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# N-nitrosamine removal by reverse osmosis for indirect potable water reuse – A critical review based on observations from laboratory, pilot and full-scale studies

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## Review

# N-nitrosamine removal by reverse osmosis for indirect potable water reuse – A critical review based on observations from laboratory-, pilot- and full-scale studies

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## ABSTRACT

N-nitrosodimethylamine (NDMA) and several other N-nitrosamines have been identified as probable human carcinogens. Here, we review key aspects related to the occurrence and removal of N-nitrosamines by reverse osmosis (RO) membranes in the context of indirect potable water reuse. A comprehensive analysis of the existing data reveals significant variations in the rejection of NDMA by RO membranes reported in the literature, ranging from negligible up to 86%. This review article provides some insight into the reasons for such variations by examining the available data on the effects of operating conditions on NDMA rejection. Amongst several operating parameters investigated so far in the literature, feed temperature, membrane permeate flux, feed solution pH and ionic strength were found to have considerable impact on NDMA rejection by RO membranes. In particular, it has been recently shown that seasonal changes in feed temperature (e.g. from 20 to 30 °C) can result in a significant decrease in NDMA rejection (from 49% to 25%). However, the combined effects of all operating parameters identified in the literature to date can only account for some of the variations in NDMA rejection that have been observed in full-scale RO plants. The impacts of membrane fouling and particularly chemical cleaning on the rejection of N-nitrosamines have not been fully investigated. Finally, this review article presents a roadmap for further research required to optimise the rejection of NDMA and other N-nitrosamines by RO membranes.

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## 1. Introduction

Water reuse has grown significantly in recent years in response to the increasing demand for water brought about by population increase, urbanisation, and diminishing and uncertain availability of freshwater resources. Many water authorities around the world have now recognised the potential value of water reuse after experiencing severe droughts as well as the environmental and economic costs of imported water [1–3]. Since the quality of reclaimed water for potable reuse is stringently regulated, reverse osmosis (RO) treatment has become an increasingly common component of the water reclamation process. RO membranes can successfully remove a wide range of contaminants including inorganic salts and trace organic chemicals [4,5]. However, the rejection of N-nitrosodimethylamine (NDMA) by RO membranes appears to be highly variable [6,7]. N-nitrosamines including NDMA can readily be formed during the disinfection of biologically-treated effluent using chlorine or chloramines [8,9]. Given the probable carcinogenic potency of NDMA and several other N-nitrosamines [10,11], the fate of these compounds in water reclamation applications is of significant interest to both the scientific community and water authority.

For indirect potable water reuse applications involving the use of the RO process, concentration of NDMA in the final product water can be controlled via several strategies. NDMA concentration can be minimised by reducing the formation of NDMA during the chloramination process. This can be achieved by dosing preformed chloramine [12] and reducing the contact time of chloramination [13,14]. However, reducing the NDMA formation may not be sufficient if a higher NDMA concentration than the regulatory level occurs in the inflow of the wastewater treatment plant (WWTP). An alternative approach is to use an additional treatment process for the removal of NDMA. Possible treatment technologies include UV/H<sub>2</sub>O<sub>2</sub> treatment process, natural attenuation during aquifer recharge, and RO filtration.

Advanced oxidation using a combination of UV radiation and dosed hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to form hydroxyl radicals has been proven to be effective for the removal of NDMA and has been applied following RO filtration in several water reclamation schemes around the world [6,15]. However, the energy consumption required by UV/H<sub>2</sub>O<sub>2</sub> treatment for the control of NDMA is high and can have a negative consequence of increasing the carbon footprint of the water reuse scheme. Moreover, it is still necessary to control the concentration of NDMA by other processes during wastewater reclamation since the removal of NDMA by UV/H<sub>2</sub>O<sub>2</sub> treatment is sometimes incomplete [6]. At a water reuse facility in Southern California, there were some periods when reclaimed water after UV/H<sub>2</sub>O<sub>2</sub> treatment had to be blended with other non-recycled sources to reduce NDMA concentration in the final product to below the 10 ng/L notification level [7].

Natural attenuation over an extended retention time in an aquifer or surface reservoir has been shown to be effective for the removal of NDMA and other N-nitrosamines [16,17]. Although

natural attenuation is likely to play a significant role as a post RO treatment process for the removal of NDMA and other N-nitrosamines, most water authorities are still reluctant to exclusively rely on this passive treatment technique. A reliable removal efficiency of NDMA and other N-nitrosamines remains a major focus for the control of these contaminants in indirect potable water recycling practices.

RO membranes are widely used for the treatment of reclaimed water for indirect potable reuse and other applications. However, the effectiveness of RO membranes for the rejection of NDMA and other N-nitrosamines is still poorly understood. Broad discrepancy exists in the existing scientific literature regarding the rejection of NDMA by RO membranes. For instance, NDMA rejection by a commonly used RO membrane (TFC-HR, Koch Membranes) was reported to be 50% at the West Basin Municipal Water District water recycling plant in California, USA [6]. At the Scottsdale Water Campus (Arizona, USA), NDMA rejections by the same type of RO membrane (TFC-HR) were reported to be 10% and 70% during two separate sampling events [6]. Compared to NDMA, little is known about the fate of other N-nitrosamines in water reclamation due to the scarcity of sampling data. This paper aims to provide a comprehensive review on the fate of N-nitrosamines and their rejections by RO treatment during water reclamation.

## 2. Indirect potable water reuse and N-nitrosamines

### 2.1. Water reclamation process

Indirect potable water reuse is generally performed through a ‘multiple barrier’ approach that incorporates both engineered and natural treatment processes as well as non-treatment measures. These multiple barriers may variably include (1) residential/industrial source control; (2) conventional wastewater treatment; (3) advanced water treatment; (4) environmental buffer and blending; and (5) drinking water treatment [3].

A notable approach for the advanced treatment of reclaimed water is the use of integrated membrane systems (Table 1). Since secondary effluents have high fouling propensity against RO membranes [18], microfiltration (MF) or ultrafiltration (UF) treatment is usually used as a pretreatment step to minimise membrane fouling in the subsequent RO process. The RO process substantially reduces the concentration of dissolved solids including macro-organic molecules and inorganic salts [19]. RO membranes can also achieve an excellent removal of a large range of trace organic chemicals [5,19–21]. Although RO membranes can remove bacteria and viruses [22,23], it is still common to deploy either UV- or chlorine-based disinfection processes as a ‘redundant’ post treatment to inactivate human pathogens (Table 1). Because the rejection of NDMA by RO membranes is highly variable and can be quite low, the advanced oxidation UV/H<sub>2</sub>O<sub>2</sub> process may also be used for the destruction of NDMA that can permeate through the RO membrane.

