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Effects of membrane fouling on N-nitrosamine rejection by nanofiltration and reverse osmosis membranes

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

Rita K. Henderson

University Of New South Wales, r.henderson@unsw.edu.au

Yvan Poussade

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

See next page for additional authors

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Authors

Takahiro Fujioka, Stuart J. Khan, James A. McDonald, Rita K. Henderson, Yvan Poussade, Jorg E. Drewes, and Long Nghiem

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Takahiro Fujioka¹, Stuart J. Khan², James A. McDonald², Rita K. Henderson², Yvan Poussade^{3,4}, Jörg E. Drewes^{2,5}, and Long D. Nghiem^{1,*}

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

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

³ Veolia Water Australia, Level 15, 127 Creek Street, QLD 4000, Australia

⁴ Seqwater, Level 2, 240 Margaret St, Brisbane City QLD 4000 Australia

⁵ Advanced Water Technology Center (AQWATEC), Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, CO 80401, USA

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

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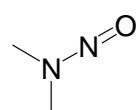
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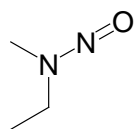
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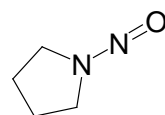
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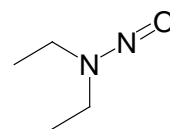
NDMA
(74 g/mol)



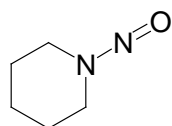
NMEA
(88 g/mol)



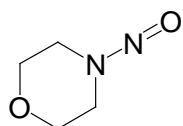
NPYR
(100 g/mol)



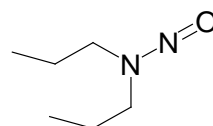
NDEA
(102 g/mol)



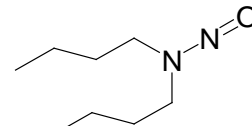
NPIP
(114 g/mol)



NMOR
(116 g/mol)



NDPA
(130 g/mol)



NDBA
(158 g/mol)

