

1

SUPPORTING INFORMATION

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3 UV/Chlorine vs. UV/H₂O₂ for water reuse at Orange County Water

4 District, CA: A pilot study

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14 **Table S1.** Selected elementary reactions considered in the kinetic model

No.	Reaction	Rate constant
1	$\text{NH}_2\text{Cl} + h\nu \rightarrow \text{NH}_2\bullet + \text{Cl}\bullet$	$\varepsilon = 371 \text{ M}^{-1} \text{ cm}^{-1}$ $\Phi = 0.294$ ²
2	$\text{NHCl}_2 + h\nu \rightarrow \text{NHCl}\bullet + \text{Cl}\bullet$	$\varepsilon = 126 \text{ M}^{-1} \text{ cm}^{-1}$ $\Phi = 0.82$ ¹
3	$\text{HOCl} + h\nu \rightarrow \bullet\text{OH} + \text{Cl}\bullet$	$\varepsilon = 58 \text{ M}^{-1} \text{ cm}^{-1}$ ² $\Phi = 0.55$ ³
4	$\text{H}_2\text{O}_2 + h\nu \rightarrow 2\bullet\text{OH}$	$\varepsilon = 19.6 \text{ M}^{-1} \text{ cm}^{-1}$ ⁴ $\Phi = 0.5$ ⁴
5	$\bullet\text{OH} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}\bullet + \text{H}_2\text{O}$	$5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ⁵ $6.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ⁶ $8.64 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ² $1.02 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁷ $2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁸
6	$\bullet\text{OH} + \text{NHCl}_2 \rightarrow \text{NCl}_2\bullet + \text{H}_2\text{O}$	$2.57 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ⁶ $6.21 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ⁹
7	$\bullet\text{OH} + \text{NCl}_3 \rightarrow \text{NCl}_2\bullet + \text{HOCl}$	$1.67 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ⁶
8	$\bullet\text{OH} + \text{HOCl} \rightarrow \text{ClO}\bullet + \text{H}_2\text{O}$	$8.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁰ $1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ¹¹ $5.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ⁷ $2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ¹²
9	$\bullet\text{OH} + \text{OCl}^- \rightarrow \text{ClO}\bullet + \text{OH}^-$	$1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁷ $8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ¹³
10	$\bullet\text{OH} + \text{NO}_2^- \rightarrow \text{OH}^- + \text{NO}_2\bullet$	$5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁴ $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ¹⁵
11	$\bullet\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2\bullet + \text{H}_2\text{O}$	$2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁵
12	$\bullet\text{OH} + \text{Cl}^- \rightarrow \text{ClOH}\bullet^-$	$4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁶
13	$\bullet\text{OH} + \text{ONOO}^- \rightarrow \text{ONOO}\bullet + \text{OH}^-$	$4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁷
14	$\bullet\text{OH} + \text{HCO}_3^- \rightarrow \text{CO}_3\bullet^- + \text{H}_2\text{O}$	$8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁵
15	$\bullet\text{OH} + \text{CO}_3^{2-} \rightarrow \text{CO}_3\bullet^- + \text{OH}^-$	$3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁵
16	$\text{Cl}\bullet + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}\bullet + \text{HCl}$	$1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁷ $2.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁸
17	$\text{Cl}\bullet + \text{HOCl} \rightarrow \text{ClO}\bullet + \text{H}^+ + \text{Cl}^-$	$3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁹
18	$\text{Cl}\bullet + \text{OCl}^- \rightarrow \text{ClO}\bullet + \text{Cl}^-$	$8.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁹
19	$\text{Cl}\bullet + \text{Cl}^- \rightarrow \text{Cl}_2\bullet^-$	$6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁹ $7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ²⁰ $8.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ²¹ $8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ²²
20	$\text{Cl}\bullet + \text{NO}_2^- \rightarrow \text{Cl}^- + \text{NO}_2\bullet$	$5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ²³
21	$\text{Cl}\bullet + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Cl}^- + \text{HO}_2\bullet$	$1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ²⁴

