Ozonation of iodide-containing waters:

Selective oxidation of iodide to iodate with

simultaneous minimization of bromate and I-

THMs

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18   **Abstract**

19   The presence of iodinated disinfection by-products (I-DBPs) in drinking water

20   poses a potential health concern since it has been shown that I-DBPs are

21   generally more genotoxic and cytotoxic than their chlorinated and brominated

22   analogues. I-DBPs are formed during oxidation/disinfection of iodide-containing

23   waters by reaction of the transient hypoiodous acid (HOI) with natural organic

24   matter (NOM). In this study, we demonstrate that ozone pre-treatment

25   selectively oxidizes iodide to iodate and avoids the formation of I-DBPs. Iodate is

26   non-toxic and is therefore a desired sink of iodine in drinking water. Complete

27   conversion of iodide to iodate while minimizing the bromate formation to below

28   the guideline value of 10 µg L^{-1} was achieved for a wide range of ozone doses in

29   five raw waters with DOC and bromide concentrations of 1.1-20 mg L^{-1} and 170-

30   940 µg L^{-1}, respectively. Lowering the pH effectively further reduced bromate

31   formation but had no impact on the extent of iodate and bromoform formation

32   (the main trihalomethane (THM) formed during ozonation). Experiments carried

33   out with pre-chlorinated/post-clarified samples already containing I-DBPs,

34   showed that ozonation effectively oxidized I-THMs. Therefore, in iodide-containing

35   waters, in which I-DBPs can be produced upon chlorination or especially

36   chloramination, a pre-ozonation step to oxidise iodide to iodate is an efficient

37   process to mitigate I-DBP formation.

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39   **Keywords:** ozone, iodide, I-DBPs, I-THMs, bromate, iodate

40

1. Introduction

Iodinated disinfection by products (DBPs) are among the most genotoxic and cytotoxic DBPs identified in drinking water (Richardson et al., 2008; Richardson et al., 2007), with iodoacetic acid being the most genotoxic DBP reported to date (Plewa et al., 2004). The formation of I-DBPs during water treatment has been well documented in iodide-containing waters, and predominantly occurs as a result of disinfection with monochloramine (Bichsel and von Gunten, 2000). When monochloramine is applied to iodide-containing waters, hypoiodous acid (HOI) is formed which then reacts with natural organic matter (NOM), resulting in iodinated organic compounds (i.e. I-DBPs). In contrast to chlorine and ozone, monochloramine is not able to further oxidize HOI to iodate (Bichsel and von Gunten, 1999), a non-toxic and therefore preferred sink of iodine (Burgi et al., 2001).

To minimize the formation of I-DBPs, several options have been considered. The most common method is the removal of DBP precursors (e.g. NOM) prior to disinfection. Conventional coagulation treatment removes a large portion of the dissolved organic carbon (DOC) (Bolto et al., 2002), however, it is not an effective process for bromide removal (Amy, 1999), and similar behavior is expected for iodide. Membrane filtration, particularly reverse osmosis, has proved to be effective in the removal of both halides and NOM (Magara et al., 1996; Xu et al., 2008), however, it is currently not economically feasible. Another option for I-DBP minimization which has been proposed is the alteration of the chloramine disinfection process to pre-chlorination followed by ammonia addition since free chlorine can oxidize iodide to iodate (Jones et al., 2011). This is an efficient way to reduce iodoform (CHI_3) formation, but, there is the potential for higher formation of other

66   iodo- trihalomethanes (I-THMs), depending on the bromide concentration and the free

67   chlorine contact time (Criquet et al., 2012).

68   In this study, we propose an alternative approach for mitigation of the formation of

69   iodo-organic compounds. Ozone rapidly oxidises iodide to iodate (Bichsel and von

70   Gunten, 1999), however, its application is often limited in bromide-containing waters

71   due to bromate formation, which has a drinking water guideline value in the USA and

72   Europe of 10 µg L^{-1} (EU, 1998; US-EPA, 2006; WHO, 2008). The presence of iodide

73   and bromide is ubiquitous in natural waters; while bromide is found at concentrations

74   up to several mg L^{-1} (Heller-Grossman et al., 2001; Magazinovic et al., 2004), iodide

75   is usually present at low concentrations (< 100 µg L^{-1}, (Richardson et al., 2008)).

76   The oxidation of iodide by ozone is very rapid (k =1.2 10^9 M^{-1}s^{-1}) (Liu et al., 2001)

77   and leads to HOI and OI$^-$, which are both quickly oxidized to iodate (k= 3.6 10^4 M^{-1}s^{-1}

78   and 1.6 10^6 M^{-1}s^{-1} respectively, (Bichsel and von Gunten, 1999). Ozonation includes

79   two oxidation pathways: direct oxidation by ozone and oxidation by the hydroxyl

80   radicals (•OH) which are formed as secondary oxidants from ozone decomposition

81   (von Gunten, 2003a). Due to the high reactivity of ozone with iodide and HOI/OI$^-$, the

82   reaction with •OH can be neglected (**Scheme S1a**) (von Gunten, 2003b).

