

1-1-2013

N-nitrosamine rejection by reverse osmosis membranes: a full-scale study

Takahiro Fujioka

University of Wollongong, tf385@uowmail.edu.au

Stuart J. Khan

University Of New South Wales, s.khan@unsw.edu.au

James A. McDonald

University Of New South Wales

Annalie Roux

Seqwater

Yvan Poussade

Veolia Water Australia, yvan.poussade@veoliawater.com.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/smartpapers>



Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

N-nitrosamine rejection by reverse osmosis membranes: a full-scale study

Abstract

This study aims to provide longitudinal and spatial insights to the rejection of N-nitrosamines by reverse osmosis (RO) membranes during sampling campaigns at three full-scale water recycling plants. Samples were collected at all individual filtration stages as well as at a cool and a warm weather period to elucidate the impact of recovery and feed temperature on the rejection of N-nitrosamines. N-nitrosodimethylamine (NDMA) was detected in all RO feed samples varying between 7 and 32 ng/L. Concentrations of most other N-nitrosamines in the feed solutions were determined to be lower than their detection limits (3e5 ng/L) but higher concentrations were detected in the feed after each filtration stage. As a notable exception, in one plant, N-nitrosomorpholine (NMOR) was observed at high concentrations in RO feed (177e475 ng/L) and permeate (34e76 ng/L). Overall rejection of NDMA among the three RO systems varied widely from 4 to 47%. Data presented here suggest that the feed temperature can influence rejection of NDMA. A considerable variation in NDMA rejection across the three RO stages (14e78%) was also observed. Overall NMOR rejections were consistently high ranging from 81 to 84%. On the other hand, overall rejection of N-nitrosodiethylamine (NDEA) varied from negligible to 53%, which was considerably lower than values reported in previous laboratory-scale studies. A comparison between results reported here and the literature indicates that there can be some discrepancy in N-nitrosamine rejection data between laboratory- and full-scale studies probably due to differences in water recoveries and operating conditions (e.g. temperature, membrane fouling, and hydraulic conditions).

Keywords

nitrosamine, n, scale, study, full, membranes, osmosis, reverse, rejection

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Fujioka, T., Khan, S. J., McDonald, J. A., Roux, A., Poussade, Y., Drewes, J. E. & Nghiem, L. D. (2013). N-nitrosamine rejection by reverse osmosis membranes: a full-scale study. *Water Research*, 47 (16), 6141-6148.

Authors

Takahiro Fujioka, Stuart J. Khan, James A. McDonald, Annalie Roux, Yvan Poussade, Jorg E. Drewes, and Long D. Nghiem

1 **N-nitrosamine rejection by reverse osmosis membranes: a full-**
2 **scale study**

3 Revised Manuscript Submitted to

4 ***Water Research***

5 July 2013

6 Takahiro Fujioka ¹, Stuart J. Khan ², James A. McDonald ², Annalie Roux ³,
7 Yvan Poussade ⁴, and Jörg E. Drewes ^{2,5}, Long D. Nghiem ^{1,*}

8 ¹ Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental
9 Engineering, The University of Wollongong, NSW 2522, Australia

10 ² UNSW Water Research Centre, School of Civil and Environmental Engineering, The
11 University of New South Wales, NSW 2052, Australia

12 ³ Seqwater, Level 2, 240 Margaret Street, Brisbane, QLD 4000, Australia

13 ⁴ Veolia Water Australia, Level 15, 127 Creek Street, Brisbane, QLD 4000, Australia

14 ⁵ Chair of Urban Water Systems Engineering, Technische Universität München, 85748
15 Garching, Germany

16 _____

17 * Corresponding author: Long Duc Nghiem, Email: longn@uow.edu.au, Ph +61 2 4221 4590

18 **Abstract**

19 This study aims to provide longitudinal and spatial insights to the rejection of N-nitrosamines
20 by reverse osmosis (RO) membranes during sampling campaigns at three full-scale water
21 recycling plants. Samples were collected at all individual filtration stages as well as at a cool
22 and a warm weather period to elucidate the impact of recovery and feed temperature on the
23 rejection of N-nitrosamines. N-nitrosodimethylamine (NDMA) was detected in all RO feed
24 samples varying between 7 and 32 ng/L. Concentrations of most other N-nitrosamines in the
25 feed solutions were determined to be lower than their detection limits (3-5 ng/L) but higher
26 concentrations were detected in the feed after each filtration stage. As a notable exception, in
27 one plant, N-nitrosomorpholine (NMOR) was observed at high concentrations in RO feed
28 (177-475 ng/L) and permeate (34-76 ng/L). Overall rejection of NDMA among the three RO
29 systems varied widely from 4 to 47%. Data presented here suggest that the feed temperature
30 can influence rejection of NDMA. A considerable variation in NDMA rejection across the
31 three RO stages (14-78%) was also observed. Overall NMOR rejections were consistently
32 high ranging from 81 to 84%. On the other hand, overall rejection of N-nitrosodiethylamine
33 (NDEA) varied from negligible to 53%, which was considerably lower than values reported
34 in previous laboratory-scale studies. A comparison between results reported here and the
35 literature indicates that there can be some discrepancy in N-nitrosamine rejection data
36 between laboratory- and full-scale studies probably due to differences in water recoveries and
37 operating conditions (e.g. temperature, membrane fouling, and hydraulic conditions).

