



## WATER RESOURCES RESEARCH GRANT PROPOSAL

**Title:** Occurrence and Formation of Nitrosamines in Drinking Water Distribution Systems

**Focus Categories:** Water Quality, Toxic Substances, Water Supply, and Nitrate Contamination

**Keywords:** Water Chemistry, Water Quality, Water Treatment, Disinfection, and Chlorination

**Duration:** July 1, 2000 to June 30, 2001

**Federal Funds Requested:** Total \$23,902 Direct \$23,902 Indirect \$0

**Non-Federal Matching Funds Pledged:** Total \$59,083 Direct \$38,625  
Indirect \$20,458

### **Principal Investigator:**

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**Congressional District:** 1<sup>st</sup>

### **Statement of Critical Regional or State Water Problem**

Many nitrosamines, especially N-dimethylnitrosamine (NDMA), are potent carcinogens. A number of past studies and current observations support the hypothesis that nitrosamine (NA) occurrence and formation could be an especially important problem in some Midwestern drinking water distribution systems. While the exact conditions and mechanisms leading to nitrosamine formation in the environment are not well understood, it is known that they are formed by reaction of nitrite with certain organic nitrogen containing (amine) compounds. These precursors to NA formation are ubiquitous in many Midwest drinking water sources or can actually be formed in distribution systems thus possibly making these supplies susceptible to nitrosamine formation. Additionally, recent observation in California suggests that NDMA formation may be related to disinfection practices, suggesting that at least this nitrosamine should also be considered a "new" disinfection by-product. Little is known, however, about the occurrence and formation potential of nitrosamines in Midwestern drinking water distribution systems. To date, no systematic studies have considered the potential for nitrosamine formation in distribution systems and possible spatial and temporal variability. Research is needed to characterize the extent of this potential problem, and to

determine how water quality, treatment, and distribution system characteristics influence it. The relationship of nitrosamine formation and occurrence to disinfection and in-system processes, especially those influenced by the pipe-water interface, needs to be ascertained. A fundamental understanding of the reaction kinetics and mechanisms would also be of great benefit in developing strategies to minimize exposure to these contaminants.

### **Statement of Results or Benefits**

This research will determine the extent of formation and occurrence of NDMA and other selected nitrosamines in several distribution systems. Information will be obtained relating the occurrence and extent of formation to water quality, treatment, and characteristics of the distribution. Laboratory studies will provide fundamental information on the formation mechanisms and kinetics and will identify controlling variables.

The anticipated benefits from this study are several fold. First, quantification of NDMA and other nitrosamine occurrence and formation in drinking water is important because this class of chemicals includes many potent carcinogens. Information obtained in both field and laboratory studies can be used in assessing the potential extent of the problem by considering the factors making supplies susceptible to nitrosamine formation. The results of this study will additionally be used to propose strategies to minimize exposure such as modifying treatment, changing source water, or perhaps instituting waste and agricultural management practices that minimize inorganic and organic nitrogen discharges to potential drinking water supplies.

### **Nature, Scope, and Objectives:**

Nitrosamines are members of a class of compounds, many of which are carcinogenic, mutagenic, and teratogenic (Loeppky et.al., 1994; O'Neill et.al., 1984). The nitrosamine, N-Nitrosodimethylamine is particularly harmful and has been most commonly found in the environment. NDMA is identified as a carcinogen under California's Health and Safety Code Section 25249.5, et seq., the Safe Drinking Water and Toxic Enforcement Act of 1986 ("Proposition 65"). It is classified as a probable human carcinogen by the US Environmental Protection Agency (US EPA). Because NDMA historically has not been considered a common drinking water contaminant, it has no state or federal drinking water maximum contaminant level. Risk assessments from the 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. The State of California has recently established a 0.002 ppb "action level" on NDMA in drinking water. The Canadian action level is currently 0.009 ppb.

Nitrosamines are likely to be found where both secondary or tertiary amines and nitrate or nitrite occur. They have therefore been found in many food products as well as soils, wastewater, and drinking water. Until recently it was generally believed that the occurrence in drinking water was primarily due to contamination in the source water.

Recent observations in California and Canada (California, 1999; Graham et. al. 1995) indicate that nitrosamines can be formed in drinking water as a consequence of treatment. Perhaps most interesting and counter intuitive, are the observations that NDMA formation appears to be somehow related to disinfection practices as evidenced by increases in concentration after chlorination of both wastewater and drinking water in California. This suggests that NDMA could also possibly be considered a "new" disinfection by-product (DBP).

