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## Global Water Research Coalition

# Analysis, Toxicity, Occurrence, Fate, and Removal of Nitrosamines in the Water Cycle

Report of the GWRC Research Strategy Workshop

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# Global Water Research Coalition

*Global cooperation for the generation of water knowledge*

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*The members of the GWRC are: the Awwa Research Foundation (US), CRC Water Quality and Treatment (Australia), EAWAG (Switzerland), Kiwa (Netherlands), PUB (Singapore), Suez Environment – CIRSEE (France), Stowa - Foundation for Applied Water Research (Netherlands), DVGW-TZW Water Technology Center (Germany), UK Water Industry Research (UK), Veolia- Anjou Recherché (France), Water Environment Research Foundation (US), Water Research Commission (South Africa), WaterReuse Foundation (US), and the Water Services Association of Australia.*

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## **EXECUTIVE SUMMARY**

Nitrosamines are known to be very toxic and carcinogenic chemicals. For most of them, carcinogenic effects have been observed at concentrations in the very low ng/L range and thus their occurrence in the aquatic environment has to be regarded as a cause for concern. On October 12 and 13, 2006 a GWRC workshop on analysis, toxicity, occurrence, fate, and removal of nitrosamines in the water cycle was hosted at TZW in Karlsruhe, Germany. With TZW as lead agent, the organisation of the workshop was supported by AwwaRF, CIRSEE, US EPA and Kiwa. At the workshop, representatives of the GWRC member organisations and invited experts presented the latest results of their research activities.

The presentations covered the state-of-the-art in analysis of nitrosamines, their toxicological evaluation, their sources, their occurrence and fate in the water cycle, and their behaviour during drinking water treatment. After a detailed discussion, knowledge gaps and needs for further research were identified. Based on a prioritisation of these research needs, all workshop participants agreed that understanding the sources and prevalence of nitrosamines in the water cycle would be of major interest for all GWRC members and thus a draft proposal for a future GWRC research project on nitrosamines was developed. The proposed project focuses on the identification of sources for nitrosamines (NDMA, NMOR) and includes the exchange of analytical methods (training, inter-laboratory comparison), an extensive occurrence study (wastewaters, raw waters (groundwater and surface waters) and potable and non-potable finished waters) in the GWRC member states and detailed laboratory-based studies on the behaviour of specific nitrosamine precursors. One of the main outcomes of the project will be a recommendation for minimisation strategies which can be used by drinking water utilities, wastewater utilities, and authorities.

# 1 INTRODUCTION

## 1.1 Background

Nitrosamines are known to be very toxic and carcinogenic chemicals. For most of them, carcinogenic effects have been observed at concentration levels in the very low ng/L range and thus their occurrence in the aquatic environment has to be regarded as a cause for concern. Only few years ago, N-nitrosodimethylamine (NDMA) was found to be a by-product during disinfection of wastewaters and drinking waters with chloramine or chlorine, but other nitrosamines, like N-nitrosomorpholine (NMOR), have recently also been detected in source waters influenced by industrial wastewater discharges. Although the toxicological data base on nitrosamines is quite complete, a comprehensive risk assessment of the occurrence of nitrosamines in drinking waters is difficult. Different action levels in drinking water have been established in different countries, most of them not only considering the toxicological data sets but also taking into account that there are other relevant sources for nitrosamine uptake. Possible sources of nitrosamines include fried bacon, cured meats, beer, non-fat dry milk, tobacco products, gastric juices, rubber products, and certain cosmetics.

In 1956, Barnes and Magee discovered during a routine screening of chemicals that NDMA produces liver tumors in rats. In the early 1970s, outbreaks of liver disorders including cancer in farm animals in Norway could be related to the consumption of herrings preserved by sodium nitrite. This finding was the starting point for a systematic investigation of the effects of nitrosamines in food. In the following years, several toxicological studies were performed to evaluate the effects of nitrosamines in cured meat. At the same time, reliable analytical methods were established that enabled the determination of nitrosamines in food and beverages.

For environmental waters however, analytical methods for the determination of nitrosamines, which provide sufficient sensitivity to monitor the low levels of concern, have become available only few years ago. Therefore, data on occurrence and fate of nitrosamines in the water cycle are still scarce. In some countries, monitoring activities have been initiated recently, mainly focusing on the occurrence of nitrosamines in drinking waters.

## 1.2 The workshop

As the issue of nitrosamines in the water cycle is part of the research agenda of several GWRC members, it was the idea to exchange the information about ongoing research activities and available results during a GWRC workshop. This workshop was hosted at the offices of TZW in Karlsruhe, Germany on October 12 and 13, 2006. With TZW as lead agent the organisation of the workshop was supported by AwwaRF, CIRSEE, US EPA and Kiwa.



At the workshop, representatives of the GWRC member organisations and invited experts presented the latest results of their research activities. The presentations covered the state-of-the-art in analysis of nitrosamines, their toxicological evaluation, their sources as well as their occurrence and fate in the water cycle, and their behaviour during drinking water treatment. After a detailed discussion of the presentations, knowledge gaps and needs for further research were identified. Based on these research needs, a draft proposal for a future GWRC research project was developed.

This workshop report will briefly summarise the presentations given during the workshop, the outcomes and conclusions as well as the research initiative launched during the workshop.

## 2 CURRENT KNOWLEDGE ON NITROSAMINES

### 2.1 Sources of nitrosamines in the aquatic environment and formation during disinfection processes

Possible sources of nitrosamines in the aquatic environment include industrial production processes (e.g. rubber or leather manufacturing, chemical industries, metal industries, pesticide or rocket fuel production), personal care products (cosmetics, tobacco products) as well as food-stuff (fried bacon, cured meats, non-fat dry milk, cheese, fish, meat, beer). Nitrosamines released from these sources can either result in direct uptake by humans or in a discharge into primary wastewaters. It is well known that nitrosamines are not well eliminated during wastewater treatment processes and thus a discharge into the respective surface waters is likely. Furthermore nitrosamines might be formed within the wastewater treatment plant (WWTP), either by nitrosation of aliphatic amines or by wastewater chloramination. Nowadays, chloramination is also recognised as a source of nitrosamines in drinking waters. In addition to this, some polyelectrolytes and ion exchange resins used during the drinking water treatment process might act as sources of nitrosamines.

Formation mechanisms for nitrosamines during chloramination of natural waters are still subject of ongoing research. Previous studies indicated that oxidation of dimethylamine by monochloramine to unsymmetrical dimethylhydrazine (UDMH) is the key reaction in the formation pathway of NDMA. Results from recent studies, however, have disproved this hypothesis and a chlorinated form of UDMH, which is formed by reaction of dimethylamine with dichloramine, is now regarded as a key element of the formation pathway. This chlorinated UDMH species can then be further oxidised to NDMA either by monochloramine or dissolved oxygen.

### 2.2 Toxicity

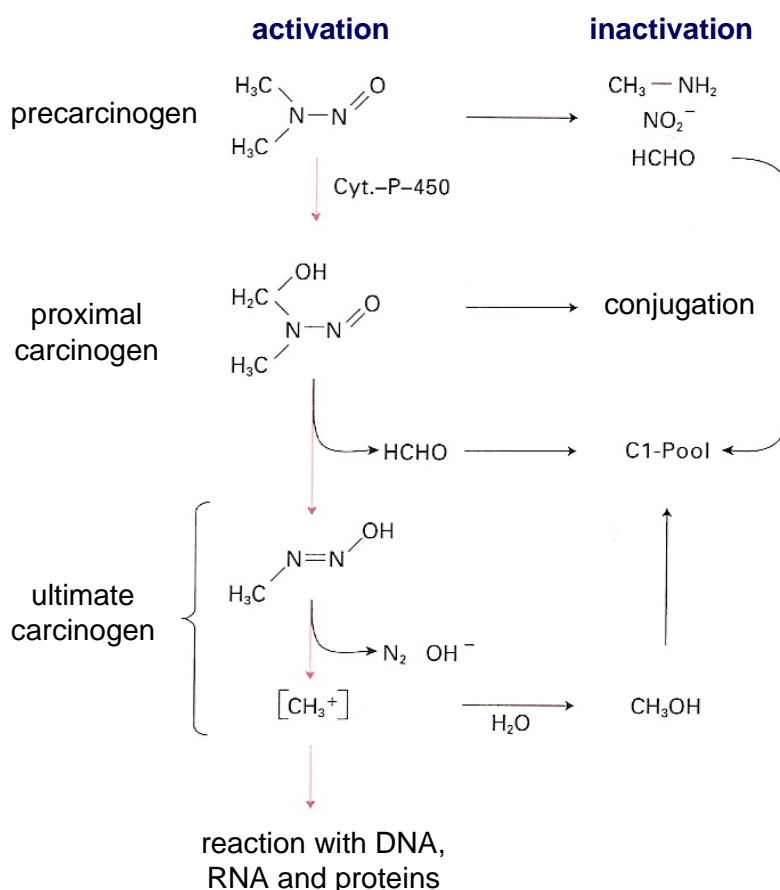
Looking at the possible exposure of humans to nitrosamines, one has to distinguish two major pathways, exogenous exposure and endogenous exposure. Exogenous exposure can be either related to industrial manufacturing processes, e.g. during manufacturing of rubber, leather, metal, during the production of pesticides or detergents, or in fish industries, or it can be related to lifestyle products as tobacco, food, cosmetics, pharmaceuticals, or household cleaners. Endogenous exposure covers the uptake of precursors including nitrite and nitrosable amines and their transformation into nitrosamines within the human body.

The per-capita exposure to NDMA is estimated to 80 to 300 ng per day. A more recent study in Spain yielded an uptake of 114 ng NDMA per day via food. NDMA levels in beer have been

determined to be between 0 and 0.5 µg/L, whereas in cured meat 0.3 to 1.0 µg/kg NDMA have been found.

Possible routes of exogenous exposure to nitrosamines include inhalation, ingestion, and dermal contact. It was found that NDMA resorption after oral intake takes place via the upper part of the small intestine. Most of the nitrosamines are efficiently metabolized during liver passage (first pass metabolism), whereby 60% of the N-alkyl nitrosamine dose is transferred to carbon dioxide. Only small amounts of the adsorbed nitrosamines are excreted via urine and faeces and only small amounts are distributed systematically in the human body. The latter process becomes more relevant at higher doses of nitrosamines.

With respect to toxicity of nitrosamines, carcinogenicity is the most relevant endpoint. Figure 1 gives a schematic presentation of the biotransformation of NDMA leading to structural changes of DNA or RNA.



**Figure 1:** Endogenous biotransformation of NDMA

Acute toxicity of nitrosamines is rather low. LD<sub>50</sub> values are 40 mg/kg for NDMA, 280 mg/kg for NDEA, and 1200 mg/kg for NDBA (rat, oral). In most cases studied so far, nitrosamine ad-

ministration resulted in liver damages. Chronic toxicity of nitrosamines leads to the same hepatotoxic effects which are often accompanied by the formation of tumors. Up to now, approximately 300 nitrosamines have been tested for toxicity and 90% have been identified as carcinogenic in a wide variety of experimental animals (more than 30 species including primates). Until now, no animal is known in which NDMA does not induce any tumor, strongly supporting the assumption that it is also carcinogenic to humans. Most of the nitrosamines act rather organ specific, e.g. for NDMA and NMOR, the liver is the target organ. NDMA administered to pregnant rats and mice may cause cancer in the offspring, i.e. NDMA is also a transplacental carcinogen.

### 2.3 Regulatory aspects

In a number of test systems for gene mutation it could be proven that NDMA is mutagenic. For genotoxic compounds, however, the establishment of a threshold value is impossible as already a very small amount of a genotoxic substance may induce cancer. Thus, threshold values for those compounds have to be based on acceptable additional cancer risks. In most countries an additional cancer risk of one in a million for lifetime exposure to a chemical is used for the deduction of threshold values. Table 1 gives an overview of the  $10^{-6}$  cancer risk levels for the most relevant nitrosamines as published by the US Department of Health and Human Services.

**Table 1: Cancer risk levels for nitrosamines (Source: US Department of Health and Human Services, 2005)**

Nitrosamine	Short form	$10^{-6}$ cancer risk level (ng/L)
N-Nitrosodimethylamine	NDMA	0.7
N-Nitrosomethylethylamine	NMEA	2
N-Nitrosodiethylamine	NDEA	0.2
N-Nitrosodi-n-propylamine	NDPA	5
N-Nitrosodi-n-butylamine	NDBA	6
N-Nitrosodiethanolamine	NDELA	10
N-Nitrosopiperidine	NPIP	0.8
N-Nitrosopyrrolidine	NPYR	16
N-Nitrosomorpholine	NMOR	0.8

In the **US**, there is no federal requirement to control nitrosamines in drinking waters. The US Environmental Protection Agency (EPA) has not yet set any maximum contaminant level goal (MCLG) or maximum contaminant level (MCL) for nitrosamines in drinking water. Up to now, nitrosamines are not covered by the Disinfection By-product Rule (DBP Rule) because during the negotiations of Stage 2 DBP Rule (1999/2000), there was very little evidence of occurrence of NDMA in drinking waters. Currently, the EPA Office of Science and Technology is preparing a draft Health Advisory for NDMA. To learn more about their national occurrence in US waters, NDMA and five other nitrosamines (NDEA, NDBA, NDPA, NMEA, and NPYR) will be monitored under the Unregulated Contaminant Monitoring Rule (UCMR). Cycle 2 of this monitoring program (UCMR2) will start in 2007 and EPA Method 521 will be used to analyse monitoring data (see Chapter 2.4). Furthermore, NDMA will likely be listed in the next Contaminant Candidate List (CCL 3) which will be published in 2008.

The California Department of Health Services (DHS) has set notification levels of 10 ng/L for NDMA (valid since 1998), 10 ng/L for NDEA (valid since 2004), and of 10 ng/L NDPA (valid since 2005). DHS recommends removing a source from service at levels of 200 ng/L NDMA, 100 ng/L NDEA, or 500 ng/L NDPA. In 2006, a draft Public Health Goal (PHG) of 3 ng/L NDMA was published by the Office of Environmental Health Hazard Assessment (OEHHA) in California.

**Canada** has added NDMA to the list of toxic substances in 2003 and has recommended risk reduction by limiting exposure (pesticides, food and water).

In **the Netherlands**, the National Institute for Public Health and the Environment (RIVM) proposed in 2004 a provisional guideline value for NDMA in drinking water of 12 ng/L.

In **Germany**, NDMA and NMOR are classified as B2 carcinogens, i.e. probable human carcinogens. In 2005, the Federal Environmental Agency (UBA) has recommended an ad-hoc guideline value of 10 ng/L for NDMA and NMOR in drinking water. This value, however, is not only based on toxicity data but also takes into account other sources of nitrosamines than drinking water.

## **2.4 Analysis of nitrosamines**

Due to their extremely high toxicity, very sensitive analytical methods are mandatory for the determination of relevant levels of nitrosamines in water.

EPA Method 521 describes the analysis of NDMA and six additional nitrosamines (NDEA, NDBA, NDPA, NMEA, NPIP, and NPYR) at low ng/L levels in water. NMOR, however, is not included in this method (because of laboratory background contamination at low concentrations). The method is based on a solid-phase extraction with coconut charcoal as sorbent and dichloromethane as eluent. Analysis of the nitrosamines is done by GC/CI-MS-MS with large-volume in-

jection. NDMA-d6, NDEA-d10 and NDPA-d14 are used as internal standards. With this method a detection limit for NDMA of 0.28 ng/L can be achieved.

Another method for the trace-level analysis of eight nitrosamines (NDMA, NMEA, NDEA, NDPA, NDBA, NMOR, NPIP, and NPYR) is based on solid-phase extraction onto a “two-layered mixed bed” consisting of a C18 layer and an activated carbon layer. Similar to the EPA method, dichloromethane is used as eluent and subsequent determination is done by GC-CI-SIM-MS with large-volume injection (50 µL). NDMA-d6, NDEA-d10, NDPA-d14, and NPYR-d8 are used as internal standards and iso-butane is used as reagent gas for chemical ionisation. Limit of quantification for NDMA is 0.36 ng/L. For the other nitrosamines, values between 0.25 and 1.1 ng/L could be achieved. The precision of the method was shown to be better than 9%, method blank values were always below 0.2 ng/L. For verification of positive NDMA results, the extract is re-analysed after UV irradiation. As NDMA is known to be photo-labile, NDMA peaks disappear after UV treatment and thus can be distinguished from possible interferences. Stability experiments have proven that the nitrosamines under investigation are stable in both river water and drinking water for more than 20 days when stored at 4°C.

In a research effort different low cost methods for analysis of NDMA and other nitrosamines in different water matrices (WWTP effluents and drinking water) were compared. For extraction of the analytes liquid-liquid extraction, solid-phase extraction onto an Ambersorb 572 resin and cartridge solid-phase extraction on different Ambersorb and Envicarb media were compared. Quantitation was done by GC/MS using chemical ionisation with methanol. Best recoveries and consequently best detection limits for a variety of nitrosamines (NDMA, NMEA, NDEA, NMOR, NPYR, NDPA, NPIP, and NDBA) were obtained for solid-phase extraction. All methods, however, were suitable for analysing nitrosamines in different matrices and all of them met the regulatory acceptance level of 70 to 130%. The SPE based methods were most effective at low levels whereas the methods using liquid-liquid extraction became acceptable for nitrosamine concentrations above 10 ng/L. Time consumption for the different methods was found to be comparable.

An alternative simple and low cost method for the extraction of NDMA, NMEA, NDEA, NDPA, NMOR, NPYR, NPIP, and NDBA is the application of solid-phase micro extraction (SPME) technique. This technique can be easily automated and can directly be coupled to a gas chromatographic system. A comparison of direct (liquid) SPME to headspace SPME with different fibre materials yielded slightly better recoveries for the headspace method. Best recoveries were obtained with a 75 µm carboxene/polydimethylsiloxane coated fibre. Addition of sodium chloride (100% saturation) also significantly enhanced the extraction yield when using headspace SPME. Detection limits with this technique are in the range of 100 ng/L (depending on composition of

the matrix) and thus too high for drinking water analysis at regulatory levels. For screening purposes at higher concentration levels, however, SPME offers an interesting alternative for pre-concentration of nitrosamines.

## **2.5 Occurrence of nitrosamines**

### **2.5.1 US**

In the United States a lot of data are available on the occurrence of nitrosamines, especially NDMA, in wastewaters and drinking waters. Between 2001 and 2004, several surveys on nitrosamine occurrence in drinking water treatment plants were performed. Most of them focused on NDMA but some also covered other nitrosamines of interest. In most of the systems using chlorination or chloramination, NDMA was detected in the effluent waters, especially when the raw water was impacted by wastewater effluents. Concentration levels ranged from few ng/L up to more than 50 ng/L and were found to be higher for systems applying chloramination than for those applying chlorination. Whenever distribution systems were included in the survey, a significant increase of NDMA levels during distribution was observed. Other nitrosamines than NDMA turned out to be of minor importance.

