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# Validating the rejection of trace organic chemicals by reverse osmosis membranes using a pilot-scale system

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# Validating the rejection of trace organic chemicals by reverse osmosis membranes using a pilot-scale system

## **Abstract**

A protocol to validate the rejection of organic chemicals of potential health risk by low pressure reverse osmosis (LPRO) membranes was developed for decision making support regarding the monitoring level required for potable water reuse. Ten organic chemicals were selected for evaluation, based on their recorded usage, the scarcity of rejection data, and difficulty in analytical determination at concentrations relevant to their potential impact on human-health. An analytical method was developed for these organic chemicals. The target rejections of 90 and 99% for neutral and charged chemicals respectively were successfully achieved under the standard operating condition with only two exceptions (i.e. bisoprolol and carazolol rejections by the TFC-HR membrane). These lower rejections by the TFC-HR can be attributed to its highestwater permeability amongst the three membranes while both bisoprolol and carazolol are positively charged. Changes in operating conditions including permeate flux, feed temperature and chemical cleaning can exert a considerable impact on conductivity rejection by the three LPRO membranes investigated here. Feed temperature showed an apparent impact on the rejection of the selected organic chemicals. However, their rejections were still higher than the target validation values. The protocol developed here can be expanded for the validation of other organic chemicals.

## **Keywords**

trace organic chemicals (TrOCs), low pressure reverse osmosis, rejection validation, operating conditions, potable water reuse

## **Disciplines**

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2 **osmosis membranes using a pilot-scale system**

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21 achieved under the standard operating condition with the exception of bisoprolol and  
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29 be expanded for the validation of other organic chemicals.

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31 validation; operating conditions; potable water reuse.

## 32 **1. Introduction**

33 The widespread occurrence of thousands of trace organic chemicals (TrOCs) of both natural  
34 and industrial origins in wastewater impacted water bodies is an important environmental  
35 issue of our time [1]. [Some of these chemicals pose toxicological threats to wildlife as well as](#)  
36 [potential adverse human health effects](#). These TrOCs are present in reclaimed water at  
37 concentrations in the range from less than one part-per-trillion (ng/L) to a few part-per-billion  
38 ( $\mu\text{g/L}$ ). Thus, they can only be detectable by some of the most advanced analytical techniques.  
39 The difficulties associated with their analysis and accurately evaluating their impact on  
40 human health present a major scientific challenge in addressing water quality problems  
41 caused by these TrOCs. One notable example is the uncertainty related to the removal of  
42 these chemicals by advanced water treatment processes, which could severely hinder the  
43 development of potable water reuse projects.

44 Concerns over possible adverse health impacts due to chronic and acute exposure to TrOCs  
45 via potable water recycling trigger the need to monitor their concentrations in the product  
46 water or to ascertain their removal efficiency. Routine monitoring is essential when there is a  
47 sufficient probability that certain TrOCs may occur in the product water at the threshold  
48 concentration which may result in adverse health impact. [On the other hand, TrOCs \(e.g.](#)  
49 [obsolete herbicides, industrial chemicals, and therapeutic drugs used in large quantity in the](#)  
50 [hospital\) often do not occur in municipal wastewater or only occur at below the detection](#)  
51 [limits of most advanced analytical techniques](#). Thus their fates during water reclamation are  
52 [largely unknown](#). To minimise the risk of accidental release of these TrOCs into the recycled  
53 [water, a multiple barrier approach including the source water control and advanced water](#)  
54 [treatment processes has been employed in many indirect potable water reuse schemes \[2\]](#).

55 The low pressure reverse osmosis (LPRO) filtration process is an important treatment  
56 component of many recent potable water recycling schemes. [LPRO membranes are expected](#)  
57 [to effectively remove a range of TrOCs](#). However, to date, only a small fraction of TrOCs has  
58 [been evaluated for their rejection by LPRO membranes \[3-7\]](#). Recent research in this area has  
59 resulted in a qualitative framework for assessing the removal of TrOCs by LPRO membranes.  
60 As a notable example, Bellona et al., (2004) [8] developed a rejection diagram to predict the  
61 rejection of TrOCs of known physiochemical properties. Bellona's rejection diagram is based

62 on the premise that the rejection of TrOCs by polyamide (PA) -based reverse osmosis (RO)  
63 membranes is mainly governed by size exclusion [8] and to a lesser extent by electrostatic  
64 interaction if the compound carries a charge. The measured rejections of most TrOCs that  
65 occur frequently in municipal wastewater at sufficiently high concentration are consistent  
66 with values estimated from this qualitative assessment framework. However, there remain  
67 many TrOCs that can potentially be introduced to municipal wastewater via uncontrolled or  
68 accidentally release but otherwise their concentrations are below the detection limits of most  
69 advanced analytical techniques. As a result, theoretical estimations of expected TrOC  
70 rejection have been suggested based on experimental results and the qualitative prediction  
71 framework by Bellona et al. [8]. Rigorous mathematic [9, 10] and artificial neural network  
72 [11] models have also been developed to predict and simulate the rejection of TrOCs by  
73 LPRO membranes under a range of operating conditions. However, the availability of these  
74 predictive tools does not replace the need to experimentally validate the rejection of TrOCs if  
75 they are not routinely monitored in potable water recycling applications.

76 Given the need to prioritise the monitoring efforts to manage the risk associated with TrOCs  
77 in recycled water, this study aims to identify whether the theoretical TrOC rejection based on  
78 the qualitative prediction framework by Bellona et al. [8] is valid using a spiral wound  
79 membrane system under a realistic range of filtration conditions. TrOCs were selected for this  
80 validation exercise based on an extensive literature review (to ensure that their rejections by  
81 LPRO membrane have not been previously reported in the literature) and a human health risk  
82 assessment. An analytical method was developed and optimised for the selected TrOCs. RO  
83 filtration experiments were conducted using three different LPRO membranes under a range  
84 of operating conditions (e.g. permeate flux, feed temperature and chemical cleaning). Overall,  
85 this study provides the insight of TrOC rejections by LPRO membrane for the validation of  
86 RO system performance. The validation protocol described is intended to be easily adaptable  
87 for a larger range of TrOCs selected on the basis of future membrane performance validation  
88 requirements.

## 89 2. Materials and methods

### 90 2.1. Chemicals

91 The selection of TrOCs for this validation exercise was based on an investigation undertaken  
92 for a large Australian water utility. In total 135 TrOCs were screened based on acceptable  
93 health-based concentrations published by the Queensland Government [12], registered usage  
94 in Australia, reported occurrences in wastewater, secondary treated effluent, and RO  
95 permeate. Bellona et al. [8] conducted a comprehensive literature review to show that TrOC  
96 rejection can be qualitatively predicted based on their physicochemical properties. Based on  
97 their physicochemical properties, TrOCs can be classified into 10 categories and the rejection  
98 of each category by RO membrane can be estimated (Supplementary Material Figure S1). For  
99 each category, an assumed rejection has been determined based on conservative estimates of  
100 0-3 Log removals of TrOCs under normal RO filtration operating conditions (Supplementary  
101 Material Table S2). The rejection categories and their assumed rejections are rough estimates  
102 based on their properties; thus, the assumed rejection values are yet to be comprehensively  
103 validated. Accordingly, a conservative validation target has been set for each category  
104 (Supplementary Material Table S2). The 10 TrOCs considered in this study have molecular  
105 weight larger than the MWCO of RO membranes and are hydrophilic at environmental pH  
106 (i.e. pH 7). Based on the qualitative prediction framework proposed here (Supplementary  
107 Material Table S2), their conservative validation targets were set at 90% for neutral (rejection  
108 category 7 and 9) and 99% for charged compounds (rejection category 10). Health ratio – a  
109 relationship between maximum reported TrOC concentration and their guideline limit – of  
110 selected chemical was high (0.1-1.3). All charged TrOCs selected here (Table 1) have over  
111 99% dissociation in pH 7.4 solution. The Log *D* value represents the distribution-coefficient  
112 at given pH indicating the hydrophobicity/hydrophilicity of a compound.

113 Di-*n*-butyl phthalate, bisoprolol, carazolol, carazolol-D7, dichloroprop, metsulfuron-methyl,  
114 molinate, penicillin V, pirimiphos-ethyl, trichlorfon, 17 $\alpha$ -estradiol, methanol, methyl-*tert*-  
115 butylether, ammonium acetate, and formic acid were purchased from Sigma-Aldrich (Castle  
116 Hill, NSW, Australia). Di-*n*-butyl phthalate-D4, carbamazepine-D10, gemfibrozil-D6 and  
117 17 $\beta$ -estradiol-D4 were purchased from CDN isotopes (Pointe-Claire, Quebec, Canada).  
118 Bisoprolol-D5 and penicillin V-D5 were purchased from Toronto Research Chemicals

119 (Toronto, Ontario, Canada). Dichloroprop-D6 and pirimiphos-ethyl-D10 were purchased  
120 from Dr Ehrenstorfer GmbH (Augsburg, Germany). All chemicals were of 98.5% purity or  
121 higher. All isotope labelled standards were of at least 98% atom abundance. A stock solution  
122 containing all selected TrOCs for rejection validation (**Table 1**) was prepared at 50-200 mg/L  
123 in methanol. A stock containing the isotope labelled versions of the target compounds was  
124 also prepared at 1 mg/L in methanol and used as the surrogate standard. A stock containing  
125 carbamazepine-D10 was prepared at 1 mg/L in methanol and used as the internal standard  
126 from compounds that did not have isotope labelled homologues. Unless otherwise stated,  
127 water used for method validation samples was taken from a Milli-Q water purification system  
128 (Millipore Kilsyth, Victoria, Australia).