38 **Keywords:** Water reuse; N-nitrosamines; NDMA; reverse osmosis (RO) membranes; full-
39 scale operation.

40 **1. Introduction**

41 As clean water sources continue to dwindle in many parts of the world, water recycling has
42 been used by water providers to secure safe and reliable supplies of water for municipal,
43 industrial and agricultural uses (Shannon et al., 2008). In many water recycling schemes,
44 reverse osmosis (RO) filtration is deployed as a key process to remove inorganic salts and
45 trace organic chemicals (Bellona et al., 2004; Dolnicar et al., 2010; Shannon et al., 2008;
46 Verliefde et al., 2008). However, among these trace organic chemicals, the rejection of N-
47 nitrosodimethylamine (NDMA) by RO membranes has often been reported to be low and
48 highly variable (Fujioka et al., 2012a). As a result, subsequent treatment by advanced
49 oxidation processes (AOPs), which is commonly based on UV-H₂O₂, is required where
50 NDMA concentrations in the final product water is stringently regulated (Plumlee et al.,
51 2008; Poussade et al., 2009). In addition to NDMA, several other N-nitrosamines have also
52 attracted scientific and regulatory attention due to their potentially carcinogenic properties
53 (Sedlak and von Gunten, 2011; USEPA, 1993). These N-nitrosamines include N-
54 nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine
55 (NDEA), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), N-
56 nitrosodipropylamine (NDPA), N-nitrosodi-n-butylamine (NDBA) and their occurrence in
57 wastewater and secondary treated effluent has been reported in the literature (Krauss et al.,
58 2010; Reyes-Contreras et al., 2012; Yoon et al., 2012). In particular, NMOR has been
59 reported at up to 12.7 µg/L in secondary treated effluent (Krasner et al., 2009). Potential
60 sources of the high NMOR concentrations in wastewater include toiletries and cosmetics
61 (Spiegelhalder and Preussmann, 1984) and rubber and tire industries (Fajen et al., 1979). For
62 the augmentation of drinking water sources, guideline values of NDMA (10 ng/L), NDEA
63 (10 ng/L) and NMOR (1 ng/L) have been recommended by the Australian Guidelines for
64 Water Recycling (NRMCC et al., 2008). On the other hand, NDMA is the only N-
65 nitrosamine considered in the Australian Drinking Water Guidelines with a recommended
66 guideline value of 100 ng/L (NHMRC and NRMCC, 2011).

67 The rejection of small neutral solutes such as N-nitrosamines by RO membranes is mainly
68 governed by size exclusion (Fujioka et al., 2012b). In general, the rejection of N-nitrosamines
69 increases in the increasing order of their molecular size (Bellona et al., 2011; Miyashita et al.,
70 2009; Steinle-Darling et al., 2007). Thus, NDMA, which is the smallest molecule among N-

71 nitrosamines, exhibits the lowest rejection (Fujioka et al., 2012a). Previous laboratory-scale
72 studies (Bellona et al., 2011; Fujioka et al., 2012b; Miyashita et al., 2009) have elucidated the
73 effects of operating conditions and feed water characteristics on the rejection of N-
74 nitrosamines. It is reported that permeate flux can play an important role in the rejection of
75 low molecular weight N-nitrosamines. Fujioka et al. (2012b) also reported that a seven-fold
76 increase in feed ionic strength (from 26 to 182 mM) could lead to some decrease in NDMA
77 rejection (from 51 to 43%) and that pH changes in the feed (from pH 6.5 to 9) could also
78 cause an increased NDMA rejection (from 37 to 51%). In addition to these water quality
79 parameters, a recent laboratory-scale study by Fujioka et al. (2013a) has reported that
80 membrane fouling by tertiary treated wastewater effluent resulted in an increase in the
81 rejection of low molecular weight N-nitrosamines including NDMA.