As already mentioned in Chapter 2.3, NDMA, NDEA, NDBA, NDPA, NMEA, and NPYR will be monitored under the Unregulated Contaminant Monitoring Rule (UCMR). Cycle 2 of this monitoring program will start in 2007 and EPA Method 521 will be used to analyse monitoring data (see Chapter 2.4).

In 2004, a survey on NDMA occurrence in US wastewaters was conducted. In the raw sewage, NDMA levels between 7 and 790 ng/L and a median concentration of 88 ng/L were found. The median value for NDMA in the primary effluent was 73 ng/L indicating that there is not much NDMA reduction during the treatment process. In a recent study on the occurrence of nitrosamines in WWTP effluents, NDMA levels between 8 and 400 ng/L and NMOR levels between 56 and 1390 ng/L were found. Other nitrosamines as NMEA, NPIP, NPYR, and NDEA were only rarely detected.

### **2.5.2 Australia**

Problems with NDMA in Australia are closely related to the special water supply situation in the country. Drinking water is transported over large distances, detention times can be up to months. Most of the distribution systems are above ground at temperatures of ca. 40 °C. As a consequence, high doses of chloramine have to be used (up to 4.2 mg/L) and booster chloramination is a common process. Recent studies have shown that under these conditions NDMA levels up to 90 ng/L can be formed. Ongoing research in Australia focuses on the establishment of a

monitoring system, on an optimisation of the treatment process to reduce chloramine levels and the identification of precursor compounds.

### **2.5.3 UK**

In the UK only limited amount of data on the occurrence of nitrosamines is available so far. First analyses of drinking water samples on NDMA were performed in winter 2006 targeting water treatment systems where NDMA most likely will be formed, i.e. those systems that use either chloramination for residual disinfection or chemical treatment or ion exchange for nitrate removal. During this monitoring, no NDMA was detected at concentrations above the limit of detection of 10 ng/L. A current project in the UK includes a survey of 15 water treatment works with about 240 samples being analysed for NDMA (besides standard water quality parameters). An improved analytical method will be used with a reporting level around 2 ng/L.

### **2.5.4 France**

Already in 1982, a screening performed by the Suez Environment subsidiary Degremont yielded the occasional presence of nitrosamines in WWTP influents and effluents. During analysis of nitrosamines in French surface waters in 1984, 11 ng/L NDMA and 114 ng/L NMOR were found in the river Seine. At this time, it was also found that nitrosamine levels might increase during drinking water treatment, especially after chlorination. Resins used for denitrification and, more recently, cationic polymers were also identified as sources of nitrosamines (NDMA, NDEA, NDPA, and NMEA).

### **2.5.5 The Netherlands**

In 1996, NDMA concentrations below 100 ng/L were reported for rivers Rhine and Meuse in the Netherlands. In 2002, improved analytical methods were used and 7 ng/L NDMA were detected in river Rhine and 2 ng/L in river Meuse. In 2003 a screening of NDMA in Dutch raw and drinking waters were performed and between < 2 and 10 ng/L were found in raw waters and < 2 ng/L in drinking waters. In 2005, NDMA was monitored on a monthly basis in river Rhine at Lobith, in the Lek Canal at Nieuwegein and in Lake IJsselmeer. In river Rhine, concentration levels around 2 ng/L were found in almost all samples under investigation. In the Lek Canal, NDMA was only sporadically found at low concentrations and in Lake IJsselmeer, NDMA levels were always below 2 ng/L. An extensive monitoring (120 samples) in 2006 at different stages of drinking water production (dune infiltration, coagulation, rapid and slow sand filtration, activated carbon filtration, ozonation and UV/H<sub>2</sub>O<sub>2</sub> treatment) yielded no positive results for NDMA.



### **2.5.6 Germany**

In Germany, monitoring of nitrosamines in effluents of municipal and industrial WWTPs was performed. NDMA and NMOR were identified as key compounds with concentrations of up to 15 µg/L for NDMA and up to 13 µg/L for NMOR. However, no further efforts were made to identify the sources of these elevated nitrosamine levels. A recent survey on the occurrence of nitrosamines in German river waters yielded NDMA concentrations between < 0.3 and 29 ng/L and NMOR levels between < 0.3 and 92 ng/L. For example in the river Rhine, maximum concentrations of up to 12 ng/L NDMA and up to 13 ng/L NMOR were found. In the river Main, which is strongly affected by industrial wastewaters, higher maximum levels of up to 29 ng/L NDMA and up to 92 ng/L NMOR could be detected.

## **2.6 Removal of nitrosamines**

### **2.6.1 Biodegradation**

Several studies described in the literature indicate that NDMA is biodegradable under environmental conditions (e.g. in soil or in municipal wastewater treatment plants). The extent of microbial degradation of NDMA in aqueous and soil systems, however, has not yet been clearly established. Furthermore, in many soil experiments there is no clear differentiation between microbial degradation and volatilisation. For water/soil systems half-lives of 12 to 448 days are reported whereby no major differences between aerobic and anaerobic conditions can be found. Degradation very much depends on the adaptation of micro-organisms, the nutrient status of the water, and the availability of competitive substrates. If nitrosamines are metabolised by microbial communities, the degradation process most likely is co-metabolic. Up to now, the metabolic degradation pathway of NDMA has not been fully elucidated, even if there are some hints on a similarity between the bacterial and the mammalian metabolism pathway. For the metabolism of NDMA in mammalian cells, three major pathways have been identified: denitrosation (leading to methylamine), demethylation (leading to the carcinogenic methyl cation), and a reductive route (leading to methylamine, with formaldehyde as intermediate).

In a project on occurrence, fate, and transport of NDMA in groundwater it was found that NDMA is not significantly transformed or removed from the system. It was found that NDMA is not being adsorbed or otherwise retarded with respect to groundwater flow. Biodegradation might occur in some parts of the aquifer but not in others and thus biodegradation was not identified as option to decrease NDMA concentrations below levels of concern.

In bench-scale filters simulating the aerobic degradation during bankfiltration or slow sand filtration, NDMA was very biodegradable whereas the other nitrosamines under investigation

(NMEA, NDEA, NDPA, NDBA, NPIP, NPYR, and NMOR) were persistent. This result of a laboratory-scale experiment was confirmed by a long-time monitoring of a riverbank filtration site in Germany where NDMA was effectively removed during underground passage while NMOR was found in the bankfiltrated water. Other nitrosamines than NDMA and NMOR were not present in the river water, and thus their behaviour could not be evaluated.

### **2.6.2 Activated carbon filtration**

NDMA exhibits a log  $K_{OW}$  value of -0.57, indicating that it is a very hydrophilic compound with high water solubility. Consequently, NDMA and also the other nitrosamines are only poorly adsorbable onto activated carbon as well as onto polymeric materials. Better adsorbability, though still poor, was found for adsorption of NDMA onto Ambersorb 572, a carbonaceous resin, and on a carbon made from coconut shells. Removal of nitrosamines by adsorption processes thus is associated with short regeneration cycles and high costs and is therefore not a cost-effective technology. For some activated carbon filters, however, an increase in removal efficiency for NDMA was observed with increasing running time. This effect can most likely be explained by an increasing biological activity of the filter with increasing running time and thus biodegradation is the dominant mechanism of NDMA removal.

### **2.6.3 Ozonation**

Ozonation also seems not to be a favourite option for removal of nitrosamines. Rate constants for the reaction of NDMA with oxidants are  $0.052 \text{ M}^{-1}\text{s}^{-1}$  for ozone,  $< 0.001 \text{ M}^{-1}\text{s}^{-1}$  for chlorine dioxide,  $1.9 \text{ M}^{-1}\text{s}^{-1}$  for iron(VI) and  $4.5 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$  for the hydroxyl radical. Thus, only the application of advanced oxidation processes (AOP) where the hydroxyl radical is the main oxidant can lead to an efficient removal of nitrosamines. Laboratory-based experiments with environmental waters, however, prove that even with advanced oxidation processes high doses of oxidants have to be applied to achieve substantial removal rates for nitrosamines.

On the other hand, pre-oxidation seems to be a good option for removal of precursor compounds leading to the formation of NDMA during subsequent chloramination or chlorination. In laboratory-based experiments ozone was found to be a more efficient oxidant for reducing the NDMA formation potential than chlorine dioxide.

### **2.6.4 Other treatment technologies**

Up to now, micro, ultra, and nano filtration for nitrosamine removal have not been investigated in more detail. However, experience shows that micro or ultrafiltration is mainly dependent on the size of the substance to be removed. Due to its small size, NDMA provides no favorable proper-

ties concerning its removal from the water phase by membrane filtration. In nano filtration, however, removal is not only based on sieving effects but also on adsorptive characteristics and affinity of the membrane material towards NDMA. Thus, depending on the membrane material, nano filtration may offer some potential for NDMA removal, even though economical considerations may prohibit the large scale implementation of this process in drinking water treatment. Furthermore, a removal of 12% for NDMA by reverse osmosis with cellulose acetate membranes is described in literature. The removal was enhanced to 40% when thin film composite membranes were used.

The most promising technology investigated in literature is the photolysis of NDMA by UV irradiation and some pilot-scale and industrial-scale applications are described in literature. A comparison of the UV dosage required for NDMA removal of one order of magnitude (approximately 1,000 mJ/cm<sup>2</sup>) with that for equivalent virus removal yields a ten times higher dosage. This means that an effective NDMA removal by UV irradiation leads to a complete disinfection of the treated water.

### 3 CONCLUSIONS

Based on the presentations given at the workshop and the very detailed discussions during and after the presentations, the following conclusions on the occurrence of nitrosamines in the water cycle can be drawn:

- There is no question about the toxicological relevance of nitrosamines. There is clear evidence that nitrosamines are carcinogenic to humans and that the concentration levels related to an additional cancer risk of one in a million for lifetime exposure are in the very low ng/L range for all of the relevant nitrosamines (e.g. 0.7 ng/L for NDMA).
- Methods for the analysis of nitrosamines in environmental waters are available and partly described in the literature section of this report. Some of them, however, do not cover all nitrosamines of interest (e.g. NMOR is not included as part of EPA method 521), while others are not sensitive enough to monitor nitrosamines down to the very low levels of concern and thus can only be used as screening methods at higher concentration levels. The available methods that enable the determination of all relevant nitrosamines at very low limits of detection are rather time-consuming and require expensive technical equipment and analytical expertise. Thus, there is a need for the development of sensitive, easy to use, low-cost method for nitrosamine analysis.
- Nitrosamine formation during chlorination and chloramination of drinking water has been extensively investigated during the last couple of years. NDMA has been identified as a compound formed during disinfection whereas the other nitrosamines are only of minor relevance. Most of the key-factors affecting the formation of NDMA during chloramination are known and operational practices for minimizing NDMA formation have been derived from laboratory-scale experiments (e.g. reducing disinfectant doses, lowering pH, minimising formation of dichloramine). In addition to this, treatment options for removal and identification of precursor compounds have been attempted in laboratory-scale experiments (e.g. biodegradation during riverbank filtration or slow sand filtration, pre-oxidation, activated carbon filtration). However, there are still open questions related to the formation mechanism of nitrosamines during disinfection and related to the identity of the precursor compound(s). Further pilot-scale and full-scale tests are necessary to further optimise operating conditions for minimising nitrosamine formation and to increase the knowledge of removal options for precursor compounds. Sorption and biodegradation of precursor compounds in the underground needs to be investigated in more detail including especially the impact of the redox milieu (e.g. biodegradation under anoxic conditions).

- Chemicals and resins used for coagulation or ion exchange are known to be important sources for nitrosamines and/or nitrosamine precursors. Therefore utilities should strive to select suitable coag/IX resins that minimise nitrosamine formation during drinking water treatment. If no appropriate resins can be found on the market, the design of alternative materials might be an interesting option. Thus, information of the manufacturers of such materials and discussions about possible alternatives are recommended.
- Occurrence data indicate that NDMA levels can increase in the distribution system. However, the underlying mechanisms and the key-factors that impact the formation of nitrosamines during water distribution are still unclear. The role of biofilms has to be investigated as well as the relevance of compounds leaching from pipe materials which might act as precursors for NDMA formation.
- Further research on nitrosamine formation during disinfection of drinking waters should also take into account other nitrogen-containing disinfection by-products (e.g. aliphatic nitro compounds).
- In addition to the formation of nitrosamines during chlorination and chloramination processes, other major sources for nitrosamine contamination seem to exist. From these sources, especially NDMA and NMOR are released into in aquatic environment. However, it is still unclear to what extent waste waters contaminate surface waters and to what extent source waters are contaminated by nitrosamines. Occurrence data for nitrosamines (especially for NMOR) in wastewaters and surface waters are limited. The nature of nitrosamine precursors and the underlying processes leading to the formation of nitrosamines, however, need further elucidation.
- Although quite a lot of research has been done on the removal of nitrosamines, UV irradiation still seems to be the only effective option for complete removal of NDMA. This technique, however, is characterised by a high energy demand and consequently is a very expensive one. Thus, cost-effective removal techniques for nitrosamines are still missing.

After a detailed discussion about prioritisation of research needs and consideration of ongoing or planned research activities, all workshop participants agreed that understanding the sources and prevalence of nitrosamines in the water cycle would be of major interest for all GWRC members. Based on the final conclusions, a project proposal for further research activities in the field of nitrosamines in the water cycle was prepared and is presented in Annex 4. The proposed project focuses on the identification of nitrosamine precursors (NDMA, NMOR), the exchange of analytical methods (training, inter-laboratory comparison), an extensive occurrence study (wastewaters, raw waters (groundwater and surface waters) and potable and non-potable finished waters)

in the GWRC member states, and detailed laboratory-based studies on the behaviour of specific precursors. One of the main outcomes of the project will be a recommendation for minimisation strategies which can be used by drinking water utilities, wastewater utilities, and authorities.

**ANNEX 1: List of workshop participants**

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<b>Name</b>	<b>Institute</b>	<b>E-mail</b>
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Hiba M. SHUKAIRY	EPA (US)	Shukairy.Hiba@epa.gov

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## **ANNEX 2: Workshop programme**

**Thursday, October 12, 2006:**

9:00 – 09:30	Welcome (Wolfgang Kühn)  Presentation of participants  Introduction: Purpose of the workshop (Frank Sacher)
09:30 – 10:30	Nitrosamines in the US: Current Status and Future Challenges (William Mitch)  Discussion
10:30 – 11:00	<i>Coffee break</i>
11:00 – 12:30	Nitrosamines – Toxicity and regulatory aspects in Europe (Carsten Schmidt)  Nitrosamines from US-EPA's perspective (Hiba Shukairy)  Analysis of nitrosamines (Auguste Bruchet & Mel Suffet, Carsten Schmidt)  Discussion
12:30 – 13:30	<i>Lunch</i>
13:30 – 15:30	Presentations of participants: Occurrence of nitrosamines  - Situation in France (Auguste Bruchet)  - Situation in Australia (Jim Morran)  - Situation in UK (David Holt)  - Situation in Germany (Carsten Schmidt)  - Situation in the Netherlands (Leo Puijker)  Discussion of presentations
15:30 – 16:00	<i>Coffee break</i>
16:00 – 17:30	Presentations of participants: Removal of nitrosamines  - Removal by biodegradation and activated carbon filtration (Carsten Schmidt)  - Removal by oxidative processes (Martin Krauss)  Research activities



- Water Reuse Foundation (Taylor Mauck)
- AwwaRF (Djanette Khiari)

Discussion of presentations,

Identification of knowledge gaps and research needs

**Friday, October 13, 2006:**

9:00 – 10:30	Summary of day 1 (Frank Sacher) Discussion and prioritisation of knowledge gaps
10:30 – 11:00	<i>Coffee break</i>
11:00 – 13:00	Preparation of project proposal(s) Follow-up actions Summary of the workshop (Frank Sacher)
13:00 – 14:00	<i>Lunch</i>
14:00	Closure of the workshop

### **ANNEX 3: List of research needs**

- Identification of sources for nitrosamines (NDMA, **NMOR**)
- Nitrosamine formation during disinfection
- Removal options for nitrosamines
- Identification of precursors
- Removal of (individual) precursor compounds
  - Pilot-scale and full-scale tests
  - Biodegradation (anoxic conditions)
  - Sorption
- Minimising nitrosamine formation
- Optimising operating conditions (contact time, pre-chlorination; take into account other DBP)
- Nitrosamine formation in distribution systems (biofilms; compounds leaching from pipe materials as precursors)
- Selection/design of better coag/IX resins
- Other nitrogen-containing DBPs
- Low-cost methods for nitrosamine analysis

### ANNEX 4: Project proposal for future research activities

<b>Project Title:</b>	<i>Understanding the sources and prevalence of nitrosamines in the water cycle</i>				
<b>Name of Proposer &amp; Affiliation:</b>					
<b>Collaborators:</b>	CIRSEE, EAWAG, KIWA, TZW, Yale University, CRC-WQT... WateReuse Foundation, AwwaRF, US-EPA,...				
<b>Estimated Total Cost of Research (Euro)</b>					
		100000	100000	100000	300000

<b>Background:</b>	<p style="text-align: center;"><b>Justification:</b></p> <p>Nitrosamines are among the most toxic and carcinogenic chemicals known. For most of them, carcinogenic effects have been observed at concentration levels in the very low ng/L range. N-nitrosodimethylamine (NDMA) was found to be a by-product of disinfection with chloramine or chlorine, but other nitrosamines like N-nitrosomorpholine (NMOR) have also been detected in source waters influenced by waste water discharges.</p> <p>During a GWRC workshop in Karlsruhe, the state-of-the-art in analysis of nitrosamines, their toxicological evaluation, their sources as well as their occurrence and fate in the water cycle, and their behaviour during drinking water treatment was presented. Knowledge gaps and needs for further research have been identified and prioritized. Based on the conclusions of the workshop, this project proposal has been prepared.</p>
<b>Consequences if work not carried out:</b>	Without understanding the sources and the mechanisms leading to the formation of, or contamination with nitrosamines it can not be guaranteed that the aquatic environment and especially the drinking water are free of carcinogenic compounds.
<b>Benefits to be achieved:</b>	
- Political	Striving to minimize health risks from carcinogenic compounds. Compliance with existing and future requirements and regulations. Recommendations for strategies to minimize nitrosamine levels in the water cycle.
- Economic	Minimizing costs for drinking water industries by improving raw water quality. Optimizing monitoring programmes with respect to nitrosamines.
- Technical	Understanding sources and mechanisms of formation of nitrosamines in the aquatic environment.