129 **[Table 1]**

## 130 *2.2. RO feed*

131 RO feed was collected from a full-scale water recycling plant in Australia. The treatment  
132 plant train prior to sampling point comprises primary treatment, bioreactor, sand filtration,  
133 and microfiltration. Conductivity and pH of the RO feed were 820  $\mu\text{S}/\text{cm}$  and 7.7,  
134 respectively.

## 135 *2.3. Pilot-scale RO filtration system and RO elements*

136 A pilot-scale cross-flow RO filtration system was used. The system comprised three 4-inch  
137 fibreglass pressure vessels, a high pressure pump (CRN 3-25, Grundfos, Bjerringbro,  
138 Denmark) and 300 L polyethylene feed reservoir (**Figure 1**). The feed stream of the three  
139 pressure vessels was connected in series. One 4 inch  $\times$  40 inch LPRO membrane element was  
140 held in each pressure vessel. Stainless steel pipes and PVC pipes were used in the feed and  
141 permeate stream, respectively. The concentrate flow was monitored at the exit of the third  
142 vessel and the permeate flow was monitored at the exit of each pressure vessel. These flows  
143 were controlled by adjusting the opening of a glove valve and the power output of the pump  
144 using a variable frequency drive. The permeate and concentrate were recirculated into the  
145 feed reservoir. A chiller/heater unit (Aqua Cooler S360PD-CT, Chester Hill, NSW, Australia)  
146 connected to stainless steel heat exchanging pipes was used to control the feed solution  
147 temperature in the feed reservoir.



148 Three different LPRO membranes namely ESPA2-4040 (Hydranautics, Oceanside, CA,  
149 USA), TFC-HR 4040 (Koch Membrane Systems, San Diego, CA, USA) and TMG10 (Toray,  
150 Tokyo, Japan) were used (Table 2). These PA-based LPRO membranes are commonly used  
151 for brackish water treatment. The ESPA2 and TFC-HR membranes have been deployed in  
152 several full-scale RO installations in the USA and Australia for potable water reuse  
153 applications [13].

154 [Figure 1]

155 [Table 2]

#### 156 2.4. Filtration protocols

157 Prior to the first filtration experiment, the analyte stock solution of the selected TrOCs was  
158 dosed into 100 L RO feed water at a ratio of 10 mL-stock/100L-water to obtain  
159 approximately 5-20 µg/L of each TrOC. The membrane system was then operated at  
160 approximately 300 kPa for at least 12 hours before the first samples were taken for analysis.  
161 The standard system operating condition used in this investigation was system permeate flux  
162 20 L/m<sup>2</sup>h and feed temperature 20 °C. The impact of feed temperature was first investigated  
163 by incrementally increasing feed temperature from 10 to 35 °C. During the experiment, the  
164 system permeate flux was maintained at 20 L/m<sup>2</sup>h. The impact of permeate flux was  
165 investigated by first adjusting permeate flux to 30 L/m<sup>2</sup>h. Then, the permeate flux was  
166 stepwise decreased down to 10 L/m<sup>2</sup>h. The feed temperature during the experiment was  
167 maintained at 20±0.1 °C. The system recovery was maintained at 25% for all experiments. It  
168 is noteworthy that full-scale RO plants are operated at up to 85% water recovery [14] and the  
169 increase in system recovery can decrease solute rejection [9].

170 Following experiments described above, chemical cleaning was conducted using NaOH  
171 solution (pH 11-11.5). The chemical cleaning protocols include: (a) flushing the RO system  
172 with 150 L of tap water; (b) recirculating NaOH solution for 1 hour at 35 °C; (c) soaking with  
173 the NaOH solution for 3 hours; (d) recirculating the NaOH solution for 1 hour at 35 °C; (e)  
174 flushing the RO system with 150 L of tap water. During the chemical recirculation, glove  
175 valve installed in the exit of the feed stream (Figure 1) was fully opened in order to minimise  
176 permeation through LPRO membranes, and feed flow was maintained at 24 L/min. Following  
177 the chemical cleaning, the membrane system was operated using the RO feed water at

178 approximately 300 kPa for at least 12 hours. Then, feed and permeate samples were collected  
179 under the standard system operating condition (i.e. system permeate flux 20 L/m<sup>2</sup>h and feed  
180 temperature 20 °C). The rejection of chemicals was calculated using the following equation.

$$181 \quad \text{Rejection } R [\%] = \left( 1 - \frac{C_p}{C_f} \right) \times 100 \quad (1)$$

182 where  $C_p$  and  $C_f$  are permeate and feed concentrations, respectively.

## 183 2.5. Analytical techniques

### 184 2.5.1. Sample collection

185 Samples were collected in 0.5 L amber glass bottles. Sample volume taken for validation was  
186 0.5 L. Immediately after sampling 100 µL of the 1 mg/L surrogate standard stock was added  
187 to each sample and well mixed before commencement of extraction. Samples were extracted  
188 immediately after sampling otherwise stored in the dark at 4 °C and extracted within 48 hours.

### 189 2.5.2. Solid phase extraction

190 Solid phase extraction (SPE) of TrOCs in each sample was performed using a method  
191 previously reported elsewhere [3]. TrOCs were extracted onto 500 mg hydrophilic/lipophilic  
192 balance (HLB) solid-phase extraction SPE cartridges (Waters, Millford, MA, USA).  
193 Cartridges were pre-conditioned with *tert*-butyl methyl ether (MTBE), methanol, and Milli-Q  
194 water. Samples were drawn through the cartridge at approximately 10 mL/min. The  
195 cartridges were then rinsed with Milli-Q water (5mL), dried and stored at 4 °C in sealed bags  
196 under nitrogen until elution. Target TrOCs were eluted from the cartridges with methanol  
197 followed by methanol/MTBE under gravity. The solvent was removed under nitrogen to  
198 approximately 1 mL using a solvent evaporator (Turbovap, Caliper Life Sciences, Hopkinton,  
199 MA, USA). The residue was transferred to a 2 mL amber auto-sampler vial. 50 µL of the  
200 internal standard was added to each sample before capping with crimped seal.

### 201 2.5.3. Liquid Chromatography (LC) – tandem Mass Spectrometry (MS)

202 TrOCs were chromatographed using an Agilent (Palo Alto, CA, USA) 1200 series HPLC  
203 system equipped with a 150 x 4.6 mm, 5 µm particle size, Luna C18 (2) column  
204 (Phenomenex, Torrence CA, USA). An API 4000 triple quadrupole mass spectrometer

205 (Applied Biosystems, Foster City, CA, USA) equipped with a turbo-V ion source employed  
206 in both positive and negative Electrospray ionisation (ESI) modes for all target compounds  
207 except 17 $\alpha$ -estradiol which was analysed using atmospheric-pressure chemical ionisation  
208 (APCI) in positive mode. Using multiple reaction monitoring (MRM) two precursor ion –  
209 product ion transitions for all target compounds and isotope labelled surrogates were  
210 monitored for unequivocal confirmation. Only the first transition was used for quantitation.  
211 Relative retention times of the analyte and isotopically labelled surrogate standard were also  
212 monitored to ensure correct identification.

213 The use of isotope labelled versions of target compounds enabled quantification by isotope  
214 dilution which enables losses due to incomplete extraction to be accounted for. An isotopic  
215 version of each of the organic chemicals investigated here was used as their internal standard  
216 to account for any losses during SPE as well as changes in the final volume. Isotopically  
217 labelled versions were not available for metsulfuron-methyl, molinate, and trichlorfon. Thus,  
218 carbamazepine D10 was used as the internal standard for these chemicals to account for any  
219 changes in the final volume.

220 Both ESI and APCI in positive and negative modes were investigated for all standards to  
221 establish the best ionization configuration. To determine suitable precursor ions a solution of  
222 each standard was directly infused into the ion source and scanned using quadrupole 1 (Q1)  
223 from  $m/z$  50 – 450. The most intense ion observed was used to determine optimal source  
224 parameters such as declustering potential, collision energy and collision cell exit potential for  
225 each of up to 8 product ions detected in quadrupole 2 (Q2). Precursor-product ion transitions  
226 were incorporated into ESI positive, ESI negative or APCI positive methods and run using  
227 the chromatographic conditions stated above. For each analyte and surrogate standard the two  
228 most intense transitions were used in the final methods.

