

# Chloramination techniques to reduce NDMA formation during disinfection

I. M. Schreiber & W. A. Mitch

*Department of Chemical Engineering, Yale University, USA*

## Abstract

Previous studies modeled NDMA formation during chlorine disinfection as arising from the oxidation of an unsymmetrical dimethylhydrazine intermediate formed from the reaction of monochloramine and dimethylamine. However, chlorination of wastewater effluents indicated that this mechanism could not account for a significant portion of the observed NDMA formation. Laboratory studies indicated that the order of reagent addition can have a significant effect on NDMA formation. Important factors included the chlorination state of organic nitrogen precursors and the formation of dichloramine. Disinfection systems were devised that maximize the formation of chlorinated organic nitrogen precursors and minimize dichloramine formation in order to minimize NDMA formation. Preliminary results from pilot testing indicate the effectiveness of these disinfection scenarios during chlorination of drinking waters and wastewaters. Evidence for a new reaction pathway to explain NDMA formation during chlorine disinfection is presented.

*Keywords:* chloramines, disinfection by-products, NDMA.

## 1 Introduction

As a result of the reduction in the allowable concentrations of trihalomethanes (THMs) and haloacetic acids (HAAs) in treated drinking waters resulting from the US EPA Disinfection Byproduct Rules, drinking water utilities are considering switching to chloramine disinfection to minimize THM and HAA formation. Increasing population densities are necessitating the use of wastewater-impacted drinking water supplies that exhibit higher levels of dissolved organic nitrogen (DON). In addition, the elevated levels of inorganic nitrogen in wastewater effluents, together with those resulting from non-point



source agricultural runoff, are fostering algal blooms in drinking water reservoirs. In turn, these algal blooms elevate DON levels in drinking water supplies. The combination of chloramines with elevated DON levels (e.g., DON  $\sim 2$  mg/L) raise the possibility that toxic organic nitrogenous disinfection byproducts may form.

The formation of *N*-nitrosodimethylamine (NDMA), an extremely potent carcinogen, during chlorine disinfection led to the temporary closure of Water Factory 21, a municipal wastewater recycling facility in Orange County, CA. This facility typifies the future dilemmas to be faced by drinking water utilities using wastewater-impacted drinking water supplies because the facility treats municipal wastewater for recharge of a drinking water aquifer. Because the molar ratio of applied chlorine is less than the ammonia concentration in the water (i.e., Cl:N < 1), chloramines are the active disinfectants. Although chlorine disinfection of municipal secondary wastewaters typically forms only 100 ng/L of NDMA, the California Notification level for NDMA is currently set at 10 ng/L and the US EPA lists the drinking water concentration that would result in a  $10^{-6}$  lifetime cancer risk level for NDMA as 0.7 ng/L [1]. Therefore, it is unclear whether the reduction in health risk resulting from reductions in THM and HAA formation by altering disinfection to chloramination may be balanced by the increased risk resulting from nitrosamine formation.

Utilities encountering unacceptable NDMA concentrations in their effluents currently employ ultraviolet (UV) treatment to remove NDMA from their effluents [1]. However, because nitrosamine formation has been found to be relatively slow, gradual NDMA formation is anticipated to result from the chloramine residual maintained in distribution systems. Moreover, one-log reductions in NDMA concentrations within the effluents of treatment plants require UV doses approximately an order of magnitude greater than those required for disinfection. The goal of the research was to identify simple methods of altering the chloramination disinfection process to minimize nitrosamine formation, and potentially avoid the need to install UV treatment systems.