**Table 1**  
Examples of advanced water treatment processes for indirect potable water reuse.

Treatment processes	Location (commissioning year)	Final water use	Capacity (m <sup>3</sup> /day)	Reference
MF/UF → RO	Scottsdale, AZ, USA (1999)	Groundwater recharge	53,000	[3]
	Terminal Island, CA, USA (2001)	Groundwater recharge	18,900	[113]
MF/UF → RO → UV	Vander Lans, CA, USA (2001)	Groundwater recharge	12,000	[113]
	Torreele, Belgium (2002)	Groundwater recharge	8800	[76]
	NeWater, Singapore Kranji (2002), Bedok (2002), Seletar (2004), Ulu pandan (2007)	Surface water augmentation into a dam	216,000	[3]
MF/UF → RO → UV + H <sub>2</sub> O <sub>2</sub>	Groundwater Replenishment Project, Orange County, CA, USA (2007)	Groundwater recharge	265,000	[3]
	Western Corridor project, Australia Bundamba (2007), Luggage Point (2008), Gibson Island (2008)	Planned future surface water augmentation into a dam	232,000	[114]

## 2.2. Occurrence of N-nitrosamines in water recycling schemes

### 2.2.1. Presence of N-nitrosamines in wastewater

In addition to NDMA, other N-nitrosamines known to occur in secondary effluent include N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine (NDEA), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), N-nitrosodipropylamine (NDPA), N-nitrosodi-*n*-butylamine (NDBA) and N-Nitrosodiphenylamine (NDPhA) [17,24,25]. The chemical structure of N-nitrosamines is generally described as R<sub>1</sub>R<sub>2</sub>N–N=O. These N-nitrosamines are neutral and small molecules ranging from 74 to 198 g/mol and most N-nitrosamines have high solubilities (Table 2). N-nitrosamines are considered hydrophilic (i.e. log *K*<sub>ow</sub> < 3) with N-nitrosodiphenylamine being the only exception (Table 2). Of these N-nitrosamines, much of the recent research has focused on the fate of NDMA during wastewater treatment and water reuse.

N-nitrosamines can be found in both domestic and industrial wastewater. Cosmetic and toiletry products contain NDMA and NMOR [26] and NDMA concentration in the range of 17–63 ng/L has been reported in raw residential sewage [6,27,28]. Industrial discharge is another potentially major pathway for NDMA to enter the sewage system. N-nitrosamines including NDMA can be formed as impurities during various manufacturing activities, such as the production of rubber, high-energy batteries, some lubricants, antifreezers, and cutting fluids [6]. Due to industrial activities, NDMA concentrations as high as 1000 ng/L have been reported in an industrial sewer system [28]. Sedlak and Kavanaugh [6] investigated the inflow of several WWTPs in California and suggested that NDMA concentrations in the inflow could vary significantly depending on the degree of industrial sewer inflow. They reported that NDMA concentration in the inflow of WWTPs located in residential areas ranged between 50 and 100 ng/L whereas an average of 150 ng/L NDMA concentrations was found at WWTPs where the contribution of the industrial discharge was over 10%. At a WWTP in the US, a variable concentration of NMOR in the range from 130 to 12700 ng/L has also been reported in the wastewater effluent at different sampling occasions, due possibly to the industrial activities [29].

### 2.2.2. NDMA precursors

Together with the increasingly reported occurrence of NDMA in domestic and industrial wastewater, the abundance of NDMA precursors in both domestic and industrial wastewater discharge has been widely reported in the literature. For the evaluation of the maximum NDMA formation that can occur in an aqueous solution, the NDMA formation potential can be used [30]. NDMA formation potentials ranging from 25 to 55 µg/L were reported in domestic wastewater in California by Sedlak and Kavanaugh [6]. They also

reported NDMA formation potentials of as high as 82.5 µg/L in an industrial wastewater.

A number of substances have been identified as NDMA precursors. These include both heterogeneous organic mixtures such as humic substances found in the natural environment [31] and some specific organic compounds containing the amine functional group such as dimethylamine, triethylamines, and dimethylaminobenzene (Fig. 1). These amine bearing organic compounds can be readily converted to NDMA during chloramination [32]. Some pharmaceuticals and personal care products (PPCPs) containing dimethylamine (DMA) or diethylamine (DEA) functional groups can also act as NDMA precursors. For example, Shen and Andrews [33] reported higher than 1% molar conversion of eight PPCPs containing these functional groups to NDMA during chloramination.




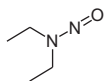
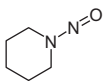
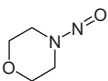
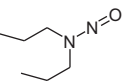
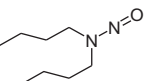
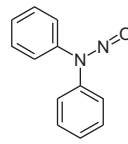
Since DMA occurs naturally in urine and faeces, DMA is ubiquitous in domestic wastewater [6,34]. In fact, faeces and urine contain an average DMA concentration of 0.4 and 15.9 mg/L, respectively [35]. Numerous studies have used DMA to elucidate mechanisms of NDMA formation [13,34,36]. Gerecke and Sedlak [37] reported that the yield of NDMA from the reaction between DMA and chloramine was only approximately 0.6%. Similarly, in the primary effluent of the Orange County Sanitation District facility (CA, USA) approximately 80 µg/L of DMA was found while NDMA formation potential was only 5 µg/L in the same sample [27].

Several other compounds such as DEA, dipropylamine (PYP), pyrrolidine (PIP) and diphenylamine (DPhA) are also suspected to be the precursor of NDEA, NPYR, NPIP and NDPhA, respectively. Amongst them, DEA, PYP and PIP are excreted through faeces and urines in the range of 0.03–9 mg/L [35], and DPhA can be found in an insecticide, a storage preservative for apples and a rubber antioxidant [38]. To date, however, most N-nitrosamine precursor studies have focused exclusively on the formation of NDMA during chloramination, and information regarding the precursors of the other N-nitrosamines is rather scarce.

### 2.2.3. NDMA formation

In general, oxidation of N-nitrosamine precursors by strong oxidants such as chlorination, chloramination, ozone, and potassium permanganate leads to a formation of NDMA [13,39–42]. Several mechanisms of NDMA formation during chloramination have been proposed [43], and they usually involve two major pathways. Unsymmetrical dimethylhydrazine (UDMH) is initially formed from NDMA precursors such as DMA by a reaction with monochloramine (NH<sub>2</sub>Cl). Then UDMH is transformed into NDMA by the oxidation of monochloramine, as shown in Eq. (1) [34,36]. The yield of NDMA formation from DMA is less than 3% and the oxidation is a gradual process taking several days [13,30].

