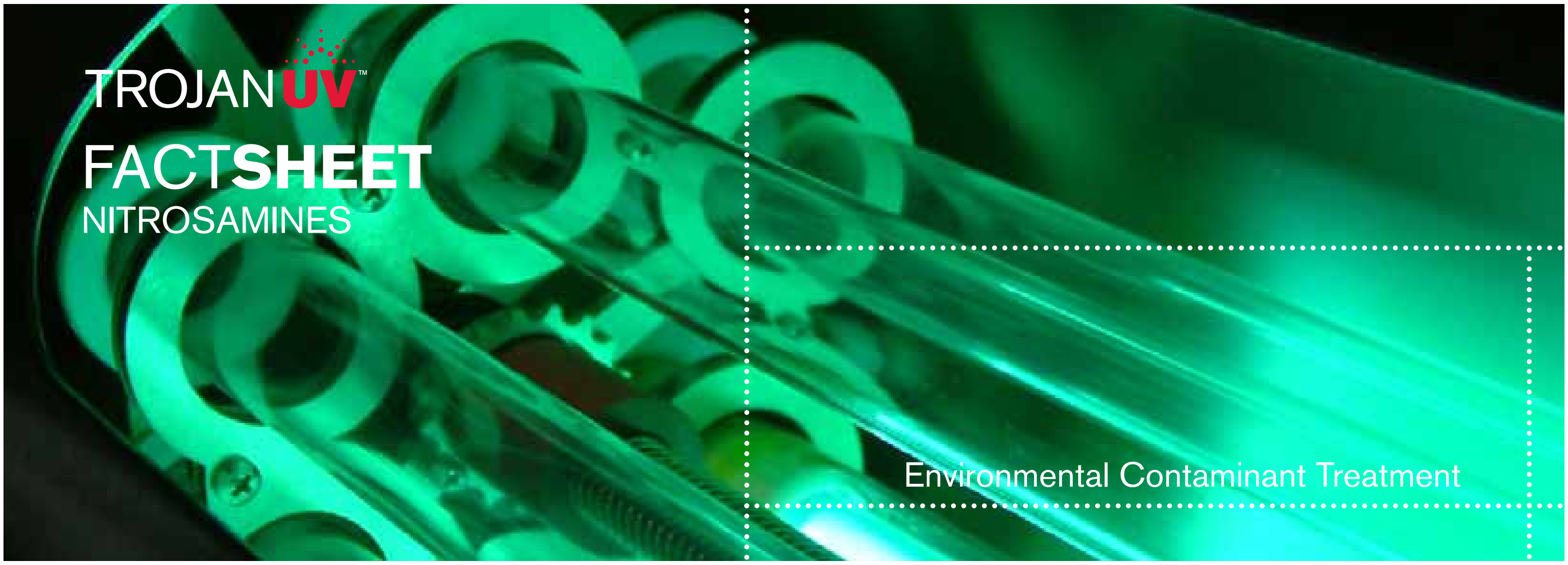



# Update on Emerging Contaminants: NDMA and Other Nitrosamines

The nitrosamine group, a group that includes *N*-nitrosodimethylamine (NDMA), has attracted increased attention from the water treatment community as potent and potentially wide-ranging water contaminants. While their presence in municipal wastewater and indirect potable reuse is relatively well understood, understanding of their presence in drinking water is limited. To improve this understanding, the nitrosamine group has been included in the Unregulated Contaminant Monitoring Rule (UCMR) 2. This summary provides an introduction to this emerging group of contaminants with a focus on NDMA.

NDMA can be formed when wastewater or drinking water is treated with chlorine or chloramines.

## INTRODUCTION TO NITROSAMINES

The nitrosamines group consists of a large number of compounds formed by various combinations of amines and nitrogen compounds. Each has the foundational structure N-N=O. There are hundreds of individual nitrosamine compounds, and nearly all are carcinogenic to animals in animal studies. A handful are of concern to the water treatment community **(Table 1)**, with perhaps the best known being NDMA.

## SOURCES AND FORMATION OF NDMA

In its pure form, NDMA is a semi-volatile, yellow, oily liquid with very little odor. However, it is more often found as a by-product or impurity of a chemical mixture. For example, during the 1950's, NDMA was a key intermediate in the electrolytic production of 1,1-dimethylhydrazine, a component of liquid rocket fuel. The finished fuel contained approximately 0.1% NDMA as an impurity. Further, as 1,1-dimethylhydrazine breaks down, NDMA is one of the more stable breakdown products. For this reason and as a result of its resistance to natural degradation, NDMA has been detected in groundwater near rocket testing facilities. NDMA was produced commercially until the mid 1970's. Today, NDMA is only produced in limited quantities for research purposes. However, NDMA can be formed in the environment given the correct conditions and the appropriate precursor compounds. While there are a number of possible formation pathways, NDMA can be formed by the combination of dimethylamine (DMA) and nitrite, particularly in slightly acidic waters. Another important formation pathway occurs during disinfection of drinking water and wastewater with chlorine and chloramines. Either disinfectant, when combined with the correct precursor compounds, has been shown to form NDMA (Mitch and Sedlak, 2002; Choi and Valentine, 2001). In fact, some water treatment processes themselves (certain water treatment polymers and ion exchange resins) may contain NDMA precursors that promote NDMA formation when exposed to chlorine or chloramines. Therefore, NDMA is often classified as a disinfection byproduct (DBP).