## 2 Materials and methods

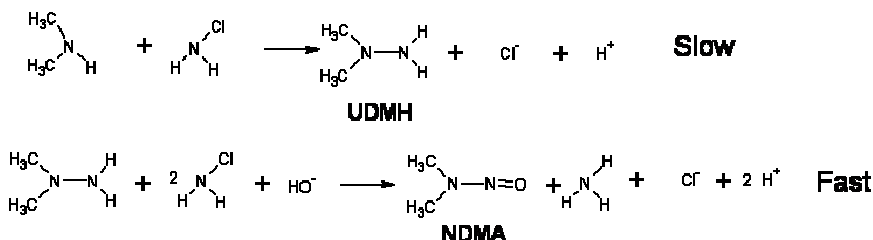
Materials and analytical methods have been described previously and are summarized below [2]. NDMA- $d_6$  was injected into aqueous solutions for isotope dilution analysis. NDMA was extracted using Ambersorb 572 resin beads (0.4 g/L). After filtration, the resin beads were extracted with methylene chloride. The methylene chloride extracts were blown down to 1 mL and analyzed by gas chromatography tandem mass spectrometry in the chemical ionization mode using methanol as the reagent gas.

Chloramines were speciated using a UV/visible spectrophotometer [2]. Measurements were conducted at the absorption maxima of monochloramine ( $\text{NH}_2\text{Cl}$ ,  $\lambda_{\text{max}} = 245$  nm) and dichloramine ( $\text{NHCl}_2$ ,  $\lambda_{\text{max}} = 295$  nm). Because absorbance peaks overlap, species concentrations were calculated by solving a matrix of absorbances at these two peaks.



### 3 Results and discussion

NDMA formation during chloramination had previously been explained as arising through the slow reaction of monochloramine ( $\text{NH}_2\text{Cl}$ ) and unprotonated dimethylamine (DMA) to form an unsymmetrical dimethylhydrazine (UDMH) intermediate [3, 4]. The UDMH intermediate is rapidly oxidized in the presence of  $\text{NH}_2\text{Cl}$  to form NDMA at low yields (i.e., < 3%):



However, aliquots of a sample of secondary municipal wastewater effluent that serves as the influent to the microfiltration process at the West Basin Municipal Water District's wastewater reclamation plant (El Segundo, CA) were subjected separately to 0.4 mM hypochlorite ( $\text{HOCl}$ ) and  $\text{NH}_2\text{Cl}$  for a 3 h contact time [2]. The  $\text{HOCl}$  formed 1150 ng/L while the  $\text{NH}_2\text{Cl}$  formed 74 ng/L. These results were surprising because the wastewater effluent contained 2.4 mM ammonia and so  $\text{NH}_2\text{Cl}$  formation was expected to predominate. When an equivalent dose of dichloramine ( $\text{NHCl}_2$ ; 0.2 mM or 0.8 meq/L) was applied to another aliquot of this sample, 8,150 ng/L NDMA formed over 3 h. These results indicated that  $\text{NHCl}_2$  formation was potentially involved in the enhanced NDMA formation observed during chlorination of wastewater effluents.

Pure inorganic chloramine (0.2 mM) and dimethylamine (1.3  $\mu\text{M}$ ) reagents were mixed in deionized water buffered at pH 6.9 with 10 mM phosphate buffer in different combinations [2]. These concentrations were selected to mimic the concentrations of hypochlorite (14 mg/L as  $\text{Cl}_2$ ) and organic nitrogen precursors for NDMA formation observed in practice. Over a 4 h contact period, the combination of  $\text{NH}_2\text{Cl}$  and chlorinated dimethylamine (CDMA) produced the least NDMA over a 4 h contact period (10 ng/L) while the combination of  $\text{NHCl}_2$  and DMA formed the most NDMA (682 ng/L). The combinations  $\text{NH}_2\text{Cl}$ /DMA and  $\text{NHCl}_2$ /CDMA produced 48 ng/L and 138 ng/L NDMA, respectively. These results indicated that the combination of  $\text{NH}_2\text{Cl}$ /CDMA would minimize NDMA formation during chloramination.

