

Report for 2001IA1601B: Occurrence and Formation of Nitrosamines in Drinking Water Distribution Systems

- Articles in Refereed Scientific Journals:
 - Choi, Junghoon and Richard Valentine. "Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product", *Water Research*, Vol. 36, No. 4, pp. 817-824, 2002.
 - Choi, Junghoon, Stephen Duirk and Richard Valentine. "Mechanistic Studies of N-nitrosodimethylamine formation in Drinking Water", *Journal of Environmental Monitoring*, (2002), 4(2), 249-252.
- Conference Proceedings:
 - Choi, Junghoon and Richard Valentine. 2001. "Formation of N-nitrosodimethylamine (NDMA) in Chloraminated Water: New disinfection by-product", *Proceedings the 221st National Meeting (Environmental Division)*, San Diego, CA, April 1-5, 2001, Vol 41, No. 1, pg 8-11.
 - Choi, Junghoon and Richard Valentine. 2001. "Studies on the Formation of Nitrosodimethylamine (NDMA) in Drinking Water: A New Chloramination Disinfection By-product", *Proceedings of the 2001 National American Water Works Association (AWWA) Annual Conference, Universities Forum-Water Science and Research Division*, Chapter TUE22, paper no. 4, 9 pp., June 17-22, 2001- Washington D.C.
 - Choi, Junghoon and Richard Valentine, 2001 "Mechanistic studies of N-nitrosodimethylamine (NDMA) formation in chloraminated drinking water", *Proceedings of the 222nd American Chemical Society (Environmental Division)*, Vol. 41(2), Paper no. 112, pp. 804-809 August 26-30, 2001, Chicago, Illinois.
 - Valentine, Richard and Junghoon Choi. A kinetic model of N-Nitrosodimethylamine (NDMA) formation during water chlorination/chloramination", *IAW 2nd World Water Congress, Preprints, Health Standards-Track 8*, Paper no. 4, 6 pp., October 15-19, Berlin, Germany, 2001.

Report Follows:

Research Background:

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.

Objective(s) of the Research Project:

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.

Progress Summary/Accomplishments for Second Year:

Work during the first year focused on the development of analytical methods for NDMA and acquiring data conclusively showing that NDMA is a water treatment disinfection by-product. During the second year reported on here, we focused on developing a comprehensive reaction model describing NDMA formation by reaction of monochloramine and dimethylamine (the hypothesized organic nitrogen precursor). Additional work implicates the possible role of bromide as a catalyst in NDMA formation in chlorinated and chloraminated water. Several water distribution systems have also been sampled for NDMA. NDMA formation appears to be associated with the practice of chloramination in support of the hypothesis that it is a disinfection by-product.

The kinetic reaction model (Table 1 and Figure 1) was developed primarily to provide kinetic evidence in support of a proposed mechanism describing NDMA formation in chlorinated water containing ammonia or in drinking waters which are chloraminated. Rate constants were obtained from the literature or fit to the data obtained only at pH 7. Therefore the model is pH specific and not of general use at other pH values without further calibration at these specific pH values. In addition, the model does not include reactions of other potentially reactive constituents such as bromide, nitrite, and NOM.

The proposed mechanism is based largely on studies of hydrazine formation (a rocket fuel) and its oxidation (Lunn et al, 1991; Castegnaro et al, 1986; Cahn and Powell, 1954). The key reactions include the formation of monochloramine from the initially added HOCl (Reaction 1), the reaction of chlorine with DMA to form dimethylchloramine, DMCA (Reaction 2), and the slow transfer of active chlorine from monochloramine to DMA to form more DMCA (Reaction 3). Formation of NDMA is initiated by the formation of 1,1-dimethylhydrazine (UDMH) intermediate from the reaction of DMA with monochloramine (Reaction 4), followed by the oxidation of UDMH by monochloramine or oxygen to NDMA (Reaction 5). It should be pointed out that NDMA is believed to be only a minor product of UDMH oxidation. Aside from NDMA formation, the reaction of UDMH with monochloramine may form other products such as tetramethyltetrazene, methylenedimethylhydrazine, and formaldehyde dimethylhydrazone (Sisler et al., 1969; Mitch and Sedlak, 2002). The presence of other natural organic matter will likely influence the efficiency of NDMA formation from competitive reactions involving intermediates.

Model results, based upon parameters either obtained from literature or determined by fitting selected data sets, generally conform quite well to experimental results at the same pH. Figures 2 and 3 show a close correspondence between measured NDMA concentrations and that predicted by the calibrated model in chloraminated water containing DMA. As can be seen, the formation of NDMA by reaction of monochloramine is relatively slow at this pH. Mitch and Sedlak (2002) reported that NDMA formation by this mechanism is a maximum near pH 8. It should be noted that addition of nitrite to DMA containing solutions yielded very little NDMA. This, as well as comparisons based on literature kinetic constants, suggests that classical nitrosation is not likely an important formation mechanism at drinking water pH conditions unless some unrecognized catalytic process is occurring.