		$2.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ²⁰
22	$\text{Cl}\bullet + \text{OH}^- \rightarrow \text{ClOH}\bullet^-$	$1.8 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ ¹⁹
23	$\text{Cl}\bullet + \text{H}_2\text{O} \rightarrow \text{ClOH}\bullet^- + \text{H}^+$	$7.2 \times 10^4 \text{ s}^{-1}$ ¹⁶ $1.6 \times 10^5 \text{ s}^{-1}$ ^{19,25} $1.8 \times 10^5 \text{ s}^{-1}$ ²⁰ $2.5 \times 10^5 \text{ s}^{-1}$ ^{23,26}
24	$\text{Cl}\bullet + \text{HCO}_3^- \rightarrow \text{CO}_3\bullet^- + \text{H}^+ + \text{Cl}^-$	$2.2 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ ²⁷ $2.4 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ²³
25	$\text{Cl}\bullet + \text{CO}_3^{2-} \rightarrow \text{CO}_3\bullet^- + \text{Cl}^-$	$5.0 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ ²⁷
26	$\text{Cl}_2\bullet^- + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}\bullet + \text{H}^+ + 2\text{Cl}^-$	$6.5 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ ¹⁸
27	$\text{Cl}_2\bullet^- + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{ClOH}\bullet^- + \text{H}^+$	$\leq 100 \text{ s}^{-1}$ ²⁰ $\leq 1300 \text{ s}^{-1}$ ²⁶
28	$\text{Cl}_2\bullet^- \rightarrow \text{Cl}\bullet + \text{Cl}^-$	$5.7 \times 10^4 \text{ s}^{-1}$ ²⁰ $6.0 \times 10^4 \text{ s}^{-1}$ ²⁸ $1.1 \times 10^5 \text{ s}^{-1}$ ¹⁶
29	$\text{Cl}_2\bullet^- + \text{Cl}\bullet \rightarrow \text{Cl}_2 + \text{Cl}^-$	$2.1 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ²⁹
30	$\text{Cl}_2\bullet^- + \text{Cl}_2\bullet^- \rightarrow 2\text{Cl}^- + \text{Cl}_2$	$9.0 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ ²⁸ $3.5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ²⁰
31	$\text{CO}_3\bullet^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2\bullet + \text{HCO}_3^-$	$4.3 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$ ³⁰
32	$\text{ClOH}\bullet^- \rightarrow \text{Cl}^- + \bullet\text{OH}$	$6.0 \times 10^9 \text{ s}^{-1}$ ²⁰
33	$\text{ClOH}\bullet^- \rightarrow \text{Cl}\bullet + \text{OH}^-$	23 s^{-1} ¹⁶
34	$\text{ClOH}\bullet^- + \text{Cl}^- \rightarrow \text{OH}^- + \text{Cl}_2\bullet^-$	$1.0 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$ ³¹
35	$\text{ClOH}\bullet^- + \text{H}^+ \rightarrow \text{Cl}\bullet + \text{H}_2\text{O}$	$2.1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ ¹⁶ $2.4 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ ²⁰ $2.6 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ ²⁵ $5.0 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ ²³
36	$\text{ClO}\bullet + \text{ClO}\bullet \rightarrow \text{Cl}_2\text{O}_2$	$2.5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ¹⁹ $7.5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ³²
37	$\bullet\text{OH} + \text{ClO}_2^- \rightarrow \text{ClO}_2\bullet + \text{OH}^-$	$6.3 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ³² $7.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ³³
38	$\bullet\text{OH} + \text{ClO}_2\bullet \rightarrow \text{ClO}_3^- + \text{H}^+$	$4.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ¹⁹
39	$\bullet\text{Cl} + \text{ClO}_2\bullet \rightarrow \text{Cl}_2\text{O}_2$	$1.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ³⁴ $4.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ⁷
40	$\text{Cl}_2\bullet^- + \text{ClO}_2\bullet \rightarrow \text{Cl}_2\text{O}_2 + \text{Cl}^-$	$1.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ³⁴
41	$\text{ClO}\bullet + \text{ClO}_2\bullet \rightarrow \text{Cl}_2\text{O}_3$	$1.4 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ³⁵
42	$\text{Cl}_2\bullet^- + \text{ClO}_2^- \rightarrow \text{ClO}_2\bullet + 2\text{Cl}^-$	$1.3 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ ¹¹
43	$\text{ClO}\bullet + \text{ClO}_2^- \rightarrow \text{OCl}^- + \text{ClO}_2\bullet$	$9.4 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ ³⁶
44	$\text{Cl}_2\text{O}_2 + \text{ClO}_2^- + \text{Cl}^- \rightarrow 2\text{ClO}_2\bullet + 2\text{Cl}^-$	$8.4 \times 10^9 \text{ M}^{-2} \text{s}^{-1}$ ³⁷
45	$\text{Cl}_2\text{O}_2 + \text{ClO}_2^- + \text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 2\text{HOCl}$	$1.2 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$ ³⁸ $5.3 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$ ³⁷
46	$\text{ClO}_2^- + \text{HOCl} + \text{H}^+ \rightarrow \text{Cl}_2\text{O}_2 + \text{H}_2\text{O}$	$1.12 \times 10^6 \text{ M}^{-2} \text{s}^{-1}$ ³⁹

47	$\text{ClO}_2^- + \text{HOCl} + \text{Cl}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^- + \text{H}^+$	$180 \text{ M}^{-2} \text{ s}^{-1}$ ³⁸
48	$\text{Cl}_2\text{O}_2 \rightarrow 2\text{ClO}\cdot$	$k_{45}/(1.3 \times 10^5)/1.93 / 0.034 \text{ s}^{-1}$ ³²
49	$\text{NH}_2\cdot + \text{O}_2 \rightarrow \text{NH}_2\text{O}_2\cdot$	$1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ⁴⁰ $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ⁴¹ $3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ⁴² $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁴³ $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁴⁴
50	$\text{NH}_2\text{O}_2\cdot \rightarrow \text{NO}\cdot + \text{H}_2\text{O}$	$1.0 \times 10^8 \text{ s}^{-1}$ ⁹
51	$\text{NH}_2\text{O}_2\cdot \rightarrow \text{transient species} \rightarrow \text{N}_2\text{O}$	$5.98 \times 10^8 \text{ s}^{-1}$ ⁹
52	$\text{NO}\cdot + \text{O}_2 \rightarrow \text{ONOO}\cdot$	$50\text{--}3000 \text{ M}^{-1} \text{ s}^{-1}$ ⁴⁵ $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ⁴⁶
53	$\text{ONOO}\cdot + \text{NO}\cdot \rightarrow 2\text{NO}_2\cdot$	$5.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ⁴⁶ $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁴⁵
54	$\text{ONOO}\cdot \rightarrow \text{NO}\cdot + \text{O}_2$	6500 s^{-1} ⁴⁵ $2.0 \times 10^5 \text{ s}^{-1}$ ⁴⁶
55	$\text{NO}\cdot + \cdot\text{OH} \rightarrow \text{HNO}_2$	$1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ⁴⁷ $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ⁴⁸
56	$\text{NO}\cdot + \text{NO}_2\cdot \rightarrow \text{N}_2\text{O}_3$	$1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁴⁹
57	$\text{NO}_2\cdot + \text{NO}_2\cdot \rightarrow \text{N}_2\text{O}_4$	$4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ⁵⁰
58	$\text{N}_2\text{O}_3 \rightarrow \text{NO}\cdot + \text{NO}_2\cdot$	$2.2 \times 10^4 \text{ s}^{-1}$ ⁵¹ $8.0 \times 10^4 \text{ s}^{-1}$ ⁴⁹ $4.3 \times 10^6 \text{ s}^{-1}$ ⁵²
59	$\text{N}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{NO}_2^- + 2\text{H}^+$	530 s^{-1} ⁴⁹ 1600 s^{-1} ⁵³ 2000 s^{-1} ⁵¹
60	$\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2\cdot$	6900 s^{-1} ⁵⁰
61	$\text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{NO}_3^- + 2\text{H}^+$	300 s^{-1} ⁵¹ 1000 s^{-1} ⁵⁰
62	$2\text{HNO} \rightarrow [\text{HONNOH}] \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$	$8.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ⁵⁴
63	$\text{HNO} + \text{O}_2 \rightarrow \text{ONOOH}$	$3.8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ ⁵⁵ $3.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ⁵⁶ $1.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ⁵⁷
64	$\text{H}^+ + \text{NH}_2\text{Cl} + \text{NO}_2^- \rightarrow \text{NH}_3 + \text{NO}_2\text{Cl}$	$7.6 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ ⁵⁸ $1.2 \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$ ⁵⁹
65	$\text{NO}_2\text{Cl} + \text{NO}_2^- \rightarrow \text{N}_2\text{O}_4 + \text{Cl}^-$	$8000 \text{ M}^{-1} \text{ s}^{-1}$ ⁶⁰
66	$\text{NO}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{Cl}^- + 2\text{H}^+$	4.8 s^{-1} ⁶⁰
67	$\text{ONOOH} \rightarrow \text{NO}_2\cdot + \cdot\text{OH}$	0.232 s^{-1} ⁶¹ 0.35 s^{-1} ⁶²
68	$\text{ONOOH} \rightarrow \text{NO}_3^- + \text{H}^+$	0.568 s^{-1} ⁶¹ 0.90 s^{-1} ⁶² 1.15 s^{-1} ⁶³
69	$\text{ONOO}^- \rightarrow \text{O}_2\cdot^- + \text{NO}\cdot$	0.02 s^{-1} ⁶⁴
70	$\text{ONOO}^- \rightarrow \text{NO}_3^-$	$8.0 \times 10^{-6} \text{ s}^{-1}$ ⁶²

