VICTORIA UNIVERSITY
MELBOURNE AUSTRALIA

A critical control point approach to the removal of chemicals of concern from water for reuse

Accepted Manuscript

A critical control point approach to the removal of chemicals of concern from water for reuse

Peter J. Scales, Kaushalya Wijekoon, Christian Ladwig, Adrian Knight, Mayumi Allinson, Graeme Allinson, Jianhua Zhang, Stephen Gray, Michael Packer, Kathy Northcott, David Sheehan

Please cite this article as: Scales, P.J., Wijekoon, K., Ladwig, C., Knight, A., Allinson, M., Allinson, G., Zhang, J., Gray, S., Packer, M., Northcott, K., Sheehan, D., A critical control point approach to the removal of chemicals of concern from water for reuse, *Water Research* (2019), doi: https://doi.org/10.1016/j.watres.2019.05.035.

EXAMPLE BARRIER CREDIT SYSTEM FOR CCP

CCP Surrogates
Residual >0.05 mg/L
Dose >11.7 mg/L
CT_{10} > 14 mg.min/L
T_{10} > 5 min

Feed Water
DOC <10 mg/L

Pathogen Credits	**LRV**
Virus	2.0
Bacteria	2.0
Protozoa	0.0
Helminths	0.0

Chemical Credits	**LRV**
Ozone class 1	0.9
Ozone class 2	0.0
Ozone class 3	0.0
Ozone class 4	0.0

Selected Barrier

Ozone ←

Process Barrier

AS

MF
BAC
RO
UV
Cl_2
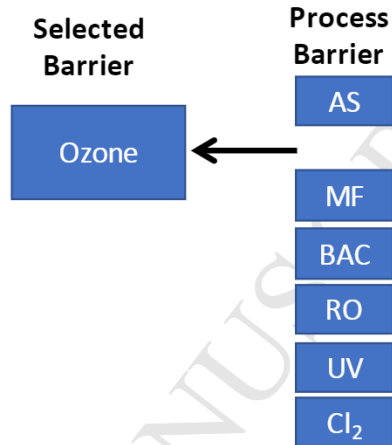
1 **A Critical Control Point Approach to the Removal of Chemicals of Concern from Water for**

2 **Reuse**

3 Peter J Scales[1]*, Kaushalya Wijekoon[1], Christian Ladwig[2], Adrian Knight[1], Mayumi Allinson[1],

4 Graeme Allinson[3], Jianhua Zhang[4], Stephen Gray[4], Michael Packer[5], Kathy Northcott[6] and

5 David Sheehan[7]

6 [1] *Particulate Fluids Processing Centre, Department of Chemical Engineering, The University*

7 *of Melbourne, 3010, Australia*

8 [2] *Department of Chemistry, Technical University Munich, Munich, Germany*

9 [3] *Centre for Environmental Sustainability and Remediation, School of Science, RMIT*

10 *University, Melbourne, 3001, Australia*

11 [4] *Institute for Sustainable Industries and Liveable Cities, Victoria University, Werribee, 3030,*

12 *Australia*

13 [5] *Australian Antarctic Division, Kingston, 7050, Australia*

14 [6] *Water Research Australia, Adelaide, 5000, Australia*

15 [7] *Coliban Water, Bendigo, 3550, Australia*

16 * *Author for correspondence: Email: peterjs@unimelb.edu.au; Phone: +61 3 8344 6480*

17

18   **Abstract**

19   The reuse of water in a range of potable and non-potable applications is an important factor in the

20   augmentation of water supply and in improving water security and productivity worldwide. A key

21   hindrance to the reuse of water is the cost of compliance testing and process validation associated

22   with ensuring that pathogen and chemicals in the feedwater are removed to a level that ensures no

23   acute or chronic health and/or environmental effects. The critical control point (CCP) approach is

24   well established and widely adopted by water utilities to provide an operational and risk

25   management framework for the removal of pathogens in the treatment system. The application of

26   a CCP approach to barriers in a treatment system for the removal of chemicals is presented. The

27   application exemplar is to a small community wastewater treatment system that aims to produce

28   potable quality water from a secondary treated wastewater effluent, however, the concepts

29   presented are generic. The example used seven treatment barriers, five of which were designed

30   and operated as CCP barriers for pathogens. The work demonstrates a method and risk

31   management framework by which three of the seven barriers could also include a CCP approach for

32   the removal of chemicals. Analogous to a CCP approach for pathogens, the potential is to reduce

33   the use of chemical analysis as a routine determinant of performance criteria. The operational

34   deployment of a CCP approach for chemicals was augmented with the development of a decision

35   tree encompassing the classification of chemicals and the total removal credits across the

36   treatment train in terms of the mechanistic removal of chemicals for each barrier. Validation of the

37   approach is shown for a activated sludge, ozone and reverse osmosis barrier.

38

39 **Key Words**

40 Chemical log reduction value, chemicals of concern, critical control point, advanced water

41 treatment, water recycling

42

43 **1   Introduction**

44 The recycling of water from wastewater and stormwater for re-use in a range of potable and non-

45 potable applications is an important factor in the augmentation of water supply and in improving

46 water productivity worldwide (Grant *et al.* 2012). Along with demand management, the

47 opportunity exists through recycle to more than double current water resources available for

48 human use in urban environments, referenced by the fact that more than 80% of all urban water in

49 the world is used only once and disposed to the environment at lower quality (UN_WWAP 2017).

50 Recycling some or all of this water would not only reduce pressures on surface and ground water

51 resources but invigorate the use of water sources deemed too contaminated for potable use.

52 Barriers to reuse are significant nonetheless. Pathogen and chemical removal from wastewater and

53 stormwater requires a multiple barrier approach, and the associated chemical and microbial

54 analysis to achieve compliance means that the water is often costlier than traditional source

55 protected surface and groundwater supplies. In addition, there is a social stigma to the planned

56 direct or indirect reuse of wastewater for potable purposes. The outcome is that desalination of

57 seawater is often chosen over wastewater reuse for potable augmentation despite the fact that

58 energy costs are higher and brine disposal limits the opportunity to coastal environments. Cost

59 effective and well-regulated processes for ensuring the quality of water in non-coastal and small

60 communities are therefore critical to water resilience in water scarce environments.

61 A key hindrance to the reuse of water is the cost of compliance testing and process validation

62 associated with ensuring that pathogen and chemicals in the feedwater are removed to a level that

63 ensures no acute or chronic health and/or environmental effects from the reuse of the water. In

64 the case of pathogens, compliance entities have validated a number of processes for the removal of

65 pathogens to minimum levels. An example is the USEPA Long Term 2 Enhanced Surface Water

66 Treatment Rule for the removal of *Cryptosporidium* (USEPA 2018). This validation is deemed

67 compliant by regulatory bodies provided that the equipment associated with the barrier is operated

68 in a consistent manner and continuous or semi-continuous monitoring of surrogates to ensure

69 performance are maintained (Hunter_Water 2005, USEPA 2018). Examples of validated barriers

70 include membrane bioreactors (MBR), UV, ozonation and chlorination as well as nano-filtration (NF)

71 and reverse osmosis (RO) membrane systems (WaterSecure 2018). The process allows the barrier

72 to be operated using, for example, conductivity measurement as a surrogate of barrier integrity in

73 the case of a RO membrane. This process significantly reduces the need for regular (daily)

74 compliance testing using microbial analysis since barrier integrity and compliance validation have

75 already been linked. Less regular (i.e. weekly or monthly) compliance validation is then acceptable,

76 significantly reducing the cost of fit for purpose water production.

77 **1.1   Critical Control Point (CCP)**

78 To define the operational boundaries of the key barriers in a water treatment process, the Critical

79 Control Point (CCP) concept is often used. The CCP approach was first developed by the food and

80 beverage industry as a preventative approach to food safety as distinct from reliance on final

81 inspection. It focused on the removal of biological, chemical and physical hazards from food and

82 the approach was used to determine the key points within the manufacturing process where

83 contamination can occur and be prevented (Ropkins *et al.* 2003). The same approach was then

84 adapted for water quality management and many water regulators now specify the use of the CCP

85 approach as the risk management framework for water treatment systems for managing operation

86 of plants (Hunter_Water 2005, NRMMC 2008). By using the CCP approach, water treatment plant

87 operators and their contracted entities are able to focus resources on monitoring these critical

88 points. These points provide the greatest information and benefit in being able to quickly correct

89 any deviations from acceptable limits and through the risk management framework, significantly

90 reduce the costs of microbial analysis (Laydon. 2011). Along with quantitative microbial risk

91 assessment (QMRA) of the required level of pathogen removal (Barker *et al.* 2013) (usually quoted

92 as a log reduction value (LRV)) to mitigate the risk of acute or chronic illness), the CCP approach can

93 be used to design and operate a multi-barrier treatment process. The basic rules for a CCP are

94 (NHMRC and NRMMC 2011, Barker *et al.* 2013):

95 • Operational parameters can be measured and critical limits can be set to define the

96   operational effectiveness of the activity (e.g. a CT measured as a chlorine residual multiplied

97   by a contact time for disinfection)

98 • Operational parameters can be monitored frequently enough to reveal any failures in a

99   timely manner (online and continuous monitoring is preferable)

100 • Procedures for corrective action (including process shutdown) can be implemented in

101   response to deviation from alert or critical limits.

102　It should be noted here that depending on the circumstances, the claimed LRV for pathogen

103　removal may vary for a given barrier and for the surrogate of performance used to monitor

104　performance. In some instances, a range of surrogate measures may be in place for a particular

105　barrier and indeed, this is the case in one instance herein where a pressure decay test and a

106　measure of residual conductivity are used as surrogates of performance of a reverse osmosis

107　barrier. It is important operationally that neither can over-ride the other in terms of process

108　shutdown. To avoid confusion and reduce the costs of CCP validation for a barrier, it is usual to use

109　one surrogate of performance per barrier with other surrogates used as quality control points

110　(advisory), unless an extra credit for a particular pathogen or chemical is necessary that is not

111　already covered by the single CCP.

112　In addition to pathogens, there are a large number of chemicals that find their way into our

113　waterways and wastewater, and the number and diversity is increasing year on year. Many national

114　regulatory authorities now publish guidelines for the maximum recommended concentrations of

115　chemicals of concern (CoC) deemed to have potential in causing acute or chronic illness. These

116　guidelines usually classify the chemicals into end use categories and although there are in excess of

117　three hundred CoC in for instance the Australian Guidelines for Water Recycling (NRMMC 2008),

118　the list can never be comprehensive in an environment where in excess of 50,000 chemicals and

119　their metabolites are common to many cities and communities. To try and circumvent the issue,

120　regulatory authorities associated with water recycling for potable applications often use a

121　surrogate list of CoC (NRMMC 2008).

122　In drawing an analogy to the highly successful CCP approach used to operationally mitigate the risk

123　of pathogens in our water supply through a focus on risk assessment and barrier integrity, the

124   surrogate list does not represent a route to significantly lowering the cost of treated water

125   compliance. Whilst useful, it still requires regular chemical analysis and is prohibitive in both cost

126   and logistics for small and remote communities (i.e. regular sampling and transport of these

127   samples to certified measurement laboratories) and restricts the likely uptake of water recycling by

128   those that are often most in need of water resilience. An approach that allows chemicals to use the

129   same CCP criteria as pathogens for a particular barrier using a decision tree that relates molecular

130   characteristics to the mechanism of removal in the barrier would seem more appropriate. The basis

131   for such an approach is already available through extensive work on CoC across various water

132   treatment barriers although the classification has not been formalised, trialled and validated at

133   scale.

134   **1.2   Demographic effect**

135   Further to the above concept, the difference between small and large communities needs

136   consideration. In the case of pathogens, it has been demonstrated that the treatment needs of a

137   small community are significantly greater than for a large municipal purified water recycling plant,

138   since pathogens shed by a few people during a disease outbreak are diluted by the bulk flow for

139   large plants but less so for small communities (Barker *et al.* 2013). Indeed, more stringent pathogen

140   log reduction values (LRV) are required for small communities (between 3-6 log higher) to meet a

141   DALY (Disability Adjusted Life Year) of less than 10^{-6}/person-yr (NRMMC 2008). In the case of CoC, a

142   similar scenario ensues whereby any chemical spills in a small community will be exacerbated since

143   the volumetric buffering capacity of the system is much reduced. As an example, a 100 person

144   community adding 200 L/day/person to the collection system using a treatment process with a

145   hydraulic residence time of six hours will have an effective dilution volume of 5,000 litres. In a

146 community of 100,000 people, the same spill would be diluted to 5 ML, a factor of 1,000 different,

147 albeit there is an implicit assumption of perfect mixing, something that is unlikely.

