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2  
3 1 **Iodate and iodo-trihalomethane formation during chlorination of iodide-containing**  
4 2 **waters: Role of bromide.**

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6 3  
7 4 **Justine Criquet<sup>a,b</sup>, Sebastien Allard<sup>b</sup>, Elisabeth Salhi<sup>a</sup>, Cynthia A. Joll<sup>b</sup>, Anna Heitz<sup>b</sup> and**  
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21 16 Phone: +41 58 765 5270

22 17  
23 18 **Abstract**

24 19  
25 20 The kinetics of iodate formation is a critical factor in mitigation of the formation of potentially  
26 21 toxic and off flavour causing iodoorganic compounds during chlorination. This study  
27 22 demonstrates that the formation of bromine through the oxidation of bromide by chlorine  
28 23 significantly enhances the oxidation of iodide to iodate in a bromide-catalysed process. The  
29 24 pH-dependent kinetics revealed species specific rate constants of  $k(\text{HOBr} + \text{IO}^-) = 1.9 \times 10^6 \text{ M}^{-1}$   
30 25  $\text{s}^{-1}$ ,  $k(\text{BrO}^- + \text{IO}^-) = 1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $k(\text{HOBr} + \text{HOI}) < 1 \text{ M}^{-1} \text{ s}^{-1}$ . The kinetics and the yield  
31 26 of iodate formation in natural waters depend mainly on the naturally occurring bromide and the  
32 27 type and concentration of dissolved organic matter (DOM). The process of free chlorine  
33 28 exposure followed by ammonia addition revealed that the formation of I-THMs, especially  
34 29 iodoform, was greatly reduced by an increase of free chlorine exposure and an increase of the  
35 30  $\text{Br}^-/\text{I}^-$  ratio. In water from Great Southern River (with a bromide concentration of 200  $\mu\text{g/L}$ ), the  
36 31 relative I-incorporation in I-THMs decreased from 18 to 2% when the free chlorine contact time  
37 32 was increased from 2 to 20 minutes (chlorine dose 1  $\text{mg Cl}_2/\text{L}$ ). This observation is inversely  
38 33 correlated with the conversion of iodide to iodate, which increased from 10 to nearly 90%.  
39 34 Increasing bromide concentration also increased the conversion of iodide to iodate: from 45 to

1  
2  
3 35 nearly 90% with a bromide concentration of 40 and 200  $\mu\text{g/L}$ , respectively and a  
4  
5 36 prechlorination time of 20 min, while the I-incorporation in I-THMs decreased from 10 to 2%.  
6  
7 37

8  
9 38 **Introduction:**  
10  
11 39

12  
13 40 Iodide in source waters is rapidly oxidized to hypiodous acid during oxidation and disinfection  
14  
15 41 with chlorine, monochloramine and ozone.<sup>1-4</sup> During oxidative water treatment, hypiodous  
16  
17 42 acid (HOI) is formed and can be further oxidized to iodate ( $\text{IO}_3^-$ ) or react with NOM to form  
18  
19 43 iodo-organic compounds as disinfection by-products (DBPs).<sup>5,6</sup> It has been shown that iodo-  
20  
21 44 trihalomethanes (I-THMs) are more toxic than their brominated and chlorinated analogues and  
22  
23 45 iodoacetic acid has been found to be the most genotoxic DBP identified to date.<sup>7,8</sup> Moreover, I-  
24  
25 46 THMs, especially iodoform, were associated with a characteristic medicinal taste and odor  
26  
27 47 which may appear in finished drinking water.<sup>9</sup> In fact, these compounds have low odor  
28  
29 48 threshold concentrations ranging from 0.03 to 8.9  $\mu\text{g/L}$ , with the lowest concentration being for  
30  
31 49 iodoform.<sup>10</sup> The occurrence of I-THMs and iodo-acids has been studied and these compounds  
32  
33 50 were found in most finished drinking waters when the iodide levels in the corresponding source  
34  
35 51 waters were between 0.4 and more than 100  $\mu\text{g/L}$ .<sup>8</sup> The formation of iodoorganic compounds  
36  
37 52 is favored in waters containing a high iodide concentration and, among existing disinfection  
38  
39 53 processes, it was shown that chloramination leads to the highest concentrations of iodo-  
40  
41 54 DBPs.<sup>5,8,9,11,12</sup> In a survey of the occurrence of DBPs in the United States, the highest I-THM  
42  
43 55 concentration was observed for a simultaneous addition of chlorine and ammonia.<sup>11</sup> Another  
44  
45 56 survey showed the relationship between the formation of I-THMs and the free chlorine contact  
46  
47 57 time, with shorter contact times inducing a higher formation of I-THMs.<sup>8</sup> These observations  
48  
49 58 are related to the further oxidation of HOI, the first oxidation product of  $\text{I}^-$ , which determines the  
50  
51 59 fate of iodine compounds in oxidative treatment. Only ozone and chlorine oxidize HOI and  $\text{IO}^-$   
52  
53 60 to  $\text{IO}_3^-$ , iodate formation does not occur with monochloramine. Iodate is the desired sink of  
54  
55 61 iodide in drinking water treatment. In contrast to bromate, iodate has been conferred a  
56  
57 62 “Generally Recognized as Safe” status by the United States Food and Drug Administration.<sup>13</sup>  
58  
59  
60

1  
2  
3 63 Chlorine species oxidize HOI by a combination of second- and third-order reactions ( $k''(\text{HOCl} +$   
4  
5 64  $\text{HOI}) = 8.2 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k'''(\text{HOCl} + \text{HOCl} + \text{HOI}) = 8.3 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$  and  $k''(\text{ClO}^- + \text{HOI}) = 52 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>4</sup>  
6  
7 65 It has been shown that an increasing chlorine dose caused a reduced level of iodinated  
8  
9 66 organic by-products due to the formation of iodate.<sup>6</sup> However, the kinetics of the formation of  
10  
11 67 iodate by chlorine is quite slow (half-life of iodide around 40 min for a chlorine concentration of  
12  
13 68 1 mg/L) and on this basis it is difficult to explain these observations. Usually natural waters  
14  
15 69 containing high concentrations of iodide also contain elevated concentrations of bromide.<sup>8</sup>  
16  
17 70 During chlorination, bromide is oxidized to HOBr (Table 2, Eq. 19).<sup>14</sup> Bromine has generally a  
18  
19 71 higher reactivity than chlorine. For example, the reaction rate of bromine with phenolic  
20  
21 72 compounds has been found to be  $10^3$  times higher than that for chlorine.<sup>15-18</sup> Several studies  
22  
23 73 considering the effect of the presence of bromide during chlorination focus only on the  
24  
25 74 differences in the extent of formation of halogenated compounds.<sup>6,19-22</sup>  
26  
27 75 In this study we investigate the influence of bromide on the kinetics of iodate formation during  
28  
29 76 chlorination of iodide-containing natural and synthetic waters. Furthermore, the effect of DOM  
30  
31 77 type and concentration on iodate formation was studied. Finally, the effect of the bromide  
32  
33 78 concentration on the mitigation process for iodo-organic compounds, based on free chlorine  
34  
35 79 followed by ammonia addition was investigated in natural waters.  
36  
37  
38

## 39 81 **Materials and Methods**

40  
41 82  
42  
43 83 **Chemicals.** All reagents used were of the highest purity. HOBr was produced through the  
44  
45 84 oxidation of  $\text{Br}^-$  by HOCl from a NaOCl stock solution (Sigma Aldrich) of 1.29 M (determined by  
46  
47 85 iodometry<sup>23</sup>).  $\text{Br}^-$  was added in a slight stoichiometric excess of  $1.05 \times [\text{HOCl}]$ . The  
48  
49 86 concentration of the HOBr stock solution ( $7 \times 10^{-2} \text{ M}$ ) was determined by photometry  
50  
51 87 ( $\epsilon_{329\text{nm}}(\text{BrO}^-) = 332 \text{ M}^{-1} \text{ cm}^{-1}$ ; after adjusting the pH of the solution to 11).<sup>15</sup> Experiments were  
52  
53 88 performed in ultra-pure water (Barnstead Nanopure (Skan); TOC <0.2 mg/L; 18.2 m $\Omega$  cm). pH  
54  
55 89 was controlled by 5 mM phosphate, borate or carbonate buffers.  
56  
57  
58  
59  
60

