng/L to 358 ± 3.1 ng/L. An ozone dose of 1 mg/L effectively reduced the mean NDMA formation to 21.3 ± 8.3 ng/L. Increasing ozone doses of 2 mg/L and 5 mg/L further decrease NDMA formation to 8.2 ± 1.5 ng/L and 4.2 ± 0.4 ng/L. Free chlorine alone decreased NDMA formation to 10.7 ± 3.8 ng/L. A combination of 2 mg/L ozone and 5 mg/L of free chlorine resulted in the lowest NDMA formation (2.4 ± 0.6 ng/L). All pre-oxidation treatments effectively destroyed ranitidine and any other NDMA precursors present in the water and decreased NDMA formation by 94% to 99%.

Final Report as of June 30, 2023 (to be submitted before August 15, 2023)

Batch experiments were performed to investigate the effectiveness of pre-oxidation at destroying NDMA precursors. Samples included: 1) raw and lime softened Crow River water, and 2) raw, lime-softened, and re-carbonated water samples collected from the St. Paul Regional Water Services (SPRWS) treatment plant during the winter. SPRWS uses the Mississippi River as its main water supply. Selected water samples also were spiked with a model NDMA precursor, ranitidine, before further testing. The effect of ozone dose (1, 2, and 5 mg/L) and water temperature (5 and 20 degrees Celsius) were investigated. Free chlorine (4.24 mg/L as Cl_2) and ozone coupled with hydrogen peroxide to promote hydroxyl radical formation were also tested.

NDMA precursor concentrations in the raw, lime softened, and re-carbonated SPRWS water samples collected in winter were 10.1 ng/L, 17 ng/L and 14 ng/L, respectively. All oxidation treatments applied to raw, lime-softened, and re-carbonated water effectively decreased the $NDMA_{UFC}$ concentrations to 1.1 ng/L to 4.6 ng/L, which were all below the Minnesota Department of Health's (MDH) guidance value of 5 ng/L and the State of California's notification level of 10 ng/L. Furthermore, the effectiveness of pre-oxidation at destroying NDMA precursors was also investigated using a water sample collected from the Crow River. $NDMA_{UFC}$ concentrations in raw and lime-softened Crow River samples were 33.7 ng/L and 36.5 ng/L, respectively. An ozone dose of 2 mg/L at 20°C was reasonably effective at destroying NDMA precursors in both raw and lime-softened Crow River water to 6.6 ng/L and 10.1 ng/L, respectively.

The ranitidine spike increased the average NDMA concentration in recarbonated water from 14 ng/L to 358 ± 3.1 ng/L. An ozone dose of 1 mg/L effectively reduced the mean NDMA formation to 21.3 ± 8.3 ng/L. Increasing ozone doses of 2 mg/L and 5 mg/L further decrease NDMA formation to 8.2 ± 1.5 ng/L and 4.2 ± 0.4 ng/L. Free chlorine alone decreased NDMA formation to 10.7 ± 3.8 ng/L. A combination of 2 mg/L ozone and 5 mg/L of free chlorine resulted in the lowest NDMA formation (2.4 ± 0.6 ng/L). All pre-oxidation treatments effectively destroyed ranitidine and any other NDMA precursors present in the water and decreased NDMA formation by 94% to 99%. Overall, these results suggest that ozone at moderate doses of about 2 mg/L is very effective at destroying NDMA precursors. Furthermore, free chlorine at typical doses and contact times used for disinfection is also effective.

IV. DISSEMINATION:

Description: Findings will be disseminated directly to the two participating utilities as a written report and an in-person presentation. Findings will also be disseminated and archived via reports to LCCMR, peer-reviewed journal publications (open access), and presentations at conferences. We will also, if and when appropriate, disseminate results via press releases to the media and via the MDH website.

The Minnesota Environment and Natural Resources Trust Fund (ENRTF) will be acknowledged through use of the trust fund logo or attribution language on project print and electronic media, publications, signage, and other communications per the ENRTF Acknowledgement Guidelines.

Dissemination Budget: $ 37,050

First Update March 1, 2020
No progress on this activity.

Second Update September 1, 2021
No progress on this activity.

Third Update March 1, 2021
No progress on this activity.

Fourth Update September 1, 2022

An update on our research will be presented at the annual conference of the Minnesota Chapter of the American Water Works Association in Duluth in mid-September.