82 The rejection of N-nitrosamines by RO membranes has been extensively investigated at the
83 laboratory scale (Bellona et al., 2011; Fujioka et al., 2012b; Miyashita et al., 2009; Steinle-
84 Darling et al., 2007). However, full-scale monitoring data to reaffirm findings from
85 laboratory-scale experiments and to assess the impact of realistic operating conditions on the
86 rejection of N-nitrosamines have rarely been reported in the peer review literature. Plumlee et
87 al. (2008) studied the removal of NDMA by different treatment processes (including RO) at
88 the Interim Water Purification Facility (Orange County, California, USA). NDMA removal
89 by the RO process varied from 24 to 56%. The authors suggested that the variation in NDMA
90 rejection observed in their study might be associated with changing feed conditions and
91 membrane fouling. However, the authors did not monitor the feed and membrane fouling
92 conditions. Farré et al. (2011) reported the fate of NDMA after each treatment process of the
93 Bundamba Water Recycling plant in Queensland, Australia. Because Farré et al. (2011) did
94 not focus on the RO process, only one overall rejection value of NDMA by the RO system
95 can be inferred from their study. Some information about the rejection of NDMA and NMOR
96 by a full-scale RO plant can also be inferred from a study by Krauss et al. (2010), who
97 investigated the fate of N-nitrosamine precursors at the Wulpen/Torreele Water Recycling
98 plant in Belgium. In comparison to NDMA, very little is known about the fate and removal of
99 other N-nitrosamines during RO filtration at full scale. The scarcity of full-scale monitoring
100 and the lack of information regarding operating conditions (e.g. permeate flux and recovery)
101 and feed water characteristics (e.g. temperature, ionic composition) significantly hinder any
102 meaningful data analysis. RO systems for wastewater recycling are typically designed using

103 three stages to achieve recovery around 85% (Fujioka et al., 2012a). Although the RO feed is
104 further concentrated after each filtration stage, no studies available to date have examined
105 rejection efficiencies for nitrosamines at subsequent stages.

106 The aim of this study was to assess the removal of eight N-nitrosamines in three full-scale
107 RO plants. N-nitrosamine rejection values obtained at different stages were systematically
108 related to the operating conditions and feed water characteristics. In addition, the difference
109 in N-nitrosamine rejections between a cool and a warm weather period at one plant was also
110 elucidated. Based on the obtained results, implications to water recycling practice were
111 highlighted and discussed.

112 **2. Materials and methods**

113 *2.1. RO systems*

114 Samples were collected from three full-scale water recycling plants denoted as A, B and C
115 located in Australia. In these plants, prior to RO filtration, secondary treated effluent is first
116 pretreated by either microfiltration (MF) or ultrafiltration (UF). In all three plants, pre-formed
117 chloramines were added to the process prior to MF or UF filtration to mitigate biofouling on
118 the RO membranes (Figure 1). The RO membranes used in these plants are from three
119 different manufacturers. The membranes used in these three plants are thin film composite
120 with a polyamide skin layer. They were characterized by similar salt (NaCl) rejection and
121 water permeability (Fujioka et al. (2013b)). The process flow diagrams of these RO systems
122 are shown in Figure 1. Samples were collected from plant A during cool (A-1) and warm (A-
123 2) weather periods. At plant A, chloramination is normally added downstream of the
124 coagulation process, which was the configuration when sampling campaign A-1 was
125 conducted (Figure 1). During an extended period of warm weather when it is necessary to
126 control algal growth during the coagulation process, chloramination can be added upstream
127 of the coagulation process. Plant A was operated in this configuration when the sampling
128 campaign A-2 took place (Figure 1). Unlike plants B and C, plant A is equipped with a
129 booster pump prior to the third stage to maintain the same average flux at all three stages
130 (Figure 1). All three systems produce reclaimed water for industrial and/or agriculture uses.
131 Plants A and B were designed for a possible indirect potable water recycling application
132 where high quality reclaimed water can be used to replenish an existing reservoir for drinking

133 water supply. Thus, the UV-H₂O₂ process was also installed after the RO process at these
134 systems for the destruction of residual NDMA in the RO permeate. Similar installation using
135 the UV-H₂O₂ process specifically for the removal of residual NDMA in the RO permeate can
136 also be found elsewhere (Drewes and Khan, 2011; Plumlee et al., 2008).

137 **[Figure 1]**

138 *2.2. Sampling protocol*

139 RO feed and permeate samples were collected from each RO stage (Figure 1). From each
140 sampling point, one sample was collected from plant C in May and December 2012 and
141 duplicate samples were collected in all other sampling events for N-nitrosamine analysis.
142 These samples (500 mL) were stored in amber glass bottles. Deuterated N-nitrosamines
143 corresponding to each target compound were used as isotope labelled surrogates. These
144 deuterated N-nitrosamines were purchased from CDN Isotopes (Pointe-Claire, Quebec,
145 Canada). A surrogate stock solution containing 100 µg/L of each deuterated N-nitrosamines
146 was prepared in pure methanol. Immediately after sample collection, the surrogate stock
147 solution was added to the sampling bottles to obtain 50 ng/L of each isotope labelled N-
148 nitrosamine. Analytical grade sodium thiosulfate (100 mg/L) was also added to the sample as
149 quenching reagent to prevent any further NDMA formation during transportation and sample
150 processing. From each sampling point, 20 mL sample was collected in plastic bottles for the
151 analysis of cations and boron and 100 mL sample was collected in amber glass bottle for the
152 analysis of anions and total organic carbon. Operating conditions and feed temperature of the
153 RO systems on the sampling day are summarised in Table 1. The difference in feed
154 temperature between the entrance and exit of each RO unit was less than 1 °C.