**Table 2**  
Physicochemical properties of the selected nitrosamines.

Compound	N-nitrosodimethylamine	N-nitrosomethylethylamine	N-nitrosopyrrolidine	N-nitrosodiethylamine	N-nitrosopiperidine	N-nitrosomorpholine	N-nitrosodipropylamine	N-nitrosodi- <i>n</i> -butylamine	N-nitrosodiphenylamine
Abbreviation	NDMA	NMEA	NPYR	NDEA	NPIP	NMOR	NDPA	NDBA	NDPhA
Structure									
Molecular FORMULA	C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O	C <sub>3</sub> H <sub>8</sub> N <sub>2</sub> O	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O	C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> O	C <sub>8</sub> H <sub>18</sub> N <sub>2</sub> O	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O
Molecular weight (g/mol)	74.05	88.06	100.06	102.08	114.08	116.06	130.11	158.14	198.22
Henry's law constant at 25 °C (atm m <sup>3</sup> /mol) <sup>a</sup>	1.20 × 10 <sup>-6</sup>	1.44 × 10 <sup>-6</sup>	1.99 × 10 <sup>-7</sup>	1.73 × 10 <sup>-6</sup>	2.81 × 10 <sup>-7</sup>	2.13 × 10 <sup>-10</sup>	3.46 × 10 <sup>-6</sup>	9.96 × 10 <sup>-6</sup>	1.38 × 10 <sup>-5</sup>
Solubility in water at 20 °C (g/L) <sup>b</sup>	1000	300	780	147	49	4714	9.9	1.2	0.035
LogKow <sup>b</sup>	-0.64	-0.15	0.23	0.34	0.74	-1.39	1.35	2.31	3.16

<sup>a</sup> EPI Suite™ v4.10, US EPA, <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>.

<sup>b</sup> GSI Environmental Inc., <http://www.gsi-net.com/en/publications/gsi-chemical-database.html>.

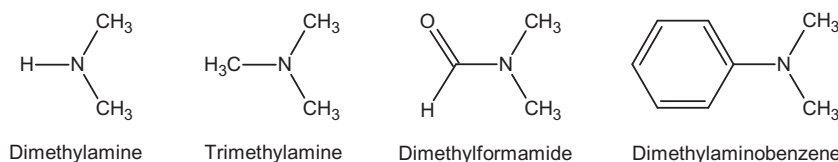
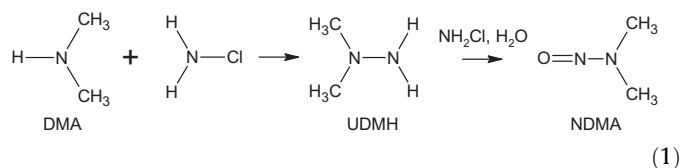
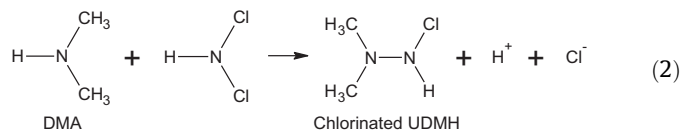


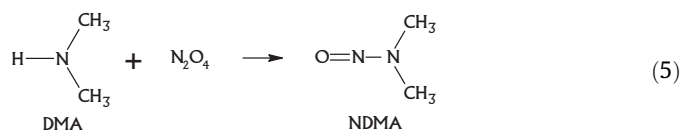
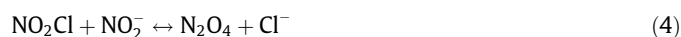
Fig. 1. NDMA precursors found in wastewater.



Schreiber and Mitch [13] have revised this formula to take into account the significant enhancement in NDMA formation by dichloramine ( $\text{NHCl}_2$ ), as shown in Eq. (2). Another study proposed that the chlorinated UDMH intermediates can be oxidised by both dissolved oxygen and chloramines. This is attributed to the weak and non-polar property of the N–Cl bond contained in the chlorinated UDMH intermediates [44].



Choi and Valentine [45] proposed another pathway for NDMA formation in the presence of DMA and chlorine. It was hypothesised that dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) is firstly formed by nitrosation enhanced by chlorine, and then a reaction between  $\text{N}_2\text{O}_4$  and DMA leads to the formation of NDMA as shown in the following equations:



The formation of NDMA by chloramination can vary significantly depending on the conditions of the chloramination process. In fact, several studies reported that NDMA concentration substantially increased with increasing reaction time and chloramine (or chlorine) dosage [8,9,34,36]. Farré et al. [12] investigated the impact of chloramination contact time on NDMA formation in the feed of a full-scale RO plant. They reported that 20–22 h of chloramination contact time led to  $170 \pm 20$  ng/L NDMA concentration, while 1–2 h of chloramination exposure resulted in only  $7 \pm 2$  ng/L NDMA concentration.

The disinfection process can be optimised to minimise the formation of NDMA. It has been demonstrated that adding ammonium chloride followed by chlorine into the wastewater forms less NDMA than adding chlorine followed by ammonium chloride [13,14]. This is because dichloramine, which forms more NDMA than monochloramine, is generated less when ammonium chloride is added earlier into the wastewater, reducing the transient occurrence of high chlorine/ammonia ratios. These findings are consistent with another laboratory-scale study where dosing preformed monochloramine into the wastewater led to far less NDMA formation potential (<1 ng/L) compared with dosing ammonium chloride and sodium hypochlorite into the wastewater (6 ng/L)

[12]. Although the formation of NDMA during water reclamation can be minimised with an appropriate chloramination conditions, a subsequent treatment process is often necessary for further removal of NDMA.

### 2.3. Health-based water quality guidelines and standards for N-nitrosamines

The occurrence of N-nitrosamines in drinking water has attracted significant scientific and regulatory attention in recent years since some have been classified as probable human carcinogens by the US Environmental Protection Agency [11] and the International Agency for Research on Cancer [10]. The occurrence of NDMA is of particular concern amongst all N-nitrosamines because NDMA concentration exceeding some enforced regulatory levels has been detected in drinking water [41,46,47]. Based on a calculated excess lifetime cancer risk of 1 in  $10^6$ , the California Office of Environmental Health Hazard Assessment have set a public health goal for NDMA in drinking water of 3 ng/L [48] (Table 3). The California Department of Public Health (CDPH) also established a notification level for NDMA, NDEA and NDPA of 10 ng/L [48]. Outside the US, an interim action level of NDMA has been determined at 9 ng/L by the Ontario Ministry of the Environment [49], while a NDMA guideline value of the World Health Organisation [50] and Australian Drinking Water Guidelines [51] is as high as 100 ng/L. The regulation of N-nitrosamines in indirect potable water reuse is much more stringent than that in conventional drinking water. Health-based guideline values of 10 ng/L for NDMA, 10 ng/L for NDEA and 1 ng/L for NMOR have been established in the Australian Guidelines for Water Recycling [52].