1  
2  
3 90 **Natural waters.** Five natural waters were collected in Switzerland and in Western Australia.  
4  
5 91 Their key water quality characteristics are summarized in Table 1. The collected waters were  
6  
7 92 filtered through 0.45  $\mu\text{m}$  membranes before storage at 4  $^{\circ}\text{C}$ . To allow a comparison of iodate  
8  
9 93 formation for the different waters, they were diluted to obtain the same DOC concentration (1.2  
10  
11 94 mg C/L) and then spiked in order to achieve the same final concentration of iodide (50  $\mu\text{g/L}$ ;  
12  
13 95 0.4  $\mu\text{M}$ ) and bromide (100  $\mu\text{g/L}$ ; 1.25  $\mu\text{M}$ ). The pH was adjusted to 8.0 and, for the waters from  
14  
15 96 Great Southern River, North West Reservoir and Great Southern Reservoir, in which  
16  
17 97 deviations of pH during chlorination occurred, a phosphate buffer (5 mM) was added.  
18  
19 98

20  
21 99 Table 1  
22  
23 100

24  
25 101 **Ions and trihalomethane analysis.**  $\text{Br}^-$  and  $\text{IO}_3^-$  analysis were performed in both laboratories  
26  
27 102 by ion chromatography (Dionex ICS 3000) on an AG-S9 column. Low quantification limits for  
28  
29 103 iodate were obtained by a post-column reaction with UV/Vis detection of  $\text{I}_3^-$  at 288 nm.<sup>24</sup> The  
30  
31 104 quantification limits were 10 and 1  $\mu\text{g/L}$  for  $\text{Br}^-$  and  $\text{IO}_3^-$ , respectively. Iodide was determined by  
32  
33 105 an ion-selective electrode (Orion 96-53 Combination iodide electrode) for the Swiss waters and  
34  
35 106 by ion chromatography for the Australian waters, with a quantification limit of 10  $\mu\text{g/L}$ . Most of  
36  
37 107 the iodate samples were analysed at least twice, an average of the values was determined, the  
38  
39 108 standard deviation of the method was around 5%.

40  
41 109 Trihalomethanes (I-THMs and THM4) were analyzed by a headspace solid-phase  
42  
43 110 microextraction-gas chromatography-mass spectrometry (SPME-GC-MS).<sup>25</sup> The error bars  
44  
45 111 (Figure 5 and S7-9) represent the values obtained by a repetition of the analysis on each  
46  
47 112 sample. More detailed information for each compound (detection, quantification limits and  
48  
49 113 reproducibility) can be found in a previous publication.<sup>25</sup>  
50  
51 114

52  
53 115 **Chlorination/bromination experiments.** Experiments were performed at  $24 \pm 1$   $^{\circ}\text{C}$  in a 500  
54  
55 116 mL batch reactor equipped with a dispenser. The oxidant concentration was measured using  
56  
57 117 the colorimetric method based on diethyl-p-phenylene diamine (DPD).<sup>23</sup> Small volumes of  
58  
59  
60

1  
2  
3 118 sodium hypochlorite or hypobromite stock solutions were added at  $t = 0$  to the different water  
4  
5 119 samples and aliquots of reaction solutions were withdrawn after 15 s - 5 h and added to an  
6  
7 120 excess ( $20 \times$ ) of sodium sulfite solution to quench the oxidants before iodate analysis. Aliquots  
8  
9 121 were also added to a DPD/phosphate buffer mixture to determine residual oxidant  
10  
11 122 concentrations. To determine the rate constants for the reaction of HOBr with HOI, triplicate  
12  
13 123 experiments were performed under pseudo first order conditions by measuring the formation of  
14  
15 124 iodate in the presence of an excess of bromine ( $[\text{HOBr}/\text{BrO}^-] = 2 \mu\text{M}$  and  $[\text{I}^-] = 0.1 \mu\text{M}$ ), the pH  
16  
17 125 range was 5.4 to 11.5.

### 126 **Chlorine-ammonia experiments for trihalomethane mitigation**

127 The natural water was diluted and spiked with aliquots of stock solutions of iodide and bromide  
128 to achieve a dissolved organic carbon (DOC) concentration of 1.2 mg C/L and desired  
129 concentrations of 50  $\mu\text{g}/\text{L}$  and from 40 to 200  $\mu\text{g}/\text{L}$ , respectively for  $\text{I}^-$  and  $\text{Br}^-$ . The reactions  
130 were initiated in 100 mL batch reactors by the addition of chlorine to yield 1 mg/L as  $\text{Cl}_2$ . At  
131 different reaction times (0, 2, 5, 10, 20 min), an aliquot of ammonium chloride solution ( $10 \times$   
132 molar excess compared to the initial chlorine concentration) was added to quench the residual  
133 chlorine by the formation of monochloramine. After 24 hours, samples were withdrawn for  
134 iodate and trihalomethane measurements. The iodate concentrations measured after the  
135 different reaction time by quenching with sulfite and after 24 hours after addition of  $\text{NH}_4\text{Cl}$  were  
136 identical. Experiments without addition of  $\text{NH}_4\text{Cl}$  (i.e. 24 h chlorination) were also performed for  
137 comparison.



## 138 Results and Discussion

139

### 140 Effect of bromide on the kinetics of iodate formation during chlorination

141 The oxidation of iodide by chlorine has been studied previously.<sup>2</sup> The first step is the oxidation  
142 of  $I^-$  to HOI and is very fast.<sup>3</sup> This reaction occurs immediately, then 2 additional moles of HOCl  
143 per mole of HOI are consumed to yield  $IO_3^-$ . Figure 1 shows the effect of bromide on iodate  
144 formation, chlorination experiments were performed in the presence of various concentrations  
145 of bromide (*i.e.* ultrapure water;  $[I^-]_0 = 1 \mu\text{M}$  (127  $\mu\text{g/L}$ );  $[\text{HOCl}]_{\text{tot},0} = 4 \mu\text{M}$ ; pH 7; with  $[\text{Br}^-]$  from  
146 0 to 2  $\mu\text{M}$  (up to 160  $\mu\text{g/L}$ )). The kinetics of the decrease of the oxidant concentrations are  
147 shown in SI (Figure S1) and represented as the sum of  $[\text{HOCl}]_{\text{tot}} + [\text{HOBr}]_{\text{tot}} + [\text{HOI}]_{\text{tot}}$ ; with  
148  $[\text{HOX}]_{\text{tot}} = [\text{HOX}] + [\text{XO}^-]$ , X = Cl, Br, I.

149

150 Figure 1

151

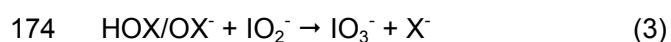
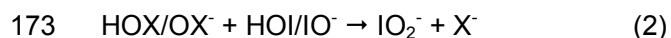
152 As demonstrated in Figure 1, the presence of bromide significantly enhances the kinetics of  
153 iodate formation compared to chlorination alone. Half of the iodide was oxidized to iodate after  
154 360, 35 and 13 min, for bromide concentrations of 0, 0.5 and 2  $\mu\text{M}$ , respectively. The much  
155 higher rate of iodate formation by HOBr (Figure 1a) (half-life of iodide of 4 and 360 min for  
156 oxidation by bromine or chlorine, respectively) explains the enhancement observed in  
157 presence of bromide during chlorination. This is due to the formation of HOBr by oxidation of  
158  $\text{Br}^-$  by HOCl (Eq. 19) followed by the reaction of bromine with HOI. Moreover, according to  
159 Figure 1b, the kinetics of iodate formation by bromine is pH-dependent, with the slowest rate  
160 occurring at low pH (7.0). With increasing pH the rate reached a maximum before decreasing  
161 again at higher pH.

