



Review

Nitrosamines and water

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ABSTRACT

This paper provides an overview of all current issues that are connected to the presence of nitrosamines in water technology. N-nitrosodimethylamine (NDMA) is the most frequently detected member of this family. Nitrosamines became the hottest topic in drinking water science when they were identified as disinfection by-products (DBPs) in chloraminated waters. The danger that they pose to consumer health seems to be much higher than that from chlorinated DBPs. This review summarizes our contemporary knowledge of these compounds in water, their occurrence, and precursors of nitrosamines in drinking and wastewaters, in addition to attempts to remove nitrosamines from water. The paper also reviews our knowledge of the mechanisms of nitrosamine formation in water technology. The current, commonly accepted mechanism of NDMA formation during chloramination of drinking waters assumes that dichloramine reacts with dimethylamine, forms unsymmetrical dimethylhydrazine and further oxidizes to NDMA. The question to answer is which precursors are responsible for delivering the DMA moiety for the reaction since the presence of DMA in water cannot explain the quantities of NDMA that are formed. There are also reports that other oxidants that are commonly used in water technology may generate NDMA. However, the mechanisms of such transformations are unknown. Methods for the removal of nitrosamines from water are described briefly. However, the research that has been undertaken on such methods seems to be at an early stage of development. It is predicted that photolytic methods may have the greatest potential for technological application.

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1. Introduction

The history of environmental pollution by nitrosamines seems to be lengthy. At first, industrial sources were blamed for polluting raw and drinking waters mainly with N-nitrosodimethylamine. (NDMA—abbreviations for nitrosamines are listed in Table 1.) The first reports that document the presence of NDMA in waters appeared in the 1970s. N-nitrosodimethylamine (NDMA) was detected in the air and water in locations that are adjacent to a factory near Baltimore (MD) that produced unsymmetrical dimethylhydrazine (UDMH) from NDMA ([1] and references therein). The reports that documents excessive NDMA concentrations in groundwater in the proximity of a rocket testing facility in California were particularly important [1]. Several studies have described NDMA formation in waters that have been treated with ion-exchange. The anion-exchange resins have quaternary amine functional groups that could serve as NDMA precursors [2–4]. However, at the beginning of the 21st century, the final disinfection of drinking waters appeared to be the main source of nitrosamines. Thus, chloramination was blamed for NDMA formation. This was ironic, because chloramination had been thought to generate a smaller number of disinfection by-products than other disinfectants. This stimulated research on the mechanisms of NDMA formation and its precursors, as well as the development of new methods of analysis, occurrence studies, and destruction methods, etc. All of the early reports of NDMA presence in water were comprehensively reviewed by Mitch et al. [1]. Another short review of NDMA issues in water industry was published by Nicholson [5]. Recently, Krasner [6] reviewed emerging disinfection by-products of health concern. The review also focused on NDMA issues. The reader can find a brief update of NDMA problems in Richardson's recent biannual reviews [7,8]. Human contact with NDMA is not limited to drinking water since nitrosamines have also been found in chlorinated swimming pool waters [9,10].

Nitrosamines (with NDMA as the most recognized member of this group) are probable human carcinogens that could seriously affect the safety of drinking water consumers. NDMA can form in chloraminated or chlorinated waters. There are reports of NDMA formation as a result of oxidation of certain precursors. Furthermore, it can form from ion-exchange resins and nitrogen-containing flocculants. Nitrosamines belong to the category of nitrogen-containing disinfection by-products (DBPs) that some researchers consider to be the most dangerous for humans [11]. The presence of ammonia nitrogen in chlorinated wastewater effluent has also been shown recently to significantly influence water genotoxicity [12]. Due to the high carcinogenic activity of nitrosamines, their maximum allowable concentration levels are generally set at a low ng/L level (for a risk of 10^{-5}), which causes serious analytical problems. After the discovery of NDMA in California well water, the State of California issued an action level of 2 ng/L for NDMA. However, this was subsequently revised to 10 ng/L, due to the difficulty in measuring it at the originally proposed level [13]. NDMA is generally present at a concentration of a few nanograms per liter in chloraminated/chlorinated drinking water, but can form or appear at much higher levels in wastewaters. NDMA is now placed on the Unregulated Contaminants Monitoring Rule (UCMR-2), where occurrence data are being collected for it and other nitrosamines on a national scale. Ontario has issued an interim maximum acceptable concentration of 9 ng/L for NDMA [14]. The Drinking Water Inspectorate of England and Wales requires monitoring of NDMA at 1 ng/L [15], while in Germany the permissible health-based values for NDMA and NMOR are equal to 10 ng/L [10,16].

The aim of this paper is to review the current state of knowledge concerning all aspects of nitrosamines formation and presence in water technology.

In general, there are two main strategies to consider concerning nitrosamines in drinking water technology: (i) to find an effective method to remove nitrosamines from water or (ii) to prevent their formation. There are no effective methods to remove nitrosamines and since they form mainly after final disinfection, the only way to avoid nitrosamines in water seems to be: (i) to understand how they are formed and (ii) to treat water with the best available methods to minimize their formation.

The present knowledge cannot fully explain how these minute amounts of nitrosamines are formed. The very low yield (approximately 1% or less) in most of the reactions considered makes predictions or determination of the actual mechanism that are responsible for the formation of the compounds even more difficult. In this review, controversies concerning the formation of NDMA in water technology processes will be emphasized. A lack of disinfection, that is distribution of biologically stable water, which does not require final disinfection with chemicals, seems to be the best way to avoid the presence of NDMA in drinking water. However, it must be realized that some surface and ground waters, particularly those affected by chlorinated wastewater treatment plant (WWTP) effluents, may require the removal of NDMA.

2. Nitrosamines

Scientists have been studying nitrosamines for more than a 100 years. However, when in 1954 Barnes and Magee [17] discovered the carcinogenic properties of the group, nitrosamines gained more attention. It has been proved that roughly 90% of nitrosamines are carcinogenic. Although NDMA is the subject of the majority of papers, other members of the group have also been detected in drinking waters. These include: N-nitrosomorpholine [18], N-nitrosopyrrolidine [18,19] N-nitrosopiperidine [19] and N-nitrosodiphenylamine [19,20]. Several secondary N-nitrosamines are of concern to USEPA. The properties of the nitrosamines are listed in Table 1.

Nitrosamines are polar compounds and usually soluble in water. Their partition coefficients in octanol/water are low and therefore the compounds are difficult to extract with organic solvents. The compounds also are not adsorbed on nonpolar surfaces to any significant extent. The Henry constants are small, which means that nitrosamines cannot be removed from water by aeration. NDMA strongly absorbs 225–250 nm radiation (at 238 nm $\epsilon_{\text{mol}} = 7380 \text{ L/M cm}$) and this property may be used for photolytic destruction of the compound in water. As a polar compound, NDMA is not bioaccumulated, but also appears to be hardly biodegradable. The large hydrophilicity, the low adsorbability and the recalcitrant nature of nitrosamines contribute to a large risk of ground water contamination. However, the most serious threat for consumers results from the generation of NDMA during final disinfection of drinking water with chloramines. The concentration of NDMA increases with distance from the water treatment facility [23–25].

3. Analysis of nitrosamines

Research on nitrosamine occurrence in waters would not be possible without the development of sensitive methods and analytical procedures. There are many methods to analyze nitrosamines and many of the compounds are routinely analyzed (e.g., in food or in rubber products) [26,27]. The methods are often based on a denitrosation reaction. The subsequent determination of the resulting secondary amines by derivatization cannot be used to determine the NDMA and related compounds in water, as secondary amines may be present in waters at concentrations three orders of magnitude higher than those of the nitrosamines.

Table 1
The properties of secondary nitrosamines (USEPA) [21].

Nitrosamine (Abbreviation)	Formula	Molecular weight (g/mol)	log $K_{o/w}$ [22]	Standard US EPA cancer classification group	MCL for $R = 10^{-5}$ (ng/L)
N-nitrosodimethylamine (NDMA)	C ₂ H ₆ N ₂ O	74,082	−0.57	B2	7
N-nitrosomethylethylamine (NMEA)	C ₃ H ₈ N ₂ O	88,108	0.04	B2	20
N-nitrosodiethylamine (NDEA)	C ₄ H ₁₀ N ₂ O	102,135	0.48	B2	2
N-nitroso-di-n-propylamine (NDPA)	C ₆ H ₁₄ N ₂ O	130,188	1.36	B2	50
N-nitroso-di-n-butylamine (NDBA)	C ₈ H ₁₈ N ₂ O	158,241	2.63	B2	60
N-nitroso-di-phenylamine (NDPhA)	C ₁₂ H ₁₀ N ₂ O	198,221	3.13	B2	70,000
N-nitrosopyrrolidine (NPYR)	C ₄ H ₈ N ₂ O	100.1	−0.19	2B (IARC)	
N-nitrosopiperidine (NPIP)	C ₅ H ₁₀ N ₂ O	114.15	0.36	B2	
N-nitrosomorpholine (NMOR)	C ₄ H ₈ N ₂ O ₂	116.12	−0.44	2B (IARC)	

MCL: maximum contaminant level for risk 10^{-5} . (The abbreviations are used throughout the text).

This limitation does not hold when post-column derivatization is used. Pérez-Ruiz et al. [28] applied post-column (HPLC) nitrosamine photolysis and tris(2,2'-bipyridyl) ruthenium (III) chemiluminescence for the detection of ng/L concentrations of NDMA, NDEA, NPIP, NMOR, NPYR. The method is based on the earlier idea of Noffsinger and Danielson [29]. Strata X (Styrene–divinylbenzene) cartridges were used for the preconcentration of the nitrosamines. This appeared to be more efficient than using active carbon. A detection limit (LODs) of a few nanograms per liter was obtained.