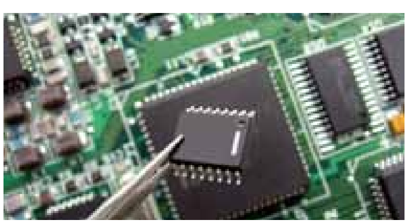
## NDMA IN WASTEWATER

NDMA can be found in relatively high concentrations (hundreds, even thousands of parts per trillion [ppt]) in wastewater due to the relative abundance of NDMA precursors and the wide use of chlorine. Dimethylamine is a common component of animal and human waste and can remain in water even after secondary wastewater treatment. Nitrates are also present in wastewater. In addition, the presence of the following industries or activities in the collection network can increase the potential for NDMA formation:

- Cosmetics manufacturing
- The manufacture of pharmaceutical and personal care products (PPCPs) such as shampoos, other hair and skin products, and cleansers

- Rubber and tire manufacturing

- Printed circuit board manufacturing



- Foods and Beverages

- Use of dithiocarbamates for root control or metals processing

Areas containing high densities of these industries are at increased risk of forming higher concentrations of NDMA in wastewater.

**What Others Are Doing:**
Several water supply projects currently take secondarytreated wastewater and treat it to standards beyond those required for drinking water. These facilities use microfiltration (MF) and reverse osmosis (RO). However, because NDMA passes through MF and RO, Trojan UV-oxidation is used as a final polishing step. Selected indirect potable reuse projects include:

- The Orange County (CA) Water District's Groundwater Replenishment System (GWRS)
- Water Replenishment District's Alamitos Barrier Recycled Water Project, and
- West Basin Municipal Water District's Water Recycling Project

This TrojanUVPhox™ at the Orange County Water District removes NDMA and any other wastewater-derived contaminants that may be present in MF and RO-treated secondary effluent.

## NITROSAMINES IN INDIRECT POTABLE REUSE

Due to the potential presence of NDMA in wastewater, water providers performing Indirect Potable Reuse (IPR) of wastewater are required by many regulators to monitor for NDMA. Due to its low molecular weight of 74.1 amu **(Table 1)**, NDMA passes through conventional and membrane treatment processes, even reverse osmosis. Without treatment with UV, NDMA can be present in finished, treated water intended for IPR (see back page for Treatment Technologies).

## NITROSAMINES IN MUNICIPAL DRINKING WATER

NDMA is a disinfection byproduct and can be present at low concentrations in treated drinking water (Barrett 2003). In addition, NDMA may be present in source water under the influence of wastewater discharge. During dry seasons, wastewater effluent may comprise a significant fraction of the volume of water present in a river or stream. A waterway experiencing this condition has become known as "effluent impacted" or "effluent dominated." The scenario in which a downstream municipality draws drinking water from this type of source is becoming more common as cities expand their reach to provide additional drinking water supplies. Inclusion of nitrosamines in the UCMR 2 will provide additional data regarding the presence of NDMA resulting from wastewater effluent or other sources in the United States drinking water supply (see Regulatory Response below).

## NITROSAMINES IN FOODS AND BEVERAGES

Nitrosamines have been detected in certain foods and beverages including cured meats, cheeses, beer and whisky. Nitrosamines form in cured meats because meats contain amines and sodium nitrite is added as a preservative. Due to toxicity concerns, however, adjustments to brewing, fermenting, and curing processes have been made and have led to a significant reduction in NDMA in these foods and beverages (Scanlan 2006).

## HEALTH RISKS

NDMA has a high chronic and acute toxicity. The USEPA, the Agency for Toxic Substances and Disease Registry, and the Department of Human Health Services, among others, have determined that based on animal testing NDMA may reasonably be considered a human carcinogen that is hazardous at low concentrations. The USEPA's Integrated Risk Information System (IRIS), a database containing toxicity information on hazardous substances, lists NDMA as a probable human carcinogen with a one in one million lifetime cancer risk (10-6) in drinking water at a concentration of 0.7 ppt consumed by a 70 kg person drinking 2 liters of water per day (de minimis levels are listed for other nitrosamines in Table 1). There is general agreement within the toxicological community that NDMA, even at very low concentrations, presents a health risk.

## UCMR 2

In August 2005, the USEPA released its second proposed Unregulated Contaminant Monitoring Rule (UCMR 2). This rule requires that utilities serving greater than 10,000 customers test for 26 environmental contaminants and submit the results to a central EPA database. Among the 26 contaminants are six nitrosamines, including NDMA (Table 1). Data collected under UCMR 2 are to assist in regulatory determination. From its distribution in drinking water, regulators determine a contaminant's potential impact on human health. The UCMR helps provide data for that effort. The first UCMR, UCMR 1, was promulgated in 1999. For a list of the other contaminants and for details on UCMR 2, visit the USEPA website http://www.epa.gov/safewater/ucmr/.