While seemingly counter intuitive, consideration of the chemical literature provides several possible explanations supporting this. Perhaps the most important is that chlorinated organic amines (organic N-chloramines) are more reactive in the formation of nitrosamines than are unchlorinated ones (Myers and Wright, 1948; Nakajima, et al., 1984). Furthermore this phenomena may also be particularly important when chloramination is practiced because of the tendency of organic N-chloramines to form in the presence of monochloramine, the primary species produced in chloraminated waters (Wolfe and Olson, 1984).

These observations as well as consideration of the available literature suggest that nitrosamine formation in some distribution systems may pose a significant health problem. This is because of the relatively large abundance of potential precursor material in the raw water, and because of several processes that may occur in distribution systems. Nitrite for example, can be found in drinking for several reasons. The common occurrence of nitrate in Midwest water from fertilizers can lead to the formation of nitrite by biological denitrification from microorganisms in the distribution system. Nitrite may also be formed by reaction with zero valent suggesting that cast iron found in unlined cast iron pipes (Cheng, 1997) may cause some nitrite formation. Another very important source is from the biological nitrification of ammonia, which is also frequently found in both surface and groundwater. Nitrification of ammonia can result in nitrite formation and is also recognized as a particular problem associated with the use of chloramines whose formation requires ammonia addition. Breakpoint chlorination, practiced to remove ammonia in order to provide a free chlorine residual, also produces some nitrate as one oxidation product (Jafvert and Valentine, 1992).

Decomposition or discharge of organic materials of plant and animal origin from agricultural, municipal, and industrial discharges, and pesticide preparations are primary sources of environmental organic nitrogen containing compounds and amines entering a distribution system. Biofilms and microbes inside pipe deposits in distribution systems, however, could also be an important source of organic nitrogen precursors. These deposits are known to be rich in organic matter and reduced iron (Tuovinen et.al. 1980). The presence of microbes in or on these deposits could also biologically catalyze the formation of nitrosamines (Kunisaki and Hayashi, 1979).

Lastly, it should be pointed out competing processes causing nitrosamine losses may complicate any assessment of their significance. A number of drinking water processes, such as reaction with ferrous iron (Dix et al. 1991) and biodegradation (Kaplan and Arthur, 1985) may occur. The concentration of nitrosamine actually observed in the field

would then be related to the relative rates of both formation and loss pathways. Perturbations of the whole system could tip the balance one way or the other. For example, an additional strategy to nitrosamine minimization and occurrence would be to somehow increase loss rates.

An approach to evaluating the occurrence and formation of nitrosamines is needed which recognizes our current understanding of the chemical, biological, and physical factors, and especially processes that may occur in distribution systems. Field studies as well as carefully controlled laboratory studies are needed to further define the mechanisms and variables involved especially the role of disinfection and the pipe-water interface. Based on the ascertained research needs, the following specific objectives with rationale were formulated for this research study:

1. Assess the spatial and temporal occurrence of selected nitrosamines, especially NDMA, in several Midwestern water distribution systems.
2. Conduct laboratory based studies to examine mechanisms and fundamental factors influencing nitrosamine formation especially disinfection, and the presence of pipe and attached deposit material.
3. Relate field and laboratory findings to provide an assessment of the significance of nitrosamine occurrence and formation as a consequent of source water quality, water treatment and distribution, and to propose strategies to minimize occurrence and formation.

### **Methods, Procedures, and Facilities**

**Field Sites.** Nitrosamine formation will be assessed in the distribution systems of several municipal utilities and the University of Iowa having different water sources, treatment, and distribution system characteristic. These have been carefully selected to include what are hypothesized to be "susceptible" systems and to allow some important comparisons.

1. **Cedar Rapids, Iowa** (see attached letter) obtains water from the Cedar River, using shallow wells and practices lime softening and chloramination. The system is predominately unlined cast iron pipe typically found with extensive tubercules and iron oxide containing deposits. Nitrate can periodically exceed the current MCL and episodes of nitrification in their system occasionally occurs.
2. **Des Moines, Iowa** (see attached letter) treats surface water by lime softening and chlorination but also can implement nitrate removal when nitrate is excessive in the supply. Des Moines currently has the largest ion exchange facility specifically designed for nitrate removal. This will allow assessment of the effect of nitrate removal. The system is primarily lined cast iron.

3. **The City of Coralville, Iowa** has a supply from the deep Jordan aquifer groundwater supply and practices lime softening and free chlorination. The system is primarily unlined cast iron.

4. **The City of Iowa, City** obtains its supply from the Iowa River (which can contain significant amounts of nitrate) and practices only direct filtration. It generally uses free chlorine but sometimes switches to chlorine dioxide when taste and odor problems arise. The system is primarily unlined cast iron. It will be studied in parallel with the University of Iowa system described below.