Tomkins et al. [30] and Tomkins and Griese, [31] developed an analytical method that quantifies NDMA in water at a level of 2–3 ng/L. It included a C₁₈ Empore disk to remove neutral organic compounds from water, an extraction of NDMA with dichloromethane, concentration of the extract, adsorption of NDMA in a carbon trap followed by thermal desorption into GC column and chemiluminescent nitrogen detection.

The methods currently used for the determination of nitrosamines are based on enrichment of nitrosamines by solid phase extraction (SPE), elution of the analytes with methylene chloride, concentration of the eluate to less than 1 ml and chromatographic (GC or HPLC) analysis with MS/MS detection [32–35]. Low N-nitrosamine recoveries are common for both liquid–liquid extraction (LLE) and SPE methods. Thus, an isotope dilution method is used to reduce uncertainty in the determination.

Charrois et al. [32] proposed the use of a combined SPE column consisting of a LiChrolut EN (bottom layer) with an Ambersorb 572 (upper layer). LiChrolut EN is an ethylvinylbenzene–divinylbenzene sorbent powder material with a high specific surface area (1200 m²/g). Ambersorb 572 is a carbonaceous spherical bead material with a high surface area of 1100 m²/g. Dichloromethane was used for elution of nitrosamines from the SPE column. The volume extracted was reduced with nitrogen gas to 200 μ l to achieve a concentration factor of 2500. Chromatography was performed with GC coupled with the mass

selective detector operating in PCI mode and ammonia as the reagent gas.

Munch and Bassett [35] developed EPA method 521 for seven nitrosamines. The SPE procedure used coconut charcoal as the adsorbent, dichloromethane extraction, concentration of the extract to less than 1 ml and analysis by GC/CI–MS/MS with methanol as the reagent.

Cheng et al. [34] developed an alternative method to analyze eight nitrosamines in water. The authors compared three methods to isolate nitrosamines: SPE with an in-house loaded Ambersorb 572 adsorbent, commercially available cartridges for SPE (CSPE) and a micro liquid–liquid extraction (MLLE) system. A concentration factor of 1250 was obtained with the SPE system and dichloromethane elution. The CSPE graphitized carbon black cartridge supplemented with 350 mg of Ambersorb 572 resin appeared to be the most efficient for nitrosamine retention. The elution was carried out with dichloromethane and, after final evaporation of the solvent, a concentration factor of 1000 was achieved. In the MLLE system, dichloromethane was used as the extractant and the final concentration of the extract to 0.5 ml led to a 200-fold enrichment. The authors [34] of the method claim that further concentration with corresponding smaller detection limits (MDLs) is possible. It is worth mentioning that, in all extractions, the salting-out effect (with NaCl) appeared to have a favorable influence on the extraction efficiency. For final determination of nitrosamines, GC–CI/MS/MS with methanol as the reagent was applied.

Krauss and Hollender [33] recently described a new analytical procedure to determine nine nitrosamines with SPE and HPLC–MS/MS. The solid phase extraction used for isolation of nitrosamines from water was carried out in two combined cartridges. One reversed phase (Oasis HLB) cartridge in the top position was used to remove nonpolar interferences and enrich less polar nitrosamines, while a carbonaceous sorbent (Bakerbond Carbon) was applied to retain most polar nitrosamines. A similar idea was employed earlier by Tomkins et al. [30]. The analytes were eluted

Table 2
MDL of various nitrosamine analysis methods (ng/L).

	Charrois et al. [32]	Krauss and Hollender [33]	Cheng et al. [34]			Munch and Bassett [35] EPA 521 method		SPME extraction Grebel et al. [36]		
			SPE	CSPE	MLLE	Lab.1	Lab.2	NCD	NPD	CI/MS
NDMA	0.7	0.4	0.78	0.70	2.3	0.28	0.33	57	890	30
NMEA	0.4	0.9	1.35	1.36	3.9	0.28	0.17	132	226	90
NDEA	0.6	0.7	1.78	0.84	2.5	0.26	0.31	87	181	64
NDPA	1.0	0.8	1.64	0.81	3.4	0.32	0.24	58	144	59
NPYR	1.2	1.0	0.84	0.54	1.8	0.35	0.20	–	–	–
NPIP	1.3	0.1	1.35	0.33	2.2	0.66	0.27	125	1016	59
NMOR	1.0	0.2	1.38	0.63	2.7	–	–	–	–	138
NDBA	1.3	3.3	1.61	0.80	3.8	0.36	0.22	193	242	79
NDPhA	–	2.4	–	–	–	–	–	–	–	–

SPE, solid phase extraction; CSPE, cartridge solid phase extraction; MLLE, micro liquid–liquid extraction; NCD, nitrogen chemiluminescence detector; NPD, nitrogen–phosphorous detector; CI/MS, chemical ionization (with ammonia)–mass spectrometry.

with dichloromethane and analyzed by HPLC with a reversed C₁₈ column and a linear ion trap/orbitrap mass spectrometer.

Solid phase microextraction (SPME) has also been tried as a method for the isolation and enrichment of nitrosamines before chromatographic analysis. Although the method was less time consuming than those described above, it did not ensure the required sensitivity [36]. The detection limits that were achieved for all of the systems described above are combined in Table 2.

A fast screening method for nitrosamines was developed by Jurado-Sánchez et al. [10]. It consists of a solid phase extraction using 250 ml water that passes through a 75 mg LiChrolut EN cartridge, elution of the analytes with 150 µl (acetonitrile–ethylacetate 1:9), concentration of the extract to 10 µl (a concentration factor of 25,000) and gas-chromatography with a nitrogen–phosphorous detector (GC-NPD) analysis on a short, 1.5 m capillary column. Two chromatographic peaks were observed—one for NDMA and NDEA and the second for NPYR, NMOR, NPIP, and NDBA. However, the results of the screening methods require further confirmation using a standard GC-MS. The limits of detection for six nitrosamines are in the range of 0.4–1.7 ng/L.

To summarize, Ambersorb 572 (a carbonaceous, spherical bead material with a high surface area of 1100 m²/g), which was first proposed by Jenkins et al. [37], is commonly used in analytical procedures as an adsorbent in SPE cartridges for nitrosamine enrichment. Dichloromethane also seems to be commonly used as the best solvent for extraction of nitrosamines in both SPE and LLE procedures. The determination of low concentrations of nitrosamines requires ca. 1000-fold enrichment of the analytes before chromatography (mainly GC) with chemical ionization and tandem mass spectrometry. Isotope dilution is used to increase the precision of analysis. Carbonaceous adsorbents should be used with care as, according to a recent report [38], carbon may catalyze the oxidation of DMA to NDMA in the presence of oxygen.

4. Occurrence studies

Nitrosamines have been found in surface and ground waters, in wastewater treatment plant influents and effluents, as well as in drinking waters.

4.1. Drinking waters

Few systematic studies of real drinking water systems are available, but the general conclusion of the studies identifies chloramination as the main source of NDMA in finished water. The chlorination of ground water that is polluted with ammonia may also result in the formation of NDMA.

One of the first occurrence studies focused on NDMA presence in US and Canadian drinking water treatment plants. The studies were carried out by Barret et al. [25]. Samples of raw waters and water treatment plant effluents from distribution systems of 21 water treatment facilities were analyzed for nitrosamine presence. Almost no NDMA was present in the raw waters. Slightly higher concentrations of NDMA were found in chloraminated waters than the chlorinated waters, although almost all results were below Canadian and US standards for drinking water (9 and 10 ng/L, respectively). The study identified anion-exchange resins as an important source of NDMA precursors as the chlorinated water from the plant applying the process had the highest concentration of the nitrosamine (25 ng/L). The study also confirmed that the chloramine reaction that leads to NDMA formation is relatively slow. This resulted in increasing concentrations of nitrosamine as the distance from the treatment plant increased [25].

The California Department of Health Services conducted a survey of nitrosamines in 32 water treatment plants. (Table 3).

The survey confirmed the presence of NDMA in some raw waters (later Zhao et al. [39] also found NDMA in some influent waters). It also indicated that chloramination is an important source of NDMA. However, the study also showed that chloramine alone is insufficient for generation of nitrosamine. The water must contain certain precursors. Analyses were undertaken for several possible factors, including chlorine residual (both free and total), pH, temperature, alkalinity, total organic carbon, nitrate-N, nitrite-N, ammonia-N, and total Kjeldahl nitrogen. No correlations could be found. The study confirmed the earlier findings of Barret et al. [25] regarding the significance of ion-exchange resins as important sources of NDMA precursors [40].

Charrois et al. [18] have surveyed 179 Ontario water treatment plants for nitrosamine presence. The study concerned influent, effluent and distribution water samples. Altogether more than 3000 samples have been analyzed. Except for NDMA, nanogram quantities of N-nitrosomorpholine and N-nitrosopyrrolidine have been detected in some waters.

The results collected by Charrois et al. [18] confirm again that some raw waters may already contain NDMA and that both chlorination and chloramination of waters may lead to the formation of nitrosamine. Although chlorination may generate some NDMA, the median concentration values of chlorinated systems were far below Canadian standards. For chloraminated systems, median NDMA concentrations were slightly higher for effluent and distribution samples, but still lower than the standard. Of the 179 drinking water systems that were surveyed, 30% were found to contain NDMA. Most NDMA concentrations were associated with facilities that use chloramine for final disinfection. It is also worth emphasizing that, in chloraminated systems, the median NDMA concentration increases in distribution systems. According to Charrois et al. [18], the presence of nitrosamines in water may be positively correlated with the presence of organic nitrogen. The results of the survey by Charrois et al. [18] are shown in Table 4.

