

Assessment of 265-nm UV-LED for direct photolysis and advanced oxidation of *N*-nitrosamines and 1,4-dioxane

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1 **Abstract**

2 The advanced oxidation process (AOP), using conventional low-pressure mercury (LP Hg)-
3 vapor UV lamps, forms a critical barrier for pathogens and contaminants of emerging concern
4 (CECs) in potable water reuse. In recent years, UV-light-emitting diode (UV-LED) has
5 attracted considerable attention as an alternative UV source because it has a long lifetime and
6 is mercury-free. This study assesses the effectiveness of 265-nm UV-LED in removal of
7 characteristic CECs, 1,4-dioxane (100 µg/L) and *N*-nitrosamines (500 ng/L), including *N*-
8 nitrosodimethylamine (NDMA), in recycled potable water. Direct photolysis using a UV-LED
9 lamp, at the maximum UV dose of 900 mJ/cm², achieved a maximum of 31% NDMA reduction,
10 as opposed to a 93% reduction by a conventional LP Hg UV lamp. We attributed this to the
11 higher emission wavelength of the UV-LED (265 nm) than that for the LP Hg UV lamp (254
12 nm). Both UV lamps failed to photolyze 1,4-dioxane. Using hydrogen peroxide or
13 monochloramine remarkably enhanced the effectiveness of the LP Hg UV-based AOP in
14 removing 1,4-dioxane, and the percentage of NDMA removed also increased slightly; however,
15 it did not improve the effectiveness of the UV-LED-based AOP. We conclude from this study
16 that despite the advantages of the UV-LED over the conventional LP Hg UV lamp, the former
17 performs ineffectively at attenuating major CECs in recycled water.

18 **Keywords:** 1,4-dioxane; NDMA; UV-LED; advanced oxidation process; potable reuse; CECs.

19 **1 Introduction**

20 Frequent droughts over the last 20 years have led to an increased use of purified wastewater
21 for augmenting drinking water supplies in many regions (WHO, 2017). The scheme of utilizing
22 recycled water as a sustainable water supply is referred to as potable reuse. Potable reuse is
23 based on subjecting secondary wastewater effluent to an advanced wastewater treatment train
24 that often includes microfiltration (MF), reverse osmosis (RO), and an advanced oxidation
25 process (AOP) (Gerrity et al., 2013). The United States of America and Australia have adopted
26 ultraviolet (UV)-based AOPs to achieve a certain level of reduction in the concentration of
27 pathogens and contaminants of emerging concern (CECs), both of which can permeate through
28 the RO process (Farré et al., 2011; Plumlee et al., 2008). The AOP usually consists of adding
29 hydrogen peroxide (H₂O₂) (3–5 mg/L) to the water, followed by photolysis using UV lamps
30 [e.g., low pressure (LP) or medium pressure (HP) mercury (Hg)-vapor-ultraviolet (UV) lamps
31 that emit monochromatic light at 254 nm or polychromatic light from 200 to 470 nm,
32 respectively] (Collins and Bolton, 2016).

33 AOP utilizes a strong oxidizing agent (e.g., hydroxyl radical, HO[•]) to degrade CECs (Deng and
34 Zhao, 2015). Other AOPs includes UV/free chlorine, UV/chloramines, and ozone/hydrogen
35 peroxide (Ikehata et al., 2006; Patton et al., 2018a; Zhang et al., 2019). In recent years, UV
36 light-emitting diodes (UV-LEDs), emitting at 265 to 285 nm, were found to be effective in
37 disinfecting wastewater, and are being increasingly tested as an alternative for LP Hg UV lamps
38 despite their polychromatic UV light emission (Hull et al., 2019; Nelson et al., 2013;
39 Nyangaresi et al., 2018; Song et al., 2016). As compared to traditional LP Hg UV lamps, UV-
40 LEDs have a shorter warm-up time and smaller footprint, whereas their capital cost can be
41 higher. The use of UV-LEDs for the removal of CECs in potable reuse has not yet been
42 explored.

43 Among the regulated CECs in potable reuse, 1,4-dioxane and *N*-nitrosodimethylamine
44 (NDMA) are two representative CECs that are designated to be degraded by the LP Hg UV-
45 based AOP. 1,4-Dioxane ($C_4H_8O_2$), an industrial solvent, can be found in treated wastewater
46 at concentrations up to 100 $\mu\text{g/L}$ (Mohr et al., 2010; Stepien et al., 2014), and the regulatory
47 level of 1,4-dioxane, for example, in California, USA, is 1 $\mu\text{g/L}$ (DDW/CAEPA, 2015). UV
48 irradiation is not very effective in degrading 1,4-dioxane—the degradation of 1,4-dioxane is
49 brought about by the hydroxyl radicals generated during the AOP (Ikehata et al., 2016; Kruithof
50 et al., 2007). Since 1,4-dioxane is one of the least degraded compounds by the UV-based AOP,
51 it has been used as a conservative surrogate indicator for the removal of other CECs. For
52 example, the State of California requires AOP in potable reuse to achieve a minimum of 0.5-
53 log (i.e., 68%) removal of 1,4-dioxane (SWRCB, 2015). Although the removal of 1,4-dioxane
54 by UV-based AOP has been extensively explored in drinking water treatment and potable reuse
55 (Ikehata et al., 2016; Patton et al., 2017; Zhang et al., 2019), the effectiveness of UV-LED
56 lamps in degrading 1,4-dioxane remains unknown.

57 The removal of NDMA, a disinfection by-product, by UV-based AOP is another concern in
58 potable reuse (Fujioka et al., 2017; Sgroi et al., 2018). The State of California has set a
59 notification level of 10 $\mu\text{g/L}$ for NDMA in drinking water (DDW/CAEPA, 2015). NDMA is
60 present in raw wastewater and is also formed during the chloramination process preceding the
61 RO process, and therefore the RO feed often has more than 20 ng/L of NDMA (Hatt et al.,
62 2013). Since NDMA is poorly rejected by RO membranes ($< 50\%$), concentration of NDMA
63 in the inflow of AOP (i.e., the RO process permeate) can be higher than its target value (10
64 ng/L). NDMA has an absorbance maximum at 227 nm—it is readily photolyzed by
65 wavelengths shorter than 260 nm (Lee et al., 2005; Sharpless and Linden, 2003). Therefore,
66 H_2O_2 dosing prior to UV irradiation barely enhances the degradation of NDMA (Collins and
67 Bolton, 2016). In recent years, chloramine has been tested as an alternative for H_2O_2 for

68 increasing the efficiency of LP Hg UV-based AOP in degrading NDMA (Chuang et al., 2017;
69 Patton et al., 2018b). Till date, there has been no study to determine the effectiveness of UV-
70 LEDs in degrading NDMA, either by direct photolysis or with the assistance of oxidizing
71 agents like H₂O₂ and chloramine.

