

# Online monitoring of bromate in treated wastewater:

## Implications for potable water reuse

Takahiro Fujioka<sup>a,\*</sup>, Sandrine Boivin<sup>a</sup>, Haruka Takeuchi<sup>b</sup>

*<sup>a</sup>Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi,  
Nagasaki 852-8521, Japan*

*<sup>b</sup>Research Center for Environmental Quality Management, Kyoto University, 1-2 Yumihama, Otsu  
520-0811, Japan*

---

\* Corresponding author: Takahiro Fujioka, Email: [tfujioka@nagasaki-u.ac.jp](mailto:tfujioka@nagasaki-u.ac.jp), Tel: +81 095 819 2695

## 1 **Abstract**

2 Continuous monitoring of bromate ions, a disinfection by-product of the ozonation of  
3 wastewater, may improve the safety of recycled water for potable use. A recently developed  
4 elemental analyzer can determine bromate ion concentrations online. However, dissolved  
5 organics present in wastewater interfere with the detection of bromate ions. The aim of this study  
6 was to develop a nanofiltration (NF) membrane-based pre-treatment system to remove the  
7 interfering substances present in treated wastewater prior to the online analysis. The NF pre-  
8 treatment system was optimized to ensure the removal of the interfering substances from the  
9 membrane bioreactor (MBR)-treated wastewater without altering the bromate ion concentration.  
10 We determined a permeate flux of 1 L/m<sup>2</sup> h and a feed temperature of 35 °C as optimal pre-  
11 treatment conditions for online analysis. Furthermore, the continuous monitoring of MBR-treated  
12 wastewater, containing different bromate ion concentrations (0–12 µg/L), for three days revealed  
13 a strong correlation between the concentrations determined using the online analyzer and liquid  
14 chromatography coupled with tandem mass spectrometry. Thus, this study demonstrates the  
15 potential utility of the online bromate ion analyzer coupled with NF pre-treatment system to  
16 monitor the rate of bromate ion formation during ozonation.

17

18 **Keywords:** Online bromate ion analyzer; nanofiltration; potable water use; disinfection by-  
19 product; ozone.

20

## 21 **1 Introduction**

22 Ozonation is a reliable water treatment process that reduces the concentrations of trace  
23 organic chemicals and pathogens, such as viruses and bacteria, in water and wastewater, as  
24 ozone is a strong oxidant. Therefore, ozonation, followed by treatment with biologically  
25 activated carbon, can be implemented prior to advanced wastewater treatment processes  
26 (AWTPs), such as microfiltration or ultrafiltration, reverse osmosis (RO) membrane, and  
27 advanced oxidation, for potable use.<sup>1, 2</sup> However, the ozonation of wastewater results in the  
28 formation of bromate ions ( $\text{BrO}_3^-$ ), carcinogenic disinfection by-products (DBPs) that are  
29 generated from the reaction between ozone and bromide ions in wastewater ( $\sim 300 \mu\text{g-Br}^-/\text{L}$ ),<sup>3</sup> at  
30 higher concentrations than the guideline-prescribed value ( $10 \mu\text{g-BrO}_3^-/\text{L}$ ).<sup>4, 5</sup> Bromate ions are  
31 one of the six major contaminants identified in chemical monitoring programs under potable  
32 reuse projects which pose a health risk.<sup>6</sup> However, thus far, RO membrane treatment has  
33 remained as the only reliable process used for the removal of bromate ions from wastewater.<sup>7, 8</sup>  
34 Therefore, controlling bromate ion formation is a significant challenge for AWTPs without an  
35 RO membrane treatment process, which has gained attention as an alternative of RO-based  
36 AWTP for potable reuse in inland locations.<sup>9-11</sup>

37 Online monitoring of bromate ion concentrations after ozonation can help improve the safety  
38 of recycled water, which will aid the implementation of countermeasures such as reduction of  
39 ozone doses up to the guideline-prescribed values. However, the bromate ion concentrations in  
40 parts-per-billion ( $\mu\text{g/L}$ ) are analyzed using laboratory-based analytical techniques such as ion  
41 chromatography coupled with suppressed conductivity followed by a post-column reaction<sup>12, 13</sup>  
42 and liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS).<sup>14</sup> Recently, a  
43 novel online technology<sup>15</sup> based on fluorescence estimation at excitation (EX) and emission

44 (EM) wavelengths of 300 and 400 nm, respectively, has been developed to monitor bromate ion  
45 concentration in drinking water. Nevertheless, wastewater contains a high concentration of  
46 dissolved organic compounds that exhibit autofluorescence at 300–400 nm and interfere with the  
47 analysis.