Additionally, in the same paper, 20 samples from Alberta public drinking water distribution systems were analyzed. In one of the utilities, the water had an exceptionally high concentration of organic nitrogen. That resulted in high concentrations of NDMA; 66 ng/L was detected in the sample taken from the middle of the distribution system, while 100 ng/L was found in the sample taken at the farthest extreme of the same system [18].

Eleven US WTPs were examined for NDMA formation by Zhao et al. [39]. The raw waters were found to contain NDMA in concentrations of 0–53 ng/L. Chemical disinfection caused an increase in NDMA concentrations; chlorination, chloramination and chlorine dioxide were shown to increase NDMA in finished waters. We have previously reported [41] that ClO₂ may oxidize DMA to NDMA. The paper of Zhao et al. [39] is the first to confirm our observations. Zhao et al. also confirmed that ozonation and chlorine dioxide efficiency for the reduction/elimination of NDMA formation depends on the nature of the nitrosamine precursors in the source water. Significantly, more NDMA (than in the untreated water) was found after advanced oxidation processes (AOP) (H₂O₂/UV) in some waters.

A nationwide survey of NDMA occurrence in Japan was carried out by Asami et al. [42] in raw and finished waters from many water treatment plants. Nitrosamine was detected in raw waters in a concentration of less than 10 ng/L. The NDMA concentrations were greater in waters containing higher levels of total nitrogen. It must be emphasized that, in Japan, chloramination is not used for final disinfection. Ozonation was shown to increase substantially the NDMA concentrations in two waters. In both cases, however, biologically active filter (BAF) treatment removed the nitrosamine efficiently. The authors noticed some positive correlation between population density and NDMA concentrations in surface waters.

Table 3

NDMA occurrence results in 32 California drinking water plants (California Department of Health Services last updated March 15, 2002) as cited in Charrois et al. [18].

		No. of samples (<i>n</i>)	Concentration		Samples > MDL
			Median (ng/L)	Max. (ng/L)	
Chlorine	Influent	11	<1	9.4	3
	Effluent	11	<1	3.3	3
	Distribution	12	<1	2.5	4
Chloramine	Influent	27	<1	3.9	9
	Effluent	31	1.8	18.3	21
	Distribution	34	1.8	15.8	27
O ₃ /chlorine	Influent	7	<1	1.3	2
	Effluent	10	<1	3.9	5
	Distribution	10	<1	6.8	3

To summarize, the available surveys have shown that about one third of raw waters is more or less polluted with NDMA. Although chloramination seems to be the most significant source of NDMA in drinking waters, it seems that all oxidants are able to form NDMA when some unidentified precursors are present in treated water.

4.2. Wastewaters

A number of nitrosamines have been found in primary effluents in wastewater treatment plants (WWTPs) in Switzerland: NDMA, NMOR, NDBA, NPIP, and NDEA with concentrations typically in the range 5–25 ng/L [43]. According to Krauss et al. [43], human urine can be considered to be a source of NDMA in concentrations of up to ca. 5 ng/L in raw wastewaters, while higher concentrations are caused by industrial wastes. NPIP was also found in human urine and its excretion found to correlate with coffee consumption [44]. Nitrosamine concentrations are highly variable, hourly and daily. Activated sludge removal efficiency was estimated at ca. 60% or higher for concentrations of NDMA exceeding ca. 15 ng/L. The secondary effluent NDMA concentrations were usually lower than 10 ng/L. Since there usually is no chemical disinfection of the treated wastewaters in European countries, there is no threat of the formation of additional amounts of nitrosamines [43].

WWTP primary sludge supernatant contained up to 1 µg/L of NDMA, whereas the final concentrations were well above 100 ng/L [45]. Nitrosamine removal was directly correlated with chemical oxygen consumption. According to Padhye et al. [45], more efficient removal of NDMA requires additional biodegradable carbon. Astonishingly high and variable concentrations of NMOR of 130–12,700 ng/L have been observed by Krasner et al. [46] at one WWTP in the USA, while, at the same facility, NDMA was found at a low level of ng/L. However, disinfection with chlorine resulted in excessive NDMA formation up to 3000 ng/L. Very high (up to 5000 ng/L) and variable concentrations of NDMA were noted in the effluents of three WWTPs by Zhou et al. [47]. The implementation of

nitrification/denitrification and sequential disinfection with chlorine decreased the nitrosamine concentrations in effluents by an order of magnitude.

Padhye et al. [45] have shown that nitrosamines (NDMA and NPYR) are present in considerable amounts in wastewaters. The highest concentrations of nitrosamines were found in primary sludge supernatant, but subsequent stages of treatment decreased the concentrations substantially. Sedlak et al. [48] found NDMA in concentrations ranging from 80 to 790 ng/L in seven wastewater treatment plant influents. Dimethylamine was present in these waters at concentrations of 50–120 µg/L and accounted for the majority of NDMA precursors. The analysis of the effluents from the WWTPs confirmed that NDMA was not removed consistently. The effluents contained unidentified NDMA precursors, while most DMA was removed by biological processes [48]. NDMA that is discharged with effluents from WWTP may readily degrade in the environment by biological or photochemical processes, while unidentified NDMA precursors are resistant to biochemical degradation. Such effluents may deliver NDMA precursors to water treatment plants (WTP) located downstream [49]. Incidentally, wastewater NDMA could reach concentrations of few micrograms per liter [46]. Similar values of NDMA in some California wastewater plant effluents have been found by Zhou et al. [47]. According to Pehlivanoglu-Mantas et al. [49], WWTP effluents containing ammonia are used for landscape or crop irrigation. Such waters are disinfected with high doses of chlorine. A full-scale system was shown to produce up to 460 ng of NDMA/L when chlorination was applied in the presence of ammonia [50]. In systems without ammonia in the wastewater effluents, only up to 20 ng of NDMA/L was detected after chlorination. The authors advise the use of lower doses of chlorine for disinfection. This seems to contradict the findings of Krasner et al. [46]. The fate of wastewater-derived disinfection by-products in surface waters was examined by Chen et al. [51] and solar photolysis appeared to be the main mechanism decreasing concentrations of NDMA in river waters.

Table 4

NDMA data from 179 Ontario water treatment plants [18].

		No. of samples (<i>n</i>)	Concentration		Samples > MDL
			Median (ng/L)	Max. (ng/L)	
Chlorine	Influent	851	<1	8	245
	Effluent	1429	<1	40	794
	Distribution	282	<1	66	100
Chloramine	Influent	142	<1	6.7	53
	Effluent	277	1.3	65	166
	Distribution	76	2.2	18	60
O ₃ /chlorine	Influent	2	<1	<1	0
	Effluent	2	<1	<1	0
	Distribution	2	<1	<1	0

To summarize, wastewater effluents may pollute the receiving (ground or surface) waters with both NDMA and NDMA precursors. The presence of nitrosamines in drinking waters seems to be connected to the application of chemical oxidation in water treatment. Chloramination is most often identified as the source of NDMA in finished waters.

Human excretion and industrial pollution are the sources of nitrosamines in wastewater influents. Human excretion results in a relatively low and stable level of nitrosamines. Industrial sources, on the other hand, are the most probable cause of incidental pollution of wastewaters with unstable concentrations of nitrosamine. According to the observations made so far, better nitrification/denitrification leads to a lower risk of NDMA formation during the final disinfection of wastewater effluents. Furthermore, better chemical oxygen demand (COD) removal seems to be connected to better removal of NDMA precursors. In USA and Canada, nitrosamine concentrations in wastewater influents and effluents vary in a very wide range (from the low $\mu\text{g/L}$ to the low ng/L). In Europe, WWTP effluents are not disinfected and therefore no threat of NDMA formation exists. However, there are also no European results concerning the presence of NDMA precursors in the effluents.

5. Precursors of NDMA in drinking water technology

According to some earlier cited papers, raw waters may already contain certain amounts of NDMA [18,25,39]. In the generation of NDMA, nitrosamine precursors are the key issue, as it is clear that nitrosamines may be formed during water treatment (and distribution) only from compounds that contain organic nitrogen. Since NDMA removal cannot be applied after final disinfection, it is necessary to identify precursors and then attempt to remove them from the water to avoid the formation of nitrosamines. A possible list of NDMA precursors contains:

- dimethylamine, if present in natural waters,
- undefined organic nitrogen as a part of natural organic matter [52,53],
- other amines (tertiary- or quaternary-) that can be oxidized to DMA during water treatment [54],
- cationic flocculants [23],
- anion exchange resins that are used for ion-exchange in water treatment [2,55].

It is obvious that dimethylamine (DMA) is the most natural and most likely precursor of NDMA. Of course, the majority of laboratory experiments on the formation of NDMA have been carried out with DMA. However, there is no systematic data on the presence of DMA in natural surface and ground waters. There are few papers that describe the determination of secondary amines in river waters. Furthermore, the results presented in this regard are rather inconsistent. According to Sacher et al. [56], concentrations of DMA in German rivers do not exceed $3 \mu\text{g/L}$. Except for DMA, morpholine was also detected in river waters by the same group of researchers. Cai et al. [57] detected about $20 \mu\text{g/L}$ of DMA in lake waters, while, according to Zhao et al. [58], more than $200 \mu\text{g/L}$ of DMA were found in another lake. Sewage-polluted waters were shown to contain more than $200 \mu\text{g/L}$ of DMA. Yet, in large rivers with a higher dilution factor, DMA was not found [59]. The data is quite inconsistent, as it represents single samplings from different surface waters and during unspecified seasons. Since the expected concentrations of DMA in natural water are usually at the $\mu\text{g/L}$ level, even reactions with less than a 1% yield may be of importance for the formation of NDMA. Although secondary amines undergo biodegradation in natural systems, the rate of this process has been shown to depend

strongly on the amine concentration [60]. Similarly, no data about the behavior of secondary amines in the water treatment technological pathway is available.