162

### 163 Kinetics and stoichiometry of iodate formation from iodide by HOBr

164 The stoichiometry of the reaction of HOBr/ $\text{BrO}^-$  with HOI/ $\text{IO}^-$  to iodate was investigated as a  
165 function of pH and at molar ratios of  $[\text{HOBr}]_{\text{tot}}:[I^-] = 4:1$ . Considering the consumption of the

1  
2  
3 166 oxidant (HOBr/BrO<sup>-</sup>) and its self-decay in water, it was found that 3.0 ± 0.2 mol of HOBr/BrO<sup>-</sup>  
4  
5 167 were consumed per mol of I<sup>-</sup> oxidized to IO<sub>3</sub><sup>-</sup> (SI, Figure S2). According to the stoichiometry  
6  
7 168 and the mass balance showing quantitative formation of iodate from iodide, it can be assumed  
8  
9 169 that no stable intermediates or IO<sub>4</sub><sup>-</sup> were formed. Therefore, it can be hypothesized that the  
10  
11 170 reaction pathway of formation of iodate through oxidation of iodide by bromine is similar to the  
12  
13 171 one proposed for chlorine (Eqs. 1-3).<sup>4</sup>



20  
21 175 X = Cl, Br

22  
23 176 The kinetics of the first step of iodide oxidation by HOBr, *i.e.*, the formation of HOI/IO<sup>-</sup>, has  
24  
25 177 been determined previously<sup>26</sup> (Table 2, Eqs. 10 and 11). Under the conditions used, the  
26  
27 178 formation of hypiodite and hypiodous acid occurs immediately. Moreover, the species  
28  
29 179 specific rate constants of Eq. 3 are assumed to be high, considering that IO<sub>2</sub><sup>-</sup> does not  
30  
31 180 accumulate in solution. Therefore, the rate limiting step is the oxidation of HOI/IO<sup>-</sup> by  
32  
33 181 HOBr/BrO<sup>-</sup> (Eq. 2) and the rate of iodate formation corresponds to the rate of the reaction (2).  
34  
35 182 To determine the kinetics of the oxidation of iodine by bromine, experiments were performed  
36  
37 183 under pseudo first order conditions ([HOBr]<sub>tot</sub>:[I<sup>-</sup>] = 20). The apparent rate constant of reaction  
38  
39 184 (2) can be determined as follows (Eqs. 4-8):

40  
41  
42 185 
$$r = \frac{d[IO_3^-]}{dt} = - \frac{d[HOI]_{tot}}{dt} \quad (4)$$

43  
44 186 where,

45  
46 187 
$$r = k''_{app} [HOI]_{tot} [HOBr]_{tot} \quad (5)$$

47  
48 188 HOBr was introduced in a large excess, hence, [HOBr]<sub>tot</sub> can be considered constant (pseudo  
49  
50 189 first order conditions):

51  
52 190 
$$r = k'_{app} [HOI]_{tot} \quad \text{with: } k'_{app} = k''_{app} [HOBr]_{tot} \quad (6)$$

53  
54 191 then,

55  
56  
57 192 
$$r = - \frac{d[HOI]_{tot}}{dt} = \frac{d[IO_3^-]}{dt} = k'_{app} [HOI]_{tot} \quad (7)$$

1  
2  
3 193 The concentration of HOI after a time  $t$  is calculated as  $[\text{HOI}]_{\text{tot},t} = [\text{HOI}]_{\text{tot},0} - [\text{IO}_3^-]_t$  with  $[\text{HOI}]_{\text{tot},0}$   
4  
5 194 =  $[\text{I}^-]_0$ ; then,

6  
7 195 
$$\ln \frac{[\text{I}^-]_0 - [\text{IO}_3^-]_t}{[\text{I}^-]_0} = -k'_{\text{app}} t \quad (8)$$
  
8  
9

10 196

11  
12 197 The apparent rate constant of the reaction between iodine and bromine was obtained by  
13  
14 198 measuring the kinetics of iodate formation as a function of pH from 7.0 to 11.5. The slopes of  
15  
16 199 the logarithmic regression lines for the different pH (Eq. 8) (SI, Figure S3) give the value of  
17  
18 200  $k'_{\text{app}}$ . The apparent second order rate constant  $k''_{\text{app}}$  is then obtained by dividing the first order  
19  
20 201 rate constant by the concentration of bromine. The derived apparent second order rate  
21  
22 202 constants of the reaction between iodine and bromine species as a function of the pH are  
23  
24 203 plotted in Figure 2.  
25

26 204

27  
28 205 Figure 2  
29

30 206

31  
32 207 The variation of the apparent second order rate constants shows a maximum at the mean of  
33  
34 208 the two pKa values ( $1/2(\text{pKa}_1 + \text{pKa}_2) = 9.6$ ) of the involved species HOBr and HOI  
35  
36 209 ( $\text{pKa}_1(\text{HOBr}/\text{BrO}^-) = 8.8$ ;  $\text{pKa}_2(\text{HOI}/\text{IO}^-) = 10.4$ ). This behaviour is common for the reaction of  
37  
38 210 two compounds HA and HB if either the protonated form HA reacts with the deprotonated form  
39  
40 211  $\text{B}^-$ , or conversely,  $\text{A}^-$  reacts with HB.<sup>27</sup> From a kinetic point of view, the two reactions ( $\text{BrO}^- +$   
41  
42 212  $\text{HOI}$  and  $\text{HOBr} + \text{IO}^-$ ; Eqs. 14 and 14a, Table 2) cannot be distinguished since they have the  
43  
44 213 same pH dependence. Rather than considering the two reactions in parallel, it is usually  
45  
46 214 assumed that only one of the two pathways is important. From a chemical point of view, HOBr  
47  
48 215 is a stronger electrophile and  $\text{IO}^-$  is a stronger nucleophile. Therefore, the reaction of HOBr  
49  
50 216 with  $\text{IO}^-$  (Table 2, Eq. 14) is considered as the dominant pathway for the reaction of the  
51  
52 217 bromine with the iodine species. Nevertheless, at low or high pH,  $\text{HOBr} + \text{HOI}$  or  $\text{OBr}^- + \text{IO}^-$ ,  
53  
54 218 respectively, might also be important reactions (see below). Consequently, the reactions  
55  
56 219 considered to represent this reaction step are Eqs. 13-15 (Table 2).  
57  
58  
59  
60

1  
2  
3 220 The species specific rate constants were determined by a non-linear least-square regression  
4  
5 221 with the experimental rate constants determined as a function of the pH (SI, Text S1). The  
6  
7 222 regression curve is represented in Figure 2 and is in good agreement with the profile of the pH-  
8  
9 223 dependent experimental data. The species specific second order rate constants were  
10  
11 224 determined to be  $k(\text{HOBr}/\text{IO}^-) = 1.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $k(\text{BrO}^-/\text{IO}^-) = 1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . Based on  
12  
13 225 this model, the reaction between HOBr and HOI was negligible with a value tending to zero.  
14  
15 226 For  $\text{pH} < 7$ , a drop of the apparent rate constant was found followed by an increase for smaller  
16  
17 227 pH values. The increase in the apparent rate constant in more acidic conditions can be  
18  
19 228 attributed to the formation of  $\text{Br}_2$ . The rate constant for the reaction of  $\text{Br}_2$  with HOI was  
20  
21 229 estimated to be  $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and this reaction becomes significant for  $\text{pH} < 7$  (SI, Text S2).

### 230 **Modeling the effect of bromide on iodate formation during chlorination**

231 To validate the kinetics of iodate formation during chlorination of bromide-containing waters,  
232 simulations of the reaction system were carried out by a kinetic model (Software Copasi<sup>28</sup>).  
233 The reaction model is shown in Table 2 (Eqs. 9-25).

234 Table 2

235

236 The results of the model calculation for of iodide oxidation by bromine are presented in Figure  
237 1b. The experiments performed in basic media were well predicted by the set of reactions  
238 taken into account shown in Table 2. However, the model showed a certain deviation  
239 compared to the experimental data obtained for  $\text{pH} 7.0$ . A small error on the measured pH  
240 value ( $\pm 0.1$ ) can affect the kinetics of iodate formation significantly. The observed difference  
241 between the experiment and model calculations is therefore within the range of experimental  
242 error. The model was subsequently applied for modeling iodate formation during chlorination of  
243 iodide-containing water in the absence and presence of bromide at  $\text{pH} 7$  (lines in Figure 1a)  
244 with good agreement with the experimental data. The increase in the rate of iodate formation in  
245 the presence of bromide is caused by the formation of bromine through the reaction of chlorine  
246 with bromide (Table 2, Eq. 19). HOBr then oxidizes HOI to  $\text{IO}_2^-$  (more rapidly than HOCl  
247 undertakes this oxidation) and thereby HOBr is reduced to  $\text{Br}^-$  (Table 2, Eqs. 13-15).