72 This study evaluates the efficiency of a UV-LED lamp unit, with an emission peak at 265 nm
73 (265-nm UV-LED), towards the removal of 1,4-dioxane and four *N*-nitrosamines (including
74 NDMA) and compares it with that of a conventional LP Hg UV lamp unit. The evaluations
75 were conducted using a laboratory scale continuous treatment system. To the best of our
76 knowledge, this is the first-of-its-kind study that assesses the performance of a 265-nm UV-
77 LED for removal of 1,4-dioxane and NDMA—two major CECs in potable reuse.

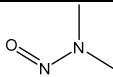
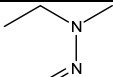
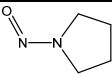
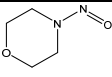
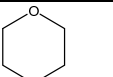
78 **2 Materials and methods**

79 **2.1 Chemicals**

80 Four *N*-nitrosamines—*N*-nitrosodimethylamine (NDMA), *N*-nitrosomethylamine
81 (NMEA), *N*-nitrosopyrrolidine (NPYR) and *N*-nitrosomorpholine (NMOR)—were purchased
82 from Agilent (Santa Clara, CA, USA) (**Table 1**). 1,4-Dioxane was purchased from Wako Pure
83 Chemical Industries (Osaka, Japan). Stock solutions (1 mg/L) of each of the above compounds
84 were prepared in pure methanol. Hydrogen peroxide (H₂O₂) solution (30% (w/w)), ammonium
85 chloride (NH₄Cl), sodium hypochlorite (NaOCl), and sodium bisulfite were purchased from
86 FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). A 400 mg/L monochloramine
87 (NH₂Cl) stock solution was prepared by mixing NH₄Cl solution with a solution containing
88 NaOCl and NaOH in pure water obtained from a water purification system (Mega Unity,
89 Organo; Tokyo, Japan). A 400 mg/L H₂O₂ stock solution was also prepared in pure water. RO-
90 treated wastewater (pH = 6.0) was prepared by passing the activated sludge effluent collected

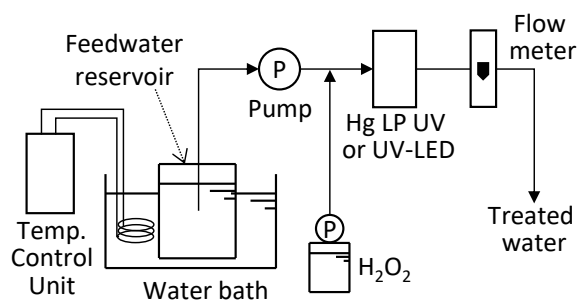
91 at a wastewater treatment plant through a 4-inch RO membrane (ESPA2, Hydranautics:
 92 Oceanside, CA, USA).

93 **Table 1** – Properties of the selected compounds.

	NDMA	NMEA	NPYR	NMOR	1,4-dioxane
Structure					
Formula	C ₂ H ₆ N ₂ O	C ₃ H ₈ N ₂ O	C ₄ H ₈ N ₂ O	C ₄ H ₈ N ₂ O ₂	C ₄ H ₈ O ₂

94 **2.2 Online UV treatment systems**

95 This study used a 2.0-W 265-nm UV-LED lamp unit (Toshiba Lighting & Technology
 96 Corporation; Yokosuka, Japan) and a 6.7 W unit with a low-pressure mercury vapor UV lamp
 97 (US/30F150/R3, Stanley Electric; Tokyo, Japan). While the LP Hg UV lamp has a
 98 monochromatic emission at a wavelength of 254 nm, the UV-LED lamp has a broader emission,
 99 with a peak at 265 nm and a full width at half maximum of approximately 13 nm. A bench-
 100 scale UV treatment system with a continuous flow configuration included the LP Hg UV or
 101 UV-LED lamp unit, a smooth-flow pump for feeding the solution (Q-100, Tacmina, Osaka,
 102 Japan), an adjustable flow pump for dosing H₂O₂ or monochloramine (KP-12, FLOM, Tokyo,
 103 Japan), 1/16 in. polytetrafluoroethylene (PTFE) tubes, a flow meter, a temperature circulator
 104 (Thermax TM-1A, AS ONE; Osaka, Japan), and a 5 L glass reservoir with a stainless steel heat
 105 exchanging coil connected to a temperature control unit (NCB-500, Tokyo Rikakikai, Tokyo,
 106 Japan) (**Fig. 1**). Water temperature was controlled at 20 ± 0.5 °C.



107
 108 **Fig. 1** – Schematic diagram of UV treatment system equipped with low-pressure mercury (LP
 109 Hg)-vapor-UV or UV-light-emitting diode (LED) lamp.

110 2.3 Test protocols

111 The stock solutions were used to obtain 500 ng/L and 100 µg/L *N*-nitrosamines and 1,4-dioxane,
112 respectively, in the RO feedwater. The dose of UV irradiation, which was determined based on
113 UV transmittance for clean water (98%) and UV dose simulation data, was incrementally
114 increased from zero to 900 mJ/cm². The power output of the 265-nm UV-LED lamp unit was
115 controlled by adjusting the amount current supplied using a variable power supply unit. For the
116 tests using the UV-LED lamp unit, the flow-rates of the feedwater and the chemical solution
117 (H₂O₂ or pure water) were maintained constant at 9.5 mL/min and 0.5 mL/min, respectively.
118 In contrast to the UV-LED, the power output of the LP Hg UV unit could only be adjusted to
119 full (24 V) or half (12 V) capacity. Therefore, the desired UV doses (ranging from 0 to 900
120 mJ/cm²) were achieved by incrementally changing the flow-rate of the feedwater (13.2 mL/min
121 to 79.2 mL/min) and the chemical solution (H₂O₂, monochloramine, or pure water; 0.69
122 mL/min to 4.2 mL/min). The output of the LP Hg UV lamp fixed at 50%. The flowrates were
123 adjusted to maintain the percentage of the chemical solution in the feed solution at 5%. Upon
124 changing operating conditions, sample collection was done only after a 10-min stabilization
125 period. UV-treated samples were collected in 1.5 mL amber vials (for *N*-nitrosamine analysis)
126 or 50 mL amber bottles (for 1,4-dioxane analysis). Immediately after sample collection, 5 mM
127 sodium sulfite solution was added to the vials to quench residual hydrogen peroxide or
128 monochloramine. The degradation rate, *k*, was calculated as follows:

$$129 \quad k = \frac{\ln\left(\frac{C_t}{C_0}\right)}{E_{UV,t}} \quad (1)$$

130 Where, *C*₀ is the initial concentration, *C*_{*t*} is concentration at time *t*, and *E*_{*UV,t*} is the UV dose at
131 time *t*.

132 **2.4 Analytical techniques**

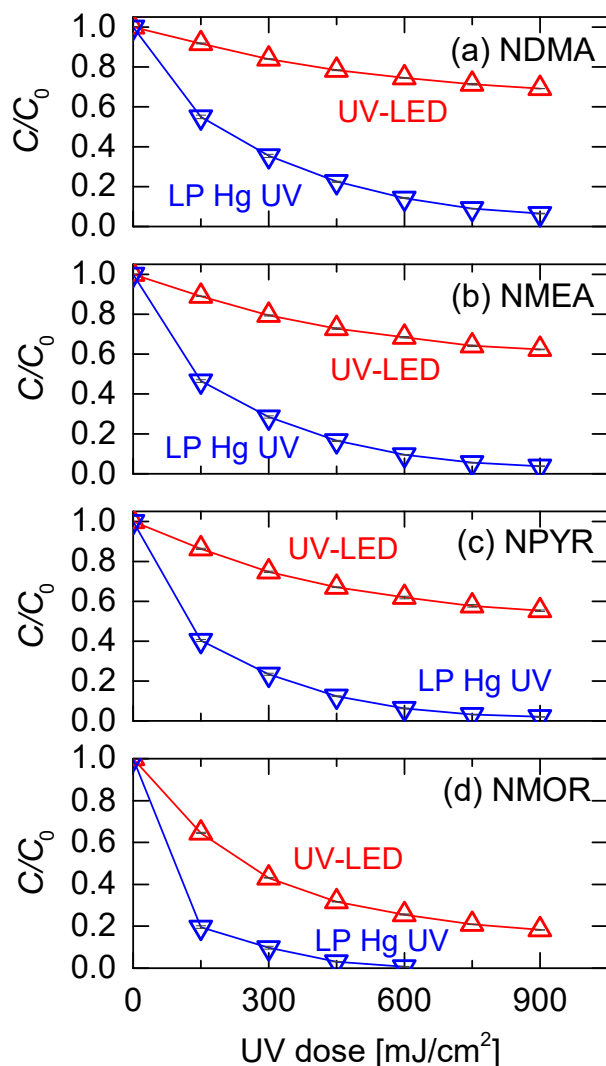
133 Concentrations of the four *N*-nitrosamines were determined using high-performance liquid
134 chromatography followed by photochemical reaction and chemiluminescence (HPLC-PR-CL)
135 (Kodamatani et al., 2018; Kodamatani et al., 2009). The method detection limits for NDMA,
136 NMEA, NPYR, and NMOR were 0.40 ng/L, 0.54 ng/L, 0.60 ng/L, and 1.4 ng/L, respectively.
137 Concentrations of 1,4-dioxane were determined by headspace-gas chromatography-mass
138 spectrometry (HG-GC/MS) using a GCMS-QP2010 SE system combined with a HS-20
139 headspace sampler (Shimadzu, Kyoto, Japan) and an Rtx-624 capillary column (60 m × 0.32
140 mm ID; film thickness 1.8 μm; Restek, PA, USA). 1,4-Dioxane-d₈ was used as the surrogate
141 standard. The method detection limit for 1,4-dioxane was 10 μg/L. Monochloramine
142 concentrations were determined using a portable colorimeter (DR900, Hach, Loveland, CO,
143 USA) with Monochlor F reagent pillows. Hydrogen peroxide concentrations were determined
144 using a portable colorimeter (DPM2-H₂O₂, Kyoritsu Chemical-Check Lab, Tokyo, Japan)
145 with reagent pillows. UV absorption spectra of *N*-nitrosamines, 1,4-dioxane, hydrogen
146 peroxide, and monochloramine were obtained using a spectrophotometer (V-730, Jasco; Tokyo,
147 Japan).

148 **3 Results and discussions**

149 **3.1 Direct photolysis**

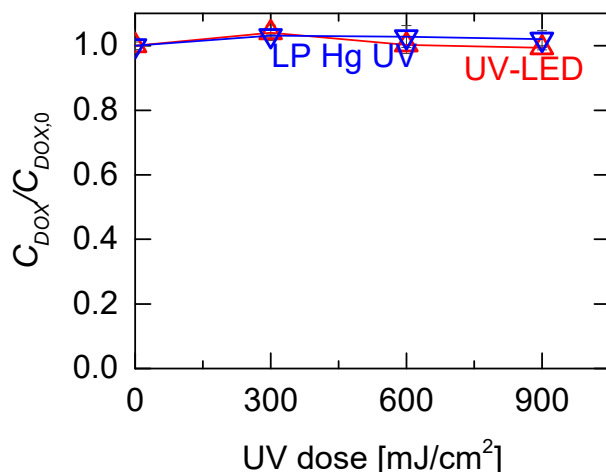
150 The LP Hg UV lamp was found to be more effective at photolyzing *N*-nitrosamines than the
151 265 nm UV-LED. In case of the LP Hg UV lamp, increasing the UV dose from zero to 900
152 mJ/cm² progressively reduced the NDMA content; 91% of NDMA was removed at a UV dose
153 of 750 mJ/cm² (**Fig. 2a**), and 93% was removed at the maximum dose of 900 mJ/cm². The
154 results indicate a marginal increase in NDMA removal efficiency can be obtained at UV doses
155 above 750 mJ/cm². The energy requirement of LP Hg UV for achieving 90% reduction of