48 The interfering substances in wastewater can be separated from bromate ions using  
49 nanofiltration (NF) membranes. Polymeric NF membranes, with a molecular weight cut-off  
50 (MWCO) of 200–400 Da,<sup>16, 17</sup> filter out a considerable portion of the organic matter ( $\geq 500$  Da)  
51 and a small proportion of bromate ions (10%–50%)<sup>18</sup> from water. The NF pre-treatment system  
52 coupled with the online elemental analyzer ensures a high rejection rate for interfering  
53 substances and a low rejection rate for bromate ions. However, the NF pre-treatment system has  
54 not been used with the online bromate ion analyzer. Thus, the efficiency of NF pre-treatment  
55 system for the separation of both bromate ions and interfering substances remains to be  
56 determined.

57 The aim of this study was to develop an NF pre-treatment system to enable the continuous  
58 monitoring of bromate ion concentrations in treated wastewater by decreasing the permeation of  
59 interfering substances. Furthermore, the effects of the pre-treatment conditions on the permeation  
60 of interfering substances and bromate ions in the treated wastewater were assessed to maximize  
61 the removal of interfering substances. Additionally, the efficiency of the optimized NF pre-  
62 treatment system was evaluated by continuously monitoring the bromate ion concentrations in  
63 the treated wastewater for three days, and the split samples were analyzed using LC–MS/MS to  
64 compare the online-monitored bromate ion concentrations with those obtained via LC–MS/MS.

65

## 66 **2 Methods**

### 67 *2.1 Materials*

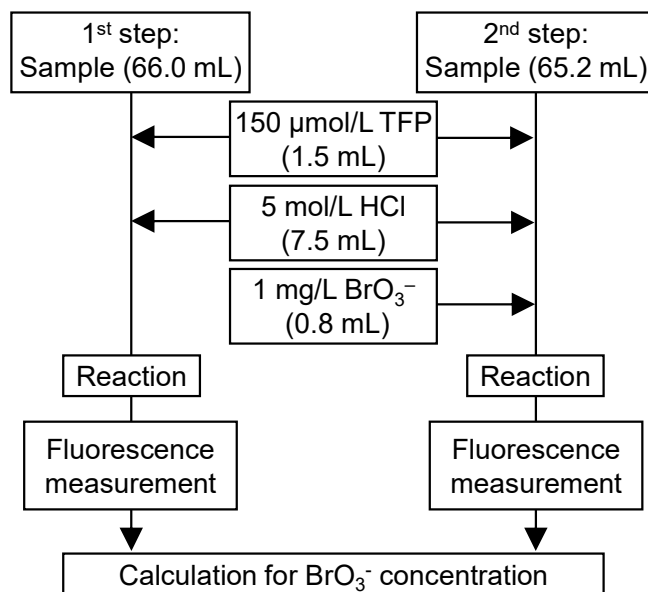
68 The standard solution of bromate ions (2,008 mg BrO<sub>3</sub><sup>-</sup>/L) was obtained from FUJIFILM  
69 Wako Pure Chemical Corp. (Osaka, Japan), and a bromate stock solution (1 mg/L) was prepared  
70 in pure water. Trifluoperazine dihydrochloride (TFP) was obtained from Tokyo Chemical  
71 Industry Co. Ltd. (Tokyo, Japan), and a TFP stock solution (150 μmol/L) was prepared in pure  
72 water. Membrane bioreactor (MBR)-treated wastewater samples, produced using hollow fiber  
73 ultrafiltration membranes with a nominal pore size of 0.05 μm, were collected from a municipal  
74 wastewater treatment plant in Japan. In addition, samples of effluent produced through primary  
75 wastewater treatment (i.e., screens followed by sedimentation) were collected at another  
76 municipal wastewater treatment plant in Japan.