71	$O_2^{\bullet-} + HO_2^{\bullet} \rightarrow HO_2^- + O_2$	$9.7 \times 10^7 M^{-1}s^{-1}$ ⁶⁵
72	$HO_2^{\bullet} + H_2O_2 \rightarrow \cdot OH + H_2O + O_2$	$3.0 M^{-1}s^{-1}$ ¹⁵
73	$O_2^{\bullet-} + H_2O_2 \rightarrow \cdot OH + OH^- + O_2$	$0.13 M^{-1}s^{-1}$ ¹⁵
74	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	$4.2 \times 10^6 M^{-1}s^{-1}$ ⁶⁶
75	$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	$280 M^{-1}s^{-1}$ ⁶⁶
76	$HOCl + NHCl_2 + OH^- \rightarrow NCl_3 + OH^- + H_2O$	$3.3 \times 10^9 M^{-2}s^{-1}$ ⁶⁷
77	$HOCl + NHCl_2 + OCl^- \rightarrow NCl_3 + OH^- + HOCl$	$1.0 \times 10^5 M^{-2}s^{-1}$ ⁶⁷
78	$NH_2Cl + H_2O \rightarrow HOCl + NH_3$	$2.1 \times 10^{-5}s^{-1}$ ⁶⁶
79	$NHCl_2 + H_2O \rightarrow HOCl + NH_2Cl$	$6.5 \times 10^{-7}s^{-1}$ ⁶⁸
80	$NCl_3 + H_2O \rightarrow HOCl + NHCl_2$	$3.2 \times 10^{-5}s^{-1}$ ⁶⁸
81	$NH_2Cl + NH_2Cl + H^+ \rightarrow NHCl_2 + NH_4^+$	$6944 M^{-2}s^{-1}$ ⁶⁹
82	$NH_2Cl + NH_2Cl + H_2CO_3 \rightarrow NHCl_2 + NH_4^+ + HCO_3^-$	$11 M^{-2}s^{-1}$ ⁶⁹
83	$NH_2Cl + NH_2Cl + HCO_3^- \rightarrow NHCl_2 + NH_3 + HCO_3^-$	$0.22 M^{-2}s^{-1}$ ⁶⁹
84	$NH_2Cl + NHCl_2 \rightarrow N_2 + 3H^+ + 3Cl^-$ (assumed products)	$0.015 M^{-1}s^{-1}$ ⁷⁰
85	$NHCl_2 + NH_3 + H^+ \rightarrow NH_2Cl + NH_2Cl + H^+$	$6.0 \times 10^4 M^{-2}s^{-1}$ ⁶⁷
86	$NHCl_2 + OH^- \rightarrow I + products$	$110 M^{-1}s^{-1}$ ⁷¹
87	$I + NHCl_2 \rightarrow HOCl + products$	$2.8 \times 10^4 M^{-1}s^{-1}$ ⁷²
88	$I + NH_2Cl \rightarrow products$	$8.3 \times 10^3 M^{-1}s^{-1}$ ⁷²
89	$NH_2Cl + NCl_3 + OH^- \rightarrow HOCl + products$	$1.4 \times 10^9 M^{-2}s^{-1}$ ⁷⁰
90	$NHCl_2 + NCl_3 + OH^- \rightarrow 2HOCl + products$	$5.6 \times 10^{10} M^{-2}s^{-1}$ ⁷⁰
91	$H_2O_2 + NH_2Cl \rightarrow products$	$0.0276 M^{-1}s^{-1}$ (24.6 °C) ⁷³
92	$HOCl + NO_2^- \rightarrow NO_2Cl + OH^-$	$7.4 \times 10^3 M^{-1}s^{-1}$ ⁷⁴ $4.4 \times 10^4 M^{-1}s^{-1}$ ⁵⁸
93	$H_2O_2 + HOCl \rightarrow Cl^- + H_2O + O_2 + H^+$	$1.1 \times 10^4 M^{-1}s^{-1}$ ¹³
94	$H_2O_2 + OCl^- \rightarrow Cl^- + H_2O + O_2$	$1.7 \times 10^5 M^{-1}s^{-1}$ ¹³
95	$\cdot OH + 1,4-dioxane \rightarrow$	$2.8 \times 10^9 M^{-1}s^{-1}$ ¹⁵ $3.1 \times 10^9 M^{-1}s^{-1}$ ⁷⁵
96	$Cl\bullet + 1,4-dioxane \rightarrow$	$4.4 \times 10^6 M^{-1}s^{-1}$ ⁷⁶ $2.8-3.4 \times 10^9 M^{-1}s^{-1}$ ⁷⁷
97	$Cl_2^{\bullet-} + 1,4-dioxane \rightarrow$	$3.3 \times 10^6 M^{-1}s^{-1}$ ⁷⁶
98	$HOCl \leftrightarrow OCl^-$ $OCl^- + H^+ \rightarrow HOCl$ $HOCl \rightarrow OCl^- + H^+$	pKa=7.5 ⁷⁸ $5.0 \times 10^{10} M^{-1}s^{-1}$ $1.58 \times 10^3 s^{-1}$
99	$H_2CO_3 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$ $HCO_3^- + H^+ \rightarrow H_2CO_3$ $H_2CO_3 \rightarrow H^+ + HCO_3^-$ $CO_3^{2-} + H^+ \rightarrow HCO_3^-$	pKa ₁ =6.3 & pKa ₂ =10.3 ⁷⁹ $1.0 \times 10^{10} M^{-1}s^{-1}$ $5.0 \times 10^3 s^{-1}$ $5.0 \times 10^{10} M^{-1}s^{-1}$