Although an increasing number of authorities have regulated N-nitrosamine concentrations for drinking or recycled water (Table 3), many water utilities have not been able to monitor their concentrations in the product water on a regular basis. Under the USEPA Unregulated Contaminant Monitoring Rule 2 (UCMR 2), an extensive screening exercise was conducted between 2008 and 2010 to identify key contaminants of concern for future monitoring and regulation [47]. From 1196 public water supplies and approximately 17,150 samples, NDMA was the most frequently detected contaminant in the samples from 25% of the public water supplies or 10% of the total samples in which a maximum concentration of 630 ng/L was reported [47]. Five N-nitrosamines (i.e. NDMA, NDEA, NDPA, NPYR and NDPhA) have also been included in the third Contaminant Candidate List (CCL3) proposed by the US EPA [53]. These N-nitrosamines are likely to be regulated in the future under the Safe Drinking Water Act of the United States [54].

### 2.4. N-nitrosamine quantification using chemical analysis

Quantifying NDMA and other N-nitrosamines at the part-per-trillion level (ng/L) is a challenging task and to date most reported detection limits are only marginally lower than their regulated values. High analytical cost is also a hurdle to engage in intensive monitoring efforts for N-nitrosamines in addition to regulatory requirements. To address the low concentration analysis, most currently available methods involve a solid-phase extraction (SPE)

**Table 3**  
Risk level and guideline level of N-nitrosamines.

Compound	US EPA classification <sup>a</sup>	IARC classification <sup>b</sup>	US EPA, IRIS 10 <sup>-6</sup> risk level (ng/L)	CDPH 10 <sup>-6</sup> risk level (ng/L)	CDPH notification level (ng/L)	Ontario MOE an interim action level (ng/L)	WHO guideline value (ng/L)	ADWG guideline value (ng/L)	AGWR guideline value (ng/L)
NDMA <sup>c,d</sup>	B2	2A	0.7	3	10	9	100	100	10
NMEA <sup>c</sup>	B2	2B	2	1.5	–	–	–	–	–
NPYR <sup>c,d</sup>	B2	2B	20	15	–	–	–	–	–
NDEA <sup>c,d</sup>	B2	2A	0.2	1	10	–	–	–	10
NPIP	–	2B	–	3.5	–	–	–	–	–
NMOR	–	2B	–	5	–	–	–	–	1
NDPA <sup>c,d</sup>	B2	2B	5	5	10	–	–	–	–
NDBA <sup>c</sup>	B2	2B	6	3	–	–	–	–	–
NDPhA <sup>d</sup>	B2	3	7000	–	–	–	–	–	–
Reference	[11]	[10]	[11]	[48]	[48]	[49]	[50]	[51]	[52]

<sup>a</sup> B2: probable human carcinogen.

<sup>b</sup> 2A: probable human carcinogen; 2B: possibly human carcinogen; 3: unclassifiable chemical as to its carcinogenicity to humans.

<sup>c</sup> Chemical is on US EPA's list of the UCMR 2.

<sup>d</sup> Chemical is on US EPA's list of the CCL3.

**Table 4**  
NDMA rejection by pilot- and full-scale RO plants.

Location	Pretreatment processes <sup>a</sup>	RO Membrane	RO stages	RO recovery (%)	RO permeate flux (L/m <sup>2</sup> h)	NDMA in RO feed (ng/L)	NDMA in RO permeate (ng/L)	NDMA rejection by RO (%)	Reference
El Segundo – train 3, West Basin Water Recycling Plant, USA	SEC–NaOCl–MF–RO	TFC–HR	3	85	17	90 60	40 43	56 28	[6] [115]
Scottsdale Water Campus, USA	SEC–NaOCl/NH <sub>4</sub> <sup>+</sup> –MF–RO	TFC–HR	3	85	18.2	330 200	100 180	70 10	[6,115]
Bundamba AWTP, Australia	SEC–NaOCl/NH <sub>4</sub> <sup>+</sup> –COAG–UF–RO	TFC–HR	3	85	NA	190	170	11	[12,77]
El Segundo – train 4, West Basin Water Recycling Plant, USA	SEC–NH <sub>4</sub> <sup>+</sup> –COAG–NaOCl–UF–RO					7	6	14	
El Segundo – train 4, West Basin Water Recycling Plant, USA	SEC–NaOCl–MF–RO	ESPA2	2	85	19.4	32	21	34	[113,115]
Interim Water Factory 21, USA	SEC–NaOCl–MF–RO	ESPA2	NA	85	20.5	18 45	14 20	22 55	[7]
Beenyup Pilot Plant, Australia	SEC–HOCl/NH <sub>4</sub> <sup>+</sup> –MF–RO	ESPA2	2	80	19.7	11 6.7	<1.6 2.5	>86 63	[116]

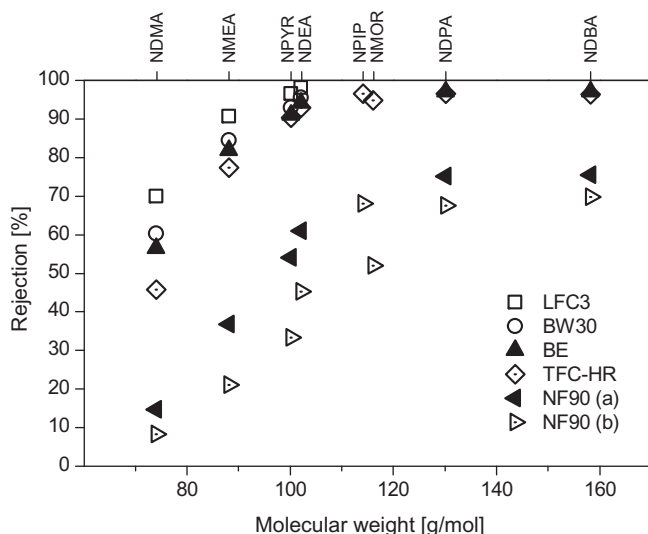
<sup>a</sup> SEC: secondary effluent; COAG: coagulation process; NaOCl/HOCl: chlorine addition; NH<sub>4</sub><sup>+</sup>: ammonia addition; MF/UF: MF/UF process; RO: RO process.

procedure followed by quantification using chromatographic-mass spectrometric analytical instruments.