On the other hand, Gerecke and Sedlak [53] and Chen and Valentine [52,61] have shown that chloramination of natural organic matter (NOM) is responsible for the formation of significant amounts of NDMA. According to Chen and Valentine [52], the oxidation of natural organic matter by chloramines is the rate-determining step in formation of NDMA. The quantity of NDMA can be correlated linearly with a decrease of SUVA value at 272 nm [52]. In a subsequent paper, Chen and Valentine [61] found that the dimethylamine present in river water at $0.5 \mu\text{g/L}$ could account only for 15% of the NDMA that was formed, while the prevailing amounts of the nitrosamine were formed from NOM. Of the six fractions of NOM, hydrophilic bases have been found to be the most potent NDMA precursors, even though their share of NOM was less than 5%. All of these facts conspire to confirm that DMA is not the single NDMA precursor. Soon, the research efforts to find the NDMA precursors became focused on dissolved organic nitrogen (DON) [62]. DON is a summary parameter concerning undefined organic nitrogen that is contained in natural organic matter. Wastewaters may contain DON at concentrations higher than those in natural waters and thus NDMA formation may be associated particularly with wastewater-impacted waters [63,64]. There are three main sources of DON in raw waters:

- effluents from wastewater plants (with relatively high NDMA formation potential (NDMA-FP)) that are located upstream of the WTP,
- SMPs – soluble microbial products – as a group of compounds from biomass decay and substrate metabolism, containing proteins [65]; SMPs were shown by Krasner et al. [66] to slightly increase NDMA-FP,
- autochthonous organic matter that contain extra- and intracellular algal organic matter.

These three sources of DON may substantially increase NDMA formation potential in raw waters [66,67].

The average DON concentration in raw waters measured for 28 US WTPs in 13 states was about 0.186 mg/L [68]. It is also interesting to note that the molecular weight distribution of DON is similar to that of dissolved organic carbon (DOC). Lee et al. [68] also found that fluorescence spectroscopy may be used as a reasonable surrogate for DON. Excitation at $270\text{--}280 \text{ nm}$ and emission at $300\text{--}350 \text{ nm}$ correlated well with protein-like material. A similar conclusion may be drawn from the work of Hua et al. [69], who indicated that fluorescence from excitation at $290\text{--}310 \text{ nm}$, emitted at $330\text{--}350 \text{ nm}$ is closely related to the NDMA formation potential. NDMA precursors are usually associated with non-humic substances. This is why waters that have a high DOC do not form much NDMA [70]. Substantial amounts of nitrosamine precursors are provided by wastewater treatment plant effluents. Certain agricultural activity may also increase DON and NDMA formation upon chloramination [70]. Since DON constitutes only a minor part of DOC, it has never been subjected to intensive research in wastewater treatment technology. DON was found to constitute barely 10% of the total dissolved nitrogen in raw waters. DON in wastewaters has been comprehensively reviewed recently by Pehlivanoglu-Mantas and Sedlak [71]. It is also worth emphasizing that DON has recently become the most unwanted part of NOM in drinking water treatment technology as it appears to be responsible for the formation of the most dangerous disinfection by-products [11,62,72,73]. The determination of DON is not easy and has been a matter of dispute [74,75]. DON may contain up to $50 \mu\text{M/L}$ of total organic nitrogen.

Anionites constitute the next group of NDMA precursors in drinking waters. The first reports on the presence of NDMA in waters treated by ion-exchange were prepared in the seventies [2–4]. Kimoto et al. [2] noted an exceptionally high concentration of NDMA when chlorine-containing water was exposed to a mixed-bed demineralization resin. Najm and Trussel [55] confirmed the formation of NDMA in chloraminated water contacted earlier with strong-base quaternary amine ion-exchangers. They also observed a significant increase in NDMA formation for resins that had been soaked in nitrite-containing water. Kemper et al. [76] continued research on NDMA release from ion-exchangers and, according to their results, resins may pollute water with NDMA when freshly used and/or when used shortly after regeneration. When, however, feed water contained chlorine or chloramine, NDMA formation was observed in the first bed volume of an ion-exchanger. The presence of nitrate enhanced NDMA formation. Resins were found to release NDMA precursors, which substantially increased the nitrosamine formation after adding chlorine or chloramine for disinfection.

Cationic treatment polymer poly (diallyldimethylammonium chloride) (poly DADMAC) has been found to be a single and significant precursor of NDMA in drinking water by Wilczak et al. [23] Various commercial DADMAC polymers showed different NDMA formation potential. Increased polymer doses caused increased NDMA formation after the chloramination of finished waters. Lower polymer doses and a longer contact time with free chlorine before the addition of ammonia resulted in lower concentrations of NDMA. According to Kohut and Andrews [77], the age of a stock solution of poly(DADMAC) did not influence its NDMA FP. While poly(epichlorohydrin) dimethylamine (polyamine) solution significantly increased NDMA formation over a time span of 0–5 h, it remained unchanged over a later period (5–50 h).

The formation of NDMA from the same polymers, polyamine and poly(DADMAC), has been examined by Park et al. [78]. In polyamines, dimethylamine end-groups appeared to be responsible for NDMA formation and, therefore, the higher the molecular mass of the polyamine, the lower is the NDMA-FP. The quaternary ammonium salt, diallyldimethyl ammonium chloride, a monomer of DADMAC appeared to be quite resistant to chloramination and cannot be blamed for NDMA formation. However, a similar tertiary amine, allyldimethylamine, readily formed nitrosodimethylamine upon chloramination [78]. Releasing DMA from polymer breakdown accounts for a major mechanism of NDMA formation upon chloramination. The same was confirmed in another paper by Park et al. [79]. Chlorine-based oxidants (NH_2Cl , Cl_2 , and ClO_2) were shown to release DMA from four examined amine-based polymers used in water treatment technology. The paper of Park et al. [79] confirms that oxidants are able to release DMA moiety from some organic compounds.

Kemper et al. [80] continued their efforts to find NDMA precursors. Contrary to Park et al. [78], they emphasized the role of quaternary amine polymers that are used in water treatment, as well as other quaternary amines that are applied widely in toiletries as an important source of NDMA. According to the results of Kemper et al., the polymerization of quaternary amines may promote nitrosamine formation upon chlorination or chloramination.

Diphenylamine appeared to be the major precursor of NDPhA. According to Zhou et al. [20] the chlorination of diphenylamine leads to the formation of NDPhA. The reaction strongly depends on pH and an increase in pH from 4 to 10 results in a 64-fold enhancement of nitrosamine formation.

6. Precursors of NDMA in wastewater technology

Wastewaters (untreated and treated) may contain a very wide range of NDMA concentrations. There are many results that are

based on an analysis of US or Canadian wastewaters, but, with the exception of the paper by Krauss et al. [43], there is a lack of European research on nitrosamine concentration in wastewaters.

According to Padhye et al. [45], DMA and other amines were also shown to be present in wastewater, but constituted barely 20–30% of NDMA-FP. The highest concentration of nitrosamine precursors was also found in raw wastewater. The treatment removed ca. 60% of the precursors. The authors [45] emphasize that about 80% precursors have an unknown structure. It is important to note that treated effluents still have high NDMA FP levels and, therefore, may impact surface waters that may be used downstream as a supply for WTPs. Organic matter isolates from several natural waters and WWTP effluents were examined for NDMA generation at NDMA formation potential conditions [81]. The “NDMA productivity” spanned three orders of magnitude from 0.01 to 7 ng/mg dissolved organic carbon (DOC). The isolates that had a low DOC/DON ratio (<20) were the major source of NDMA and the isolates of DOC from WWTPs yielded NDMA at an order of magnitude higher than DOC isolates from other sources. Another survey of 23 US WWTPs has shown that the hydrophilic fraction of DOC is closely related to NDMA FP. Thus, it is necessary to identify the WWTP process that would preferentially remove this fraction of DOC. In this context, nitrification was found to play a key role in the removal of precursors for nitrogenous disinfection byproducts including NDMA [82].

Disinfection of the effluents with chlorine or chloramine leads to the formation of nitrosamines. The concentrations of nitrosamines depend on chlorine:organic nitrogen ratio; Krasner et al. [46] have found that a lower $\text{Cl}_2:\text{N}$ (<10) ratio generates much more NDMA than chlorine that is applied at the ratio >10.

Apart from the unidentified organic nitrogen precursors of NDMA, several compounds detected in wastewaters have been found to produce NDMA with an exceptionally high yield upon chloramination or ozonation.