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3 248 Therefore, bromide acts as a catalyst in the formation of iodate during chlorination. This has  
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5 249 been shown previously for the transformation of chlorpyrifos during chlorination.<sup>32</sup> Bromide  
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7 250 catalysis is also known from other oxidation processes such as the enhanced ammonia  
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9 251 oxidation during ozonation of ammonia- and bromide-containing waters, and the formation of  
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11 252 *N*-nitrosodimethylamine during ozonation of dimethylsulfoxide- and bromide-containing  
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13 253 waters.<sup>33,34</sup>

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### 16 17 255 **Iodate formation during chlorination of iodide-containing natural waters**

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19 256 To further elucidate the reaction pathways of iodate formation, chlorination experiments were  
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21 257 performed with two natural waters spiked with iodide ( $0.40 \mu\text{M} \approx 50 \mu\text{g/L}$ ) and various  
22  
23 258 concentrations of bromide. Bromide concentrations were in the range of natural waters from  
24  
25 259  $0.19 \mu\text{M}$  ( $15 \mu\text{g/L}$ ) up to  $6.25 \mu\text{M}$  ( $500 \mu\text{g/L}$ ). The formation of iodate is presented as a function  
26  
27 260 of the oxidant exposure (sum of chlorine, bromine and iodine exposures) in Figure 3. This  
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29 261 representation takes into account the different rates of consumption of the oxidants due to  
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31 262 differences in the water composition.

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34  
35 264 Figure 3

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39 266 According to Figure 3, as found in ultrapure water, increasing the bromide concentrations in  
40  
41 267 natural waters significantly enhanced the rate of iodate formation. The experiments on both  
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43 268 waters were performed at the same pH (8) to avoid an effect of this parameter on the kinetics  
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45 269 of iodate formation. The main difference between the two waters was the DOC level: Lake  
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47 270 Greifensee water ( $3.5 \text{ mg C/L}$ ) had a DOC concentration that was 3 times higher than the DOC  
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49 271 concentration of Lake Zurich water ( $1.2 \text{ mg C/L}$ ). Comparison of Figures 3a and b shows that  
50  
51 272 the rate of iodate formation was higher for the water with the lower DOC concentration at the  
52  
53 273 same bromide concentration. Hypoiodous and hypobromous acids are scavenged to a higher  
54  
55 274 proportion when the concentration of dissolved organic matter (DOM) is higher. This is  
56  
57 275 reflected by the fact that the iodate yield in the natural waters is not 100% based on the initial  
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3 276 iodide concentration. In addition to the kinetic enhancement, it is important to note that a  
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5 277 higher bromide level also improves the relative conversion of iodide to iodate by lowering the  
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7 278 effect of the competitive reactions with DOM. The faster reaction of bromine species compared  
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9 279 to chlorine species with hypiodous acid decreases the life-time of HOI, thereby reducing its  
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11 280 likelihood of reaction with DOM and favoring iodate as a sink for iodine. The stability of the  
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13 281 oxidants (HOCl + HOBr + HOI) was also influenced by the bromide concentration (SI, Figure  
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15 282 S4). An increase in the consumption rate of the total oxidant concentration was observed with  
16  
17 283 increasing bromide concentration. In natural waters, this can mainly be explained by the higher  
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19 284 reactivity of HOBr compared to HOCl towards DOM.<sup>6,35</sup> During chlorination, a substantial  
20  
21 285 portion of bromide disappeared and was probably incorporated into organic matter (SI, Figure  
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23 286 S5). This fraction was different for the two waters and was independent of the initial bromide  
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25 287 concentration. Bromide in these waters decreased about 50 and 40% based on the initial  
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27 288 concentration in Lake Zurich and Lake Greifensee waters, respectively. Modeling of the effect  
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29 289 of bromide on iodate formation during chlorination of iodide-containing natural waters was  
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31 290 difficult due to the unknown speciation of the different oxidant species, HOCl, HOBr and HOI,  
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33 291 and lack of information on the reactivity of those species with DOM which is different for each  
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35 292 natural water.

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37 293 To compare the influence of the type of DOM on iodate formation, experiments with natural  
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39 294 waters from different origins (lakes, reservoirs and a river from both Switzerland and Australia;  
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41 295 Table 1) were performed. Chlorination experiments were conducted at pH 8.0 with the natural  
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43 296 waters adjusted to the same DOC concentration (1.2 mg C/L), with iodide and bromide  
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45 297 concentrations of  $50 \pm 2$  and  $105 \pm 5$   $\mu\text{g/L}$  (0.4 and 1.3  $\mu\text{M}$ ), respectively. The formation of  
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47 298 iodate as a function of the oxidant exposures is presented in Figure 4.

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49 299

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51 300 Figure 4

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56 302 Despite the same experimental conditions (pH,  $[\text{I}^-]$ ,  $[\text{Br}^-]$ , DOC concentration), the kinetics of  
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58 303 iodate formation varied depending on the water type. In particular, the experiment performed

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3 304 using the Great Southern Reservoir water showed completely different iodate formation.  
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5 305 Different types of DOM have different reactivities towards hypohalous acids and are  
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7 306 responsible for differences in extent and rate of iodate formation due to incorporation of  
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9 307 halogens into the DOM. In fact, the kinetics of iodate formation generally decreased with  
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11 308 increasing SUVA (SI, Figure S6). This is likely related to the more aromatic character of the  
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13 309 organic matter (higher SUVA), which constitutes a target for quenching the moieties HOI and  
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15 310 HOBr, thereby increasing the competition of the DOM for consumption of the HOI versus  
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17 311 oxidation of HOI to iodate. However, the SUVA alone does not explain completely the  
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19 312 differences in the kinetics of iodate formation. For example, Lake Zurich and Great Southern  
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21 313 River waters showed the same trend for iodate formation but had quite different SUVA values  
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23 314 (2.6 and 4.1, respectively). Therefore, SUVA can only serve as a very general parameter to  
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25 315 understand the relative kinetics of iodate formation in natural waters and more detailed  
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27 316 structural information on DOM would be needed to draw more quantitative conclusions. As  
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29 317 noted previously, bromide incorporation into organic matter differs from one water source to  
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31 318 another. In the five investigated waters, bromide incorporation was found to vary from 30 to  
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33 319 70% without any correlation to the kinetics of iodate formation (results not shown). However,  
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35 320 the experiments performed at two DOC concentrations for Lake Griefensee (1.2 and 3.5 mg  
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37 321 C/L) show that the kinetics of iodate formation (Figure 3b and 4) and the incorporation of  
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39 322 bromine was related to the DOC concentration. Half of the maximum yield of iodate (*i.e.*  
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41 323 formation of 0.2  $\mu\text{M}$  of iodate) was reached for an oxidant exposure of 7 and 24 mg  $\text{Cl}_2/\text{L} \times$   
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43 324 min, for a DOC concentration of 1.2 and 3.5 mg C/L, respectively. Moreover, the incorporation  
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45 325 of bromine into organic matter was higher for the higher organic matter content (30 and 40%  
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47 326 for DOC concentrations of 1.2 and 3.5 mg C/L, respectively). The observations of iodate  
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49 327 formation and bromide incorporation into organic matter indicate a significant dependence on  
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51 328 the DOC concentration. Therefore, the conversion factor of iodide to iodate could be much  
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53 329 lower in waters rich in organic matter.  
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**333 Formation of iodo-trihalomethanes (I-THMs)**

334 Trihalomethane formation may serve as a model for the formation of halo-organic compounds.

335 Chloramination with a sufficient free chlorine contact time followed by ammonia addition, rather

336 than preformed monochloramine, has been previously suggested<sup>8,21,22</sup> as a mitigation strategy

337 for the minimization of I-DBPs, since exposure to free chlorine should promote the formation of

338 iodate. This mitigation process was tested on one of the natural waters (Great Southern River,

339 after dilution and spiking: [I<sup>-</sup>] = 50 µg/L; pH 8; DOC = 1.2 mg C/L). The free chlorine contact

340 time was varied such that the full range of conversion of iodide to iodate (from 0 up to nearly

341 90%) was achieved to elucidate the optimum conditions for minimal formation of I-THMs. This

342 was done for three different bromide concentrations (40, 100 and 200 µg/L). After a certain

343 chlorine contact time (0, 2, 5, 10 and 20 min), ammonia was added to reduce the formation of

344 bromo- and chloro-organic compounds. The formation of trihalomethanes, the four regulated

345 THMs (THM4) and I-THMs, was analysed after 24 hours. Figure 5 presents the iodine

346 incorporation into I-THMs and the corresponding iodate formation. A detailed speciation of

347 trihalomethanes is given in SI (Figures S7 and S8). For the calculation of the incorporation of

348 iodine, the molar concentrations of individual I-THMs were multiplied by the number of iodine

349 atoms in the I-THM. With this value, the percentage of iodine incorporated into the I-THMs can

350 be compared to the percentage of iodine yielding IO<sub>3</sub><sup>-</sup>.