229 The instrument was calibrated at the beginning of each analytical run. Using working stocks,  
230 method calibration standards were prepared at 0.5, 1, 5, 10, 50, 100, 500 and 1000 ng/mL in  
231 methanol. For each calibration standard, 100 ng and 50 ng of surrogate and internal standard  
232 respectively were added so that a relative response versus relative concentration curve can be  
233 generated. At least six calibration points were used for each target compound. Recoveries of  
234 target compounds from both Milli-Q grade and RO feed water were determined by spiking

235 and extracting samples at 10, 100 and 1000 ng/L. Due to presence of some compounds in RO  
236 feed water, recoveries were determined only at 100 ng/L for this matrix.

#### 237 2.5.4. General water quality analysis

238 During RO filtration experiments, pH, electrical conductivity and temperature of solutions  
239 was measured using Orion 4-Star Plus pH/conductivity meter (Thermo Fisher Scientific,  
240 Waltham, MA, USA).

### 241 **3. Results and discussion**

#### 242 *3.1. Analytical technique development and validation*

243 Recoveries of the other TrOCs from Milli-Q water and RO feed are summarised in  
244 [Supplementary Material Table S3](#). All target TrOCs were recovered within satisfactory  
245 tolerances with the exception of molinate and trichlofon which were poorly recovered. To  
246 mitigate this low recovery, higher feed concentrations for these two compounds were used for  
247 the RO filtration work. On the other hand, di-n-butyl phthalate recoveries were significantly  
248 affected by background contamination, thus its reporting levels were adjusted in this  
249 investigation accordingly. It is noteworthy that for quantification purpose any variations in  
250 recovery of the target analysts were corrected using the isotopic standards [to remove any](#)  
251 [interference from the variation in recovery](#).

252 The calibrations and reporting detection limits of the tested TrOCs are summarised in  
253 [Supplementary Material Table S4](#). The instrument detection limit (IDL) was determined as  
254 the lowest concentration of a standard that affords a signal to noise ratio (s/n) of 3 or greater.  
255 The method detection limit (MDL) was the concentration of a target compound in sample that  
256 has been processed through the entire method giving a s/n greater or equal to 3. Reporting  
257 limits were determined as being the greatest value of either the 2<sup>nd</sup> lowest calibration point or  
258 3 times the MDL. Reporting limits were also dependant on any background contamination  
259 present in analysed samples. Reporting limits in the RO feed were up to five times higher  
260 than those in Milli-Q water ([Supplementary Material Table S4](#)). Details of the optimization  
261 are summarized in [Supplementary Material Table S5 and S6](#). The molecular structures of all  
262 precursor ions and proposed structures of the monitored product ions are summarized in  
263 [Supplementary Material Table S7](#).

264 Of the 10 TrOCs, dichloroprop, bisoprolol, varazolol, and molinate were detected in the RO  
265 feed solution collected at a full-scale plant at slightly above their reporting detection limits of  
266 5, 20, 7, and 11 ng/L, respectively. The concentrations of other TrOCs were below the  
267 detection limits reported in [Supplementary Material Table S4](#). For validation purpose, if the  
268 target TrOC was not detectable in the RO permeate, the reporting detection limit was used to  
269 calculate a minimum rejection value.

### 270 3.2. Validation during RO filtration

#### 271 3.2.1. Effects of physicochemical properties of TrOCs and membranes

272 The target validation rejection of 90% of neutral TrOCs could be readily achieved by all three  
273 LPRO membranes ([Table 3](#)). The neutral TrOCs selected here have the molecular weight of  
274 over 180 g/mol whereas the molecular weight cut-off of LPRO membranes is reported to be  
275 about 100 g/mol [15]. In fact, Fujioka et al. [16] evaluated the rejection of neutral compounds  
276 (i.e. N-nitrosamines) using a laboratory-scale setup and reported that neutral compounds with  
277 the molecular weight of over 114 g/mol exhibited greater than 90% rejection by five different  
278 LPRO membranes that are often used for water recycling applications.

279 The target validation rejection of 99% of charged chemicals were also achieved using all  
280 three LPRO membranes with only two exceptions. Rejections of bisoprolol and carazolol by  
281 the TFC-HR membrane were 97.7% and 97.2%, respectively ([Table 3](#)). These two TrOCs are  
282 positively charged and TFC-HR has the highest water permeability compared to the other  
283 LPRO membranes investigated here. The low rejection of these positively charged TrOCs  
284 can be explained by electrostatic attraction with the negatively charged active skin layer  
285 surface of the LPRO membranes, causing a localised increase in concentration at the  
286 membrane surface, and leading to a low rejection. Verliefde et al. [17] called this  
287 phenomenon as “charge concentration polarisation”. The target validation rejection of 99%  
288 was achieved with all negatively charged TrOCs (i.e. dichloroprop, metsulfuron-methyl and  
289 penicillin V) examined here. [The active skin layer of typical LPRO membranes is negatively  
290 changed \[18, 19\]. In fact, two of the LPRO membranes used in this study \(ESPA2 and TFC-  
291 HR\) have a negative charge \(-11 and -23 mV, respectively\) at the test solution pH \(i.e. pH  
292 7.7\) \[20\]. Thus, high rejection of negatively charged TrOCs can be obtained due to  
293 electrostatic repulsion between these solutes and the membrane surface.](#)

294 Penicillin V was successfully incorporated in the analytical method described earlier.  
295 However, it was detectable in the RO permeate of the TMG membrane only (Table 3). Thus,  
296 the validation of Penicillin V rejection was omitted from subsequent experiments. Significant  
297 decrease in pirimiphos-ethyl concentration in the RO feed was observed. Concentration of  
298 this TrOC in the feed decreased from 10,000 ng/L to 80-140 ng/L after 12 hours of filtration.  
299 Pirimiphos-ethyl has the highest hydrophobicity among TrOCs selected here ( $\text{Log } D = 5.1$ ).  
300 Thus, its adsorption onto membrane surface due to hydrophobic interaction can possibly be  
301 attributed to the decreasing pirimiphos-ethyl concentration in the feed [21, 22]. It is  
302 noteworthy that pirimiphos-ethyl rejection calculation was conservative and was based on its  
303 measured concentrations in the feed and permeate. Nevertheless, the calculated rejection (94-  
304 96%) was still above the target validation value of 90%.

305 The validation was further examined using the rejections of eight other TrOCs (i.e. N-  
306 nitrosamines) that were evaluated by RO membranes (i.e. ESPA2 and TFC-HR) using the  
307 same pilot-scale system [9, 23]. N-nitrosamines are uncharged and generally hydrophilic at  
308 the environment pH (e.g. pH 6-8). The target validation rejection of each N-nitrosamine was  
309 achieved under the standard operating conditions (Table 4). The results reported here support  
310 that the rejection targets determined based on the qualitative prediction framework can be  
311 applicable to estimate the rejection of a variety of TrOCs.

312 [Table 3]

313 [Table 4]

314 There was an apparent variation in the rejection of TrOCs among the three tested RO  
315 membranes (i.e. ESPA2, TFC-HR and TMG). Although the relationship between membrane  
316 permeability and conductivity rejection could be clearly observed, this relationship is not  
317 readily transferable to the rejection of TrOCs (Figure 2). Nevertheless, it is apparent that the  
318 ESPA2 which has the lowest water permeability amongst the three membranes examined  
319 here exhibits high and less scattered TrOC rejection. On the other hand, rejections of the nine  
320 TrOCs to be validated in this study by the TMG and TFC-HR membranes scattered quite  
321 widely. In the pore-flow model, membrane permeability increases and solute rejection  
322 decreases with increasing the free-volume hole-size of RO membrane active skin layer [24].  
323 In addition to free-volume hole-size, the porosity of the active skin layer has been suggested

324 as an important factor determining the membrane's separation performance [25].  
325 Nevertheless, the porosity of the active skin layer cannot be accurately quantified by any  
326 analytical techniques available to date.

327 **[Figure 2]**

### 328 3.2.2. Effects of operating conditions

329 Variation in operating conditions is often seen at full-scale RO plants. For example, seasonal  
330 variation in RO feed temperature at a full-scale plant can be over 10 °C [26, 27]. Although  
331 full-scale RO systems deployed for water recycling applications commonly employ a similar  
332 average flux of 17-21 L/m<sup>2</sup>h [14], a large variation in local permeate flux (e.g. 10-25 L/m<sup>2</sup>h)  
333 in an RO stage can also be expected [9]. Changes in these operating conditions including  
334 permeate flux, feed temperature may exert a considerable influence on the rejection of TrOCs  
335 by LPRO membrane [28]. Chemical cleaning may modify the PA structure of the RO active  
336 skin layer, causing a deterioration in TrOC rejection [29]. Thus, the impact of operating  
337 conditions and chemical cleaning on the validation results was investigated in this study.