148 For chemicals that are added as a result of standard domestic activities, for example,

149 pharmaceuticals and personal care products (PPCPs) and their metabolites, there is little difference

150 expected between a large municipal and small community, save for greater variability as a result of

151 demographic, industrial and societal influences that are not homogenized within the small

152 community. In this context, a study on small communities is representative of a worst-case scenario

153 and yet, except for a chemical spill scenario, the feed to a large and small community wastewater

154 treatment plant is expected to be very similar, save for industrial inputs. Testing of a treatment

155 plant for a small community using a large community feed is thus considered viable since a spill

156 scenario can be considered as part of the risk management framework and everyday product

157 concentrations in wastewater feed will be similar.

158 **1.3   Multiple barrier approach**

159 A multiple barrier approach has been applied in the production of potable water for centuries. The

160 selection of barriers seeks to optimise the removal capabilities of different steps in the treatment

161 process. Typically, the barriers include five main functions, namely source water protection,

162 coagulation/flocculation/sedimentation, filtration, disinfection and distribution system protection

163 (Hunter_Water 2005). To monitor the key points in the water treatment chain, the CCP concept is

164 often used. Various guideline document outline that the CCP method is one approach which can

165 successfully assist in reviewing the preventative measures for potable water quality management

166 (NRMMC 2008, Laydon. 2011). The approach also specifies within the preventative measures for

167 recycled water management that CCP analysis can be used in managing effluent quality to ensure it

168 is fit for purpose (DPI 2015). Guideline documents usually detail the criteria that a preventative

169 measure must meet for selection as a CCP, inclusive of operational requirements (NHMRC and

170 NRMMC 2011).

171 Feedwater quality, ozonation, microfiltration, reverse osmosis, ultraviolet radiation, and

172 chlorination were identified as CCP locations for the treatment system designed herein for the case

173 of pathogen removal. A minimum log reduction value (LRV) and the associated operational and risk

174 criteria to achieve the LRV were then considered (Zhang *et al.* 2017). This barrier list is not

175 intended to be exhaustive, just a necessary minimum to achieve potable water with an acceptable

176 risk of pathogen exposure in a small community scenario (Barker *et al.* 2013). The testing and

177 validation of the barriers to achieve pathogen compliance is detailed elsewhere (Zhang *et al.* 2016a,

178 Zhang *et al.* 2016c). The surrogates of performance chosen and the LRV of pathogens associated

179 with each of the barriers was based on pre-validation scenarios from around the world and limited

180 additional validation (Zhang *et al.* 2016c) was performed as part of the activity. For the feed water

181 type involved, the combinations of performance surrogate and claimed LRV are thus considered

182 typical but clearly not exhaustive of the multiple operations across the globe.

183 Besides pathogens, water supplies may also be polluted with trace organic chemicals, metals,

184 nutrients, radionuclides, radioactive tracers and disinfection by-products. The latter are a

185 consequence of oxidation steps such as ozonation, advanced oxidation and chlorination. As many of

186 these chemicals have a potential to cause harm to health and/or the environment, chemical

187 residual concentrations are considered as problematic and are of concern. Since input sources vary,

188 the removal of CoC from water to achieve a fit for purpose quality is very challenging. Published

189 work on the removal performance of CoCs in wastewater mainly focus on specific types of

190 chemicals or the behaviour of specific barriers, however, none of them has used the CCP concept as

191 the approach to test the overall performance of the combined barriers. Also, classification of CoCs

192 according to their end use or broad molecular description   (NRMMC 2006, NRMMC 2008), whilst

193 useful in determining the maximum guideline concentration in the product water and the likely

194 route to a particular toxic effect, is not useful in defining whether a molecule would be removed by

195 a particular barrier (Tadkaew *et al.* 2011).

196 **1.4   Advanced water treatment plant (AWTP)**

197 This study comprises the testing of the CCP concept for CoC removal using a small scale (20 m^3/day)

198 semi-batch containerised advanced water treatment plant (AWTP) using the secondary effluent of a

199 municipal (50,000 person equivalent) treatment plant as a feed. The AWTP was designed for

200 installation into an Antarctic community of 150 persons (maximum), 20 persons (minimum) and

201 was commissioned and then tested for nine months to determine the suitability for deployment.

202 The variation in feed between summer (150 persons) and winter (20 persons) dictated a need for

203 semi-batch operation. The logistics of regular (daily, weekly or even monthly) water quality

204 monitoring using sophisticated chemical analysis across a broad spectrum of chemicals and

205 surrogates was considered impossible since the community is isolated for at least 7 months per

206 year. Simple on-site laboratory tests and passive sampling were considered achievable. A greater

207 level of sophistication was available during the test period although the key consideration was

208 always the remote operational status.

209 The Advanced Water Treatment Plant (AWTP) for Australian Antarctic Division's (AAD) Davis Station

210 was located at Selfs Point Wastewater Treatment Plant (SPWWTP), Hobart, Australia during the test

211 period. Although only a low capacity plant, it was the actual plant that is now deployed in

212 Antarctica and was used as the testing device herein to demonstrate the performance and

213 reliability in the reduction of CoC using the CCP approach. It was designed especially for potable

214 water production for small communities. The plant consists of seven barriers including ozone,

215 ceramic micro-filtration (CMF), biologically activated carbon (BAC), reverse osmosis (RO), ultra-

216 violet radiation (UV), calcite dissolution and chlorination (Cl_2), and was preceded by a secondary

217 effluent treatment plant (activated sludge (AS)). At the application site in Antarctica, the secondary

218 treatment step also includes an MBR unit with a polymeric ultrafiltration configuration, although

219 the secondary effluent or the results presented here was from a clarifier. Earlier work has shown

220 that except for the calcite filter, which acts as a water stabilizer and the BAC, all the other barriers

221 have LRV claims for pathogen removal and associated CCP criteria, indicating they are all functional

222 barriers for pathogens. These claims are summarised in Table 1.

223 Table 1: Claimed LRVs for pathogens for the AWTP and CCPs for each barrier (Bartlett *et al.* 2015).

Barrier	CCP	LRV*		
		Virus	Bacteria	Protozoa
Ozonation	CT	2	2	0
Ceramic MF	PDT	1	1	4
BAC	Turbidity	0	0	0
RO	Conductivity and PDT	1.5	1.5	2
UV	Measured dose	4	4	4
Calcite Filter	pH	0	0	0
Chlorination	CT	4	4	0
Total claimed LRVs		12.5	12.5	10

224 * The LRVs are credited based on the USEPA Long Term 2 Enhanced Surface Water Treatment Rule (USEPA 2018). CT =

225 residual concentration x contact time, PDT = pressure decay test. For ozonation, the contact time was a T_{10}, namely the

226 time at which 10% of a surrogate appeared in the effluent.

227 In the assessment of CoC removal, calcite dissolution is considered a water stabilization step and Cl_2

228 provides no obvious chemical removal (indeed, chemicals are added in both barriers) and molecular

229 destruction by the UV barrier, whilst possible, was not able to be quantified to a particular class of

230 chemicals. Therefore, these three barriers are not considered as functional barriers for CoC removal

231 in this study. It is noted none the less that advanced oxidation (using UV peroxide, UV ozone, or UV

232   hypochlorite) is often used as a key chemical removal step and there is an opportunity to develop

233   protocols and claims for these barriers based on the principles outlined. This means that the seven-

234   barrier process of the AWTP plus the AS, with six barriers functional for pathogen removal, can

235   really only be considered a maximum five barrier process for the quantification of chemical

236   removal.

237   Using a CCP approach and LRV assessment, the AS, ozone, CMF, BAC and RO barriers are

238   investigated as functional barriers for CoC removal in this work. Given that a removal mechanism

239   specific to a class of molecules could not be assigned to the CMF and BAC barriers, analysis of the

240   AS, ozone and RO barriers is completed in detail here. The potential for MBR removal of chemicals

241   is also considered although no validation data is presented since this barrier was not operational

242   during testing. As a consequence of the CCP approach, the maximum feed concentrations of

243   chemicals in the wastewater collection system that would have the potential to cause compliance

244   breaches are also calculated. The results of this assessment are considered generalizable to direct

245   potable water reuse. Also, a decision tree is established for the classification and assignment of

246   total credits for any CoC. The decision tree takes into account the attributes of a particular

247   molecule that would cause it to be removed or indeed generated at a treatment barrier. These

248   attributes include mass, volume, water-oil partition characteristics, bond structure, bond type and

249   charge. This is combined with the guideline limits for potable water to assess the effectiveness of

250   the AWTP barriers.

251   The study aims to provide a case study for the use of the CCP approach for the removal of

252   chemicals of concern from water for potable reuse. The case study chosen, that of a small plant

253   associated with a small community, represents the worse-case scenario in risk management terms

254 for the removal of chemicals, although the barriers analysed are generic to a wide range of recycle

255 plants and the analysis of each of these barriers is independent of the scale of the plant. It is

256 acknowledged that the barrier types and conditions are not comprehensive, but the barrier

257 operational conditions chosen are considered applicable to a wide range of scenarios.

258 **2   Experimental Section**

259 **2.1   AWTP operation**

260 The AWTP was located at Selfs Point Wastewater Treatment Plant (SPWWTP), Hobart, Australia.

261 The AWTP had seven process units including ozonation, CMF, BAC, RO, UV disinfection, calcite

262 filtration and chlorination (Cl_2). In its final application state, the AWTP is preceded by an MBR

263 within the secondary treatment plant (AS plant with clarifier as tested here). There were two

264 output streams of the AWTP, namely a RO concentrate and a product stream stored for potential

265 potable use. A schematic of the process flowsheet is shown in Figure 1.

266

MBR → Ozone → CMF → BAC → RO → UV → Calcite Contactor → Cl_2 → Storage

Ocean Discharge
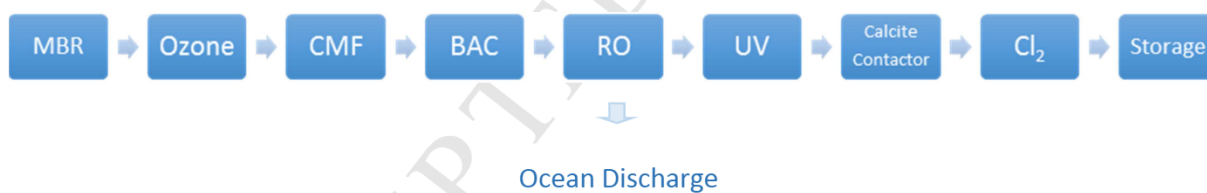
267 Figure 1: Schematic of the AWTP flowsheet

268 **2.1.1   Ozone**

269 A packaged ozone system (Wedeco OCS-GSO) and its operation are described elsewhere (Zhang *et*

270 *al.* 2016a). The plant commenced operation with target, alert and critical limits for ozone residual

12

271   or ozone dose as shown in Table 2. These were taken as critical control point (CCP) limits for the

272   ozone barrier. The target ozone levels were chosen based on pathogen reduction requirements.

273   The CoC reduction criteria and chemical classification, including the propensity of a particular

274   chemical type to be destroyed by ozone (specified as a LRV), were chosen based on the description

275   of Dickenson et al (Dickenson *et al.* 2009) and the feedwater characteristics. Of critical interest

276   here was the concentration of total organic carbon (TOC) in the feed to the ozone barrier. Data

277   from the literature in terms of ozone dose and residual to achieve a given LRV of a particular class

278   of chemical, when compared to that required to achieve the pathogen credits of the barrier (see

279   Table 1) were such that the pathogen based CCP criteria were considered adequate in this instance.

280   Other surrogate and higher order criteria may be required if either a higher chemical or pathogen

281   removal credit is deemed desirable.