## REGULATORY RESPONSE

The province of Ontario, Canada has set a drinking water standard for NDMA of 9 ppt. Ontario is the only state, provincial, or federal government that has promulgated a formal drinking water standard for a nitrosamine. However, at the state level in the U.S., the California Department of Health Services has set notification levels for NDMA, NDEA, and NDPA at 10 ppt. In addition, in early 2006, California became the first U.S. state to set a public health goal for NDMA (at 3 ppt). This action is a precursor to formal regulation. At the federal level in the U.S., NDMA is listed on the 2001 CERCLA Priority List of Hazardous Substances and, as has been mentioned, the nitrosamine group is included in the second proposed UCMR (see inset above). Playing a role in very low regulatory standards is the improvement of analytical methods for detecting NDMA. Laboratories, currently using high resolution GC/MS techniques, can detect and report NDMA at sub part per trillion levels.

## TREATMENT TECHNOLOGIES

NDMA and other nitrosamines are not easily removed from water because they are generally highly soluble, resist adsorption, and have low volatility. Thus, traditional treatment technologies such as flocculation, sand filtration, carbon adsorption and air stripping fail to sufficiently remove NDMA. Even advanced treatment technologies such as membranes and ozone are inadequate. NDMA passes through reverse osmosis membranes due to its low molecular weight and ozone is ineffective because the reaction rates of NDMA with ozone and the hydroxyl radical are relatively slow (for example, the reaction rate of NDMA with the hydroxyl radical is ten times slower than that of 1,4-dioxane, another recalcitrant environmental contaminant). However, NDMA does degrade relatively quickly when exposed to ultraviolet light (a process known as UV-photolysis).

This is cost-effectively performed in optimized UV reactors containing lamps with the spectral characteristics needed to destroy NDMA. For this reason, Trojan's UV technologies are very effective in removing NDMA from water.

In addition, the use of UV as a disinfection technology in the wastewater or drinking water plant limits the formation of NDMA as a by-product of disinfection with chlorine or chloramines. Therefore, UV is effective in two ways:

1. V treats NDMA and other nitrosamines by direct UV-photolysis

2. UV disinfection prevents the formation of NDMA by significantly reducing or eliminating the use of chlorine or chloramines.

**Table 1.** Nitrosamines included in the UCMR 2

| Nitrosamine | Acronym | Risk Level* (ppt) | Chemical Formula | Molecular Weight (amu) |
|---|---|---|---|---|
| *N*-nitrosodimethylamine | NDMA | 0.7 | $(CH_3)_2N\text{-}N{=}O$ | 74.1 |
| *N*-nitrosodiethylamine | NDEA | 0.2 | $(C_2H_5)_2N\text{-}N{=}O$ | 102.1 |
| *N*-nitrosodibutylamine | NDBA | 6 | $(C_4H_9)_2N\text{-}N{=}O$ | 158.3 |
| *N*-nitrosodipropylamine | NDPA | 5 | $(C_3H_7)_2N\text{-}N{=}O$ | 130.2 |
| *N*-nitrosomethylethylamine | NMEA | 1.5 | $C_3H_8N\text{-}N{=}O$ | 88.13 |
| *N*-nitrosopyrrolidine | NPYR | 20 | $C_4H_8N\text{-}N{=}O$ | 100.1 |

* $10^{-5}$ risk level in drinking water [IRIS and CDHS webites]

# FACTSHEET

## TROJAN – TREATING MULTIPLE CONTAMINANTS WITH ONE UV SYSTEM

As an added benefit to NDMA treatment, upon passing through a Trojan UV-oxidation system the water is treated for chlorineresistant pathogenic microorganisms. In addition, UV in conjunction with hydrogen peroxide (UV-oxidation) treats other organic compounds that may be present in the water. Examples of compounds amenable to treatment by UV-oxidation include a variety of potential endocrine disruptors and pharmaceuticals, 1,4-dioxane, volatile organic compounds (VOCs), pesticides, and taste and odor-causing compounds such as MIB and geosmin.

For more information regarding the treatment of multiple contaminants using Trojan's UV solutions, including nitrosamines treatment, please contact Trojan.

This TrojanUVPhox™ at the California Domestic Water Company is one of five Trojan projects in the San Gabriel Valley, CA that treats NDMA in drinking water to less than 2 parts per trillion.

**References:**

Mitch, W. A., and D. L. Sedlak. 2002. Formation of *N*-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. Environ. Sci. Technol. Vol. 36, No. 4. pp. 588-595.

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Barrett, S., et. al. Occurrence of NDMA in Drinking Water: a North American Survey, 2001-2002, AWWA Annual Conference 2003.

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North America T. 519.457.3400 F. 519.457.3030 www.trojanuv.com
Europe (please contact our UK office) T. +44 (1905) 771117 F. +44 (1905) 772270