Fifth Update March 1, 2022
An update on our research was presented by graduate students Jiaqi Li and Eric Noe at the annual conference of the Minnesota Chapter of the American Water Works Association in Duluth in mid-September.

Update as of June 30, 2022:
Project extended to June 30, 2023 by LCCMR 6/30/22 as a result of M.L. 2022, Chp.94, Sec. 2, Subd. 19, legislative extension criteria being met.

Sixth Update as of September 1, 2022:
An update on our research was presented by graduate students Jiaqi Li and Eric Noe at the annual conference of the American Chemical Society in San Diego in mid-March.

Seventh Update as of March 1, 2023:
A journal article on the testing of pre-oxidation for NDMA precursor destruction was submitted to the peer-reviewed scientific journal *Environmental Engineering Science* in February 2022.

Final Report as of June 30, 2023 (to be submitted before August 15, 2023):
The findings of the project were presented at the annual conference of the Minnesota Chapter of the American Water Works Association in 2021, at the annual conference of the American Chemical Society in 2022, and at the annual conference of the AEESP in 2023.

A journal article concerning the pre-oxidation for NDMA precursor destruction was published in the journal *Environmental Engineering Science*. A journal article concerning the spatial and seasonal variations of NDMA precursors in the Crow River watershed and the effect of lime softening on NDMA formation was accepted by the journal *Environmental Science & Technology.*

V. ADDITIONAL BUDGET INFORMATION:

A. Personnel and Capital Expenditures

Explanation of Capital Expenditures Greater Than $5,000: N/A

Explanation of Use of Classified Staff: N/A

Total Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation:

Enter Total Estimated Personnel Hours for entire duration of project: 5460	Divide total personnel hours by 2,080 hours in 1 yr = TOTAL FTE: 2.63

Total Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation:

Enter Total Estimated Contract Personnel Hours for entire duration of project: N/A	Divide total contract hours by 2,080 hours in 1 yr = TOTAL FTE: N/A

VI. PROJECT PARTNERS:

Name	Title	Affiliation	Role
William Arnold	Professor	University of Minnesota	Co-Investigator

A. Partners outside of project manager's organization receiving ENRTF funding: N/A

Name	Title	Affiliation	Role
-None -			

B. Partners outside of project manager's organization NOT receiving ENRTF funding

Name	Title	Affiliation	Role
George Kraynick	Water Quality Manager	MWTDS	Sampling, sharing data
Jim Bode	Water Production Manager	SPRWS	Sampling in Crow River

VII. LONG-TERM- IMPLEMENTATION AND FUNDING:

The main goals of the proposed research are to identify significant sources of NDMA precursors to the Upper Mississippi River and to develop pollution prevention strategies for reducing precursor inputs. For example, if it is found that a certain class of antibiotics given to farm animals is an important precursor, then one possible **strategy** would be to suggest a ban on that class of antibiotics for animal use. The **project impact** will be improved drinking water quality and protection of the health and safety of Minnesotans, particularly those in the Twin Cities and surrounding suburbs served by the Minneapolis and St. Paul water utilities.

C. Funding History: N/A

VIII. REPORTING REQUIREMENTS:

- Project status update reports will be submitted March 1 and September 1 each year of the project
- A final report and associated products will be submitted between June 30 and August 15, 2023