	Identifying operational or technical options for reduction of nitrosamine levels in waste waters and surface waters. Improving our understanding of various internationally used nitrosamine methods.
<b>Aiming to achieve:</b>	<b>Objectives:</b> Identifying and understanding sources and mechanisms of formation of nitrosamines (esp. NDMA and NMOR) in the aquatic environment.
<b>Specific questions answered:</b>	To what extent are source waters contaminated by nitrosamines? To what extent do waste waters contaminate surface waters? What is the source of NMOR? Are there specific sources for nitrosamines (e.g. IX resins, special production processes)?
<b>Tasks set for contractor:</b>	<b>Identification of sources for nitrosamines (NDMA, NMOR)</b> Phase 1: Exchange of analytical methods, training, inter-laboratory comparison Phase 2: Occurrence study (waste waters, raw water (groundwater and surface water) and potable and non-potable finished waters) in the GWRC member states <ul style="list-style-type: none"> <li>• Survey of existing occurrence and formation data</li> <li>• Planning of additional monitoring (identification of water utilities, identification of sampling sites that might have high nitrosamine levels, e.g. industrial waste waters (chemical, pharmaceutical, rubber industries, municipal wastewaters, coag/IX resins, pipe materials); the selection should include sites representative of all types of sources and should take into account regional aspects</li> <li>• Statistical design of the study</li> </ul> Phase 3: Detailed study on behaviour of specific precursors (laboratory-based studies based on existing knowledge and on the outcome of Phase 2) Phase 4: Evaluation of data Phase 5: Recommendations for minimization strategies (e.g. for drinking water utilities, waste water utilities, authorities,...) Phase 6: Identification of further knowledge gaps and research needs
<b>Deliverables:</b>	Final report summarizing information on sources and extent of nitrosamine contamination in the water cycle. Strategies for minimizing nitrosamine levels in the water cycle.
<b>Completion date to maximise benefits:</b>	2009
<b>Target audience for the output?</b>	Waste water industry, drinking water utilities, regulators, environmental protection agencies, pharmaceutical and chemical industries, consumers.

<p><b>Which groups should receive any reports resulting from this work?</b></p>	<p>GWRC member organisations and target audience.</p>
<p><b>Should the output be submitted for independent peer review to add authority to the work?</b></p>	<p>No.</p>

## ANNEX 5: Presentations of the workshop participants

### William A. Mitch: Nitrosamines in the US: Current Status and Future Challenges

– GWRC, 2006 –

## Nitrosamines in the US: Current Status and Future Challenges

William A. Mitch  
Department of Chemical Engineering  
Environmental Engineering Program  
Yale University

### Outline

- Nitrosamine Regulations
- Nitrosamine Occurrence
- Nitrosamine Precursors
- Nitrosamine Formation during Chlorination/Chloramination
  - Formation from secondary amines
  - Practical, cheap solutions
- Future Challenges

### Nitrosamine Regulations

- US EPA – no MCL
  - Not on CCL 2 → but in the future? Widespread occurrence
  - 10<sup>-6</sup> lifetime cancer risk drinking water concentrations similar

Nitrosamine	ng/L	
NDMA	0.7	IRIS
NDEA	0.2	
NMEA	2	

- States
  - CA DHS
    - NDMA – 10 ng/L notification (1998), 200 ng/L response
    - NDEA – 10 ng/L notification (2004), 100 ng/L response
    - NDPA – 10 ng/L notification (2005), 500 ng/L response
  - MADEP
    - NDMA – 10 ng/L guideline

### NDMA Occurrence in Drinking Water

- Awwarf – 2001-2002 survey of 21 plants (Barrett et al., 2003)
  - Only 1 detection in the influent, but not confirmed
  - Most plant effluents < 10 ng/L, but increase in distribution system
    - Highest for chloramination, and chlorine/anion exchange plants
- Luo et al., 2003
  - 11 plants with 3-48 ng/L NDMA
  - 4 > 10 ng/L (chloramines form more)
- Charrois et al., 2004
  - Chloraminated surface water (probably with wastewater impacts)
    - 67 ng/L in effluent, up to 180 ng/L in distribution system
    - 2-4 ng/L NPYR, and 1 ng/L NMOR

### NDMA Occurrence in Drinking Water

- Awwarf 3014 – ongoing
  - Analysis of NDMA, NMEA, NDEA, NPYR, NPIP, NMOR in 12 treatment plants
    - using chlorine, chlorine/chloramine, ozone/chlorine, ozone/chloramines
    - impacted by wastewater effluents, algal blooms or no impacts
    - also measuring precursor levels
- Awwarf 4019 – coming soon
  - Measurement of N-DBP formation during UV/chlorination or UV/chloramination
  - Includes nitrosamines
- Drinking Water Precursors Summary:
  - Coagulation polymers – more later
  - Anion exchange resins (nitrate/perchlorate)
    - May not require chloramines? (Najm and Trussell, 2001)
  - NOM? Or wastewater impacts?

### NDMA Occurrence in Wastewater

- Sedlak et al. 2004
  - raw sewage – 7-790 ng/L NDMA (median 88 ng/L)
  - residential sections – 17-63 ng/L – **mostly residential sources**
  - **industrial inputs can be important**
    - metam sodium for root control – 2,000 ng/L in sewer line
    - stock = 1.1 million ng/L
    - dimethyldithiocarbamate in printed circuit board operations
      - up to 56,000 ng/L in manufacturing plant effluents
      - small flows, but accounted for 22% of OCSD's NDMA inputs
    - auto antifreeze – 350,000 ng/L
    - **QCSD successfully worked with industry to limit discharges**
  - primary effluent (median 73 ng/L) – not much loss since not particle-bound
  - precursors in influent – DMA → 81 µg/L median
    - accounts for most of precursors

### NDMA Occurrence in Wastewater

- **Mitch and Sedlak, 2004; Sedlak et al., 2004**
  - secondary treatment
    - variable NDMA removal – 0-75%
    - >95% removal of DMA → not an important precursor
      - precursor concentrations – 2000-4000 ng/L
  - dimethylamides – hydrolyze to release DMA (dimethylformamide)
  - tertiary amines with DMA functional groups are precursors
    - DMA-based tertiary amine coag. polymers formed 400x more NDMA than DMA
    - quaternary amines are **NOT precursors**
    - tetramethylamine did not form NDMA during FP test

CN(C)R

### NDMA Occurrence in Wastewater

- **Schreiber and Mitch, 2006**
  - Measured 6 nitrosamines in WWTP effluents in CT
  - NDMA 8-400 ng/L
  - NMOR 56-1390 ng/L
    - no formation potential → industrial contaminant?
  - NMEA, NPIP, NPYR, NDEA rarely detected

### NDMA Precursors Occurrence in WW

- **Mitch and Sedlak, 2004**
  - particle-associated precursors from coag polymers – 50% of total
  - rest are low molecular weight (< 1000 Da)
  - polar – readily removed by RO
  - not very biodegradable – persist through nitrification/denitrification
  - WW precursors are THE important precursor source except for coag polymers and IX resins

(Gerecke and Sedlak, 2003; Mitch and Sedlak, 2004)

(Gerecke and Sedlak, 2003; Mitch and Sedlak, 2004)

### WW Impacts on DW Supplies - Precursors

- **Schreiber and Mitch, 2006**

Precursors accumulate in Quinnipiac River (CT) with WW discharges → Impact downstream users

River is 20-40% WW depending on season

→ WW impacts most likely source of NDMA precursors

→ NMOR – no formation potential

### WW Impacts on DW Supplies - WaterReuse

- **Pehlivanoglu-Mantas and Sedlak, 2005**
  - NDMA precursors decline by ~25% over 30 d in activated sludge inocula
- **Pehlivanoglu-Mantas et al., 2005**
  - Chlorination of WW containing ammonia for irrigation (2000 mg-min/L)
    - 120-490 ng/L in distribution systems
    - Long contact times lead to steady increases in NDMA
  - Chlorination of WW without ammonia for irrigation
    - no significant increase
- **Gan et al., 2006**
  - Irrigation with 114-1820 ng/L → < 5 ng/L in leachate from turfgrass
    - Lab studies indicate volatilization, not biodegradation
    - Aerobic biodegradation does occur (Sharp et al., 2005)

### Secondary Amines → Nitrosamines

Primary nitrosamines are unstable

#### Previous NDMA Formation Pathway Hypothesis

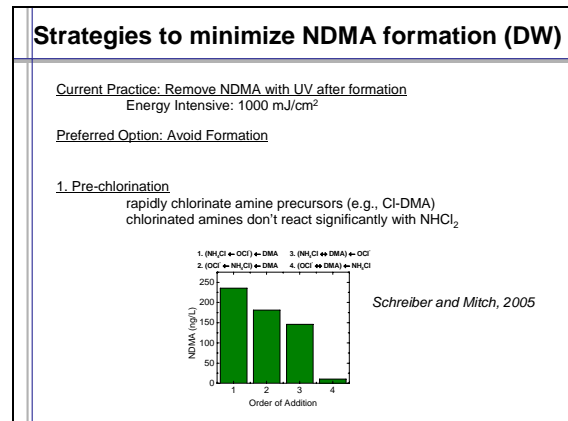
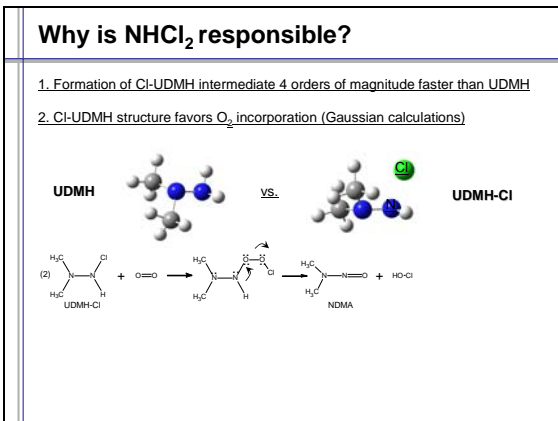
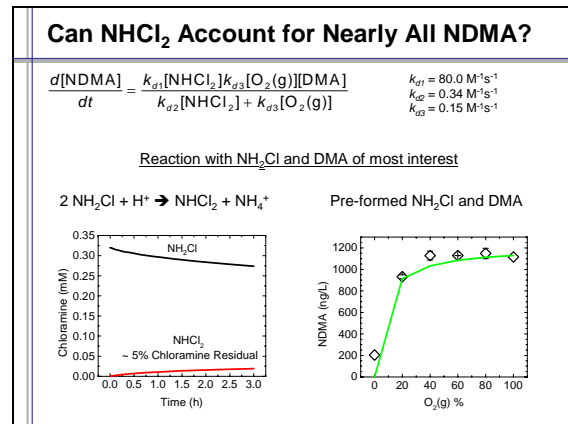
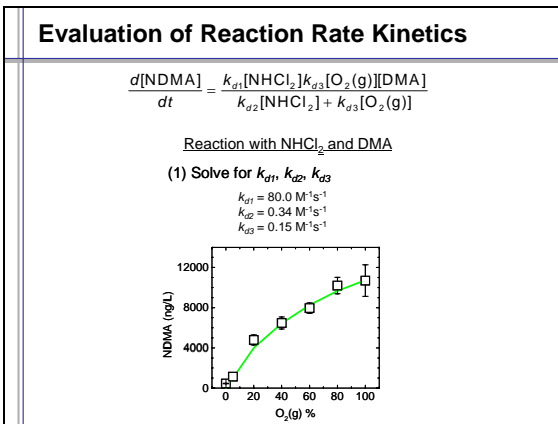
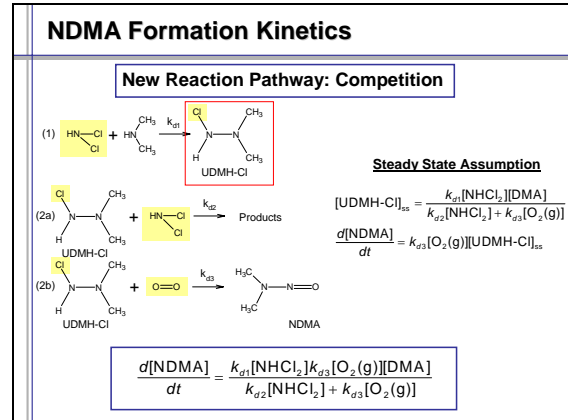
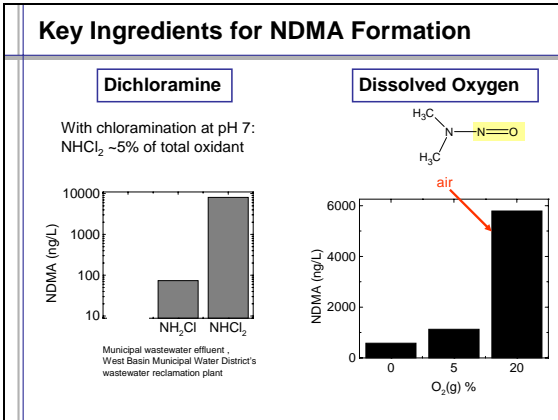
(Mitch and Sedlak, 2002; Choi and Valentine, 2002)

$$(1) \text{H}_2\text{N}-\text{Cl} + \text{H}_2\text{C}(\text{CH}_3)_2 \xrightarrow{k_1} \text{H}_2\text{N}-\text{C}(\text{CH}_3)_2 + \text{Cl}^- + \text{H}^+ \text{ slow}$$

$$(2) \text{H}_2\text{N}-\text{Cl} + \text{H}_2\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)_2 \xrightarrow{k_2} \text{H}_2\text{N}-\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)_2 + \text{NH}_4^+ + \text{Cl}^- \text{ fast}$$

**Problem: More NDMA formation from DMA than UDMH**

(Schreiber and Mitch, ES&T, Research ASAP)





### Strategies to minimize NDMA formation (WW)

**Preferred Option: Avoid Formation:**  
Minimize  $\text{NHCl}_2$  and  $\text{O}_2$

**2. Apply Pre-formed  $\text{NH}_2\text{Cl}$  to waters with  $\text{NH}_4^+$**   
Takes time to form significant  $\text{NHCl}_2$  via

$$2 \text{NH}_2\text{Cl} + \text{H}^+ \rightarrow \text{NHCl}_2 + \text{NH}_4^+$$

HOCI Injection

Cl:N > 1 here  
pH ≈ 7-8

• =  $\text{NH}_3$   
• =  $\text{NH}_2\text{Cl}$

$\text{NH}_3$  HOCl  
pH > 8.5

### Pilot Test: West Basin WWTP

Current = injection of free chlorine into  $\text{NH}_3$ -containing solution at pH 7

Method	$\text{NHCl}_2$	$\text{NH}_2\text{Cl}$
Current	~2.0	~1.5
Pre-Form	~0.5	~3.5

Method	NDMA (% increase)
Current	~160
Preform	~20

(Mitch et al., 2005)

### Strategies to minimize NDMA formation

**3. Reduce dissolved oxygen concentration**

Municipal wastewater effluent, Wallingford WPCF, Connecticut

Potential Configuration for WWTP

$\text{NH}_3$   $\text{Cl}_2$  tap water pH > 8.5

### Future Challenges

**1. Define Precursors?**

NDMA precursors are:  
Coagulants/IX resins  
WW NOM → not DMA (except sewage)

NMOR → no precursors

Other nitrosamines  
not secondary amines  
may not be WW-related  
→ but less important

NOM precursors operationally defined for treatment  
low molecular weight  
Sacher results (PAC)  
tertiary amines

mostly human waste → can't prevent

### Future Challenges

**2. Pilot Test Solutions?**

Drinking water – pre-chlorination/post chloramination

WW – activated sludge effluent de-aeration  
- pre-formed chloramine application

GAC-PAC

### Future Challenges

**3. Design better coag./IX resins**

Previous research has identified several concerns...

**BUT**

1. Lab studies indicate quaternary amines aren't precursors  
→ what is?
2. Both applications seem to require quaternary amines  
→ change to ethyl groups → NDEA, etc.

→ Work with manufacturers to design a better resin? Think outside the box?


## Carsten K. Schmidt: Toxicity of nitrosamines and regulatory aspects in Germany

TZW

### Toxicity of nitrosamines and regulatory aspects in Germany

Carsten K. Schmidt

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DVGW

TZW

### Historical milestones I

- Nitrosamines were first described in the chemical literature over 100 years ago, but did first not receive much attention
- in 1956 Barnes and Magee reported that NDMA produced liver tumors in rats (discovery during routine screening of chemicals)
- in the early 1970s there were outbreaks of liver disorders, including cancer, in various farm animals in Norway that consumed herring meal preserved by sodium nitrite - findings of NDMA in fish meal → starting sign for investigation of human food
- in the late 1960s researchers at the University of Nebraska Medical Center were studying nitrosamine formation from the drug aminopyrine
- mysteriously, when they used a new batch of aminopyrine, no nitrosamines were formed any longer (new batch was formulated with ascorbic acid as preservative)

DVGW

TZW

### Historical milestones II

- during the 1970s and 1980s, reliable analytical methods were established to determine nitrosamine levels in foods and beverages
- these methods were later also applied to a variety of other consumer products, occupational settings, and body fluids
- in the late 1970s, extensive attention was focused on the issue of nitrosamines in cured meats, and the removal of sodium nitrite as food additive was considered
- problem: effectiveness of nitrite against Clostridium botulinum (toxin production)
- solution: limitation of nitrite and admixture of ascorbic acid
- in 1980, several European scientists detected NDMA in beer, being formed by direct-fire drying of barley malt (gramine and NO<sub>x</sub>)
- solution: indirect-fire drying
- beer now contains only 2 % of the amount of NDMA that was present 20 years ago
- only recently: NDMA in drinking water, condoms, and balloons

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### Nitrosamines in food, body fluids, and occupational exposure

- Fried bacon
- Cured meats
- Beer
- Nonfat dry milk
- Tobacco products
- Gastric juices
- Rubber products
- Rubber manufacturing
- Metal industries
- Pesticide production and use
- Certain cosmetics
- Certain chemical manufacturing

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### Exposure to nitrosamines

total exposure

**exogenous exposure**

- lifestyle**
  - tobacco, tobacco smoke
  - food
  - cosmetics
  - pharmaceuticals
  - household cleaners
  - internal air
- work-related**
  - rubber industries
  - leather industries
  - metal industries
  - production of detergents
  - pesticide production
  - fish industry

**endogenous exposure**

- uptake of precursors**
  - nitrite
  - nitrogen oxides
  - nitrosable amines
- formation of precursors**
  - nitrate, nitrite (saliva, gastric juice)
  - amine formation

- estimated per-capita exposure to NDMA: 80-300 ng per day
- most recent study from Spain: 114 ng NDMA per day via food
- NDMA levels in beer: 0-0.5 µg/L
- NDMA levels in cured meat 0.3-1.0 µg/kg
- total exposure to volatile nitrosamines: 200-1000 ng per day

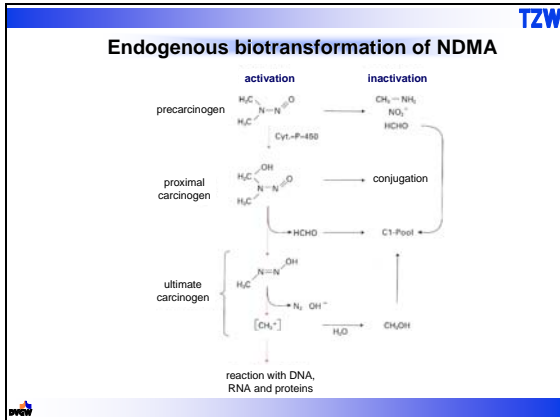
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TZW

### Uptake and distribution

- probable routes of exposure: inhalation, ingestion, and dermal contact
- NDMA resorption after oral intake via the upper part of the small intestine
- most nitrosamines are efficiently metabolized during liver passage (first pass)
- 60 % of the N-alkyl-nitrosamine dose is thereby transferred to CO<sub>2</sub>
- only small amounts are excreted via urine and faeces
- only small amounts are distributed systemically (more relevant at higher doses)

DVGW



### Health Effects

- acute toxicity (LD<sub>50</sub> rat, oral) - clinical signs: liver damages for NDMA: 40 mg/kg, NDEA: 280 mg/kg, NDMA: 1200 mg/kg
- chronic toxicity: similar hepatotoxic signs, often accompanied by tumors
- NDMA administered to pregnant rats and mice by several routes, has been shown to cause cancer in the offspring (transplacental carcinogen)
- with respect to toxicity, the carcinogenic action is the most relevant endpoint
- approximately 300 nitrosamines have been tested, and 90 % of them have been found to be carcinogenic in a wide variety of experimental animals (more than 30 species including primates)
- most nitrosamines are organ specific: target of NDMA and NMOR → liver
- until now, no animal is known in which NDMA does not induce any tumor, supporting the assumption that it is also carcinogenic to humans

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### Carcinogenicity

- NDMA was shown to be mutagenic in a number of test systems for genmutation: *Escherichia coli*, *Salmonella typhimurium*, *Neurospora crassa*
- produces mitotic recombination in *Sacharoyus cerevisiae*
- produces lethal mutations in *Drosophilla melanogaster*
- produces chromosomal aberrations in mammalian cells
- positive responses in bacterial cells are dependent upon addition of a mammalian metabolism system (S9 mix)
- NDMA is genotoxic, similar results for other nitrosamines
- risk assessment of genotoxic compounds is difficult
- genotoxic carcinogens: establishment of a threshold value impossible
- even a very small amount of the substance theoretically produces a finite increased risk of cancer
- assessment: additional cancer risk of one in a million (1:10<sup>6</sup>) for lifetime exposure

TZW

### Cancer risk levels for nitrosamines

Nitrosamine	Short form	10 <sup>-6</sup> cancer risk level (ng/L)
N-Nitrosodimethylamine	NDMA	0.7
N-Nitrosoethylmethylamine	NEMA	2
N-Nitrosodiethylamine	NDEA	0.2
N-Nitrosodi-n-propylamine	NDPA	5
N-Nitrosodi-n-butylamine	NDBA	6
N-Nitrosodiethanolamine	NDEIA	10
N-Nitrosopiperidine	NPIP	0.8
N-Nitrosopyrrolidine	NPYR	16
N-Nitrosomorpholine	NMOR	0.8

Source: U.S. Department of Health and Human Services (2005)

EPA generally uses the linearized multistage (LMS) model which fits linear dose-response curves to low doses. It is consistent with a no-threshold model of carcinogenesis.