77

### 78 *2.2 Analytical methods*

79 Bromate ion concentrations were determined using a prototype online bromate ion analyzer  
80 (METAWATER Co. Ltd., Tokyo, Japan) based on the changes in fluorescence intensities,  
81 resulting from the reaction between TFP and bromate ions.<sup>15</sup> The overall procedure is depicted in  
82 **Fig. 1**. First, approximately 150 mL auto-collected wastewater samples, which were subjected to  
83 acidification with 0.5 M HCl, were mixed with 3.0 μM TFP stock solution for 1 min.  
84 Subsequently, fluorescence intensities were estimated at EX and EM of 300 nm and 400 nm,  
85 respectively. Second, the wastewater samples were analyzed via a method similar to the  
86 abovementioned method, using 10 μg/L of bromate ions. The bromate ion concentrations were  
87 then determined using the fluorescence intensity estimates of the two analyses (that is, with and  
88 without the bromate ion standard solution). Each analysis duration was 90 min, and a sample

89 volume of approximately 450 mL was used. A standard curve was generated using bromate  
90 solutions (in pure water) with concentrations of 0, 2.5, 5.0, and 10  $\mu\text{g/L}$ .



91

92 **Fig. 1** Flow diagram of the online process used to determine bromate ion concentration.

93

94 Bromate ion concentrations in the manually-collected samples were determined using LC-  
95 MS/MS (ACQUITY UPLC system and ACQUITY TQD MS/MS, Waters Co.; Milford, MA,  
96 USA) equipped with an ACQUITY UPLC BEH Amide column ( $2.1 \times 150$  mm,  $1.7 \mu\text{m}$ , Waters  
97 Co.; Milford, MA, USA) (**Supplementary Table S1**). Water samples were diluted with  
98 acetonitrile (LC-MS grade, FUJIFILM Wako Pure Chemical; Osaka, Japan) since the BEH  
99 Amide is a hydrophilic interaction chromatography column, and an 80/20 (v/v) mixture of  
100 acetonitrile and the water sample was injected into the analytical system. A binary gradient with  
101 a flow rate of 0.3 mL/min was used. The mobile phases A and B were 50 mM ammonium  
102 formate and acetonitrile, respectively. The mass spectrometer was operated using electrospray  
103 ionization in negative ion mode. Multiple reaction monitoring (MRM) mode was used to  
104 quantify ions in the samples, with precursor and product ion transitions corresponding to 127 m/z

105 and 111 m/z, respectively. Moreover, the concentrations of the interfering substances in the  
106 wastewater samples were characterized using the excitation–emission matrix (EEM) spectra  
107 obtained using the RF-6000 spectrophotometer (Shimadzu Co., Kyoto, Japan).

108

### 109 **2.3 The NF pretreatment system**

110 Spiral-wound polyamide NF membrane elements (NF270-1812-250; Pure-Pro Water  
111 Corporation, Kaohsiung, Taiwan; effective membrane area = 0.6 m<sup>2</sup>) were installed in an NF  
112 pre-treatment system (**Supplementary Fig. S1**) to separate the interfering substances from the  
113 bromate ions. The NF membrane elements were assembled using the NF membranes (NF270,  
114 DuPont Water Solutions, Wilmington, DE, USA) with an MWCO of 300 Da, according to the  
115 manufacturer's instructions.

116

### 117 **2.4 Experimental protocols**

118 Prior to each test, the NF pre-treatment system with the NF membrane module was  
119 conditioned by conducting filtration of pure water for two days. After replacing pure water with  
120 22.5 L of MBR-treated wastewater, the rate of inflow to the membrane module was set at 700  
121 mL/min. The permeate flux and feed temperature were adjusted to 1–10 L/m<sup>2</sup> h and 10–35 °C,  
122 respectively. The bromate stock solution was added into the feed tank in a stepwise manner from  
123 0 µg/L to 12 µg/L, and the permeate was collected in an equipped collection tank. The permeate  
124 was transferred from the collection tank to the online bromate ion analyzer using a 1/8"  
125 polytetrafluoroethylene pipe. Both the permeate and the concentrate were recirculated during the  
126 test period. The entire volume of the feed was replaced after 1.3 and 2.8 d. Feed and permeate  
127 samples collected from the feed and permeate collection tanks, respectively, were manually

128 analyzed using LC–MS/MS and the RF-6000 spectrophotometer. When bromate ion  
129 concentrations were analyzed in the primary wastewater treatment effluent samples, the permeate  
130 flux and feed temperature during the NF pre-treatment were adjusted to 1 L/m<sup>2</sup> h and 35 °C,  
131 respectively. A bromate stock solution was added into the primary wastewater treatment effluent  
132 at a concentration of 4 µg/L.