5. **University of Iowa** runs its own 12-MGD water plant for its own use. The supply is obtained from the Iowa River approximately 1/2 mile from the Iowa City treatment plant. Unlike Iowa City, it practices lime softening. This significantly lowers the organic content in comparison to Iowa City thus providing an ideal situation to compare the effect of organic precursor removal. The water is chlorinated.

**Field Measurements.** Studies will focus on measurements of dimethylnitrosamine over a representative spatial distribution of sampling points as well as in different seasons. Additional semi-volatile nitrosamines (e.g. diethyl and dibutylnitrosamine) will be measured pending evaluation of our analytical systems as discussed in the analytical section. Measurements will also be made on chlorine and chloramine concentration, dissolved oxygen, dissolved organic carbon, ammonia, organic nitrogen, and nitrate and nitrite. A "simulated distribution system" or SDS type of study will also be conducted. This entails taking samples at the influent of the water distribution system then periodically sampling for the various constituents. The results will be compared to those obtained from samples taken directly from the systems. Differences reflect in-system processes.

**Laboratory Studies.** These studies will involve the use of field collected as well as laboratory prepared waters. The studies are primarily designed to evaluate the kinetics of both formation and loss reactions, and the role of chlorination and chloramination. Control of the reaction conditions can be accomplished so that relatively high nitrosamine concentrations can be produced to facilitate analysis. Two types of reactors will be used. Pure water phase reactions will be studied using a batch reactors as well as with a special reactor. Evaluation of in-system processes and effects will be made using a recirculating pipe-loop reactor constructed to mimic a section of a distribution system. The specific purpose is to more carefully examine processes that may only occur in the distribution system. This will consist of one-foot sections of pipe set up with a recirculating bath provides for pH, dissolved oxygen control. The pipe section will be collected from Cedar Rapids or Iowa City.

Important parameters to be varied include pH, nitrite, and precursor concentration. Model precursors will include dimethyl and diethylamine and some common proteins and extracted humic substances. It is hypothesized that one role of chlorination and

chloramination may be to oxidize some proteins to more reactive NA precursors. Loss studies will utilize additions of NDMA and possibly several other nitrosamines pending evaluation of our analytical capabilities. Chloramines will be formed in-situ or preformed than added to solutions.

**Analytical Methods.** It is recognized that the most important analytical task will be to determine nitrosamine concentrations especially at very low but environmentally important levels in the range of 2-100 ng/L. Two analytical approaches will be initially evaluated that are capable of measuring a small suite of semi-volatile nitrosamines but especially NDMA the primary focus of this research. Relatively high concentrations of nitrosamines will be measured using EPA method 8070A. This method requires solvent extraction followed by GC analysis using a nitrogen-phosphorus detector. The Method Detection Limits range from 0.15 µg/L (150 ng/L) for N-nitrosodimethylamine to 0.81 µg/L for N-nitrosodiphenylamine.

Low levels will be measured using the method developed by Plomley (1994). This involves an extraction step followed by gas chromatography/tandem mass spectrometry (GC/MS/MS) using a quadrupole ion trap mass spectrometer in chemical ionization (CI) mode. It has been successfully used for the determination of NDMA in water samples at a concentration of about 1 ng/L (Plomley et al.,1994). Ion trap MS/MS capability using a Finnigan MAT GCQ™ GC/MS system is available at the University of Iowa Environmental Engineering and Science Laboratory where the laboratory part of this study will be conducted.

Organic nitrogen will be determined by Kjeldahl analysis (APHA-AWWA-WPCF, 1992) in water samples subjected to concentration by membrane RO . Dissolved organic carbon will be measured using a Shimadzu TOC analyzer. Ammonia will be determined by an Orion ammonia specific probe, and nitrate and nitrite by ion chromatography. Chlorine and chloramines will be determined by DPD-FAS titration (APHA-AWWA-WPCF, 1992). A membrane probe (Yellow Springs) will measure dissolved oxygen.