It has been found that tertiary amines may be oxidized to secondary amines [83]. Therefore, oxidation processes may be a source of DMA moiety. Chlorination or chloramination of tertiary amines leads to the formation of aldehydes and secondary amines. Secondary amines become important precursors of nitrosamines during chloramination [84]. Similarly, diuron was shown to degrade in the environment with the formation of dimethylamine [85]. Chlorination or chloramination of waters that have been polluted with the herbicide led to NDMA formation. The presence of ammonia strongly enhanced the NDMA yield, while the presence of nitrates was shown to have a weaker effect on the NDMA yield enhancement [86]. According to Chen and Young [86], diuron is oxidized with chlorine and results in the formation of DMA and/or chlorodimethylamine. DMA may be subsequently nitrosated with N_2O_4 . While in the presence of ammonia, chlorodimethylamine, may react with dichloramine. Tolyfluanid, a widely used fungicide, was shown by Schmidt and Brauch [87] to be a source of NDMA in some German drinking waters. The fungicide is microbially converted to dimethylsulfamide, which appears to be a very stable and persistent water pollutant. It cannot be efficiently removed by river bank filtration, adsorption by active carbon, coagulation or nanofiltration. However, upon ozonation, the compound is easily converted with a high yield (52%!) to NDMA. In one of the examined treatment plants, such a series of reactions led to more than 300 ng NDMA/L in drinking water. The more general conclusion of Schmidt and Brauch's [87] work is that oxidation may also lead to NDMA formation if precursors containing dimethylamine group are present in water. Ozonation of dyes that contain a dimethylamine group was also shown to produce large amounts of NDMA; 50 $\mu\text{M/L}$ dye solutions were able to yield more than 1000 ng NDMA/L. Furthermore, an increase in the pH (in the range 6–8) and the presence of nitrites enhanced NDMA formation [88]. The

paper of Oya et al. [88] confirms the conclusions of a recently published work by our group concerning ozonation of DMA [89]. The same Japanese group has identified two other compounds that can form NDMA upon ozonation. They are 4,4'-hexamethylenebis(1,1-dimethylsemicarbazide) (HMDS) and 1,1,1',1'-tetramethyl-4,4'-(methylenedi-p-phenylene)disemicarbazide (TDMS). Both compounds are used in industry to prevent the yellowing of polyurethane fibers. The presence of HMDS or TDMS in industrial wastewaters considerably increased the concentrations of NDMA after wastewater ozonation and, consequently, the NDMA concentrations in receiving river water. Both compounds contain dimethylamine groups. Furthermore, the groups are bonded to nitrogen atoms. The compounds have been identified as efficient NDMA precursors [90].

Wastewaters may contain NDMA from humans and industry; the removal efficiency varies from case to case. Wastewaters may contain identified NDMA precursors, such as DMA and other specific compounds originating from agricultural or industrial wastes that can be oxidized to NDMA. Wastewater effluents may also contain unidentified NDMA precursors that can pollute receiving surface or ground waters, while at the same time increasing their NDMA formation potential. Unidentified NDMA precursors are resistant to photolysis and biodegradation.

7. Removal of nitrosamine precursors by water treatment processes

Now the question of whether water treatment technology can remove DON or/and NDMA precursors arises.

Water treatment processes remove on average ca. 20% of the DON and about 29% of the DOC [91]. Lee and Westerhoff [92] investigated the fate of DON during coagulation and found that a dual coagulation strategy (using alum + polymer) was slightly more efficient than coagulation using alum alone, as it improved DON removal by 15–20%. This was also confirmed by Krasner et al. [70]. According to the same paper, prechlorination and ozonation decreased NDMA formation potential. The survey of 16 US WTPs showed that the mean concentration of DON in plant influents was 0.29 mg N/L. On average, the treatment removed one third of the DON. The DON that remained was responsible for the formation of highly undesired nitrogenous DBPs, including NDMA. Four treatment processes [91] were examined for NDMA FP removal efficiency, but only filtration through biologically active carbon resulted in an unequivocal decrease of the parameter. Biodegradation also efficiently removed NDMA formed by ozonation [42]. Coagulation was shown to increase, as well as decrease, the formation potential. An increase of NDMA FP after coagulation was observed in the processes that apply organic flocculants [67]. Ozonation is generally believed to decrease NDMA FP, although its median efficiency in the 16 plants surveyed appeared to be barely 10%. In some cases, even a 46% increase of NDMA concentration was found. Japanese results from several water treatment plants also indicate that ozonation may increase NDMA concentrations in treated waters [42]. Another example of nitrosamine detection after ozonation can be found in the paper of Planas et al. [16] where an increase of NDMA concentration and formation of several other nitrosamines was observed. The general belief that oxidation decreases nitrosamine formation potential is based on the results of two papers by Lee et al. [93,94], where several NDMA suspected precursors (organic compounds with dimethylamine- or trimethylamine groups) were oxidized with relatively high doses of oxidants (ozone, chlorine dioxide, ferrate and hydroxyl radicals) and then reacted with chloramine. However, there are several reports that state that oxidation of DMA may lead to the formation of NDMA [41,95,96], particularly at a higher pH. Zhao et al.

[39] have also shown that raw water oxidation with chlorine dioxide or ozone may increase NDMA content in treated waters. Lime softening also gave equivocal results, increasing the potential in one case by 20% and decreasing it in another case by 12% [91]. The NDMA FP in drinking water treatment does not depend solely on the NDMA precursors. Other parameters of water may influence the formation of nitrosamines as well. For example, a temperature increase resulted in the formation of higher amounts of NDMA [67] and bromides also were shown to increase the formation of NDMA. Contrary to these two parameters, the presence of nitrites did not impact on nitrosamine formation [67]. The treatment of raw waters impacted by WWTP effluents may result in the formation of excessive amounts of NDMA upon chlorination. Krasner et al. [97] have shown that NDMA formation may be minimized when longer chlorination contact times are applied. For well-nitrified WWTP effluents, the NDMA formation potential during post chloramination depends only slightly on a Cl:N ratio.

Water treatment processes have shown that both a decrease and an increase in NDMA FP are possible. Filtration through biologically active carbon consistently lower nitrosamine concentration. Coagulation may decrease NDMA FP but also may increase it, depending on the polymers used in the process. Ozonation gave various results, sometimes increasing NDMA FP and sometimes decreasing it. In general, the scarcity of data concerning particular processes does not enable any generalization.

8. Mechanisms of NDMA formation

The nitrosation of secondary amines is a well known reaction. The reaction pathways by means of N_2O_3 , H_2ONO^+/NO^+ and XNO species have been identified. The reaction proceeds at an acidic pH, and most rapidly at pH 3.4 [98]. The yield of nitrosation decreases sharply with increasing pH and is very low at a neutral or basic pH. However, several catalytic mechanisms of the reaction have been discovered. Photochemical reactions [99], formaldehyde [100] or fulvic acid [101] catalyzed reactions, may proceed at a neutral or even basic pH. The reader will find other examples of nitrosation reactions in nature in the review by Mitch et al. [1] There are also some theoretical papers predicting catalytic nitrosation of DMA in the presence of carbon dioxide and carbonyl compounds [102,103].

In all earlier observations, NDMA formation during water treatment was suspected to proceed by the nitrosation pathway. However, Najm and Trussel [55] were the first to notice that chloramination is responsible for nitrosamine formation. According to them [55], the rate constant of the nitrosation reaction and concentrations of the reagents (DMA and nitrites) indicated that the reaction would be extremely slow and could not be responsible for NDMA formation. A literature search revealed that chloramine reacts with dimethylamine relatively slowly, forming unsymmetrical dimethylhydrazine (UDMH). UDMH may be easily oxidized to various compounds, with NDMA among them, as a low yield by-product. In 2002, two research groups [104–107] demonstrated that the UDMH pathway may take place in chloraminated drinking waters. Mitch and Sedlak [104] proved that the maximum NDMA formation rates are between pH 6 and pH 8. Other experiments have shown that oxidation of UDMH is not a rate-determining step and that UDMH may be oxidized by chlorine, as well as by other oxidants. The proposed mechanism did not explain NDMA formation upon chlorination of DMA (in the absence of ammonia). Choi and Valentine [105] have confirmed that NDMA formation increased with increased monochloramine concentrations. They have also confirmed that chloramine is a source of the nitrogen in the NDMA molecule. In the same paper, they have also shown that nitrite and DMA at a pH 7 may form some NDMA, but that its yield is about one sixth of that of the chloramine-DMA reaction. Both groups rec-

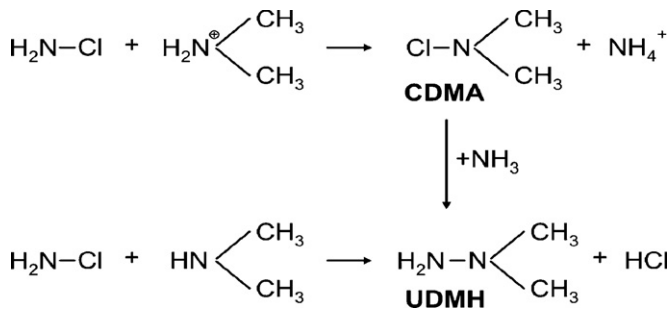


Fig. 1. Formation of unsymmetrical dimethylhydrazine (UDMH) [104,105] (CDMA: chlorodimethylamine).

ognized monochloramine as being responsible for the oxidation of UDMH [104–107]. Thus, the model of NDMA formation that was proposed by the two groups consisted of the:

- formation of monochloramine, formation of dimethylhydrazine,
- oxidation of UDMH by monochloramine to NDMA,
- reversible chlorine transfer reaction between free chlorine/monochloramine and DMA (occurring along with the first two steps).

The reactions leading to formation of UMDH and further products of UMDH oxidation are illustrated in Figs. 1 and 2.

It soon appeared that, due to a very low molar yield of NDMA formation by the UDMH pathway, DMA concentrations could not account for the amounts of nitrosamine observed in real wastewater effluents. Thus, there had to be other NDMA precursors. To assess the ability of waters to generate NDMA, Mitch et al. [108] developed the first NDMA precursor test. A similar test was published by Dotson et al. [81]. Gerecke and Sedlak [53] also realized that DMA is not the single NDMA source and identified natural organic matter (NOM) as a possible nitrosamine precursor. However, they emphasized that NOM that was not influenced by WWTP effluents would not form excessive amounts of NDMA. Bromides, according to Gerecke and Sedlak [53], did not enhance NDMA formation. This statement was later found to be falsified, for example, in the paper of Krasner et al. [67]. The chlorination of DMA in the absence of ammonia, but in the presence of nitrite, was also shown to generate NDMA; the mechanism of the reaction has been well explained by Choi and Valentine [109]. The enhanced HOCl nitrosation pathway involves the formation of dinitrogen tetroxide and nitrosation of DMA. The reaction is, however, slow and is not expected to contribute much in NDMA formation (see Fig. 3).