Figure 1

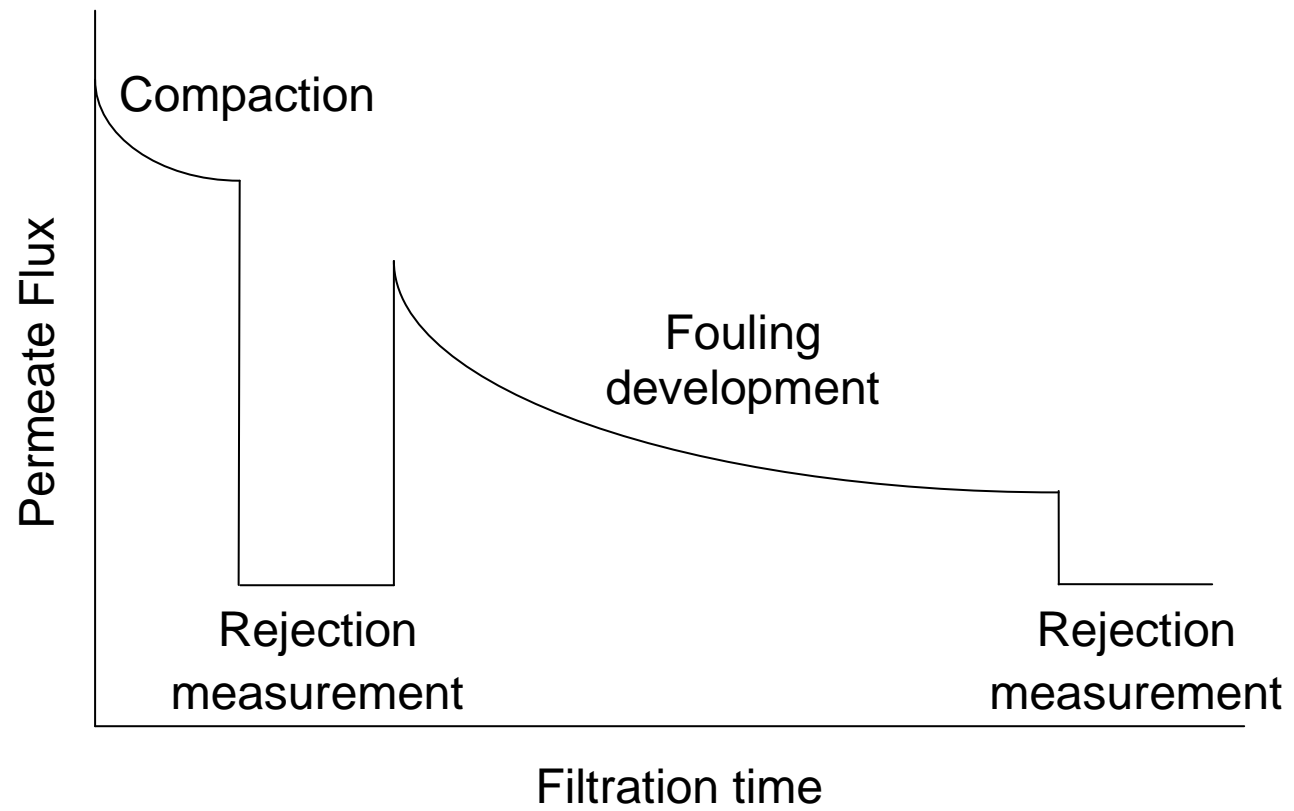


Figure 2

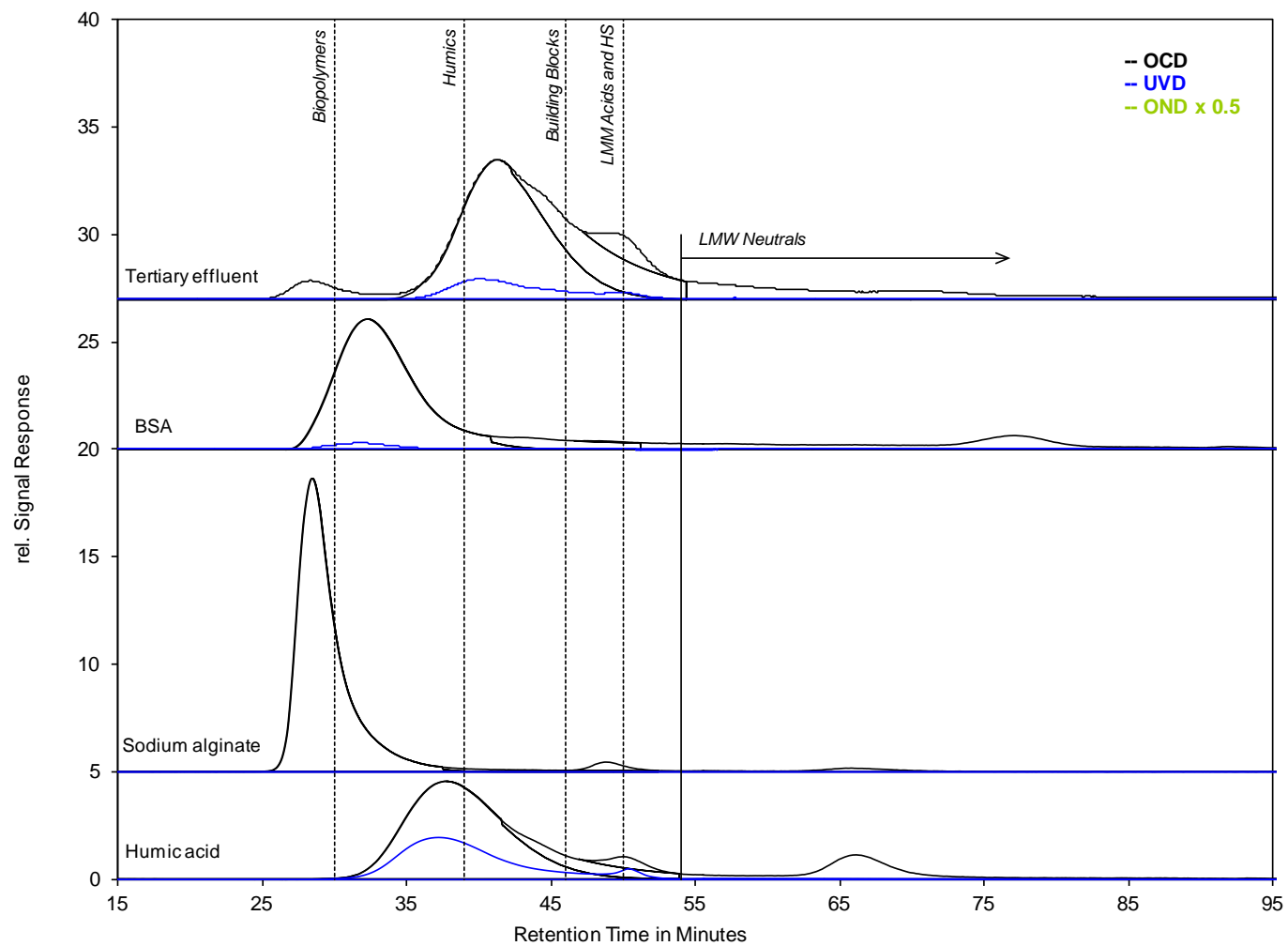


Figure 3

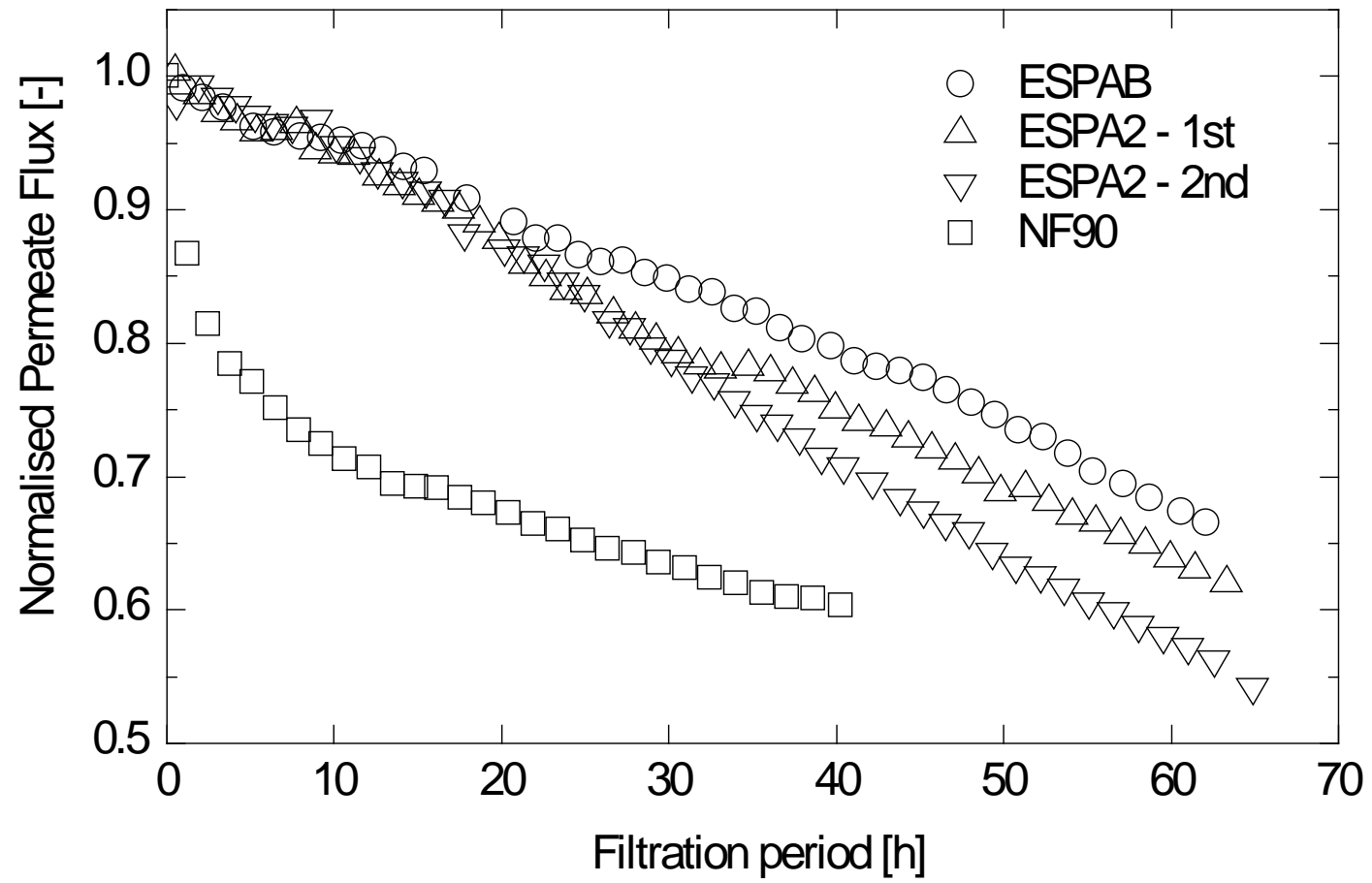


Figure 4

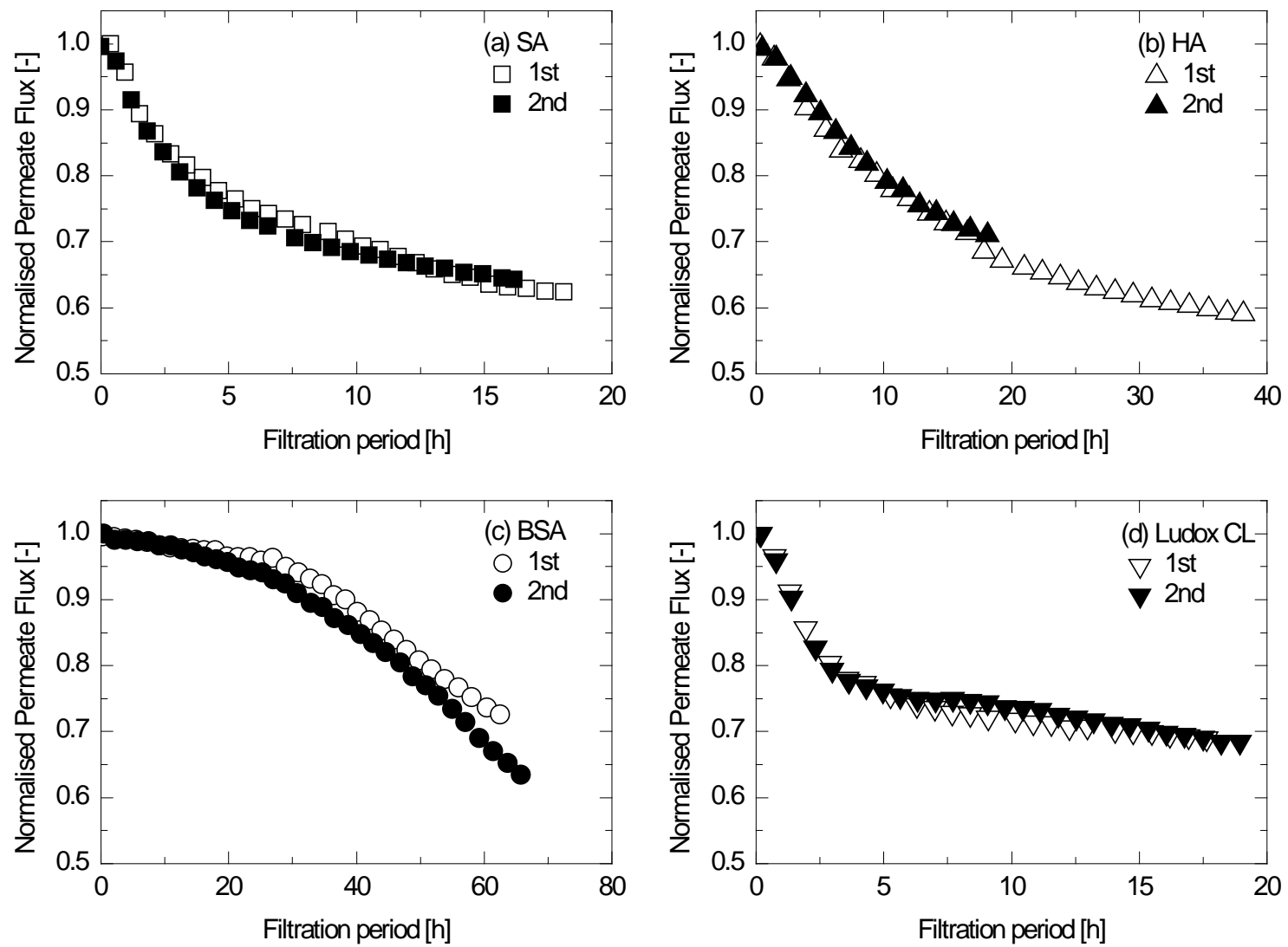