155 **[Table 1]**

156 *2.3. Analytical technique*

157 An analytical method previously developed for the determination N-nitrosamines in drinking
158 water and treated municipal effluent was employed (McDonald et al., 2012). The method
159 uses solid phase extraction (SPE), gas chromatography and analysis by tandem mass
160 spectrometry with electron impact ionization. Eight N-nitrosamines investigated in this study
161 have molecular weight in the range from 74 to 158 g/mol (Supplementary Material Figure

162 S1). These eight target N-nitrosamines are hydrophilic in the operating pH range of the RO
163 plants (pH 6-8). Further details of their physicochemical characteristics can be found
164 elsewhere (Fujioka et al., 2012a). The use of direct isotope dilution ensures accurate
165 quantification, accounting for analytical variability that may occur during sample processing,
166 extraction and instrumental analysis. SPE was conducted using Supelclean™ Coconut
167 Charcoal SPE cartridges purchased from Supelco (St Louis, MO, USA). The concentrations
168 of N-nitrosamines were quantified using an Agilent 7890A gas chromatograph coupled with
169 an Agilent 7000B triple quadrupole mass spectrometer. Calibration curves were established
170 for each N-nitrosamine with a range of 0.5-500 ng/L. The NMOR calibration curve was
171 extended to account for the NMOR concentration of over 400 ng/L. The quantitative
172 detection limits of this technique were 3 ng/L for NDMA, NDEA, NPIP, and NMOR, and 5
173 ng/L for NMEA, NPYR, NDPA, and NDBA.

174 Total organic carbon (TOC) concentration was determined using a TOC-V_{CSH} analyser
175 (Shimadzu, Japan). Conductivity and pH were measured using an Orion 4-Star Plus
176 pH/conductivity meter (Thermo scientific, USA). Cation and boron concentration were
177 determined using an Inductive Coupled Plasma - Mass Spectrometer (7500CS, Agilent
178 Technologies, Wilmington, DE, USA) following the protocol previously reported by Tu et al.
179 (2011). Anion concentrations were determined using an ion chromatography system
180 (Shimadzu, Tokyo, Japan).

181 **[Figure 2]**

182 2.4. Calculation

183 The rejection of N-nitrosamines and other solutes in each RO stage and combined RO stages
184 was calculated using the following equations.

$$185 \text{ Each stage rejection } R_i [\%] = \left(1 - \frac{C_{pi}}{C_{fi}} \right) \times 100 \quad (1)$$

$$186 \text{ Overall rejection } R_T [\%] = \left(1 - \frac{C_{pT}}{C_{f1}} \right) \times 100 \quad (2)$$

187 where i is the number of stage, C_{pi} is the solute concentration in the RO permeate of the stage
188 i , C_{fi} is the solute concentration in the RO feed of the stage i , and C_{pT} is the solute
189 concentration in the combined RO permeate.

190 **3. Results and discussion**

191 *3.1. Organic and inorganic constituent removal*

192 The feed waters to the three RO systems differed markedly in TOC concentration and salinity
193 (Supplementary Material Table S2). In particular, the feed water to plant A exhibited a
194 relatively high conductivity (salinity) at approximately 2.5 mS/cm. The sewer catchment of
195 plant A is predominantly in a low-lying coastal area and is subjected to seawater intrusion. In
196 fact, due to seawater ingresses, boron concentration in the feed to plant A was also higher
197 compared to plant B and C. Despite the high feed water salinity, the quality of RO permeate
198 at plant A was comparable to that at the other two RO systems. Most common cations and
199 anions in the feed water can be rejected well by the RO membranes. As a result, the permeate
200 at all three RO systems was of high quality with respect to basic water quality parameters. In
201 agreement with the 85% water recovery (Table 1) of these RO systems, TOC and
202 conductivity concentrations in the final concentrates were approximately six times greater
203 than those in the feed waters (Supplementary Material Table S2).