282

283 Table 2: CCP values for the ozone barrier, with either ozone residual or an ozone dose as the target
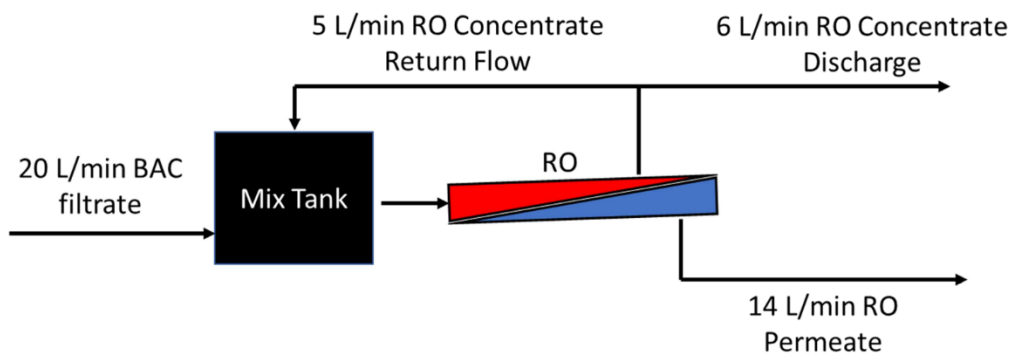
284 criteria

Key Control Measures	Ozone residual (mg/L)	Ozone dose (mg/L)
Target Criteria	0.25	14
Alert Limit	<0.1	<12
Critical Limit	<0.05	<11.7

285

286

2.1.2 Reverse Osmosis (RO)

288 The RO system consisted of five 10.2 cm (4") BW30 (Dow Filmtec) membranes in series and is

289 described elsewhere (Zhang *et al.* 2016a). A simple process flow diagram for the RO barrier is

290 shown in Figure 2.

291

292 Figure 2: Process flow diagram for RO

14

2.2 Sampling and data analysis

294 Unfiltered water samples were collected from 8 locations in the AWTP. These locations were the

295 feed (post AS), post ozone, post CMF, post BAC, RO concentrate, RO permeate, post UV and plant

296 outlet (Figure 3). All outlets were flamed and then flushed before sampling. Additionally, a sample

297 of feed water to the Selfs Point wastewater treatment plant was also taken.
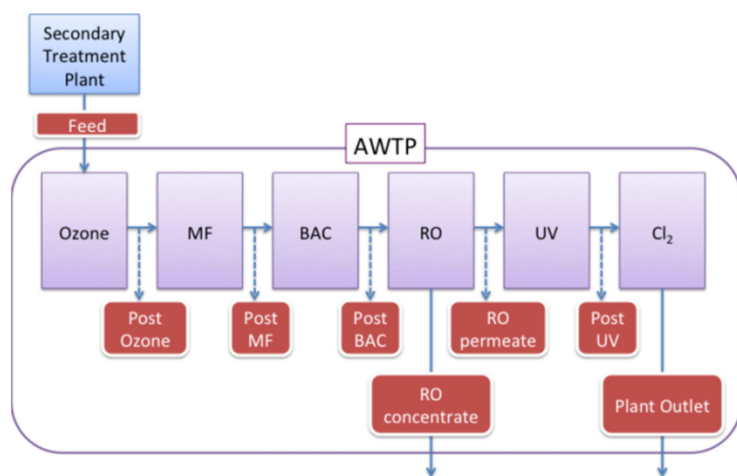
298

299 Figure 3: Summary of sampling locations in the AWTP

300 The samples were sent stored on ice to a laboratory in the School of Chemistry at the University of

301 Melbourne. The analytical analysis of all samples and the subsequent data analysis is described in

302 detail in Allinson et al. (Allinson *et al.* 2018).

303

304 The Limit of Reporting (LOR) were determined according to Method 1030C in Standard Methods for

305 the Analysis of Water and Wastewater (Eaton *et al.* 2005). Where statistical comparisons required

306 all data to have a numerical value, then concentrations less than the LOR values were set at 0.5

307 times the LOR value.

3 Results and discussion

3.1 Critical Control Point identification and LRV credits

3.1.1 Feed assessment and the role of secondary (activated sludge) treatment

The final installation of the AWTP is inclusive of a membrane bioreactor, which is expected to show better performance for the removal of micropollutants compared to a more conventional activated sludge treatment process inclusive of clarification (Clara *et al.* 2005a, Reif *et al.* 2008, Radjenović *et al.* 2009), since the membrane acts as a more complete physical barrier to the passage of particulate/suspended solids. The membrane also acts as a barrier to dissolved organic species through adsorption and entrapment in the fouling layer (Steinle-Darling *et al.* 2007, Fujioka *et al.* 2013, Fujioka *et al.* 2017). The extended solids residence time (SRT) of an MBR enhances the growth of slow growing microorganisms and prolongs biodegradation of micropollutants (Clara *et al.* 2005a, Clara *et al.* 2005b). None the less, a standard activated sludge (AS) process was used during this testing and as with all such processes, including those with an MBR, adsorption of micropollutants onto sludge and/or biodegradation (Clara *et al.* 2005a, Wijekoon *et al.* 2013b) are expected to be the most important micro-pollutant removal mechanisms. Molecules that do not adsorb on to sludge (hydrophilic or less hydrophobic) or that are not readily biodegradable within the hydraulic residence time of the activated sludge process will have a propensity to pass through the barrier.

There are few systematic studies of the mechanistic removal of organic pollutants by activated sludge treatment. Tadkaew et al. (Tadkaew *et al.* 2011) used a range of challenge additions of organic COCs including endocrine disrupting chemicals (EDCs), pesticides, and pharmaceutically

329 active chemicals (PhACs) to a synthetic wastewater to test a 40nm pore sized MBR. Three molecular

330 features were identified as directly connected to the removal efficiency (Isma *et al.* 2014) and a

331 classification is designated as:

332 **AS Class 1:** Hydrophobicity: all molecules with a hydrophobicity greater than log D@pH 8 of

333 3.2 showed >85% removal (LRV>0.8) where D is the partition coefficient between a

334 hydrophilic and a lyophilic phase, relative to octanol=8.0

335 **AS Class 2:** Non-Class 1 chemicals with electron withdrawing groups: molecules with electron

336 withdrawing groups such as chlorine, fluorine, bromine or amide are observed to

337 be recalcitrant to removal with <20% removal.

338 **AS Class 3:** Non-Class 1 molecules with electron donating groups: these chemicals are more

339 easily attacked and showed good removal in many cases. This includes a very wide

340 variety of functional groups, exclusive of those in AS Class 2.

341 Kovalova et al. (Kovalova *et al.* 2012), in their study on micropollutant removal from hospital

342 wastewater provided consistent results to Tadkaew et al. (Tadkaew *et al.* 2011). Based on a range

343 of literature reviewed in Kovalova (Kovalova *et al.* 2012) and the Tadkaew (Tadkaew *et al.* 2011)

344 studies, it was concluded that the only claim that could be made for the removal of CoC that was

345 consistent across all literature for a standard secondary activated sludge process or for an MBR

346 system was for the class of chemicals determined to be hydrophobic (Log D @ pH 8>3.2) (**AS Class**

347 **1**). This chemical grouping was expected to be consistently removed to better than 85% (LRV>0.8)

348 (Tadkaew *et al.* 2011, Kovalova *et al.* 2012) and the main removal mechanism for this chemical

349 grouping was adsorption to the biomass that in turn assisted prolonged biodegradation or

350 transformation (Clara *et al.* 2005a, Radjenović *et al.* 2009, Wijekoon *et al.* 2013b). A key difficulty

351 with a AS with clarifier or an MBR system is to define an operational surrogate that can be used to

352 set alert and critical control points in a CCP system. It is usual to set multiple criteria in this

353 instance. Examples include turbidity of the clarified overflow (since AS Class 1 molecules are

354 adsorbed to the biomass) and a combined measure of the reduction of either DOC or nitrogen. The

355 latter is a performance surrogate in terms of hydraulic residence time and biological activity.

356 Although no MBR was operational during testing, the CoC removal mechanism was tested assuming

357 that the clarification system was a worst-case scenario mimic of an MBR whereby feedwater

358 turbidity was taken as a CCP. In cases where the turbidity exceeded 5 NTU, the plant was not

359 operated. Samples of the feed to the Selfs Point plant (primary wastewater) were filtered through

360 standard Whatman filter papers and analysis completed using the AIQS-DB methodology. Many of

361 the semi volatile chemicals in the feed sample to the plant saturated the GC-MS detector and non-

362 volatile compound levels were so high that they saturated the LC-MS column completely, which

363 negated further work. As a result, 34 chemicals that were within the measurement range in the

364 primary influent were chosen for further analysis. Dilution of the feed to the GC-MS and LC-MS was

365 not performed to rectify the saturation issue as the initial detection analysis is quite time

366 consuming for the AIQS-DB method and the saturation was not confirmed until more than a month

367 after the initial run. Among the 34 chemicals, the K_{ow} (LogD) data for 21 chemicals is available from

368 the on-line "ChemSpider" database (Royal Society of Chemistry 2019). For a further 11 straight

369 chain alkane chemicals, the K_{ow} was assumed (based on chemical structure) to be greater than 10.

370 Only 3 chemicals had a K_{ow} less than 3.2. The removal efficiency across the secondary waste water

371 treatment plant was then assessed through sampling of the secondary waste water clarifier (feed to

372 the AWTP). Samples were taken under high and low flow conditions although the hydraulic

373 residence time was not significantly different across any 24-hour period. The data and associated

374 analysis are shown in the supplementary information (Table S1) for one primary feed sampling

375 event. It should be noted that the clarifier overflow of the secondary treatment plant (feed to the

376 AWTP) was sampled weekly for a period of nine months as well as specifically for high and low flow

377 periods of operation (as detailed in Table S1).

378 Although only 3 of the 34 chemicals considered here had a Log D value below 3.2, a minimum LRV

379 of 1.25 was measured for all chemicals across the secondary (AS) treatment process that was the

380 feed to the AWTP. Therefore, the operational data indicate this minimum LRV was not restricted to

381 chemicals with a Log D >3.2, as chemicals with a Log D < 3.2 were also removed to similar extent

382 (Tadkaew *et al.* 2011). However, the removal mechanism for the Log D < 3.2 chemicals is not

383 singular or well defined. Other characteristics such as the presence of electron donating or

384 withdrawing groups and their strengths (Tadkaew *et al.* 2011, Wijekoon *et al.* 2013b), and the

385 extent to which the molecule is assimilable makes assessment difficult. Molecules of LogD <3.2 with

386 strong electron donating groups tend to biodegrade easily while molecules with strong electron

387 withdrawing groups would be expected to be retained in the clarifier overflow. The data here is

388 limited, since the number of molecules in the feed analysis was limited. Indeed, over seventy

389 chemicals were detected regularly in the feed to the AWTP and many of these were beyond the

390 saturation limit of the detector in the sampling associated with the feed to the Selfs Point plant.

391 Taking both the consistency of the analysis data in this study and the literature data into account, it

392 would seem that a claim of an LRV of 0.8 for organic chemicals with a Log D >3.2 is justified, since

393 the main mechanism of removal is associated with particle attachment and this is enhanced for an

394 MBR. The operational CCP for the MBR in Antarctica is <0.1 NTU with a critical limit of 0.2 NTU to

395 achieve pathogen removal requirements. The CoC removal criteria should be easily achieved at this

396 operational state.

397

398

399 Other chemicals of interest include nitrogen and radiolytic compounds. Since total nitrogen (TN) is a

400 feed water quality control parameter of the AWTP, it was monitored on-line in the feedwater.

401 Removal to an LRV of greater than 1 was observed across the 9 months of operation. Radiolytic

402 compounds such as particulate radioactive tracers were not measured and although good removal

403 would be expected, no data is available from this study.

404 A conservative LRV of 0.8 for AS Class 1 chemicals and 1.0 for TN for a AS system is supported based

405 on the data from the Selfs Point Waste Water Treatment Plant and previous literature. This will be

406 considered further later and although not validated, is an important consideration in the treatment

407 of chemical spills to small community wastewater treatment plants where the water is being re-

408 used.

409 **3.1.2 Ozone**

410 Using the experimental results and protocols developed by WaterVal for pathogen control

411 (WaterSecure 2017a), protocols for chemical control for ozonation were formulated and validated.

412 The WaterVal procedure provides a recommended approach to validation that is based on the

413 following nine elements (originally written for pathogens but reformulated here),

414   1. Identification of the mechanisms of chemical removal by the treatment process unit,

415   2. Identification of target chemicals and or surrogates that are the subject of the validation

416   study,

417   3. Identification of factors that affect the efficacy of the treatment process unit in reducing the

418   target chemical,

419   4. Identification of operational monitoring parameters that can be measured continually and

420   are related to the reduction of the target chemical,

421   5. Identification of the validation method to demonstrate the capability of the treatment

422   process unit,

423   6. Description of a method to collect and analyse data to formulate evidence-based

424   conclusions,

425   7. Description of a method to determine the critical limits, as well as an operational monitoring

426   and control strategy,

427   8. Description of a method to determine the LRV for each chemical group in each specific

428   treatment process unit performing within defined critical limits,

429   9. Provision of a means for revalidation or additional onsite validation where proposed

430   modifications are inconsistent with the previous validation test conditions

431   Data for the removal of organic CoC across the AWTP barriers, as measured by GC-MS and LC-MS

432   (Kadokami et al. 2005) according to the AIQS-DB methodology as a composite of monthly data (for

433   9 months) is reported in detail in an earlier publication (Allinson et al. 2018) as well as removal of

434   DOC and TN across barriers for an average of 30 weekly sampling events (Zhang *et al.* 2016b, Zhang

435   *et al.* 2017).

