

Nitrosamines: A review of formation pathways, precursors, control, and occurrence in drinking water

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Abstract. Nitrogenous disinfection by-products (N-DBPs) are emerging by-products that may be present in drinking water as by-products of water treatment plant (WTP) operations. Nitrosamines are N-DBPs that form by reaction of chloramine with certain organic nitrogen-containing compounds; however, the exact processes and environments in which nitrosamines form are still not well understood. Organic nitrogen precursors react within the WTP and distribution system, forming the toxic by-products during chloramination, or while in distribution. To best control the formation potential of nitrosamines, precursors must be removed from source water prior to chloramine disinfection. These nitrosamine forming precursors are abundant in source waters worldwide, presenting a need for further study of the mechanisms that reduce the formation potential of nitrosamines in chloramination WTPs.

1 Introduction

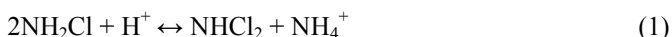
Nitrogenous disinfection byproducts (N-DBPs) are toxic pollutants of emerging concern that may be present in source waters from industrial or wastewater discharge, septic systems, or as byproducts of water treatment plant (WTP) operations. Specifically, N-DBPs such as nitrosamines can form by the reaction of precursors within a treatment plant or chloraminated distribution system [1, 2]. Many nitrosamines that have been studied are classified as probable carcinogens, as indicated by the U.S. Environmental Protection Agency's (USEPA's) Integrated Risk Information System (IRIS) database. [1, 3] documented the reactions of chloramines with organic nitrogen precursors as the primary mechanism responsible for N-DBP formation in WTPs. These precursors to nitrosamine formation are abundant in many global drinking water sources and can be formed in the distribution systems, making these supplies particularly susceptible to nitrosamine formation. This review provides an assessment of formation pathways and precursors of nitrosamines, mechanisms for control of nitrosamine formation, and the global occurrence of nitrosamines in drinking water.

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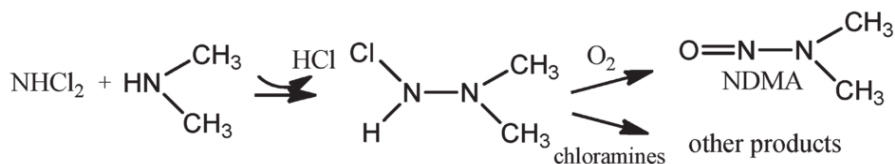
2 Nitrosamine formation in drinking water: chloramination

Drinking water treatment is a major pathway to nitrosamine formation. Previous studies have documented nitrosamine formation from several mechanisms of WTP operations, including chloramination, ozonation, and chlorine-nitrite interaction [2]. The degree of influence on formation of nitrosamines varies between all WTP processes.

Chloramine disinfection is the most important pathway for nitrosamine formation [4]. Findings from [3, 5] showed nitrosamine formation occurred by reaction of monochloramine and amine precursors. [1] later explained that both monochloramine (NH_2Cl) and dichloramine (NHCl_2) coexist under typical chloramine disinfection conditions, and both are responsible for nearly all nitrosamine formation in drinking water treatment:



[4] demonstrated the formation of N-nitrosodimethylamine (NDMA) and other nitrosamines from reactions that occur during chloramination (Scheme 1). A nucleophilic substitution reaction between dimethylamine and NHCl_2 forms a chlorinated unsymmetrical dimethylhydrazine intermediate (Cl-UDMH). Oxidation of Cl-UDMH by dissolved oxygen forms NDMA and other nitrosamines. This particular formation pathway has a slow reaction process, often days, indicating that nitrosamines continue formation and accumulation within a chloraminated distribution system [6, 7].



Scheme 1 – From [4].

3 Nitrosamine precursors in source waters

Source waters utilized for consumption are extremely influential to nitrosamine formation potential. Quality of source water is largely dependent on factors such as watershed and source water type. Seasonal variation is also known to have significant impact on disinfection byproducts [8]. Through proper assessment of source water before disinfection, WTPs can provide potable water while preventing the formation of nitrosamines.

Evaluation of nitrosamine formation potential begins with proper source water assessment. Watershed variation generates differences in precursor type and relating concentrations. Amines are expected to be the major nitrosamine forming precursor during chloramination [2]. Although the reaction time is much slower, amides are the other major category of organic nitrogen precursors [9].

Signatures of amine and amide precursors exist multiple watershed types, including urban and agricultural. Source water containing high concentrations of precursors is likely impaired by treated wastewater, industrial effluents, or herbicides diuron and dimethyldithiocarbamate [9-13].