Figure 5

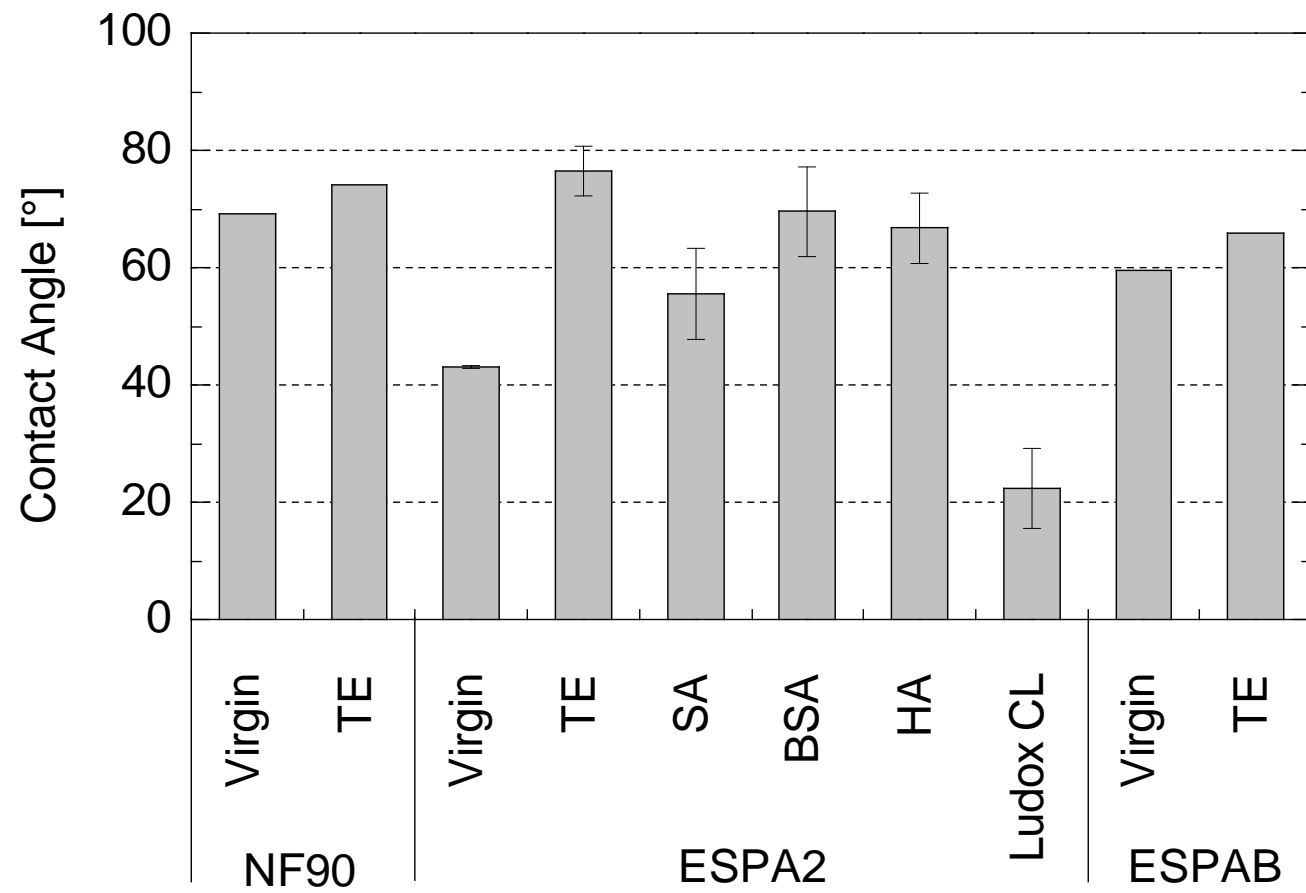


Figure 6

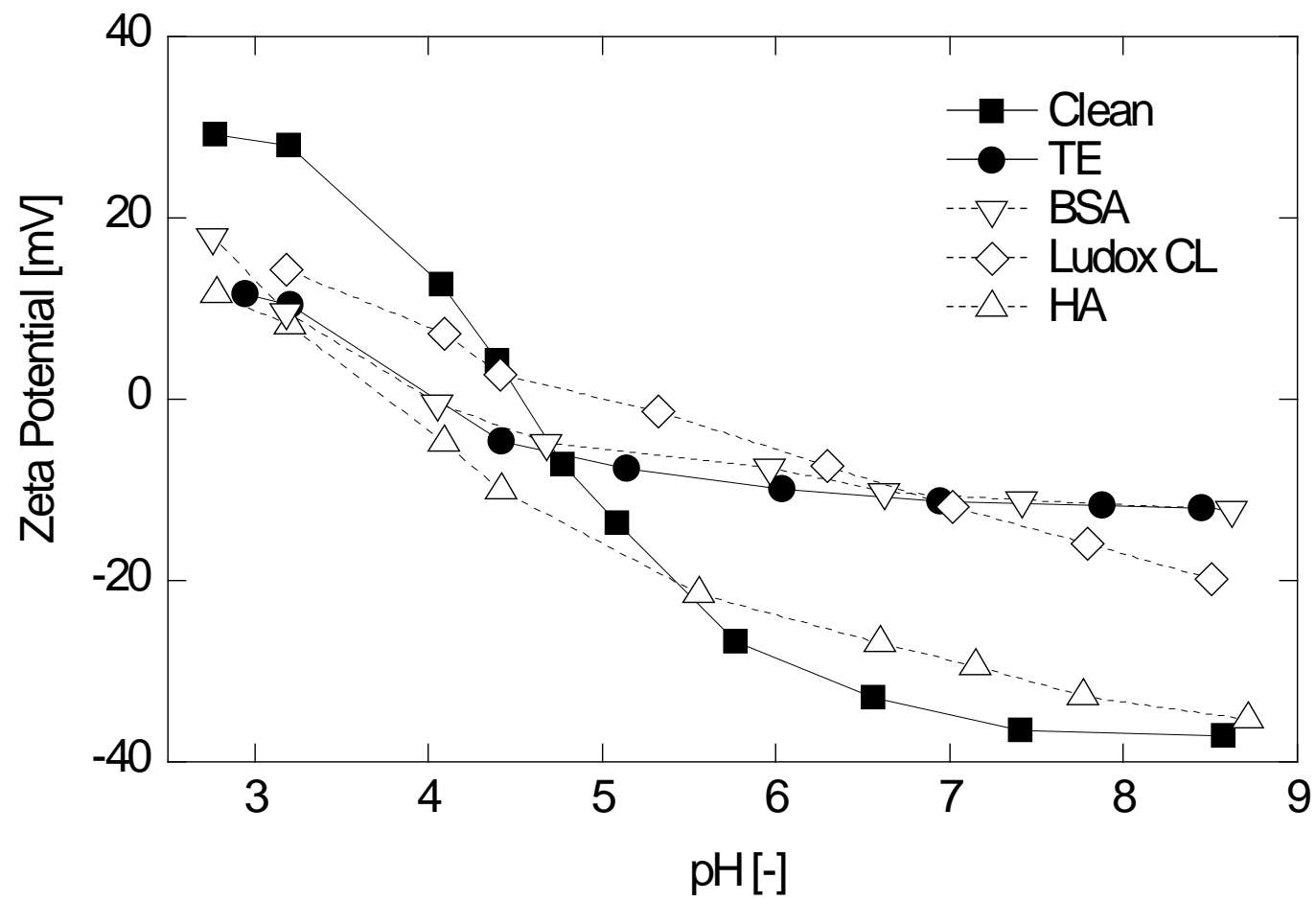


Figure 7

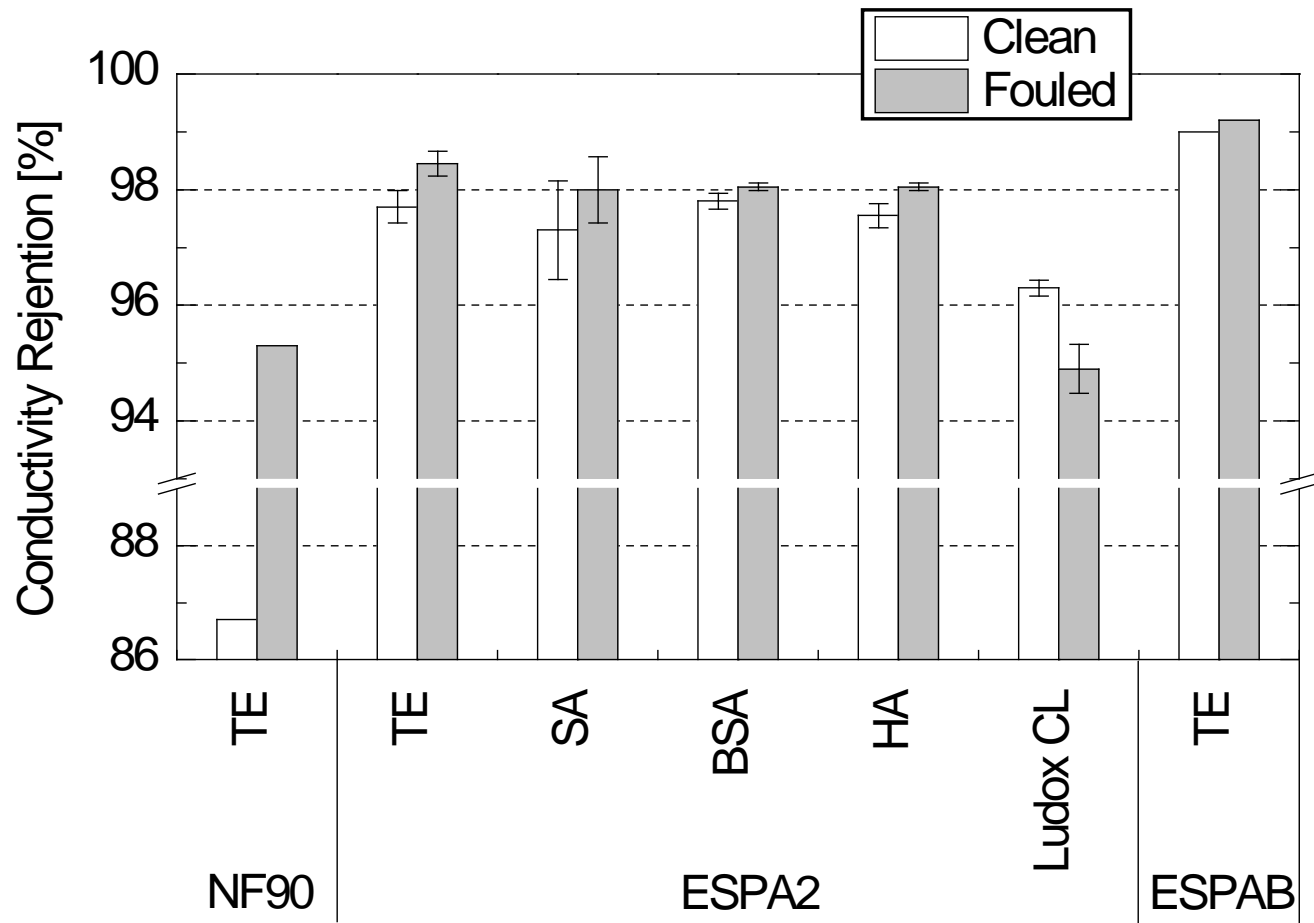
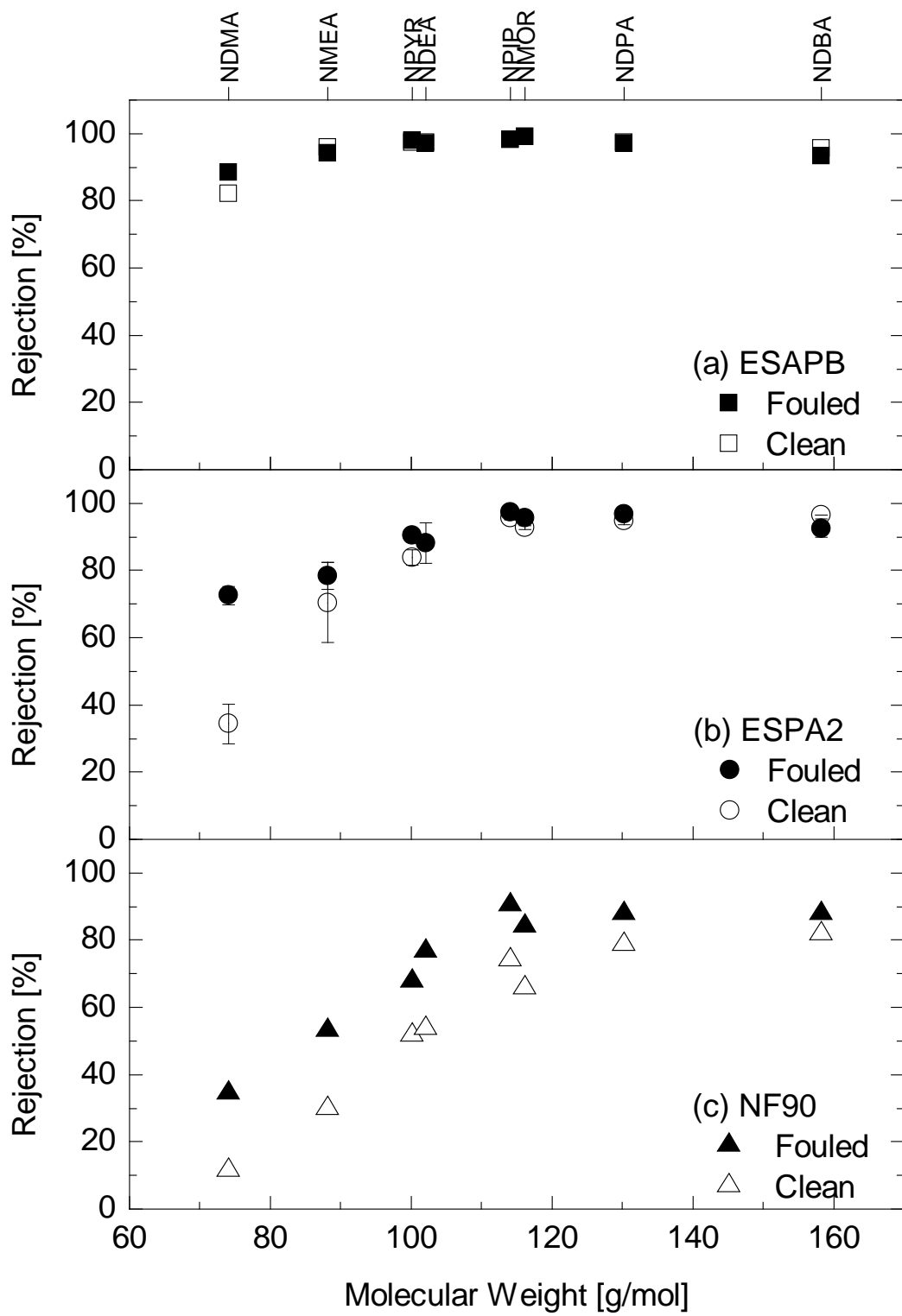