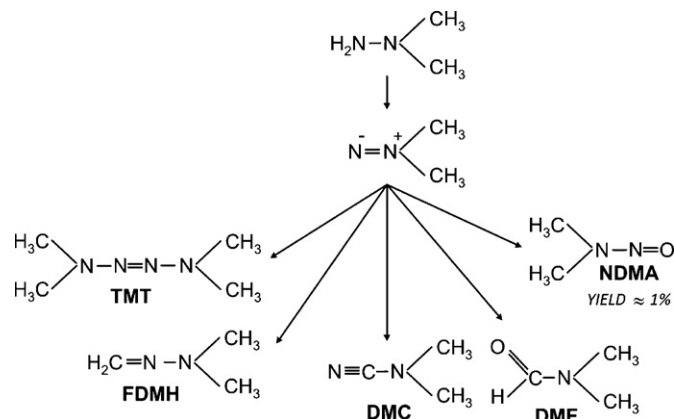


Fig. 2. Unsymmetrical dimethylhydrazine oxidation by-products.

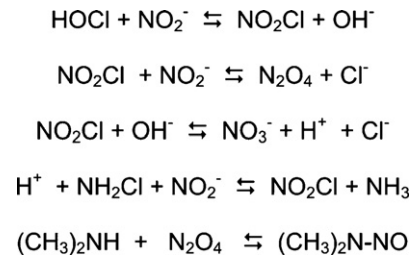


Fig. 3. Nitrosation pathway as proposed by Choi and Valentine [109].

Schreiber and Mitch [110] modified the previous hypothetical mechanism of NDMA formation by demonstrating that NDMA formation depends on dichloramine, rather than monochloramine, concentration. According to the new hypothesis, dichloramine reacted with DMA, resulting in a chlorinated derivative of UDMH, which was subsequently oxidized by dissolved oxygen. The NDMA yield was shown to be positively related to the oxygen concentration. Thus, the new hypothesis of NDMA formation by chloramination of DMA was assumed to follow the reactions illustrated in Fig. 4.

Although Schreiber and Mitch [110] proved the importance of both dichloramine and dissolved oxygen for the formation of NDMA, the weak side of the hypothesis is the formation of a stronger oxidant (HOCl) upon the action of a weaker oxidant (O_2). The authors have, however, proved consistent enhancement of the formation of several nitrosamines (NDEA, NMOR, NPIP, and NPYR) upon the presence of both dichloramine and oxygen. This appears today to be a commonly accepted mechanism of NDMA formation upon chloramination of DMA aqueous solutions.

In real WWTP or WTP conditions, the formation of monochloramine exceeds the formation of dichloramine [111]. However, even at a neutral pH, low quantities of NHCl_2 may be responsible for 2–10 times greater generation of NDMA. Higher dichloramine concentrations are observed when chlorine is added to waters containing ammonia. When ammonia is added to prechlorinated water or wastewater, less NDMA may be generated. That is why efficient nitrification in wastewater treatment plants may also diminish the amounts of nitrosamine that are formed after final disinfection of the effluents. In general, water treatment plants should avoid conditions that are favorable for dichloramine formation.

Breakpoint chlorination has also attracted researchers' interest as it can obviously lead to conditions in which NDMA formation may occur, since the maximum concentrations of the reagents are observed near the breakpoint [111]. Furthermore, when chloramination is used for disinfection, unintentional nitrification in distribution system often leads to the formation of nitrites. The nitrites may enhance NDMA concentrations [112]. According to Schreiber and Mitch [112], nitrosamine formation will be much lower when breakpoint chlorination is conducted without significant free chlorine residual. Charrois et al. [18] have found that chlorine that was applied at doses of 0.6–0.8 $\text{Cl}_2:\text{N}(\text{NH}_3)$ resulted in maximum NDMA formation. Prechlorination (before chloramination) with a contact time ca. 2 h resulted in significant NDMA reductions compared to chloramination process without prechlorination. Such a strategy also appeared to be successful in the case of the minimization of NDMA concentrations in chloraminated wastewaters [97].

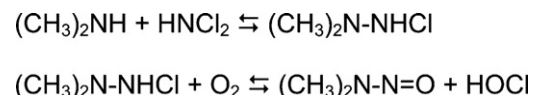


Fig. 4. NDMA formation mechanism modified by Schreiber and Mitch [110].

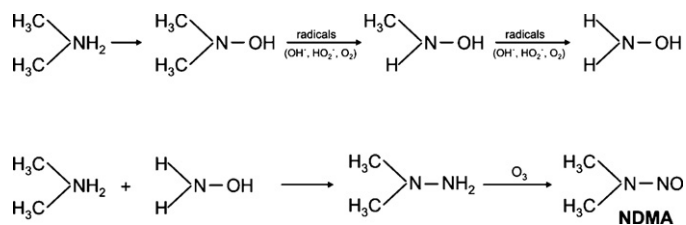


Fig. 5. Mechanism of NDMA formation by ozonation of DMA as proposed by Yang et al. [113].

Chlorination and chloramination are the main sources of NDMA in wastewaters and drinking waters. However, there have been several reports of NDMA formation upon the application of other strong oxidants, such as ozone, chlorine dioxide, KMnO₄ or ferrate (VI) [16,39,41,42,87–89,95,96]. In general, when oxidants are in contact with dimethylamine, part of the DMA is oxidized to nitrites and nitrates (formaldehyde and formic acids are also commonly detected). Thus, it is suspected that the reaction mechanism involves direct nitrosation. The yields of the reactions are small and pH-dependent. The ozonation of DMA forms NDMA with a yield of 0.4% at a pH 10.5. At a pH < 8 practically no NDMA can be expected. The reactions are likely to be of a radical type as the presence of tert-butyl alcohol strongly retards NDMA formation [89].

Permanganate was also shown to oxidize DMA, while generating small amounts of NDMA, particularly in the presence of nitrites [96]. NDMA formation was pH- and contact time-dependent (a higher pH favored nitrosamine generation). However, MnO₂ appeared to catalyze NDMA formation. This seems to be a more important observation. It is also necessary to mention that all of the oxidants were shown to destroy part of the DMA to leave nitrites, nitrates, formaldehyde and formic acid. The formation of NDMA upon the ozonation of DMA was confirmed by Yang et al. [113]. They proposed a mechanism of NDMA formation that is based on the generation of hydroxylamine as a by-product of DMA oxidation. According to the hypothesis of Yang et al. [113], the formation of nitrosamines proceeds through UDMH formation and then oxidation of the hydrazine. The reaction paths are shown in Fig. 5.

There are some real examples of NDMA formation by the ozonation of wastewaters [87,88,91,114]. A few examples of NDMA formation during ozonation in drinking water treatment technology may also be found [16,42,91]. The formation of NDMA was also evidenced after the ClO₂ application [39] for the oxidation of raw waters. However, it seems today that other oxidants that are used in water treatment technology do not significantly threaten to contaminate drinking waters with nitrosamine. The oxidation of the potential nitrosamine precursors with ozone, chlorine dioxide and ferrate (VI) appeared to decrease substantially the NDMA formation potential in subsequent chloramination [93,94]. On the other hand, the ozonation of some commercial dyes with dimethylamine group was shown to generate NDMA [88].

Another possibility for NDMA formation, particularly in natural waters, was shown by Lee and Yoon [115]. NDMA formation may be induced by UV-A irradiation when DMA and nitrites are present in water. The reaction was enhanced by increasing the concentrations of the substrates, as well as by an alkali pH with the maximum yield observed at a pH 10. Radical scavengers and the presence of oxygen decreased NDMA formation.

Although chloramination is commonly blamed for the formation of NDMA, it is worth emphasizing that the yield of the UMDH path is usually very low and does not exceed a few percent. In most water treatment plants, the UMDH path does not lead to NDMA concentrations that exceed California or Ontario regulations (see Tables 2–5). The yield of NDMA in the chloramine reaction with

undefined NOM precursor seems to be higher than that with free (or rather protonated) amine (e.g., see [61]). Additionally, the yield of NDMA in a direct ozonation of DMA does not exceed ca. 1% [89]. However, the ozonation reactions with some known precursor molecules (e.g., dimethylsulfamide [87]) may lead to ca. 52% transformation of the compound to NDMA. Similarly, ozonation of some anti-yellowing factors led to NDMA formation with a 10–27% molecular conversion factor [88,90]. A particularly high molecular conversion of the ozonated compound to NDMA is observed when the dimethylamine group is connected to a nitrogen atom. (See the examples provided by Schmidt and Brauch [87] or by Oya et al. [88]) A very high NDMA yield is also observed when compounds that contain dimethylamine moiety are connected to another nitrogen atom through the sulfone (–SO₂–) group [87]. Ozone destroys some dyes with dimethylamino groups with a high yield of DMA [116]. However, the overall conversions of the dyes to NDMA do not exceed 1% [88]. Therefore, the presence of dimethylamine group in the precursor compound does not seem to be the single condition that leads to the high NDMA yield upon ozonation [88]. NDMA yields from a variety of compounds upon ozonation are shown in Table 5.

Similar conclusions may be drawn from the results that were presented by Lee et al. [93,94] where releasing DMA from precursor molecules (as a result of oxidation) caused no increase in NDMA formation upon chloramination.