For quantitative determination of N-nitrosamines in water samples, many recent methods use gas chromatography coupled with different detection techniques such as mass spectrometry (GC–MS) [55,56], tandem mass spectrometry (GC–MS/MS) [57–59] or high resolution mass spectrometry (GC–HRMS) [60,61]. These methods use deuterated N-nitrosamines (i.e. d<sub>6</sub>-NDMA and d<sub>14</sub>-NDPA) as an internal standard for calibrations and/or surrogate for recoveries. The US EPA has defined that Method 521 [57] be used for analysing N-nitrosamines under the USEPA Unregulated Contaminant Monitoring Rule 2. Method 521 is based on coconut charcoal SPE, GC–MS/MS, large volume injector and chemical ionisation (CI) operation mode with CI reagent gas (methanol or acetonitrile). Method 521 provides a reporting detection limit of 1.6 ng/L for NDMA and the reporting detection limits of the other N-nitrosamines (NMEA, NDEA, NDPA, NDBA, NPYR and NPIP) range from 1.2 to 2.1 ng/L. The Ontario Ministry of Environment sets a different testing method for Ontario drinking water samples using GC–HRMS after an SPE procedure using the Ambersorb 572 adsorbent [60]. In the method, the reporting detection limit of NDMA is 0.99 ng/L. Recent developments in N-nitrosamine analysis include a simple technique using selective

ion storage mode of GC/MS with chemical ionisation [62], a sensitive GC–MS/MS technique using electron ionisation [63] and high-field asymmetric waveform ion mobility spectrometry with time-of-flight mass spectrometry [64].

Due to the polar characteristic and high water solubility of N-nitrosamines, liquid chromatography (LC) technique has been increasingly developed. Compared to GC methods, LC technique particularly has an advantage on detecting both thermally stable and unstable N-nitrosamines (i.e. NDPhA) [65]. To date several LC–MS/MS techniques have been reported [7,24,66]. Positive electrospray ionisation (ESI) combined with multiple reaction monitoring mode is used in these methods. Zhao et al. [24] investigated nine N-nitrosamines in water samples using SPE–LC(ESI)–MS/MS and reported that detection limits of N-nitrosamines are in the range from 0.1 to 10.6 ng/L with 41–111% recoveries. Another SPE–LC(ESI)–MS/MS technique has been developed with a detection limit of 2 ng/L NDMA and over 90% recovery [7]. The other recent techniques include a method using SPE and LC(ESI)–HRMS detection [66] and SPE–LC–MS/MS with atmospheric pressure chemical ionisation [67]. Although these LC–MS/MS or LC–HRMS methods can be an alternative technique to GC-based techniques, very few water utilities have affordable routine access to LC–MS/MS and LC–HRMS.



**Fig. 2.** Rejection of N-nitrosamines by four RO (LFC3, BW30, BE and TFC-HR) and an NF (NF90) membrane [25,72,73] obtained from laboratory-scale study (a and b denote two separate studies).

### 2.5. Removal of N-nitrosamines during water reclamation

N-nitrosamines have relatively low molecular weights and are stable in aqueous solution, and thus are not sufficiently removed by most conventional water and wastewater treatment processes. The removal of NDMA by secondary treatment is poor and highly variable [6] and the removal of NDMA by coagulation has been reported to be negligible [68]. Less than 10% NDMA removal by UF treatment was reported at a full-scale plant [12]. Granular activated carbon adsorption also exhibited limited effectiveness for NDMA removal [69,70], with the removal of NDMA in the range of 20–50% [71]. Although RO membranes have been proven for complete or near complete removal of a large range of trace organic chemicals, there exists significant discrepancy in NDMA rejections both from laboratory- and full-scale data. This discrepancy will be further discussed in the next section.

## 3. N-nitrosamine removal by RO membranes

### 3.1. Rejection of N-nitrosamines in laboratory-scale studies

N-nitrosamines are neutral compounds at the typical environmental pH range of 4–10. Similar to other neutral trace organic compounds, the rejection of N-nitrosamines appears to be primarily governed by steric hindrance (size exclusion) effect based on the interaction between the pore size within an active skin layer (or so-called free-volume hole-size in membrane polymer chains) and the molecular size (Fig. 2). It is noteworthy that all of the RO membranes listed in Fig. 2 are typically used for brackish water desalting and softening. There is a strong correlation between molecular weight of N-nitrosamines and their rejections for a given membrane [25,72,73]. An overall trend of increasing rejection in the increasing order of molecular width of the N-nitrosamines has also been demonstrated by Fujioka et al. [73], when they examined the rejection of eight N-nitrosamines by NF/RO membranes. A strong correlation between the rejection of N-nitrosamines by a NF membrane (NF270) and the Stokes radius of the N-nitrosamines was also reported by Bellona et al. [74]. The rejection of NDMA, the smallest compound amongst all N-nitrosamines, was consistently found to be lowest by all types of membrane reported in the literature. While molecular size is a major factor governing

the rejection of N-nitrosamines by NF/RO membranes, their rejection may also be influenced to some extent by other physicochemical properties such as hydrophobicity. Fujioka et al. [73] reported a small but clear discernible peculiarity regarding the rejection of NMOR when they examined the correlation between molecular weight and N-nitrosamine rejection by several NF/RO membranes. Despite the similarity in molecular weight between NMOR (116 g/mol) and NPIP (114 g/mol), NMOR rejection by the TFC-HR and NF90 membranes was 2% and 16% lower than that of NPIP, respectively.

Laboratory-scale studies available to date have consistently indicated that the rejection of NDMA by RO membranes (such as the BE, BW30, LFC3, and TFC-HR membranes) was between 50% and 70% (Fig. 2). On the other hand, NDMA rejection by NF membranes (such as the NF90) reported in laboratory-scale studies was negligible and typically below 15%. The impact of membrane type on N-nitrosamine rejection is less profound with higher molecular weight N-nitrosamines.

It is noted that the rejection of NDPhA has not been reported in the literature. Nevertheless, NDPhA has the highest molecular weight amongst the N-nitrosamines of concern and it is expected to be well removed by RO membranes.

### 3.2. Rejection of N-nitrosamines and N-nitrosamine precursors in pilot- and full-scale installations

#### 3.2.1. Rejection of N-nitrosamines

In comparison to other trace organic chemicals, pilot- and full-scale data regarding the rejection of N-nitrosamines by RO membranes are very scarce. To date, monitoring effort in pilot- and full-scale investigations has focused almost exclusively on NDMA. The rejections of other N-nitrosamines are rarely reported in the literature. While NDMA rejection by RO membranes reported in most laboratory-scale studies was in the range of 50–70% (Section 3.1), it is striking to note a substantial discrepancy in the rejection of NDMA recorded from pilot- and full-scale RO plants (Table 4). These plants had similar pretreatment processes and were operated with almost identical water recovery ratios and average RO permeate fluxes. In these water reclamation plants, chloramination was performed by injecting sodium hypochlorite (NaOCl) and ammonia simultaneously prior to MF or UF to control biofouling. The concentration of chloramine in the RO feed was usually maintained at between 1 and 5 mg/L. The average permeate flux and water recovery of all RO plants were approximately 20 L/m<sup>2</sup> h and 80–85%, respectively (Table 4).