Figure 8



1031

1032 **Figure 9**

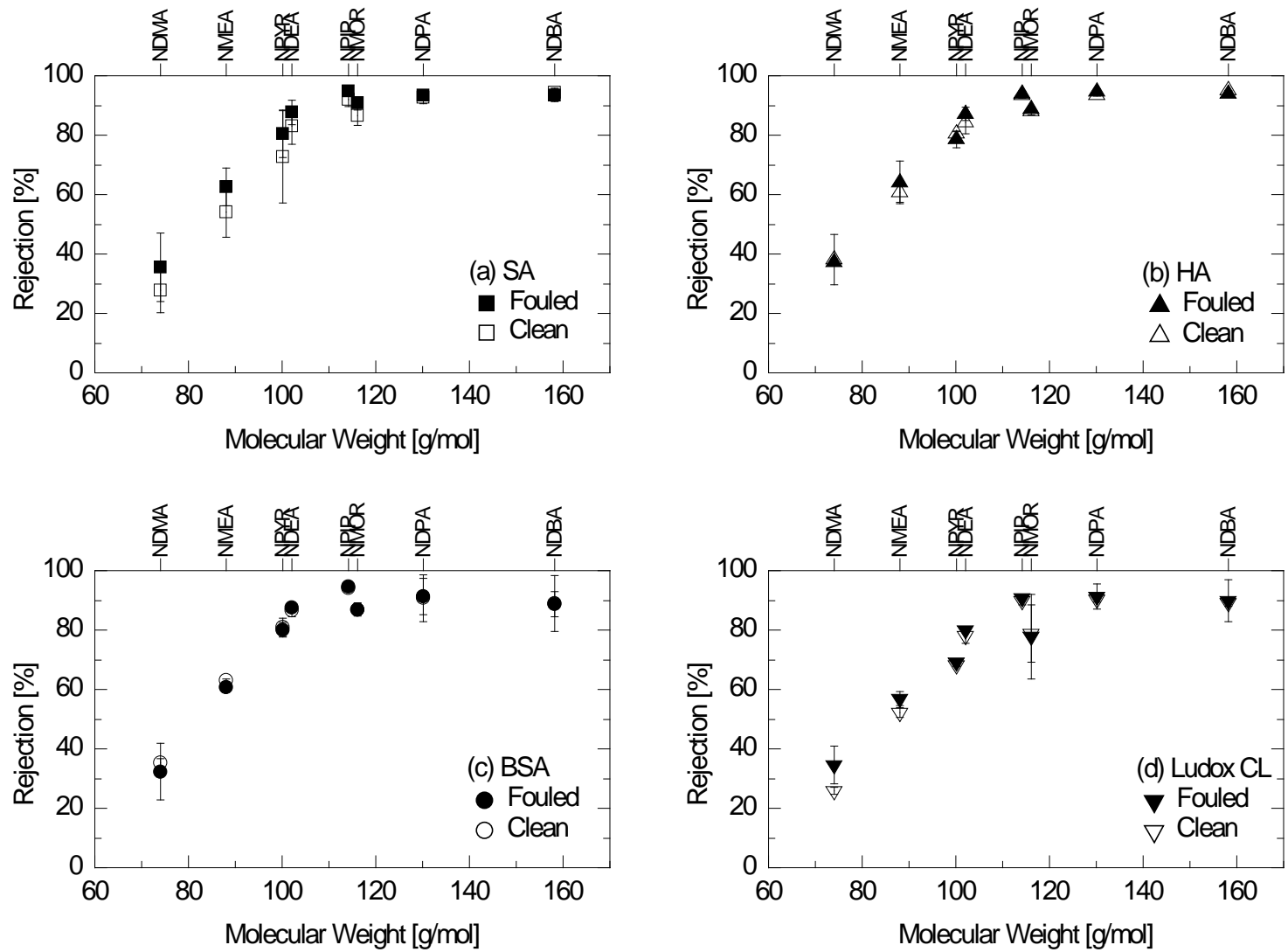


Figure 10

1 **Abstract**

2 The impact of fouling on N-nitrosamine rejection by nanofiltration (NF) and reverse osmosis
3 (RO) membranes was investigated in this study. Membrane fouling was simulated using
4 tertiary treated effluent and several model fouling solutions (that contained sodium alginate,
5 bovine serum albumin, humic acid or colloidal silica) to elucidate the changes in rejection
6 behaviour of N-nitrosamines. In general, the rejection of N-nitrosamines increased when the
7 membranes were fouled by tertiary effluent. The rejection of small molecular weight N-
8 nitrosamines was most affected by membrane fouling. In particular, the rejection of N-
9 nitrosodimethylamine (NDMA) by the ESPA2 membrane increased from 34 to 73% after
10 membrane fouling caused by tertiary effluent. The results also indicate that the impact was
11 less apparent for the lowest permeability membrane (i.e., ESPAB), and the rejection of N-
12 nitrosamines by the ESPAB membrane was over 82% regardless of membrane fouling. The
13 effect of membrane fouling caused by model foulants on N-nitrosamine rejection was
14 considerably less than that caused by tertiary effluent. Size exclusion chromatography
15 analyses revealed that the tertiary effluent contains a high fraction of low molecular weight (<
16 500 g/mol) organic substances. It appears that these low molecular weight foulants present in
17 the tertiary effluent can restrict the solute pathway within the active skin layer of membranes,
18 resulting in the observed increase of solute rejection.

19 **Keywords:** Water recycling, N-nitrosamines, NDMA, reverse osmosis, organic fouling,
20 colloidal fouling.

21

22 **1. Introduction**

23 Augmentation of potable water sources with reclaimed municipal effluent is an important
24 strategy to secure a reliable water supply in regions and countries with severe water scarcity.
25 However, a major concern over this alternative source of water supply is the occurrence of
26 trace organic chemicals which may induce adverse and chronic health effects. Notable
27 amongst these trace organic chemicals is N-nitrosodimethylamine (NDMA) which is an N-
28 nitrosamine that can be formed during the chloramination of the treated effluent [1]. In
29 addition to NDMA, other N-nitrosamines known to occur in treated effluent include N-
30 nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine
31 (NDEA), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), N-
32 nitrosodipropylamine (NDPA), N-nitrosodi-n-butylamine (NDBA) [2-4]. Some of these N-
33 nitrosamines have been identified as probable carcinogenic agents and thus their
34 concentrations in drinking water and recycled water intended for potable consumption have
35 been regulated by water authorities around the world [5-6]. The Australian Guidelines for
36 Water Recycling have recommended the maximum value of NDMA, NDEA, and NMOR in
37 recycled water intended for potable supply of 10, 10, and 1 ng/L, respectively [7]. Both
38 reverse osmosis (RO) and nanofiltration (NF) membranes have been frequently used in water
39 reclamation partly to ensure adequate removal of emerging trace chemicals, little is known
40 about their capacity to remove N-nitrosamines in full-scale installations. Reported percentage
41 rejections of NDMA vary greatly in full-scale plants from almost negligible to 86% and the
42 underlying reason for such significant variation in NDMA rejection remains unclear [8-11].

43 To date, only a few laboratory-scale studies have investigated N-nitrosamine rejection
44 capability of NF/RO membranes using clean matrix solutions [3, 12-13]. These studies
45 reported that the rejection of NDMA by RO membranes was in the range from 50 to 70%.
46 The rejection of N-nitrosamines increased in the order of increasing molecular weight and the
47 steric hindrance mechanism was identified as a predominant rejection mechanism of N-
48 nitrosamines by NF/RO membranes [3, 12-13]. Feed solution characteristics (i.e., pH, ionic
49 strength and temperature of the feed solution) also affected the rejection of NDMA and in
50 some cases other N-nitrosamines [3, 13]. In particular, Fujioka et al. [13] reported a
51 significant drop in NDMA rejection (from 49 to 25%) for an increase in feed temperature
52 from 20 to 30 °C. Nevertheless, the variations in these feed solution characteristics explain

53 only some of the variations in NDMA rejections that were reported in the previous full-scale
54 studies.

55 Municipal wastewater usually contains a large amount of organic and inorganic matter,
56 resulting in the formation of organic and colloidal fouling, bio-fouling and inorganic scales
57 on RO membranes [14-15]. It has been established in the literature that membrane fouling
58 can either increase or decrease the separation efficiency of NF/RO membranes [14, 16-18].
59 However, apart from a laboratory-scale study conducted by Steinle-Darling et al. [3] who
60 investigated the rejection of several N-nitrosamines by an RO membrane (ESPA3) artificially
61 fouled with sodium alginate, to date little attention has been given to the effects of membrane
62 fouling on the rejection of N-nitrosamines. Steinle-Darling et al. [3] reported that membrane
63 fouling by sodium alginate on the ESPA3 membrane caused a reduction in NDMA rejection
64 (from 56 to 37%).