133

### 134 **3 Results and Discussion**

#### 135 **3.1 Importance of the NF pre-treatment system**

136 The inconclusive direct online analysis of bromate ions in the MBR-treated wastewater  
137 samples could be attributed to the high concentrations of interfering substances that emitted auto-  
138 fluorescence at EX300/EM400, which exceeded the detection limit of the online analyzer. The  
139 major sources of the interference at these wavelengths were humic acid-like fluorophores, with  
140 EX/EM of 320–360 nm/400–450 nm (denoted as peak C) (Supplementary Fig. S2a).<sup>19</sup> The  
141 intensity of humic acid-like fluorophores can be considerably reduced by conducting NF pre-  
142 treatment (Supplementary Fig. S2b). NF pre-treatment can remove many interfering substances  
143 in the MBR-treated wastewater because the NF270 membrane has an MWCO of approximately  
144 300 Da, and humic substances, including humic acids and humic acid-like substances, have  
145 molecular weights > 350 Da.<sup>20,21</sup>

146

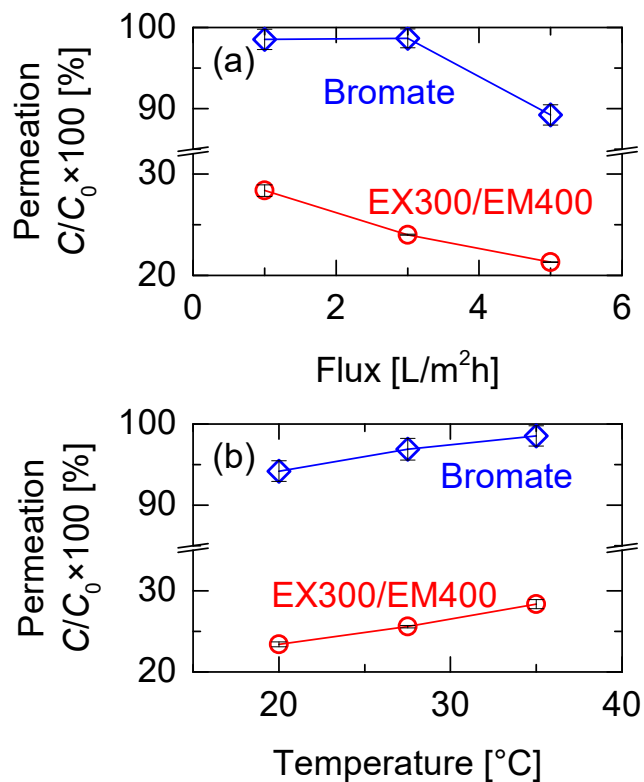
#### 147 **3.2 Optimization of pre-treatment conditions**

148 The permeate flux and feed temperature during the NF pre-treatment were optimized by  
149 assessing the permeation of bromate ions and interfering substances, indicated by the  
150 fluorescence intensities EX300/EM400, in the MBR-treated wastewater. A permeate flux of 1.0



151 L/m<sup>2</sup> h at a feed temperature of 35 °C helped achieve 99% permeation of bromate ions (that is,  
152 almost no bromate ions were removed) and 28% permeation of the interfering substances (that is,  
153 72% of the interfering substances were removed) (**Fig. 2a**). No errors were observed with the use  
154 of the online bromate ion analyzer, and this was attributable to the NF-treated wastewater,  
155 indicating an adequate removal of the interfering substances. A permeate flux < 1.0 L/m<sup>2</sup> h could  
156 not be achieved because of the friction loss in the NF pre-treatment system to maintain a cross-  
157 flow rate of 700 mL/min. Although increasing the permeate flux to 5 L/m<sup>2</sup> h decreased the  
158 permeation of the interfering substances up to 21%, bromate ion permeation also decreased  
159 (89%), suggesting that 11% of the bromate ions were rejected by the NF membrane. The changes  
160 in solute permeation occur owing to the changes in solute and solution permeation; solute  
161 permeation through membranes is less affected by changes in the permeate flux.<sup>22</sup>

162 Furthermore, increased feed temperatures affected the permeation of both bromate ions and  
163 interfering substances. An increase in feed temperature from 20 °C to 35 °C resulted in an  
164 increase in the permeation of interfering substances from 21% to 28%, while increasing the  
165 permeation of bromate ions from 94% to 99% (**Fig. 2b**). The changes in solute permeation are  
166 affected by temperature variations because of the changes in the membrane pore size and the  
167 permeability of solutes; at high temperatures, the pore size of the NF membrane and the  
168 permeability coefficient of solutes increase.<sup>23, 24</sup> The permeation of bromate ions and interfering  
169 substances revealed a similar increasing trend based on the changes in permeate flux and feed  
170 temperature (**Fig. S3**). Thus, complete separation of bromate ions from the interfering substances  
171 using the NF270 membrane was impossible. As the minimum removal of bromate ions by the  
172 NF membrane is a preferred pre-treatment approach, the lowest permeate flux (1.0 L/m<sup>2</sup>h) and  
173 the highest feed temperature (35 °C) can be selected as the optimal conditions.