TZW

### Regulatory aspects in Germany

- NDMA and NMOR classification -- B2; probable human carcinogens
- **Federal Environment Agency in Germany (UBA)** only „recommendation“ - not regulated in German „Drinking Water Directive“ ad-hoc guideline values (based on 2 liters drinking water consumption for 70 years)
  - NDMA: 10 ng/L      NMOR: 10 ng/L
- also based on the philosophy: if an individual were to drink 2 liters drinking water containing <10 ng NDMA/L over 70 years, that person shall have no more than a one in one million increased chance of developing cancer
- assessment takes also estimates of the general daily nitrosamine intake into account
- better lower levels: „concentrations should be as low as reasonably achievable“


TZW

### Regulatory aspects in the US

- so far, no drinking water maximum contaminant level goal (MCLG) or maximum contaminant level (MCL) set by the U.S. EPA
- Notification level by the California Department of Health Services (DHS)
  - 1998: 10 ng/L NDMA      2004: 10 ng/L NDEA      2005: 10 ng/L NDPA
- DHS recommends to remove the source from service at
  - 100 ng/L NDEA      200 ng/L NDMA      500 ng/L NDPA
- 2006 draft Public Health Goal (PHG) by the OEHHA of 3 ng/L NDMA

TZW

## Hiba Shukaairy: NDMA – EPA’s Perspective



**NDMA  
EPA’s Perspective**

Hiba Shukaairy  
USEPA Technical Support Center  
Cincinnati, Ohio

Global Water Research Coalition  
NDMA Workshop  
October 12, 2006

### Outline

- Regulatory Perspective
- Why Address NDMA Issues?
- Analytical Methods
- The Need for National Occurrence Data
  - Unregulated Contaminant Monitoring Rule
- Relative Source Contributions
- What’s Next?

### Disinfection Byproducts (DBPs) - Historical Regulatory Perspective

- THM Rule in 1979
  - MCL for TTHM 100 ug/L
  - Compliance based on a running annual average
- Negotiated Rulemaking Process
  - Stage 1 DBP Proposed Rule 1994
  - Information Collection Rule 1996
  - Notice of Data Availability 1997
  - Final Stage 1 DBP Rule 1998
    - TTHM 80 ug/L as a running annual average (RAA)
    - HAA5 60 ug/L as an RAA

### Why the Need for the Stage 2 Regulations?

- Potential health effects of concern: reproductive and developmental effects and cancer risks.
- High levels of DBPs are projected to occur in distribution systems even under Stage 1 DBPR.
  - Some populations would continue to have exposure above Stage 1 MCLs (80/60 ppb TTHM/HAA5)
  - Higher concentrations are of health concern
- Statutory requirement under SDWA 1996 Amendments (Section 1412(b)(2)(C))

### Stage 2 DBP Rule Development

- Stage 2 DBPR & LT2ESWTR negotiated together with Federal Advisory Committee
  - FACA met from 3/30/99 to 9/6/00
  - 21 members from different stakeholder groups
  - Agreement in Principle signed September 2000
- Many Stakeholders participated in the process
  - Water suppliers
  - Environmental and public health groups
  - Local, State and Federal governments
  - Chemical and equipment manufacturers
- The goal is to balance risks
  - Protection from both microbial pathogens and DBPs

### Summary of the Stage 2 DBP Rule

- Builds upon existing rules in M-DBP Suite
- Identifies more appropriate monitoring sites for DBPs
  - Initial distribution system evaluations (IDSEs) to investigate TTHM and HAA5 levels in the distribution system
- Improves protection of public health by reducing exposure to DBPs
  - MCLs remain at the same level as the Stage 1 DBP Rule
  - Locational Running Annual Averages (LRAAs) to calculate compliance
- Ensures equitable public health protection for all consumers
- Specifies requirement for consecutive systems
- Population based monitoring requirements

### What about NDMA?

- NDMA was not addressed during the regulatory negotiations
  - Very little evidence of occurrence at that time
- Known adverse health effects with a 10<sup>-6</sup> cancer risk level of 0.7 ng/L based on 2L water per day consumption
- Contaminant from industrial sources such as liquid rocket fuel, solvent in plastic industry and manufacture of pesticides
- Contaminant from reactions with resins and coagulant based cationic polymers
  - Quaternary amines and DADMAC
- Nitrosamines can be formed from the reaction between disinfectants and organic carbon and nitrogen in the water
- Exposure to NDMA is also from food products (beer, cured meat and cheeses); and from tobacco & air near industries
- Nitrosamines are found in wastewater effluents and are a concern in water reuse

### Regulatory Perspective

- Currently, no US Federal requirements to control NDMA
- California – established a notification level for NDMA, NDEA and NDPA at 10 ng/L
  - Established 3 ng/L as a draft Public Health Goal
- Canada has added NDMA to the list of Toxic Substances in 2003
  - Risk reduction by limiting exposure (pesticides, food and water)
- EPA Office of Science and Technology is preparing a draft Health Advisory to be finalized in early 2007
- National occurrence data needed to inform regulatory decisions
- Robust method required to allow for National occurrence data gathering

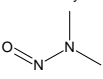
### Analytical Method Development

- EPA Lead is Jean W. Munch, USEPA, Office of Research and Development, National Exposure Research Laboratory, Cincinnati
- Reference: Munch, J. W. and Bassett, M.V., "Method development for the analysis of N-Nitrosodimethylamine and other N-Nitrosamines in drinking water at low nanogram/L concentrations using solid phase extraction and gas chromatography with chemical ionization tandem mass spectrometry." *Journal of AOAC International*, Vol. 89, No. 2, 2006, p 486-497.
- EPA Method 521 described in detail on EPA website
  - [www.epa.gov/nerlcwww/ordmeth.htm](http://www.epa.gov/nerlcwww/ordmeth.htm)

### EPA Method 521

- Analysis of NDMA and 6 additional nitrosamines at low ng/L
- Solid phase extraction with coconut charcoal as the sorbent and dichloromethane as the eluent
- Water sample is 0.5 L concentrated to 1 mL
- Analysis by GC/CI-MS/MS
- Large volume injection
- MDL = 0.28 ng/L
- MRL of 2 ng/L (LCMRL 1.3 – 1.6 ng/L)

### Nitrosamines

NDMA and Company		
	Compound	Abbr.
 <p>NDMA</p>	N-nitrosodimethylamine	
	N-nitrosodiethylamine	NDEA
	N-nitrosodi-n-butylamine	NDBA
	N-nitrosodi-n-propylamine	NDPA
	N-nitrosomethylethylamine	NMEA
	N-nitrosomorpholine	NMOR
	N-nitrosopiperidine	NPIP
N-nitrosopyrrolidine	NPYR	

### What One Part per Trillion (ng/L) Really Means.... Some Examples

- 1 minute in 2,000,000 years.
- 1 M&M in 1,000,000 tons of M&Ms.
- 1 heartbeat in 36,000 years.
- 1 inch in 16,000,000 miles.

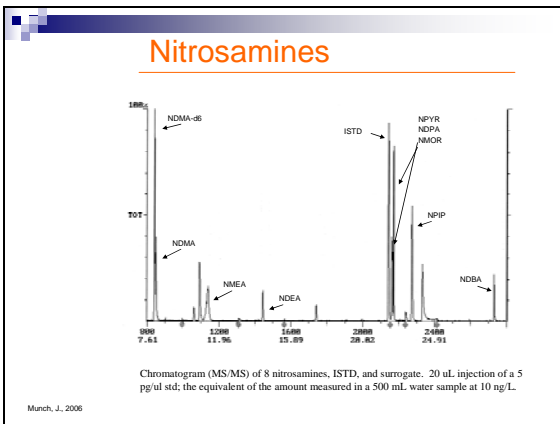
### Challenges in Method Development

- Nitrosamines are miscible in water. Therefore, difficult to extract from the water matrix
- Due to health concern at low levels, it is imperative to measure low concentrations. Therefore, low detection limits needed for the method
- Low response found with electron ionization MS and other GC detectors
- Need Surrogate (NDMA-d6) and internal standards (NDPA-d14 & NDEA-d10)
- N-nitrosamines can be contaminants in rubber products – samples and extracts should not come in contact with rubber products
- N-nitrosomorpholine was not included in the method because of laboratory background contamination at low concentrations

### Nitrosamines Extraction Techniques

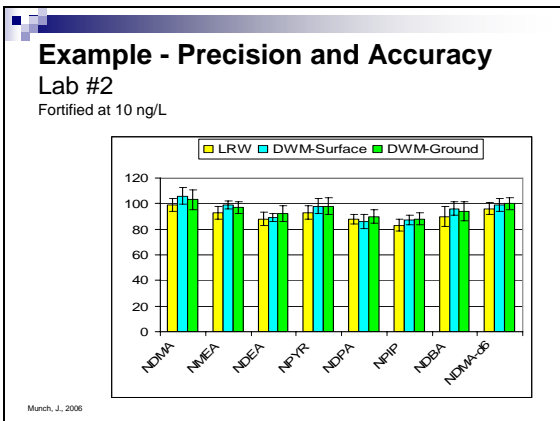
CARTRIDGE SPE (2g coconut charcoal)

March, J. 2006



### Method Performance Testing

- Solid phase extraction
  - Charcoal
  - Sample volume
  - Sample flow rate
- Selection and optimization of GC/MS/MS parameters
- Method precision and accuracy tested
  - Various water matrices (SW, GW and high TOC water)
  - Two labs



### The Contaminant Candidate List: Setting Priorities for the Future

- SDWA requires a CCL list every 5 years
  - List contaminants known or anticipated to occur in public water supplies
  - Consider adverse health effects
  - CCL 1 (1998); CCL 2 (2005); CCL 3 (2008)
- Make regulatory determinations on a 5 year cycle
  - Determination on *at least* 5 contaminants
  - First determination final July 2003; next preliminary determination expected 2006
- SDWA Regulatory Determination (1412(b)(1)) requires regulation of contaminants that have adverse health effects and occur nationally
  - Regulation results in public health risk reduction

## Unregulated Contaminant Monitoring Rule

### Monitoring for Emerging Contaminants of Concern

- Finished drinking water occurrence for select CCL contaminants
  - Determine distribution and concentration range
- Use data in future regulatory decision-making
- Limited to 30 contaminants per 5-year cycle
- Direct implementation by EPA with support from State partnerships
  - Guidance and outreach
- UCMR cycle 2 (UCMR 2) – assessment and screening approaches for monitoring proposed to begin in 2007

## Unregulated Contaminant Monitoring Rule - NDMA

### Monitoring for Emerging Contaminants of Concern

- UCMR cycle 2 (UCMR 2) - monitoring proposed to begin in 2007
- Monitoring done as part of the screening survey
- NDMA and 5 other nitrosamines proposed for monitoring
  - N-nitrosodiethylamine (NDEA)
  - N-nitroso-di-n-butylamine (NDBA)
  - N-nitroso-di-n-propylamine (NDPA)
  - N-nitrosomethylethylamine (NMEA)
  - N-nitrosopyrrolidine (NPYR)
- EPA Method 521 proposed for monitoring
  - EPA lab approval is required for nitrosamine analysis
- Monitoring proposed in the finished water and in one distribution system location
  - Disinfectant use (Chlorine versus chloramine) will be reported

## Relative Source Contribution

- NDMA can be formed during food processing and preservation (0.1 to 20 ug/kg reported)
  - Addition of nitrite and nitrate
  - Preservation by smoking
  - Food drying and pickling
  - Food stored under humid conditions by bacteria
- Indoor air can be contaminated from smoke and in some industrial urban locations
- WHO reports that NDMA in drinking water contributes below 10 percent of the total exposure (WHO Background Document, 2006)
- NCEA (ORD) evaluated proportional intake and deduced that the contribution of drinking water to average daily exposure is low relative to food and air exposure

## What's Next for Nitrosamines?

- NDMA will likely be listed on CCL3
- Microbial disinfection Byproduct Rules will undergo statutory six-year review (Cycle ending in 2015)
- Risk balancing for microbial and DBP regulations
- EPA will evaluate occurrence data gathered during UCMR2
- EPA will evaluate formation and control studies
  - Evaluate factors that contribute to the formation
  - Address the need for treatment technologies to control risk
- Continue addressing the relative source contribution
- Data will inform regulatory decisions for nitrosamines

## Summary of EPA's Studies for Nitrosamines

- Data collection and analysis of National nitrosamine occurrence data from UCMR2
- A 4-Lab study measures 8 nitrosamines in chlorinated concentrates (in addition to raw and treated water) in conjunction with animal testing (repro/develop effects)
- Further discussions on relative contributions from the drinking water

## For Additional Information

- [shukairy.hiba@epa.gov](mailto:shukairy.hiba@epa.gov)  
513 569-7943
- Safe drinking water hotline
  - email address [hotline-sdwa@epa.gov](mailto:hotline-sdwa@epa.gov)
  - telephone 703 412-3330
  - 800 426-4791
- [www.epa.gov/ogwdw/safewater](http://www.epa.gov/ogwdw/safewater)
- Method 521 [munch.jean@epa.gov](mailto:munch.jean@epa.gov)
- UCMR2 [munch.dave@epa.gov](mailto:munch.dave@epa.gov)



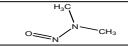
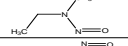
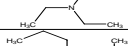
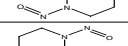
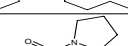
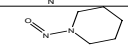
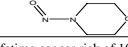
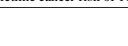
**Auguste Bruchet: Analysis of nitrosamines (presentation on behalf of Mel Suffet)**

## Development of Low Cost Method(s) for NDMA Analysis

**R. C. Cheng and C. Andrews-Tate**  
**Long Beach Water Department**  
**C. J. Hwang and C. Guo**  
**Metropolitan Water District of S. California**  
**Janel Grebel and Mel Suffet**  
**Env. Sci. and Eng. Program**  
**UCLA,**  
**Los Angeles, CA**  
*Funded by Water Reuse Foundation -*

## Acknowledgments


- 💧 WaterReuse Foundation
- 💧 US Bureau of Reclamation
- 💧 LA County Sanitation Districts
- 💧 Orange County Water District
- 💧 Central & West Basin Municipal Water Districts
- 💧 Castaic Lake Water Agency

Compound	10 <sup>-6</sup> Cancer Risk Water Conc.*	Structure
N-nitrosodimethylamine	0.7 ng/L	
N-nitrosomethylethylamine	2.0 ng/L	
N-nitrosodiethylamine	0.2 ng/L	
N-nitrosodi-n-propylamine	5.0 ng/L	
N-nitrosodi-n-butylamine	6.0 ng/L	
N-nitrosopyrrolidine	20.0 ng/L	
N-nitrosopiperidine	Unavailable	
N-nitrosomorpholine	Unavailable	

\*Based on USEPA, 1993 Integrated Risk Information System for lifetime cancer risk of 10<sup>-6</sup>



## Analytical Challenges

- 💧 Minute quantities (< 10 ng/L in potable water)
- 💧 Accuracy and reproducibility
- 💧 Other nitrosamines
- 💧 Time consuming and costly




## Extraction Methods Examined

- 💧 **Liquid phase (LLE)**
  - ⊗ manual or continuous
  - ⊗ **micro LLE (reduced volume), one extraction step**
- 💧 **Solid phase (Amb SPE)**
  - ⊗ Ambersorb 572 as resin
  - ⊗ **contact time = 2 hrs**
- 💧 **Cartridge solid phase (CSPE)**
  - ⊗ Ambersorb, Envicarb media
  - ⊗ **Potentially automatable**

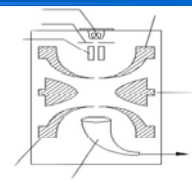



## Quantitation (GC/MS)

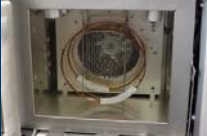
Long Beach Water Department:



1079 Injector  
-Temp. program  
-Split ratio  
-Split time

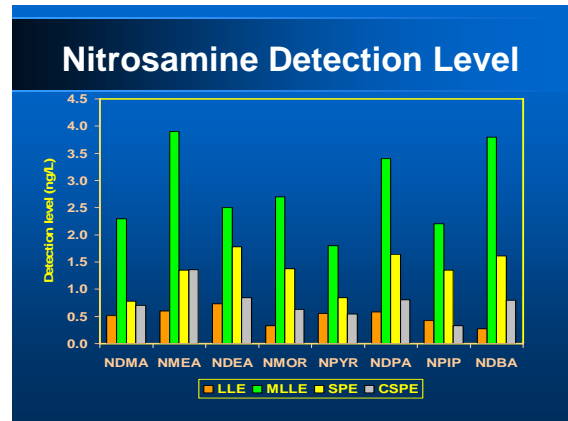
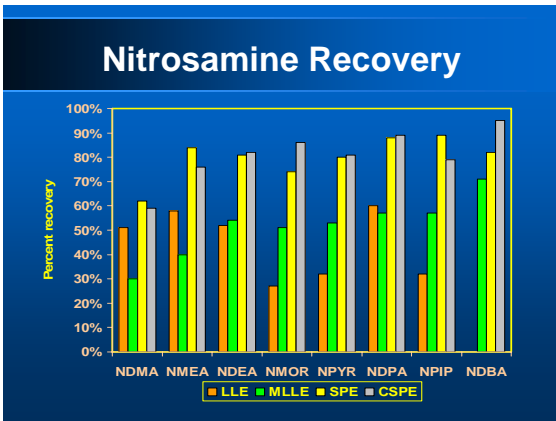


Varian 3800 GC  
-Temp. program  
-Column  
-DB-VRX  
-HP-VOC



Varian 2000 Ion trap  
-Chemical Ionization (methanol)





### Participating Laboratories

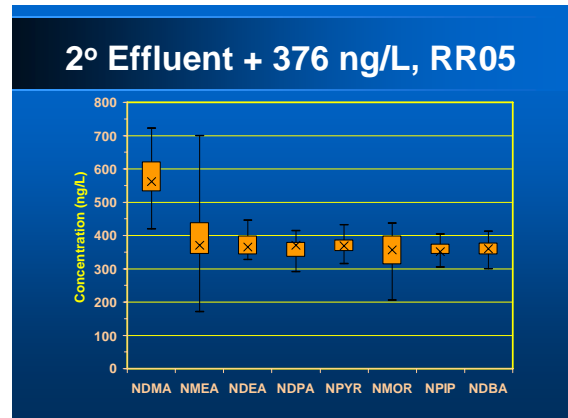
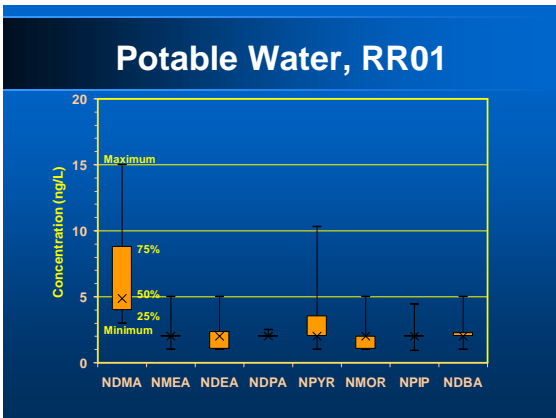
Type Lab	Amb-Envi		Amb SPE	LLE
	MLLE	CSPE		
Regulatory	2	---	1	---
Commercial	2	1	1	4
Utility	2	2	2	2
<b>Total</b>	<b>6</b>	<b>3</b>	<b>4</b>	<b>6</b>

U.S. Labs - 8  
Canadian Labs - 4

### Samples Tested

Sample	Source	pH	Turbidity (NTU)	Conduct (µmho/cm)	Cl <sub>2</sub> (mg/L)	NA Spike (ng/L)
RR-01	Potable	8.32	0.30	423	2.8	0
RR-02	Potable (spiked)	7.97	0.13	403	2.8	12.7
RR-03	RO Effluent	4.73	0.11	65	0.05	0
RR-04	2° Effluent	7.41	1.07	824	0.04	0
RR-05	2° Effluent (spiked)	7.28	0.23	838	0.04	376
RR-06	3° Effluent	7.42	0.39	912	3.64	0

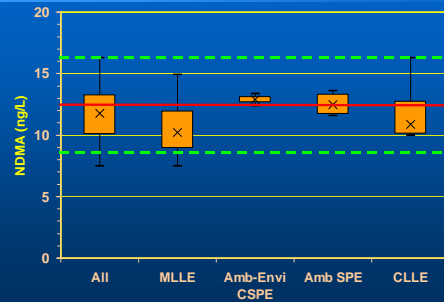
Samples 1, 4 spiked for low and high nitrosamine recoveries



### Low Level Accuracy/Precision

- ◆ Low level = RR02 - RR01
- ◆ Should be ~ 12.7 ng/L for all NA (accuracy)
- ◆ Examine data spread for precision

### NDMA Low Spike Recovery NDMA = 12.7 ng/L



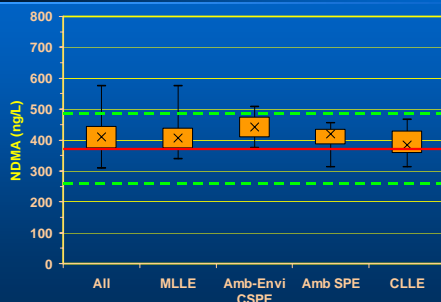
### Low Concentration Method Ranking

Nitrosamine	MLE	Amb-Envi CSPE	Amb SPE	CLLE
NDMA	4	1	2	3
NMEA	3	1	2	4
NDEA	4	3	2	1
NDPA	1	3	2	4
NPYR	2	4	1	3
NMOR	2	1	4	3
NPIP	3	4	2	1
NDBA	4	1	3	2
Total	23	18	18	21

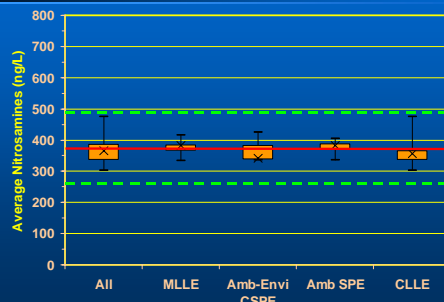
### High Level Accuracy/Precision

- ◆ Low level = RR05 - RR04(Sec WW Eff)
- ◆ Should be ~ 376 ng/L for all NA (accuracy)
- ◆ Examine data spread for precision

### NDMA High Spike Recovery NDMA = 376 ng/L



### Avg. NA High Spike Recovery Average Nitrosamine = 376 ng/L



### High Concentration Method Ranking

Nitrosamine	MLLE	Amb-Envi		CLLE
		CSPE	Amb SPE	
NDMA	2	4	3	1
NMEA	2	4	3	1
NDEA	2	3	1	4
NDPA	1	3	2	4
NPYR	1	2	3	4
NMOR	3	4	1	2
NPIP	3	4	1	2
NDBA	1	4	2	3
Total	15	28	16	20

### Analytical Time Required

	MLLE	Amb-Envi		LLE
		CSPE	Amb SPE	
No. samples	6	6	6	6
No. analyzed, w/stds	6 - 19	16 - 30	16 - 43	20 - 34
Sample prep (hr)	1 - 2	1 - 8.5	1 - 2	1 - 2
Extr/Sepn/Desorp (hr)	4 - 6	3 - 20	5 - 7	16 - 22
Quant/Detect (hr)	7 - 8	6 - 8	6 - 18	7 - 12
QA/QC/Report (hr)	1 - 5	1 - 8	2 - 5	1 - 2
Total (hr)	16 - 23	11 - 44	15 - 27	30 - 32
Time/sample (w/stds) (hr)	2.7 - 3.8	1.8 - 7.3	2.5 - 4.5	5.0 - 5.3

### Conclusions

- ◆ LLE, MLLE, Mod SPE, and Amb-Envi CSPE tested
- ◆ Different water matrices tested
- ◆ NDMA >> other NAs in all samples
- ◆ All methods met regulatory acceptance guidelines of 70 - 130%
- ◆ All methods able to analyze broad range of NA concentrations in different matrices

### Conclusions (cont'd)

- ◆ SPE methods effective at low levels
- ◆ MLLE method acceptable at > 10 ng/L
- ◆ LLE, Amb SPE, Amb-Envi CSPE can achieve ~ 2 ng/L reporting limit (if DLR = 3x MDL)
- ◆ DLR for other NAs ~ 5 ng/L
- ◆ Analytical times for alternative methods less than or equal to LLE

### SPME

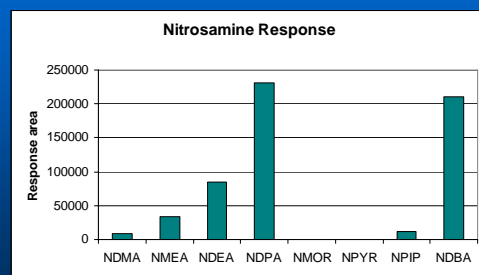
Mel Suffet, Janel Grebel  
UCLA, LA, CA

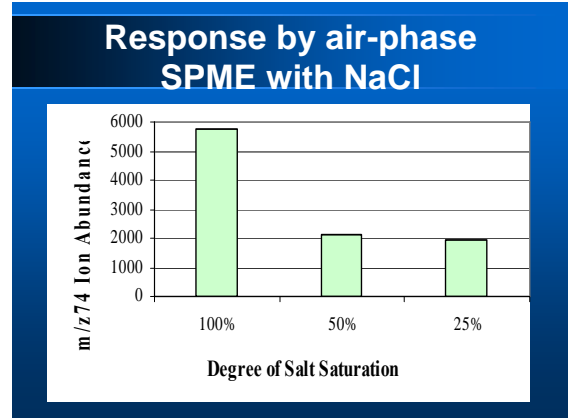
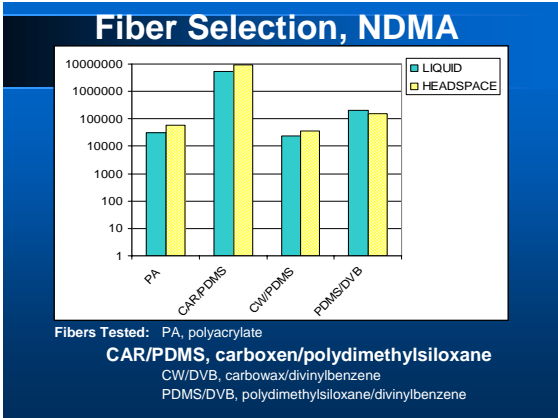
Connie Young, Rodger Baird  
LA County Sanitation Districts

Michael Scimanti  
MWD of Southern California

- ◆ SPME dependent on equilibrium between water matrix, headspace, and SPME fiber. This equilibrium is dependent on analyte concentration in each phase. Only a fraction of the total analyte present is extracted.

### Nitrosamine Extraction (500 ng/L)





### Competition Study

- ◆ Treatment plant water matrix could lead to adsorption competition on the SPME fiber
- ◆ Potential competition problems
  - Humic Substances
  - 1,1-Dimethylhydrazine (UMDH)

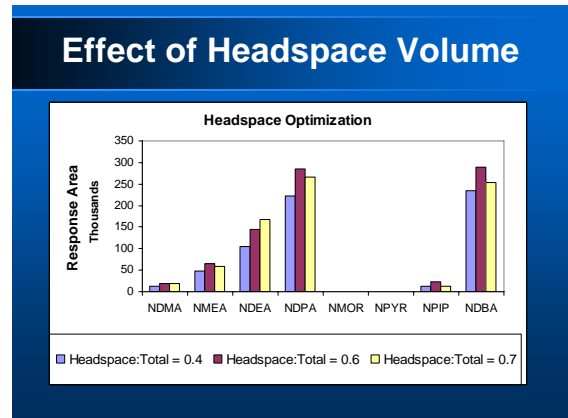
### Competition Study, cont'd

Method	Water Matrix	NDMA (ng/L)
SPME	2 effluent <sup>a</sup> (no Cl)	17.9
LLE	2 effluent (no Cl)	11.2
SPME	2 effluent (no Cl), - spiked with 200 ng/L NDMA	2
-----		
SPME	Wastewater Final effluent <sup>b</sup>	210
LLE	Wastewater Final effluent	183
-----		
SPME	Organic-free water with 250 ng/L UDMH, - spiked with 30ng/L NDMA	37.6
	Tap water with 250 ng/L UDMH, - spiked with 30 ng/L NDMA	41.2

<sup>a</sup> 9.6 mg/L of TOC and pH 7.27  
<sup>b</sup> 8.3 mg/L of TOC and pH 7.11

### Extraction Conditions

SPME Fiber	75 um CAR/PDMS
Sample volume	7 mL
Vial volume	15mL
Salt addition	NaCl, 2.4g
Extraction Temperature	65 deg C
Extraction Time	45 min
Desorption Temperature	220 deg C
Desorption Time	2 min



Spike Recoveries from Secondary Wastewater Effluent

n=2 for 200 ng/L nitrosamine spike

Sample	NCD		NPD		CI/MS	
	Amount	Spike Recovery	Amount	Spike Recovery	Amount	Spike Recovery
Secondary Effluent	ng/L	%	ng/L	%	ng/L	%
NDMA	320	94	705	259	435	166
NMEA	223	112	236	119	92	46
NDEA	192	96	146	73	221	111
NDPA	205	103	206	103	229	115
NDBA	205	102	245	123	206	103
NPIP	230	115	---	---	146	73
NPYR	ND <sup>a</sup>	ND <sup>a</sup>	ND <sup>a</sup>	ND <sup>a</sup>	N/A <sup>b</sup>	N/A <sup>b</sup>
NMOR	ND <sup>a</sup>	ND <sup>a</sup>	ND <sup>a</sup>	ND <sup>a</sup>	236	136

<sup>a</sup>Detected at 95°C with high detection limits

<sup>b</sup>Compound not resolved by chromatographic column

### Extraction Conditions

Organization	LAGSD	MWD	UCLA
SPME Fiber	75 um CAR/PDMS	85 um CAR/PDMS	75 um CAR/PDMS
Sample volume	5 mL	10 mL	10 mL
Vial volume	7 mL	40 mL	40 mL
Salt addition	NaCl, saturated	NaCl, 2.5g	NaCl, 3.5g
Extraction Temperature	95 deg C	65 deg C	65 deg C
Extraction Time	30 min	45 min	45 min
Desorption Temperature	250 deg C	220 deg C	220 deg C
Desorption Time	???	5 min	2 min
Instrument Detection	ThermoFinnigan	Varian Saturn 2200	NCD
Ionization/detection mode	ammonia CI/MS	acetonitrile CI/MS	NA

## Summary

- |                                                                                                                                                                        |                                                                                                                                        |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> <li>◆ Advantages</li> <li>--no solvent required</li> <li>--simple method</li> <li>--low cost</li> <li>--easily automated</li> </ul> | <ul style="list-style-type: none"> <li>◆ Disadvantages</li> <li>--detection limit too high to analysis at regulatory levels</li> </ul> |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|

**Applications:**

SPME could be a good screening method for higher nitrosamine concentrations


# Carsten K. Schmidt: Determination of N-nitrosamines in water via LVI-GC-PCI-SIM-MS after solid-phase extraction

TZW

## Determination of N-Nitrosamines in water via LVI-GC-PCI-SIM-MS after solid-phase extraction

Carsten K. Schmidt  
Thomas Lustinetz, Silke Glöckler, Heinz-Jürgen Brauch

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## N-Nitrosamines

CN(N=O)C  
**NDMA**  
 (CAS 62-75-9)

CCN(N=O)C  
**NEMA**  
 (CAS 10595-95-6)

CCN(N=O)CC  
**NDEA**  
 (CAS 55-18-5)

CCN(N=O)CC  
**NDPA**  
 (CAS 621-64-7)

CCN(N=O)CC  
**NDBA**  
 (CAS 924-16-3)

C1CCN(N=O)CC1  
**NMOR**  
 (CAS 59-89-2)

C1CCN(N=O)CC1  
**NPYP**  
 (CAS 100-75-4)

C1CCN(N=O)C1  
**NPYR**  
 (CAS 930-55-2)

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## Sample Preparation

Water Sample 500 mL

Adjustment to pH 3

Addition of Internal Standards

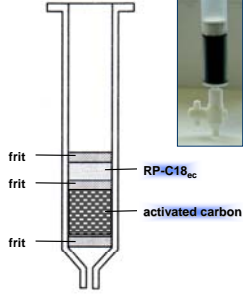
Solid-Phase Extraction  
two-layered mixed bed<sup>®</sup> C18<sub>ec</sub> + activated carbon

Elution with Dichloromethane

Drying of the Eluate over Na<sub>2</sub>SO<sub>4</sub>

Concentration of the Eluate  
with a rotary evaporator to 150 µL


LVI-GC-PCI-MS-SIM-Analysis  
Injection of 50 µL



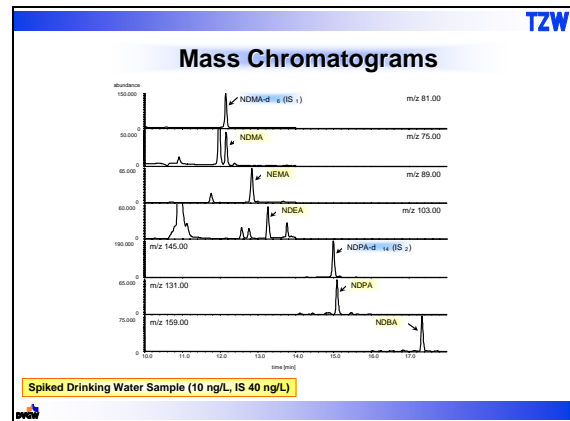
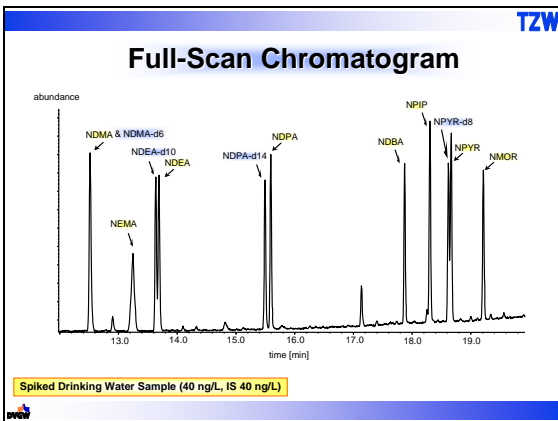
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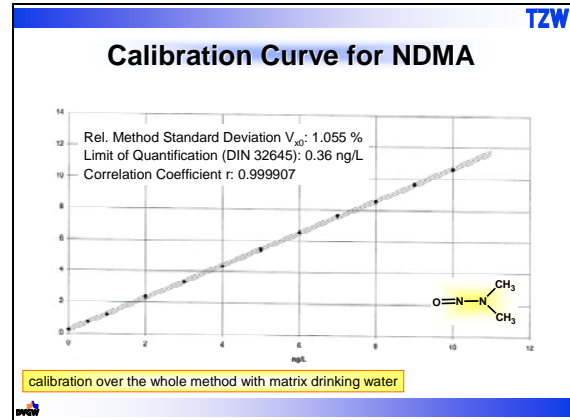
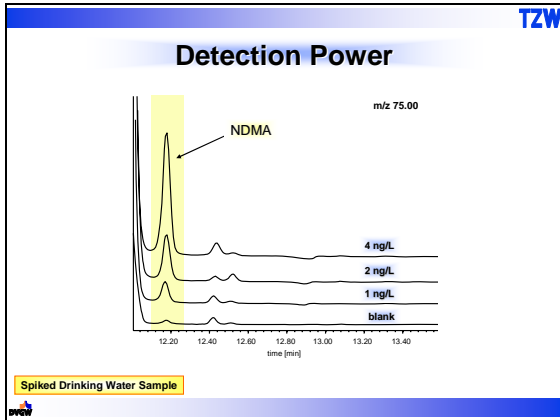
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## GC/MS-Determination (LVI-GC-PCI-MS-SIM)