65 The aim of this work was to provide insights into the effects of membrane fouling on the
66 rejection of N-nitrosamines by NF/RO membranes. The effects of membrane fouling were
67 investigated by comparing the rejections of N-nitrosamines by clean and fouled membranes.
68 Tertiary treated effluent and four different model foulants (namely sodium alginate, bovine
69 serum albumin, humic acid and colloidal silica) were used to induce membrane fouling. The
70 tertiary treated effluent and model foulants were characterised in detail to systematically
71 elucidate the effects of membrane fouling on the rejection of N-nitrosamines by NF/RO
72 membranes.

73 **2. Materials and methods**

74 *2.1. NF/RO membranes*

75 Three NF/RO membranes – namely the NF90, ESPA2, and ESPAB – were used in this
76 investigation. These are thin-film composite polyamide membranes with a microporous
77 supporting layer and were supplied as flat sheet samples. Key properties of these membranes
78 are shown in Table 1. The NF90 (Dow Filmtec, Minneapolis, MN, USA) is an NF membrane
79 typically used for softening of brackish water. The ESPA2 (Hydranautics, Oceanside, CA,
80 USA) is a low pressure reverse osmosis membrane that is widely applied for water
81 reclamation applications. The ESPAB (Hydranautics, Oceanside, CA, USA) is also low
82 pressure reverse osmosis but it has been designed to achieve a high boron rejection.

83

[Table 1]

84 2.2. Chemicals

85 The eight N-nitrosamines used in this study (Figure 1) were of analytical grade and were
86 purchased from Sigma-Aldrich (St Louis, MO, USA). Their physicochemical properties have
87 been described in detail elsewhere [13]. N-nitrosamine stock solution was prepared in pure
88 methanol with 250 µg/L of each N-nitrosamine. A deuterated surrogate standard was used for
89 each N-nitrosamine under investigation. These surrogate standards include N-
90 nitrosodimethylamine-D6, N-nitrosomethylethylamine-D3, N-nitrosopyrrolidine-D8, N-
91 nitrosodiethylamine-D10, N-nitrosopiperidine-D10, N-nitrosomorpholine-D8, N-
92 nitrosodipropylamine-D14 and N-nitrosodi-n-butylamine-D9, and were purchased from CDN
93 isotopes (Pointe-Claire, Quebec, Canada). A surrogate stock solution containing 100 µg/L of
94 each deuterated N-nitrosamine was prepared in pure methanol. The stock solutions were
95 stored at -18 °C and used within one month of preparation.

96 Analytical grade NaCl, CaCl₂ and NaHCO₃ were purchased from Ajax Finechem (Taren
97 Point, NSW, Australia). Sodium alginate (SA), bovine serum albumin (BSA), humic acid
98 (HA) and colloidal silica (Ludox CL, 30% weight suspension in water) were selected as
99 model foulants to simulate polysaccharides, proteins, refractory organic matter and colloidal
100 particles, respectively. These model foulants were purchased from Sigma-Aldrich (St Louis,
101 MO, USA). The Ludox CL is a positively charged silica particle whose surface is coated with
102 a layer of aluminium [19]. The hydrodynamic diameter of the Ludox CL is from
103 approximately 40 nm at below pH 6 to 233 nm at pH 10 due to aggregation effects in
104 different pH solutions [19].

105

[Figure1]

106 2.3. Tertiary treated effluent

107 Tertiary treated effluent sample was collected from an advanced water recycling plant in New
108 South Wales, Australia. The treatment train of the plant prior to the sampling point includes
109 screening, bioreactor and sand filtration, and the sample was collected after sand filtration.

110 2.4. Membrane filtration system

111 A laboratory-scale cross flow NF/RO filtration system was used in this study (Supplementary
112 Material Figure S1). A detailed description of this system is available elsewhere [13]. The
113 system consisted of a cross-flow stainless steel cell with effective membrane area of 4 cm by
114 10 cm and a channel height of 2 mm. The feed solution was kept in a stainless reservoir and
115 was fed to the membrane cell by a high pressure pump (Hydra-Cell, Wanner Engineering Inc.,
116 Minneapolis, MN, USA). The permeate flow and cross-flow velocity were regulated by a
117 bypass valve and a back-pressure regulator (Swagelok, Solon, OH, USA). The permeate flow
118 was monitored using a digital flow meter (FlowCal, GJC Instruments Ltd, Cheshire, UK)
119 which was connected to a computer. A stainless steel heat exchanging coil was submerged
120 into the feed reservoir and was connected to a chillier/heater unit (Neslab RTE 7, Thermo
121 Scientific Inc., Waltham, MA, USA) to control the temperature of the feed solution.

122 2.5. Experimental protocols

123 Rejection measurement and membrane fouling development were sequentially carried out
124 with four steps: (1) compaction; (2) measuring N-nitrosamine rejection without membrane
125 fouling; (3) fouling development; and (4) remeasuring N-nitrosamine rejection by fouled
126 membrane (Figure 2). Because full-scale RO plants are generally operated with a constant
127 (average) permeate flux which is approximately 20 L/m²h [20] and feed pressure increases as
128 fouling progresses to maintain the permeate flux, the constant permeate flux of 20 L/m²h was
129 used to evaluate N-nitrosamine rejection before and after fouling. Throughout the
130 experiments, cross flow velocity and feed temperature in the reservoir were always kept
131 constant at 0.42 m/s and 20 ± 0.1 °C, respectively. The details of these four steps are as
132 follows.

133 Step 1: The membrane sample was first compacted using Milli-Q water at 1,800 kPa until the
134 permeate flux was stabilised.

135 Step 2: Following the compaction step, the Milli-Q water in the filtration system was
136 replaced with either the tertiary effluent or synthetic solution containing a particular model
137 foulant (e.g. SA, HA, BSA or Ludox CL) and background electrolytes (20 mM NaCl, 1 mM
138 CaCl₂ and 1 mM NaHCO₃). The concentrations of SA, BSA and HA in the feed solution
139 were adjusted to make up approximately 10 mg/L as total organic carbon (TOC). The Ludox

140 CL was suspended in the same background electrolyte solution (20 mM NaCl, 1 mM CaCl₂
141 and 1 mM NaHCO₃) to obtain 100 mg/L of colloidal silica. After the replacement of feed
142 solutions, stock N-nitrosamine solution was spiked into the feed solution at environmentally
143 relevant concentration (i.e., 250 ng/L). The permeate flux was also adjusted at 20 L/m²h
144 which is a typical value for most water reclamation RO plants [20]. The system was operated
145 for 1 h prior to the collection of the feed and permeate samples for analysis. This sampling
146 point represents the performance of the membrane under a clean condition.

147 Step 3: After the first sampling event, membrane fouling was promoted by adjusting the
148 permeate flux to 60 L/m²h. The system was then continuously operated with a constant feed
149 pressure. The fouling development step ended after the permeate flux reached 45 L/m²h (i.e.,
150 decreased by 25%).

151 Step 4: The permeate flux was adjusted to 20 L/m²h and the system was stabilised for 1 h
152 prior to the second sampling of the feed and permeate. This sampling point represents the
153 performance of the membrane under a fouled condition.

154 **[Figure 2]**

155 *2.6. Analytical techniques*

156 2.6.1. Size exclusion chromatography analyses

157 Characterisation of dissolved organic carbon (DOC) composition in the tertiary effluent and
158 model foulant solution samples was carried out with a size exclusion chromatography
159 technique using a Liquid Chromatography - Organic Carbon Detection (LC-OCD) Model 8
160 system (DOC-LABOR, Karlsruhe, Germany). The LC-OCD system is equipped with a UV-
161 detector (254 nm) as well as organic carbon and nitrogen detectors. Chromatographic
162 separation is undertaken using a Toyopearl[®] TSK HW-50S column (Tosoh Bioscience,
163 Tokyo, Japan). Prior to the analysis, calibration of humic substance molecular weights was
164 conducted using IHSS Humic acid and IHSS Fulvic acid. Calibrations of detectors for total
165 organic carbon and total organic nitrogen were also conducted using potassium hydrogen
166 phthalate and potassium nitrate, respectively. For the analysis, a mobile phase (phosphate
167 buffer, pH 6.37, 2.5 g/L KH₂PO₄ and 1.5g/L Na₂HPO₄·H₂O) was set at a flow rate of 1.1
168 mL/min. In the LC-OCD system, an injected sample of 1 mL was pre-filtered with an in-line

169 0.45 μm PES-filter located in front of the column and detectors. Software provided by the
170 manufacturer (ChromCALC, DOC-LABOR, Karlsruhe, Germany) was used for the
171 quantification of the organic matter compositions. Further details can also be found in
172 previous studies [21-22].

173 2.6.2. Contact angle measurement

174 Contact angle of membrane surface was measured using the standard sessile drop method.
175 This was performed with a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ).
176 Prior to the measurement, virgin and fouled membrane samples were dried for over 24 h in
177 the dark. The dry membrane was fixed on the stage of the instrument and contact angle of the
178 membrane was measured with a water droplet (Milli-Q water). The contact angle of each
179 membrane was determined with an average of ten droplets.

180 2.6.3. Zeta potential measurement

181 Zeta potential of the virgin and fouled membrane surface was determined and calculated
182 using the Fairbrother-Mastin streaming potential method. The measurement of the streaming
183 potential was performed between pH 3 and 8.5 with a SurPASS Electrokinetic Analyser
184 (Anton Paar GmbH, Graz, Austria). In the measurement, 1 mM KCl was used as a
185 background electrolyte solution. The background solution pH was adjusted by a titration of
186 either KOH (1M) or HCl (1M) solutions. During the analysis, the background solution
187 temperature was $25\pm 1^\circ\text{C}$.

188 2.6.4. Basic analytical techniques

189 Turbidity was analysed using a 2100N laboratory turbidity meter (Hach, USA). Conductivity
190 and pH were measured using an Orion 4-Star Plus pH/conductivity meter (Thermo scientific,
191 USA). TOC concentration was determined using a TOC-VSH analyser (Shimadzu, Japan)
192 based on the non-purgeable organic carbon (NPOC) method. Cations and anions were
193 analysed using an Inductive Coupled Plasma – Mass Spectrometer (7500CS, Agilent
194 Technologies, Wilmington, DE, USA) and an ion chromatography (IC) system (Shimadzu,
195 Tokyo, Japan), respectively.