351

352 Figure 5

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354 Considering the monochloramination experiment (no free chlorine contact time, t = 0 min in

355 Figure 5), only a few THM4 were formed with traces of brominated THMs, as monochloramine

356 hardly oxidizes bromide (SI, Figures S7 and S8). Although the I-THMs were predominant in

357 this case compared to the THM4, a relatively low incorporation of iodine into I-THMs of around

358 6% of the initial iodide content, independent of the bromide concentration was observed. In this

359 process, iodoform was formed in a relatively high concentration, representing up to 90% of the



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3 360 iodine incorporation into I-THMs. These results are in accordance with those previously  
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5 361 published<sup>5,9,21,22,36</sup> in which chloramination of raw waters showed substantial formation of  
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7 362 iodoform.

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10 363 The formation and the speciation of iodinated THMs depend on the free chlorine contact time  
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12 364 and the bromide concentration. The iodine incorporation into I-THMs increased for a short  
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14 365 chlorination time compared to chloramination but decreased for higher free chlorine exposures.

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16 366 The lower formation of I-THMs with increasing free chlorine contact time was correlated with  
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18 367 the conversion of iodide to iodate. According to Figure 5, the iodine incorporation was lowered  
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20 368 from 18 to 2% of the initial iodide content, while the iodate concentration increased from 10 to  
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22 369 nearly 90%, for an increase of the prechlorination time from 2 up to 20 min in the presence of  
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24 370 200 µg/L of bromide. Moreover, increasing concentrations of bromide clearly reduced the  
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26 371 formation of I-THMs by favoring the formation of iodate. For the experiments performed with  
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28 372 the highest prechlorination time, an increase of the bromide level from 40 to 200 µg/L resulted  
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30 373 in a decrease of the iodine incorporated in I-THMs by a factor > 4 and an improvement of  
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32 374 iodide conversion to iodate from 45 to nearly 90% of the initial iodide concentration. At the  
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34 375 same time, the formation of Br-THMs was kept low, with a bromine incorporation between 4.5  
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36 376 and more than 10 times lower than the one observed during the 24h-chlorination performed  
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38 377 under the same conditions for varying Br<sup>-</sup> concentrations. The highest formation of THM4  
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40 378 observed for the chlorine-ammonia process occurred for the highest free chlorine contact time  
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42 379 and highest bromide concentration. However, this concentration (9 µg/L) was significantly  
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44 380 lower than the one observed for the 24h-chlorination (around 40 µg/L) (SI, Figure S8 and Table  
45  
46 381 S1). Considering the increasing iodate formation with increasing prechlorination time (Figure  
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48 382 5), the higher formation of I-THMs after a short prechlorination time compared to the  
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50 383 chloramination process was not expected.<sup>5</sup> This behaviour was also noticed by Jones et al.<sup>21</sup>  
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52 384 who showed a higher formation of I-THMs by chlorination than by the chloramination process  
53  
54 385 in some cases. This was attributed to the additional formation of brominated I-THMs during  
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56 386 chlorination which are not formed during chloramination. In our experiments, the formation of  
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58 387 brominated I-THMs effectively occurred with chlorination (SI, Figure S7) and contributed to the  
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3 388 overall increase of I-THMs, but the formation of iodoform also increased with a short  
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5 389 prechlorination time. As shown in a previous study,<sup>5</sup> the formation of iodoform readily depends  
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7 390 on the chlorination dose and exposure, decreasing with an increasing exposure. In our study,  
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9 391 the highest concentrations of iodoform were observed for the smaller prechlorination contact  
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11 392 times and exposures (from 0 to 5 min). Thereafter, the concentration of this product decreased  
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13 393 with increasing chlorine exposure. The same trend was also observed for the highly iodinated  
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15 394 compounds (CHCl<sub>2</sub> and CHBr<sub>2</sub>). Therefore, increased chlorination can limit the formation of  
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17 395 the highly iodinated THMs, and especially the formation of CHI<sub>3</sub>, which may be problematic  
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19 396 due to its taste and odor.<sup>10</sup> It can also be expected that highly toxic mono-iodinated  
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21 397 compounds, such as iodo acetic acids, will behave in the same manner. However, the chlorine  
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23 398 dose is an important parameter: the prechlorination exposure should be high enough to  
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25 399 transform iodide into iodate and avoid the formation of high concentrations of iodinated  
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27 400 compounds. In our experiments, the formation of I-THMs was decreased to a large extent after  
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29 401 10 minutes for the experiment performed with the higher bromide concentration; a longer  
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31 402 contact time was needed in the case of lower concentrations of bromide. Furthermore, in  
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33 403 addition to the formation of I-THMs, more information is needed about the formation of other  
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35 404 iodo-organic compounds, especially iodoacetic acid, under realistic conditions without omitting  
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37 405 the role of bromide. During chlorination, iodate formation was controlled by HOBr even at low  
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39 406 bromide levels. Considering a chlorine dose of 1 mg Cl<sub>2</sub>/L at pH 7, a concentration of  
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41 407 approximately 25 µg/L of bromide is sufficient to induce half of the iodate formation through the  
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43 408 reaction of HOI with HOBr. This concentration drops to <10 µg/L for pH 8.

#### 409 **Practical implications**

410 A process based on free chlorine followed by chloramine to reduce the formation of I-organics  
411 has been proposed in several studies.<sup>4,9,11,21,22,36-38</sup> Our study reveals that bromide plays an  
412 important role in this process, notably by enhancing the preferred conversion of iodide to  
413 iodate. The balance between the formation of iodate and iodoorganic compounds formation  
414 depends on the water quality, *i.e.* the concentration and nature of the natural organic matter,  
415 the bromide concentration and the chlorine consumption rate. To determine the optimum pre-

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3 416 chlorine exposure, we propose an assessment of iodate formation. In fact, the plot of I-  
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5 417 incorporation vs. iodate formation (SI, Figure S9) shows that, under our experimental  
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7 418 conditions, the formation of I-THMs was minimal for a conversion of  $\geq 60\%$  of iodide to iodate,  
8  
9 419 independent of the bromide level. Since we have a limited data set, more information is  
10  
11 420 needed to validate this procedure.

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14  
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19  
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#### 21 22 23 425 **Supporting Information Available**

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26 426 Two texts, one table and nine figures with further information addressing calculations and  
27  
28 427 additional data. This information is available free of charge via the Internet at  
29  
30 428 <http://pubs.acs.org/> .

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532 Table 1. Natural water characteristics.

	DOC (mg C/L)	SUVA (L/mg C.m)	I <sup>-</sup> (µg/L)	Br <sup>-</sup> (µg/L)
<b>Lake Zurich</b>	1.2	2.6	< 10	15
<b>Lake Greifensee</b>	3.5	1.8	< 10	50
<b>North West Reservoir</b>	2.8	1.7	31	168
<b>Great Southern River</b>	12.0	4.1	17	412
<b>Great Southern Reservoir</b>	20.0	4.9	<10	400