IX. SEE ADDITIONAL WORK PLAN COMPONENTS:

A. Budget Spreadsheet
B. Visual Component or Map

Attachment B

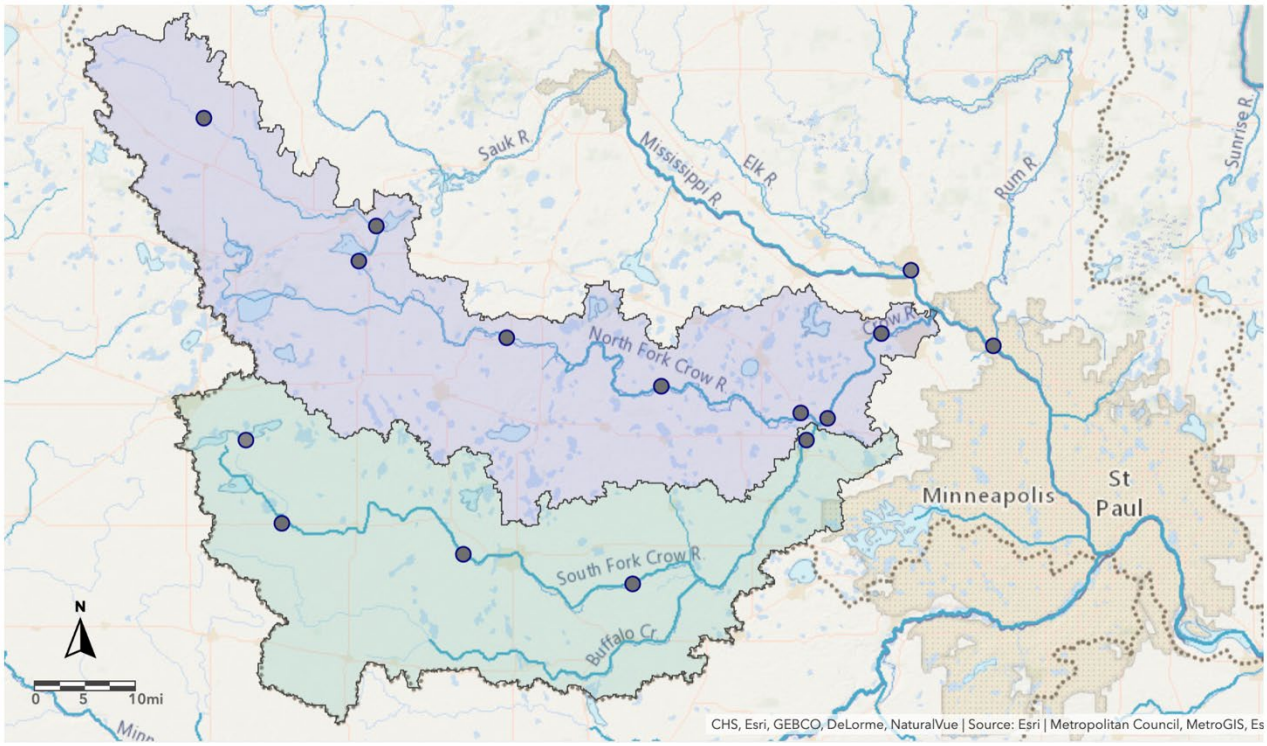


Figure 1. A map of sampling locations (black points) along the two tributaries (North Fork of the Crow River, South Fork of the Crow River), main stem of the Crow River, and upstream and downstream the confluent point of Crow river and Mississippi River. The watersheds for the North Fork Crow River and main stem of the Crow River are colored in purple while the watershed for South Fork of the Crow River is colored in green. The map is reproduced with permission from Esri. Map image is the intellectual property of Esri and is used herein under license. Copyright © Esri and its licensors.