196 2.6.5. N-nitrosamine concentration analysis

197 The analysis of each N-nitrosamine concentration in this study is based on the gas
198 chromatography coupled with tandem mass spectrometry (GC-MS/MS) technique using
199 electron ionisation in a combination with the solid phase extraction (SPE) method previously
200 described by McDonald et al [23]. Prior to the SPE process, the SPE cartridges
201 (SupelcleanTM Coconut Charcoal SPE cartridges (2 g/mL), Supelco, St Louis, MO, USA)
202 were cleaned with 6 mL dichloromethane, 6 mL methanol and 12 mL of Milli-Q water.
203 Accurate quantitation (accounting for incomplete SPE recovery) was undertaken by direct-
204 analogue isotope dilution for all nitrosamines by adding 100 µL surrogate stock solution into
205 200 mL of each sample to make up 50 ng/L of each N-nitrosamine surrogate. N-nitrosamines
206 in the samples were then extracted by SPE at a flow rate of 5 mL/min. The cartridges were
207 rinsed with 3 mL Milli-Q water and dried with high purity nitrogen gas for at least 60
208 minutes. The dried SPE cartridges were then eluted using 12 mL dichloromethane, and 100
209 µL of toluene was added in the eluent. The eluent was then concentrated to 1 mL with a
210 Turbovap LV (Caliper Life Sciences, Hopkinton, MA, USA) under a gentle nitrogen stream.
211 The concentrations of N-nitrosamines were quantified using an Agilent 7890A gas
212 chromatograph (GC) coupled with an Agilent 7000B triple quadrupole mass spectrometer
213 (MS/MS). Calibration curves were established for each N-nitrosamine in the range of 1-400
214 ng/L. The NMOR calibration curve was extended to account for the NMOR concentration of
215 over 400 ng/L. The quantitative detection limits of this technique for NDMA, NDEA and
216 NDPA were 5 ng/L. The quantitative detection limits for all other N-nitrosamines used in this
217 study were 10 ng/L.

218 **3. Results and discussion**

219 *3.1. Characteristics of the tertiary effluent and model foulants*

220 Ionic composition and organic content of the tertiary effluent used in this study (Table 3) was
221 similar to that of most water reclamation plants. Nevertheless, the conductivity of this tertiary
222 treated effluent (Table 2) was slightly lower than the typical range of 1200-1700 µS/cm,
223 which is often found in the literature [24-25]. The tertiary effluent used in this study had not
224 been subjected to chloramination, with the exception of NMOR, and all other N-nitrosamines
225 were not detectable in the tertiary effluent sample. The concentration of NMOR in this
226 tertiary effluent was 1350 ng/L. NMOR can be found in toiletry and cosmetic products [26]

227 and rubber and tire industry, elevated concentration of NMOR in treated effluent has
228 previously been reported [27]. The water recycling plant where the tertiary treated effluent
229 was collected is known to have a very high load of industrial wastewaters in its catchment.

230 **[Table 2]**

231 The organic contents of secondary effluents have been generally characterised to comprise a
232 number of size fractions commonly referred to as biopolymers (polysaccharides, proteins and
233 colloidal organics) ($\gg 20,000$ Da), humic substances (approximately 1000 Da), building
234 blocks (300-500 Da) and low molecular weight (LMW) acids (< 350 Da) and neutrals (< 350
235 Da) [21-22, 28-29]. The building blocks block fraction represents breakdown products, or
236 intermediates during the degradation, of humic substances such as fulvic acid [22, 30]. The
237 tertiary effluent used in this study has a diverse molecular weight distribution (Figure 3). The
238 DOC concentration of fractions of biopolymers (10%), humic substances (46%), building
239 blocks (17%) and LMW neutrals (23%) in the tertiary effluent (Table 3) was in good
240 agreement with a previous study carried out by Henderson et al. [28]. Model foulants used in
241 this investigation had significant differences in their physicochemical characteristics which
242 were expected to assist in identifying the impact of fouling on membrane separation
243 performance. The major fraction of SA and BSA solutions was biopolymers (> 20000 g/mol),
244 which is consistent with a previous study [31] showing a molecular weight of 12000-80000
245 g/mol (SA) and 67000 g/mol (BSA). The molecular weight of HA analysed here was in the
246 range of approximately 1000 g/mol and this is in good agreement of the average molecular
247 weight of HA (1000 g/mol) reported in the literature [22]. All three organic model foulant
248 also contained some fraction of building blocks (300-500 g/mol) and LMW neutrals (< 350
249 g/mol) (Table 3).

250 **[Figure 3]**

251 **[Table 3]**

252 *3.2. Membrane fouling behaviour*

253 Significant membrane fouling was observed with all three membranes investigated in this
254 study when tertiary effluent was used at the elevated initial permeate flux of $60 \text{ L/m}^2\text{h}$ (which
255 is approximately three times the value used in most full scale RO systems for water recycling

256 applications). The profile of membrane permeability measured before and after fouling is
257 presented in Table S2 of the Supplementary Material. Membrane fouling behaviour of the
258 NF90 differs significantly from that of the ESPA2 and ESPAB membranes (Figure 4). Flux
259 decline was most severe for the NF90 membrane followed by the ESPA2 and ESPAB
260 membranes. The permeate flux of the NF90 membrane dropped by 30% within the first 12 h
261 system operation, and then decreased linearly as filtration progressed. In contrast, the two RO
262 membranes (ESPAB and ESPA2) showed an almost linear flux decline from the beginning of
263 the filtration. The flux decline of the ESPA2 and ESPAB membranes using tertiary effluent
264 reached 30% with 40-50 h and 60 h filtration, respectively. Interestingly, the rate of flux
265 decline amongst the three membranes increased in the order of increasing pure water
266 membrane permeability (Table 1). Similar observations were reported in previous laboratory-
267 scale studies [16, 32].

268 **[Figure 4]**

269 When the model foulants were used, significant variation in membrane fouling was observed.
270 When the ESPA2 membrane was fouled with either SA or HA, permeate flux dropped
271 rapidly within 10–20 h of system operation (Figure 5a-b). These observed curves of
272 membrane fouling are consistent with a previous study [33]. The rapid flux decline in the
273 early stage may have resulted from the formation of an alginate and humic acid fouling layer
274 on the membrane surface, resulting in a substantial resistance to permeate flow [16, 34]. In
275 fact, it is known that the HA foulant layer can account for a cake layer as thick as 4 μm [35],
276 while a skin layer thickness of RO membrane is usually less than 0.3 μm [36]. In contrast,
277 membrane fouling by BSA used here progressed slowly and linearly until 30 h system
278 operation, and then the slope of the permeate flux decline became steeper (Figure 5c). This
279 trend of the permeate flux decline is again in good agreement with a previous study [31].
280 Permeate flux with Ludox CL dropped significantly within 5 h of system operation, then
281 gradually decreased as filtration progressed (Figure 5d). This observation is consistent with a
282 previous laboratory-study from which it was suggested that the hydrophobic interactions and
283 electrostatic attraction forces between charged colloid particles and membrane surface were
284 key causes for colloidal membrane fouling in the early filtration stage [19].

285 **[Figure 5]**

286 3.3. Characteristics of fouled membranes

287 The membrane surface hydrophobicity (measured by contact angle) increased significantly
288 when the NF/RO membranes were fouled by tertiary effluent (Figure 6). The contact angle of
289 the ESPA2 membrane increased from 43 to 79° due to the membrane fouling. While the three
290 virgin membranes (NF90, ESPA2 and ESPAB) have a wide range of contact angle values
291 (43-69°), the fouled membrane surface revealed a very similar contact angle (in the range of
292 66-79°). The type of foulants can also have a major impact on the hydrophobicity of
293 membranes. The hydrophobicity of ESPA2 membranes increased as a result of membrane
294 fouling by SA, HA and BSA, whereas a considerable reduction in hydrophobicity was
295 observed with Ludox CL (Figure 6). The contact angle of each fouled membrane analysed
296 here was in good agreement with results reported by Beyer et al. [33] who also investigated
297 the hydrophobicity of fouled membranes by various model foulants using the NF270
298 membrane. Results reported here suggest that the hydrophobicity of the fouled membrane
299 surface depends mainly on the hydrophobicity of the foulants.

300 The impact of fouling on the membrane surface charge was also examined by analysing zeta
301 potentials of clean and fouled ESPA2 membranes. Consistent with a previous study [35], the
302 zeta potential of the fouled membranes became less negative at high pH (i.e., pH8) and less
303 positive at low pH (Figure 7). Amongst the model foulants, the zeta potential of BSA was
304 similar to tertiary effluent at all pH values tested. Although organic matter eluting in tertiary
305 effluent has a high concentration of material with similar molecular size to humic substances
306 (Table 3), the measured zeta potential of fouled membranes by the tertiary effluent and HA
307 were distinctly different (Figure 7). These results suggest that the material of the tertiary
308 effluent eluting in the humic substance fraction is similar to humic acid and fulvic acid
309 standards in terms of molecular size but has different charge characteristics. It is noted that
310 the zeta potential analysis of the SA fouled membrane was not conducted because of the re-
311 formation of alginate gel which clogged of the flow through cell of the Electrokinetic
312 Analyser.