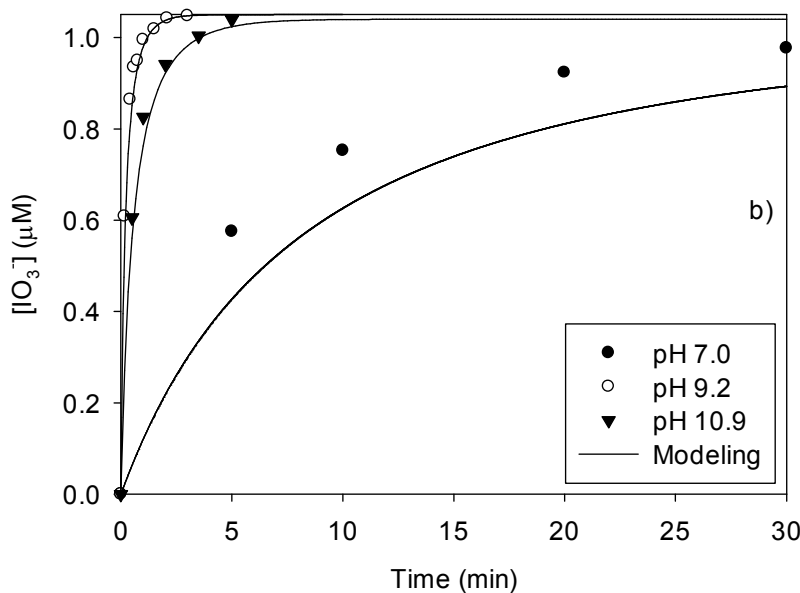
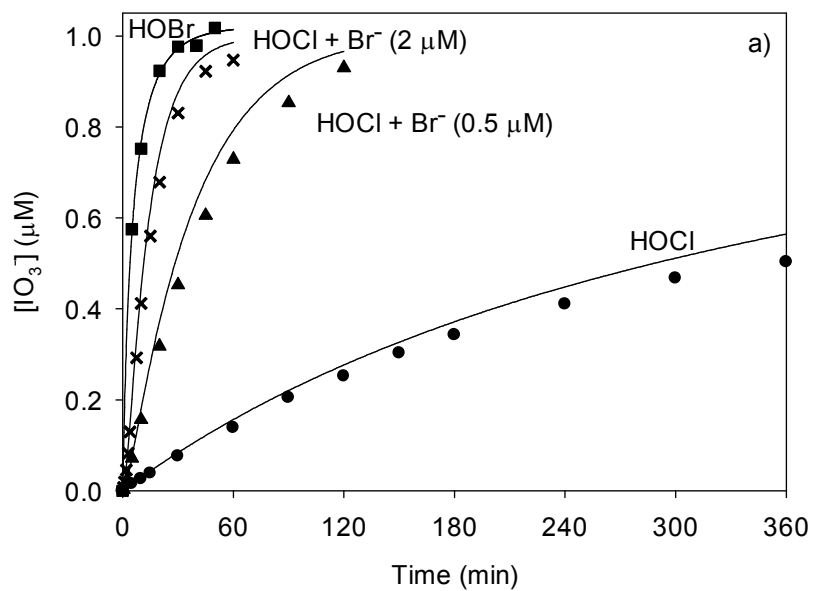
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534 Table 2. Rate constants for the reactions occurring in the chlorine-bromide-iodide system.  
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Eq.	Reaction	Rate constants (M <sup>-1</sup> s <sup>-1</sup> )	pKa	<i>k''<sub>app</sub></i> (M <sup>-1</sup> s <sup>-1</sup> )		References
				pH 7	pH 8	
9	BrO <sup>-</sup> + H <sup>+</sup> ⇌ HOBr		8.8			29
10	HOBr + I <sup>-</sup> → HOI + Br <sup>-</sup>	5.0 × 10 <sup>9</sup>				26
11	BrO <sup>-</sup> + I <sup>-</sup> → IO <sup>-</sup> + Br <sup>-</sup>	6.8 × 10 <sup>5</sup>				26
12	IO <sup>-</sup> + H <sup>+</sup> ⇌ HOI		10.4			30
13	HOBr + HOI → IO <sub>2</sub> <sup>-</sup> + Br <sup>-</sup> + 2 H <sup>+</sup>	Not significant				This work
14	HOBr + IO <sup>-</sup> → IO <sub>2</sub> <sup>-</sup> + Br <sup>-</sup> + H <sup>+</sup>	1.9 × 10 <sup>6</sup>		740	6500	This work
14a	BrO <sup>-</sup> + HOI → IO <sub>2</sub> <sup>-</sup> + Br <sup>-</sup> + H <sup>+</sup>	-				<sup>a</sup>
15	BrO <sup>-</sup> + IO <sup>-</sup> → IO <sub>2</sub> <sup>-</sup> + Br <sup>-</sup>	1.8 × 10 <sup>3</sup>		12	1030	This work
16	HOBr + IO <sub>2</sub> <sup>-</sup> → IO <sub>3</sub> <sup>-</sup> + Br <sup>-</sup> + H <sup>+</sup>	High				Suggested in this work
17	BrO <sup>-</sup> + IO <sub>2</sub> <sup>-</sup> → IO <sub>3</sub> <sup>-</sup> + Br <sup>-</sup>	High				Suggested in this work
18	ClO <sup>-</sup> + H <sup>+</sup> ⇌ HOCl		7.53			31
19	HOCl + Br <sup>-</sup> → HOBr + Cl <sup>-</sup>	1550				14
20	ClO <sup>-</sup> + Br <sup>-</sup> → BrO <sup>-</sup> + Cl <sup>-</sup>	9 × 10 <sup>-4</sup>				14
21	HOCl + I <sup>-</sup> → HOI + Cl <sup>-</sup>	4.3 × 10 <sup>8</sup>				3
22	HOCl + HOI → IO <sub>2</sub> <sup>-</sup> + Cl <sup>-</sup> + 2 H <sup>+</sup>	8.2				4
23	ClO <sup>-</sup> + HOI → IO <sub>2</sub> <sup>-</sup> + Cl <sup>-</sup> + H <sup>+</sup>	52				4
24	HOCl + IO <sub>2</sub> <sup>-</sup> → IO <sub>3</sub> <sup>-</sup>	High				Suggested in this work
25	ClO <sup>-</sup> + IO <sub>2</sub> <sup>-</sup> → IO <sub>3</sub> <sup>-</sup> + Cl <sup>-</sup>	High				Suggested in this work

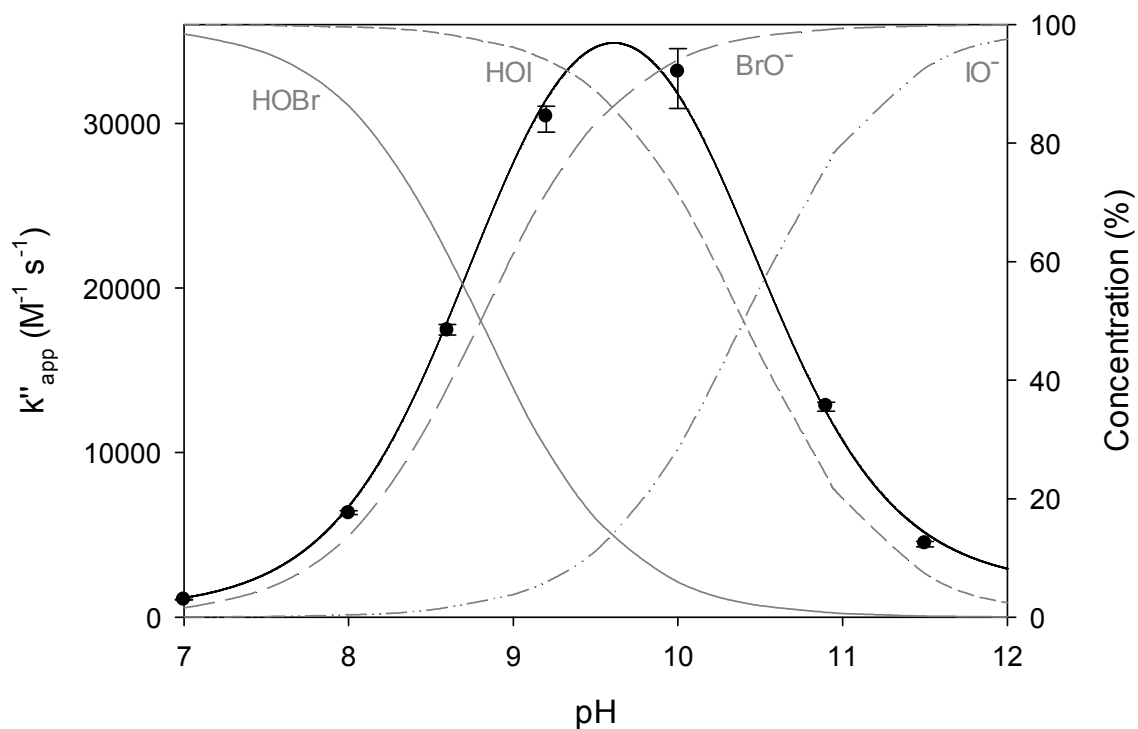
536 <sup>a</sup>Reaction 14a is not taken into account as reaction 14 describes the behaviour of these  
537 species as *f*(pH).  
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543  
544 Figure 1. Kinetics of iodate formation from iodide-containing waters: a) during chlorination in  
545 presence of various concentrations of bromide or during bromination (ultrapure water, pH 7.0  $\pm$   
546 0.1 (phosphate buffer, 5 mM);  $[I^-]_0 = 1 \mu\text{M}$ ;  $[Br^-]_0 = 0.5$  or  $2 \mu\text{M}$ ,  $[HOBr]_0$  or  $[HOCl]_0 = 4 \mu\text{M}$ ); b)  
547 during bromination at various pH values ( $[I^-]_0 = 1 \mu\text{M}$ ;  $[HOBr]_0 = 4 \mu\text{M}$  (phosphate, borate or  
548 carbonate buffer, 5 mM)). Symbols: experimental data; Lines: Modeling considering the  
549 reactions in Table 2 (see text).