	$\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+$	2.5 s^{-1}
100	$\text{HO}_2^\bullet \leftrightarrow \text{O}_2^{\bullet-}$ $\text{O}_2^{\bullet-} + \text{H}^+ \rightarrow \text{HO}_2^\bullet$ $\text{HO}_2^\bullet \rightarrow \text{O}_2^{\bullet-} + \text{H}^+$	$\text{pKa} = 4.8$ ⁶⁵ $5.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ $7.9 \times 10^5 \text{ s}^{-1}$
101	$\text{ONOOH} \leftrightarrow \text{ONOO}^-$ $\text{ONOO}^- + \text{H}^+ \rightarrow \text{ONOOH}$ $\text{ONOOH} \rightarrow \text{ONOO}^- + \text{H}^+$	$\text{pKa} = 6.6$ ⁶² $5.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ $1.26 \times 10^4 \text{ s}^{-1}$
102	$\text{NDMA} + h\nu \rightarrow$	$\varepsilon = 1650 \text{ M}^{-1} \text{ cm}^{-1}$ ⁸⁰ $\Phi = 0.28$ ⁸⁰

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17 **Section S1.** 1,4-Dioxane analysis
18 A Gas Chromatograph (7890A, Agilent Technologies) equipped with triple-axis detector (5975C,
19 VL MSD, Agilent Technologies) and autosampler (GC sampler 80, Agilent Technologies) was
20 used to analyze 1,4-dioxane. An automated solid-phase microextraction (SPME) unit is connected
21 to the GC-MS autosampler for 1,4-dioxane extraction from the sample using a method developed
22 in-house. A ZB-WAXPlus (30 m \times 0.25 mm \times 0.5 μ m) GC column was used with a temperature
23 program (37 °C for 5 min \rightarrow 85 °C at 10 °C min $^{-1}$ \rightarrow 200 °C for 1.6 min) and helium as a carrier
24 gas (1 mL min $^{-1}$). The MS source, MS Quad, and transfer line temperatures were maintained at
25 230, 150, and 280 °C, respectively. The instrument was used in the electron impact ionization
26 mode (electron energy of 70 eV at 230 °C).

27

- 28 **Section S2.** The photolysis rate and reactive radical formation rate from oxidants.
 29 The direct photolysis rate of a specific compound M can be calculated using the fundamental
 30 expression of photolysis rate constant shown in equation S1⁸¹:

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$$k_{d,M} = \frac{\varepsilon_M \times \Phi_M \times ln(10)}{U_{254}} \quad (S1)$$

32 where ε_M is the molar absorption coefficient at 254 nm ($M^{-1} \text{ cm}^{-1}$), Φ_M is the quantum yield (mol
 33 einstein $^{-1}$; dimensionless parameter), and $U_{253.7}$ is the molar photon energy (J einstein $^{-1}$) at 253.7
 34 nm. The $\cdot\text{OH}$ and $\text{Cl}\cdot$ radicals are the primary radical species responsible for 1,4-dioxane treatment
 35 in the UV/HOCl and UV/ H_2O_2 AOPs in the presence of chloramines. In this study, $\text{NH}_2\cdot$ and
 36 $\text{NHCl}\cdot$ are not considered as reactive radical species toward 1,4-dioxane. The radical generation
 37 rates were calculated according to the reactive radical formation yield from each oxidant. Table
 38 S2 lists the photochemical properties of oxidants.