338 Conductivity rejection by the ESPA2 membrane decreased from 99.3 to 98.3% as the  
339 permeate flux decreased from 30 to 10 L/m<sup>2</sup>h (Figure 3a). On the other hand, the rejection of  
340 these TrOCs by the ESPA2 membrane remained almost constant for the increased permeate  
341 flux. A similar trend was observed for the TMG membrane (Figure 3c). When the TFC-HR  
342 membrane was used, the impact of the increased permeate flux was particularly apparent for  
343 the rejection of two positively charged TrOCs (i.e. carazolol and bisoprolol) (Figure 3b).  
344 These two TrOCs exhibited the lowest rejections (97-98%) among the TrOCs that  
345 concentrations in the permeate were above their reporting detection limits.

346 **[Figure 3]**

347 In general, an increase in feed temperature resulted in a decrease in conductivity rejection,  
348 while the impact on TrOC rejection was negligible (Figure 4). Regardless of the variation in  
349 feed temperature, rejections of both neutral and charged TrOCs by the ESPA2 membrane  
350 were above the target validation values (Figure 4). Similar results were observed with the  
351 TMG membrane except the two positively charged TrOCs (i.e. carazolol and bisoprolol) at  
352 feed temperature of 30 and 35 °C (Figure 4). The rejections of these positively charged

353 TrOCs by the TFC-HR membrane were also observed at lower than their rejection validations  
354 (Figure 4). The decreased TrOC rejection against increased feed temperature is likely to  
355 occur due to an increase in diffusivity of solutes through membrane [28]. The results reported  
356 here indicate that the rejections of positively charged TrOCs selected here by the TFC-HR  
357 membrane are more likely to fall below their target rejection validations during a hot weather  
358 period.

359 **[Figure 4]**

360 Effects of chemical cleaning were also investigated. Chemical cleaning resulted in a small but  
361 discernible decrease in conductivity rejection by all LPRO membranes (Figure 5). This  
362 implies that chemical cleaning can cause a negative impact on solute rejection. In fact, feed  
363 pressure to maintain the permeate flux of 20 L/m<sup>2</sup>h commonly decreased by 3-5% for all  
364 LPRO membranes as a result of chemical cleaning, indicating that permeability of the  
365 membranes increased. A previous study has reported the rejection of several TrOCs is  
366 inversely proportional to membrane permeability [16]. However, the impact of chemical  
367 cleaning on TrOC rejection was not apparent. After chemical cleaning, the rejection of  
368 trichlorfon by the ESPA2 membrane decreased to below the validation target of 90% (Figure  
369 5a). It is noteworthy that when the filtration experiment was performed after the chemical  
370 cleaning, trichlorfon concentrations in the feed and permeate were very low (48 and <5 ng/L,  
371 respectively), resulting in a rather low rejection value. Despite the inconclusive nature of the  
372 data reported here regarding the impact of chemical cleaning on TrOC rejection, it is  
373 noteworthy that extended chemical cleaning *simulating multiple chemical cleanings over the*  
374 *years* may cause deterioration in compound rejection as previously reported in the literature  
375 [29].

376 **[Figure 5]**

#### 377 **4. Conclusions**

378 A protocol to validate the rejection of TrOCs was developed for decision making support  
379 regarding the monitoring level required for potable water reuse. Analytical method was  
380 successfully developed for quantifying the concentration of 10 TrOCs initially selected in this  
381 study. The results show that LPRO membranes can achieve more than 90% of all neutral  
382 TrOCs selected *which ensures that the rejection diagram previously developed based on their*



383 physicochemical properties is valid. However, the validation target of 99% of two charged  
384 TrOCs (i.e. bisoprolol and carazolol) could not be achieved with the TFC-HR membrane.  
385 This may be because bisoprolol and carazolol are both positively charged and the TFC-HR  
386 has the highest water permeability amongst all three LPRO membranes investigated here.  
387 The results also demonstrate that LPRO membrane with low water permeability is more  
388 likely to satisfy the validation target. Operating conditions including permeate flux, feed  
389 temperature and chemical cleaning can exert a considerable impact on conductivity rejection  
390 by the three LPRO membranes investigated here. However, only feed temperature showed an  
391 apparent impact on the rejection of TrOCs. The decreased rejection of TrOCs with increasing  
392 temperature may be due to the increased diffusivity through the membranes. Indeed, the  
393 rejection of positively charged TrOCs is more likely to fall below their target rejection  
394 validation value during the summer when the feed temperature is high.

## 395 5. Acknowledgements

396 This work was supported by Seqwater.

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487 **Table 1:** Physicochemical characteristics, [regulated concentrations](#) and [rejection categories](#) of the selected TrOCs.

TrOC <sup>a</sup>	Molecular formula [-]	Molecular weight [g/mol]	pK <sub>a</sub> (pK <sub>b</sub> ) <sup>b</sup> [-]	Log <i>D</i> at pH 7.4 <sup>c</sup> [-]	PHR guideline value <sup>d</sup>	Maximum reported concentration in source water <sup>e</sup> [µg/L]	Health ratio <sup>e</sup>	Rejection category <sup>e,f</sup>	Validation target [%]	
Neutral	molinate (n)	C <sub>8</sub> H <sub>15</sub> NOS	n.a.	2.7	5	<0.5	<0.100	7	90	
	trichlorfon (n)	C <sub>4</sub> H <sub>8</sub> Cl <sub>3</sub> O <sub>4</sub> P	10.1	0.5	5	<1	<0.200	9	90	
	17 $\alpha$ -estradiol (n)	C <sub>18</sub> H <sub>24</sub> O <sub>2</sub>	272.4	10.3	4.1	0.175	0.074	0.423	7	90
	di-n-butyl phthalate (n)	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	278.3	n.a.	4.8	35	10.4	0.297	7	90
	pirimiphos-ethyl (n)	C <sub>13</sub> H <sub>24</sub> N <sub>3</sub> O <sub>3</sub> PS	333.4	(5.1)	5.1	0.5	<0.5	1.000	7	90
Charged	dichloroprop (-)	C <sub>9</sub> H <sub>8</sub> Cl <sub>2</sub> O <sub>3</sub>	3.0	-0.7	n.a.	n.a.	n.a.	10	99	
	carazolol (+)	C <sub>18</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	(9.7)	1.4	0.35	0.12	0.343	10	99	
	bisoprolol (+)	C <sub>18</sub> H <sub>31</sub> NO <sub>4</sub>	(9.7)	0.1	0.63	0.37	0.587	10	99	
	penicillin V (-)	C <sub>16</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub> S	350.4	3.4	-1.9	1.5	2	1.333	10	99
	metsulfuron-methyl (-)	C <sub>14</sub> H <sub>15</sub> N <sub>5</sub> O <sub>6</sub> S	381.4	3.5	-0.3	30	<20	0.667	10	99

488 <sup>a</sup> (n) neutral; (+) positively charged; (-) negatively charged.

489 <sup>b</sup> Chemaxon (<http://www.chemicalize.org/>).

490 <sup>c</sup> Chemspider (<http://www.chemspider.com/>), data calculated using Advanced Chemistry Development (ACD/Labs).

491 <sup>d</sup> [Public Health Regulation 2005 \[12\]](#).

492 <sup>e</sup> [Viridis Consultants Pty Ltd, Chemical Classification, Review and classification of regulated chemicals for recycled water augmentation of drinking water supplies in South East Queensland, \(2011\)](#).

493 <sup>f</sup> [Supplementary Material Table S2](#).

494 n.a.: not available.

496 **Table 2:** Performance data of membrane element provided by manufacturer.

Membrane type	Manufacturer	Membrane area [m <sup>2</sup> ]	Product flow rate [m <sup>3</sup> /day]	Salt rejection [%]	Water permeability <sup>d</sup> [L/m <sup>2</sup> hbar]
ESPA2	Hydranautics	7.9	7.2 <sup>a</sup>	99.6 <sup>a</sup>	4.4
TFC-HR	KMS	7.9	8.6 <sup>b</sup>	99.55 <sup>b</sup>	5.7
TMG10	Toray	8.0	9.1 <sup>c</sup>	99.5 <sup>c</sup>	5.5

497 <sup>a</sup> Filtration condition: 1500 ppm NaCl, 1.05 MPa, 25 °C, pH 6.5-7.0 and 15% recovery.

498 <sup>b</sup> Filtration condition: 2000 ppm NaCl, 1.55 MPa, 25 °C, pH 7.5 and 15% recovery.

499 <sup>c</sup> Filtration condition: 500 ppm NaCl, 0.96 MPa, 25 °C, pH 7.0 and 15% recovery.

500 <sup>d</sup> Measured with deionised water at 20 °C feed temperature using a single spiral wound  
 501 element.

502 **Table 3:** Rejection of TrOCs in the RO feed by the (a) ESPA2, (b) TFC-HR and (c) TMG  
 503 membranes (system permeate flux 20 L/m<sup>2</sup>h, feed pH 7.65, system recovery 25%, feed  
 504 temperature 20.0 ± 0.1°C). Values reported here are the average and ranges of duplicate  
 505 samples.