156 NDMA is consistent with previous studies (Mezyk et al., 2004; Sharpless and Linden, 2003).
157 In addition, we determined the degradation rate of NDMA using LP Hg UV to be 3×10^{-3}
158 cm^2/mJ , which is similar to the value determined in a previous study ($2.6 \times 10^{-3} \text{cm}^2/\text{mJ}$) (Velo-
159 Gala et al., 2019). The results indicate that the data obtained in this study using the online LP
160 Hg UV treatment system are comparable to previous studies in terms of NDMA removal
161 performance. The percentage reduction was higher for the other three *N*-nitrosamines (NMEA,
162 NPYR, and NMOR), but their degradation also showed a similar dependence on UV dosage
163 (**Fig. 2b-d**). The UV-LED was not as effective at degrading NDMA. For example, at the
164 highest UV dose of $900 \text{mJ}/\text{cm}^2$, UV-LED achieved only 31% reduction of NDMA (**Fig. 2a**).
165 The percentage reduction of the other three *N*-nitrosamines (NMEA, NPYR, and NMOR) was
166 also lower than that by LP Hg UV (**Fig. 2b-d**). The higher-molecular-weight compounds were
167 found to be degraded to a greater extent.



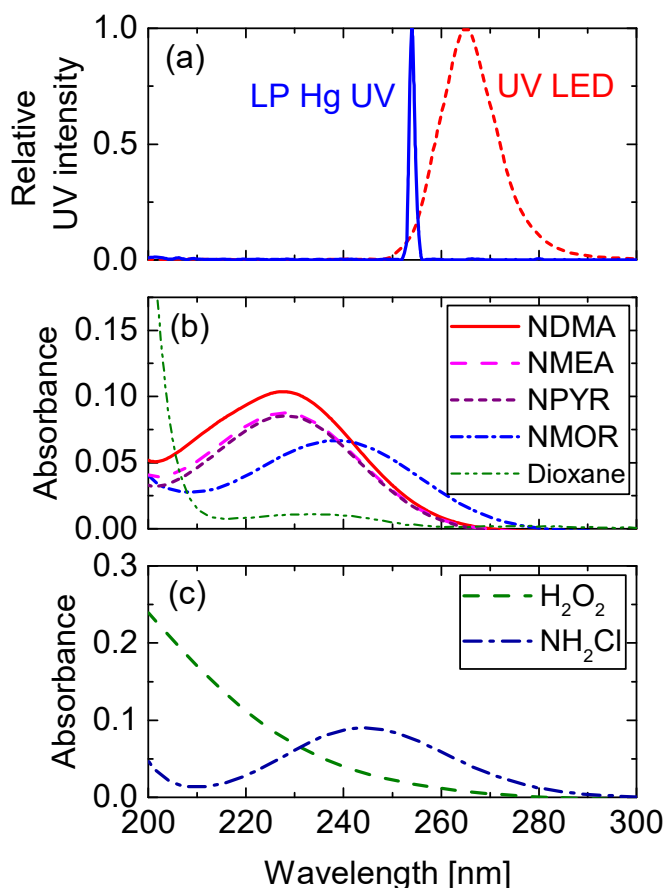
168
 169 **Fig. 2** – Degradation of the four *N*-nitrosamines by direct photolysis (using 265-nm UV-LED
 170 or LP Hg UV) as a function of UV dose.

171 Compared to the *N*-nitrosamines, 1,4-dioxane was very resistant towards direct photolysis by
 172 LP Hg UV or UV-LED—almost no change in its concentration was observed even at the
 173 highest UV dose of 900 mJ/cm^2 (**Fig. 3**). The results indicate that direct photolysis is not
 174 effective at degrading 1,4-dioxane, which is consistent with previous studies (Kruithof et al.,
 175 2007; Lee et al., 2020).



176
 177 **Fig. 3** – Degradation of 1,4-dioxane (DOX) by direct photolysis (using 265-nm UV-LED or
 178 LP Hg UV) as a function of UV dose.

179 The reasons for the low efficiency of 265-nm UV-LED lamp as compared to LP Hg UV lamp
 180 were further explored based on their respective emission spectra and the absorption spectra of
 181 the contaminants, since the photolysis of target chemicals occurs when they absorb the
 182 wavelengths provided by the UV lamps. The LP Hg UV has sharp emission peak at 254 nm,
 183 whereas the UV-LED has a broad emission centered at 265 nm (**Fig. 4a**). Thus, UV-LED would
 184 be more efficient at photolyzing chemicals that absorb at wavelengths larger than 260 nm.
 185 However, *N*-nitrosamines, including NDMA, absorb wavelengths shorter than 240 nm; they
 186 have a lower absorbance at higher wavelengths (**Fig. 4b**). *N*-nitrosamines absorb the LP Hg
 187 UV emission better than that the UV-LED emission, and therefore the former will be more
 188 efficient at photolyzing the *N*-nitrosamines than the latter, which is in line with the observations
 189 of this study (**Fig. 2**). In contrast to *N*-nitrosamines, 1,4-dioxane does not absorb wavelengths
 190 larger than 250 nm (**Fig. 4b**). The results indicate that direct photolysis of 1,4-dioxane is
 191 ineffective with either the LP Hg UV or the UV-LED lamp.