39

40 **Table S2.** Photochemical properties of oxidants

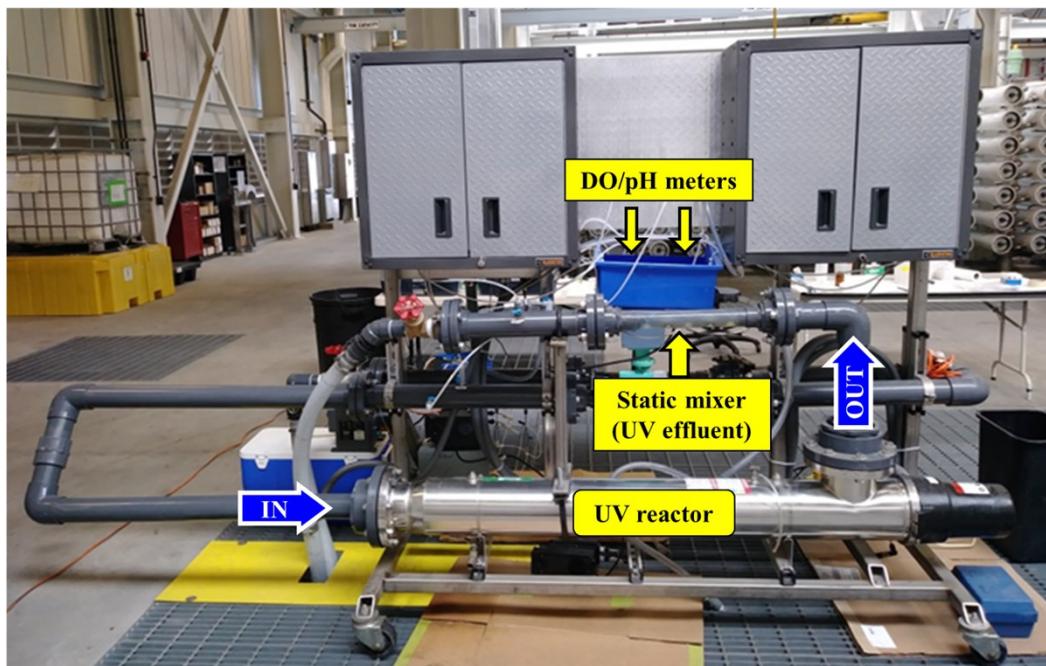
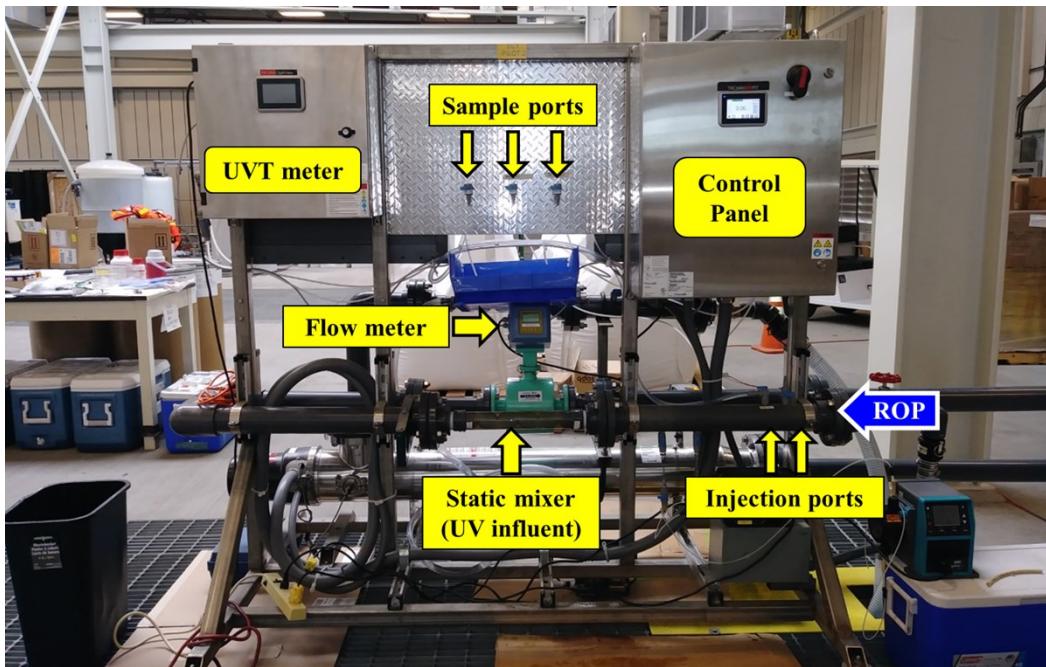
	Molar absorption coefficient, ε $M^{-1} \text{ cm}^{-1}$	Quantum yield, Φ	Direct photolysis rate constant, k_d' ($\text{cm}^2 \text{ mJ}^{-1}$)	Reactive radical generation rate, constant k_{radical}' ($\text{cm}^2 \text{ mJ}^{-1}$)
NH ₂ Cl	371 ¹	0.296 ²	5.33×10^{-4}	5.33×10^{-4}
NHCl ₂	126 ¹	0.82 ¹	5.05×10^{-4}	5.05×10^{-4}
HOCl	58 ²	0.55 ³	1.56×10^{-4}	3.12×10^{-4}
H ₂ O ₂	19.6 ⁴	0.5 ⁴	0.48×10^{-4}	0.96×10^{-4}

41

42 **Section S3.** Bench-scale tests using a closed-loop recirculation UV reactor
43 A bench-scale UV system (UVMax™ D4 reactor, Viqua, Canada) equipped with one 43W-low-
44 pressure Hg-vapor arc lamp was used to treat water sample volumes up to 8L in a recirculation
45 mode. The lamp emits primarily the 253.7 nm wavelength and the average UV fluence rate in
46 milliQ water was determined as $5.5 \pm 0.1 \text{ mW cm}^{-2}$ using very low concentrations (μM) of either
47 sulfamethoxazole or H_2O_2 as chemical probes.

48

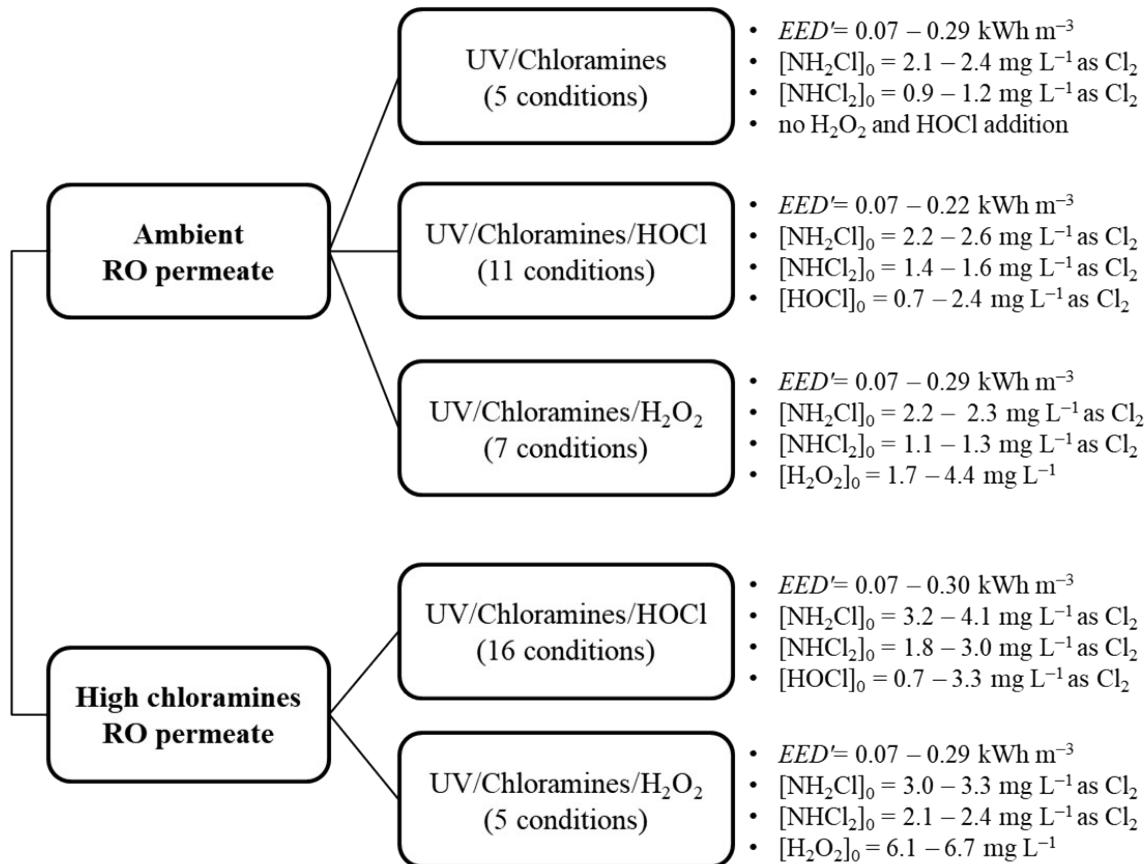
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52 **Figure S1.** The pilot system comprising a TrojanUVPhox™08AL20 reactor, a flow meter,
 53 injection ports, static mixers, sample ports, online UV effluent transmittance instrument, and real-
 54 time pH and DO meters.