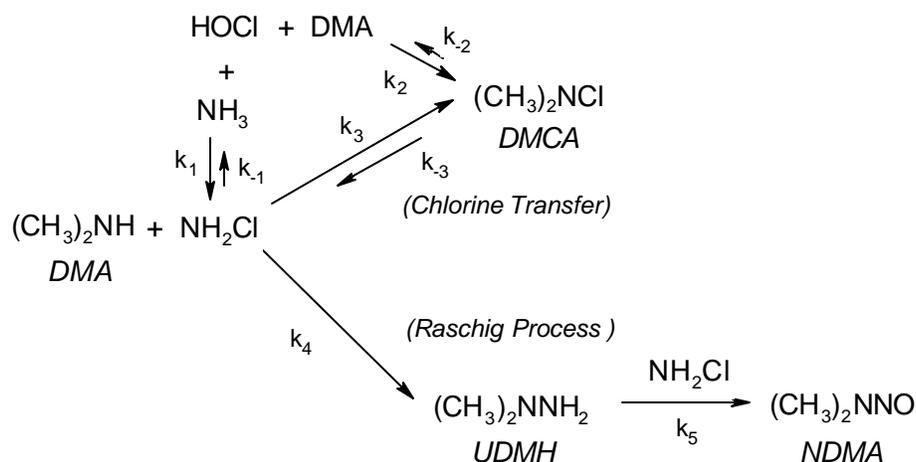


Figure 1. Mechanism of NDMA formation in chlorinated waters containing DMA and ammonia.

Table 1. Proposed reactions and rate constants for NDMA formation from DMA and monochloramine.

| Reaction | Rate constant at pH 7 (25°C) | Reference |
|--|--|---|
| (1) $\text{HOCl} + \text{NH}_3 \xrightleftharpoons[k_{-1}]{k_1} \text{NH}_2\text{Cl} + \text{H}_2\text{O}$ | $k_1 = 4.17 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ $k_{-1} = 2.11 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ | Morris J. C. and Isaac R. A. (1981) |
| (2) $\text{HOCl} + (\text{CH}_3)_2\text{NH} \xrightleftharpoons[k_{-2}]{k_2} (\text{CH}_3)_2\text{NCl} + \text{H}_2\text{O}$ | $k_2 = 4.23 \times 10^4 \text{ M}^{-1} \text{ s}^{-1 \text{ a}}$ $k_{-2} = 1.60 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1 \text{ a}}$ | Yoon J. and Jensen J. N. (1993) |
| (3) $\text{NH}_2\text{Cl} + (\text{CH}_3)_2\text{NH} \xrightleftharpoons[k_{-3}]{k_3} (\text{CH}_3)_2\text{NCl} + \text{NH}_3$ | $k_3 = 1.40 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ $k_{-3} = 5.83 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1 \text{ a}}$ | Yoon J. and Jensen J. N. (1993); Isaac R. A. and Morris J. (1983) |
| (4) $\text{NH}_2\text{Cl} + (\text{CH}_3)_2\text{NH} \xrightarrow{k_4} (\text{CH}_3)_2\text{NNH}_2 + \text{H}^+ + \text{Cl}^-$ | $k_4 = 1.28 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ | This model |
| (5) $(\text{CH}_3)_2\text{NNH}_2 + 2\text{NH}_2\text{Cl} + \text{H}_2\text{O} \xrightarrow{k_5} (\text{CH}_3)_2\text{NNO} + 2\text{NH}_3 + 2\text{H}^+ + 2\text{Cl}^-$ | $k_5 = 1.11 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ | This model |

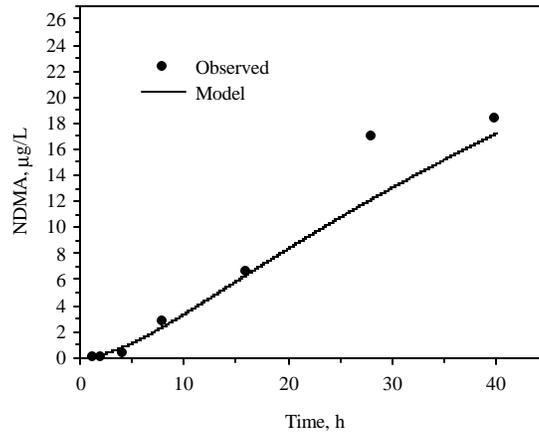


Figure 2. NDMA formation as a function of time. 0.1 mM of DMA was reacted with 0.1 mM of monochloramine. pH 7.0 ± 0.1 , 1 mM bicarbonate buffer. Model results are calculated based upon reactions and rate constants shown in Table 1.

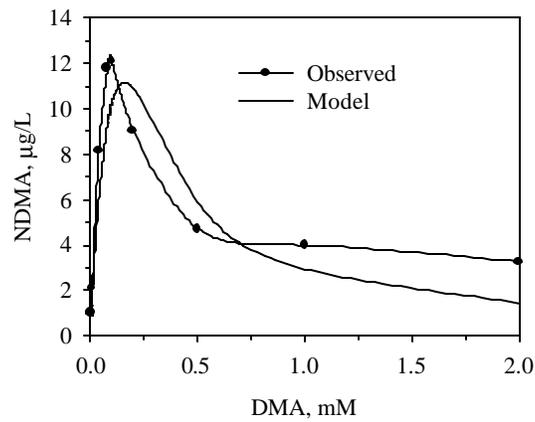


Figure 3. NDMA formation from preformed monochloramine after 24 hours as a function of DMA concentration. Monochloramine 0.1 mM, pH 7.0, 1 mM bicarbonate, 25 °C.

Additional work shows that the presence of bromide can also increase the formation of NDMA. This is presumed to be through the formation of monobromamine, an analog of monochloramine, formed by the oxidation of bromide by either free chlorine or by monochloramine. In general, its effect is also manifested much more quickly than the reaction of monochloramine. This is believed due to the general increased reactivity of monobromamine compared to monochloramine.

Consistent with this general formation mechanism, significant NDMA formation in some chloraminated distribution systems was observed sometimes in the range of 10-20 ng/L. The highest formation was observed in distribution systems obtaining their source water from supplies impacted municipal and agricultural waste disposal.