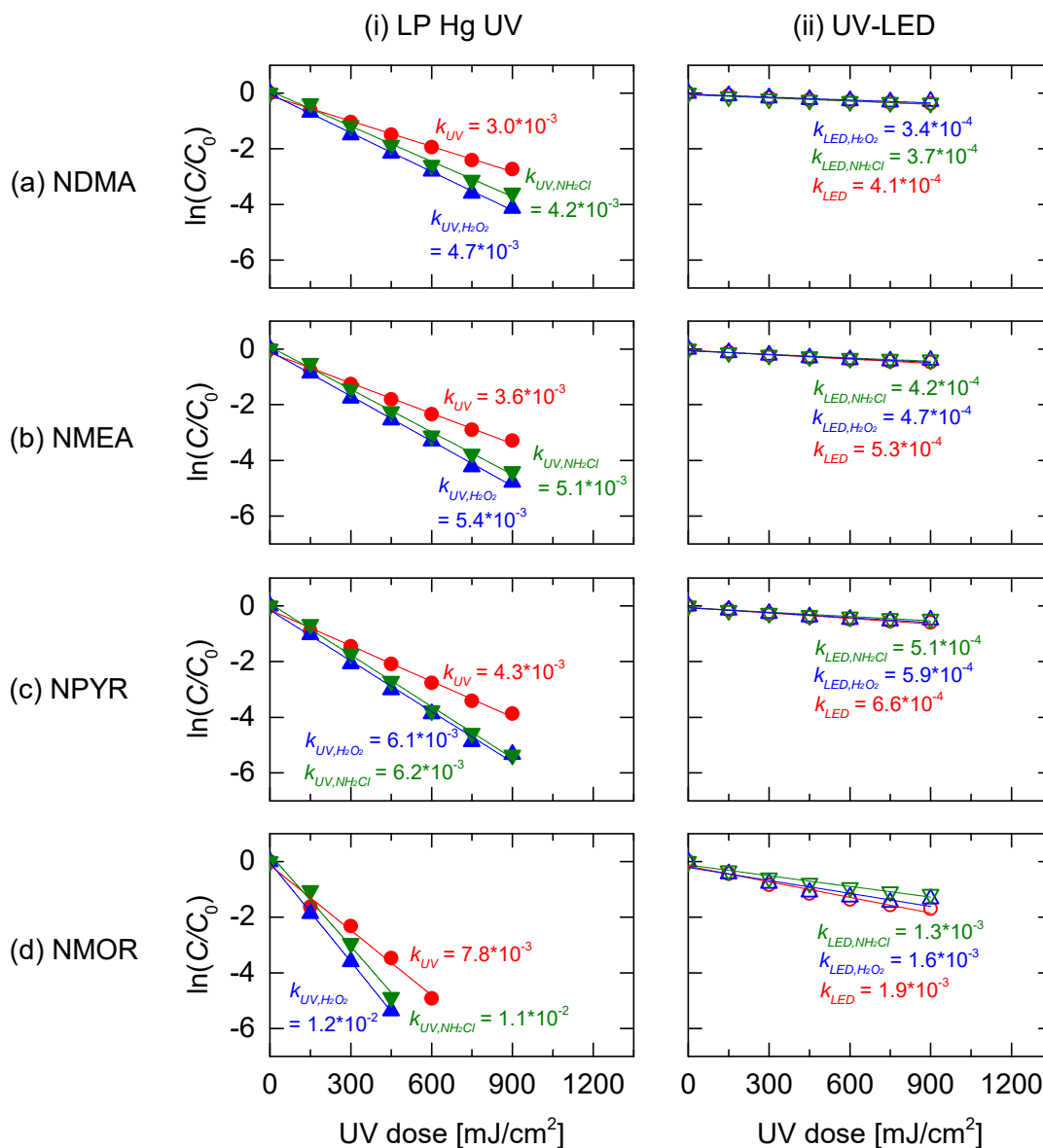


192
 193 **Fig. 4** – (a) Relative UV intensity of the LP Hg UV and 265-nm UV-LED lamps, and UV
 194 absorption spectra of (b) *N*-nitrosamines (1 mg/L for each compound) and 1,4-dioxane (1,000
 195 mg/L), and (c) hydrogen peroxide (H₂O₂; 30 mg/L) and monochloramine (NH₂Cl; 6.7 mg/L).

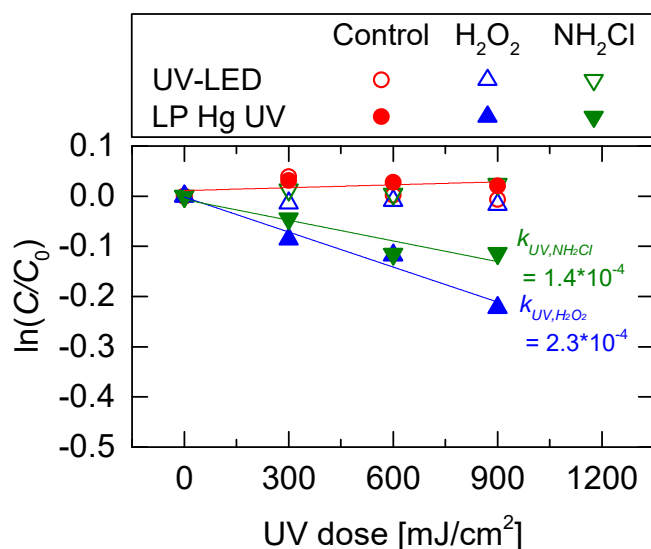
196 **3.2 Advanced oxidation**

197 Advanced oxidation using the LP Hg UV lamp and H₂O₂ or NH₂Cl generally enhanced the
 198 degradation of *N*-nitrosamines compared with direct photolysis alone. Both H₂O₂ and NH₂Cl
 199 absorb 254-nm emission of the LP Hg UV lamp, (**Fig. 4c**) thus photolyzing to give hydroxyl
 200 radicals can be formed with the LP Hg UV unit. The degradation constant of NDMA by the
 201 LP Hg UV-based AOP using H₂O₂ or NH₂Cl was 4.2×10^{-3} or 4.7×10^{-3} cm²/mJ,
 202 respectively—this is higher than the control (3.0×10^{-3} cm²/mJ) (**Fig. 5a**). Similar improvement
 203 was also observed in the degradation of the other three *N*-nitrosamines (**Fig. 5b-d**). The
 204 degradation constants of *N*-nitrosamines were generally similar for the AOPs with H₂O₂ or
 205 NH₂Cl, however the degradation constant of NDMA was greater for AOP with H₂O₂ than the

206 AOP with NH_2Cl . We note that this enhancement can depend on the water quality or operating
 207 conditions. Like *N*-nitrosamines, the degradation of 1,4-dioxane was similarly enhanced (**Fig.**
 208 **6**). The effectiveness of the AOP with H_2O_2 was greater than that with NH_2Cl , which is
 209 consistent with a previous study (Zhang et al., 2019). Overall, the results indicate that the
 210 hydroxyl radicals formed from H_2O_2 or NH_2Cl can slightly enhance the degradation of both *N*-
 211 nitrosamines and 1,4-dioxane.