174

175 **Fig. 2** Effects of (a) permeate flux and (b) feed temperature of the NF pre-treatment system on  
 176 the permeation of bromate ions and the interfering substances in the MBR-treated wastewater  
 177 represented by the fluorescence intensities (EX300/EM400). The standard permeate flux and  
 178 feed temperature were 1 L/m<sup>2</sup> h and 35 °C, respectively. Bromate ion concentrations were  
 179 adjusted to 12 µg/L.

180

181 Bromate ion concentrations in the primary wastewater treatment effluent were also analyzed  
 182 to assess the versatility of the NF pre-treatment system and identify its optimal treatment  
 183 conditions (i.e., permeate flux of 1.0 L/m<sup>2</sup> h and feed temperature of 35 °C). Results showed that  
 184 the permeation of bromate ions and interfering substances was 100% and 28%, respectively,  
 185 during the NF pre-treatment, which was comparable to that of the MBR-treated wastewater. The

186 online bromate ion analyzer did not show instrumental errors, despite high concentrations of  
187 interfering substances in the primary wastewater effluent. The intensity of humic acid-like  
188 fluorophores was substantially reduced using the NF pre-treatment system (**Supplementary Fig.**  
189 **S4**). For a primary wastewater treatment effluent sample with bromate ion concentrations of 0.0  
190 or 5.0  $\mu\text{g/L}$ , determined using LC-MS/MS, the online analyzer coupled with the optimized NF  
191 pre-treatment system provided similar bromate ion concentrations (0.3 and 4.3  $\mu\text{g/L}$ ). Therefore,  
192 a permeate flux of 1  $\text{L/m}^2 \text{ h}$  and a feed temperature of 35  $^\circ\text{C}$  were selected as the optimal  
193 conditions in this study because removing approximately 70 % of the interfering substances was  
194 adequate to eliminate instrumental errors.