Parameter	Target Rejection [%]	Rejection [%]/Validation					
		ESPA2		TFC-HR		TMG	
molinate	90	99.8±0.0	Yes	98.3±0.3	Yes	99.8±0.0	Yes
trichlorfon	90	99.9±0.0*	Yes	99.9±0.0*	Yes	99.4±0.0*	Yes
17 $\alpha$ -estradiol	90	99.8±0.0	Yes	98.1±0.1	Yes	98.7±0.0	Yes
di-n-butyl phthalate	90	97.3±0.0*	Yes	96.5±0.4	Yes	91.5±0.0	Yes
pirimiphos-ethyl	90	96.0±0.0*	Yes	93.8±0.0*	Yes	96.3±0.0*	Yes
dichloroprop	99	99.9±0.0*	Yes	99.4±0.0	Yes	99.9±0.0*	Yes
carazolol	99	99.8±0.0	Yes	97.7±0.2	No	99.5±0.1	Yes
bisoprolol	99	99.8±0.0	Yes	97.2±0.2	No	99.5±0.0	Yes
penicillin V	99	N.D.	-	N.D.	-	99.5±0.0*	Yes
metsulfuron-methyl	99	99.9±0.0*	Yes	99.3±0.0	Yes	99.9±0.0*	Yes

506 \* Permeate concentration was below their detection limits.

507 N.D.: feed concentration was below their detection limits.

508 **Table 4:** Rejection of N-nitrosamines in the RO feed by the ESPA2 and TFC-HR membranes (system permeate flux 20 L/m<sup>2</sup>h, feed pH 8, system  
 509 recovery 25%, feed temperature 20.0 ± 0.1°C).

Parameter	Molecular weight [g/mol]	Log D at pH 8	Molecular width (MWd) [nm]	Rejection category <sup>a</sup>	Target Rejection <sup>a</sup> [%]	Rejection [%]/Validation			
						ESPA2 [9]		TFC-HR [23]	
N-nitrosodimethylamine	74.1	0.04	0.270	3	0	56	Yes	31	Yes
N-nitrosomethylethylamine	88.1	0.4	0.306	3	0	83	Yes	64	Yes
N-nitrosopyrrolidine	100.1	0.44	0.318	8	20	93	Yes	71	Yes
N-nitrosodiethylamine	102.1	0.75	0.322	8	20	94	Yes	85	Yes
N-nitrosopiperidine	114.1	0.89	0.325	8	20	98	Yes	94	Yes
N-nitrosomorpholine	116.1	-0.18	0.317	8	20	97	Yes	79	Yes
N-nitrosodipropylamine	130.1	1.80	0.365	8	20	98	Yes	94	Yes
N-nitrosodi-n-butylamine	158.1	2.69	0.405	7	90	97	Yes	N.A.	

510 <sup>a</sup> Supplementary Material Table S2.

511 N.A.: not available.

512 **LIST OF FIGURES**

513 **Figure 1:** Schematic diagram of the pilot RO filtration system.

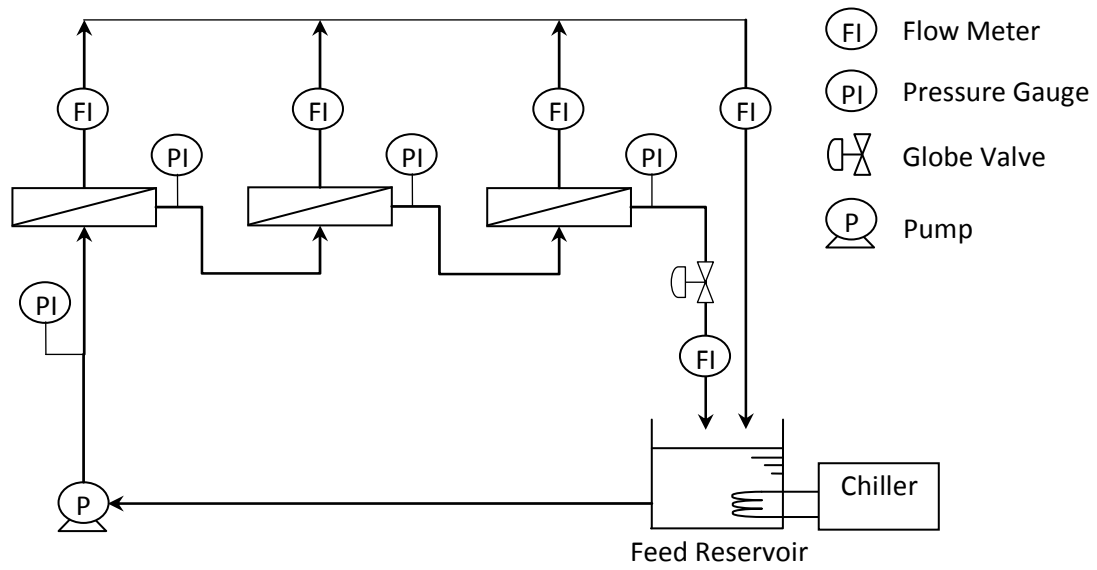
514 **Figure 2:** Rejection of conductivity and TrOCs in the RO feed as a function of water  
515 permeability of LPRO membrane. Open symbol indicates that the permeate concentration was  
516 below the instrumental detection limit.

517 **Figure 3:** Effects of average permeate flux on the rejection of conductivity and TrOCs in the  
518 RO feed by the (a) ESPA2, (b) TFC-HR and (c) TMG membranes. Values reported here are  
519 the averages of duplicate samples. Open symbol indicates that the permeate concentration was  
520 below the instrumental detection limit. Dotted lines show the target validation rejections of  
521 the neutral and charged TrOCs.

522 **Figure 4:** Effects of feed temperature on the rejection of conductivity and TrOCs in the RO  
523 feed by the (a) ESPA2, (b) TFC-HR and (c) TMG membranes. Values reported here are the  
524 averages of duplicate samples. Open symbol indicates that the permeate concentration was  
525 below the instrumental detection limit. Dotted lines show the target validation rejections of  
526 the neutral and charged TrOCs.

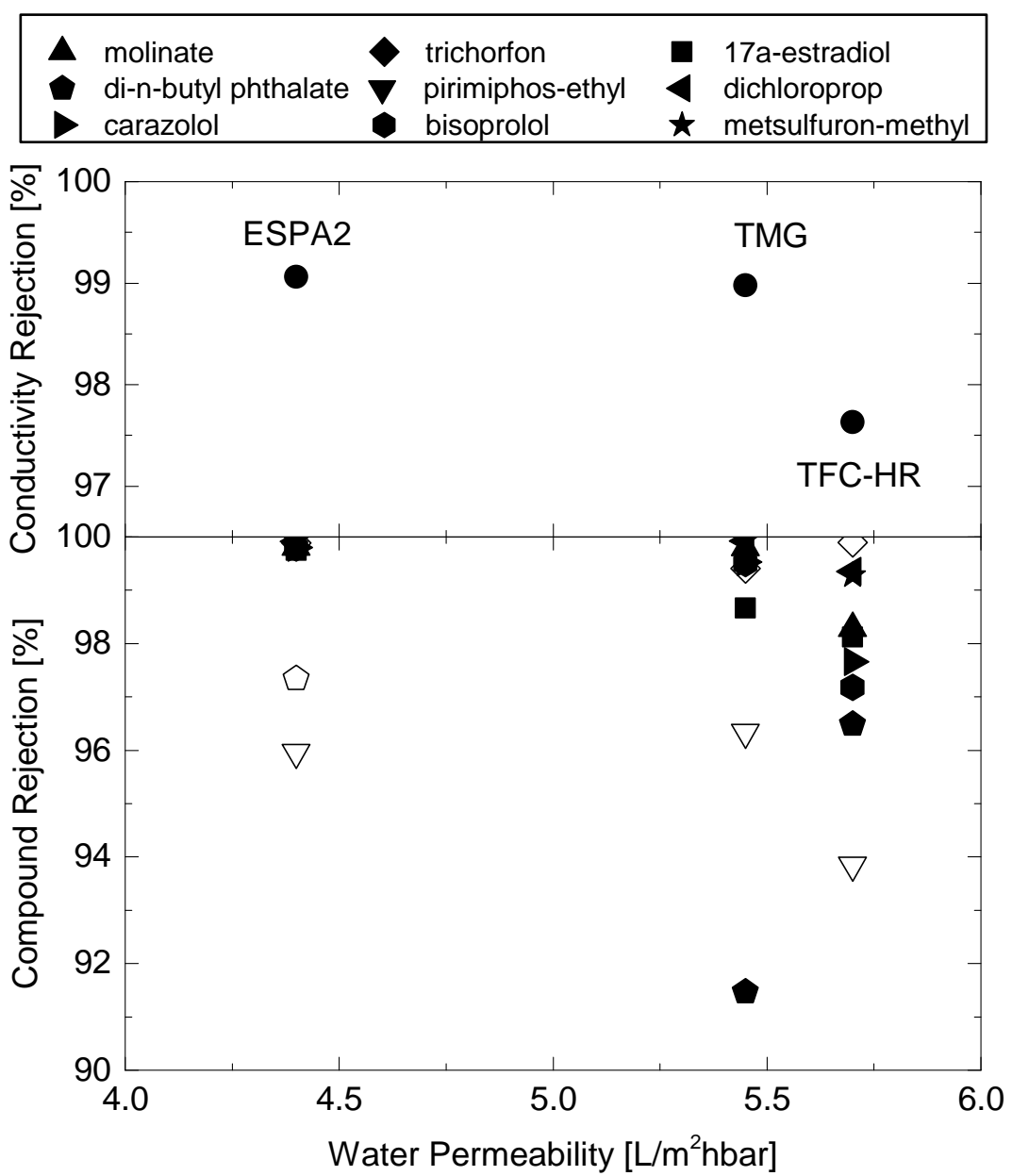
527 **Figure 5:** Effects of chemical cleaning on the rejection of conductivity and TrOCs in the RO  
528 feed water by the (a) ESPA2, (b) TFC-HR and (c) TMG membranes. Values reported here are  
529 the averages of duplicate samples. Open symbol indicates that the permeate concentration was  
530 below the instrumental detection limit. Dotted lines show the target validation rejections of  
531 the neutral and charged TrOCs.