436

437   From the operational data of the AWTP (Allinson *et al.* 2018), an overall 60% reduction in CoC was

438   achieved across the ozone barrier. However, for chemicals inclusive of TN and total DOC in solution,

439   ozone showed little or no effect (Zhang *et al.* 2017). This is expected since mechanistically it is

440   difficult to envisage mineralisation of organic chemicals, but it is expected that there should be

441   significant fragmentation. Assimilable organic carbon is produced during ozonation hence DOC

442   reduction is not expected, however, following ozonation, barriers such as activated carbon,

443   biologically activated carbon, membranes and sand filtration have been used to reduce the

444   concentration of assimilable organic carbon (Hollender *et al.* 2009, Zhang *et al.* 2016a).

445   Ozonation has been identified as an effective process of removing a wide spectrum of CoC both in

446   wastewater treatment and water treatment (Ternes *et al.* 2003, Snyder *et al.* 2006, Broséus *et al.*

447   2009, Margot *et al.* 2013). Effective removal is mainly attributed to the high oxidation potential of

448   OH radicals. Huber et al. (Huber *et al.* 2005), reported between 90-99 % removal of eleven

449   commonly found pharmaceutical and personal care products (PPCPs) in a pilot scale wastewater

450   treatment system, at an ozone dose 2-5 mg O_3/L. This dose level is significantly below the critical

451   limit of the ozone barrier of the AWTP but it has been shown that the absolute dose is not a

452   preferred criterion since the dose should reflect the initial ozone demand (IOD) in the feed water

453   (Dickenson *et al.* 2009, Wert *et al.* 2009). A CCP criteria that includes both a dose relative to the

454   IOD and a CT may be indicated.

455 In the presence of an excess of ozone and a sufficient reaction time, chemicals with tertiary amino

456 groups and aniline moieties (e.g., diclofenac and sulfanamides) and chemicals with an activated

457 aromatic ring and double bonds (e.g., carbamazepine and trimethoprim) can be significantly

458 reduced during ozonation at a relatively low ozone dose of as little as 2-3 mg O_3/L (Hollender *et al.*

459 2009). The efficiency of ozonation, especially at low ozone dose, is attributed to the high rate

460 constants for the reaction of those chemicals with ozone, low DOC concentration (<5 mg/L), an

461 absence of competitors such as nitrite (~0.05 mg/L) and a neutral pH, which leads to high ozone

462 stability (Hollender *et al.* 2009). The target ozone dose for the AWTP was 14 mg/L. This was

463 designed to be high relative to the TN and DOC concentration so as to ensure the presence of OH

464 radicals, not just ozone, for the destruction of CoC.

465 Analysis showed that nitrosamines including NDMA, NDEA and 9 other new molecules were

466 produced after ozone oxidation, mainly aliphatic chemicals (6 aliphatic, 3 aromatic). The occurrence

467 of reactive inorganic nitrogenous intermediates such as hydroxylamine and dinitrogen tetroxide

468 (N_2O_4) are mainly attributed to the formation of nitrosamines during ozonation (Lei *et al.* 2009).

469 NDMA is a known disinfection by-product of ozonation (Gerrity *et al.* 2015) and was under

470 continuous concentration detection through each barrier. NDMA can be effectively removed by

471 biodegradation due to the presence of an electron-donating group (i.e. dimethyl amine) (Krauss *et*

472 *al.* 2009, Wijekoon *et al.* 2013a). The data is presented in an earlier publication (Allinson *et al.* 2018)

473 and shows that a small reduction in NDMA was achieved after the biological activated carbon

474 barrier but that the RO membrane system was critical in the reduction to non-detectable levels.

475 As noted, literature data for molecular changes solely across ozone barriers under operational

476 conditions are very limited. The data is usually for combined ozone-BAC scenarios (Hubner *et al.*

477   2015) although the study of Lee *et al.* looks at removal both before and after BAC and provides

478   detailed information on the ozone dose to DOC ratio in an operational plant (Lee *et al.* 2012). In

479   addition, ozone dose and contact time reported in literature are for their own specific cases and are

480   often not reported and/or are very different from the operational scenario of the AWTP. Ozonation

481   efficiency for the removal of CoC is significantly affected by the instantaneous ozone demand (IOD),

482   wherein a higher ozone dose than the IOD assures occurrence of OH radicals to oxidize recalcitrant

483   chemicals. Whilst an ozone dose below the IOD destroys molecules susceptible to ozone oxidation,

484   it is hard to quantify removal unless there is an excess of OH radicals. At an O_3 dose equal or higher

485   than the IOD, significant OH formation takes place. As indicated earlier, the organic concentration

486   strongly influences the available OH radical concentration. At an ozone:TOC ratio of 0.6 or higher,

487   substantial OH formation can always be assumed (Dickenson *et al.* 2009, Wert *et al.* 2009). For

488   higher ratios, almost all organic molecules, not depending on their structure, are removed

489   efficiently, often below the detection limit. With increasing ozone contact time, the chemical

490   removal increases and typically the reaction completes after a few seconds to minutes (EPA 2011).

491   In Dickenson et al.'s pilot study (Dickenson *et al.* 2009), the ozone dose was varied across a range of

492   2.1 to 7.0 mg/L to give an ozone/TOC ratio from 0.3 to 1.0 mg/mg with data reported

493   predominately (Snyder *et al.* 2006, Wert *et al.* 2009) for the 0.6 to 1.0 range. The contact time

494   varied from 2 to 18 minutes. Using the extended integrated method based on the ozone residual

495   concentration at outlet and T_{10} in the reactor, the calculated ozone CT_{10} value was between 4 and

496   11 mg.min/L (Rakness *et al.* 2005). The T_{10} in the reactor was measured using tracer studies. No

497   CT_{10} value is given for the study by Lee et al. but contact times between 5 and 15 minutes and

498   ozone/TOC ratios of 0.4 to 2 are reported (Lee *et al.* 2012). In the AWTP, the ozone dose was such

499   that the ozone/TOC ratio was always >1.0 and the CT_{10} was >14 mg.min/L at a minimum contact

500   time > 5 minutes for all operational times where an ozone residual was detected. There was a

501   period of operation where this was not the case although no change in performance against

502   pathogen or chemical LRV's was noted in this period. In the pilot study of Dickenson *et al.*

503   (Dickenson *et al.* 2009), they investigated the response to ozone of different molecular types. By

504   assuming the instantaneous ozone demand (IOD) had been exceeded, they categorized the

505   ozonation potential of chemicals into four key molecular groups. The groupings are outlined in

506   Table 6.

507

508 Table 3: Molecular categories for ozonation

Class	RE (%)	Molecular Characteristics	Other indicators
Ozone 1	>90	Electron rich aromatic systems with hydroxyl, amino, acylamino, alkoxy or alkyl groups Deprotonated amines Nonaromatic alkenes	Ozone second order reaction rate $>103\ M^{-1}\,s^{-1}$
Ozone 2	>50 <90	aliphatic alkane, ketone, alcohol, acid, ether, and amide or and nitro aromatic chemicals	
Ozone 3	>25 <50	Nitrosamines	Formation and removal are competitive.
Ozone 4	<25	Halogen containing aliphatic and aromatic chemicals	Strong electron withdrawing groups (EWG's)

509

510 An analysis was completed on the nine data sets accumulated over the monthly sampling events in

511 the AWTP using GC-MS and LC-MS analysis as well as a separate nitrosamine study. The feed and

512 post ozone data were compared and categorized using the Dickenson *et al.* classification. The

513   detailed results are provided in Table S2 of the supplementary information. A summary of the data

514   is shown in Table 4.

515

516   Table 4: Removal data across the ozone barrier by class of compound

Class	RE (%)	Removal observations	Exceptions
Ozone 1	>90	N=24 chemicals >90 % N=20 50-90% N=1 increased N=3	50-90% - 4-Methyl-2,6-di-t-butylphenol(BHT) Increased – Fenubucarb, Dimethyl phthalate, Benzyl alcohol
Ozone 2	50-90	N=19 chemicals >90% N=7 50-90% N=2 25-50% N=3 <25% N=2 increased N=5	25-50% - Cholestanol, 24-Ethyl coprostanol, Stigmastanol <25% - Methyl myristate, beta-Sitosterol Increased Tris(1,3-dichloro-2-propyl) phosphate, Octanol, 9Z)-9-Tetradecenoic acid, methyl ester, Coprostanone,
Ozone 3	25-50	N=2 chemicals Increased N=2	Increased - NDMA, NDEA
Ozone 4	<25	N=10 chemicals >90% N=8 25-50% N=1 increased N=1	Increased - Tris(2-chloroethyl) phosphate

517

518   Chemicals in the Class 1 categorisation (Table 4), nominally electron rich aromatic molecules and

519   non-aromatic alkenes, were removed very effectively by ozone, often to the point of non-detection

520   and all were well below guideline values associated with the Australian Drinking Water Guidelines

521   (ADWG) and the Australian Guidelines for Water Recycle (AGWR) (tabulated information is shown

522   in the supplementary information). The three chemicals that increased in concentration were still

523   well below guideline values and can be classed as either an ozone by-product in the case of

524   dimethyl phthalate and as possible anomalies in the other two cases since these were not observed

525   in the feed and detected only once in the effluent in nine samplings. The concentrations in each

526   case were close to the LOR. Therefore, 21 out of 24 chemicals in Class 1 were reduced in

527   concentration and all to substantially below guideline values. The latter is not a criterion for

528   operation of a CCP, just a necessary outcome if no other barriers exist for chemical removal. The

529   average removal efficiency of the 21 chemicals was >98.6% with a range of 86.6-100%. This was

530   consistent with literature expectations for the role of ozone at doses greater than the IOD and with

531   a high CT_{10} as measured by the extended integration method (Kadokami *et al.* 2005). Therefore, the

532   data is consistent with the claim that the ozone barrier, operated under CCP criteria to remove

533   pathogens, could be operated under the same criteria to remove chemicals where the classification

534   is systematic with the Class 1 designation of Dickenson *et al.* Under these conditions, an LRV for

535   electron rich aromatic chemicals of 0.9 is indicated for this barrier. The performance of the barrier

536   for the other classes of compound was also consistent with literature and the mechanistic

537   removal/formation classification, but the LRV is too low and inconsistent to make a claim for LRV

538   credits under CCP operational conditions.

540 ### 3.1.3 Reverse Osmosis (RO)

541 Using experimental results and protocols developed by WaterVal (WaterSecure 2017b) for

542 pathogen control, protocols for chemical control for reverse osmosis were formulated and

543 validated. The nine elements of the WaterVal validation protocol were listed earlier.

544 The operational data from the AWTP shows a good rejection of both organic (Allinson *et al.* 2018)

545 and inorganic species including DOC, TN and NDMA (Zhang *et al.* 2016a) across the RO barrier. The

546 general mechanisms of RO rejection of chemicals are size exclusion and steric hindrance for all

547 kinds of molecules and electrostatic interaction and rejection for ionic species (Bellona *et al.* 2004a,

548 Kimura *et al.* 2004, Alturki A.A. *et al.* 2010). To a lesser extent, adsorption to the membrane and

549 hydrophobic-hydrophobic interactions take place and influence the rejection rate (Kiso *et al.* 2001,

550 Bellona *et al.* 2004a, Nghiem *et al.* 2004). For uncharged molecules, size exclusion is the most

551 important rejection mechanism. Electrostatic interactions lead to high rejection, even for very small

552 ions (Kimura *et al.* 2004).