83   In contrast, the mechanism for bromate formation is complex and involves both ozone

84   and •OH (**Scheme S1b**) (for a more detailed explanation see (von Gunten, 2003b)).

85   The oxidation of bromide by ozone is slow (k = 160 M^{-1}s^{-1}) and even if the rate

86   constants for Br$^-$ and HOBr/OBr$^-$ oxidation by •OH radicals (k = 1.1 10^9 M^{-1}s^{-1}, k = 2

87    $10^9 \times$ M^{-1}s^{-1} and 4.5 $\times$ 10^9 M^{-1}s^{-1} respectively) are high, the extent of the reaction is

88   still small due to the low steady state concentration of •OH. Based on these kinetic

89   considerations, it can be hypothesized that iodide can be selectively oxidized to iodate

90   by ozone whilst, bromate formation will be minimal. The rate-limiting step during

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91 bromate formation is the oxidation of HOBr/BrO⁻. As a consequence, an

92 accumulation of HOBr has been observed in previous studies, which may lead to

93 formation of Br-DBPs (Haag and Hoigne, 1983; Pinkernell and von Gunten, 2001).

94 In this paper, we investigated the oxidation of iodide to iodate by ozone and the

95 simultaneous formation of bromate from bromide, to assess the potential of ozonation

96 for mitigation of iodide-related water problems. Furthermore, the formation of Br-

97 THMs in the ozonation process was investigated to illustrate the difficulty in

98 balancing the formation of bromate against the formation of other Br-DBPs. Finally, a

99 post-clarified water which had been pre-chlorinated was trialled to give a more

100 complete understanding of the influence of a pre-ozonation step under real drinking

101 water treatment conditions, especially with regard to the behavior of I-THMs.

102

103 2.Materials and methods

104 2.1.Water samples

105

106 Samples were collected from surface water (HR, DR, and QR), groundwater (GB) and

107 a drinking water treatment plant (JG), to explore a wide scope of water matrices. The

108 water quality data for the five waters are shown in **Table 1**. The groundwater plant

109 treatment process consists of initial chlorination followed by coagulation with

110 aluminium sulfate. The flocs are allowed to settle in a clarifier and are sand filtered

111 before final disinfection in the clearwater tank prior to entering the reservoir. The JG

112 sample was collected prior to the sand filter (post-clarified).

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116   2.2.Reagents and analytical methods

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118   Deionised water from an ELGA purification system (resistivity of 18.2 mΩ, TOC of 1

119   µg L^{-1}) was used for all experiments.

120   All solvents and reagents used in this study were of analytical grade purity (AR grade

121   ≥ 99% pure or better). Ozone stock solutions were prepared by continuously bubbling

122   ozone-containing oxygen from an ozone generator (American Ozone Systems Inc)

123   through a Dreschel bottle into ice-cooled deionised water (Bader and Hoigne, 1981).

124   Iodide, bromide, bromate, and iodate were measured simultaneously via ion-

125   chromatography using a Dionex ICS3000 (AG9HC/AS9HC) followed by a post-

126   column reaction, according to a published method (Salhi and von Gunten, 1999). The

127   limits of detection (LOD) were calculated using the EPA Method Detection Limit

128   (US-EPA, 2004) and were 5 µg L^{-1} for iodide, 2 µg L^{-1} for bromide, 0.5 µg L^{-1} for

129   bromate, and 1 µg L^{-1} for iodate.

130   The ozone concentration of the stock solution was standardized by measurement of

131   the UV absorbance ($\varepsilon_{258\ nm}$ = 3000 $M^{-1}cm^{-1}$) using a UVmini-1240 spectrophotometer

132   (Shimadzu) and was approximately 1mM. The concentrations of dissolved ozone in

133   the experiments were determined by the indigo method (Bader and Hoigne, 1981).

134   THMs were analyzed by head-space solid phase micro-extraction gas chromatography

135   and mass spectrometry (Allard et al., 2012).

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137   2.3.Experimental procedures

138

139   Kinetic experiments were carried out at pH 6.5, 7.5 (the pH was adjusted by adding

140   dilute (0.1 M) hydrochloric acid or sodium hydroxide solutions) and pH 8 (1 mM

141   phosphate buffer). For certain reaction times, samples (8 mL) were dispensed into a

142   tube containing buffered indigo tri-sulfonate to quench the ozone reaction and

143   analyzed for ozone via the residual indigo absorbance at 600 nm. An additional

144   sample (8 mL) was taken for analysis of bromate and iodate. This sample was

145   quenched with indigo tri-sulfonate without the phosphate buffer to avoid interference

146   during the ion chromatographic separation.