<b>GC</b>	Instrument: Agilent Technologies 6890 Column: DB-WAX (30 m x 0.25 mm x 0.5 µm) Carrier Gas: Helium, 1.2 mL/min (constant flow) Temperature-Program: 35°C isotherm, 3 min 10°C/min -220°C 220°C isotherm, 2 min	
	Cold Injection System: Gerstel KAS4 <sup>plus</sup> Injection Volume: 50 µL	
<b>MS</b>	Instrument: Agilent Technologies MSD 5973 N CI-Reagent Gas: iso-butane MSD: SIM-Mode (further verification of peak identities via UV irradiation)	

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### Features of the Method

compound	limit of determination according to DIN 32645 [ng/L]	rel. method standard deviation $V_{rel}$ [%]
NDMA	0.36	1.1
NEMA	0.67	1.8
NDEA	0.25	0.74
NDPA	0.84	2.5
NDBA	1.0	2.9
NPIP	1.1	3.4
NPYR	0.37	1.1
NMOR	1.1	4.6

calibration over the whole method with matrix drinking water

### Validation of the Method

sample volume: 500 mL

limits of quantification: 0.3 - 1.1 ng/L (NDMA: 0.4 ng/L) acc. to DIN 32645

linear range: 0-100 ng/L

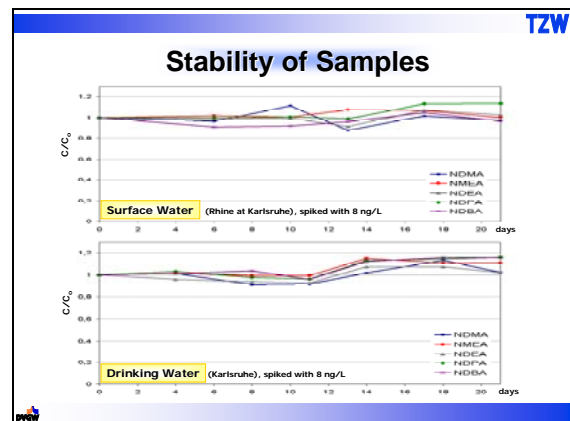
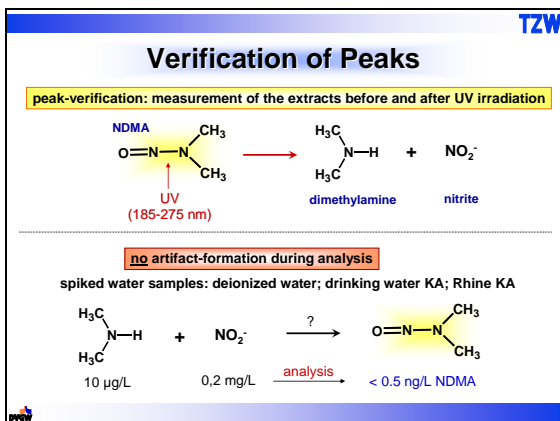
recoveries: 50-70 % (independent of the matrix)

coefficients of correlation:  $r > 0.998$

precision of the method: COV < 9 %

accuracy: rel. systematic error < 12 %



method blank values: < 0.2 ng/L



## Auguste Bruchet: Nitrosamines and the Suez Environment group

Nitrosamines  
and  
the Suez Environment group

A. Bruchet,

**First contact with Nitrosamines : 1982**

In 1982, our subsidiary Degremont was testing a new resin denitratation process.

Extensive analysis was carried out by IRCHA (France) with 7 preparation methods « Total Extraction »:

- 1) LLE at pH 7 with Chloroform
- 2) LLE at pH 2-3 with Chloroform

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**First contact with Nitrosamines : 1982**

- 4) Flocculation at pH 8 followed by soxhlet extraction with  $\text{CHCl}_3/\text{EtOH}$
- 5) IRA 68,  $\text{Cl}^-$ , elution by NaOH
- 6) XAD<sub>2</sub>, elution by EtOH, Ether,  $\text{CH}_2\text{Cl}_2$ , EtOH
- 7) GAC, soxhlet extraction with chloroform

After analysis, combination of extracts and reuptake in chloroform/ethanol

« This technique allows to recover almost all micropollutants except volatiles without transformation »

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**First contact with Nitrosamines : results**

Many groups of compounds investigated by GC including:

- Nitrosamines
- Biogenic amines (e.g. methylamine)

Pilot plant, line III :

Inlet Nitrosamines 2+ Biogenic amines 2+, 1+

Outlet Nitrosamines 2+ Biogenic amines 2+, 1+

Conclusion: systematic presence of biogenic amines, occasional presence of Nitrosamines.

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**Approval of denitratation process: full scale plant**

In 1984, monitoring of first full scale plant showed individual levels of nitrosamines\* <50 ng/L (NDEA, NDPA, NPIP, NDBA, NDPA) = LOD at that time

⇒ Process was approved

\*results published in TSM, March 1986

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**Second contact: pHD work on Nitrogenous organic compounds (E. Schmitt, 1984)**

Analysis of nitrosamines by GC-TEA in 3 water resources\*\*

	NDMA	NDEA	NMor	Others *(Total)
Seine River, Croissy	<LOD	<LOD	<LOD	<LOD
Seine River Aubergenville	11	>LOD	114	24
La Houle River	<LOD	4	<LOD	18

\*Extracts treated with denitrosation reactions by Ni-Al, KOH or UV, to avoid interferences.  
\*\* GC RT does not correspond to standards injected

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### Evolution of nitrosamines during treatment of artificially recharged groundwater (GC-TEA)

Sample	NDMA	NDEA	NMor	x	y	Total
<b>Recharge</b>						
Seine river	<	<	<	<	<	<
Prechlorination	<	4	<	6	<	<b>10</b>
Clarified water	3	7	<	6	<	16
<b>Ground water</b>						
Plant inlet	<	5	15	50	<	70
Nitrification	6	5	8	24	<	43
O3/GAC	<	6	5	<	4	37
Chlorinated	<	<	8	64	<	<b>72</b>

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### Monitoring of resin denitration process (full scale plant)

French circular from 1985 requires a periodical analysis of nitrosamines for this process

April 1996

	Raw water	After denitration
NDEA	<1.4	230
NDMA	<1.4	44
NDPA	<2.1	33
NMEA	<1.4	3

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### Monitoring of treated water (96-98) for NDEA, NDMA, NDPA, NMEA, NMOR

1996 : subsequent campaigns (1 sample per month) showed total nitrosamines ranging from 11 to 32 ng/l

1997-1998 : 1 sample/trimester. 3 results above 50 ng/L and other results between 13.2 and 84 ng/L

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### Evolution of nitrosamines (ng/l) determined by GC-TEA along a treatment plant (Bruchet, AWWA 2003)

Compound	Raw water canal 1 DOC 3 ppm	Raw water canal 2 DOC 3.2ppm	Treated Water line 1 DOC 1.9ppm THM 3.6 ppb
N-Nitrosodimethylamine NDMA	<0.4	1.8	<b>22</b>
N-Nitrosomethylamine NMEA	<0.3	<0.3	2.6
N-Nitrosodiethylamine NDEA	0.6	<0.2	<0.2
N-Nitrosodipropylamine NDPA	<0.3	<0.3	<0.3
N-Nitrosodipropylamine NDPA	<0.2	<0.2	<0.2
N-Nitrosopiperidine NPIP	<b>2.9</b>	<b>15.4</b>	<b>11.9</b>
N-Nitrosopyrrolidine NPYR	3.5	3.5	<0.3
N-Nitrosomorpholine NMOR	<b>535</b>	<b>1089</b>	<b>621.7</b>
N-Nitrosodibutylamine NDBA	<0.3	9	<0.3

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### Formation of Nitrosamines in a French groundwater treated with cationic polymers

	Nov 11 / 2004 2ppm FeCl3 + 0.5ppm A			Feb/2005 2ppm FeCl3 + 0.5ppm A			Nov/26 / 2004 2ppm FeCl3 + 0.2ppm B		
	Ozonated µg/l	Chlorinated µg/l	Distribution µg/l	Ozonated µg/l	Chlorinated µg/l	Distribution µg/l	O3 µg/l	Cl2 µg/l	DS µg/l
NDMA	< 0.015	0.1	0.05	< 0.015	< 0.015	0.015	4	< 0.015	< 0.015
NDEA	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
N-Nitrosodimethylamine	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
N-Nitrosodiethylamine	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
N-Nitrosodipropylamine	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
NPIP	< 0.03	< 0.03	0.04	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
NPYR	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
NMOR	< 0.06	0.31	0.24	< 0.06	0.51	0.47	0.09	0.12	0.12
NDBA	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.12	0.08

ymet A: polyDADMAC; polymer B: EpilDMA

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Jim Morran: N-Nitrosodimethylamine in Australia

## N-NITROSODIMETHYLAMINE In Australia




Jim Morran  
CRC Water Quality and Treatment



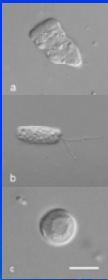


### Why Chloramine?

- Above ground systems
- Temperature ~ 40 C
- Long distances
- Detention time ~ months

Disinfectant residue  
Amoebic Meningitis

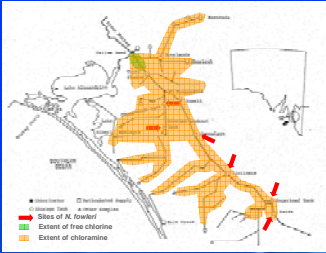






### Naegleria fowleri





### Chloramine impact

### NDMA occurrence



- High DOC, Bromide, nutrients and algae
- High chloramine dose – 4.2mg/L
- Booster chloramination
- Nitrification – breakpoint chlorination & rechloramination

NDMA 0 – 90 ng/L

### NDMA study

- Develop reliable analysis
- Monitor systems
- Optimise water treatment
- Identify precursors/surrogates



**NDMA study**

Project Leader: Dr Gayle Newcombe  
Gayle.Newcombe@sawater.com.au

Jim.Morran@sawater.com.au



water

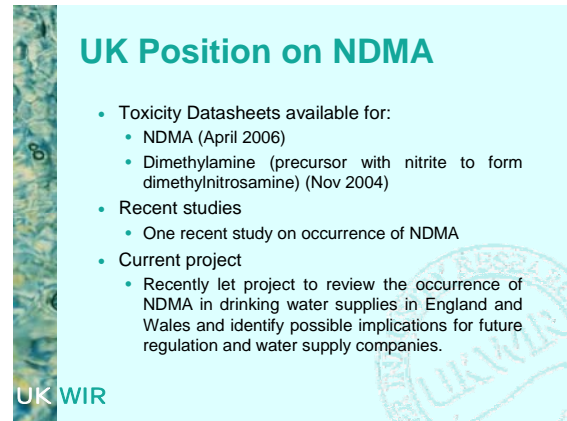
## David Holt: Occurrence of nitrosamines – Situation in UK



Occurrence of Nitrosamines  
– Situation in UK

Dr David Holt  
UKWIR Project manager

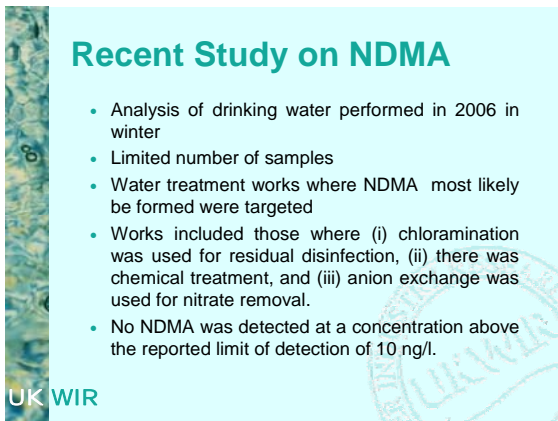
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UK Position on NDMA

- Toxicity Datasheets available for:
  - NDMA (April 2006)
  - Dimethylamine (precursor with nitrite to form dimethylnitrosamine) (Nov 2004)
- Recent studies
  - One recent study on occurrence of NDMA
- Current project
  - Recently let project to review the occurrence of NDMA in drinking water supplies in England and Wales and identify possible implications for future regulation and water supply companies.

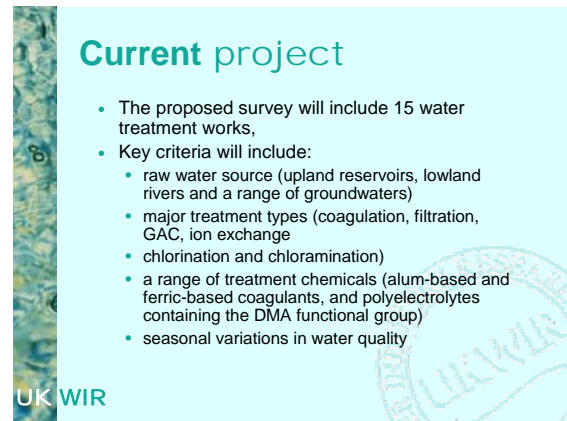
UKWIR



Recent Study on NDMA

- Analysis of drinking water performed in 2006 in winter
- Limited number of samples
- Water treatment works where NDMA most likely be formed were targeted
- Works included those where (i) chloramination was used for residual disinfection, (ii) there was chemical treatment, and (iii) anion exchange was used for nitrate removal.
- No NDMA was detected at a concentration above the reported limit of detection of 10 ng/l.

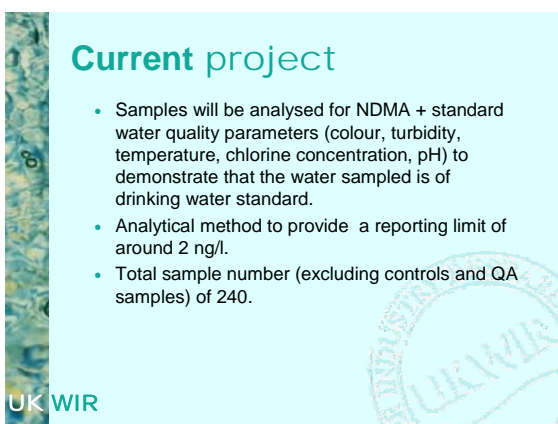
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Current project

- The proposed survey will include 15 water treatment works,
- Key criteria will include:
  - raw water source (upland reservoirs, lowland rivers and a range of groundwaters)
  - major treatment types (coagulation, filtration, GAC, ion exchange)
  - chlorination and chloramination)
  - a range of treatment chemicals (alum-based and ferric-based coagulants, and polyelectrolytes containing the DMA functional group)
  - seasonal variations in water quality

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Current project

- Samples will be analysed for NDMA + standard water quality parameters (colour, turbidity, temperature, chlorine concentration, pH) to demonstrate that the water sampled is of drinking water standard.
- Analytical method to provide a reporting limit of around 2 ng/l.
- Total sample number (excluding controls and QA samples) of 240.

UKWIR

## Carsten K. Schmidt: Occurrence of nitrosamines in the aquatic environment – Results from Germany and general aspects

TZW

### Occurrence of Nitrosamines in the Aquatic Environment

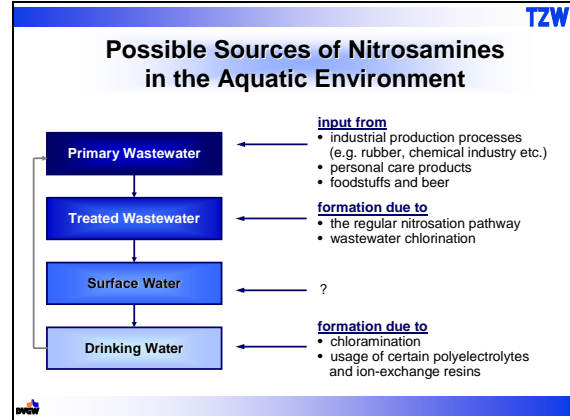
Results from Germany and General Aspects

Carsten K. Schmidt

DVGW-Technologiezentrum Wasser, Abteilung Analytik  
Karlsruher Str. 84, D-76139 Karlsruhe, e-mail: c.schmidt@tzw.de



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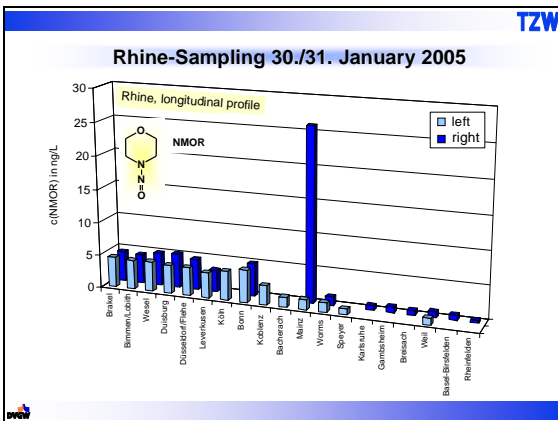
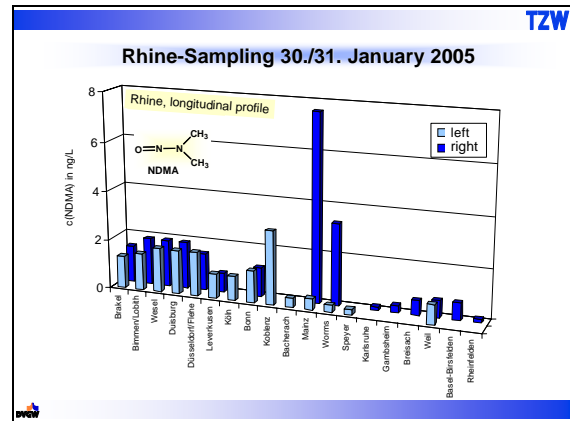
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### Nitrosamines in Surface Waters

River	NDMA [ng/L]	NMOR [ng/L]
Rhine at Karlsruhe	<0.3 ... 0.8	0.5 ... 1.1
Rhine at Düsseldorf	1.8 ... 12	0.6 ... 13
Main at Bischofsheim	0.6 ... 29	1.0 ... 92
Emscher (mouth)	1.9 ... 4.5	8.2 ... 19
Lippe (mouth)	<0.3 ... 0.5	1.6 ... 2.7
Neckar at Neckartailfingen	0.4 ... 0.7	0.8 ... 3.1
Pfingz at Karlsruhe	<0.3 ... 0.5	1.1 ... 2.9
Wupper (mouth)	0.3 ... 2.1	1.7 ... 10
Lake Constance	<0.3	<0.3
South Platte River at Brighton*	.... 6.1	.... 100
Quinnipiac River (Connecticut)**	.... 15	.... 100