Although ozonation of some specific compounds was shown to lead to NDMA with high conversion factors, biological filtration, which usually follows ozonation, was fortunately shown to reduce NDMA concentrations [42,91]. On the other hand, the ozonation that is used in WWTPs may lead to the pollution of receiving waters with NDMA. Ozone is also used in modern swimming pools to destroy anthropogenic amines [117]. Thus, theoretically, some amounts of NDMA may also be expected in those facilities that apply ozonation. Very high ozone doses are applied for the oxidation of some industrial wastewaters [117]. It is also possible that we can discover some sources of NDMA there.

9. Destruction of the nitrosamines

Due to the toxicity of NDMA, the destruction and/or removal methods of the compound from water have also attracted the attention of researchers. Since nitrosamines are rather persistent chemicals, advanced oxidation processes (AOPs), photolytic methods, radiolytic destruction, chemical reduction and also biodegradation are currently being examined.

9.1. Photolytic reactions and advanced oxidation processes

The NDMA molecule strongly absorbs 225–250 nm radiation (with a maximum at $\lambda = 238$ nm $\epsilon_{\text{mol}} = 7380$ L/M cm) [1]. However, the absorption is also pH-dependent [118,119]. Therefore, one might expect photolytic destruction to also depend on the solution's pH. Indeed, Xu et al. [118,120] have shown that an acidic pH favors the destruction of nitrosamine, while an alkali pH may substantially retard the process. The earlier work of Stefan and Bolton [121] indicated also that the photolytic destruction of NDMA is favored by acidic conditions. UV irradiation was also shown to readily degrade NPYR and NPIP [122]. NPIP photolysis was pH-dependent while NPYR degradation was independent of pH. Parent amines were the main byproducts of the photolysis. Further degradation led to simple primary alkylamines [122].

Free radical destruction of NDMA was shown to be a rather low-efficiency process due to the relatively slow reaction of the NDMA carbon-centered radicals with dissolved oxygen. The slowness of the process implied a regeneration of the parent compound [123]. Furthermore, the reactions with hydrated electrons were not effi-

Table 5
NDMA formation yields upon ozonation of several precursors.

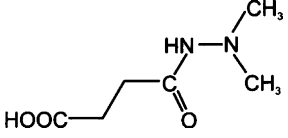
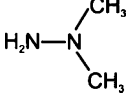
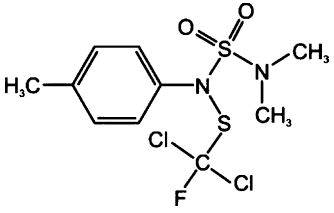
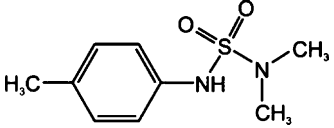
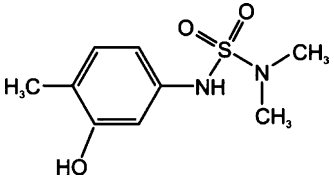
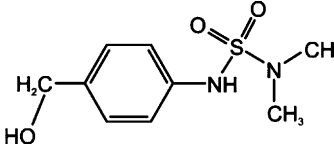
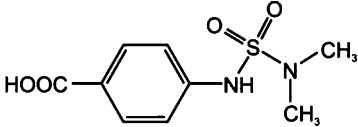
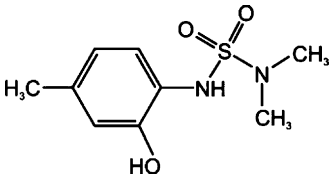
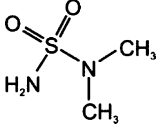
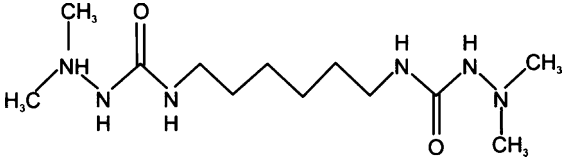
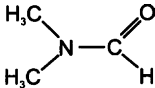
Compound	Formula	NDMA yield upon ozonation	Reference
1. Diaminozide		55%	Schmidt and Brauch [87]
2. 1,1,-Dimethylhydrazine (UMDH)		80%	
3. Tolyfluanid		9%	
4. N,N-dimethyl-N'-p-tolylsulphamide (DMST)		15%	
5. 3-OH-DMST		25%	
6. OH-methyl-DMST		22%	
7. COOH-DMST		18%	
8. 2OH-DMST		27%	
9. N,N-dimethylsulfamide (DMS)		52%	
10. 4,4'-Hexamethylene bis(1,1'-dimethyl semicarbazide) (HDMS,)		10%	Kosaka et al. [90]

Table 5 (Continued)

Compound	Formula	NDMA yield upon ozonation	Reference
11	1,1,1',1'-Tetramethyl-4,4'-(methylene-di-p-phenylene)disemicarbazide (TMDS ₄)	27%	
12	Methylene blue (MB)	8.3×10^{-3}	Oya et al. [88]
13	N,N-dimethylaminobenzene (DMAB)	6.4×10^{-3}	
14	N,N-dimethyl-p-phenylenediamine (DMPD)	4.3×10^{-2}	
15	Methyl orange (MO)	7.2×10^{-3}	
16	Methyl violet B (MVB)	1.2×10^{-2}	
17	Auramine	1.3×10^{-2}	
18	Brilliant green (BG)	$<1.0 \times 10^{-4}$	

Table 5 (Continued)

	Compound	Formula	NDMA yield upon ozonation	Reference
19	N,N-dimethylformamide (DMF)		3.5×10^{-4}	

cient as the adduct anion transformed again to the parent NDMA. According to the results observed in electron pulse radiolysis of NDMA, the AOPs' perspectives for the reduction of nitrosamine concentration are not significant [123]. Electron-pulse radiolysis may effectively destroy higher nitrosamines [124]. Ozonation and AOPs that are based on ozone/hydrogen peroxide were investigated by Lee et al. [54]. Ozonation alone was found to be not sufficiently efficient—destroying barely 13% of NDMA at a neutral pH. The O_3/H_2O_2 process, on the other hand, was able to remove more than 80% of the NDMA in 5 min contact time. Xu et al. [125] also confirmed the low efficiency of ozonation for NDMA destruction. However, the UV/O_3 process was shown to be quite efficient. Split injections of the oxidants could improve the process efficiency. Methylamine was the main by-product of NDMA destruction by the ozone/ H_2O_2 process [54]. However, in some natural waters, regeneration of NDMA was observed to lower the overall destruction ratio. Bromides may limit the application of the AOPs for nitrosamine destruction, due to a danger of bromate formation.

UV irradiation is almost as efficient in NDMA removal as the UV/O_3 process. However, there are substantial differences between the by-products of the two processes. DMA and nitrites are the main products of irradiation alone, while mainly nitrates are found after the AOP. Therefore, UV-irradiated waters may have a high NDMA regeneration potential upon subsequent chlorination [125]. The paper was further discussed in the literature [126,127].

Photolytic destruction of nitrosamines was also examined by Plumlee and Reinhard [128]. According to their model, photolysis seems to be a much more efficient method of NDMA destruction than biodegradation, even at relatively low levels of solar radiation. Plumlee and Reinhard [128] observed an average degradation of NDMA of 42% from tertiary WWTP effluents in solar channels with an 83 min residence time. The NDMA half-lives that were calculated for London's latitude should be about 8–38 h and shorter for equatorial latitudes. The values corresponded well to those reported by Pehlivanoglu-Mantas and Sedlak [50]. According to Chen et al. [51], solar photolysis appeared to be the main mechanism that decreases the concentration of NDMA in river waters.

The photocatalytic degradation of quaternary ammonium salts in TiO_2 suspensions led Kim and Choi [129] to observe that nitrogen-containing organic compounds were photocatalytically mineralized to nitrates (NO_3^-) and ammonia (NH_4^+), which seems to be a unique property as they are both oxidized and reduced. A similar conclusion can be drawn from the results of UV/TiO_2 degradation of NDMA. The mechanism of photocatalytic degradation of NDMA on TiO_2 and modified TiO_2 was also investigated by Lee et al. [130]. The degradation was initiated by hydroxyl radicals. The presence of oxalate enabled the reductive destruction of NDMA into DMA. The pH value was a key factor in determining the main degradation paths. Both silica-loaded and Nafion-coated TiO_2 favored the formation of DMA over methylamine (MA), while the fluorinated TiO_2 surface directed the NDMA destruction, mainly to the formation of MA. In a subsequent paper by the same group [131], NDMA photolytic destruction in oxygen-saturated solutions appeared to be more efficient than destruction in N_2 -saturated water. Xu et al. [118] also confirmed that NDMA photocatalytic destruction was more efficient in oxygen-saturated solutions. The presence of NOM slows the destruction of nitrosamines by UV radiation [118]. The

pulsed-UV process was found to be highly effective in destroying NDMA, since it delivered both continuous-wave UV, as well as higher intensity irradiation. However, other strongly UV absorbing species present in water, such as NOM and/or nitrates, could decrease the efficiency of the destruction [132].

To summarize, AOPs are expected to efficiently reduce NDMA concentration in the absence of bromides. Photolysis seems to be a very efficient way of NDMA removal from water. Solar photodestruction, in particular, could be used to remove nitrosamines from wastewater effluents. However, a high level of DOC and the presence of nitrates may decrease the efficiency of the photolysis. The presence of oxygen in the water enhances NDMA destruction.

9.2. Reverse osmosis (RO)

Reverse osmosis did not appear to be very efficient in NDMA rejection; typically a 50–65% removal (or less) from wastewater effluents was observed by Plumlee et al. [133]. However, the combination of RO with UV treatment enabled the achievement of final concentrations of NDMA that are lower than the California drinking water notification level of 10 ng/L. Due to the low molecular mass and polarity of the NDMA molecule, one cannot expect a high degree of rejection of the nitrosamine by RO membranes. Yet, when the nitrosamine molecular mass increases, rejection also increases. While only a 60% rejection rate was observed for NDMA, even a 92–98% removal may be expected for NDEA and a complete removal for NPIP, NMOR or NDBA [134].