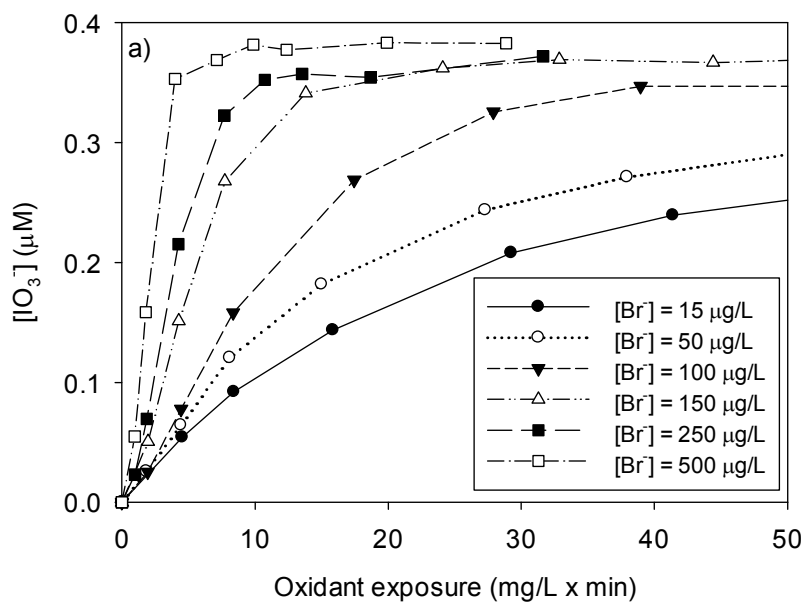




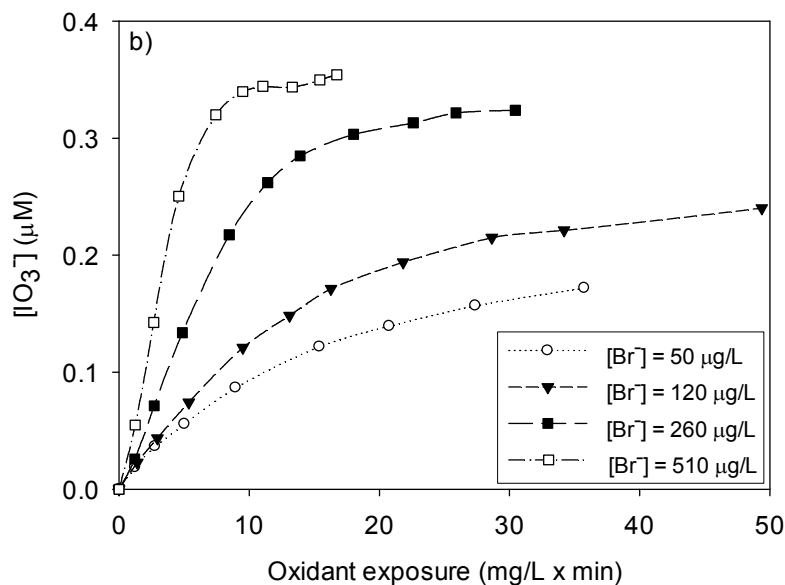
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551 Figure 2. pH dependence of the relative distribution of the main aqueous bromine and iodine  
552 species (grey) and the apparent second-order rate constant for the reaction of HOBr with HOI  
553 ( $pK_{a1}(\text{HOBr}/\text{BrO}^-) = 8.8$ ;  $pK_{a2}(\text{HOI}/\text{IO}^-) = 10.4$ ) (black) ●: experimental data; —: model  
554 calculations (see text).  
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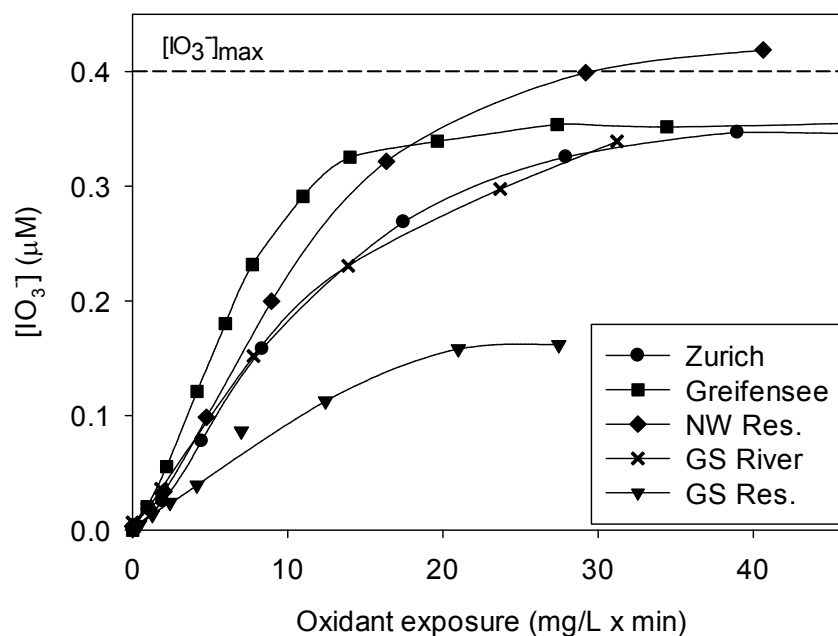
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558 Figure 3. Influence of bromide concentration on iodate formation during chlorination of iodide-  
 559 containing natural waters ( $[I^-]_0 = 0.4 \mu\text{M}$ ;  $50 \mu\text{g/L}$ ) at pH 8.0. a) Lake Zurich water:  $[\text{HOCl}]_0 =$   
 560  $1.0 \text{ mg Cl}_2/\text{L}$ ;  $\text{DOC} = 1.2 \text{ mg C/L}$ ;  $[\text{Br}^-]_0 = 15\text{-}500 \mu\text{g/L}$  ( $0.19\text{-}6.3 \mu\text{M}$ ). b) Lake Greifensee water:  
 561  $[\text{HOCl}]_0 = 1.8 \text{ mg Cl}_2/\text{L}$ ;  $\text{DOC} = 3.5 \text{ mg C/L}$ ;  $[\text{Br}^-]_0 = 50\text{-}510 \mu\text{g/L}$  ( $0.63\text{-}6.4 \mu\text{M}$ ). Lines are used  
 562 to guide the eye. Oxidant:  $[\text{HOCl}] + [\text{HOBr}] + [\text{HOI}]$ .

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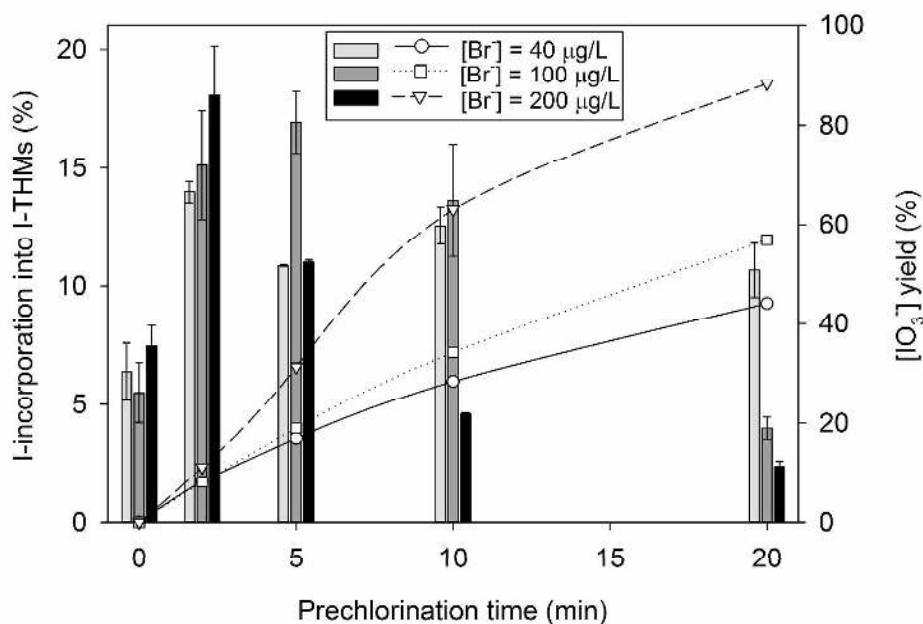
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567 Figure 4. Kinetics of iodate formation for various natural waters (Table 1). Concentrations after  
 568 dilution and spiking:  $[I^-]_0 = 50 \pm 2 \mu\text{g/L}$  ( $0.4 \mu\text{M}$ );  $[\text{Br}^-]_0 = 105 \pm 5 \mu\text{g/L}$  ( $1.3 \mu\text{M}$ );  $\text{pH} = 8.0 \pm 0.1$ ;  
 569  $\text{DOC} = 1.2 \pm 0.1 \text{ mg C/L}$ ;  $[\text{HOCl}]_0 = 1\text{-}5 \text{ mg Cl}_2/\text{L}$ . Lines are used to guide the eye.