Chloramines are generally formed in situ from the combination of ammonia and hypochlorite or chlorine gas at drinking water and wastewater treatment plants. A series of experiments were performed to indicate how the order of reagent addition affects  $\text{NHCl}_2$  and NDMA formation. DMA (0.9  $\mu\text{M}$ ), hypochlorite (0.2 mM) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ; 0.005–0.68 mM) were applied in various orders to deionized water buffered at pH 6.9 with 10 mM

phosphate buffer [2]. Breakpoint chlorination occurs at a Cl:N molar ratio  $> 1.5$ . The results indicated that  $\text{NHCl}_2$  formation increased at the expense of  $\text{NH}_2\text{Cl}$  as the Cl:N molar ratio increased until they were approximately equal (0.2 meq/L) at the breakpoint.  $\text{NHCl}_2$  concentrations were highest for scenarios that involved the addition of hypochlorite after  $\text{NH}_4\text{Cl}$ . Above the breakpoint, only free chlorine was detectable.

Below the breakpoint, NDMA concentrations were highest for the scenario involving the addition of hypochlorite after  $\text{NH}_4\text{Cl}$ , followed by the addition of DMA [2]. This addition order would favour the reaction of  $\text{NHCl}_2$  with DMA. NDMA formation was minimized when hypochlorite was added to DMA, followed by the addition of  $\text{NH}_4\text{Cl}$ . This scenario would favour the reaction of CDMA with  $\text{NH}_2\text{Cl}$ . However, at the 1.5 Cl:N molar ratio at which breakpoint reactions occur, NDMA formation over a 6 h contact time for all scenarios increased from levels of 10-250 ng/L to  $\sim 1800$  ng/L. Above the breakpoint, NDMA formation never exceeded 40 ng/L. The enhanced NDMA formation observed near the breakpoint is important for drinking water utilities because the Cl:N molar ratio of 1 at which they typically chloramine approaches the 1.5 molar ratio of the breakpoint.

It was hypothesized that the enhanced  $\text{NHCl}_2$  formation when  $\text{HOCl}$  is added after  $\text{NH}_4\text{Cl}$  is related to the rapidity of the chloramine formation reactions [2]. At the reagent concentrations applied in this study, chloramine formation half-lives are less than 1 second. Half-lives of reagent mixing may be comparable to those of chloramine formation. When  $\text{HOCl}$  is added to a well-mixed solution of  $\text{NH}_4\text{Cl}$ , the Cl:N molar ratio would be  $> 1$  at the point of  $\text{HOCl}$  application prior to its mixing into solution even if the Cl:N molar ratio after mixing is  $< 1$ . If the chloramine formation reactions are fast relative to mixing, these conditions could foster  $\text{NHCl}_2$  formation prior to complete mixing. As the  $\text{HOCl}$  stock concentration becomes more concentrated the local Cl:N molar ratio would be enhanced and  $\text{NHCl}_2$  formation should increase. When the  $\text{HOCl}$  stock concentration was increased from 14.4-144 mM, the concentration of  $\text{NHCl}_2$  increased approximately 50% [2].

Several alterations to the chloramination process were identified that could foster the reaction between chlorinated organic nitrogen precursors and  $\text{NH}_2\text{Cl}$  to minimize nitrosamine formation during chloramination [2]. For waters containing negligible ammonia concentrations (e.g., most drinking waters and nitrified wastewater effluents), chlorine should be added upstream of  $\text{NH}_4\text{Cl}$  to promote the chlorination of organic nitrogen precursors prior to chloramine formation. This option is not available to waters containing significant ammonia concentrations because chlorination of organic nitrogen precursors would compete with chloramine formation. For all waters, chloramines could be formed under conditions that promote  $\text{NH}_2\text{Cl}$  formation prior to their application to the water stream. Such conditions include  $\text{pH} > 8.5$  and the application of  $\text{NH}_4\text{Cl}$  after chlorine. This latter condition, related to the mixing phenomenon mentioned previously, becomes particularly important under full-scale treatment conditions where chlorine and hypochlorite stocks are much more concentrated