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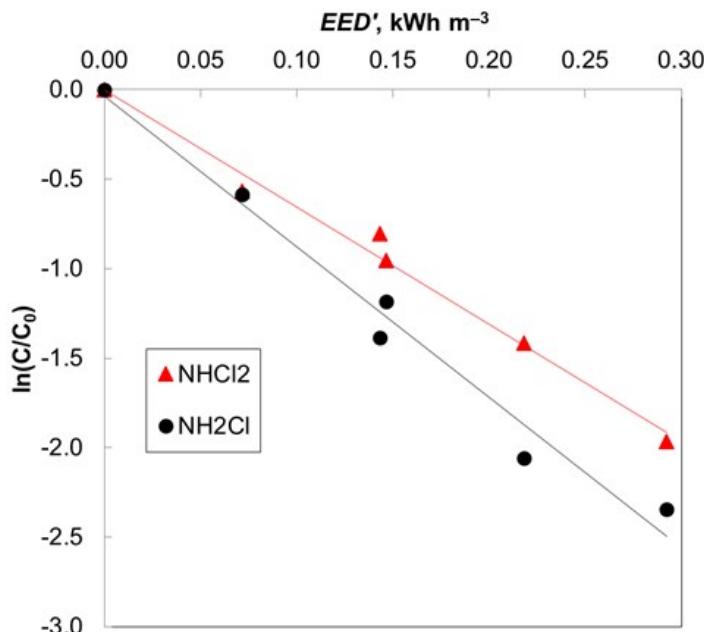
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59 **Figure S2.** Pilot test description including the electrical energy dose (EED') corrected for the lamp
60 efficiency at the operating %BPL, RO permeate quality, and oxidant concentrations.

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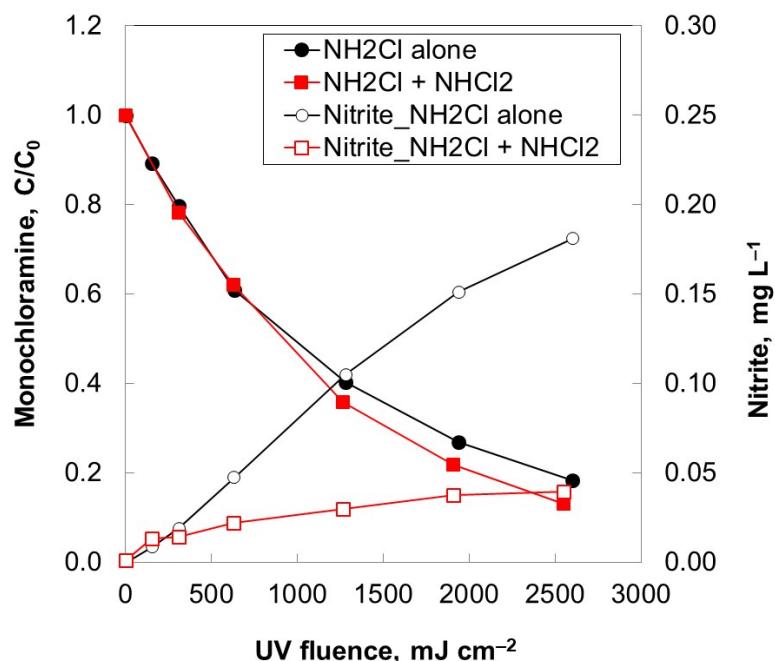


64 **Figure S3.** Photodegradation of chloramines in RO permeate at ambient quality conditions.

65 $[\text{NH}_2\text{Cl}]_0 = 2.1\text{--}2.4 \text{ mg L}^{-1}$ as Cl_2 ; $[\text{NHCl}_2]_0 = 0.9\text{--}1.2 \text{ mg L}^{-1}$ as Cl_2 ; pH 5.1–5.3; 97.1–97.5% T.

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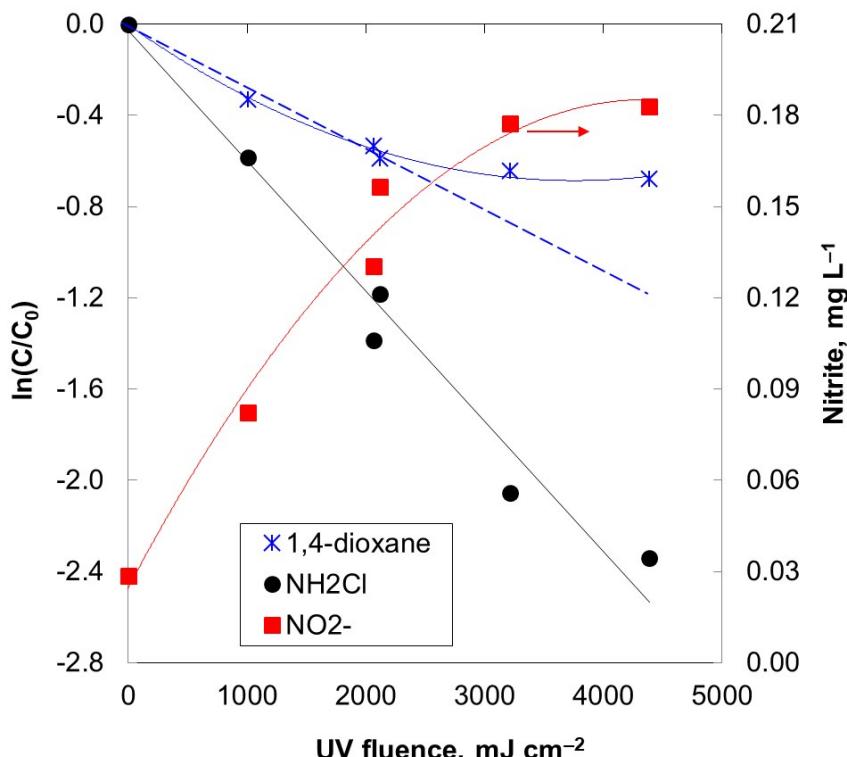
70 **Figure S4.** Formation of NO_2^- from photodegradation of NH_2Cl in the presence and the absence
71 of NHCl_2 in the bench-scale tests: $[\text{NH}_2\text{Cl}]_0 = 0.9 - 1.1 \text{ mg L}^{-1}$ as Cl_2 ; $[\text{NHCl}_2]_0 = 2.2 \text{ mg L}^{-1}$ as Cl_2 ;
72 $E_0 = 5.5 \pm 0.1 \text{ mW cm}^{-2}$; pH 5.5 (phosphate buffer).