204 The rejections of TOC, cations (sodium, magnesium, potassium and calcium), anions
205 (chloride, nitrate and sulphate) and boric acid by all three RO systems are summarised in
206 Figure S3 of the Supplementary Material. Divalent ions (i.e. magnesium, calcium and
207 sulphate) were consistently removed over 99%. On the other hand, in agreement with a
208 previous study by Bellona and Drewes (2007), nitrate rejection was slightly lower than that of
209 all other ions. The rejection of boric acid was in the range of 15-30%, which is consistent
210 with the fact that boric acid has a small molecular size and is uncharged at pH below 8 (Tu et
211 al., 2010). The difference between the charged and uncharged solutes observed here can be
212 attributed to the electrostatic interaction and size exclusion rejection mechanisms. In addition
213 to size exclusion, electrostatic repulsion can also play an important role in the rejection of
214 charged solutes by NF/RO membranes (Bellona et al., 2004).

215 3.2. *N*-nitrosamine removal

216 3.2.1. Occurrence of N-nitrosamines in the RO feed water

217 NDMA was detected in all RO feed water samples (Figure 2). NDMA concentrations (7-16
218 ng/L) detected in the RO feed solutions were below or only marginally higher than the value
219 (i.e. 10 ng/L) in the final product water stipulated by the Australian Guidelines for Water
220 Recycling, with samples from A-2 being the only exception. In A-2, chloramine was added
221 upstream of the coagulation process and thus resulting in an increase in NDMA formation.
222 Results in Figure 2 are consistent with those obtained from previous studies (Farré et al.,
223 2011; Mitch et al., 2005; Plumlee et al., 2008). For typical water recycling plants where
224 NDMA in raw water can be controlled to similar levels found in this study, reducing NDMA
225 formation in the feed (Mitch et al., 2005) and RO filtration can be implemented to meet the
226 guideline value without relying on an additional subsequent treatment process such as AOP.

227 In addition to NDMA, several other N-nitrosamines (i.e. NPYR, NDEA, NPIP, NMOR and
228 NDBA) were also detected in some but not all RO feed water samples (Supplementary
229 Material Figure S4). NMEA, which is the second lowest molecular weight compound among
230 the N-nitrosamines investigated here, was not detected during any sampling campaign.
231 Surprisingly, a comparatively high NMOR concentration (177-475 ng/L) was observed in the
232 feed water at plant C. Compared to plant C, NMOR concentrations detected in the RO feed in
233 plants A-2 and B configurations were low. It is noted that NMOR concentrations in A-1, B
234 and C-1 were not reported due to unsatisfactory variation between duplicate samples and
235 poor recovery of the isotopically labelled internal standard. In fact, a sampling program
236 conducted in plant A from 2010 to 2012 revealed low NMOR concentrations (< 21 ng/L) in
237 the RO feed (Supplementary Material Figure S5) which indicates that a very high NMOR
238 concentration like plant C has not been identified in plant A. Likewise, a sampling program
239 conducted in plant B from 2009 to 2011 also showed a relatively low NMOR concentrations
240 in the range from 9 to 57 ng/L in the RO feed (Supplementary Material Figure S5). The
241 results reported here suggest that high NMOR concentrations in RO feed may be site specific
242 and could relate to certain industrial dischargers. The source of NMOR appears to be site
243 specific and further research is necessary to identify sources of NMOR within the catchment
244 of plant C.

245 After each stage, concentrations of the N-nitrosamines increased to quantifiable levels due to
246 the concentration effect leading to higher feed concentrations in subsequent stages (Figure 2).
247 As a result, the highest N-nitrosamine concentration was consistently observed in the final
248 RO concentrate. For example, NDMA concentrations in the final RO concentrate were two to
249 six times higher than those in the RO feed. Likewise, NMOR concentrations in the RO
250 concentrate were approximately six times higher than those in the RO feed.

251 **[Figure 2]**

252 3.2.2. N-nitrosamine concentrations in the RO permeate

253 NDMA concentrations in the RO permeate were detected above the detection limit (3 ng/L)
254 at least once in samples from each plant (Figure 3). However, most of these detections did not
255 exceed the guideline value of 10 ng/L, again with a sample collected from A-2 being the only
256 exception. Of the seven remaining N-nitrosamines, only NDEA, NMOR and NDBA were
257 detected in RO permeate samples (Supplementary Material Figure S6). NMOR concentration
258 in the RO permeate samples of plant C varied between 34 and 76 ng/L, which was
259 comparatively higher than the other N-nitrosamines. This is because NMOR concentration in
260 the RO feed of plant C was also higher than all other N-nitrosamines (Figure 3). Once again,
261 NMOR concentrations in A-1, B and C-1 are noted as not available due to a large variation in
262 analysed NMOR concentration between duplicate samples and poor recovery of the
263 isotopically labelled internal standard.

