Background

N-Nitrosodimethylamine (NDMA) is a member of a chemical class, the N-nitrosoamines, which are suspected carcinogens. Their cancer potencies are reported to be higher than those of the trihalomethanes[1]. NDMA was first detected in groundwaters of Northern California (Rancho Cordova) in 1998 and Southern California in 1999 near rocket engine testing facilities at concentrations as high as 40,000 ng/L on site and 20,000 ng/L off site[1]. NDMA is a semi-volatile organic chemical and has the molecular formula O=N-N(CH3)2. NDMA is soluble in water (3,978 mg/L) and is not likely to bioaccumulate, biodegrade, adsorb to particulate matter or volatilize. Sunlight may result in limited NDMA reduction. Consistently, transport of NDMA is not retarded through soil columns[1].

NDMA occurrence is not limited only to the regions near rocket fuel facilities. NDMA detected at other sites appeared to be associated with chlorine/chloramine disinfection of water and wastewater, especially in locations where chlorinated wastewater effluent was used for aquifer recharge. Chlorination of wastewater resulted in significant NDMA formation (hundreds ng/L), with a direct relationship between NDMA concentration and chlorine dose. More recently NDMA was detected in treated drinking water at low levels (10 ng/L)[2] from sources that were not impacted by wastewater effluent or industrial sources, especially when monochloramine was used to maintain a chlorine residual[1].

A variety of studies have been conducted on health effects, occurrence and treatment, as well as surveys in drinking water NDMA occurrence in California and nationwide. Regulatory action is pending.

Sources

NDMA is found in the diet, in various meat and cured meat products (600 to 1,000 ng/kg in fried pork bacon), fish and fish products, beer (50 to 5,900 ng/kg), milk (90 to 100 ng/L)[3], cheese, soybean oil, canned fruit, and apple brandy. In the body, NDMA is formed when acidic conditions in the stomach catalyze the reaction between nitrite and dimethylamine (DMA). Historical non-dietary sources of NDMA include unsymmetrical dimethylhydrazine (UDMH, a rocket fuel component which used NDMA during synthesis), cutting oils, tobacco smoke, herbicides, pesticides, rubber products, and drugs formulated with aminopyrine. Recently discovered sources of NDMA precursors include carpet dyes, dithiocarbamates and methyl-dithiocarbamates from circuit board manufacturers and foaming sewer herbicide (Metam Sodium). NDMA occurrence in drinking water may result from industrial groundwater

contamination (rocket fuel), from the chlorination/chloramination of cationic polymers, from the use of ion exchange resins, and as a chlorination/chloramination byproduct. NDMA is also found in sewage influent from industrial sources (carbamate users, etc.) and is formed during the chlorination of secondary effluent at wastewater treatment plants.

Regulatory Considerations

The EPA IRIS classification of NDMA is B2, meaning that it can be reasonably anticipated to be a human carcinogen based on animal studies, however inadequate human data exist.   Some animal studies have shown induction of tumors at multiple sites in both rodents and non-rodent mammals exposed by various routes. The unit risk factor for 10^{-6} risk is 0.00143 µg/L in drinking water, resulting in a hypothetical guidance concentration for a 10^{-6} risk level of 0.7 ng/L (ppt). The California Office of Environmental Health Hazard Assessment (OEHHA) has performed their own risk assessment, resulting in a slightly different 10^{-6} risk guidance level of 2 ng/L (ppt). There is currently no maximum contaminant level (MCL) for NDMA, though an action level of 10 ng/L was set in 2002 by the California Department of Health Services, based in part on the discovery of NDMA as a byproduct of chlorination and chloramination of drinking water. The detection limit for NDMA in drinking water matrices currently ranges from 0.5 to 2 ng/L.

Occurrence in Drinking Water

In 1989, a survey of 145 drinking water plants in Ontario, Canada indicated that NDMA concentrations in the treated water from most of the plants were less than 5 ng/L with some samples exceeding 9 ng/L[4].   In 2001, the California Department of Health Services conducted a similar survey of drinking water systems[5]. Their results indicated that 3 of 20 chloraminated supplies contained NDMA levels greater than 10 ng/L; none of eight supplies using free chlorine disinfection had NDMA levels above 5 ng/L; and one of four water supplies using anion exchange treatment had NDMA levels above 10 ng/L.

A 2001-2002 survey of NDMA in 21 North American water systems[6] indicated the median NDMA concentrations in treatment plant effluents was less than 1 ng/L, for either chlorinated or chloraminated systems. The median distribution system concentrations was less than 2 ng/L for chloraminated water and less than 1 ng/L for chlorinated water. The highest NDMA concentrations were found in groundwater treated with anion exchange resin and chlorination. The next highest concentrations were found in groundwater treated with lime softening and chloramination.   Most samples were below the CDHS action level of 10 ng/L. There were more samples with NDMA values between 2.5 and 10 ng/L in chloraminated systems than for chlorinated systems, both in treatment plant effluents and distribution systems. The survey is on-going.