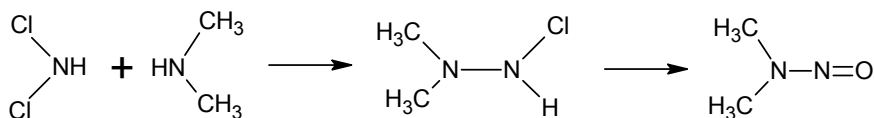
(e.g., hypochlorite stocks  $\sim 1.5$  M) than the stocks used in laboratory experiments

The efficacy of this treatment scenario was tested on the pilot scale at the West Basin Municipal Water District's wastewater reclamation facility [5]. Chloramines were pre-formed in a stock dosing tank by applying HOCl (14% solution) to  $\text{NH}_4\text{Cl}$  in various orders to tap water adjusted to pH 7.0 or 8.5 using hydrochloric acid or sodium hydroxide. HOCl and  $\text{NH}_4\text{Cl}$  were added to achieve initial concentrations of 2 mM and 2.6 mM, respectively. The first reagent was completely mixed prior to addition of the second reagent. Once both reagents were mixed, the chloramine solution was applied to the wastewater upstream of the pilot microfiltration units to achieve initial oxidant concentrations of 5 mg/L as  $\text{Cl}_2$ , the dose typically applied at the plant. Composite NDMA samples (6 h) were taken of the wastewater after passage through the microfilter (an approximate 4 minute contact time) and compared to composite NDMA samples of the wastewater influent prior to chloramine application. A control scenario was included that involved the application of HOCl without  $\text{NH}_4\text{Cl}$ . This scenario approaches the current operating conditions observed at the plant where chlorine is applied directly to the wastewater stream.

$\text{NHCl}_2$  concentrations in the stock tank were maximized for the scenario involving the addition of HOCl after  $\text{NH}_4\text{Cl}$  to tap water pre-adjusted to pH 7.0 [5]. The addition of  $\text{NH}_4\text{Cl}$  after HOCl to tap water pre-adjusted to pH 8.5 produced no detectable  $\text{NHCl}_2$ . Scenarios involving the addition of  $\text{NH}_4\text{Cl}$  after HOCl to pH 7.0 tap water or HOCl after  $\text{NH}_4\text{Cl}$  to pH 8.5 tap water produced intermediate  $\text{NHCl}_2$  concentrations.

The scenario that maximized  $\text{NHCl}_2$  formation also formed the maximum concentration of NDMA [5]. The control scenario formed statistically significant concentrations of NDMA, but the absolute formation was always  $< 3$  ng/L. Although  $\text{NHCl}_2$  formation is fostered under this scenario, concurrent chlorination of organic nitrogen precursors would inhibit NDMA formation. For the remaining scenarios, NDMA formation was not significant. Because NDMA formation is a slow reaction, the 4-minute contact time obtainable with the pilot plant configuration was not sufficient to enable significant NDMA formation.

These results suggest that the NDMA formation pathway should be modified to include the importance of  $\text{NHCl}_2$  as a reagent and the potential formation of a chlorinated UDMH intermediate [2]:



## References

- [1] Mitch, W.A., Sharp, J.O., Trussell, R.R., Valentine, R.L., Alvarez-Cohen, L., Sedlak, D.L. N-nitrosodimethylamine (NDMA) as a drinking water contaminant: A review. *Environ. Eng. Sci.* **20**, pp. 389-404, 2003.



- [2] Schreiber, I.M., Mitch, W.A. The influence of the order of reagent addition on N-nitrosodimethylamine formation. *Environ. Sci. Technol.*, **39** (10), pp. 3811-3818, 2005.
- [3] Mitch, W.A., Sedlak, D.L. Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. *Environ. Sci. Technol.* **36**, pp. 588-595, 2002.
- [4] Choi, J.H., Valentine, R.L. Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product. *Water Res.* **36**, pp. 817-824, 2002.
- [5] Mitch, W.A., Oelker, G.L., Hawley, E.L., Deeb, R.A., Sedlak, D.L. Minimization of NDMA formation during chlorine disinfection of municipal wastewater by application of pre-formed chloramines. *Environ. Eng. Sci.*, *submitted*.