264 In all cases, the concentration of N-nitrosamines in the RO permeate increased in later stages
265 due to the increased concentration in the RO feed for each stage (Figure 3). As a result, N-
266 nitrosamine concentrations in the overall RO permeate (i.e. the combined RO permeate of the
267 first, second and third stages) were higher than those in the first stage. The results here
268 indicate that rejection estimates obtained from laboratory-scale systems, which are operated
269 at low water recovery, may result in an underestimation of N-nitrosamine concentrations in
270 the RO permeate. Although the permeation of NDMA through RO membranes can be
271 managed by a subsequent UV-H₂O₂ based AOP, little is known about its removal efficiency
272 for NMOR and other N-nitrosamines. The results reported here also suggest that, in addition
273 to NDMA, it is necessary to monitor the concentration of several other N-nitrosamines
274 particularly NMOR in secondary treated effluent and the corresponding RO permeate.

275

[Figure 3]

276 3.3. Rejections by RO membranes

277 3.3.1. Overall rejection

278 Overall NDMA rejections varied significantly with a range of 4-47% among the three RO
279 systems (Figure 4). In plant A, two distinct overall NDMA rejections (36 and 4%) were
280 observed during different sampling occasions. Plant A was operated under the same operating
281 conditions (e.g. recovery and permeate flux) during the two sampling events (i.e. A-1 and A-
282 2), but their feed water temperature differed (19.4 and 28.0 °C) (Table 1). A previous
283 laboratory-scale study revealed that an increase in feed temperature from 20 to 30 °C resulted
284 in a reduction of NDMA rejection from 49 to 24% (Fujioka et al., 2012b).

285 NDEA rejection at plant A and C varied between zero and 53% (Figure 4). This is
286 considerably lower than the values (86-95%) reported in a recent laboratory-scale study using
287 low pressure RO membranes and synthetic clean water solutions (Fujioka et al., 2012b).
288 Although the mechanism underlining this phenomenon is still unknown, the results reported
289 here indicate that RO filtration in treated wastewater can result in a significant reduction in
290 NDEA rejection. In fact, in a laboratory-scale study Fujioka et al. (2013a) reported a
291 considerable deterioration in NDEA rejection using tertiary effluent as feed water. Overall,
292 NMOR rejection was high and each stage exhibited rejection ranges of 87-91% (Figure 4)
293 which is consistent with previous laboratory-scale studies (Fujioka et al., 2013a; Fujioka et al.,
294 2012b).

295

[Figure 4]

296 3.3.2. Rejection at each stage

297 In plant B, 16 inch membrane elements were used whereas 8 inch membrane elements were
298 used in plants A and C. Thus, the hydraulic distribution of plant B can differ significantly
299 from that of plant A and C. At plant B, a significant variation in NDMA rejection (14-78%)
300 was observed among the three RO stages (Figure 5). Changes in the permeate flux after each
301 filtration stage may contribute to this variation to some extent (Fujioka et al. 2012b).
302 However, because permeate flux was not monitored in each individual stage at plant B, it was
303 not possible to confirm this hypothesis. Rejection of N-nitrosamines was further investigated

304 using the two sampling events at plant A, focusing on the difference in NDMA rejection
305 among the three stages. As RO filtration progressed, feed pH increased slightly and feed
306 conductivity increased significantly for both sampling events (Figure 6). During the first
307 sampling event (A-1) an increase in NDMA rejection from the first stage to third stage was
308 observed. In general, an increase in feed conductivity (or ionic strength) results in a decrease
309 in N-nitrosamine rejection (Fujioka et al., 2012b). However, the current study revealed an
310 opposite trend which indicates that another factor such as membrane fouling may have been
311 developed more extensively in later stages and may have compensated the decreased trend of
312 NDMA rejection. On the other hand, during the second sampling event (A-2), NDMA
313 rejections decreased as RO filtration progressed to later stages (Figure 6). The results
314 reported here indicate that NDMA rejections among three RO stages may vary significantly
315 even when operating conditions (i.e. permeate flux and recovery) were maintained constant.

316 [Figure 5]

317 [Figure 6]

318 **4. Conclusions**

319 NDMA was detected in all feed samples at the three full-scale RO trains investigated in this
320 study. Although most other N-nitrosamines were not detected in the RO feed, several N-
321 nitrosamines became detectable as the feed was further concentrated after each filtration stage.
322 N-nitrosamine concentrations in the final RO concentrate were up to six times higher than
323 those in the RO feed. As a notable exception, one of the three plants exhibited high NMOR
324 concentrations (177-475 ng/L) in the feed, resulting in high NMOR concentrations (34-76
325 ng/L) in the permeate. In most cases, NDMA, NDEA and NDBA were detected below the
326 Australian guideline value in the RO permeate. Overall rejection of NDMA and NDEA
327 among the three RO systems varied significantly with a range of 4-47% and 0-53%,
328 respectively. NDMA rejections among three RO stages also exhibited a significant variation
329 in several cases. These rejection variations may have resulted from the difference in feed
330 temperature and possibly membrane fouling. These findings suggest that N-nitrosamine
331 rejection estimates derived from laboratory-scale flat-sheet membrane studies, which are
332 operated at very low water recovery, may not be representative of full-scale operation. On the
333 other hand, overall NMOR rejections were equally high with a range of 81-84%. The findings
334 of this study provide insights for potential variations in N-nitrosamine rejection among