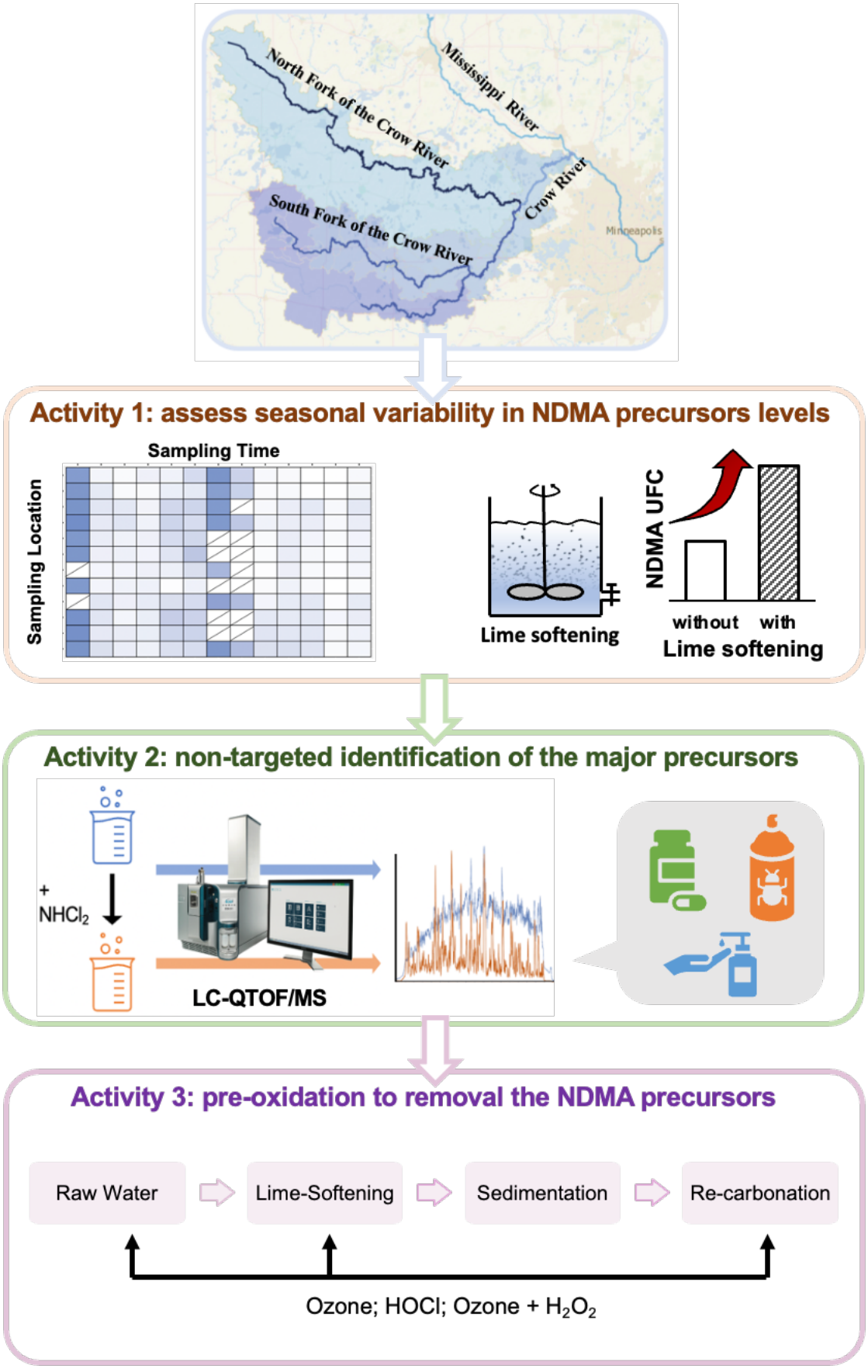


Figure 2. Visualization of this project: Improving Drinking Water for Minnesotans through Pollution Prevention

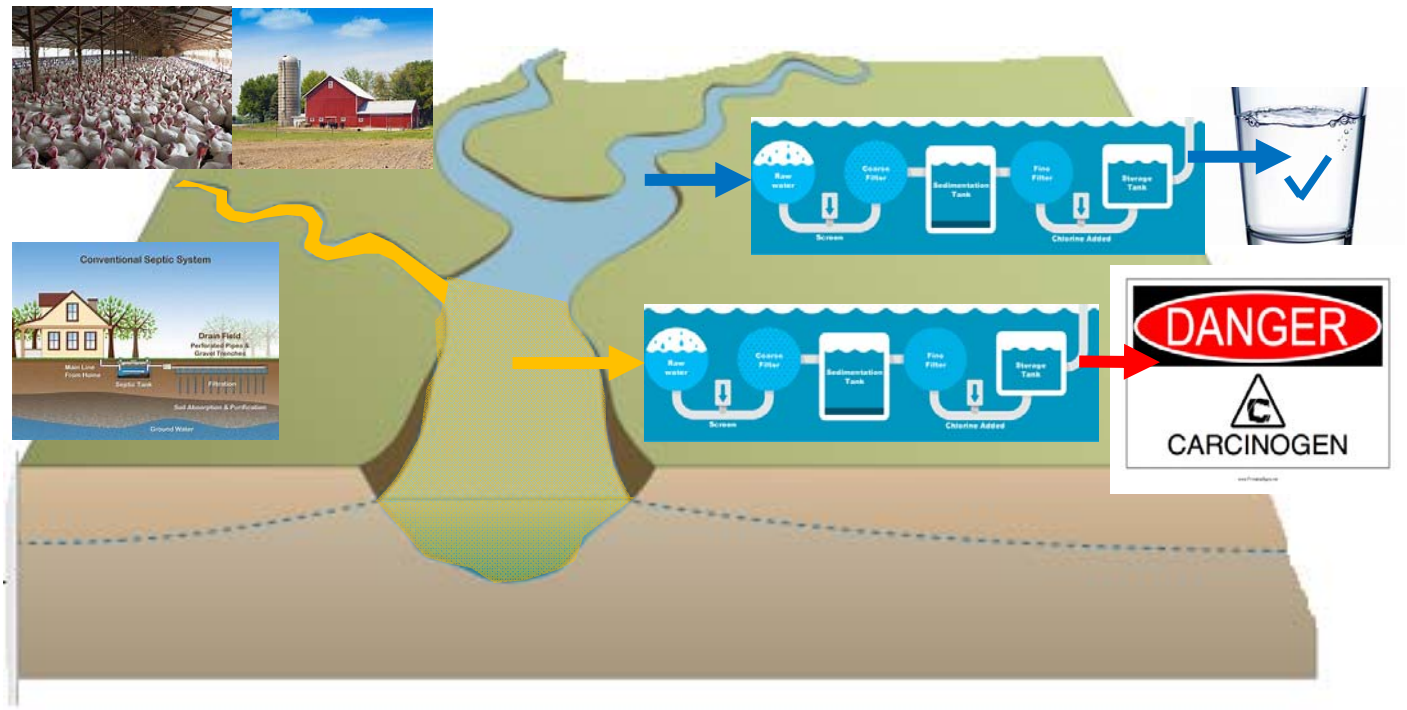
Attachment A:
Environment and Natural Resources Trust Fund
M.L. 2019 Budget Spreadsheet- FINAL
Legal Citation:
Project Manager: Raymond M. Hozalski
Project Title: Improving Drinking Water for Minnesotans through Pollution Prevention
Organization: University of Minnesota
Project Budget: $345,000
Project Length and Completion Date: 3 years, June 30, 2023
Today's Date: 8/15/23