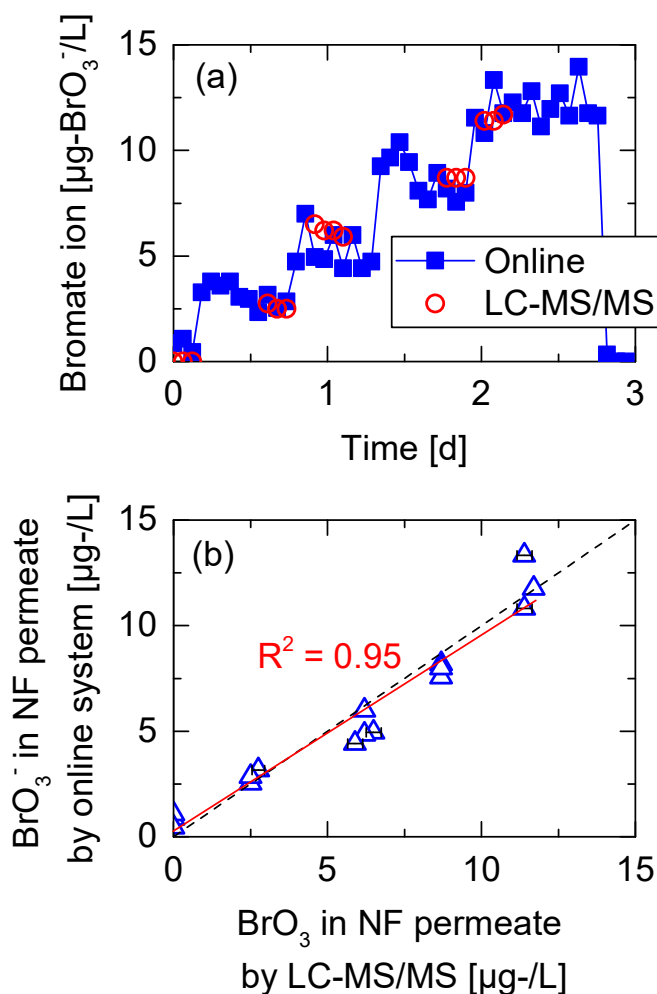
195

### 196 **3.3 Validations in the online analysis results**

197 The efficiency of the online analyzer coupled with the optimized NF pre-treatment system  
198 was successfully demonstrated by monitoring MBR-treated wastewater, containing variable  
199 concentrations of bromate ions, over a course of three days (16 analyses/d) (**Fig. 3a**). During the  
200 experimental period, small variations were observed in bromate ion concentrations determined  
201 by using the online analyzer. For example, when an MBR-treated wastewater sample, containing  
202 a low target concentration of 3.0  $\mu\text{g/L}$ , was analyzed from 0.2 d to 0.7 d, a variation of  $3.1 \pm 0.5$   
203  $\mu\text{g/L}$  was observed. Similar variations were observed at three different target concentrations (6.0,  
204 9.0, and 12.0  $\mu\text{g/L}$ ).

205 The accuracy of the online analytical data was determined by analyzing bromate ion  
206 concentrations in the split samples using LC-MS/MS. A strong linear correlation ( $R^2 = 0.95$ ) was  
207 observed between bromate ion concentrations of 0 and 12  $\mu\text{g/L}$  (**Fig. 3b**). Moreover, stable  
208 permeation rates for bromate ions ( $94\% \pm 7\%$ ) (**Supplementary Fig. S5**) and the interfering

209 substances (approximately 20%) (**Supplementary Fig. S6**) were observed. Based on the  
210 efficiency and accuracy of the online analyzer, the online-determined bromate ion concentration  
211 can be used to continuously monitor changes in bromate ion concentrations in treated  
212 wastewaters.



213  
214 **Fig. 3** (a) Bromate ion concentrations determined using liquid chromatography coupled with  
215 tandem mass spectrometry (LC–MS/MS) and the online bromate ion analyzer coupled with the  
216 NF pretreatment system (feed temperature: 35 °C; permeate flux: 1 L/m<sup>2</sup> h; transmembrane  
217 pressure: 30 kPa) and (b) correlation of the bromate ion concentrations analyzed using the two  
218 methods.

219

220        However, further investigations are warranted to determine the potential of the NF pre-  
221 treatment system to estimate the quality parameters of different types of wastewater. For  
222 example, a 20%–30% decrease in the level of interfering substances may not be sufficient for  
223 wastewater samples containing high concentrations of the interfering substances. Therefore,  
224 altering the permeation of bromate ions using the NF membrane (such as, a higher permeate flux  
225 leading to an increased removal of both bromate ions and interfering substances) may be  
226 necessary. Additionally, the minimal interference in the online bromate ion analyzer can be  
227 ensured by identifying NF membranes that can be used to remove humic acid-like substances  
228 without affecting the permeation of bromate ions. Another concern is the long-term stability of  
229 the NF pre-treatment system. The permeate flux in this study (1 L/m<sup>2</sup> h) was much lower than  
230 those used in representative NF treatment systems (20–40 L/m<sup>2</sup> h), inducing less membrane  
231 fouling. In addition, the transmembrane pressure of the NF pre-treatment system remained  
232 constant over three days, suggesting that membrane fouling was negligible. However, long-term  
233 operation over several months may gradually promote membrane fouling, affecting the  
234 permeation of bromate ions and interfering substances. To ensure that the NF pre-treatment is  
235 continuous, stable, and efficient, membranes must be periodically replaced or membrane foulants  
236 must be removed by chemical cleaning. Therefore, on-site, long-term monitoring is warranted to  
237 assess the long-term viability of the NF pre-treatment system.

238

### 239 ***3.4 Implications for on-site use***

240        This study demonstrated the potential utility of an online bromate ion analyzer in combination  
241 with an NF pre-treatment system for detecting high bromate ion concentrations in treated

242 wastewater. High bromate ion concentrations after ozonation can result from: (a) ozone  
243 generator or ozone-dosing control system failures (e.g., high ozone doses), (b) unpredictable  
244 increases in bromide ion concentrations in untreated wastewater, and (c) unpredictable formation  
245 of bromate ions, resulting from changes in the water quality of the ozonation influent, such as  
246 spikes in dissolved organic matter concentrations. Therefore, monitoring bromate ion  
247 concentrations immediately after ozonation will allow plant operators to implement  
248 countermeasures, such as ozone dose reductions. It is important to note that polymeric NF  
249 membranes and many components of the online bromate ion analyzer are not ozone-resistant.  
250 Therefore, residual ozone needs to be quenched by adding reducing agents (e.g., sodium  
251 thiosulfate) before it is measured by the online bromate ion analyzer.