335 different RO systems and RO stages. Nevertheless, it is prudent to note the causes of some
336 variations reported here were not sufficiently identified due to changes in multiple parameters
337 during full-scale RO operation. Therefore, additional work is necessary to examine the
338 impact of each cause (e.g. fouling and feed temperature) using a pilot- or full-scale RO
339 systems.

340 **5. Acknowledgements**

341 This work was supported by the Australian Research Council Linkage Projects LP0990705
342 (with industry support from Veolia Water and Seqwater). The authors acknowledge the
343 University of Wollongong for a PhD scholarship awarded to Takahiro Fujioka. Mr Kha Le
344 Tu is thanked for his assistance with ICP-MS analysis.

345 **6. References**

346 Bellona, C., Budgell, K., Ball, D., Spangler, K., Drewes, J.E. and Chellam, S. (2011) Models
347 to predict organic contaminant removal by RO and NF membranes. *IDA Journal* 3(2),
348 40-44.

349 Bellona, C. and Drewes, J.E. (2007) Viability of a low-pressure nanofilter in treating recycled
350 water for water reuse applications: A pilot-scale study. *Water Research* 41(17), 3948-
351 3958.

352 Bellona, C., Drewes, J.E., Xu, P. and Amy, G. (2004) Factors affecting the rejection of
353 organic solutes during NF/RO treatment - A literature review. *Water Research* 38(12),
354 2795-2809.

355 Dolnicar, S., Hurlimann, A. and Nghiem, L.D. (2010) The effect of information on public
356 acceptance - The case of water from alternative sources. *Journal of Environmental*
357 *Management* 91(6), 1288-1293.

358 Drewes, J. and Khan, S. (2011) *Water Quality & Treatment: A Handbook on Drinking Water*,
359 6th Edition. American Water Works Association and Edzwald, J.K. (eds), McGraw-
360 Hill Professional.

361 Fajen, J.M., Carson, G.A., Rounbehler, D.P., Fan, T.Y., Vita, R., Goff, U.E., Wolf, M.H.,
362 Edwards, G.S., Fine, D.H., Reinhold, V. and Biemann, K. (1979) N-nitrosamines in
363 the rubber and tire industry. *Science (New York, N.Y.)* 205(4412), 1262-1264.

364 Farré, M.J., Döderer, K., Hearn, L., Poussade, Y., Keller, J. and Gernjak, W. (2011)
365 Understanding the operational parameters affecting NDMA formation at Advanced
366 Water Treatment Plants. *Journal of Hazardous Materials* 185(2-3), 1575-1581.

367 Fujioka, T., Khan, S.J., McDonald, J.A., Henderson, R.K., Poussade, Y., Drewes, J.E. and
368 Nghiem, L.D. (2013a) Effects of membrane fouling on N-nitrosamine rejection by