9.3. Biodegradation and phytoremediation

The extent of the knowledge of NDMA biodegradation before 2003 was outlined by Mitch et al. [1]. At that time, there was a lack of clear evidence of the biodegradation of NDMA in ground waters and no data on the efficiency of NDMA removal by biologically active filters. Later results [42,91] proved the efficiency of the filters for the removal of nitrosamines during drinking water treatment. Aerobic biodegradation in ground waters may also remove substantial amounts of NDMA [47], although there are also some contradictory reports [135].

Zhou et al. [47] observed the fate of nitrosamine that has been discharged with water reclamation plant effluents to a system of surface and ground waters over 7 years and found that in situ biodegradation of NDMA occurs in ground waters. They clearly documented that ca. 80% of NDMA mass discharged with the effluents were biodegraded during a 600-day observation period. The biodegradation occurred under anaerobic conditions. According to Zhou et al. [47], the half-life of NDMA in the system was observed to be less than 70 days. Contrary to this well proved process of NDMA biodegradation, Patterson et al. [135] did not observe the destruction of nitrosamine (NDMA and NMOR) under anaerobic conditions, and according to them, the expected half-life of NDMA was longer than 100 days. Earlier research of Gunnison et al. [136] on the biodegradability of NDMA indicated a half-life of nitrosamine at about 12–38 days. The NDMA was likely to remain in the aqueous phase of the soil as it adsorbs negligibly. According to Gunnison et al. [136], biodegradation seems to be the major attenuation mechanism for nitrosamine in soils. However, the soils should

contain the necessary co-factors and nutrients to support microbial mineralization. Since NDMA environmental concentrations are very low, it is unlikely that bacteria would be able to sustain growth on nitrosamine as the primary substrate. Co-metabolic degradation, rather than metabolic degradation, should be expected to be the dominant degradation mechanism. Sharp et al. [137] have shown that a variety of monooxygenase-expressing organisms are capable of NDMA biodegradation.

Several strains of bacteria were found to transform NDMA to less harmful compounds in both aerobic and anaerobic conditions. *Pseudomonas mendocina* KR1 [138] was observed to oxidize (with atmospheric oxygen) NDMA to N-nitrodimethylamine, which was further metabolized to N-nitromethylamine. The strain was first grown on toluene. Aerobic biodegradation of NDMA was also possible by *Rhodococcus ruber* ENV425 [139,140]. Rodococci are soil heterotrophs of the order *Actinomycetes*. The following by-products of the degradation have been identified: methylamine, nitric oxide, nitrite, nitrate and formate. The strain mineralized more than 60% of the NDMA carbon to CO₂. The enzyme responsible for NDMA degradation has been identified [140]. The very high efficiency of the nitrosamine destruction was emphasized.

NDMA bioreduction with H₂ as the electron donor in a membrane biofilm reactor was investigated by Chung et al. [141]. The paper shows that detoxification depends on the availability and pressure of H₂. The NDMA degradation occurred rapidly under denitrifying conditions and with environmental inoculum.

The first attempts to determine NDMA removal efficiency by phytoremediation from soils irrigated with WWTP effluents were also mentioned in Mitch's review [1]. Yifru and Nzengung [142] examined black willow and hybrid poplar for the removal of NDMA. The transpiration of water appeared to be the main path of nitrosamine removal. Thus, higher removal rates were observed in summer months than in winter time. About half of the NDMA mass was phytovolatilized, while the other half could be recovered from leaves, stems and branches. The degradation of NDMA in landscape soils was found to depend on vegetation cover. The compound may be expected to persist longer in soils with sparse vegetation, low organic content and limited microbial activity [143]. However, in a subsequent paper by the same group, the fast decay of NDMA after irrigation was explained by volatilization, as barely 3% of labeled NDMA was incorporated into plants [144,145]. According to the observations above, irrigation of turf grass soils is not likely to contaminate ground waters that contain NDMA, despite the very high concentrations of NDMA in WWTP effluents [144,145]. Yet, Haruta et al. [146] found that irrigation of soils by reclaimed wastewaters may pollute ground waters when the hydraulic conductivity of the soils is high.

In summary, NDMA can only be co-metabolized, while monooxygenase enzymes are responsible for its removal. Biodegradation may be expected by various natural bacteria consortia, but the process seems to require relatively long retention times. The phytoremediation of NDMA-polluted soils seems to be possible, but the vegetation cover determines the efficiency of the process. However, sparse vegetation and high hydraulic conductivity of soils may lead to the contamination of ground waters that contain NDMA as the compound does not adsorb to soils.

9.4. Chemical reduction of NDMA

Another possible way to remove NDMA from water is by chemical (catalytic) reduction. Such a pathway of nitrosamine removal could be applied to polluted ground waters (e.g., by permeable reactive barriers) or WWTP effluents. The use of zero-valent iron as a reductor for the removal of NDMA was attempted. However, much better results have been achieved with Ni-plated iron [147,148]. DMA and ammonia were found to be the main by-products of the

reduction. The gradual loss of Ni/Fe reactivity was observed in a continuous experiment.

Davie et al. [149] studied catalytic reduction of NDMA by hydrogen gas over metallic and bimetallic catalysts. A high efficiency of reduction was observed. In a subsequent work by the same group [150], a bimetallic catalyst (Pd/In) appeared to be more efficient than the catalyst based on Pd. It is necessary to note that the experiments were carried out in pure aqueous solutions of NDMA and, therefore, the influence of normal water constituents on the reaction efficiency has not been assessed. Frierdrich et al. [151] have shown that porous Ni catalyst (Raney Ni) is highly efficient in the reduction of NDMA by H₂. Raney Ni is, however, very inconvenient to use due to its sensitivity to air oxygen. A typical NDMA half-life in H₂/catalyst conditions was only 1.5 min. Furthermore, the presence of NOM and the majority of common ions in water have not affected the removal efficiency. Bicarbonates could decrease the rate of nitrosamine reduction by 40–50%. Additionally, very high concentrations of nitrates (much higher than their usual presence in water) could be detrimental for NDMA removal. To avoid difficulties with the application of Raney Ni catalyst, the same group proposed to use Ni catalyst amended with boron [152]. Ni/B catalyst is characterized by a lower surface area than Raney Ni, but appears to be equally efficient in H₂ reduction of nitrosamine. Catalytic NDMA reduction with H₂ leaves DMA and nitrogen as the main byproducts.

At this stage of research in the field, it is difficult to judge the technological applicability of the processes for NDMA removal.

10. Conclusions

Nitrosamines, and particularly NDMA, due to their carcinogenic properties may pose some threat to drinking water consumers. However according to Fristachi and Rice [153] exposure of U.S. population on NDMA in finished drinking water is low relative to other ingestion route NDMA sources. The occurrence of NDMA in drinking water may be caused by the pollution of raw waters by nitrosamine or the formation of nitrosamine during water treatment processes. Chloramination has been proved to be the main source of NDMA in drinking water. The formation of nitrosamine during water (or wastewater) treatment requires the presence of N-containing precursors. The precursors are the most mysterious part of the nitrosamine formation process. Dimethylamine rarely seems to be the only or most important NDMA precursor.

Ozonation (and other oxidants) may also be responsible for the formation of appreciable amounts of NMDA, particularly when certain precursors are available in treated waters. Fortunately, biological filtration, which usually follows ozonation in drinking water technology, removes most of the nitrosamine.

NDMA (and other nitrosamines) may be present in wastewater influents from two sources—human excretion and industrial wastewaters. Wastewaters may also contain a variety of NDMA precursors—identified and unidentified. Furthermore, treated wastewaters may pollute receiving waters with NDMA and/or NDMA precursors. NDMA was shown to disappear in natural systems due to photolytic destruction or biodegradation, but NDMA precursors are much more persistent in the environment. Thus, wastewater effluents may pose some threat to water treatment facilities that are located downstream.

There are not many research papers concerning the occurrence of NDMA in European drinking waters. However, the presence of NDMA in our waters seems to be less probable due to the different approach to water treatment in Europe. The drinking water in many western European cities is treated to become biostable and therefore requires no final disinfection. In Eastern Europe, chlorination (or Cl₂ + ClO₂) is used for final disinfection. Ozonation may pose

some danger of NDMA formation in both drinking and wastewater treatment, but only in the presence of certain precursors. So far, this research field has been only partially explored. Several methods of nitrosamine destruction are currently under investigation. Photolytic methods seem to have the greatest potential for application.

Research needs

Limiting the risk associated with the presence of nitrosamines in drinking water seems to be the main target of research that is focused on compounds in water technology. Much work has been done so far, but some fields still have been insufficiently explored.

On the basis of the literature reviewed, the following research needs may be identified:

1. Nothing is known about NDMA pollution of surface or ground waters in Europe.
2. Systematic research on the presence of secondary amines in surface waters is possibly needed. Also, the behavior of secondary amines during various processes of drinking water treatment is largely unknown.
3. The identification of specific N-containing compounds that are present in aqueous NOM (particularly those present in the hydrophilic base fraction) that can be easily oxidized to NDMA should be undertaken.
4. More research is necessary on the NDMA removal efficiency of particular processes in drinking water treatment technology. The current results are too limited and equivocal.
5. Due to some controversies concerning NDMA formation from N-containing flocculants, more research in this field is necessary.
6. The identification of the N-containing NDMA precursors (responsible for NDMA formation potential) that are present in wastewaters would be helpful.
7. The removal of NDMA precursors in wastewater treatment technology requires more research.

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