252

## 253 **4 Conclusion**

254 To the best of our knowledge, this is the first study demonstrating the potential of the NF pre-  
255 treatment system coupled with an online analyzer for monitoring bromate ion concentrations in  
256 MBR-treated wastewater samples. In contrast with the conventional table-top analytical methods  
257 used, such as LC–MS/MS, the online analyzer provides a continuous profile of the bromate ions  
258 concentrations during water recycling. Although the accuracy of the online analyzer may be  
259 lower than that of the conventional table-top analytical methods, the online-monitored data can  
260 be utilized as an indicator of high bromate ion concentrations exceeding the guideline-prescribed  
261 value (10 µg/L). The detection of high bromate ion concentrations can serve as a cautionary  
262 measure and may help improve the safety of potable water.

263

## 264 **Acknowledgements**

265 The authors thank METAWATER Co. Ltd. (Dr. Kyungju Kim, Mr. Naoki Kanekawa, and Dr.  
266 Dabide Yamaguchi) for loaning an online bromate ion analyzer and providing technical  
267 assistance.

268

## 269 **Conflicts of interest**

270 The authors declare no competing financial interest.

271

## 272 **Supplementary Information**

273 Table S1. LC-MS/MS conditions for bromate analysis

274 Figure S1. Description of nanofiltration pre-treatment system

275 Figure S2. Excitation and emission spectra of membrane bioreactor effluent

276 Figure S3. The relationship between bromate ion permeation and EX300/EM400 permeation

277 Figure S4. Excitation and emission spectra of primary wastewater treatment effluent

278 Figure S5. Bromate concentrations before and after NF pre-treatment

279 Figure S6. Permeation of interfering substances

280

## 281 **References**

- 282 1. B. M. Pecson, S. C. Triolo, S. Olivieri, E. C. Chen, A. N. Pisarenko, C.-C. Yang, A.  
283 Olivieri, C. N. Haas, R. S. Trussell and R. R. Trussell, Reliability of pathogen control in  
284 direct potable reuse: Performance evaluation and QMRA of a full-scale 1 MGD advanced  
285 treatment train. *Water Res.*, 2017, **122**, 258-268.
- 286 2. J. L. Shi, S. L. Plata, M. Kleimans, A. E. Childress and D. L. McCurry, Formation and  
287 Fate of Nitromethane in Ozone-Based Water Reuse Processes. *Environ. Sci. Technol.*,  
288 2021, **55**, 6281-6289.
- 289 3. B. N. Jahan, L. Li and K. R. Pagilla, Fate and reduction of bromate formed in advanced  
290 water treatment ozonation systems: A critical review. *Chemosphere*, 2021, **266**, 128964.