The rejection of NDMA by the same membrane reported at different RO plants can vary significantly. For example, NDMA rejection by the TFC-HR membrane in the range of 14–70% was reported at the Bundamba Advanced WTP (Queensland, Australia), the West Basin Municipal Water District WTP (California, USA), and the Scottsdale Water Campus (Arizona, USA) (Table 4). Similarly, there also exists substantial discrepancy in NDMA rejection ranging from 22% to 86% at three different plants using the ESPA2 membrane (Table 4). It is also worth noting that substantial difference in NDMA rejection can be found even at the same plant. Two distinct NDMA rejections (10% and 70%) were recorded at different sampling occasions at the Scottsdale Water Campus [6]. Approximately 30% difference in NDMA rejection was also reported at the Interim Water Factory 21 (USA) [7]. As discussed above, although these plants were operated with a similar water recovery and average permeate flux, the exact operating conditions may vary significantly from one another. In order to account for variability in rejection performance by a single plant, Khan and McDonald [75] have demonstrated the use of probability density functions to more comprehensively describe the RO rejection of NDMA, NDEA and NDPA. The variation in the removal of NDMA



by the RO process demonstrated in Table 4 can be attributed to such differences in operating conditions amongst the different plants or sampling events. Further discussion of the impact of operating conditions on the rejection of NDMA and other N-nitrosamines is provided in Section 3.3.

### 3.2.2. Rejection of N-nitrosamine precursors

To measure the rejection of NDMA precursors by RO membranes, NDMA formation potential is usually used as a surrogate. Results reported from laboratory- and pilot-scale studies show that the rejection of NDMA formation potential by most RO membranes is more than 97% [8,32,76]. Farré et al. [77] reported over 98.5% NDMA formation potential rejection by the TFC-HR membrane at the Bundamba AWTP (Australia). It is noteworthy that the elevated NDMA formation potential in the RO concentrate can be reduced using a nitrification–denitrification process [77]. NDMA formation potential may also be rejected to a certain extent by MF and UF membranes. At the Torreele plant (Belgium), up to 10% NDMA formation potential rejection by an UF membrane was reported [76]. Similarly, NDMA formation potential rejection in the range of 10–90% by a MF membrane was reported in a pilot study at the Interim Water Factory 21 [6].

Because NDMA formation potential can occur at high concentration (i.e. 500–3200 ng/L) prior to RO filtration [6,32,77], some NDMA formation potential may still be detected in the RO permeate. For example, approximately 6 ng/L of NDMA formation potential was reported in the RO permeate treated by the TFC-HR membrane at the Bundamba AWTP [77]. On the other hand, NDMA formation potential in the range from 12 to 52 ng/L was also detected in the RO permeate in a pilot study at the Interim Water Factory 21 [6]. Because NDMA yield from NDMA formation potential by chloramination and chlorination is very low (Section 2.2.2), the remaining NDMA precursors in the RO permeate is not likely to adversely impact the RO permeate quality.

The investigation of NDMA precursor is frequently carried out with DMA. In a typical water recycling application, it occurs in the feed water to the RO process in the range of 3–12 µg/L [6,32]. The molecular weight of DMA is low (45 g/mol), however, its basicity constant ( $pK_b$ ) is 3.36 and thus it is positively charged at pH below or near neutral pH ( $(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \leftrightarrow (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$ ). As a result, DMA is very well rejected by RO membranes. Mitch and Sedlak [32] reported over 99% DMA rejection (from 8 to 11 µg/L to below 0.09 µg/L) at a WWTP using an unspecified RO membrane. In a laboratory-scale study, Miyashita et al. [72] also demonstrated a very high DMA rejection of 99.5% and 99.2% by RO (Saehan BE) and NF (NF90) membranes, respectively. Despite the similarity in rejection between NDMA formation potential and DMA, Mitch and Sedlak [32] suggested an average contribution of only 14% of DMA into the total dissolved NDMA formation potential in secondary effluent. Although the majority of NDMA formation potential found in the feed to the RO process have been reported to be small and low molecular weight compounds (< 2.5 kDa) [76,78], there is very little information available regarding specific NDMA precursors prior to RO treatment.

The rejection data of the other N-nitrosamine formation potential using pilot- or full-scale RO treatment is scarcely available. Krauss et al. [76] reported over 98% of NPYR formation potential rejection and over 94% of NPIP formation potential rejection by an RO membrane, showing a similar rejection efficiency to the rejection of NDMA.

## 3.3. Factors affecting N-nitrosamine rejections

### 3.3.1. Feed concentration

Although most RO plants (Table 4) are operated with similar water recovery and average permeate flux, the exact operating

conditions may vary significantly from one to another. A notable parameter is the concentration of NDMA in the feed, which may vary over a wide range from 7 to 330 ng/L (Table 4). However, recent laboratory-scale studies have conclusively demonstrated that the impact of feed concentration on the rejection of NDMA is negligible [72,73]. Miyashita et al. [72] reported less than 5% variation in NDMA rejection by the Saehan BE membrane when the feed concentration of NDMA varied from 0.4 to 900 µg/L. A similar observation was reported by Fujioka et al. [73] who examined the rejection of NDMA and seven other N-nitrosamines by the TFC-HR membrane in the range of 250–1500 ng/L feed concentration.

Previous studies using NF membranes also reported that solute concentration in the feed does not affect its rejection [79,80]. Transport of uncharged solutes such as N-nitrosamines through porous membranes is governed by diffusive and convective flows inside the pores, which is commonly expressed with the hydrodynamic model (Eq. (6)) [81,82].

$$J_s = -D_p \frac{dC}{dx} + J_v K_c C \quad (6)$$

where  $J_s$  is solute flux;  $D_p$  is the diffusion coefficient of the solute in the pore;  $x$  is position in a pore from inlet;  $C$  is solute concentration at axial position  $x$  in the pore;  $J_v$  is water flux; and  $K_c$  is the hindrance factor for convection. Although RO membranes generally have non-porous active skin layer, free-volume spaces in the membrane polymer chains can be considered as fictive pore radius [83] and the hydrodynamic model may be still effective [82]. In fact, the free-volume hole-size in the active skin layer of RO membranes have been analysed by previous studies [84,85] using the positron annihilation lifetime spectroscopy technique. In the hydrodynamic model, the solute rejection ( $R_j$ ) is expressed as the following equation [82].

$$R_j = 1 - \frac{C_p}{C_f} = 1 - \frac{\Phi K_c}{1 - [1 - \Phi K_c] \exp\left(-\frac{K_{d,v} \Delta x}{D_p}\right)} \quad (7)$$

where  $C_p$  is solute concentration in the permeate;  $C_f$  is solute concentration in the feed; and  $\Phi$  is steric partition factor. The solute rejection, which is associated with the membrane polymer matrix, water flux and solute characteristics, is solute concentration independent and this may explain the negligible impact of feed concentration on NDMA rejection described above.