553 Despite the myriad of possible mechanisms, the principal mechanism to remove chemicals with a

554 molecular weight greater than the molecular weight cut off (MWCO) of the membrane is size

555 exclusion. The MWCO of RO membranes is typically in the range of 100–300 Dalton (Da) for organic

556 molecules with a rejection of 96.5 % (LRV 1.5) and up to 99 % (LRV 2.0) or greater for inorganic ionic

557 solutes (Ahrens *et al.* 2010). However, the MWCO provides an estimate of the sieving effect only

558 and does not take into account the hydrophobicity, charge and geometry of the molecule,

559 temperature and flux effects, all of which can also affect rejection (Kiso *et al.* 2001, Bellona *et al.*

560 2004b).

561 Several studies indicate that the molecular weight and consequentially derived molecular weight

562 cut-offs are not particularly reliable predictors for chemical rejection (Drewes *et al.* 2003, Agenson

563 and Urase 2007, Alturki *et al.* 2010, Doederer *et al.* 2014). Only at a certain molecular weight

564 significantly higher than the MWCO do molecules seem to be always rejected by the membrane

565 due to size exclusion. A better predictor of exclusion is the molecular diameter or width, which was

566 successfully used by Alturki *et al.*(Alturki A.A. *et al.* 2010) and Doederer *et al.* (Doederer *et al.* 2014)

567 to predict rejection. However, this information is not directly available in common databases and

568 has to be calculated. A good surrogate appears to be the molar volume which can be obtained in

569 databases for every chemical (i.e. http://www.chemspider.com/).

570 Charged molecules possess a hydration shell, which makes the combination of actual ion and

571 hydration shell too bulky to pass the membrane. Therefore, all charged molecules are rejected

572 efficiently, albeit there are indications that positively and negatively charged chemicals can behave

573 differently, possibly due to adsorption. Alturki *et al.* (Alturki A.A. *et al.* 2010) demonstrated that

574 rejection of hydrophobic molecules by RO is not as effective as ionic and hydrophilic species, but a

575 combination of 40 TrOCs ranging in partition coefficient (1.21 to 6.19@pH 8) and size (151 to 454

576 MW) were removed to below detection limits from an initial dose of 2 g/L. This represents a LRV>2

577 for a Limit of Reporting (LOR) of 0.005 g/L.

578 Conductivity across the process was used for on-line verification in the AWTP and was a CCP

579 monitoring parameter for pathogen reduction. Typical operational LRV data for ionic species

580 (predominately inorganic salts) is reported elsewhere (Zhang *et al.* 2016a).

581 The data for operation of the AWTP indicated that the DOC in the feed to the RO was reduced from

582 an average value across all samplings of 6.27 mg/L to a value of <0.26 mg/L, a reduction of 95.8% or

583 LRV of 1.38. For TN, the average feed concentration was 6.89 mg/L. This was reduced to an average

584 of 0.28 mg/L (n= 30 weeks of readings), a reduction of 95.9% or LRV of 1.39.

585 The classification of CoC varies across the world, but commonly, the classification is based on end

586 use and the human response of the molecules. One example is the classification used in the the

587 AGWR (NRMMC 2008) where molecules are classified as: inorganic chemicals; disinfection by-

588 products; pesticides; fragrances; pharmaceuticals and metabolites; fire retardants; dioxins and

589 dioxin like chemicals; miscellaneous organic chemicals – PCB's, PAH's, phthalates, organotins, etc.;

590 radiological; and chelating agents .

591 Based on the operational data from the AWTP over nine-months of operation along with literature

592 analysis (NRMMC 2006, Snyder et al. 2006), the classification of molecules used in the AGWR is not

593 considered useful in determining whether a molecule would be removed by a particular barrier, as

594 there was often a range of molecular attributes within a particular class. A new classification based

595 on the mechanistic propensity of a particular compound to be removed by the RO barrier is

596 suggested. Similar to the designation of hydrophobicity as a key determinant of removal for the

597 activated sludge barrier and the presence of an electron rich moiety for removal by ozone, a set of

598 criteria were considered for RO. This classification was for polyamide (PA) based RO membranes

599 with a NaCl rejection of greater than 96.5 % (as was used here).

600 RO Class 1: Organic ionic species. Mechanism of removal: (a) electrostatic interactions between

601 charged solute and the negatively charged membrane surface (Bellona et al. 2004a, Alturki A.A. et

602 al. 2010) and (b) electrostatic repulsion of negatively charged hydrophilic solutes (Kimura et al.

603   2004, Alturki A.A. *et al.* 2010). The pH must be at least one above or below the pK_a or pK_b of the

604   molecule respectively.

605   RO Class 2: Organic neutral molecules, molar volume > 120 cm^3, Mechanism of removal: size

606   exclusion and steric hindrance (Bellona *et al.* 2004a, Kimura *et al.* 2004, Alturki A.A. *et al.* 2010)

607   RO Class 3: Organic neutral molecules, molar volume < 120 cm^3, electron withdrawing groups,

608   Mechanism of removal: not reliable due to small size (Bellona *et al.* 2004a, Kimura *et al.* 2004,

609   Alturki A.A. *et al.* 2010)

610   RO Class 4: Organic neutral molecules, molar volume < 120 cm^3, only electron donating groups or

611   electron donating and electron withdrawing groups. Mechanism of removal: not reliable due to

612   small size (Bellona *et al.* 2004a, Kimura *et al.* 2004, Alturki A.A. *et al.* 2010)

613   RO Class 5: Inorganic ionic species, Mechanism of removal: (a) electrostatic interactions between

614   charged solute and negatively charged membrane surface (Bellona *et al.* 2004a, Alturki A.A. *et al.*

615   2010) and (b) electrostatic repulsion of negatively charged hydrophilic solutes (Bellona *et al.* 2004a,

616   Kimura *et al.* 2004)

617   RO Class 6: Inorganic non-ionic species. Mechanism of removal: poorly removed due to extremely

618   small size and hydrophilicity (Kezia *et al.* 2013)

619   RO Class 7: Particulate radioactive tracers. Mechanism of removal: size exclusion, similar to the

620   removal of viruses and particulates

621   Literature data is now presented alongside data from the AWTP. As noted earlier, in excess of

622   seventy organic molecules were found regularly in the feed to the AWTP across the 9 month test

623   period. Many of these were removed in the first three barriers to below the LOR. The cumulative

624   DOC removal was consistently in the range 55-60% across the ozone, CMF and BAC barriers.

625   Figure 4 shows data from previous literature (Comerton *et al.* 2008, Alturki *et al.* 2010, Appleman *et*

626   *al.* 2014, Fujioka *et al.* 2015, Zhang *et al.* 2017) for RO Class 1 chemicals (organic ionic). The

627   literature data was for similar RO membranes in terms of surface layer and MWCO (polyamide,

628   rejection >96.5%).   A minimum LRV = 1 is observed for all chemicals of this group, with most

629   rejected to a considerably higher level. There is no data from the AWTP here as although there

630   were RO Class 1 chemicals in the feed (Allinson *et al.* 2018), , they were not detected in the

631   permeate of the RO membrane and their concentration in the feed was not greater than 5x the

632   LOR. Under these circumstances, any LRV calculation would be an underestimate of the actual LRV

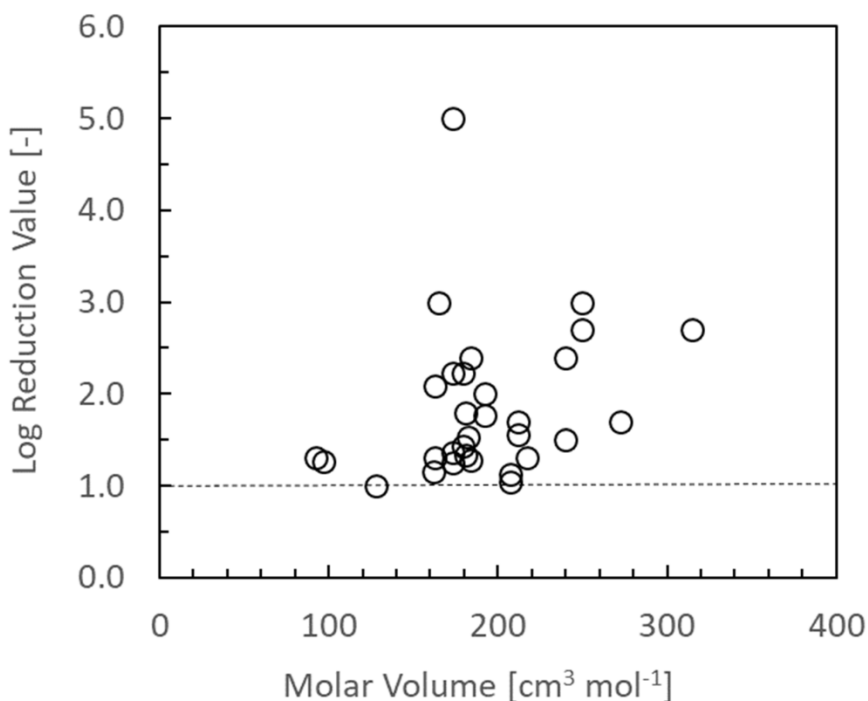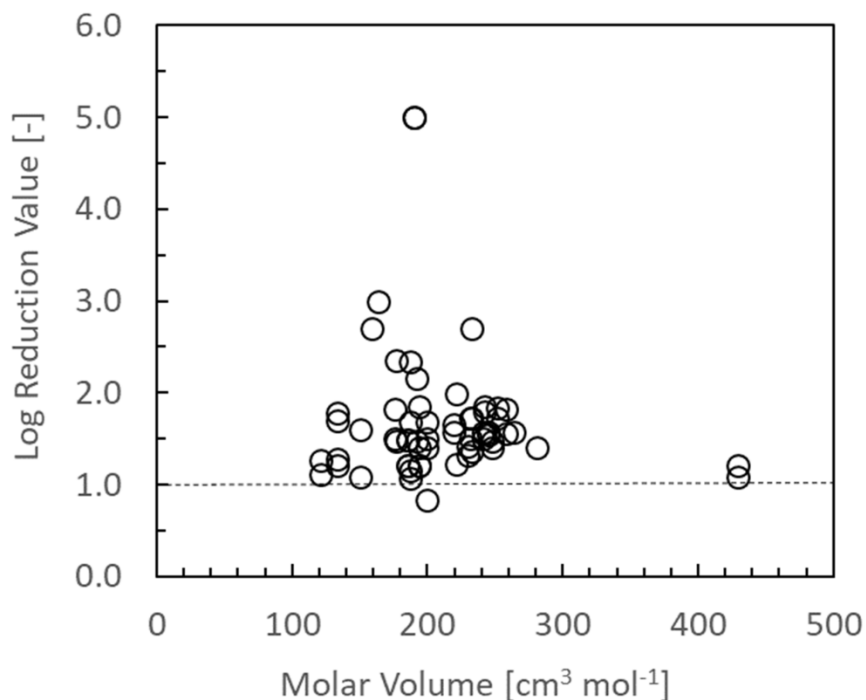633   and may imply a poor rejection. This would be inaccurate.

634

Figure 4: Performance of rejection of Class 1 molecules for an RO barrier of the type used in the AWTP and operated such that NaCl rejection was >96.5% (LRV 1.5).

635   Data for RO Class 2 molecules is shown in Figure 5. They have a molar volume above the limit of

636   120 cm^3 mol^{-1} and although one might expect rejection rate to improve with molar volume, the

637   literature (Comerton *et al.* 2008, Alturki *et al.* 2010, Appleman *et al.* 2014, Doederer *et al.* 2014,

638   Altalyan *et al.* 2016) is not supportive of this expectation. However, a large number of the

639   molecules in the literature were rejected to the extent that they could not be detected in the RO

640   permeate. A lack of knowledge of the LOR in these systems meant that an LRV could not be

641   determined in many cases. For the AWTP data, a rejection of between 90-99 % is observed,

642   regardless of molar volume, however the criteria for inclusion in the data set was, as for the Class 1

643   molecules, not met. This is an issue with results where the input concentration is not controlled

644   and reflects a dilemma of all field scale work where spiking of chemicals is not an option for a wide

645   range of pollutants. It is noted that wherever the criteria for LRV determination was met, an LRV of

646   > 1 was observed for all chemicals in this class except for one data point (LRV=0.84) for bisphenol A

647   from the laboratory scale work of Alturki *et al.* (Alturki *et al.* 2010).

648

Figure 5: Performance of rejection of Class 2 molecules for an RO barrier of the type used in the

AWTP and operated such that NaCl rejection was >96.5% (LRV 1.5).