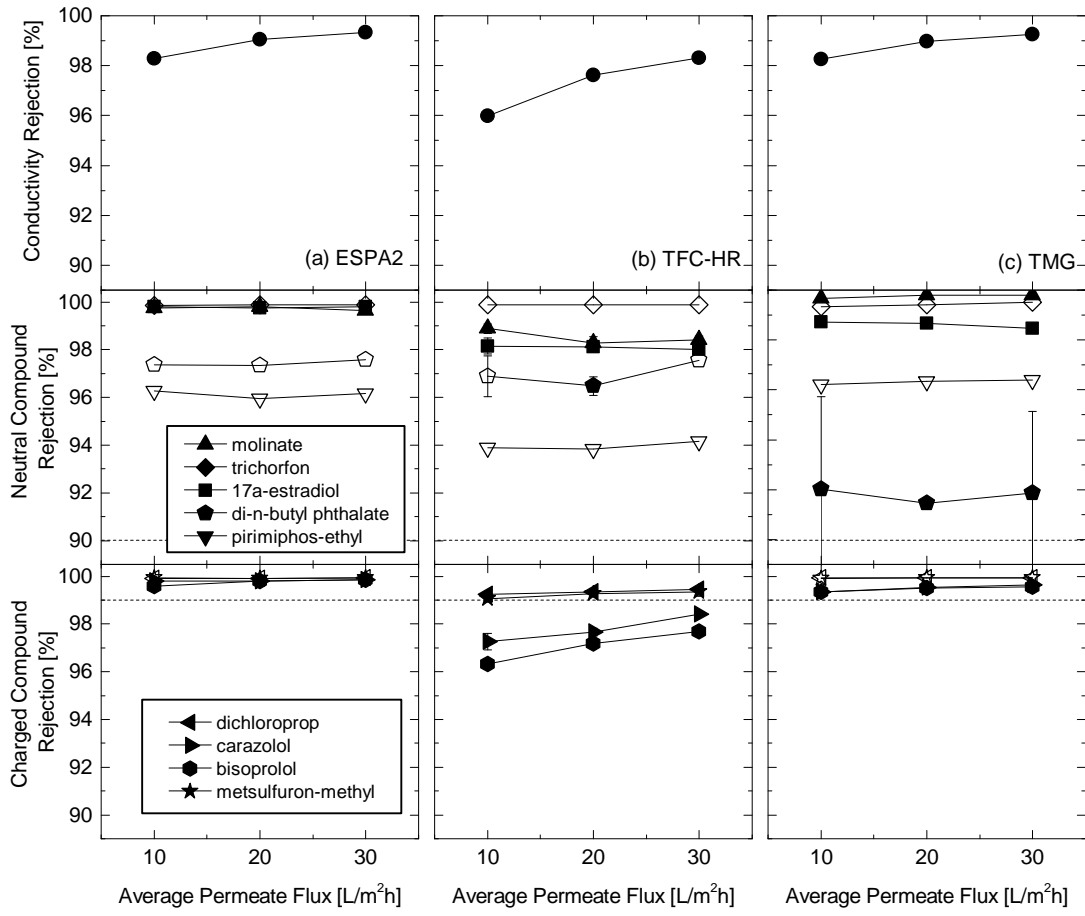
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533 **Figure 1**



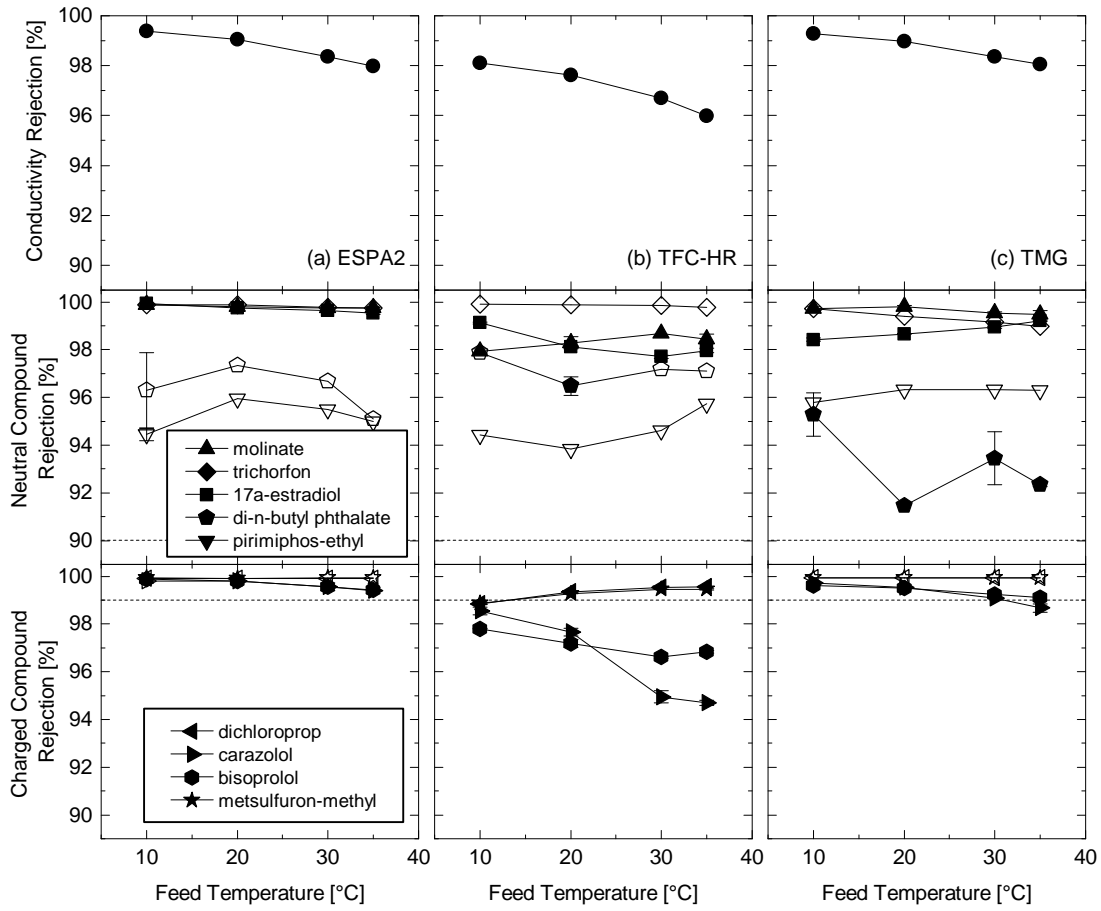
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535 **Figure 2**



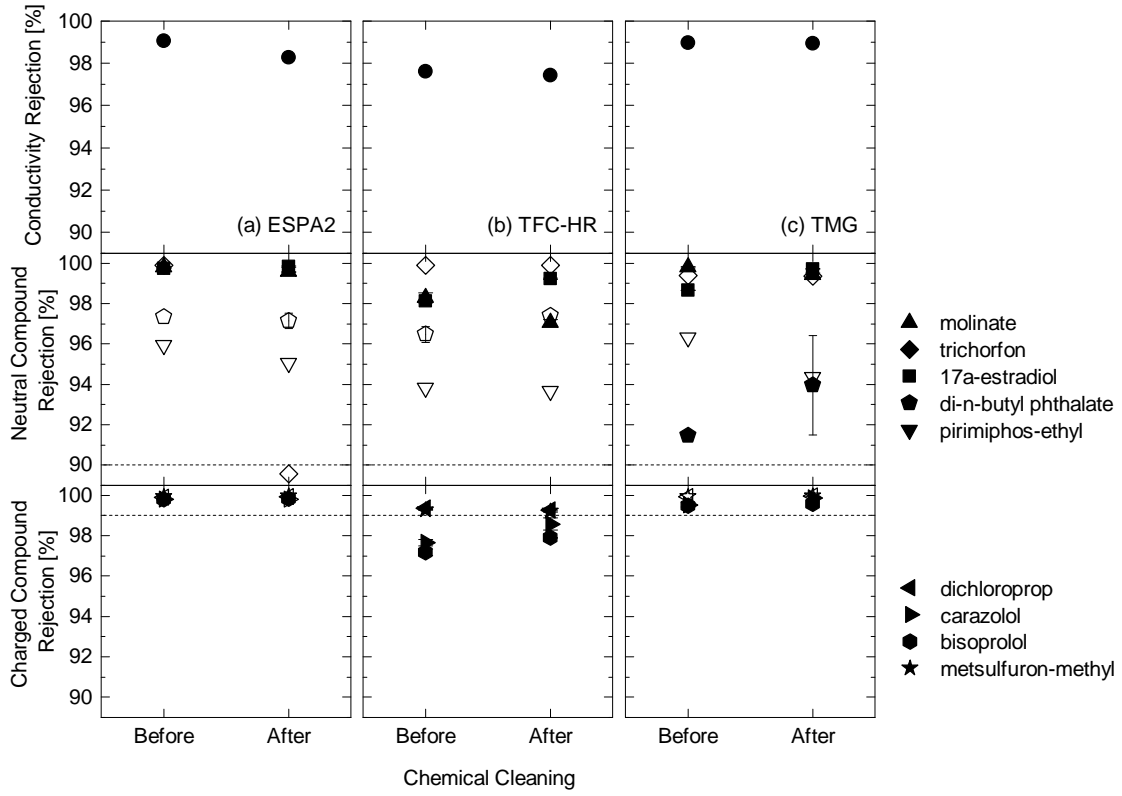
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537 **Figure 3**