### 3.3.2. Permeate flux

Permeate flux is an important operating parameter for a membrane filtration system. Miyashita et al. [72] examined the rejection of six N-nitrosamines by RO membranes (BE membrane) using a laboratory-scale filtration system and reported that their rejections increased with increasing permeates flux. They reported that NDMA rejections increased from 42% to 52% as permeate flux increased from 17 to 28 L/m<sup>2</sup> h. In a laboratory-scale study using the TFC-HR membrane, Fujioka et al. [73] also reported that an increase in permeate flux in the range from 10 to 20 L/m<sup>2</sup> h caused a significant increase in NDMA rejection ranging from 34% to 49%. Increasing permeate flux from 20 to 42 L/m<sup>2</sup> h resulted in a smaller increase in NDMA rejection in the range from 49% to 59%. Fujioka et al. [73] examined the rejection of the other N-nitrosamines by the TFC-HR membrane and found that the impact of permeate flux on N-nitrosamine rejection was less pronounced in the increasing order of their molecular weight. They reported that NMEA rejection increased from 69% to 79% and NPYR rejection increased from 80% to 84% for an increase in permeate flux ranging from 10 to 20 L/m<sup>2</sup> h.

Water flux ( $J_v$ ) and solute flux ( $J_s$ ) can be described with Eqs. (8) and (9) in the solute-diffusion model [86].

$$J_v = A(\Delta P - \Delta\pi) \quad (8)$$

$$J_s = B(C_{fo} - C_{pl}) \quad (9)$$

where  $A$  is called the water permeability constant;  $B$  is called the salt permeability constant;  $\Delta P$  is the difference in hydrostatic pressure across the membrane;  $\Delta\pi$  is the difference in osmotic pressure across the membrane;  $C_{fo}$  is the feed solute concentration at the interface of the membrane surface; and  $C_{pl}$  is the permeate solute concentration at the interface of the membrane in the permeate side. According to these equations, water flux increases with applied feed pressure, while solute flux is not pressure-dependent. Solute rejection thus increases when water flux increases by increasing pressure. In practice, the average permeate flux of RO systems used for water recycling is usually set at approximately 20 L/m<sup>2</sup> h (Table 4). However, differences in the local permeate flux amongst different elements in an RO pressure vessel can be intensified by feed pressure loss, osmotic pressure increase and membrane fouling [18,87]. Thus, variations in permeate flux that occur in an RO pressure vessel are likely to affect the rejection of low molecular weight compounds such as NDMA.

### 3.3.3. Feed pH

The influence of feed pH on the rejection of seven N-nitrosamines was investigated in a laboratory-scale study using the ESPA3 membrane [25]. They revealed higher NDMA rejection (56%) at pH 10 than at pH 3 (49%). For the other six N-nitrosamines, the impact of feed pH was not pronounced. A similar impact of feed pH was also observed in a laboratory-scale study carried by Fujioka et al. [73]. The authors reported that NDMA rejection by the TFC-HR membrane increased from 33% to 37% as the feed solution pH changed from 5 to 6.5. This change in feed solution pH also led to changes in the rejection of NMEA, the second smallest compound amongst N-nitrosamines, in the range of 68–75%. In contrast, the impact on the other N-nitrosamines was negligible.

The rejection of small and neutral compounds can be influenced by the feed solution pH and the rejection usually increases with increasing pH [88,89]. It is assumed that high pH causes an extended chain conformation of the membrane polymer matrix which results in narrower pore size of membrane, and the rejection of neutral compounds thus increases. On the other hand, chain groups existing on the membrane surface lose electrostatic repulsion at low pH range, resulting in looser pore size and low rejections [89,90]. It can be inferred from these studies that an increase in feed pH led to tighter membrane pore structure that results in an increase in the rejection of small N-nitrosamines (i.e. NDMA and NMEA). In general, changes in feed pH of full-scale water reclamation plants only occur in a small range (i.e. pH 5–8) [91] and most full-scale RO plants adjust feed pH to 6.3–6.5 to minimise scaling. Thus, feed pH is unlikely to be a major cause of the variations in NDMA rejection in full-scale RO plants.

### 3.3.4. Total dissolved solids concentration

Total dissolved solids (TDSs) concentration can induce an observable impact on the rejection of N-nitrosamines. Steinle-Darling et al. [25] investigated the impact of TDS (ionic strength) on the rejections of the seven N-nitrosamines using a laboratory-scale system and the ESPA3 membrane. They reported that NDMA rejections with deionised feed solution and 100 mM NaCl feed solution were 56% and 41%, respectively. On the other hand, the rejections of the other six N-nitrosamines for the two TDS feed solutions were equivalent. A similar impact of TDS concentration on NDMA rejection was also reported by Fujioka et al. [73] when they examined the rejection of eight N-nitrosamines by the TFC-HR membrane using a laboratory-scale system. They reported that NDMA rejection decreased from 52% to 34% as TDS concentration increased

from 26 to 260 mM. They also found that the change in TDS concentration resulted in a minor impact on the rejection of the other N-nitrosamines.

TDS concentration of RO feed for water recycling applications can vary across a range of 10–30 mM [92–94]. Therefore, it is likely that feed TDS variations will play a role in NDMA rejection variations. In addition to TDS variations in the RO feed, and TDS are gradually accumulated in the feed toward a tail-element (the last membrane element amongst serially-connected membrane elements in a vessel) because salt rejection by RO membrane is well over 90% [21]. This concentration effect results in a significant variation in total TDS concentration within RO system. The permeability of a membrane and the rejection of salts typically decrease as TDS concentration increases [95,96]. Drewes et al. [19] demonstrated that the conductivity of the feed substantially increased from 1249 to 5164  $\mu\text{S}/\text{cm}$  after passing through two subsequent RO stages during water reclamation. Consequently, the conductivity of the various membranes permeates throughout the RO system increased from 22  $\mu\text{S}/\text{cm}$  (1st stage permeate) to 65  $\mu\text{S}/\text{cm}$  (3rd stage permeate). Several studies demonstrated that an increase in TDS concentration in the RO feed also resulted in a decrease in neutral solute rejections [97–99]. They suggested that the decreasing solute rejection resulted from the enlargement in pore sizes of a membrane and changes of the solute size caused by increasing TDS concentration in the feed. It is thus reasonable to hypothesise that a high TDS concentration can decrease NDMA rejection by RO membranes.

### 3.3.5. Feed temperature

Some seasonal and diurnal variation in the temperature of the feed solution is inevitable in most WWTPs. To the best of our knowledge, so far there is only one laboratory-scale study available regarding the impact of feed temperature on the rejection of N-nitrosamines. Fujioka et al. [73] reported that NDMA rejection by the TFC-HR membrane decreased from 49% to 24% as the feed temperature increased from 20 to 30 °C. The rejection of the other N-nitrosamines was also affected by changes in feed temperature. The impact of feed temperature was less pronounced for higher molecular weight N-nitrosamines. For the increase of feed temperature in the range from 20 to 30 °C, the rejection of NMEA and NPYR dropped from 81% to 62% and 90% to 74%, respectively.