313 **[Figure 6]**

314 **[Figure 7]**

315 3.4. *Effects of membrane fouling on inorganic salt retention*

316 Membrane fouling by tertiary effluent led to an increase in conductivity (salt) rejection for all
317 membranes with an exception of Ludox CL used in this investigation (Figure 8). In particular,
318 conductivity rejection by the NF90 membrane increased significantly from 87 to 95%.
319 Similarly, when the ESPA2 membrane was fouled by organic model foulants (SA, HA and
320 BSA), conductivity rejection also increased. Because the fouling layer and skin layer surfaces
321 of the RO membranes were negatively charged at pH 8 (Figure 7), the conductivity rejection
322 increase may be attributed to an additional repelling force occurring between the fouling
323 layer and salts. Tang et al. [32] investigated the impact of humic acid fouling using several
324 NF/RO membranes and suggested that an increase in conductivity rejection with humic acid
325 fouling may be attributed to an increase in repelling force between Cl^- anions and the cake
326 layer where negatively charged humic acid is deposited (Donnan exclusion mechanism). In
327 addition to the additional repelling force, conductivity rejection can increase when the
328 pathways of the solute such as membrane pore (or so-called free-volume space in polymer
329 chain [37]) and the local defects of the active skin layer are restricted with foulants. Tu et al.
330 [38] reported a considerable increase in boron rejection when organic fouling occurred, and
331 they suggested that the increase in boron rejection was due to the plugging of local defects or
332 hot spots on the membrane active skin layer. In the present work, low molecular weight
333 organic foulants present in the tertiary effluent may have narrowed down the pores within the
334 active skin layer and/or blocked the local defects on the active skin layer surface. This
335 additional restriction of the solute pathway may explain why the increase in conductivity
336 rejection observed using tertiary effluent was higher than that using BSA despite their similar
337 zeta potential of fouled membrane surface. On the other hand, the results reported here also
338 revealed a reduction in conductivity rejection with Ludox CL fouling. Colloidal cake fouling
339 layer depositing on membrane surface hinders back diffusion of rejected salt from the
340 membrane surface to bulk solution, and the higher concentration gradient across the
341 membrane is likely to result in a decrease in salt rejection (cake enhanced concentration
342 polarisation) [31, 39]. Because the fouled membrane by colloids remarkably decreased salt
343 rejection from 96.3% to 94.9%, the cake enhanced concentration polarisation may have
344 played an important role in salt rejection using the fouled membrane.

345 **[Figure 8]**

346 3.5. *Effects of membrane fouling on N-nitrosamine rejection*

347 The rejection of small organic compounds by NF/RO membranes can be governed by steric
348 hindrance, electrostatic interactions and adsorption onto the membrane surface [40]. All N-
349 nitrosamines used are hydrophilic and uncharged at neutral pH, thus the electrostatic
350 interactions and adsorption effects do not play a major role on their rejection performances.
351 Previous studies also reported that N-nitrosamine rejection by NF/RO membranes in clean
352 water matrices reached a steady state condition within a 45 min filtration period [3, 12].
353 Preliminary experimental results (Supplementary Material Figure S3) revealed no significant
354 changes in the rejection of N-nitrosamines with the exception of NDEA after 1 and 48 h of
355 filtration even in tertiary effluent feed. These results indicate that 1 h filtration is sufficient to
356 evaluate the rejection of most N-nitrosamines in tertiary effluent. During the preliminary
357 experiment, the concentration of some N-nitrosamines (i.e, NDMA, NMEA and NDBA) in
358 the feed decreased as the filtration progressed. These N-nitrosamines have been reported to
359 be readily biodegradable [4], and the reduction in these N-nitrosamines was possibly caused
360 by biodegradation. [A previous laboratory-scale study using the TFC-HR membrane \[13\] and](#)
361 [preliminary experimental results using the ESPA2 membrane \(Supplementary Material](#)
362 [Figure S4\) revealed that the effect of feed N-nitrosamine concentration on their rejections by](#)
363 [these RO membranes is negligible in the range from 0.25 to 1.5 µg/L of each N-nitrosamine.](#)
364 [Although the impact of N-nitrosamine concentration may vary depending on the specific](#)
365 [membrane, the changes in N-nitrosamine feed concentration observed in this study are not](#)
366 [expected to play an important role in the evaluation of N-nitrosamine rejections.](#)

367 In general, membrane fouling by tertiary effluent caused an increase in N-nitrosamine
368 rejection (Figure 9). This was particularly apparent for low molecular weight N-nitrosamines
369 such as NDMA. For example, the rejection of NDMA by the NF90 and ESPA2 membranes
370 increased in the range from 11 to 34% and from 34 to 73%, respectively. In contrast,
371 membrane fouling on the ESPAB membrane resulted in only a slight increase (from 82 to
372 88%) in NDMA rejection. The results reported here also indicate that the ESPAB membrane
373 is very effective for the removal of N-nitrosamines regardless of membrane fouling. As
374 expected, during these filtration tests the concentrations of NDMA, NMEA and NDBA in the
375 feed (i.e., tertiary effluent) decreased by up to 82%. The impact of SA fouling was minor, but
376 nevertheless discernible for low molecular weight N-nitrosamines such as NDMA (Figure

377 10). On the other hand, membrane fouling of HA, BSA and Ludox CL had a negligible
378 impact on the rejection of N-nitrosamines.

379 The clear difference in the impact of membrane fouling observed between tertiary effluent
380 (Figure 9) and model foulants (Figure 10) is intriguing. For the separation mechanism of N-
381 nitrosamines, the rejection of N-nitrosamines by NF/RO membranes has been reported to be
382 mainly governed by steric hindrance where the interaction between N-nitrosamine molecule
383 size and pore size of the active skin layer plays an important role in their rejection [13].
384 Because the molecular size of N-nitrosamines does not change under the experimental
385 conditions, the increased rejection of some N-nitrosamines using the tertiary effluent is likely
386 to be attributed to changes in membrane characteristics. It can be suggested that the pathway
387 of solutes (such as membrane pore and local defects of the active skin layer) on RO
388 membranes can be restricted with foulants present in the tertiary effluent (Section 3.4) or due
389 to cake layer compression caused by the applied pressure increase, and these changes in the
390 solute pathway leads to an increase of N-nitrosamine rejection.

391 **[Figure 9]**

392 **[Figure 10]**

393 **4. Conclusions**

394 Membrane fouling by tertiary effluent and organic model foulants (i.e., sodium alginate,
395 bovine serum albumin and humic acid) led to an increase in conductivity rejection due to
396 enhanced electrostatic interactions between the fouling layer and inorganic salts. On the other
397 hand, colloidal fouling using Ludox CL caused a reduction in conductivity retention.
398 Membrane fouling by tertiary effluent also increased the rejection of N-nitrosamines. The
399 rejection of low molecular weight N-nitrosamines such as NDMA was most affected by
400 membrane fouling and the impact was most pronounced for membranes that have high
401 membrane permeability. Although the ESPA2 and ESPAB membranes were comparable in
402 terms of membrane permeability and fouling susceptibility the rejection of N-nitrosamines by
403 the ESPAB membrane was very high (over 82%) regardless the impact of membrane fouling.
404 In contrast to the results using tertiary effluent, membrane fouling by model foulants revealed
405 only a negligible impact on N-nitrosamine rejection. Because the tertiary effluent used in this
406 investigation contained a high fraction of low molecular weight organic substances, these

407 foulants may have restricted the pathway of solutes on the active skin layer of the RO
408 membrane, resulting in an increase in N-nitrosamine rejection. The present findings provide
409 valuable insights for predicting NDMA rejection variations observed during full-scale RO
410 plant operation. In addition, the results reported here indicate that changes in NDMA
411 rejection may be predicted by analysing conductivity rejection because both rejections
412 increased as fouling progressed. During a full-scale RO plant operation fouled membranes
413 are generally cleaned by chemical cleaning when membrane permeability drops by 15-20%.
414 Future work is, therefore, necessary to examine the impact of chemical cleaning on the
415 rejection of N-nitrosamines.

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- 547

548 **Table 1:** Properties of the membranes used in this study.

| Membrane | Pure water permeability ^a [L/m ² hbar] | Conductivity rejection ^b [%] |
|----------|---|--|
| NF90 | 11.7 ± 1.1 | 81.2 ± 2.5 |
| ESPA2 | 5.5 ± 0.3 | 98.1 ± 0.3 |
| ESPAB | 3.9 ± 0.2 | 99.3 ± 0.4 |

549 ^a Determined with Milli-Q water at 1,000 kPa and 20 °C feed temperature. Errors represent
 550 the standard deviation of three replicates.

551 ^b Analysed with feed solution contained 20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂ at
 552 permeate flux 20 L/m²h, cross flow velocity 40.2 cm/s, feed pH 8.0 ± 0.1 and feed
 553 temperature 20.0 ± 0.1 °C.

554 **Table 2:** Water quality of the tertiary effluent.

| Parameter | Value |
|-------------------------------|----------------|
| Turbidity | 0.7 NTU |
| Conductivity | 790 μ S/cm |
| pH | 7.8 |
| TOC | 9.3 mg/L |
| Na ⁺ | 106 mg/L |
| Mg ²⁺ | 14 mg/L |
| K ⁺ | 17 mg/L |
| Ca ²⁺ | 23 mg/L |
| Fe ²⁺ | 13 mg/L |
| Cl ⁻ | 177 mg/L |
| NO ₃ ⁻ | 43 mg/L |
| SO ₄ ²⁻ | 46 mg/L |

555

556 **Table 3:** Organic matter fractions in each feed solution.

| | Tertiary effluent | BSA | Sodium alginate | Humic acid |
|---------------------|-------------------|------|-----------------|------------|
| Hydrophobic [%] | 11.1 | n.q. | 2.0 | 0.4 |
| Hydrophilic | | | | |
| Biopolymer [%] | 9.8 | 79.5 | 91.1 | 5.6 |
| Humics [%] | 50.8 | n.q. | n.q. | 68.4 |
| (Mean MW [g/mol]) | (467) | | | (850) |
| Building blocks [%] | 15.1 | 8.1 | 2.2 | 9.2 |
| LMW neutrals [%] | 12.6 | 22.4 | 2.6 | 16.4 |
| LMW acid [%] | 0.6 | 0.2 | 2.1 | n.q. |

557 *n.q., not quantifiable

Effects of membrane fouling on N-nitrosamine rejection by nanofiltration and reverse osmosis membranes

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

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

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

³ Veolia Water Australia, Level 15, 127 Creek Street, QLD 4000, Australia

⁴ Seqwater, Level 2, 240 Margaret St, Brisbane City QLD 4000 Australia

⁵ Advanced Water Technology Center (AQWATEC), Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, CO 80401, USA