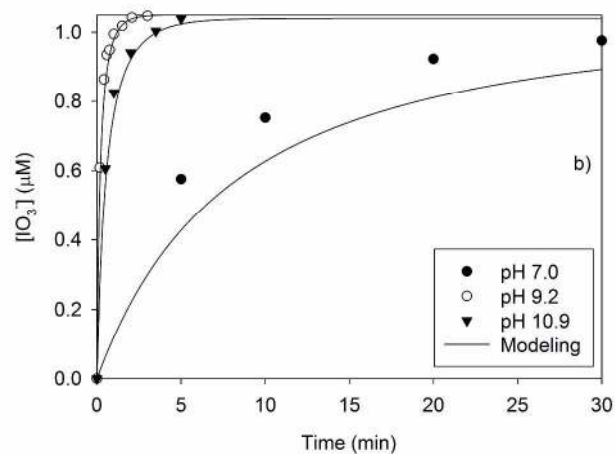
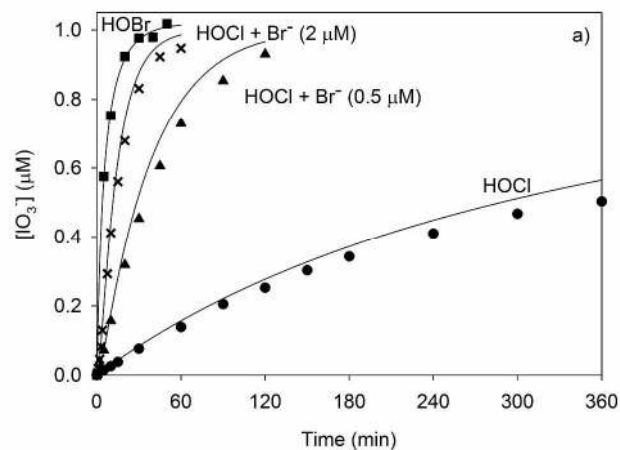
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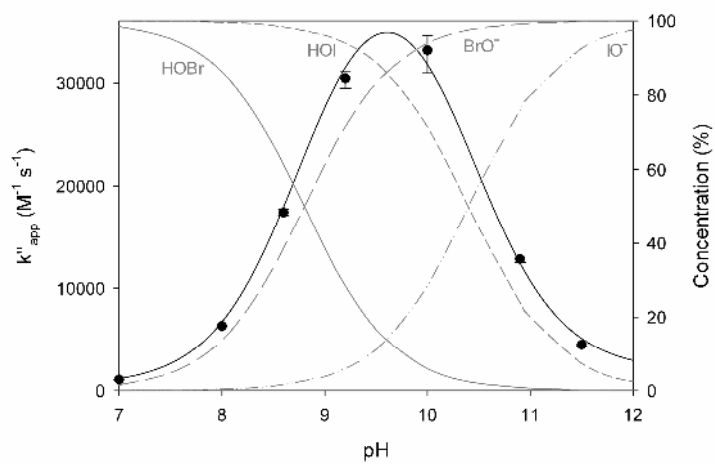
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572 Figure 5. Iodine incorporation into I-THMs (bars) and iodate yield (lines) for various  
 573 prechlorination contact times and varying bromide concentrations for Great Southern River  
 574 water (concentrations after dilution and spiking:  $[I^-]_0 = 50 \mu\text{g/L}$ ;  $[\text{Br}^-]_0 = 40, 100$  and  $200 \mu\text{g/L}$ ;  
 575  $\text{pH} 8.0$ ;  $\text{DOC} = 1.2 \text{ mg C/L}$ ). Chlorine dose:  $1 \text{ mg Cl}_2/\text{L}$  ( $15 \mu\text{M}$ ), ammonia addition:  $75 \mu\text{M}$ .  $t = 0$  min,  
 576 ammonia addition before the addition of chlorine. I-THMs were analysed after 24h to  
 577 simulate contact times in distribution systems.

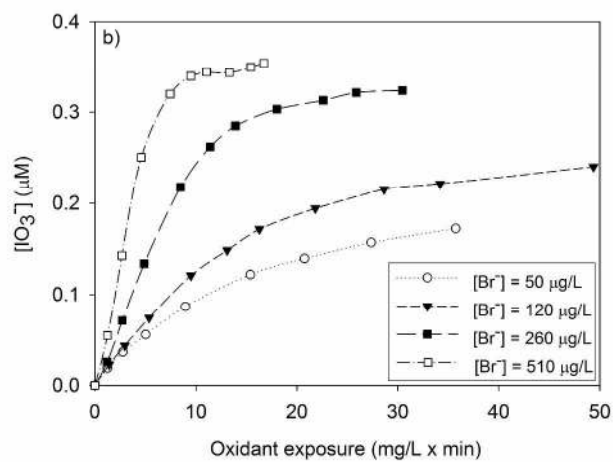
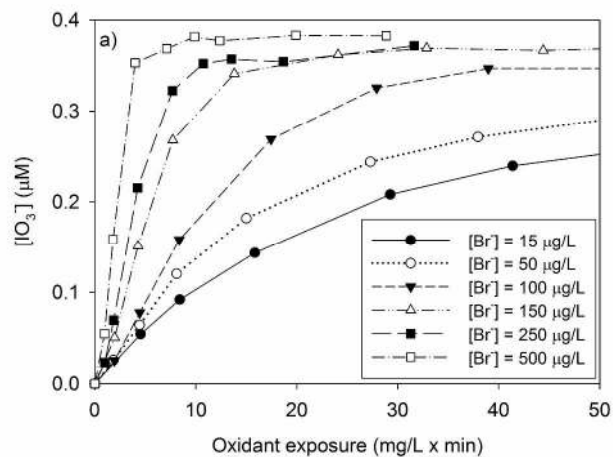
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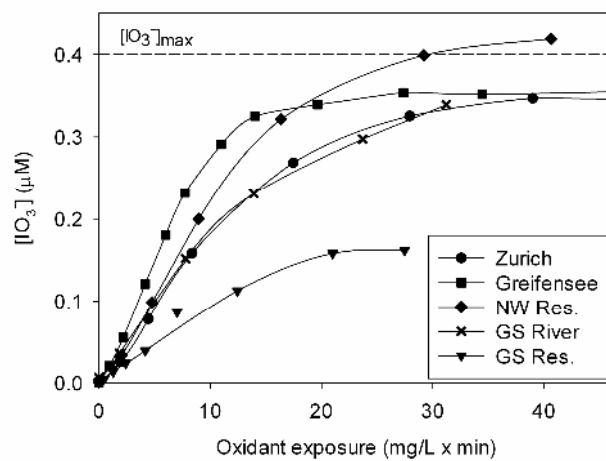
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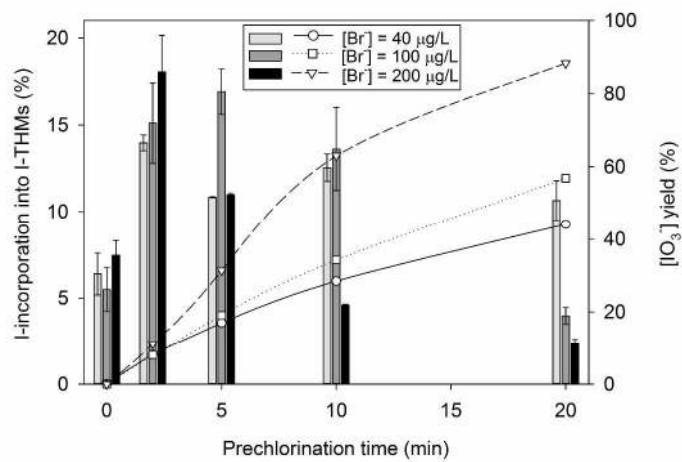
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