538

539 **Figure 4**



540

541 **Figure 5**

# **Validating the rejection of trace organic chemicals by reverse osmosis membranes using a pilot-scale system**

Takahiro Fujioka <sup>1,\*</sup>, Stuart J. Khan <sup>2</sup>, James A. McDonald <sup>2</sup>, Long D. Nghiem <sup>1</sup>

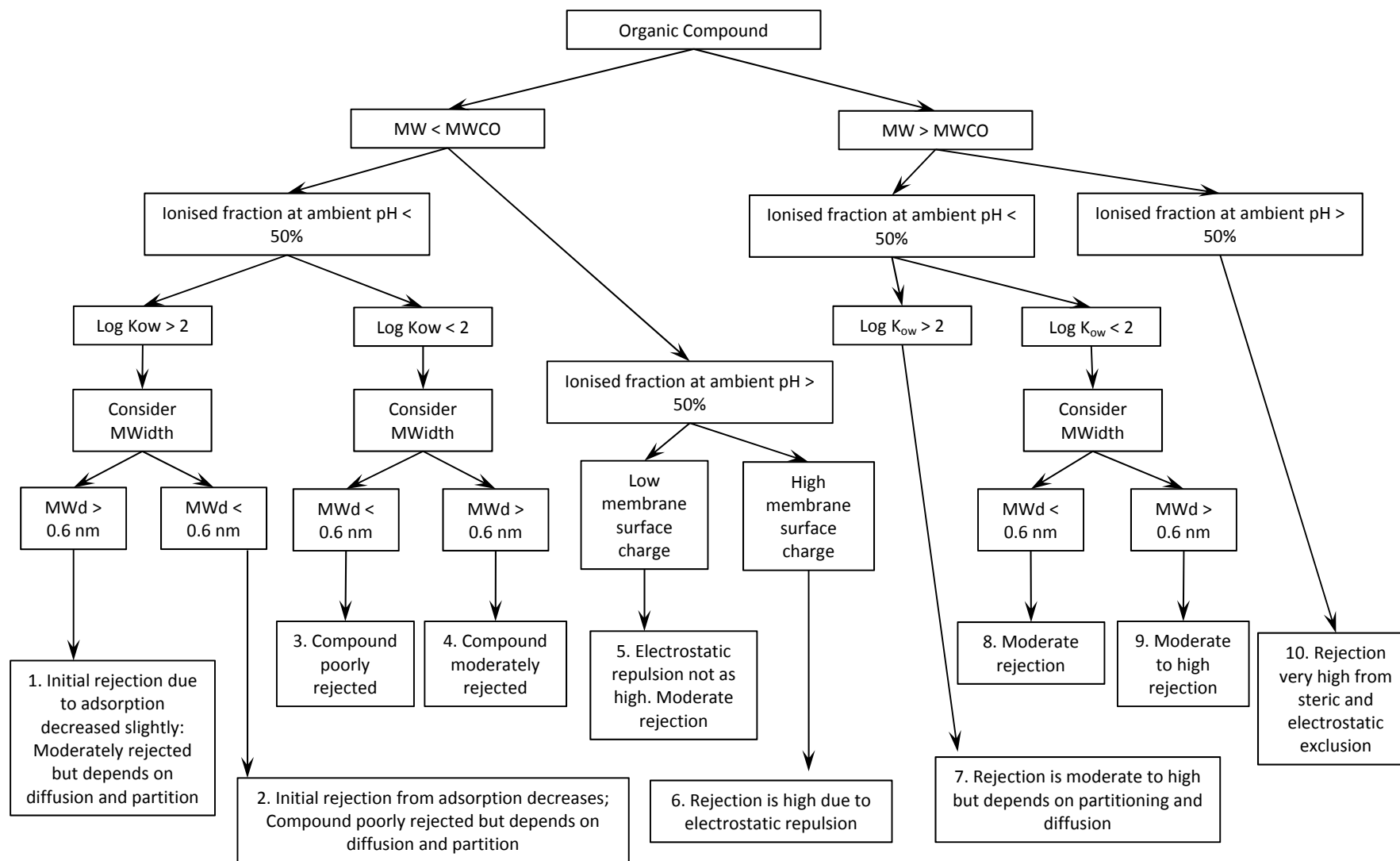
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## **SUPPLEMENTARY MATERIAL**

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**Figure S1:** Modified membrane rejection diagram. (Viridis Consultants Pty Ltd, Chemical Classification, Review and classification of regulated chemicals for recycled water augmentation of drinking water supplies in South East Queensland, (2011)).

1 **Table S2:** Rejection categories, assumed rejection and validation target. (Viridis  
 2 Consultants Pty Ltd, Chemical Classification, Review and classification of regulated  
 3 chemicals for recycled water augmentation of drinking water supplies in South East  
 4 Queensland, (2011)).

Rejection category	Description	Assumed rejection [%]	Validation target [%]
1	Initial rejection due to adsorption decreases slightly; Moderately rejected but depend on diffusion and partition	20-90	20
2	Initial rejection from adsorption decreases; Compound poorly rejected but depends on diffusion and partition	0-10	0
3	Compound poorly rejected	0-10	0
4	Compound moderately rejected	20-90	20
5	Electrostatic repulsion not as high: Moderate rejection	20-90	20
6	Rejection is high due to electrostatic repulsion	99-99.9	99
7	Rejection moderate to high but depends on partitioning and diffusion	90-99	90
8	Moderate rejection	20-90	20
9	Moderate to high rejection	90-99	90
10	Rejection very high from steric and electrostatic exclusion	99-99.9	99

5



6 **Table S3:** Recoveries of TrOCs with spiking concentrations of 10, 100, and 1,000 ng/L from  
 7 Milli-Q water and RO feed (mean  $\pm$  standard deviation of three replicates).

TrOC	Milli-Q			RO feed
	10 ng/L	100 ng/L	1,000 ng/L	100 ng/L
17 $\alpha$ -estradiol	81 $\pm$ 2	81 $\pm$ 2	79 $\pm$ 3	120 $\pm$ 2
dichloroprop	96 $\pm$ 4	88 $\pm$ 1	84 $\pm$ 3	95 $\pm$ 2
di- <i>n</i> -butyl phthalate	566 $\pm$ 4	154 $\pm$ 1	101 $\pm$ 2	455 $\pm$ 8
bisoprolol	79 $\pm$ 11	83 $\pm$ 4	78 $\pm$ 6	117 $\pm$ 2
carazolol	81 $\pm$ 16	86 $\pm$ 12	78 $\pm$ 7	106 $\pm$ 4
metsulfuron-methyl	80 $\pm$ 31	88 $\pm$ 10	93 $\pm$ 6	85 $\pm$ 20
molinate	30 $\pm$ 20	36 $\pm$ 15	35 $\pm$ 8	45 $\pm$ 15
pirimiphos-ethyl	86 $\pm$ 3	83 $\pm$ 1	78 $\pm$ 4	98 $\pm$ 2
trichorfon	37 $\pm$ 15	41 $\pm$ 23	37 $\pm$ 13	30 $\pm$ 14
penicillin V	86 $\pm$ 12	84 $\pm$ 7	75 $\pm$ 3	99 $\pm$ 9