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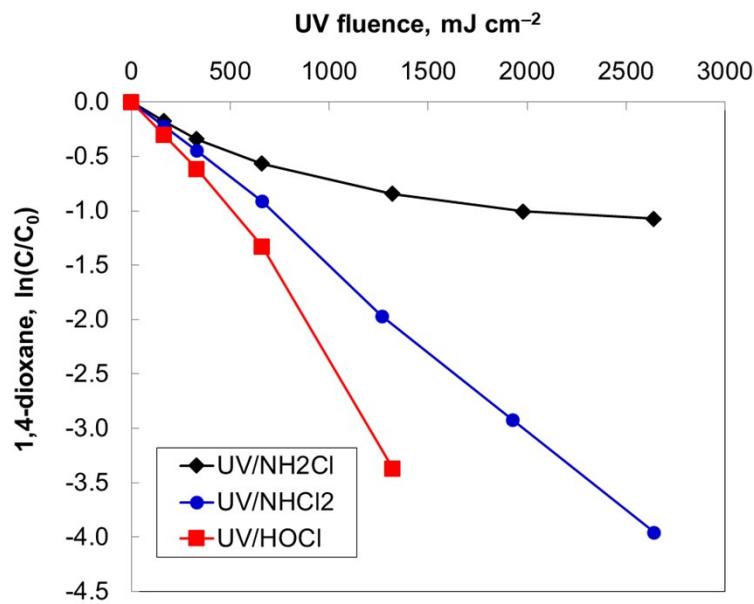
77

78 **Figure S5.** The degradation of NH_2Cl and 1,4-dioxane and NO_2^- formation in the UV/chloramine
 79 process at OCWD with RO permeate at ambient chloramine concentrations. $[\text{NH}_2\text{Cl}]_0 = 2.1\text{--}2.4$
 80 mg L^{-1} as Cl_2 , $[\text{NHCl}_2]_0 = 0.9\text{--}1.2 \text{ mg L}^{-1}$ as Cl_2 , $[1,4\text{-dioxane}]_0 = 0.19 \text{ mg L}^{-1}$, pH 5.1–5.3, and
 81 97.1–97.5% T . The symbols represent the experimental data; the black line is the regression line
 82 for the *pseudo*-first-order kinetics of NH_2Cl decay; the solid blue and red lines represent best fits
 83 for 1,4-dioxane and NO_2^- experimental data, respectively; the blue dashed line indicates the trend
 84 for a *pseudo*-first order kinetics of 1,4-dioxane decay.

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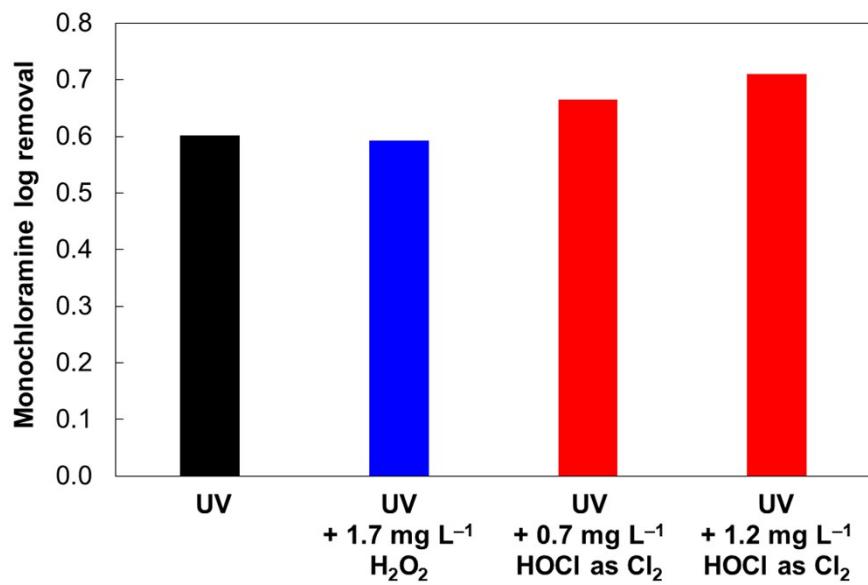
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89 **Figure S6.** Degradation of 1,4-dioxane with the UV/NH₂Cl, UV/NHCl₂, and UV/HOCl processes
90 in milliQ water using the bench-scale UV reactor. Test conditions: [oxidant]₀= 0.05 mmol L⁻¹;
91 [1,4-dioxane]₀ = 0.048±0.005 mg L⁻¹; $E_0= 5.5\pm0.1 \text{ mW cm}^{-2}$; pH 5.5.