Tsuru et al. [100] investigated the impact of feed temperature on the rejection of neutral solutes using a NF ceramic membrane and found that their rejections significantly increased with increasing feed temperature due to the increasing diffusivity of the solutes. In addition to the increased diffusivity, effective pore radius of a NF organic membrane has been suggested to increase with increasing feed temperature due to thermal expansion of pores within the active skin layer, which causes more passage of neutral solutes through membranes [101,102]. In fact, Ben Amar et al. [103] also reported that the rejection of neutral solute (arabinose) decreased from 50% to 42% when the feed temperature increased from 22 to 30 °C using an organic NF membrane (Desal 5 DK). These mechanisms reported in the literature may explain the observed decrease in the rejection of N-nitrosamines by RO membranes with an increase in feed temperature. In any water reclamation plants, the seasonal variation in RO feed temperature can be over 10 °C [104]. Thus, changes in the feed temperature can possibly account for up to 25% variation in NDMA rejection.

### 3.3.6. Membrane fouling and membrane ageing

Membrane fouling is inevitable in most if not all NF/RO filtration processes. The separation of small organic molecules by NF/RO filtration can be significantly influenced by membrane fouling [105–108]. Surprisingly, apart from a study by Steinle-Darling et al. [25] who investigated the rejection of several N-nitrosamines

by an RO membrane artificially fouled with sodium alginate, to date little attention has been given to the effects of membrane fouling on the rejection of N-nitrosamines. Nevertheless, data reported by Steinle-Darling et al. [25] confirms that the impact of membrane fouling caused by alginate on NDMA rejection can be significant. Due to membrane fouling, the permeate flux decreased by 15% and the rejections of NDMA and NMEA decreased from 56% to 39% and 79% to 68%, respectively [25]. The authors attributed the decrease in NDMA and NMEA rejection to the cake-enhanced concentration polarisation phenomenon as previously reported in the literature [106,109]. It is noteworthy that some of the reduction in NDMA and NMEA rejection observed by Steinle-Darling et al. [25] can also be attributed to a decrease in the permeate flux as discussed previously in Section 3.3.2. Further investigation is required to separate the impact of membrane fouling and flux decline and to develop a systematic understanding of the influence of other forms of membrane fouling on the rejection of N-nitrosamines.

Of a particular note is the dearth of information regarding the influence of membrane ageing on the rejection of N-nitrosamines. Membrane ageing caused by prolonged exposure to hypochlorite has been shown to have a negative impact on the rejection of inorganic salts and several trace organic compounds [110,111]. The membrane ageing process can also be exacerbated by occasional chemical cleaning which is used to restore the permeate flux once the membrane has been fouled. A recent study reported by Simon et al. [112] demonstrated that caustic cleaning at pH 12 could lead to a significant reduction in the rejection of carbamazepine which is a pharmaceutically active compound from 80% to 50%. These recent results highlight the need for a systematic investigation of the impact of membrane ageing on the rejection of N-nitrosamines. Thus, the impact of membrane ageing may also account for some of the variations in the rejection of NDMA that have been observed in the literature.

#### 3.4. Future research roadmap

The significant variations in the rejection of NDMA and the lack of rejection data of other N-nitrosamines and their precursors discussed above underscore the current research gap regarding the fate and transport of these contaminants during RO treatment for indirect potable water reuse. Additional research work is expected in the near future and will likely to focus on three key areas:

- (i) Impact of membrane fouling and membrane ageing on the rejection of N-nitrosamines;
- (ii) Modelling of N-nitrosamine rejection at pilot- or full-scale level taking into account the changes in feed water composition and hydraulic variation throughout the system; and
- (iii) Identifying a suitable surrogate parameter for routine assessment of NDMA rejection.

As discussed above, future studies addressing the impact of membrane fouling and membrane ageing on the rejection of N-nitrosamines could also explain for some of the variations in their rejection amongst different pilot-/full-scale RO plants. Recent research has confirmed that the rejection of N-nitrosamines can be simulated using the existing irreversible thermodynamic model [73]. However, such modelling capacity is limited to a flat-sheet membrane sample at the laboratory scale. Further expansion of this modelling capacity is needed to take into account variation in the hydraulic condition along the spiral wound membrane element and between different membrane elements in the system and thus allowing for a systematic evaluation of the impact of permeate flux on the rejection of NDMA and other N-nitrosamines (see Section 3.3.2). The monitoring of N-nitrosamines rejection in

pilot- and full-scale RO plants is severely hindered by the difficulties associated with the analysis of NDMA at the regulatory levels (Section 2.4). Because the rejection of NDMA by RO membranes is governed mostly by steric hindrance, it may be possible to identify a solute that both has similar rejection behaviour to that of NDMA and ubiquitously occurs in reclaimed water at a sufficiently high concentration for routine analysis. Such a surrogate, if it can be identified, is not expected to completely replace the need for the actual analysis of NDMA. However, it will be of immense benefit to the study of NDMA rejection at the pilot- and full-scale level and can serve as an early warning when low NDMA rejection occurs.

#### 4. Conclusions

Data represented in the literature suggest that steric hindrance appears to be the primary mechanism governing the rejection of N-nitrosamine by RO membranes. Considering all N-nitrosamines, studies available to date have focused mostly on the rejection of NDMA. Several investigations focusing on the other N-nitrosamines have revealed that their rejection by RO membranes can be significantly higher than that of NDMA (which has the lowest molecular weight amongst all N-nitrosamines). This review reveals significant variation in NDMA rejection amongst laboratory-, pilot- and full-scale studies (sometimes even by the same RO membrane). The rejection of NDMA by a typical brackish water RO membrane obtained from laboratory-scale studies ranged from 50% to 70%. In contrast, the rejections of NDMA reported at pilot- and full-scale varied significantly, from negligible to over 70%. The variation in NDMA rejection observed across studies can be partially explained by the differences in operating conditions (i.e. recovery, permeate flux, and feed pH) and feed solution characteristics (i.e. ionic strength and temperature). In particular, evidence reported in the literatures suggests that seasonal changes in feed water temperature are likely to play an important role in NDMA rejection. For example, an increase in feed temperature by 10 °C could account for as much as 25% reduction in NDMA rejection by a conventional RO membrane. However, the combined effects of all operating parameters cannot fully account for the variations in NDMA rejection that were observed at full-scale RO installations. The impact of membrane fouling and chemical cleaning on rejection of N-nitrosamines has not yet been systematically investigated. In addition, further research on the development of a predictive model is also needed to allow for the full understanding and optimisation of NDMA rejection in full-scale RO systems.

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