8

9 **Table S4:** Method quality parameters

TrOC	Method	Calibration range [ng/L]	R <sup>2</sup>	IDL [pg on column]	MDL [ng/L]	Reporting limit [ng/L]	
						Milli-Q	RO feed
17 $\alpha$ -estradiol	APCI positive	0.5 - 1000	0.999	5	0.1	5	5
dichloroprop	ESI negative	0.5 - 1000	0.995	11	0.5	5	5
di-n-butyl phthalate	ESI positive	0.5 - 1000	0.985	6	0.02	50	250
bisoprolol		0.5 - 1000	0.991	2	0.01	5	20
carazolol		1 - 1000	0.994	6	0.02	5	10
metsulfuron-methyl		0.5 - 1000	0.993	2	0.01	5	5
molinate		0.5 - 1000	0.990	213	1	5	10
penicillin V		0.5 - 1000	0.994	3	0.1	5	5
pirimiphos-ethyl		0.5 - 1000	0.990	69	0.5	5	5
trichlorfon		1 - 1000	0.996	32	0.4	5	5

10

11 **Table S5:** Optimized chemical dependent acquisition parameters

TrOC	Retention time [min]	Precursor ion molecular weight [g/mol]	Product ion molecular weight [g/mol]	Declustering potential [V]	Collision energy [eV]	Collision cell exit potential [V]
<b>ESI positive</b>						
molinate-1	9.1	188.1	125.5	51	19	22
molinate-2	9.1	188.1	82.9	51	25	14
trichorfon-1	5.4	256.9	109.0	76	27	18
trichorfon-2	5.4	256.9	126.7	76	25	22
di- <i>n</i> -butylphthalate-1	10.1	279.2	148.9	61	19	26
di- <i>n</i> -butylphthalate-2	10.2	279.2	204.7	61	11	12
di- <i>n</i> -butylphthalate-D4-1	10.1	283.2	209.0	41	11	12
di- <i>n</i> -butylphthalate-D4-2	10.1	283.2	152.7	41	19	26
pirimiphos-ethyl-1	10.5	334.1	198.1	61	31	16
pirimiphos-ethyl-2	10.5	334.1	181.9	61	31	16
pirimiphos-ethyl-D10-1	10.5	344.1	198.7	91	33	18
pirimiphos-ethyl-D10-2	10.5	344.1	183.0	91	33	12
carazolol-1	5.2	299.1	115.6	76	29	20
carazolol-2	5.2	299.1	221.6	76	29	18
carazolol-D7-1	5.2	306.2	122.8	81	29	22
carazolol-D7-2	5.2	306.2	221.6	81	29	20
bisoprolol-1	5.8	326.2	115.8	76	25	20
bisoprolol-2	5.8	326.2	73.5	76	43	12
bisoprolol-D5-1	5.8	331.2	120.8	96	25	10
bisoprolol-D5-2	5.8	331.2	78.9	96	43	12
penicillin V-1	5.7	383.1	159.8	71	23	14
penicillin V-2	5.7	383.1	113.9	71	51	20
penicillin-V-D5-1	5.7	388.1	160.0	71	23	28
penicillin-V-D5-2	5.7	388.1	113.6	71	55	20
metsulfuron-methyl-1	4.5	382.0	167.0	71	23	10
metsulfuron-methyl-2	4.5	382.0	198.6	71	31	34
carbamazepine-D10	7.1	247.1	204.3	51	29	10
<b>ESI negative</b>						
dichloroprop-1	6.1	232.8	160.7	-50	-18	-9
dichloroprop-2	6.1	232.8	124.5	-50	-40	-9
dichloroprop-D6-1	6.1	238.8	163.2	-50	-18	-7
dichloroprop-D6-2	6.1	238.8	126.7	-50	-40	-5
<b>APCI positive</b>						
17 $\alpha$ -estradiol-1	10.2	255.2	159.3	61	27	10
17 $\alpha$ -estradiol-2	10.2	255.2	133.2	61	27	10
17 $\alpha$ -estradiol-1-D4-1	10	259.1	161.1	61	27	8
17 $\alpha$ -estradiol-1-D4-2	10	259.1	135.1	61	25	11

12

### 13 **Optimisation of ion source parameters**

14 When employing the ESI mode, the mobile phases consisted of 5 mM ammonium acetate in  
15 water (A) and 100% methanol (B) was pumped at a flow rate of 800  $\mu\text{L}/\text{min}$ . For positive  
16 ESI analysis the eluents were held at 10% B for 0.50 min and then linearly ramped to 50% at  
17 0.51 min. Thereafter, the eluents were increased linearly to 100% at 8 min, then held at 100%  
18 B for 2 min with a total run time of 14.4 min. For negative ESI analysis, 10% B were held for  
19 0.50 min, stepped to 60% B at 0.51 min and increased linearly to 100% B at 8 min, then held  
20 at 100% B for 3 min with a total run time of 14.4 min. A 5 min equilibration step at 10% B  
21 was used at the beginning of each run.

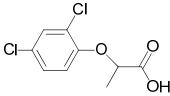
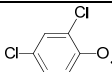

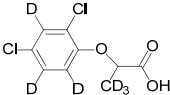
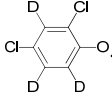

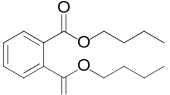
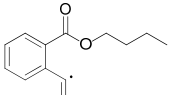

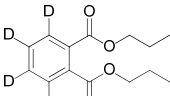
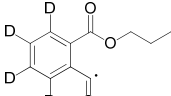

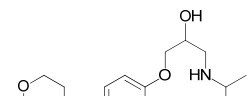


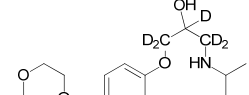


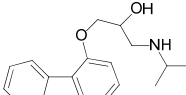


22 When employing the APCI mode, the eluents consisted of 0.1% v/v formic acid in water (A)  
23 and methanol (B) with the following ramp at a flow rate of 700  $\mu\text{L}/\text{min}$ . 60% B were held for  
24 5 min, increased linearly to 100% B at 20 min, and then held at 100% B for 3 min with a total  
25 run time of 13 min. A 3 min equilibrium step preceded injection. An injection volume of 10  
26  $\mu\text{L}$  was used for all methods.

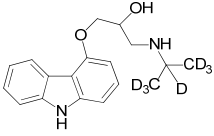
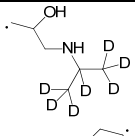
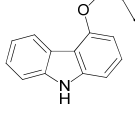
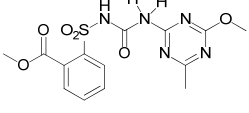
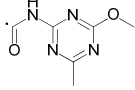
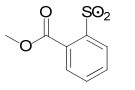
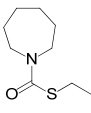


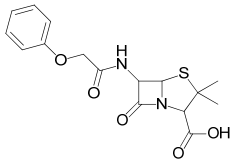


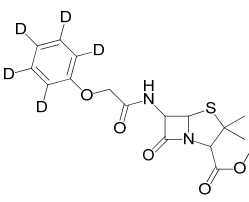


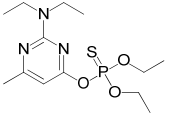


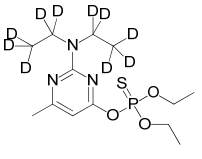


27 **Table S6:** Optimised ion source parameters

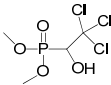

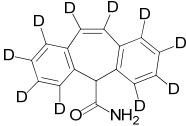
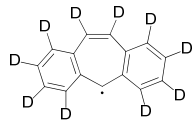
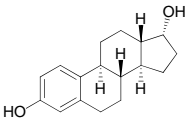
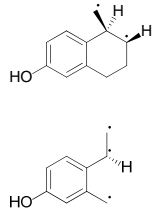
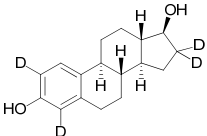
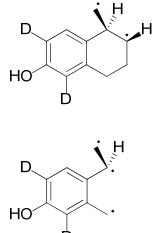
	ESI positive	ESI negative	APCI positive
curtain gas [psig]	19	19	15
collision gas [psig]	high	high	high
nebulizer current [mA]	3	-3	3
temperature [ $^{\circ}\text{C}$ ]	550	550	450
ion source gas 1 [psig]	60	60	40
ion source gas 2 [psig]	50	50	N/A
run time [min]	14.4	14.4	13

28

29 **Table S7:** Molecular structures of target chemicals and proposed structures for product ions.

	Q1	structure	Q2	proposed structure
Dichloroprop	233		161	
			125	
Dichloroprop D6	239		163	
			127	
Di- <i>n</i> -butyl phthalate	279		205	
			149	
Di- <i>n</i> -butyl phthalate D4	283		209	
			153	
Bisoprolol	326		116	
			74	
Bisoprolol D5	331		121	
			79	
Carazolol	299		116	
			222	

	Q1	structure	Q2	proposed structure
Carazolol D7	306		123	
			222	
Metsulfuron-methyl	382		167	
			199	
Molinate	188		126	
			83	
Penicillin V	383		160	
			114	
Penicillin V-D5	388		160	
			114	
Pirimiphos-ethyl	334		198	
			182	
Pirimiphos-ethyl-D10	344		199	
			183	

	Q1	structure	Q2	proposed structure
Trichlorfon	257		109  127	
Carbamazepine D10	247		204	
17 $\alpha$ -estradiol	255		159  133	
17 $\alpha$ -estradiol-D4	259		161  135	

30