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Revised Budget 8/15/23	Amount Spent	Balance
BUDGET ITEM			
Personnel (Wages and Benefits)	$ 283,764	$ 283,764	$ -
Raymond Hozalski, Project Manager (75% salary, 25% fringe benefits). 8% FTE for years 1 - 3. Overall project coordination, lead Task 1 and Task 3 studies, co-lead Task 4. $57,644			
William Arnold, Co-Project Manager (75% salary, 25% fringe benefits). 6% FTE for years 1 - 3. Lead Task 2 studies, co-lead Task 4. $50,979			
Graduate student Research assistant 1, Perform environment fate studies for Task 1, perform computations in Task 3 (55% salary, 45% fringe benefits) 50% FTE for years 1-3. $139,876			
Undergraduate researchers. Assist with laboratory experiments. 16 hrs per week during the calendar year for years 1 and 2 only. (100% salary). $19,797			
Post-doctoral researcher, Train graduate student to perform river sampling and experiments (80% salary, 20% fringe benefits) 100% FTE for 3 weeks in year 1. $3,704			
Equipment/Tools/Supplies			
Laboratory Supplies (chemical and isotopically labelled standards, chemical reagents, necessary glassware, solvents, consumable supplies, laboratory notebooks, software licenses, instrument	$ 35,538	$ 35,538	$ -
Analytical time for quantification of NDMA in water samples.	$ 10,000	$ 7,300	$ 2,700
Analytical time for identification of precursor chemicals using mass spectrometry.	$ 10,000	$ 5,455	$ 4,545
Travel expenses in Minnesota			
University vehicle rental and hotel stays to collect water samples. Presenation of results at local conferences. Reimbursement will be according to University of Minnesota guidlines.	$ 5,477	$ 5,477	$ -
Other (Open access fees for peer-reviewed journal papers)			
Publication charges to make to make published journal articles (2-3) immediately available via open access to maximize data availability and dissemination.	$ 221	$ -	$ 221
COLUMN TOTAL	$ 345,000	$ 337,534	$ 7,466

OTHER FUNDS CONTRIBUTED TO THE PROJECT	Status (secured or pending)	Budget	Spent	Balance
Non-State:		$ -	$ -	
State: U of MN (In-kind; Indirect costs not charged to project)	Secured	$ 167,067	$ 114,247	$ 52,820
In kind: Because the project is overhead free, laboratory space, electricty, and other facilities/adminstrative costs (54% of direct costs excluding permanent equipment and graduate student tuition benefits) are provided in-kind.		$ -	$ -	$ -

PAST AND CURRENT ENRTF APPROPRIATIONS	Amount legally obligated but not yet spent	Budget	Spent	Balance
Current appropriation:		$ -	$ -	$ -
Past appropriations:		$ -	$ -	$ -

The carcinogen NDMA is formed when chlorine disinfectants react with precursors in human and/or animal waste discharges.



Outcomes:

1. Quantify carcinogen-forming precursor levels.
2. Identify times and places where maximum precursor inputs occur.
3. Optimize drinking water disinfection to minimize carcinogen formation.
4. Protect human health via pollution prevention.