651

Data for RO Class 3 molecules are shown in Figure 6. The data (Doederer *et al.* 2014, Altalyan *et al.*

2016, Allinson *et al.* 2018) confirms, including that from the AWTP, that most chemicals in this class

are rejected to some extent but once the molar volume decreases significantly below 120 cm^3 mol^{-1}

, for molecules that do not have a negatively polarised centre (caused by the presence of an

electron withdrawing group), neither a reliable minimum removal nor a mechanism for rejection

can be claimed. There is also evidence that rejection of some molecules in this class is increased by

fouling and others where fouling is detrimental to removal. Operating the barrier according to the

protocols defined earlier ensured that cleaning was always performed once the trans membrane

660   pressure reached a fixed value. As such, the data reported here is for unfouled or weakly fouled
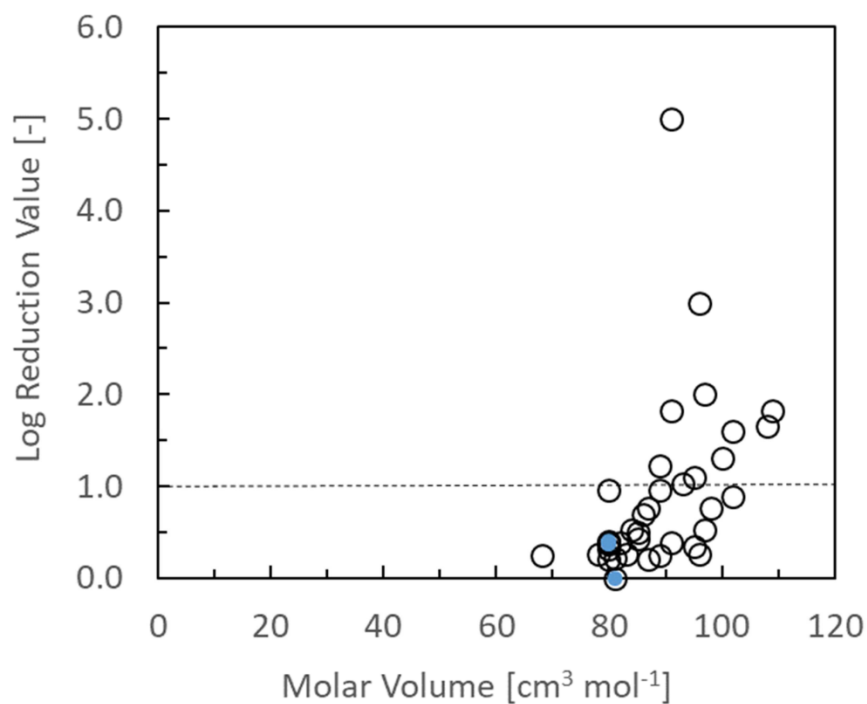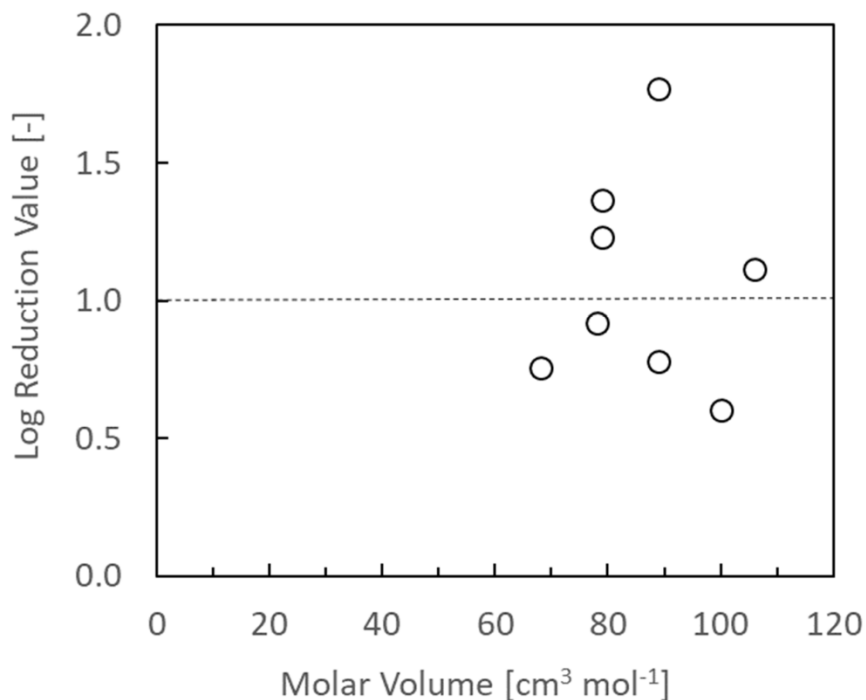
661   membranes.

Figure 6: Performance of rejection of RO Class 3 molecules for an RO barrier of the type used in the AWTP and operated such that NaCl rejection was >96.5% (LRV 1.5). Filled data points are from the AWTP.

662   Data for RO Class 4 molecules is shown in Figure 7. The list of molecules in this class, for which data

663   is available, is not extensive and includes halo-methanes and halo-ethanes amongst others. The

664   rejection of molecules of this type would need to be specifically validated and preferably by the

665   supplier of the RO unit (i.e. pre-commissioning) since many are harmful to health. An LRV of 0.5 is

666   deemed possible with appropriate validation. The results of all validated data found in the

literature (Altalyan *et al.* 2016) are from one source. There was no data from the AWTP in this

668   class.

669

670   Figure 7: Performance of rejection of RO Class 4 molecules for an RO barrier of the type used in the

671   AWTP and operated such that NaCl rejection was >96.5% (LRV 1.5).

672   The performance for RO Class 5 molecules is shown in Figure 8. The data indicates that all inorganic

673   ions are rejected to an LRV>1 and most to an LRV>1.5. Only the smallest positively charged species

674   are removed to less than an LRV of 1.5, although the study that reported the data (Malamis *et al.*

675   2012) for sodium, potassium, magnesium and manganese is at odds with the standard validation of

676   most RO membranes using seawater and NaCl rejection as the criteria for operation.   In general, an

677   LRV of > 1.5 is achieved. The results of all data found in the literature (Ozaki *et al.* 2002, Ipek 2005,

678   Mohsen-Nia *et al.* 2007, Malamis *et al.* 2012, Zhang *et al.* 2015) are shown in Figure 8. Since a CCP

679   using conductance as the surrogate of performance across the RO barrier of the AWTP (Zhang *et al.*

680 2016a) showed greater than LRV 1.5 performance for the entire operation, the AWTP data is

681 consistent with a proposed credit for RO Class 5 molecules and ions of LRV 1.5. The data from the

682 AWTP was for bromate, bromide and iodide.
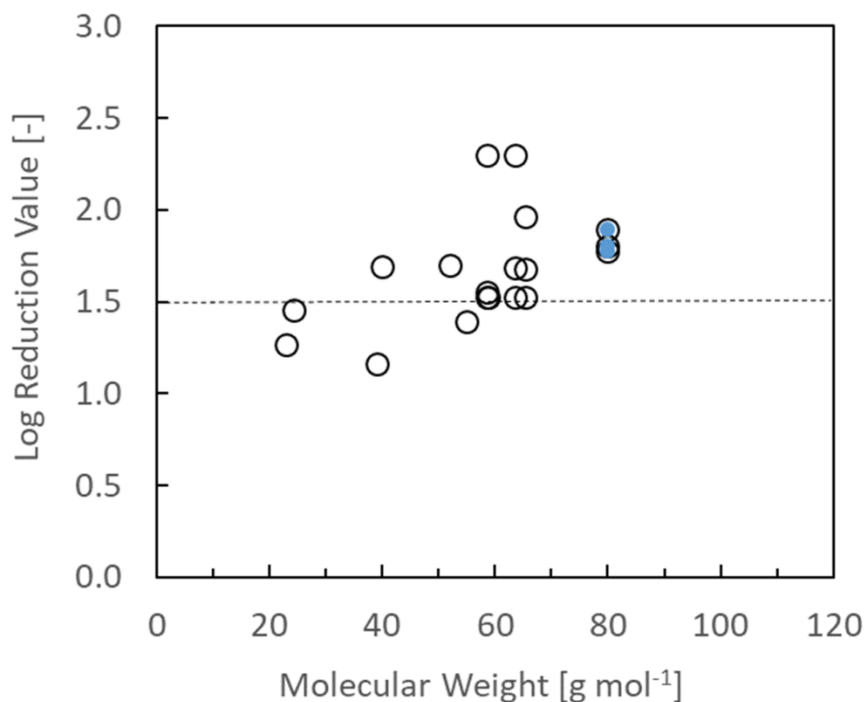
683

684 Figure 8: Performance of rejection of RO Class 5 molecules for an RO barrier of the type used in the
685 AWTP and operated such that NaCl rejection was >96.5% (LRV 1.5).

686 RO Class 6 is a for water soluble uncharged inorganic ions. Boron is the obvious member of this

687 class. Because of its extremely small size and strong hydrophilicity it can neither be rejected due to

688 size exclusion nor due to adsorption. It is poorly rejected (Kezia et al. 2013) and no LRV claim would

689 seem appropriate. RO Class 7 is for particulate radioactive tracers. Qualitative data shows good

690 rejection since the systems of interest are the same or greater in size to viruses and as such, a

691 similar rejection is assumed. Validation with a particulate surrogate would be required, albeit with a

692 sub-micron sized particle.   Other radionuclides fall into the other classes depending on their

693 molecular or atomic structure.

694 As the result of mechanistic studies and literature research, along with the data from the AWTP, a

695 range LRVs (shown in Table 5) would be deemed achievable under CCP operational conditions for a

696 polyamide RO membrane operating with a NaCl rejection >96.5% (LRV 1.5). Given that the highest

697 claim is for inorganic ionic species (RO Class 5) and this class is of itself validated continuously with

698 on-line conductivity measurement, it is expected that these figures are robust to non-membrane

699 failures (o-ring or glue line leaks) since such leaks should be detected with sufficient sensitivity to

700 identify when the CCP was close to alert or alarm levels.

701 Table 5:   Proposed achievable LRV for RO Class 1-7 molecules, ions, atoms and particulate

702 radioactive tracers based on literature data and new data presented herein.

RO Class	LRV
1: Organic ionic species	1.0
2: Organic neutral species, MV > 120 cm³/mol	1.0
3: Organic neutral species, MV < 120cm³/mol, EWG	0.0
4: Organic neutral species, MV < 120 cm³/mol, EDG/other	0.5
5: Inorganic ionic species	1.5
6: Inorganic non-ionic species	0.0
7: Particulate radioactive tracers	1.5

703

704

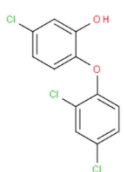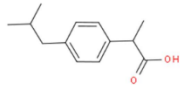**3.2   LRV calculation examples and decision tree for chemical removal**

706   Triclosan and ibuprofen, two common molecules that fall into the category of Pharmaceutical and

707   Personal Care Products (PPCP) found in the discharge in the secondary effluent of wastewater

708   treatment processes, were taken as examples to exemplify how a barrier credit process or decision

709   tree for achieving a total credits for a particular molecule would work in an analogous manner to

710   the allocated credits for pathogens (as per Table 1). A summary of the credits allocated to each

711   barrier chemical classification is shown in Table 6. A comparison on their characteristics and the

712   proposed credits is shown in Table 7, along with the calculated value for the maximum

713   concentration in the feed and the maximum spill volume. The characteristics (sometimes multiple)

714   of each molecule in terms of its mechanism of removal has been associated to a classification and

715   the associated removal credit for each barrier (i.e. a decision tree system) in Table 7. For example,

716   the charge state, hydrophobicity, molecular size and the electron withdrawing or donating nature

717   are critical to the classification across the RO, AS, RO and ozone barriers respectively since they are

718   directly related to the dominant mechanism of removal.

719   Table 6: Overview of LRV credits proposed for each class of chemical across each of the AS, ozone

720   and RO barriers. NB: Each classification is not the same for each barrier. Refer to earlier sections.