**Schedule:** An estimated project schedule is shown in Table 1.

Table 1. Proposed Project Schedule

Task	Starting date	Completion date
1. Project start-up/purchase supplies	July 1, 2000	Sept. 30, 2000
2. Training,develop analytical methods	August 1, 2000	Nov. 30, 2000
3. Winter 2000-2001 Field Measurements	Dec. 31, 2000	Feb. 30, 2001
4. Spring 2001 Field Measurement	April. 1, 2001	May 30, 2001
5. Summer 2001 Field Measurement	July 1, 2001	Aug. 30, 2001
6. Fall 2001 Field Measurements	Oct. 30, 2001	Dec. 1, 2001
7. Lab Studies-precursors and water quality	Jan. 30, 2001	July. 30, 2001
8. Lab Studies-role of disinfection	Sept. 1, 2001	Jan. 30, 2002
9. Lab Studies- role pipe surfaces	Feb. 1, 2002	April. 30, 2002
10.Final report/thesis writing	May 1, 2002	June 30, 2002

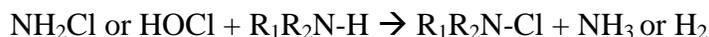
## Related Research

Considerable research has been conducted on the occurrence and formation of nitrosamines in a wide variety of matrices. The vast majority of research has been aimed specifically at formation and toxicological studies as related to health or to by-product formation in industrial manufacturing. Laboratory based "theoretical" studies have focused largely on elucidation of reaction mechanisms and kinetics. These studies have revealed many aspects of nitrosamine formation but are not easily related to observations in environmental matrices such as water or to complex environments such as distribution systems. The net formation of simple alkyl nitrosamines can be written as,



but in actuality may involve several different complex mechanisms and many nitrosating intermediates derived from nitrite such as nitrosyl chloride NOCl (Loeppky and Micheljda 1994). Nitrosyl chloride may also be an intermediate in the oxidation of nitrite by monochloramine (Margerum et al. 1994) suggesting one possible role of monochloramine in enhancing nitrosamine formation.

Particularly relevant to the proposed work is that of Myers and Wright (1948) and Nakajima et al (1984) who have shown that the organic N-chloramines are much more reactive than alkylamines. Organic chloramines readily form in the presence of free chlorine or monochloramine (Wolfe, 1986)



This reaction could also account for increased formation of nitrosamines from chlorination provided that the free chlorine or chloramine does not first oxidize nitrite to nitrate thus reducing the concentration of a critical reactant. Monochloramine is much less reactive with nitrite than free chlorine and recent work has shown that both monochloramine and nitrite can co-exist in water for extended periods. Nitrosamine formation in the presence of disinfectants may be determined by the relative rates of one of relative rates of nitrite oxidation vs formation of organic N-chloramines.

More reactive organic precursors may also be formed by oxidative reactions with nitrogen containing organic compounds. It is well established that oxidation of natural organic matter occurs and that large organic nitrogen containing compounds are frequently degraded to smaller ones. Interestingly one study (Demir et.al, 1992), showed that chloropicrin, a common nitrogen containing disinfectant by-product arising from reaction monochloramine and humic matter, is also an excellent NDMA precursor. Perhaps a related observation, Weerasooriya and Dissanayake (1989) reported that fulvic acid, one class of humic matter, is also a precursor in the presence of nitrite.

Environmentally oriented studies have been generally empirical in nature and have focussed primarily on determining if, not how, nitrosamines may be formed in water. No studies have considered the possible role of the distribution system and pipe-water interface. Ayanaaba and Alexander (1974) were the first to demonstrate formation

NDMA in Lake Water at neutral pH values when dosed with nitrite and dimethylamine and trimethylamine. Concern for formation in drinking water first occurred in Canada where formation was noted in winter months at concentrations sometimes exceed 100 ng/L, much above the 9 ng/L Canadian Maximum Acceptable Concentration (Jobb et al. 1992). Graham et al. (1995) reported on a study of the factors affecting NDMA formation during drinking water treatment using a miniature water treatment plant and dosing various precursors to the water. They concluded that pH did not play a major role in NDMA formation but that it did increase with increasing added nitrite. Addition of excess free chlorine reduced NDMA formation but it was noted that at the dosages utilized, no nitrite was apparently present and available to react. They offered the alternative hypothesis that NDMA may have reacted with the excess chlorine. They noted that the herbicide Thiram was also a much more effective precursor than dimethylamine and that temperature had little effect on NDMA. They hypothesized that field observations of higher NDMA formation during the winter were related to the stability and occurrence of organic nitrogen precursors.

Recently two experiences in California have again raised the issue of the nitrosamines in drinking water. Unfortunately none of these have yet to be reported publicly beyond the California Department of Health Services homepage (California, 1999). The first was the finding by the Los Angeles Municipal Water District (Ken Reich, 1999) that highly purified wastewater intended for indirect reuse sometimes contained approximately of 1 µg/L of NDMA. Furthermore it was found only after chlorination of the partially nitrified effluent. As the flag of concern went up, preliminary studies were then made by the Municipal Water District (Sylvia Barret, 1999) which found significant concentrations of NDMA in chloraminated drinking water.

### **Literature Cited**

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