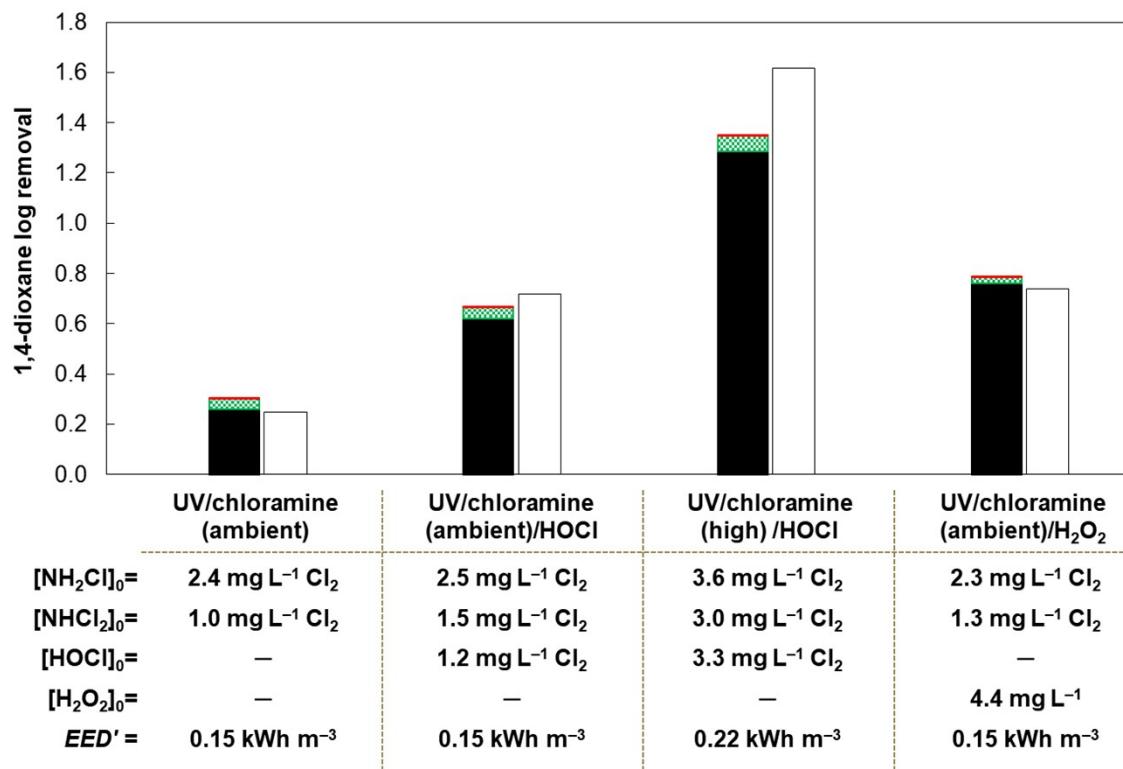
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93

94 **Figure S7.** The log-removal of NH_2Cl in UV/chloramine, UV/chloramine/ H_2O_2 , and
 95 UV/chloramine/HOCl processes at $EED' = 0.145 \text{ kWh m}^{-3}$ RO permeate at ambient chloramine
 96 concentrations: $[\text{NH}_2\text{Cl}]_0 = 2.2 \text{ mg L}^{-1}$ as Cl_2 (UV/chloramine and UV/chloramine/ H_2O_2);
 97 $[\text{NH}_2\text{Cl}]_0 = 2.5 \text{ mg L}^{-1}$ as Cl_2 (UV/chloramine/HOCl).

98

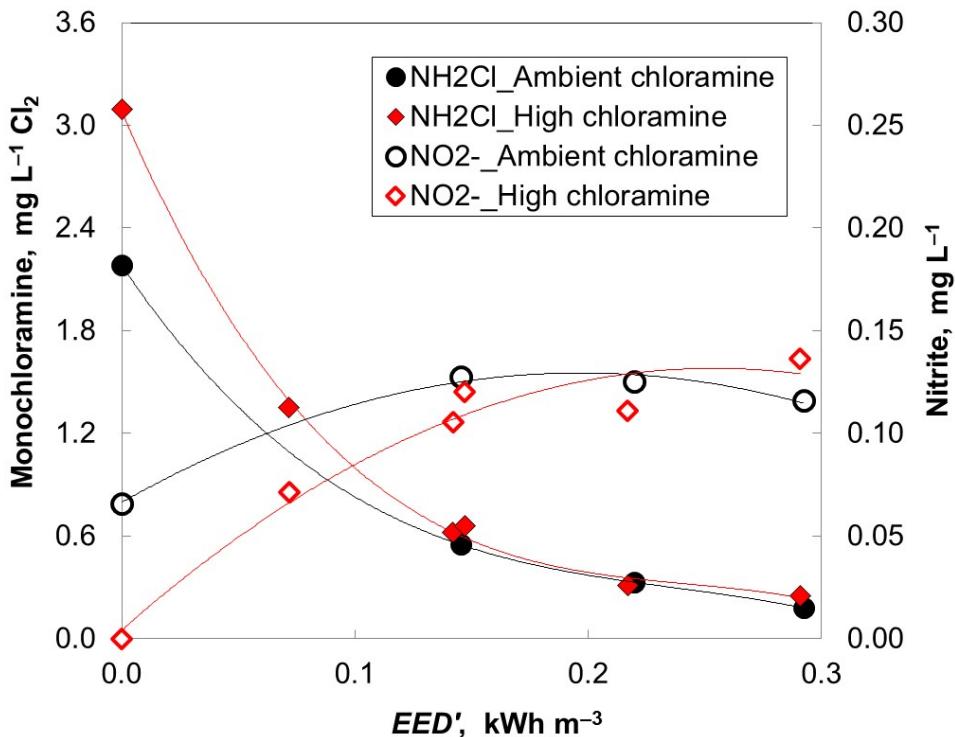


99

100 **Figure S8.** Contribution of radical species to 1,4-dioxane log-removal in the UV/chloramine and
 101 UV/chloramine/H₂O₂ processes at ambient chloramine condition, and in the UV/chloramine/HOCl
 102 process at both ambient and high chloramine conditions. Experimental data (empty bars) *vs.*
 103 model-predicted data (solid bars); radical contributions: •OH (black); Cl• (green); Cl₂•⁻ (red).

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107

108 **Figure S9.** Chloramine decay and nitrite formation in the UV/chloramine/H₂O₂ process during the
 109 pilot tests with the RO permeate at ambient and high chloramine concentrations. Conditions:
 110 [H₂O₂]₀= 1.7 mg L⁻¹ and 97.1% T (ambient chloramine levels); [H₂O₂]₀=6.1–6.7 mg L⁻¹ and
 111 95.7% T (high chloramine levels); pH 5.0–5.3.

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