Chemical Class	BARRIER	LRV	BARRIER	LRV	BARRIER	LRV
1	AS	0.8	OZONE	1.0	RO	1.0
2	AS	0.0	OZONE	0.0	RO	1.0
3	AS	0.0	OZONE	0.0	RO	0.0
4			OZONE	0.0	RO	0.5
5					RO	1.5
6					RO	0.0
7					RO	1.5

721   Table 7: Proposed classification and LRV credits and comparison of Triclosan and Ibuprofen

Name	Triclosan	Ibuprofen
Structure		
General Classification	Aromatic (EWG)	Aromatic (EDG)
pKa and charge at pH 8	7.9 (neutral)	5.2 (negative)
MW	289.542	206.281
Kow	4.76 (hydrophobic)	2.23 (hydrophilic)
AGWR max value (µg/L)	0.35	400
AS Class and (LRV)	1 (0.8)	3 (0.0)
Ozone Class and (LRV)	4 (0.0)	1 (0.9)
RO Class and (LRV)	2 (1.0)	1 (1.0)
Total LRV	1.8	1.9
Maximum WWTP feed concentration (µg/L)	22.1	31,773

722

723 In addition to the LRV credit for each barrier, the influence of a spill into the small wastewater

724 treatment system can be predicted and a dilution factor into the waste treatment system

725 calculated. This can be added to the LRV value in terms of the management of risk. For additions

726 that are ubiquitous and part of normally daily activities, this is not appropriate. In this scenario, the

727 process allows a calculation of the maximum allowable concentration in the feed, a parameter that

728 is easier to measure than in product waters where the concentrations are quite often close to the

729   LOR (Allinson *et al.* 2018). These values are shown in Table 7 and can be nominally calculated for

730   any chemical where a prescribed guideline limit is known or where a human health value can be

731   calculated (Allinson *et al.* 2018).

732   For a spill, any calculation needs to consider the hydraulic residence and volume of the system. For

733   the AWTP, this was 6 hours and 5,000 L at a person equivalent of 140 L per day for 150 people. The

734   small volume of the system and lower than typical water use represents a worse-case scenario

735   relative to larger treatment systems. A dilution factor or equivalent LRV can be assigned based on

736   the concentration per litre in the spill and the spill volume relative to the volume of the treatment

737   system.

738   Triclosan is a commonly used additive in disinfectants, soaps, toothpastes and mouthwashes at a

739   concentration of 0.1-1%, typically 0.5%. A 2 mL triclosan based disinfectant and/or toothpaste use

740   per person per day would supply around 0.01 g of triclosan per person to the wastewater system.

741   At 140 L of water use per day, this would result in a feed concentration of 71 $\propto$g/L. This is more

742   than triple the maximum calculated value in Table 7. Alternatively, a spill of 20 mL of triclosan

743   disinfectant solution into the waste water system (5 g/L equivalent concentration), would see a

744   dilution factor of 250,000 based on the hydraulic residence time and system volume for a small

745   community model (5000 L wastewater holding volume). This would result in a concentration in the

746   feed of 20 $\propto$g/L. This is in line with the maximum calculated value for removal to guideline limit

747   values. In both scenarios, source control is indicated. The data from the AWTP study reflects a

748   higher removal rate than (LRV 1.8) but from a regulatory perspective, operation of a CCP barrier

749   model for chemicals suggests that without specific validation for chemicals of concern (too

750   expensive for small communities), that source control and extra barrier measures are indicated. As

751 an example of performance, the data in the supplementary information section shows that

752 triclosan was actually removed quite effectively by the ozone barrier with an LRV of 1.24 (as against

753 a claim of 0.0). This is not unexpected for such a barrier operating at ozone dose levels well above

754 the IOD whereby it is expected that the presence of the OH radical will result in indiscriminate

755 molecular destruction.

756 Ibuprofen is a drug used for treating pain, fever, and inflammation. It is typically supplied as tablets

757 containing 200mg active ingredient. The calculated value in Table 7 to achieve regulatory guideline

758 limits is 31,773 $\propto$g/L. With ubiquitous use of say 5 tablets per person per day (close to the

759 recommended maximum daily dose) and no metabolic destruction in-vivo, the feed concentration

760 to the waste water treatment plant would still only be 7200 $\propto$g/L. Indeed, it would take over 1000

761 tablets solubilised into the waste collection system to cause an issue (5000L wastewater holding

762 volume), which was unlikely to happen. In this instance, source control is not indicated, although

763 measurements of the feed concentration at periodic intervals would be required to identify a

764 maximum concentration for the barrier system for removal of this chemical. Indeed, the suitability

765 of a particular single or multiple barrier system operating to CCP principles could be evaluated for

766 any chemical to a maximum desirable discharge concentration.

767 **4   Conclusions**

768 A detailed investigation of barrier performance and CCP classification of chemicals around a

769 activated sludge, ozone and reverse osmosis barrier has been performed using the operational data

770 from an Advanced Water Treatment Plant (AWTP) operated at Self Point Wastewater Treatment

771 Plant in Tasmania, Australia as well as (predominately) data from published literature.

772   The seven barriers associated with the AWTP were evaluated as well as an activated sludge process

773   that preceded the AWTP. No credible chemical removal was associated with five of the seven

774   AWTP barriers, although the microfiltration (MF), biologically activated carbon (BAC) and to a lesser

775   extent, UV barriers, were observed to be effective in the reduction of trace organic chemicals.

776   However, the mechanism of removal of trace organic chemicals for these barriers was not well

777   defined and the data did not allow classification of the removal to a particular class that would

778   likely satisfy a regulatory authority that there was a known and systematic relationship between

779   mechanism of removal, a specific molecular attribute (i.e. molar volume, state of charge,

780   hydrophobicity, etc.), operating conditions and the removal achieved. The BAC was effective in the

781   removal of assimilable organic carbon (AOC).

782   The individual chemical classifications developed for each of the activated sludge, ozone and

783   reverse osmosis barriers were reflective of the molecular mechanisms of removal of a particular

784   chemical by the barrier in the scenario considered herein. The classification is nominally generic

785   and not based on the end use of the chemical. On this basis, the study is considered a first

786   demonstration of the use of a multi-barrier chemical decision-tree based approach to the

787   classification of the removal of a chemical by a treatment plant under CCP constraints. It is

788   acknowledged none the less that further testing across a broader set of conditions (i.e.

789   temperature, different water hardness) is essential to establishing the efficacy of the approach,

790   including limitations across a broad set of water conditions.

791   A log reduction value for the removal of each chemical class of each barrier was then assigned

792   based on operational data for the barrier operating to a CCP condition for the water type and CCP

793   conditions considered here. This approach allows an operational plant to be designed with a clear

794 knowledge of the likely removal of a particular chemical to a regulatory standard such as a

795 maximum permissible guideline limit, based only on a knowledge of feed concentrations. It is

796 envisaged that after validation across a broader set of water and operational conditions, the

797 implementation of this process will substantially reduce the need for chemical analysis on product

798 water from treatment plants since a plant operated to CCP limits for each barrier should then only

799 need periodic verification of barrier performance.

800 **5   Acknowledgements**

805 **6   References**

806 Agenson, K. O. and T. Urase (2007). Change in membrane performance due to organic fouling in
807 nanofiltration (NF)/reverse osmosis (RO) applications. Great Britain, Elsevier Science B.V.,
808 Amsterdam.**:** 147.

809 Ahrens, S., S. Taniyasu, L. Yeung, N. Yamashita, P. Lam and R. Einghaus (2010). "Distribution of
810 polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay,
811 Japan. ." Chemosphere, **79**: 266-272.

812 Allinson, M., K. Kadokami, S. Shiraishi, D. Nakajima, J. Zhang, A. Knight, S. Gray, P. Scales and G.
813 Allinson (2018). "Wastewater recycling in Antarctica: Performance assessment of an advanced
814 water treatment plant in removing trace organic chemicals." Journal of Environmental
815 Management **224**: 122-129.

816 Altalyan, H., B. Jones, J. Bradd, L. Nghiem and Y. Alyazichi (2016). " Removal of volatile organic
817 compounds (VOCs) from groundwater by reverse osmosis and nanofiltration." Journal of Water
818 Process Engineering **9**: 9-21.

819 Alturki A.A., T. Nichanan, J. A. McDonald, S. J. Khan, W. E. Price and L. D. Nghiem (2010).
820 "Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect
821 potable water reuse applications." Journal of Membrane Science **365**(1-2): 206-215.

822 Alturki, A. A., N. Tadkaew, J. A. McDonald, S. J. Khan, W. E. Price and L. D. Nghiem (2010).
823 "Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect
824 potable water reuse applications." Journal of Membrane Science **365**: 206-215.

825 Appleman, T. D., C. P. Higgins, O. Quiñones, B. J. Vanderford, C. Kolstad, J. C. Zeigler-Holady and E.
826 R. V. Dickenson (2014). "Treatment of poly- and perfluoroalkyl substances in U.S. full-scale water
827 treatment systems." Water Research **51**: 246-255.

828 Barker, S. F., M. Packer, P. J. Scales, S. Gray, I. Snape and A. J. Hamilton (2013). "Pathogen reduction
829 requirements for direct potable reuse in Antarctica: Evaluating human health risks in small
830 communities." Science of The Total Environment **461**(Supplement C): 723-733.

831 Bartlett, S., K. Northcott, P. J. Scales, D. Sheehan and S. Gray (2015). Demonstration of robust water
832 recycling: Hazard analysis and critical control point report., Demonstration of robust water recycling
833 (Project number 3170), Australian Water Recycling Centre of Excellence, ISBN 978-1-922202-57-4.

834 Bellona, C., Drewes J.E., P. Xu and G. Amy (2004a). "Factors affecting the rejection of organic
835 solutes during NF/RO treatment—a literature review." Water Research **38**(12): 2795-2809.

836 Bellona, C., J. E. Drewes, P. Xu and G. Amy (2004b). "Factors affecting the rejection of organic
837 solutes during NF/RO treatment—a literature review." Water Research **38**(12): 2795-2809.

838 Broséus, R., S. Vincent, K. Aboulfadl, A. Daneshvar, S. Sauvé, B. Barbeau and M. Prévost (2009).
839 "Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water
840 treatment." Water Research **43**(18): 4707-4717.

841 Clara, M., N. Kreuzinger, B. Strenn, O. Gans and H. Kroiss (2005a). "The solids retention time—a
842 suitable design parameter to evaluate the capacity of wastewater treatment plants to remove
843 micropollutants." Water Research **39**(1): 97-106.

844 Clara, M., B. Strenn, O. Gans, E. Martinez, N. Kreuzinger and H. Kroiss (2005b). "Removal of selected
845 pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and
846 conventional wastewater treatment plants." Water Research **39**(19): 4797-4807.

847 Comerton, A. M., R. C. Andrews, D. M. Bagley and C. Hao (2008). "The rejection of endocrine
848 disrupting and pharmaceutically active compounds by NF and RO membranes as a function of
849 compound and water matrix properties." Journal of Membrane Science **313**(1-2): 323-335.

850 Dickenson, E. R. V., J. E. Drewes, D. L. Sedlak, E. C. Wert and S. A. Snyder (2009). "Applying
851 Surrogates and Indicators to Assess Removal Efficiency of Trace Organic Chemicals during Chemical
852 Oxidation of Wastewaters." Environmental Science & Technology **43**(16): 6242-6247.

853 Doederer, K., M. Farré, M. Pidou, H. Weinberg and W. Gernjak (2014). "Rejection of disinfection by-
854 products by RO and NF membranes: Influence of solute properties and operational parameters."
855 Journal of Membrane Science **467**: 195-205.

856 DPI (2015). Recyled Water: Information Sheet Number 4, Critical Control Points Department of
857 Primary Industries, New South Wales Government, Sydney, Australia.

858 Drewes, J. E., M. Reinhard and P. Fox (2003). "Comparing microfiltration-reverse osmosis and soil-
859 aquifer treatment for indirect potable reuse of water." Water Research **37**(15): 3612-3621.

860 Eaton, A. D., E. W. Rice and R. B. Baird (2005). Standard Methods for the Examination of Water and
861 Wastewater. Washington, American Public Health Association.

862 EPA (2011). Water Treatment Manual : Disinfection The Environmental Protection Agency , Ireland

863 Fujioka, T., S. Khan, J. McDonald and L. Nghiem (2015). "Validating the rejection of trace organic
864 chemicals by reverse osmosis membranes using a pilot-scale system." Desalination **358**: 18-26.

865 Fujioka, T., S. J. Khan, J. A. McDonald, R. K. Henderson, Y. Poussade, J. E. Drewes and L. D. Nghiem
866 (2013). "Effects of membrane fouling on N-nitrosamine rejection by nanofiltration and reverse
867 osmosis membranes." Journal of Membrane Science **427**: 311-319.

868 Fujioka, T., H. Kodamatani, H. Aizawa, S. Gray, K. P. Ishida and L. D. Nghiem (2017). "Role of
869 membrane fouling substances on the rejection of N-nitrosamines by reverse osmosis." Water
870 Research **118**: 187-195.