Formation in Drinking Water

For NDMA to be formed, reactive chlorine, such as monochloramine or chlorine and ammonia must be present. In addition, precursors such as dimethylamine or other organic amines, N-based cationic polyelectrolytes, or ion exchange resins must be present. Table 1 summarizes potential pathways for NDMA formation.

Table 1: Summary of Pathways of NDMA Formation

SIGNIFICANCE OF PATHWAY IN DRINKING WATER	*MAJOR PRECURSORS OR REACTANTS*	*ADDITIONAL COMMENTS*
1. Most common pathway	Chloramines + dimethylamine (DMA) or tertiary amines with DMA functional groups, or unsymmetrical dimethylhydrazine (UDMH)	Maximum at pH 7–8. UDMH is the rocket fuel component and primary reactant to form NDMA in contaminated ground waters. UDMH is also an intermediate of the reaction with DMA.
2. Order of magnitude slower rate than for (1)	Hypochlorite + DMA	Helps control NDMA formation with chloramines (see 3)
3. Order of magnitude slower rate than for (1).	Chloramines + chlorinated DMA	Sequential application of Cl_2 and NH_3 at the treatment plant helps reduce NDMA formation
4. Significant formation of NDMA observed in the laboratory setting	Hypochlorite + Nitrites + DMA	Rapid enhanced formation, especially at pH > 8.5. Not demonstrated in drinking water applications
5. Nitrosation pathway significant in food curing processes with nitrites and in the gas phase in cigarette smoke. Lower formation than for (4) in water	Nitrites + DMA	Slow at neutral and high pH, maximum at pH 3.4. Can occur in vivo in the acidic environment of the stomach. The estimated daily intake of NDMA for an average German diet is 0.2 μg/day[1]. Nitrification does not appear to contribute to NDMA, possibly due to pH being too high.
6. Lower formation than for (4)	Chloramines + Nitrites + DMA	Slower reaction, possibly due to scavenging of monochloramine by nitrite
7. Significant formation of NDMA observed in the laboratory setting	Bromamines + DMA	Bromamines are generally more reactive than chloramines. Could be significant for sources with high bromide content
8. Significant formation and elution observed at the plants with anion exchange resins	Quarternary amines in ion-exchange resins can leach NDMA even with distilled water or react with chlorine or chloramines. The presence of nitrite increased NDMA formation.	

Chlorination

Agricultural runoff can introduce DMA and nitrite into surface water streams that can produce NDMA in water treatment plant using chlorination processes such as sodium hypochlorite[7,8].

Chloramination

The concentration of NDMA formed as a byproduct of chloramination appears to depend heavily on the chloramine dose, and may not be strongly influenced by the presence of natural organic matter or organic nitrogen. In a 2001 study[9], it was found that increasing the chloramine dose from 1 mg/L to 5 mg/L more than doubled the resultant NDMA concentration. Their findings suggested that chloramine doses in the ranges generally used for drinking water treatment might result in NDMA formation in the range of the potential regulatory window.

Subsequent research[10,11] demonstrated an alternative formation mechanism (to the well known nitrosation of DMA by the nitrosyl cation) involving the oxidation of DMA to UDMH by chloramines and the further oxidation of UDMH by chloramines to NDMA.

The NDMA formation mechanism of the combination of dimethyl amine and the nitrosyl cation is somewhat plausible since nitrosyl cation may be formed under acidic conditions by the hydrolysis of nitrite, a product of ammonia oxidation. The water conditions for the SFPUC, however, are basic so it is uncertain to what degree the addition of ammonia would enhance NDMA formation.

The presence of bromide in source waters is thought to further catalyze NDMA formation from chloramination, as shown in Figure 1. NDMA formation appears to be significantly enhanced by the presence of bromide[12]. Bromide and ammonia compete for HOCl in strongly pH-governed reactions, forming monochloramine and hypobromous acid (HOBr). HOBr readily reacts with ammonia to produce bromamines in a mechanism similar to that proposed for monochloramine formation from HOCl and ammonia. Bromamines then follow a similar path to monochloramines in forming NDMA. The increased negative charge of brominated nitrogen in monobromamine results in a faster rate of nucleophilic substitution by DMA to form UDMH. The increased rate of UDMH formation in this manner results in the increased rate of UDMH oxidation by bromamines and increased NDMA formation.
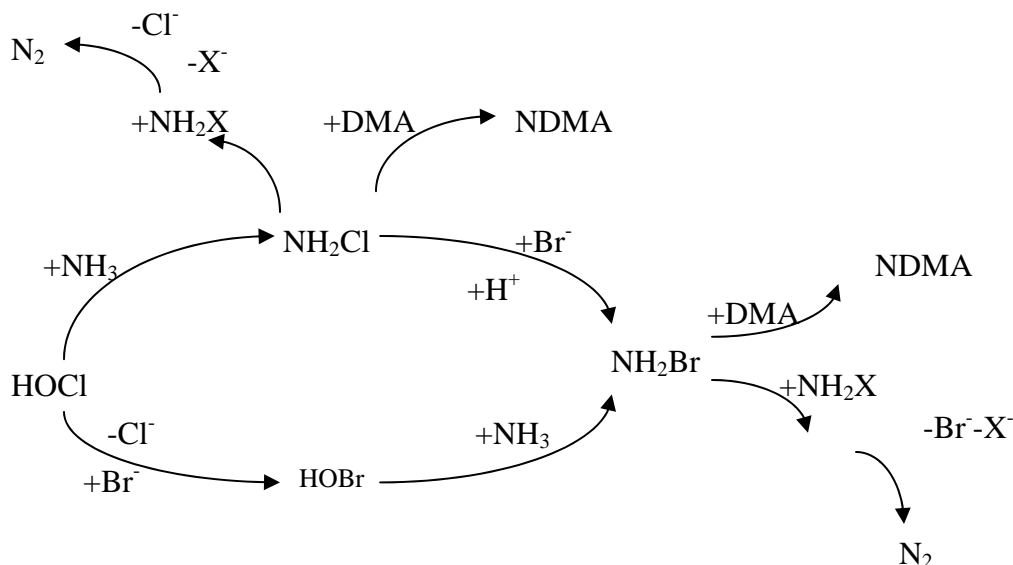
Figure 1 NDMA Formation Mechanism for the Chloramine/Bromamine Pathway (X is Cl or Br)