- 369 nanofiltration and reverse osmosis membranes. *Journal of Membrane Science* 427(0),
370 311-319.
- 371 Fujioka, T., Khan, S.J., McDonald, J.A., Roux, A., Poussade, Y., Drewes, J.E. and Nghiem,
372 L.D. (2013b) N-nitrosamine rejection by nanofiltration and reverse osmosis
373 membranes: The importance of membrane characteristics. *Desalination* 316(1), 67-75.
- 374 Fujioka, T., Khan, S.J., Poussade, Y., Drewes, J.E. and Nghiem, L.D. (2012a) N-nitrosamine
375 removal by reverse osmosis for indirect potable water reuse – A critical review based
376 on observations from laboratory-, pilot- and full-scale studies. *Separation and
377 Purification Technology* 98(0), 503-515.
- 378 Fujioka, T., Nghiem, L.D., Khan, S.J., McDonald, J.A., Poussade, Y. and Drewes, J.E.
379 (2012b) Effects of feed solution characteristics on the rejection of N-nitrosamines by
380 reverse osmosis membranes. *Journal of Membrane Science* 409–410(0), 66-74.
- 381 Krasner, S.W., Westerhoff, P., Chen, B., Rittmann, B.E. and Amy, G. (2009) Occurrence of
382 disinfection byproducts in United States wastewater treatment plant effluents.
383 *Environmental Science & Technology* 43(21), 8320-8325.
- 384 Krauss, M., Longrée, P., van Houtte, E., Cauwenberghs, J. and Hollender, J. (2010)
385 Assessing the fate of Nitrosamine precursors in wastewater treatment by
386 physicochemical fractionation. *Environmental Science & Technology* 44(20), 7871-
387 7877.
- 388 McDonald, J.A., Harden, N.B., Nghiem, L.D. and Khan, S.J. (2012) Analysis of N-
389 nitrosamines in water by isotope dilution gas chromatography-electron ionisation
390 tandem mass spectrometry. *Talanta* 99, 146-152.
- 391 Mitch, W.A., Oelker, G.L., Hawley, E.L., Deeb, R.A. and Sedlak, D.L. (2005) Minimization
392 of NDMA formation during chlorine disinfection of municipal wastewater by
393 application of pre-formed chloramines. *Environmental Engineering Science* 22(6),
394 882-890.
- 395 Miyashita, Y., Park, S.-H., Hyung, H., Huang, C.-H. and Kim, J.-H. (2009) Removal of N-
396 Nitrosamines and their precursors by nanofiltration and reverse osmosis membranes.
397 *Journal of Environmental Engineering* 135(9), 788-795.
- 398 NHMRC and NRMCC (2011) Australian drinking water guidelines paper 6 national water
399 quality management strategy, National Health and Medical Research Council,
400 National Resource Management Ministerial Council, Commonwealth of Australia,
401 Canberra.
- 402 NRMCC, EPHC and AHMC (2008) Australian guidelines for water recycling: Managing
403 health and environmental risks (Phase 2): Augmentation of drinking water supplies,
404 Environment Protection and Heritage Council, National Health and Medical Research
405 Council, Natural Resource Management Ministerial Council, Canberra.

- 406 Plumlee, M.H., López-Mesas, M., Heidlberger, A., Ishida, K.P. and Reinhard, M. (2008) N-
407 nitrosodimethylamine (NDMA) removal by reverse osmosis and UV treatment and
408 analysis via LC-MS/MS. *Water Research* 42(1-2), 347-355.
- 409 Poussade, Y., Roux, A., Walker, T. and Zavlanos, V. (2009) Advanced oxidation for indirect
410 potable reuse: a practical application in Australia. *Water Science & Technology* 60(9),
411 2419-2424.
- 412 Reyes-Contreras, C., Domínguez, C. and Bayona, J.M. (2012) Determination of nitrosamines
413 and caffeine metabolites in wastewaters using gas chromatography mass spectrometry
414 and ionic liquid stationary phases. *Journal of Chromatography A* 1261(0), 164-170.
- 415 Sedlak, D.L. and von Gunten, U. (2011) The Chlorine Dilemma. *Science* 331(6013), 42-43.
- 416 Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Marinas, B.J. and Mayes, A.M.
417 (2008) Science and technology for water purification in the coming decades. *Nature*
418 452(7185), 301-310.
- 419 Spiegelhalder, B. and Preussmann, R. (1984) Contamination of toiletries and cosmetic
420 products with volatile and nonvolatile N-nitroso carcinogens. *Journal of Cancer*
421 *Research and Clinical Oncology* 108(1), 160-163.
- 422 Steinle-Darling, E., Zedda, M., Plumlee, M.H., Ridgway, H.F. and Reinhard, M. (2007)
423 Evaluating the impacts of membrane type, coating, fouling, chemical properties and
424 water chemistry on reverse osmosis rejection of seven nitrosoalkylamines, including
425 NDMA. *Water Research* 41(17), 3959-3967.
- 426 Tu, K.L., Nghiem, L.D. and Chivas, A.R. (2010) Boron removal by reverse osmosis
427 membranes in seawater desalination applications. *Separation and Purification*
428 *Technology* 75(2), 87-101.
- 429 Tu, K.L., Nghiem, L.D. and Chivas, A.R. (2011) Coupling effects of feed solution pH and
430 ionic strength on the rejection of boron by NF/RO membranes. *Chemical Engineering*
431 *Journal* 168(2), 700-706.
- 432 USEPA (1993) N-Nitrosodimethylamine (CASRN 62-75-9) - Integrated risk information
433 system (IRIS). <http://www.epa.gov/iris/subst/0045.htm>.
- 434 Verliefde, A.R.D., Heijman, S.G.J., Cornelissen, E.R., Amy, G.L., Van der Bruggen, B. and
435 van Dijk, J.C. (2008) Rejection of trace organic pollutants with high pressure
436 membranes (NF/RO). *Environmental Progress* 27(2), 180-188.
- 437 Yoon, S., Nakada, N. and Tanaka, H. (2012) A new method for quantifying N-nitrosamines
438 in wastewater samples by gas chromatography—triple quadrupole mass spectrometry.
439 *Talanta* 97(0), 256-261.