212
 213 **Fig. 5** – Degradation of *N*-nitrosamines by AOP with (i) LP Hg UV or (ii) 265-nm UV-LED
 214 and hydrogen peroxide (H_2O_2 ; 20 mg/L) or monochloramine (NH_2Cl ; 20 mg/L) as a function
 215 of UV dose. Control values are those achieved by direct photolysis.



216
 217 **Fig. 6** – Degradation of 1,4-dioxane by AOP with 265-nm UV-LED and LP Hg UV and
 218 hydrogen peroxide (H₂O₂; 20 mg/L) or monochloramine (NH₂Cl; 20 mg/L) as a function of
 219 UV dose. Control values are those achieved by direct photolysis.

220 In contrast to the LP Hg UV, the 265-nm UV-LED is not as effective at photolyzing H₂O₂ or
 221 NH₂Cl into hydroxyl radicals, since both H₂O₂ and NH₂Cl have low absorbance at wavelengths
 222 larger than 254 nm (**Fig. 4c**). Therefore, the enhancement of degradation of contaminants due
 223 to H₂O₂ or NH₂Cl is also expected to be lower for the UV-LED-based AOP. The UV-LED-
 224 based AOP with H₂O₂ or NH₂Cl showed no improvement over direct photolysis in the
 225 degradation of *N*-nitrosamines. The degradation constants of NDMA by the UV-LED-based
 226 AOPs with H₂O₂ and NH₂Cl were $4.4 \times 10^{-4} \text{ cm}^2/\text{mJ}$ and $3.7 \times 10^{-4} \text{ cm}^2/\text{mJ}$, respectively, which
 227 are lower than that by direct photolysis ($3.0 \times 10^{-4} \text{ cm}^2/\text{mJ}$) (**Fig. 5a**). Similar observations
 228 were made for the other three *N*-nitrosamines (**Fig. 5b-d**). This indicates that the absorption of
 229 photons by H₂O₂ or NH₂Cl molecules inhibited the direct photolysis of the *N*-nitrosamines.
 230 Similarly, the addition of H₂O₂ or NH₂Cl led to no enhancement in 1,4-dioxane degradation as
 231 compared to direct photolysis (**Fig. 6**). This indicates that UV-LED is not suitable for the
 232 advanced oxidation of 1,4-dioxane with H₂O₂ or NH₂Cl. It is noted that 1,4-dioxane
 233 degradation may be enhanced by using hypochlorite (^oCl) ions as the auxiliary agent since

234 hypochlorite ions have a higher quantum yield and absorb at a higher wavelength of 292 nm
235 (Gao et al., 2019).

236 **3.3 Limitations and implications**

237 The results of this study show that degradation of *N*-nitrosamines and 1,4-dioxane by direct
238 photolysis and AOP is less effective with the 265-nm UV-LED lamp than with the conventional
239 LP Hg UV. The lower efficiency of the UV-LED lamp indicates that a higher UV dose (i.e.,
240 power input) is required to achieve the efficiency of conventional LP Hg UV lamps. UV-LED
241 is superior to LP Hg UV in terms of safety (mercury-free) and lifetime (Autin et al., 2013; Song
242 et al., 2016). Therefore, the feasibility of UV-LED for CEC removal should be based on types
243 of target contaminants, evaluation of capital and operating costs, and environmental impact.
244 Those CECs that absorb around the emission wavelength of the UV-LED, such as ciprofloxacin
245 and microcystin-LR, could be effectively attenuated by UV-LED photolysis or UV-LED-based
246 AOP (Liu et al., 2017; Matafonova and Batoev, 2018; Ou et al., 2016). A major challenge for
247 the UV-LED technology tested in this study was that its UV emission wavelength (265 nm)
248 did not match the UV absorption of target contaminants (*N*-nitrosamines) or that of H₂O₂ and
249 NH₂Cl (**Fig. 4**). Shorter UV wavelengths are preferable for the removal of *N*-nitrosamines
250 (Sakai et al., 2012). Therefore, development of UV-LEDs that emit at shorter UV wavelengths
251 (≤ 254 nm) could improve their efficiency in photolyzing *N*-nitrosamines. In addition, UV-
252 LEDs emitting at shorter wavelengths could enhance the formation of hydroxyl radicals from
253 H₂O₂ or NH₂Cl, which in turn would help degrade 1,4-dioxane. Another method of improving
254 the UV-LED AOP is by using hypochlorite ions instead of H₂O₂ or NH₂Cl along with the 285-
255 nm emitting UV-LED (Carra et al., 2020; Gao et al., 2020). However, *N*-nitrosamine photolysis
256 would be very limited at 285 nm. Moreover, the UV/chlorine AOP is very complex—it could
257 lead to formation of additional disinfection by-products (Gao et al., 2019; Reckhow et al., 2010;

258 Wang et al., 2015)—and may not be suitable for application in the final polishing step of the
259 potable reuse scheme. Overall, the development of UV-LED lamps that emit shorter UV
260 wavelengths UV light could make LEDs a viable alternative to LP Hg UV lamps in full-scale
261 AOPs in potable reuse (i.e., RO post-treatment).

262 **4 Conclusions**

263 The effectiveness of 265-nm UV-LED in degrading *N*-nitrosamines and 1,4-dioxane was
264 evaluated and compared with that of LP Hg UV lamp. The degradation of *N*-nitrosamines by
265 direct photolysis with UV-LED or LP Hg UV increased with increasing UV dose. However,
266 UV-LED was less efficient than LP Hg UV. Almost no removal of 1,4-dioxane was achieved
267 by direct photolysis using either UV-LED or LP Hg UV. These trends were well explained by
268 the UV emission wavelengths of the UV lamps and the UV absorbance range of *N*-nitrosamines
269 and 1,4-dioxane. While the addition of H₂O₂ or NH₂Cl resulted in enhanced efficiency of LP
270 Hg UV-based AOP towards degradation of *N*-nitrosamines and 1,4-dioxane, it led to a
271 negligible change in case of UV-LED-based AOP. The results of this study indicate that the
272 conventional LP Hg UV is better than the 265-nm UV-LED in terms of degradation of *N*-
273 nitrosamines and 1,4-dioxane. In conclusion, development of LEDs that emit shorter UV
274 wavelengths is required for the UV-LED technology to be applied in potable reuse.