Treatment – Removal

NDMA is highly soluble and cannot be removed by granular activated carbon (GAC) or air stripping. Ozone also does not directly react with NDMA or its precursors in water or air. Although hydroxyl radicals produced from ozone and hydrogen peroxide could be used to remove NDMA, the ozonation efficiency is limited by the presence of hydroxyl radical scavengers. Iron oxides can be used to reduce NDMA to DMA and ammonia; however, due to the slow kinetics of the reaction, this treatment method is not cost effective. Bioremediation has the potential for treatment of NDMA contaminated water, but field results of biodegradation of NDMA are limited. Despite the existence of NDMA-degrading bacteria in soil, for example at the Rocky Mountain Arsenal, no significant loss of NDMA was observed during the passage through the aquifer.   It is likely that a complex interaction exists between dissolved organic nutrients necessary for the growth of bacteria capable of degrading NDMA[1]. In addition to the lack of clear evidence for bioremediation of NDMA in groundwater, there is no information regarding the potential for biological removal of NDMA within drinking water treatment systems such as biofiltration units[1].

The most commonly applied removal method for NDMA is direct removal using photolysis by UV. Direct photolysis with UV light in the 200 - 260 nm range is highly effective at NDMA removal, but this process may simply produce the NDMA precursors DMA and nitrite. UV can be applied through the use of low and medium pressure UV lamps and pulsed UV systems. UV is currently considered the best available technology, as it is the most effective process for NDMA destruction.   The NDMA absorbs the UV energy which breaks the N-N bond. The UV dosage required

for one order of magnitude decrease in NDMA concentration is approximately 1,000 mJ/cm2, which is approximately 25 times higher than that required for equivalent Cryptosporidium inactivation. Therefore, UV treatment for NDMA will be feasible but more expensive than UV treatment for disinfection[1]. Advanced oxidation can interfere with NDMA formation and re-formation by destroying interfering compounds and precursors, and can also destroy NDMA once it is formed. Hydrogen peroxide addition is recommended for NDMA removal applications to prevent NDMA reformation and provide other oxidation benefits, though use of hydrogen peroxide is problematic for maintaining disinfectant residuals in drinking water systems. Reverse osmosis removes approximately 50% of NDMA, as shown by thin-film composite membranes in wastewater recycling plants[1].

Removal of NDMA can also be achieved indirectly by removing NDMA precursors, such as DMA and trimethylamine. Like NDMA, however, these precursors are not susceptible to treatment by air stripping and adsorption filters such as GAC. Although UV is effective at treating NDMA, it is relatively ineffective on the NDMA precursors. Biological treatment methods and advanced treatment systems, such as microfiltration and reverse osmosis, are more effective in removing the NDMA precursors, DMA and trimethylamine. Hydrogen peroxide also may inhibit NDMA reformation by oxidizing precursors.

SFPUC Monitoring

Chloramine conversion monitoring in April 2004 indicated that only one out of 8 locations had a detectable concentration of NDMA (detection limit is 2 parts per trillion). That location had an NDMA level of 4 parts per trillion.

Summary

NDMA formation is expected to modestly increase with the transition to chloramines, though due to the excellent quality of the pristine Hetch Hetchy source, (e.g., low in organic nitrogen and bromide, plus free from agricultural run-off) this is expected to be low.

The SFPUC experience should be similar to that of East Bay Municipal Utility District, a large chloraminated surface water supply system in California. EBMUD limited NDMA formation in the distribution system to low levels near or at detection below 1 – 2 ng/L with the chloramines at pH around 9.0 and even with long detention times, as long as no major precursor material is present in the raw water and treatment cationic polymer usage is optimized[13]. With the SFPUC source largely deriving from Hetch Hetchy in Yosemite National Park, the levels of organic materials are very low, the pH is maintained above 8.5 and chloramination practices are being optimized – all these factors will contribute to limiting NDMA exposure to customers. In addition, further coagulant optimization is planned for the facilities that treat a small fraction of the SFPUC supply to maximize NDMA control.

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