- 291 4. H. Vatankhah, A. Szczuka, W. A. Mitch, N. Almaraz, J. Brannum and C. Bellona,  
 292 Evaluation of Enhanced Ozone–Biologically Active Filtration Treatment for the Removal  
 293 of 1,4-Dioxane and Disinfection Byproduct Precursors from Wastewater Effluent.  
 294 *Environ. Sci. Technol.*, 2019, **53**, 2720-2730.
- 295 5. J. Hooper, D. Funk, K. Bell, M. Noibi, K. Vickstrom, C. Schulz, E. Machek and C.-H.  
 296 Huang, Pilot testing of direct and indirect potable water reuse using multi-stage ozone-  
 297 biofiltration without reverse osmosis. *Water Res.*, 2020, **169**, 115178.
- 298 6. CSWRCB, *Investigation on the feasibility of developing uniform water recycling criteria*  
 299 *for direct potable reuse*, Sacramento, CA, 2016.
- 300 7. M. Noibi, J. Hooper, K. Bell and D. Funk, Direct potable reuse using full advanced  
 301 treatment versus ozone biofiltration: A cost comparison. *AWWA Water Science*, 2020, **2**,  
 302 e1210.
- 303 8. G. Tchobanoglous, J. Cotruvo, J. Crook, E. McDonald, A. Olivieri, A. Salveson and R. S.  
 304 Trussell, *Framework for direct potable reuse*, WaterReuse Association, American Water  
 305 Works Association, Water Environment Federation, National Water Research Institute,  
 306 Alexandria, VA, 2015.
- 307 9. C. Dow, S. Ahmad, K. Stave and D. Gerrity, Evaluating the sustainability of indirect  
 308 potable reuse and direct potable reuse: a southern Nevada case study. *AWWA Water*  
 309 *Science*, 2019, **1**, e1153.
- 310 10. F. Bacaro, E. Dickenson, R. A. Trenholm and D. Gerrity, N-Nitrosodimethylamine  
 311 (NDMA) formation and mitigation in potable reuse treatment trains employing ozone and  
 312 biofiltration. *Environ. Sci.: Water Res. Technol.*, 2019, **5**, 713-725.
- 313 11. M. Park, T. Anumol and S. A. Snyder, Modeling approaches to predict removal of trace  
 314 organic compounds by ozone oxidation in potable reuse applications. *Environ. Sci.:*  
 315 *Water Res. Technol.*, 2015, **1**, 699-708.
- 316 12. S. A. Snyder, B. J. Vanderford and D. J. Rexing, Trace Analysis of Bromate, Chlorate,  
 317 Iodate, and Perchlorate in Natural and Bottled Waters. *Environ. Sci. Technol.*, 2005, **39**,  
 318 4586-4593.
- 319 13. R. Butler, L. Lytton, A. R. Godley, I. E. Tothill and E. Cartmell, Bromate analysis in  
 320 groundwater and wastewater samples. *J. Environ. Monit.*, 2005, **7**, 999-1006.
- 321 14. B. Ruffino, G. V. Korshin and M. Zanetti, Use of spectroscopic indicators for the  
 322 monitoring of bromate generation in ozonated wastewater containing variable  
 323 concentrations of bromide. *Water Res.*, 2020, **182**, 116009.
- 324 15. T. Ohtomo, R. Yatabe, Y. Tanaka, J. Kato, S. Igarashi and S. T. Tower, Fluorescence  
 325 detection-FIA for ppb levels of bromate with trifluoperazine. *Journal of flow injection*  
 326 *analysis*, 2009, **26**, 127-131.
- 327 16. L. D. Nghiem, A. I. Schäfer and M. Elimelech, Pharmaceutical retention mechanisms by  
 328 nanofiltration membranes. *Environ. Sci. Technol.*, 2005, **39**, 7698-7705.
- 329 17. T. Fujioka, S. J. Khan, J. A. McDonald and L. D. Nghiem, Rejection of trace organic  
 330 chemicals by a nanofiltration membrane: the role of molecular properties and effects of  
 331 caustic cleaning. *Environ. Sci.: Water Res. Technol.*, 2015, **1**, 846-854.
- 332 18. D. Lin, H. Liang and G. Li, Factors affecting the removal of bromate and bromide in  
 333 water by nanofiltration. *Environ. Sci. Pollut. R.*, 2020, **27**, 24639-24649.
- 334 19. E. M. Carstea, J. Bridgeman, A. Baker and D. M. Reynolds, Fluorescence spectroscopy  
 335 for wastewater monitoring: A review. *Water Res.*, 2016, **95**, 205-219.



- 336 20. S. A. Huber, A. Balz, M. Abert and W. Pronk, Characterisation of aquatic humic and  
337 non-humic matter with size-exclusion chromatography – organic carbon detection –  
338 organic nitrogen detection (LC-OCD-OND). *Water Res.*, 2011, **45**, 879-885.
- 339 21. S.-H. Yoon, Potential and limitation of fluorescence-based membrane integrity  
340 monitoring (FMIM) for reverse osmosis membranes. *Water Res.*, 2019, **154**, 287-297.
- 341 22. J. G. Wijmans and R. W. Baker, The solution-diffusion model: a review. *J. Membr. Sci.*,  
342 1995, **107**, 1-21.
- 343 23. R. R. Sharma, R. Agrawal and S. Chellam, Temperature effects on sieving characteristics  
344 of thin-film composite nanofiltration membranes: pore size distributions and transport  
345 parameters. *J. Membr. Sci.*, 2003, **223**, 69-87.
- 346 24. T. Tsuru, K. Ogawa, M. Kanezashi and T. Yoshioka, Permeation characteristics of  
347 electrolytes and neutral solutes through titania nanofiltration membranes at high  
348 temperatures. *Langmuir*, 2010, **26**, 10897-10905.  
349