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278 **6 REFERENCES**

279 Autin, O., Romelot, C., Rust, L., Hart, J., Jarvis, P., MacAdam, J., Parsons, S.A., Jefferson, B.,
280 2013. Evaluation of a UV-light emitting diodes unit for the removal of micropollutants in water
281 for low energy advanced oxidation processes. *Chemosphere* 92(6), 745-751.

- 282 Carra, I., Fernandez Lozano, J., Autin, O., Bolton, J.R., Jarvis, P., 2020. Disinfection by-
283 product formation during UV/Chlorine treatment of pesticides in a novel UV-LED reactor at
284 285 nm and the mitigation impact of GAC treatment. *Sci. Total Environ.* 712, 136413.
- 285 Chuang, Y.-H., Chen, S., Chinn, C.J., Mitch, W.A., 2017. Comparing the UV/Monochloramine
286 and UV/Free Chlorine Advanced Oxidation Processes (AOPs) to the UV/Hydrogen Peroxide
287 AOP Under Scenarios Relevant to Potable Reuse. *Environ. Sci. Technol.* 51(23), 13859-13868.
- 288 Collins, J., Bolton, J.R., 2016. *Advanced oxidation handbook*. American Water Works
289 Association.
- 290 DDW/CAEPA, 2015. *N-Nitrosodimethylamine (NDMA) Notification Level*
291 (<http://www.waterboards.ca.gov>). Division of Drinking Water, State Water Resources Control
292 Board, California Environmental Protection Agency (accessed 1 November 2017).
- 293 Deng, Y., Zhao, R., 2015. Advanced oxidation processes (AOPs) in wastewater treatment.
294 *Current Pollution Reports* 1(3), 167-176.
- 295 Farré, M.J., Döderer, K., Hearn, L., Poussade, Y., Keller, J., Gernjak, W., 2011. Understanding
296 the operational parameters affecting NDMA formation at Advanced Water Treatment Plants.
297 *J. Hazard. Mater.* 185(2-3), 1575-1581.
- 298 Fujioka, T., Masaki, S., Kodamatani, H., Ikehata, K., 2017. Degradation of N-
299 Nitrosodimethylamine by UV-Based Advanced Oxidation Processes for Potable Reuse: a Short
300 Review. *Current Pollution Reports* 3(2), 79-87.
- 301 Gao, Z.-C., Lin, Y.-L., Xu, B., Xia, Y., Hu, C.-Y., Zhang, T.-Y., Cao, T.-C., Chu, W.-H., Gao,
302 N.-Y., 2019. Effect of UV wavelength on humic acid degradation and disinfection by-product
303 formation during the UV/chlorine process. *Water Res.* 154, 199-209.
- 304 Gao, Z.-C., Lin, Y.-L., Xu, B., Xia, Y., Hu, C.-Y., Zhang, T.-Y., Cao, T.-C., Pan, Y., Gao, N.-
305 Y., 2020. A comparison of dissolved organic matter transformation in low pressure ultraviolet
306 (LPUV) and ultraviolet light-emitting diode (UV-LED)/chlorine processes. *Sci. Total Environ.*
307 702, 134942.
- 308 Gerrity, D., Pecson, B., Trussell, R.S., Trussell, R.R., 2013. Potable reuse treatment trains
309 throughout the world. *J. Water Supply Res Technol.-Aqua* 62(6), 321-338.
- 310 Hatt, J.W., Lamy, C., Germain, E., Tupper, M., Judd, S.J., 2013. NDMA formation in
311 secondary wastewater effluent. *Chemosphere* 91(1), 83-87.
- 312 Hull, N.M., Herold, W.H., Linden, K.G., 2019. UV LED water disinfection: Validation and
313 small system demonstration study. *AWWA Water Science* 1(4), e1148.
- 314 Ikehata, K., Jodeiri Naghashkar, N., Gamal El-Din, M., 2006. Degradation of Aqueous
315 Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review. *Ozone: Science*
316 *& Engineering* 28(6), 353-414.
- 317 Ikehata, K., Wang-Staley, L., Qu, X., Li, Y., 2016. Treatment of Groundwater Contaminated
318 with 1,4-Dioxane, Tetrahydrofuran, and Chlorinated Volatile Organic Compounds Using
319 Advanced Oxidation Processes. *Ozone: Science & Engineering* 38(6), 413-424.