\* Hoppe et al. 2006, \*\* Schreiber and Mich 2006

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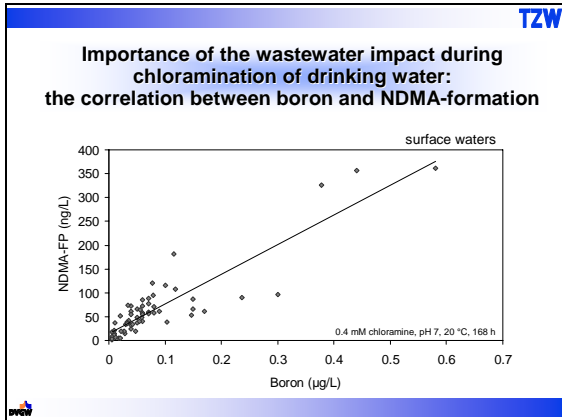


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### Nitrosamines in Effluents of municipal and industrial wastewater treatment plants

Wastewater Effluents	NDMA [ng/L]	NMOR [ng/L]
Sample A	8.100	590
Sample B	<20	<20
Sample C	2.0	5.6
Sample D	26	28
Sample E	68	130
Sample F	<20	<20
Sample G	15.000	13.000
Sample H	<1	1.3
Sample I	24	900
Sample J	160	<1
Sample K	71	1.9
Sample L	<1	<1
Sample M	15.000	7.100
Sample N	170	1.100
Sample O	630	1.600
Sample P	3.9	<1

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## Leo Puijker: NDMA in surface water and drinking water in the Netherlands

Leo Puijker, October 2006

**kiwa**  
Partner for progress

**NDMA in surface water and drinking water in the Netherlands**

GWRC-workshop Nitrosamines, October, 12 – 13, Karlsruhe

**Properties NDMA**

- **N-nitrosodimethylamine (NDMA)**
  - MW 74,08

CN(C)N=O

- Very soluble in water
  - >>100 gram/l
- Mobile compound
  - Log Kow -0.6
- Boiling point 151 °C
- UV absorption 200-270 nm; max ~223 nm

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**Nitrosamines**

component	synonym	CAS nr	BR form	log KOW
n-nitrosodimethylamine	NDMA	62-75-9	C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O	-0,60
n-nitrosomethylethylamine	NMEA	10595-95-6	C <sub>3</sub> H <sub>8</sub> N <sub>2</sub> O	-0,15
n-nitrosodiethylamine	NDEA	55-18-5	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O	0,34
n-nitrosopyrrolidine	NPYR	930-55-2	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O	0,23
n-nitrosomorpholine	NMOR	59-89-2	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	-0,43
n-nitrosodi-n-propylamine	NDPA	621-64-7	C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> O	1,33
n-nitrosopiperidine	NPIP	100-75-4	C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O	0,72
n-nitroso-n-dibutylamine	NDBA	924-16-3	C <sub>8</sub> H <sub>18</sub> N <sub>2</sub> O	2,31

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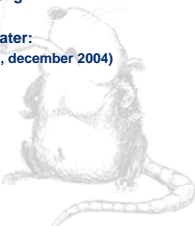
**NDMA: sources**

- **Industrial contaminant (byproduct)**
  - Leather, rubber, dyes, pesticides, rocket fuel etc.
- **Feed**
  - Beer, whisky, cheese, conserved fruit, meat and fish
- **Personal care products**
  - Cosmetics, shampoo, gels, conditioners, etc.
- **Natural sources**
  - Fish, algae, faeces
- **Water treatment**
  - Ion exchangers, chloramine disinfection byproduct, aluminium and polymer coagulants

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**NDMA: toxicity**

- **NDMA, genotoxic and human carcinogen**
  - Maximum accepted risk level 10<sup>-6</sup>
- **Acute toxicity: LD50 in rats 20-40 mg/kg**
- **(Proposed) guidelines for drinking water:**
  - RIVM, 2004 12 ng/l (provisional, december 2004)
  - RIVM, 1989 45 ng/l
  - WHO, 2003 20 ng/l
  - US, EPA, 1993 0.7 ng/l



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**Development of analytical method at Kiwa WR**

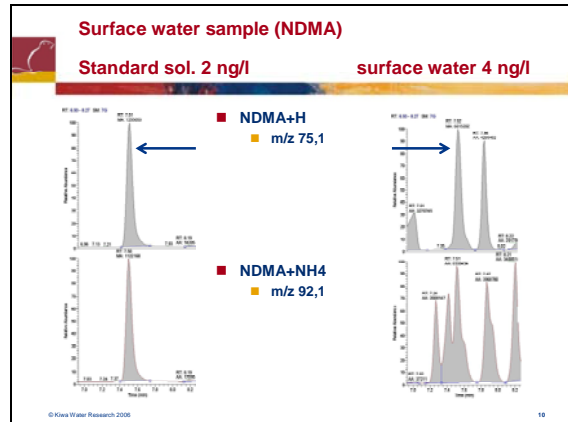
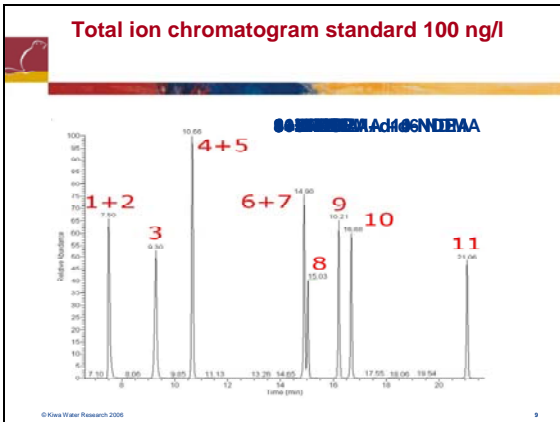
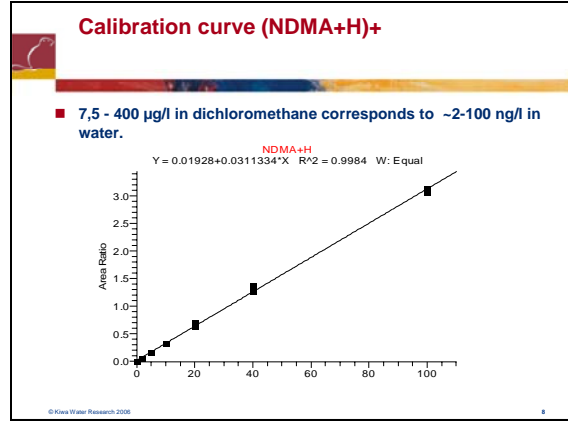
- **LLE with dichloromethane GCMS-EI**
  - Not specific
  - >10 ng/l
  - Recovery 20-30 %
- **CLLE with dichloromethane GCMS-CI-**
  - Automated extraction
  - Recovery ~50 %
- **Clean-up C18-disk, SPE two cartridges in serie (amborsorb 572) GCMS-CI+**
  - Recovery ~60 %
  - Complicated
- **SPE (coconut charcoal) GCMS-CI+**
  - 'Clean' extract
  - Recovery ~80-100 %
  - Simple

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### Analytical method at Kiwa WR

- **SPE extraction 1000 ml**
  - D6-NDMA, internal standard
  - Elution dichloromethane
- **Large volume injection 50 µl**
  - PTV injector, sintered glass liner
  - Column with trifluoropropyl phase by Varian VF200-MS of Restek RTX- 200
- **GCMS-Cl<sup>+</sup> Ammonia**
  - (M+H)<sup>+</sup> en (M+NH<sub>4</sub>)<sup>+</sup>
- **External calibration**
  - Correction for sensitivity of d10-nitrosodiethylamine and d14-nitrosodi-n-propylamine
- **NDMA and other nitrosamines included**

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### Detection limits

■ Limits of detection (LOD) and quantification (LOQ) in nanogram/liter

component	LOD	LOQ
NDMA	1	1
NMEA	2	2
NDEA	3	3
NPYR	3	3
NMOR	3	3
NDPA	3	3
NPiP	3	3
NDBA	1	3

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### Mean recoveries (%) at a level of 20 ng/l in water

component	drinking water n = 3	standard deviation	surface water n = 4	standard deviation
NDMA	81	20	75	15
NMEA	79	14	79	13
NDEA	82	7	77	6
NPYR	72	12	75	10
NMOR	90	4	94	8
NDPA	84	3	81	9
NPiP	69	12	71	9
NDBA	68	19	62	17

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### Occurrence NDMA: historical data

- In the Netherlands:
  - conc. <100 ng/l in the river Rhine and Meuse in 1996 (ref.: RIWA "Van Genderen report")
  - 2002; 7 ng/l in Rhine, 2 ng/l in the Meuse
  - In 2003, raw water 0-10 ng/l, drinking water ≤ 2 ng/l

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### NDMA (ng/l) in surface water from river Rhine in 2005 (RIWA)

- Month/2005: j f m a m j j a s o n d
- Rhine Lobith 2 < 2 2 3 1 3 3 3 3 3 2
- Lek Canal Nieuwegein < 2 1 < < < < < < < 1
- Lake IJsselmeer < < < < < < < < < < 1

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### NDMA (ng/l) at different stages in drinking water production

- Total number of analyses 120: all results < l.o.d. (1 ng/l):
  - After dune infiltration
  - Coagulation, rapid sand filtration
  - Slow sand filtration
  - Activated carbon filtration
  - Ozone
  - UV/H<sub>2</sub>O<sub>2</sub>

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### Final conclusion

- At this moment NDMA is not an issue in drinking water sources and drinking water in the Netherlands
- No frequent monitoring
  - Not a part of monitoring programs
- Confirmation of research results is needed when chloramine is proposed for disinfection

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# Carsten K. Schmidt: Removal of nitrosamines – Biodegradation and activated carbon treatment

TZW

## Removal of Nitrosamines Biodegradation and Activated Carbon Treatment

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### Is NDMA biodegradable in the aquatic environment ?

- Fournier et al. (2006) Biotransformation of N-nitrosodimethylamine by *Pseudomonas mendocina* KR1, *Appl Environ Microbiol* 72, 6693-6698
- Bradley et al. (2005) Biodegradation of N-nitrosodimethylamine in soil from a water reclamation facility, *Bioremed J* 9, 115-120
- Sedlak et al. (2005) Sources and fate of nitrosodimethylamine and its precursors in municipal wastewater treatment plants, *Water Environ Res* 77, 32-39
- Sharp et al. (2005) Aerobic biodegradation of N-nitrosodimethylamine (NDMA) by axenic bacterial strains, *Biotechnol Bioeng* 89, 608-618
- Yang et al. (2005) Degradation of N-nitrosodimethylamine in landscape soils, *J Environ Qual* 34, 336-341
- Gunnison et al. (2000) Attenuation mechanisms of N-nitrosodimethylamine at an operating intercept and treat groundwater remediation system, *J Hazard Mater B* 73, 179-197
- Kaplan and Kaplan (1985) Biodegradation of N-nitrosodimethylamine in aqueous and soil systems, *Appl Environ Microbiol* 50, 1077-1086
- Malik and Testai (1981) Transformation of nitrosamines in soil and in vitro by soil microorganisms, *Bull Environ Contam Toxicol* 27, 115-121

→ in principle: yes, but ...

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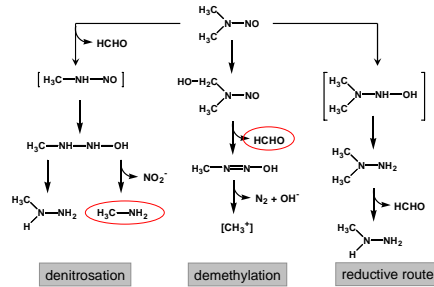
### Characteristics of Nitrosamine Biodegradation

- extent of microbial degradation of NDMA in aqueous and soil systems has not been clearly established
- soil experiments problematic: microbial degradation or volatilization ?
- quite persistent (elimination rates about 30-80 %)
- reported half-lives for NDMA in the system water/soil: 12-448 days
- no major differences: aerobic and anaerobic redox conditions
- degradation dependent on adaptation of microorganisms, nutrient status of the water, and competitive substrates
- nitrosamines can be mineralized by microbial communities under certain conditions with the degradation process being most probably co-metabolic
- it is not clear how nitrosamines behave during riverbank filtration, artificial recharge, biofiltration units
- the metabolic pathway of NDMA during microbial degradation has not been fully elucidated in the aquatic environment
- some hints on an analogy between bacterial and mammalian biochemical metabolism pathway, identified intermediates: formaldehyde and methylamine

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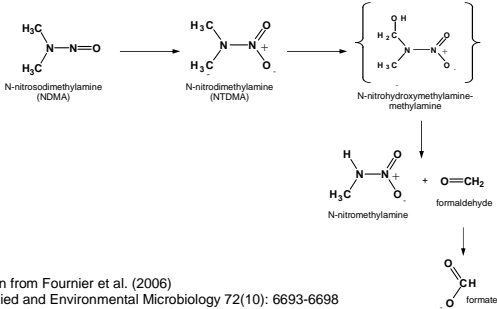
### Metabolism of NDMA by mammalian cells



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### Pathway of NDMA metabolism by *Pseudomonas mendocina* KR1

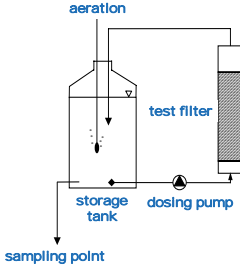


taken from Fournier et al. (2006)  
*Applied and Environmental Microbiology* 72(10): 6693-6698

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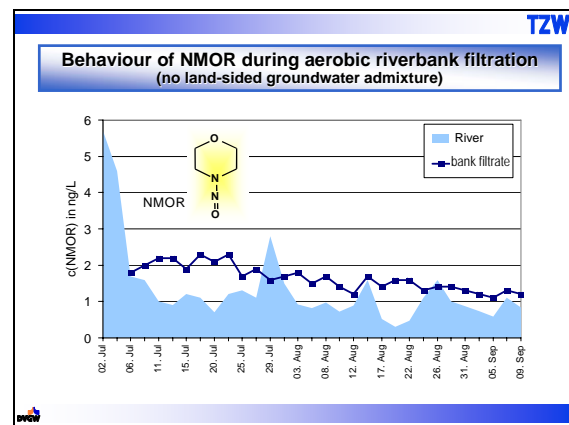
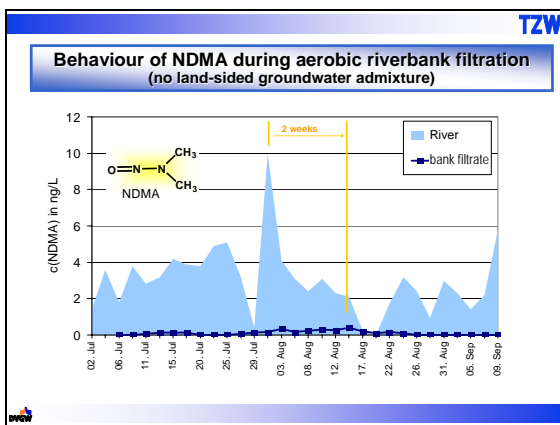
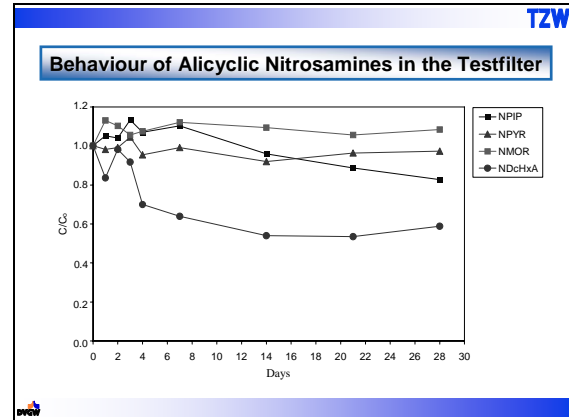
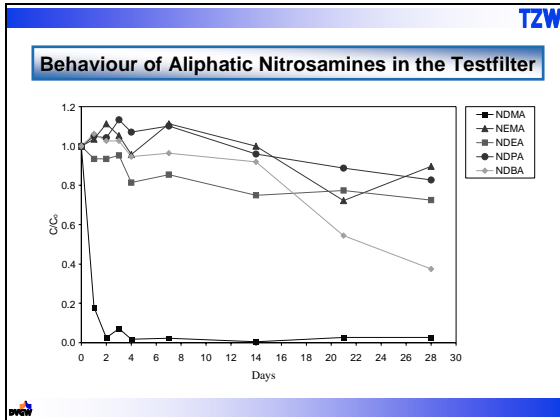
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### Aerobic Testfilter Experiments in the Laboratory



- aerated closed-loop apparatus
- 15 L storage tank filled with 10 L surface water (River Rhine)
- carrier material: porous glass beads (no adsorption capability)
- spiking level for single compounds: 100 ng/L
- 250 mL samples were taken regularly

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### Activated Carbon Filtration

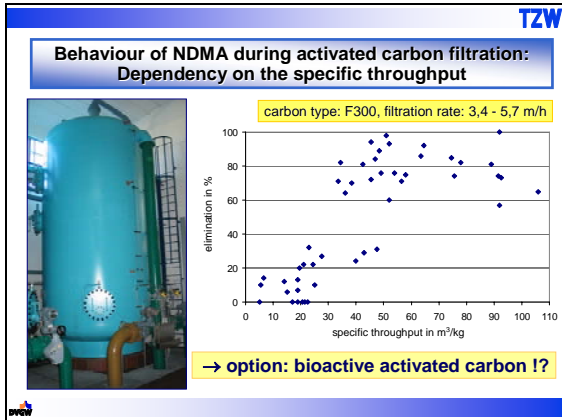
- NDMA:  $\log K_{ow} = -0.57$
- nitrosamines are highly hydrophilic and only poorly adsorbable on GAC as well as on polymer materials
- best results for NDMA removal were obtained with Ambersorb 572, a carbonaceous resin, followed by coconut shell carbon
- when compared to deionized water, the performance of all tested activated carbon types deteriorated in source water due to competitive action of other water constituents
- Freundlich parameters for Ambersorb 572 amounted to  $K = 9.65 \mu\text{g/g}$ ,  $1/n = 1.17$
- organic compounds commonly treated by carbon adsorption exhibit K values of  $>100 \mu\text{g/g}$  and  $1/n$  values below 0.6
- adsorption performance is thus rather bad and implies high costs due to short regeneration cycles

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### Freundlich Parameters for NDMA