871 Gerrity, D., A. N. Pisarenko, E. Marti, R. A. Trenholm, F. Gerringer, J. Reungoat and E. Dickenson
872 (2015). "Nitrosamines in pilot-scale and full-scale wastewater treatment plants with ozonation."
873 Water Research **72**(Supplement C): 251-261.

874 Grant, S. B., J.-D. Saphores, D. L. Feldman, A. J. Hamilton, T. D. Fletcher, P. L. M. Cook, M.
875 Stewardson, B. F. Sanders, L. A. Levin, R. F. Ambrose, A. Deletic, R. Brown, S. C. Jiang, D. Rosso, W. J.
876 Cooper and I. Marusic (2012). "Taking the 'waste' out of 'wastewater' for human water security and
877 ecosystem sustainability." Science **337**(6095): 681-686.

878 Hollender, J., S. G. Zimmermann, S. Koepke, M. Krauss, C. S. McArdell, C. Ort, H. Singer, U. von
879 Gunten and H. Siegrist (2009). "Elimination of Organic Micropollutants in a Municipal Wastewater
880 Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration."
881 Environmental Science & Technology **43**(20): 7862-7869.

882 Huber, M. M., A. Göbel, A. Joss, N. Hermann, D. Löffler, C. S. McArdell, A. Ried, H. Siegrist, T. A.
883 Ternes and U. von Gunten (2005). "Oxidation of pharmaceuticals during ozonation of municipal
884 wastewater effluents: A pilot study." Environmental Science and Technology **39**(11): 4290-4299.

885 Hubner, U., U. von Gunten and M. Jekel (2015). "Evaluation of the persistence of transformation
886 products from ozonation of trace organic compounds - a critical review." Water Res **68**: 150-170.

887 Hunter_Water (2005). Water Quality Management: A multiple barrier approach. Hunter Water,
888 Newcastle, Australia.

889 Ipek, U. (2005). "Removal of Ni(II) and Zn(II) from an aqueous solution by reverse osmosis."
890 Desalination **174**: 161-169.

891 Isma, M. I. A., A. Idris, R. Omar and A. R. P. Razreena (2014). "Effects of SRT and HRT on Treatment
892 Performance of MBR and Membrane Fouling." International Journal of Chemical, Molecular,
893 Nuclear, Materials and Metallurgical Engineering **8**(6): 488-492.

894 Kadokami, K., K. Tanada, K. Taneda and K. Nakagawa (2005). "Novel gas chromatography–mass
895 spectrometry database for automatic identification and quantification of micropollutants." Journal
896 of Chromatography A **1089**(1): 219-226.

897 Kezia, K., J. Lee, A. J. Hill and S. E. Kentish (2013). "Convective transport of boron through a brackish
898 water reverse osmosis membrane." Journal of Membrane Science **445**(Supplement C): 160-169.

899 Kimura, K., S. Toshima, G. Amy and Y. Watanabe (2004). "Rejection of neutral endocrine disrupting
900 compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes." Journal of
901 Membrane Science **245**(1-2): 71-78.

902 Kiso, Y., Y. Sugiura, T. Kitao and K. Nishimura (2001). "Effects of hydrophobicity and molecular size
903 on rejection of aromatic pesticides with nanofiltration membranes." Journal of Membrane Science
904 **192**(1–2): 1-10.

905 Kovalova, L., H. Siegrist, H. Singer, A. Wittmer and C. S. McArdell (2012). "Hospital Wastewater
906 Treatment by Membrane Bioreactor: Performance and Efficiency for Organic Micropollutant
907 Elimination." Environmental Science & Technology **46**(3): 1536-1545.

908 Krauss, M., P. Longrée, F. Dorusch, C. Ort and J. Hollender (2009). "Occurrence and removal of N-
909 nitrosamines in wastewater treatment plants." Water Research **43**(17): 4381-4391.

910 Laydon., C. (2011). Critical control point analysis: the operational benefits. 36th Annual Qld Water
911 Industry Operations Workshop. Toowoomba Queensland Water Industry Operators Association
912 Australia 73-79.

913 Lee, C. O., K. J. Howe and B. M. Thomson (2012). "Ozone and biofiltration as an alternative to
914 reverse osmosis for removing PPCPs and micropollutants from treated wastewater." Water
915 Research **46**: 1005-1014.

916 Lei, Y., C. Zhonglin, S. Jimin, X. U. Zhenzhen, L. Heng, T. Jiayu, B. E. N. Yue, Z. Xu, S. H. I. Wenxin and
917 L. I. Guibai (2009). "Reinvestigation of the nitrosamine-formation mechanism during ozonation."
918 Environmental Science and Technology **43**(14): 5481-5487.

919 Malamis, S., E. Katsou, K. Takopoulos, P. Demetriou and M. Loizidou (2012). "Assessment of metal
920 removal, biomass activity and RO concentrate treatment in an MBR–RO system." Journal of
921 Hazardous Materials **209-210**: 1-8.

922 Margot, J., C. Kienle, A. Magnet, M. Weil, L. Rossi, L. F. de Alencastro, C. Abegglen, D. Thonney, N.
923 Chèvre, M. Schärer and D. A. Barry (2013). "Treatment of micropollutants in municipal wastewater:
924 Ozone or powdered activated carbon?" Science of The Total Environment **461**(Supplement C): 480-
925 498.

926 Mohsen-Nia, M., P. Montazeri and H. Modarress (2007). "Removal of Cu2+ and Ni2+ from
927 wastewater with a chelating agent and reverse osmosis processes." Desalination **217**: 276-281.

928 Nghiem, L. D., A. I. Schäfer and M. Elimelech (2004). "Removal of Natural Hormones by
929 Nanofiltration Membranes: Measurement, Modeling, and Mechanisms." Environmental Science &
930 Technology **38**(6): 1888-1896.

931 NHMRC and NRMMC (2011). Australian Drinking Water Guidelines. N. H. a. M. R. Council. Australia

932 NRMMC (2006). National Guidelines for Water Recycling: Managing Health and Environmental Risks
933 National Resource Management Ministerial Council, Australian Health Ministers Conference
934 Canberra, Australia.

935 NRMMC (2008). Australian guidelines for water recycling: Managing health and environmental risks
936 (Phase 2). Augmentation of drinking water supplies. Canberra, Australia, Environment Protection

937 and Heritage Council, the National Health and Medical Research Council and the Natural Resource
938 Management Ministerial Council.

939 Ozaki, H., K. Sharma and W. Saktaywin (2002). "Performance of an ultra-low-pressure reverse
940 osmosis membrane (ULPROM) for separating heavy metal: effects of interference parameters."
941 Desalination **144**: 287-294.

942 Radjenović, J., M. Petrović and D. Barceló (2009). "Fate and distribution of pharmaceuticals in
943 wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced
944 membrane bioreactor (MBR) treatment." Water Research **43**(3): 831-841.

945 Rakness, K. L., I. Najm, M. Elovitz, D. Rexing and S. Via (2005). "Cryptosporidium Log-inactivation
946 with Ozone Using Effluent CT10, Geometric Mean CT10, Extended Integrated CT10 and Extended
947 CSTR Calculations." Ozone: Science & Engineering **27**(5): 335-350.

948 Reif, R., S. Suárez, F. Omil and J. M. Lema (2008). "Fate of pharmaceuticals and cosmetic ingredients
949 during the operation of a MBR treating sewage." Desalination **221**(1): 511-517.

950 Ropkins, K., A. Ferguson and A. J. Beck (2003). "Development of hazard analysis by critical control
951 points (HACCP) procedures to control organic chemical hazards in the agricultural production of raw
952 food commodities." Critical Reviews in Food Science and Nutrition **43**(3): 287-316.

953 Royal Society of Chemistry. (2019). ""chemspider.com," "   Retrieved 5/02/2019, 2019, from
954 http://www.chemspider.com/.

955 Snyder, S. A., E. C. Wert, D. J. Rexing, R. E. Zegers and D. D. Drury (2006). "Ozone Oxidation of
956 Endocrine Disruptors and Pharmaceuticals in Surface Water and Wastewater." Ozone: Science &
957 Engineering **28**(6): 445-460.

958 Steinle-Darling, E., M. Zedda, M. H. Plumlee, H. F. Ridgway and M. Reinhard (2007). "Evaluating the
959 impacts of membrane type, coating, fouling, chemical properties and water chemistry on reverse
960 osmosis rejection of seven nitrosoalklyamines, including NDMA." Water Research **41**: 3959-3967.

961 Tadkaew, N., F. I. Hai, J. A. McDonald, S. J. Khan and L. D. Nghiem (2011). "Removal of trace
962 organics by MBR treatment: The role of molecular properties." Water Research **45**(8): 2439-2451.

963 Ternes, T. A., J. Stüber, N. Herrmann, D. McDowell, A. Ried, M. Kampmann and B. Teiser (2003).
964 "Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from
965 wastewater?" Water Research **37**(8): 1976-1982.

966 UN_WWAP (2017). The United Nations World Water Development Report 2017, Wastewater, the
967 untapped resource. Paris, UNESCO: pp. 198.

968 USEPA. (2018). "Long Term 2 Enhanced Surface Water Treatment Rule Documents." Drinking Water
969 Requirements for States and Public Water Systems   Retrieved 10/08/2018, 2018, from
970 https://www.epa.gov/dwreginfo/long-term-2-enhanced-surface-water-treatment-rule-documents.

971 WaterSecure (2017a). Ozone disinfection: WaterVal validation protocol Australian WaterSecure
972 Innovations Ltd, Brisbane, Australia.

973 WaterSecure (2017b). Reverse osmosis and nanofiltration, WaterVal validation protocol Australian
974 WaterSecure Innovations Ltd, Brisbane, Australia.

975 WaterSecure. (2018). "WaterVal validation protocols." Retrieved 10/08/2018, from
976 https://www.waterra.com.au/research/waterval/.

977 Wert, E. C., F. L. Rosario-Ortiz and S. A. Snyder (2009). "Effect of ozone exposure on the oxidation of
978 trace organic contaminants in wastewater." Water Research **43**(4): 1005-1014.

979 Wijekoon, K. C., T. Fujioka, J. A. McDonald, S. J. Khan, F. I. Hai, W. E. Price and L. D. Nghiem (2013a).
980 "Removal of N-nitrosamines by an aerobic membrane bioreactor." Bioresource Technology
981 **141**(Supplement C): 41-45.

982 Wijekoon, K. C., F. I. Hai, J. Kang, W. E. Price, W. Guo, H. H. Ngo and L. D. Nghiem (2013b). "The fate
983 of pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides during MBR
984 treatment." Bioresource Technology **144**(Supplement C): 247-254.

985 Zhang, J., M. C. Duke, K. Northcott, M. Packer, M. Allinson, G. Allinson, K. Kadokami, J. Tan, S. Allard,
986 J.-P. Croue, A. Knight, P. J. Scales and S. R. Gray (2017). "Small scale direct potable reuse (DPR)
987 project for a remote area." Water **9**(94): 1-25.

988 Zhang, J., A. Knight, M. Duke, K. Northcott, M. Packer, P. J. Scales and S. R. Gray (2016a). "A new
989 integrated potable reuse process for a small remote community in Antarctica." Safety Process and
990 Environment Protection **104**: 196-208.

991 Zhang, J., A. Knight, P. Scales, M. Packer, K. Northcott, J.-P. Croué, S. Allard, J. Tan and S. Gray
992 (2015). Demonstration of robust water recycling: Operating performance and water quality report,
993 Demonstration of robust water recycling (Project number 3170), Australian Water Recycling Centre
994 of Excellence, ISBN 978-1-922202-58-1.

995 Zhang, J., K. Northcott, M. Duke, P. J. Scales and S. R. Gray (2016b). "Influence of pre-treatment
996 combinations on RO membrane fouling." Desalination **393**: 120-126.

997 Zhang, J. H., M. Cran, K. Northcott, M. Packer, M. Duke, N. Milne, P. Scales, A. Knight and S. R. Gray
998 (2016c). "Assessment of pressure decay test for RO protozoa removal validation in remote
999 operations." Desalination **386**: 19-24.

1000

Highlights

- A critical control point approach for the removal of chemicals in water recycle is presented
- The critical control point approach is detailed for three barriers
- A combined chemical log reduction value credits approach is demonstrated for a multi-barrier plant

Editor

Water Research

Dear Editor

I confirm that the authors do not have a conflict of interest in presenting the work and that it is not been submitted elsewhere for publication.

Yours sincerely

Peter Scales