- 320 Kodamatani, H., Roback, S.L., Plumlee, M.H., Ishida, K.P., Masunaga, H., Maruyama, N.,
321 Fujioka, T., 2018. An inline ion-exchange system in a chemiluminescence-based analyzer for
322 direct analysis of N-nitrosamines in treated wastewater. *J. Chromatogr. A* 1553, 51-56.
- 323 Kodamatani, H., Yamazaki, S., Saito, K., Amponsaa-Karikari, A., Kishikawa, N., Kuroda, N.,
324 Tomiyasu, T., Komatsu, Y., 2009. Highly sensitive method for determination of N-
325 nitrosamines using high-performance liquid chromatography with online UV irradiation and
326 luminol chemiluminescence detection. *J. Chromatogr. A* 1216(1), 92-98.
- 327 Kruithof, J.C., Kamp, P.C., Martijn, B.J., 2007. UV/H₂O₂ treatment: A practical solution for
328 organic contaminant control and primary disinfection. *Ozone: Science & Engineering: The*
329 *Journal of the International Ozone Association* 29(4), 273 - 280.
- 330 Lee, C.-S., Venkatesan, A.K., Walker, H.W., Gobler, C.J., 2020. Impact of groundwater quality
331 and associated byproduct formation during UV/hydrogen peroxide treatment of 1,4-dioxane.
332 *Water Res.* 173, 115534.
- 333 Lee, C., Choi, W., Kim, Y.G., Yoon, J., 2005. UV photolytic mechanism of N-
334 Nitrosodimethylamine in water: Dual pathways to methylamine versus dimethylamine.
335 *Environ. Sci. Technol.* 39(7), 2101-2106.
- 336 Liu, J., Ye, J.-s., Ou, H.-s., Lin, J., 2017. Effectiveness and intermediates of microcystin-LR
337 degradation by UV/H₂O₂ via 265 nm ultraviolet light-emitting diodes. *Environ. Sci. Pollut. R.*
338 24(5), 4676-4684.
- 339 Matafonova, G., Batoev, V., 2018. Recent advances in application of UV light-emitting diodes
340 for degrading organic pollutants in water through advanced oxidation processes: A review.
341 *Water Res.* 132, 177-189.
- 342 Mezyk, S., Cooper, W., Madden, K., Bartels, D., 2004. Free radical destruction of N-
343 nitrosodimethylamine in water. *Environ. Sci. Technol.* 38(11), 3161-3167.
- 344 Mohr, T.K.G., Stickney, J.A., DiGuseppi, W.H., 2010. *Environmental Investigation and*
345 *Remediation: 1,4-Dioxane and other Solvent Stabilizers.* CRC Press, Boca Raton.
- 346 Nelson, K.Y., McMartin, D.W., Yost, C.K., Runtz, K.J., Ono, T., 2013. Point-of-use water
347 disinfection using UV light-emitting diodes to reduce bacterial contamination. *Environ. Sci.*
348 *Pollut. R.* 20(8), 5441-5448.
- 349 Nyangaresi, P.O., Qin, Y., Chen, G., Zhang, B., Lu, Y., Shen, L., 2018. Effects of single and
350 combined UV-LEDs on inactivation and subsequent reactivation of *E. coli* in water disinfection.
351 *Water Res.* 147, 331-341.
- 352 Ou, H.-s., Ye, J.-s., Ma, S., Wei, C.-h., Gao, N.-y., He, J.-z., 2016. Degradation of ciprofloxacin
353 by UV and UV/H₂O₂ via multiple-wavelength ultraviolet light-emitting diodes: Effectiveness,
354 intermediates and antibacterial activity. *Chem. Eng. J.* 289, 391-401.
- 355 Patton, S., Li, W., Couch, K.D., Mezyk, S.P., Ishida, K.P., Liu, H., 2017. Impact of the
356 Ultraviolet Photolysis of Monochloramine on 1,4-Dioxane Removal: New Insights into Potable
357 Water Reuse. *Environ. Sci. Technol. Letters* 4(1), 26-30.

- 358 Patton, S., Romano, M., Naddeo, V., Ishida, K.P., Liu, H., 2018a. Photolysis of Mono- and
359 Dichloramines in UV/Hydrogen Peroxide: Effects on 1,4-Dioxane Removal and Relevance in
360 Water Reuse. *Environ. Sci. Technol.*
- 361 Patton, S., Romano, M., Naddeo, V., Ishida, K.P., Liu, H., 2018b. Photolysis of Mono- and
362 Dichloramines in UV/Hydrogen Peroxide: Effects on 1,4-Dioxane Removal and Relevance in
363 Water Reuse. *Environ. Sci. Technol.* 52(20), 11720-11727.
- 364 Plumlee, M.H., López-Mesas, M., Heidlberger, A., Ishida, K.P., Reinhard, M., 2008. N-
365 nitrosodimethylamine (NDMA) removal by reverse osmosis and UV treatment and analysis
366 via LC-MS/MS. *Water Res.* 42(1-2), 347-355.
- 367 Reckhow, D.A., Linden, K.G., Kim, J., Shemer, H., Makdissy, G., 2010. Effect of UV
368 treatment on DBP formation. *J. AWWA* 102(6), 100-113.
- 369 Sakai, H., Takamatsu, T., Kosaka, K., Kamiko, N., Takizawa, S., 2012. Effects of wavelength
370 and water quality on photodegradation of *N*-Nitrosodimethylamine (NDMA). *Chemosphere*
371 89(6), 702-707.
- 372 Sgroi, M., Vagliasindi, F.G.A., Snyder, S.A., Roccaro, P., 2018. N-Nitrosodimethylamine
373 (NDMA) and its precursors in water and wastewater: A review on formation and removal.
374 *Chemosphere* 191, 685-703.
- 375 Sharpless, C.M., Linden, K.G., 2003. Experimental and model comparisons of low- and
376 medium-pressure Hg lamps for the direct and H₂O₂ assisted UV photodegradation of N-
377 Nitrosodimethylamine in simulated drinking water. *Environ. Sci. Technol.* 37(9), 1933-1940.
- 378 Song, K., Mohseni, M., Taghipour, F., 2016. Application of ultraviolet light-emitting diodes
379 (UV-LEDs) for water disinfection: A review. *Water Res.* 94, 341-349.
- 380 Stepien, D.K., Diehl, P., Helm, J., Thoms, A., Püttmann, W., 2014. Fate of 1,4-dioxane in the
381 aquatic environment: From sewage to drinking water. *Water Res.* 48(Supplement C), 406-419.
- 382 SWRCB, 2015. California Code of Regulations, Title 22: Social Security, Division 4:
383 Environmental Health, Chapter 3: Water Recycling Criteria. State Water Resources Control
384 Board.
- 385 Velo-Gala, I., Farré, M.J., Radjenovic, J., Gernjak, W., 2019. N-Nitrosodimethylamine
386 (NDMA) Degradation by the Ultraviolet/Peroxodisulfate Process. *Environ. Sci. Technol.*
387 *Letters* 6(2), 106-111.
- 388 Wang, D., Bolton, J.R., Andrews, S.A., Hofmann, R., 2015. Formation of disinfection by-
389 products in the ultraviolet/chlorine advanced oxidation process. *Sci. Total Environ.* 518-519,
390 49-57.
- 391 WHO, 2017. Potable reuse: guidance for producing safe drinking-water. World Health
392 Organization, Geneva.
- 393 Zhang, Z., Chuang, Y.-H., Szczuka, A., Ishida, K.P., Roback, S., Plumlee, M.H., Mitch, W.A.,
394 2019. Pilot-scale evaluation of oxidant speciation, 1,4-dioxane degradation and disinfection
395 byproduct formation during UV/hydrogen peroxide, UV/free chlorine and UV/chloramines
396 advanced oxidation process treatment for potable reuse. *Water Res.* 164, 114939.