Adsorbent	Description	Freundlich parameters		Reference			
		K (µg/g)	1/n				
Filtrosorb F400	industrial grade carbon	14.5	n.d.	0.602	n.d.	(Kommitsceni et al. 2003)	
Filtrosorb F300	industrial grade carbon	1.00	n.d.	1.138	n.d.	(Kommitsceni et al. 2003)	
BCP/MOD1	bituminous based but differently activated compared to F300/F400	61.5	1.17	0.754	0.973	(Kommitsceni et al. 2003)	
Cesstar	catalytically enhanced coal	7.52	n.d.	0.336	n.d.	(Kommitsceni et al. 2003)	
PCB	coconut-shell based coal	4.94	9.08	0.864	0.744	(Kommitsceni et al. 2003)	
Altech 5776	coconut-shell charcoal	4.26	1.31	0.894	1.11	(Kommitsceni et al. 2003)	
Ambersorb 600	hydrophobic carbonaceous resin	10.2	4.09	0.669	0.866	(Kommitsceni et al. 2003)	
Ambersorb 572	hydrophilic carbonaceous resin	4.92	2.17	0.93	1.07	(Kommitsceni et al. 2003)	
Filtrosorb F400	contaminated and spiked groundwater	n.d.	0.96	1.27	n.d.	1.00	1.18 (Fleming et al. 1996)
CSC	coconut-shell carbon - contaminated and spiked groundwater	n.d.	0.31	2.57	n.d.	0.82	0.93 (Fleming et al. 1996)
Ambersorb 572	hydrophilic carbonaceous resin - contaminated and spiked groundwater	n.d.	9.65	28.37	n.d.	1.17	2.25 (Fleming et al. 1996)
Ambersorb 563	carbonaceous resin - contaminated and spiked groundwater	n.d.	2.09	7.35	n.d.	0.98	1.87 (Fleming et al. 1996)

GW: groundwater; n.d.: not determined



## Martin Krauss: Advanced oxidation technologies for treatment and formation prevention of NDMA in water

Advanced Oxidation Technologies  
for Treatment and Formation Prevention  
of NDMA in Water

Changha Lee & Urs von Gunten  
(Martin Krauss)

Seoul National University of Aquatic Science and Technology, Graduate School of Aquatic Science and Technology, and School of Chemical and Biological Engineering, Seoul National University (SNU), Korea

GWRC

### Two strategies for reducing NDMA level in water using oxidation technology

Background

Part 1  
Part 2

- Oxidative degradation of NDMA (Part 1)
- Reduction of NDMA formation potential by pre-oxidation of NDMA precursors (Part 2)

Possible oxidants:  $\cdot\text{OH}$ ,  $\text{O}_3$ ,  $\text{ClO}_2$ ,  $\text{HOCl}$  and  $\text{Fe(VI)}$

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Background

Part 1  
Part 2

### Oxidative degradation of NDMA by ozone

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### Oxidative degradation of NDMA

Rate Constants for Reactions of NDMA with oxidants

Background

Part 1  
Part 2

$\text{O}_3$ :  $0.052 \pm 0.002 \text{ M}^{-1} \text{ s}^{-1}$   
 $\text{ClO}_2$ :  $< 0.001 \text{ M}^{-1} \text{ s}^{-1}$   
 $\text{Fe(VI)}$ :  $1.9 \text{ M}^{-1} \text{ s}^{-1}$   
 $\cdot\text{OH}$ :  $4.5 \pm 0.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$

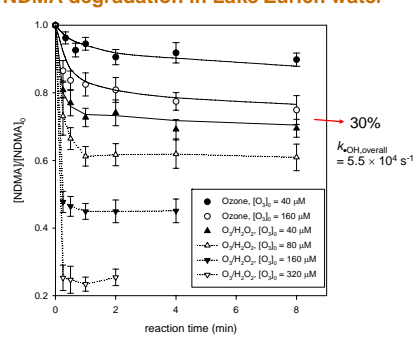
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### NDMA degradation in Lake Zurich water

Background

Part 1  
Part 2



$([\text{NDMA}]_0 = 1 \mu\text{M}, \text{ratio of } [\text{O}_3]_0/[\text{H}_2\text{O}_2]_0 = 2. \text{ Solid lines represent the model predictions})$

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### Pre-oxidation of NDMA precursors using $\text{O}_3$ and $\text{ClO}_2$ (Part 2)

Background

Part 1  
Part 2

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### Selection of model NDMA precursors

**Background**  
Part 1  
Part 2

Mitch and Sedlak, 2004 (ES&T)  
Mangino et al., 1985 (J. Agric. Food. Chem)  
Poocharoen et al., 1992 (J. Agric. Food. Chem)

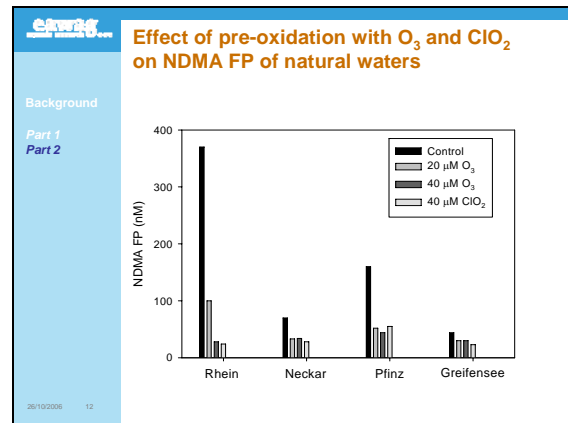
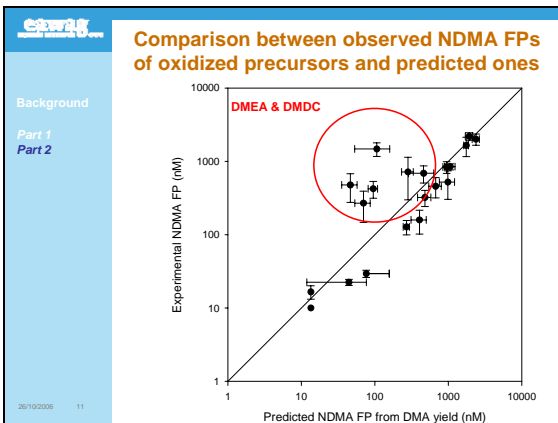
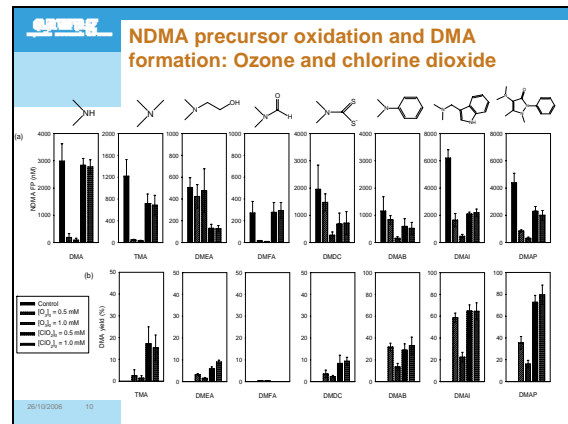
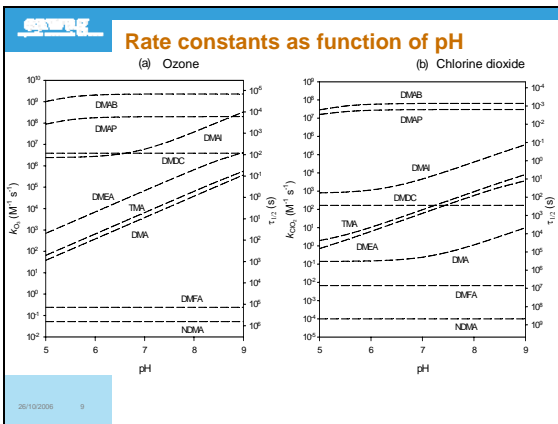
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### Determination of rate constants

**Background**  
Part 1  
Part 2

Compound	pK <sub>a</sub>	k <sub>O<sub>3</sub></sub> (M <sup>-1</sup> s <sup>-1</sup> )	k <sub>ClO<sub>2</sub></sub> (M <sup>-1</sup> s <sup>-1</sup> )	k <sub>OH</sub> (M <sup>-1</sup> s <sup>-1</sup> )
NDMA	< 1	5.2×10 <sup>-2</sup>	< 10 <sup>-3</sup>	4.5×10 <sup>8</sup>
H <sup>+</sup> -DMA	10.7	< 1×10 <sup>-1</sup>	< 1.4×10 <sup>-1</sup>	6.0×10 <sup>7</sup>
DMA		1.9×10 <sup>7</sup>	5×10 <sup>2</sup>	6.1×10 <sup>8</sup>
H <sup>+</sup> -TMA	9.8	-	< 1	4.0×10 <sup>8</sup>
TMA		4.1×10 <sup>8</sup>	6×10 <sup>4</sup>	1.3×10 <sup>10</sup>
H <sup>+</sup> -DMEA	9.2	< 2×10 <sup>-1</sup>	< 1×10 <sup>-1</sup>	5.3×10 <sup>8</sup>
DMEA		1.1×10 <sup>7</sup>	9.7×10 <sup>3</sup>	1.0×10 <sup>10</sup>
DMFA	< 1	2.4×10 <sup>-1</sup>	6.7×10 <sup>-3</sup>	1.7×10 <sup>9</sup>
DMDC	3.22	3.9×10 <sup>6</sup>	2.8×10 <sup>2</sup>	4.2×10 <sup>9</sup>
H <sup>+</sup> -DMAB	5.1	-	-	2.2×10 <sup>9</sup>
DMAB		2.3×10 <sup>9</sup>	6.5×10 <sup>7</sup>	1.4×10 <sup>10</sup>
H <sup>+</sup> -DMAI	10.0	2.4×10 <sup>6</sup>	7.7×10 <sup>2</sup>	6.9×10 <sup>9</sup>
DMAI		3.6×10 <sup>9</sup>	3.9×10 <sup>6</sup>	3.0×10 <sup>10</sup>
H <sup>+</sup> -DMAP	5.1	1.4×10 <sup>5</sup>	> 5×10 <sup>6</sup>	-
DMAP		2.0×10 <sup>8</sup>	≈ 3×10 <sup>7</sup>	3.6×10 <sup>9</sup>

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**ewag**

## Conclusions

1. Rate constants for reactions of NDMA with ozone and  $\bullet\text{OH}$  show that the reaction with  $\bullet\text{OH}$  dominates the NDMA degradation during ozonation.
2. Conventional ozonation could not significantly remove NDMA.  $\text{O}_3/\text{H}_2\text{O}_2$  AOP required  $> 160 \mu\text{M}$  ozone ( $[\text{O}_3]/[\text{H}_2\text{O}_2]_0 = 2:1$ ) for  $> 50\%$  NDMA removal.
3. DMAB, DMAI and DMAP were found to be fast-reacting compounds for both reactions of ozone and chlorine dioxide, whereas NDMA and DMFA reacted very slowly with the oxidants.
4. The pre-oxidation of NDMA precursors with ozone showed more effective reduction of NDMA FP than that with chlorine dioxide.
5. DMA is a main oxidized product responsible for NDMA FP in most cases, but DMEA and DMDC produce probably other products having NDMA FP.


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**Thank you very much  
for your attention!**

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## Taylor Mauck: WaterReuse Foundation – Germane Research



GERMANE RESEARCH

Taylor Mauck  
Project Manager


### The Reports

1. Investigation of N-Nitrosodimethylamine (NDMA) Fate and Transport
2. Alternative Methods for the Analysis of NDMA and Other Nitrosamines in Water and Wastewater
3. Removal and Destruction of NDMA and NDMA Precursors during Wastewater Treatment

### Objective



To assess the potential for NDMA in wastewater effluent to enter potable water supplies through landscape irrigation and groundwater recharge systems.

Conducted between 2002 and 2005 by a team of researchers from the University of California (UC) Berkeley, UC Riverside, Arizona State University, and Todd Engineers.




### Scope

- Fate and Transport of NDMA and NDMA Precursors in Groundwater
- Sorption and Biotransformation of NDMA and NDMA Precursors in Soils



### NDMA Occurrence, Fate, and Transport in Groundwater

- A review of field data from six different sites where NDMA was released to groundwater through a variety of mechanisms.
  - Intentional release
  - Unintentional release



### The Data

- Water quality data
- Data for other constituents other than NDMA
- Operational data
- Groundwater flow information
- Aquifer delineation and aquifer parameters
- Plume maps



### Decreasing NDMA Concentrations

1. Well location or construction
2. Mixing in the well
3. Sorption onto sediment particles
4. NDMA dispersed (spread out) in the aquifer
5. NDMA mixed with native groundwater
6. NDMA transformed  
e.g., biodegradation, chemical reaction

### Fate and Transport of NDMA In Groundwater Summary and Conclusions

- NDMA is not being sorbed or otherwise retarded with respect to groundwater flow
- Dispersion is not a major factor in most of the NDMA plumes analyzed
- NDMA mass is spread laterally and vertically by induced gradients from pumping wells

### Fate and Transport of NDMA In Groundwater Summary and Conclusions

- NDMA is not significantly transformed or removed from the system
- It is difficult to determine whether degradation is removing a significant mass of NDMA from the groundwater system
- Biodegradation may be occurring in some parts of the aquifer and not in others
- Biodegradation does not appear to have decreased NDMA concentrations below levels of concern

### NDMA Behavior in Soils

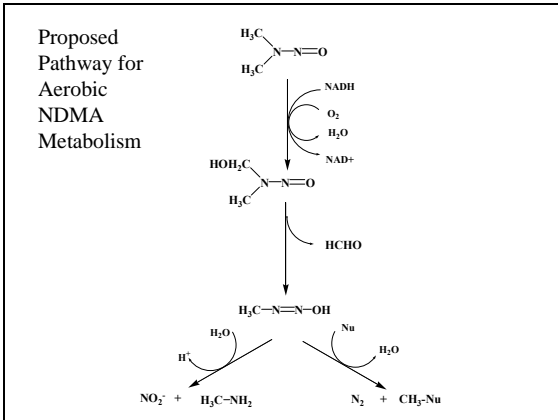
- Biotransformation and adsorption on surfaces  
– high polarity
- Sorption is important to NDMA fate and transport  
– opportunities for bacteria to degrade the compound

### Understanding Biotransformation and Sorption

- Three sets of experiments conducted:
1. **Characterization of NDMA biodegradation by pure strains of bacteria.**
  2. Studies designed to assess NDMA sorption and biotransformation
    - Mixed bacterial cultures under conditions encountered in soils where landscape irrigation is practiced.
  3. Assess the stability of NDMA precursors in the presence of bacteria
    - NDMA precursors from municipal WWTPs were exposed to a mixed bacterial culture.

### Bacteria and Enzymes Capable of NDMA Mineralization

- Four strains of common soil microbes are capable of degrading NDMA on the time scale of hours to days
- These strains express genes for monooxygenase enzymes.
- *Rhodococcus sp. RR1*  
– Propane-induced; 40x activity



### Understanding Biotransformation and Sorption

- Three sets of experiments conducted:
  1. Characterization of NDMA biodegradation by pure strains of bacteria.
  2. **Studies designed to assess NDMA sorption and biotransformation**
    - Mixed bacterial cultures under conditions encountered in soils where landscape irrigation is practiced.
  3. Assess the stability of NDMA precursors in the presence of bacteria
    - NDMA precursors from municipal WWTPs were exposed to a mixed bacterial culture.


### NDMA Adsorption in Landscape Soils

- Adsorption tested for the following soil types: Tree (Bare Surface), Ground Cover, and Turfgrass
- Adsorption in all three soils was weak and the difference between soils was small.
  - NDMA mobile in landscape soils, transport retarded by sorption to soil

### NDMA Sorption and Biotransformation in Soils


- The persistence of NDMA differed significantly among different landscape soil types.
  - different microbial activity in these soils
- The rate of degradation followed in the order:
 

Groundcover soil > turfgrass soil > bare-surface soil



### Biodegradation of NDMA Precursors

- Indirect potable reuse and landscape irrigation applications



### Biodegradation of NDMA Precursors

- Wastewater-derived NDMA precursors were relatively stable in the presence of bacteria collected from WWTPs
  - Loss of < 30% over periods of up to 30 days
- Unlikely to degrade in effluent-dominated surface water. Dilution is the only process that will reduce the concentrations of NDMA precursors
  - Typical hydraulic residence times are < 3 days

- Sorption and biotransformation data suggests that sorption coupled with biodegradation might result in removal of NDMA as it leaches through the vadose zone.
- Sorption experiments and previous data indicate that NDMA precursors might persist long enough to leach through the vadose zone.

## Laboratory vs. Field Conditions

Existence of biodegradation pathways for NDMA does not guarantee the degradation of NDMA in field conditions where microbial ecology and transport processes are more complex

- e.g., water reuse projects such as landscape irrigation and groundwater recharge

## Fate of NDMA and NDMA Precursors: Landscape Irrigation

- Wastewater effluent from Riverside Wastewater Treatment Plant applied by spray irrigation to turfgrass plots
- Samples collected from lysimeters installed below the vadose zone

## Irrigation Study Conclusions

- NDMA concentrations relatively high
- High irrigation rates used
- Sandy soil used
- Concentration of NDMA precursors reduced
- Turfgrass effective in preventing NDMA from leaching through the soil profile
  - Degradation
  - Uptake
  - Gas-phase diffusion

## Fate of NDMA and NDMA Precursors In Saturated Columns

- Saturated column, NDMA removal occurred
- Partial NDMA degradation under anaerobic conditions
  - Sufficient labile organic carbon
  - Oxygenase not only mechanism through which degradation can occur
- Disappearance of NDMA precursors
  - Precursors relatively stable under aerobic conditions
  - Additional research needed

## Conclusions

- NDMA removal can occur
  - Groundwater recharge & landscape application
  - Sorption unimportant to NDMA transport
  - NDMA biotransformation under certain conditions
- NDMA Precursors
  - Resistant to biodegradation
  - Unlikely to degrade under conditions encountered in effluent-dominated surface waters
  - Appear to be removed in groundwater systems
    - Presumably through sorption coupled with slow biodegradation

### Future Research Needs

- Assess the sorption of NDMA precursors on soils and the role of soil bacteria in NDMA degradation
- Investigating organisms responsible for NDMA degradation
- Investigating the pathways of NDMA biotransformation
- Identify NDMA precursors present in municipal wastewater effluent
- Role of labile organic carbon in degradation of NDMA and related organic compounds in water reuse systems

## **ANNEX 6: References**

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**ANNEX 7: Abbreviations**

AOP	Advanced oxidation process
CCL	Contaminant Candidate List
CI	Chemical ionisation
DHS	California Department of Health Services
DNA	Deoxyribonucleic acid
EPA	Environmental Protection Agency
GC	Gas chromatography
GWRC	Global Water Research Coalition
MCL	Maximum contaminant level
MCLG	Maximum contaminant level goal
MS	Mass spectrometer
NDBA	N-Nitrosodi-n-butylamine
NDEA	N-Nitrosodiethylamine
NDELA	N-Nitrosodiethanolamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodi-n-propylamine
NMEA	N-Nitrosomethylethylamine
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyrrolidine
OEHHA	California Office of Environmental Health Hazard Assessment
PHG	Public Health Goal
RIVM	Dutch National Institute for Public Health and the Environment
RNA	Ribonucleic acid
SPE	Solid-phase extraction
SPME	Solid-phase micro extraction
TZW	Technologiezentrum Wasser
UBA	German Federal Environmental Agency
UCMR	Unregulated Contaminant Monitoring Rule
UDMH	Unsymmetrical dimethylhydrazine
WWTP	Wastewater treatment plant