Surface runoff enriched with heavy metals, nutrients and sediments, rubber fragments, and other contaminants is an essential source of non-point source pollution to receiving water bodies such as drinking water reservoirs [14, 15]. Forested watersheds naturally offer

more protection to source water, rather than urban or agricultural watersheds. Forested buffers located around a reservoir system limit the direct influence of contaminated runoff on quality of source water. Buffer areas change the quantity of water available for runoff through interception, evapotranspiration, infiltration, percolation, and absorption, resulting in different physical, chemical, and biological processes in the receiving water bodies [14].

4 Control of nitrosamine formation

Removal of nitrosamines following drinking water treatment is a difficult task, as many nitrosamines are hydrophilic ($\log K_{ow} = -0.57$ for NDMA), and will poorly sorb to activated carbon, and other sorbents [7, 16]. NDMA has a relatively high vapor pressure at 2.7 mm Hg at 20°C [17]. The estimated Henry's Law constant for NDMA is low at 2.6×10^{-7} atm-m³/mol at 20°C, due to the high water solubility of NDMA [16, 18]. Due to the chemical and physical properties of NDMA, volatilization from air stripping during water treatment is unlikely to result in significant removal from solution [7].

Removal of nitrosamine precursors before disinfection is a vital process to control nitrosamine formation during drinking water treatment. Furthermore, nitrosamines will typically not be present in drinking waters treated by activated carbon prior to chloramination [2]. Sorption of precursors exposed to powdered activated carbon (PAC) at a dose of 5 mg/L for 7 days, showed 50% reduction of NDMA formation potential [19]. During the same study, water exposed to a PAC dose of 20 mg/L for 7 days produced an NDMA formation potential reduction of 90%. Water was in contact with PAC for 7 days to assure establishment of adsorption equilibrium, even though conventional treatment contact times typically last hours [19].

A study conducted by [20] demonstrated that by using granular activated carbon (GAC) to treat a mixture of 90% surface water and 10% wastewater at a 10-minute simulated empty bed contact time, NDMA formation potential breakthrough was less than 20% after 10,000 bed volumes. Also, GAC demonstrated 60-80% reduction of NDMA formation potential in surface waters during pilot- and full-scale studies [20].

5 Global occurrence of nitrosamines

The presence of nitrosamines is worldwide and relatively similar among all detection locations. Given the expectations from known formation pathways, North American studies found that NDMA formation is closely associated with chloramination than with chlorination [15, 21-23]. Water treatment plants with long disinfection chloramine contact times (12-18 hours) tended to have greater NDMA concentrations in the plant effluent than those with short (0.5-2 hours) contact times, due to the long time-scales of nitrosamine formation [24]. One large study collected drinking water samples under the second Unregulated Contaminants Monitoring Rule (UCMR2). NDMA was detected in 34% of chloramination plant effluents [23]. Other nitrosamines N-nitrosodiethylamine (NDEA), N-nitrosopyrrolidine (NPYR), N-nitrosodi-n-butylamine (NDBA), and N-nitrosomethylethylamine (NMEA) were also detected, but each at less than 1% occurrence [23].

[25] performed a nitrosamine occurrence study in England and Wales. Out of 41 surveyed plants, only 3 had detectable concentrations of NDMA; however, the levels were always below 6 ng/L. Another UK study conducted by [26] found NDMA concentrations just above the method detection limit (0.9 ng/L) in a few isolated samples from one distribution system. WTP practices in the UK typically operate with a set 30 minute pre-chlorine contact time, and low chloramine disinfection dose (0.5 mg/L), explaining why

such low NDMA concentrations are found in chloraminated drinking waters of the UK [26].

High nitrosamine occurrence was seen in Australia due to the high prevalence of chloramination WTPs. One study detected NDMA in 75% of chloraminated waters, where 37% of the detections had NDMA concentrations >10 ng/L [27]. Besides the high rate of chloramination WTPs, wastewater recycling, and high source water ammonia concentrations are accountable for such high levels of NDMA in drinking water in Australia [27, 28].

The occurrence of nitrosamines in China can be explained by circumstances other than drinking water treatment practices. In recent surveys of Chinese waters, nitrosamines frequently occurred due to impairment from domestic and industrial wastewaters [29, 30]. Due to the influence of industrial and domestic wastewaters, nitrosamines other than NDMA such as NPYR, NMOR, and NPIP, were detected more frequently in China than in other countries [29-31].

6 Conclusion

Nitrosamines produced as byproducts of WTP operations is a global water quality concern. The use of chloramines as a disinfectant provides a significant pathway for the formation of nitrosamines. Reduction of nitrosamine formation potential begins with proper assessment of source waters that are being treated for drinking purposes. Identifying point sources of pollution and determining land use within a source water catchment provides information on the type and amount of precursors that could be present in a receiving source water. To further reduce nitrosamine formation potential during water treatment, chloramination WTP operators need to follow procedures that remove precursors before chloramine disinfection. By adopting this practice, and implementing source water protection strategies, there will be less risk of consuming nitrosamine contaminated drinking water in areas supplied by chloraminated distribution systems.

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