SUPPLEMENTARY MATERIAL

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

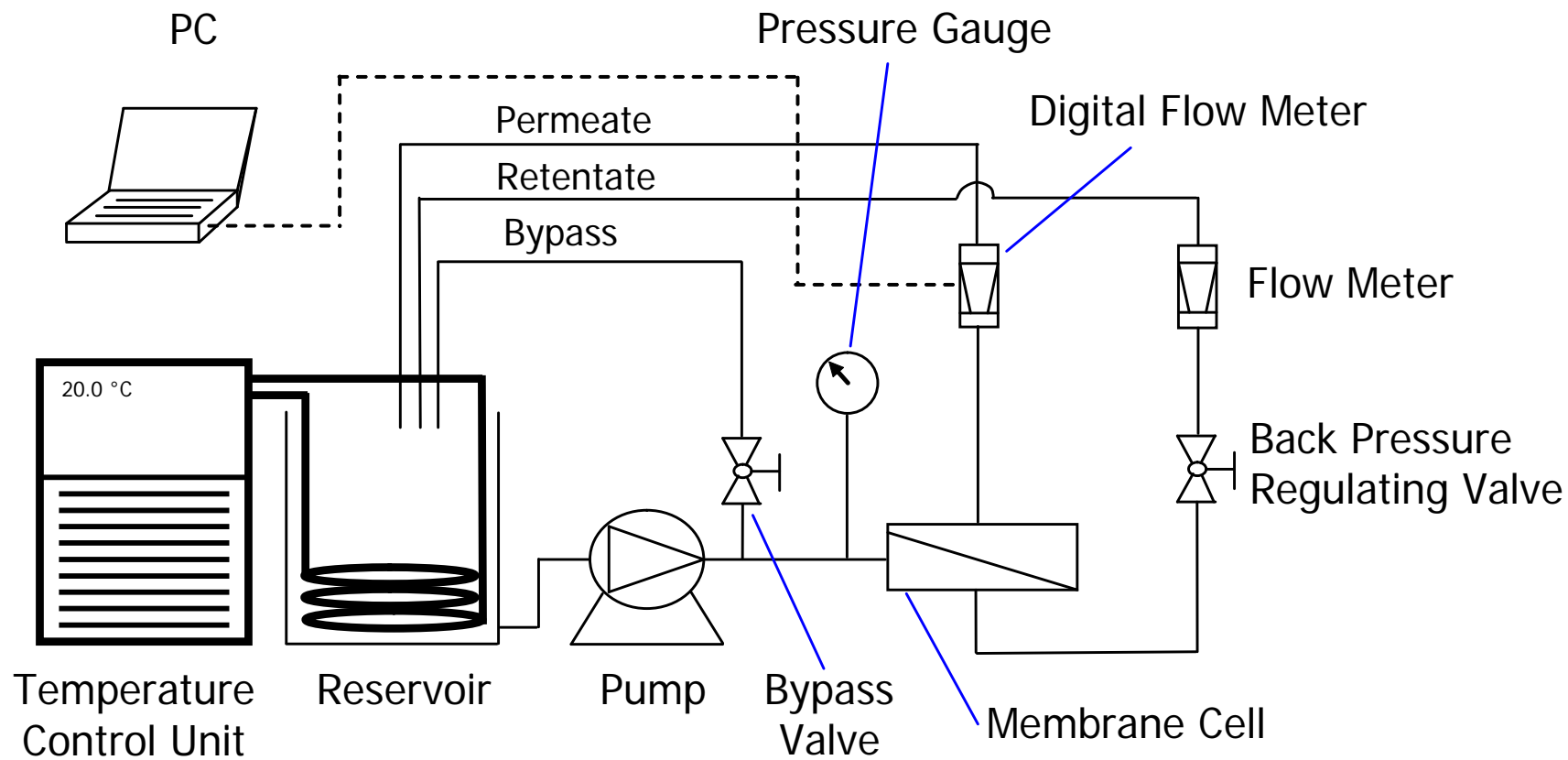


Figure S1: Schematic diagram of the cross flow filtration system.

Table S2: Membrane permeability by the clean and fouled membranes.

| Membrane | Feed solution | | Clean | Fouled |
|----------|-------------------|-----|--|--|
| | | | [Lm ⁻² h ⁻¹ bar ⁻¹ at 20°C] | [Lm ⁻² h ⁻¹ bar ⁻¹ at 20°C] |
| NF90 | Tertiary effluent | | 11.1 | 5.7 |
| ESPAB | Tertiary effluent | | 3.3 | 2.7 |
| ESPA2 | Tertiary effluent | 1st | 4.9 | 3.6 |
| | | 2nd | 5.0 | 3.5 |
| | Sodium alginate | 1st | 4.5 | 2.6 |
| | | 2nd | 4.6 | 3.0 |
| | Humic acid | 1st | 5.0 | 2.9 |
| | | 2nd | 5.0 | 3.6 |
| | BSA | 1st | 4.7 | 4.0 |
| | | 2nd | 4.7 | 3.7 |
| | Ludox CL | 1st | 4.9 | 3.5 |
| | | 2nd | 4.7 | 3.3 |

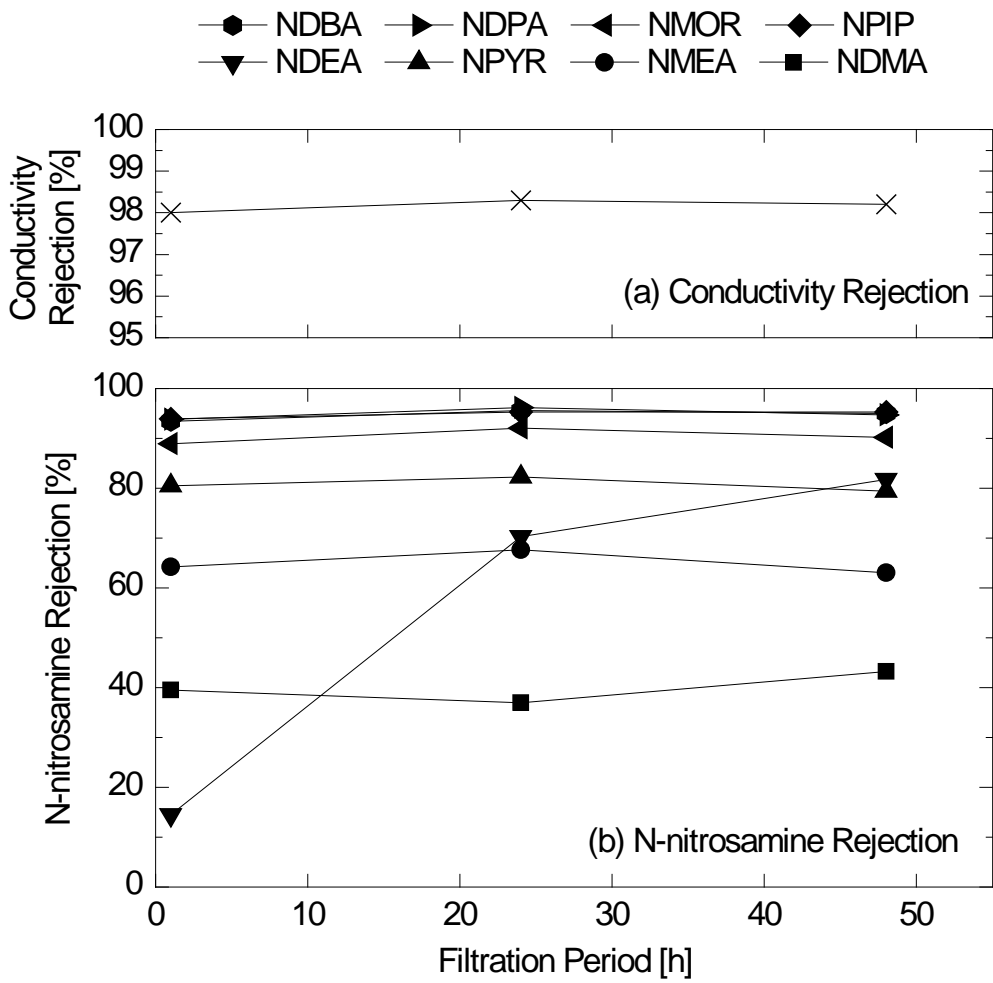


Figure S3: (a) Conductivity rejection and (b) N-nitrosamine rejection by the ESPA2 membrane as a function of filtration period (permeate flux 20 L/m²h, crossflow velocity 40.2 cm/s, feed temperature 20.0 ± 0.1 °C).

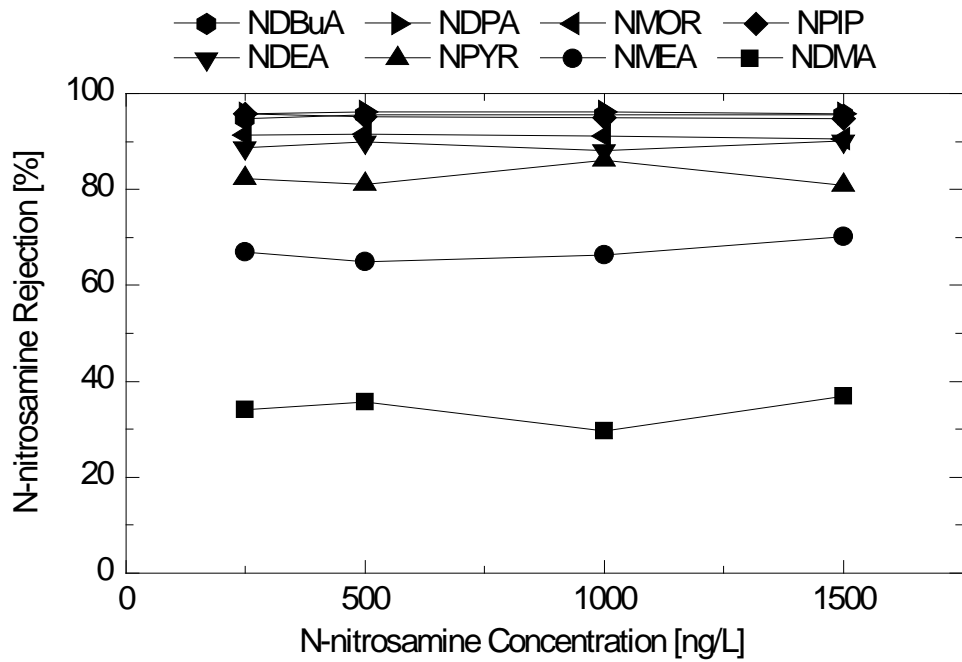


Figure S4: Rejection of N-nitrosamines by ESPA2 membrane as a function of nitrosamine concentration in the feed (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, permeate flux 20 L/m²h, crossflow velocity 40.2 cm/s, feed pH 8.0 ± 0.1, feed temperature 20.0 ± 0.1 °C).