147   For ozone dose experiments, aliquots of ozone stock solution (1 to 5 mL) were added

148   to the water samples to reach the desired initial concentration (0 – 100 μM), and upon

149   ozone addition, the solutions were mixed for 10 seconds. After complete consumption

150   of the oxidant, these solutions were sub-sampled into 40 mL vials with teflon-lined

151   caps (for THM analysis), and 10 mL plastic test tubes with caps (for bromate, and

152   iodate analysis). All vessels were filled so that they had no headspace, and were

153   stored at 4°C prior to analysis.

154

155   3.Results and discussion

156   3.1. Comparative kinetics of iodate and bromate formation

157

158   The kinetics of iodate and bromate formation in DR water were investigated (**Figure**

159   **S1**). Iodate is presented as normalised iodate formation ($[IO_3^-]/[IO_3^-]_{max}$). Bromate is

160   presented as normalised bromate formation ($[BrO_3^-]/[BrO_3^-]_{max}$) to be able to compare

161   the extent of bromide and iodide conversion, and as concentrations ($\mu g\ L^{-1}$) for

162   comparison with the drinking water standard of 10 $\mu g\ L^{-1}$. $[IO_3^-]_{max}$ was determined

163   from the full oxidation of iodide to iodate and $[BrO_3^-]_{max}$ was calculated from $[Br^-]_{ini}$.

164   Iodide is fully oxidized to iodate for an ozone exposure ≤ 0.4 mg L^{-1} x min (less than

165   15 s). At this ozone exposure, about 2.5% of bromide was converted to bromate

166   yielding a bromate concentration of ~ 4 µg L^{-1}. Generally, bromate formation was

167   much slower than iodate formation and increased until a plateau was reached at 11 µg

168   L^{-1}, for an ozone exposure of 4.9 mg L^{-1} x min. At the end of the ozonation, 7% of the

169   initial bromide was oxidized to bromate, whereas 100% of the iodide was converted

170   to iodate.

171   These observations are consistent with kinetic considerations, as the rate of iodate

172   formation (Bichsel and von Gunten, 1999) has been demonstrated to be several orders

173   of magnitude higher than the formation of bromate (von Gunten and Hoigne, 1994).

174   These findings demonstrate that, by using optimal ozone exposure, a complete iodide-

175   iodate conversion is feasible whilst bromate remains < 10 µg L^{-1}. However, the

176   optimal ozone dose will depend on the water matrix characteristics.

177

178   3.2.Ozonation of iodide- and bromide- containing waters : effect of the water matrix

179

180   To investigate the factors affecting iodate and bromate formation, experiments were

181   carried out with various natural waters **(Table 1)**. O$_3$ doses were varied and samples

182   were withdrawn after complete consumption of the oxidant. When the same

183   experimental conditions were evaluated, i.e. the raw waters were diluted to the same

184   DOC concentration and iodide and bromide added ([DOC] = 1.3 mgC L^{-1}, [I$^-$] = 50 µg

185   L^{-1}, [Br$^-$] = 100 µg L^{-1}, pH = 8), similar behavior was observed. Iodate formation was

186   already observed at the lowest ozone dose tested ($\approx$ 4 µM = 0.2 mg L^{-1}) and increased

187   with increasing ozone dose until complete conversion of iodide to iodate occurred

188   (**Figure 1**). 100% Oxidation of iodide to iodate was observed for an ozone dose of 8

189   µM for HR, 11 µM for DR and $\approx$ 14 µM for QR. Bromate formation showed a

190   different pattern with no bromate formation for ozone doses < 14 µM, followed by a

191 continuous and linear increase of bromate for increasing ozone doses (**Figure 1 and**

192 **S2**). 100% Oxidation of iodide to iodate with no bromate formation was achieved for

193 ozone doses below 14 μM in all waters. Bromate concentrations remained below 10

194 μg L^{-1} for ozone doses up to 17 μM (0.85 mg L^{-1}) in HR and ≈ 30 μM (1.5 mg L^{-1}) in

195 DR and QR.

196

197 However, some significant differences were observed for the selected waters. As

198 illustrated in **Figure 1**, the concentration of bromate formed in the HR water was

199 more than twice the concentration in the DR and QR waters. The higher carbonate

200 alkalinity of HR (70 mg L^{-1} CaCO$_3$) compared to DR and QR (< 1.5 mg L^{-1} CaCO$_3$)

201 after dilution of the raw waters to the same DOC concentration might explain the

202 enhanced bromate formation in HR. The presence of carbonate leads to a higher

203 ozone stability and hence a higher ozone exposure (von Gunten, 2003a). It has also

204 been demonstrated that carbonate and bicarbonate react with •OH to form the

205 carbonate radical (•CO$_3^-$), which can then react with HOBr to form •OBr, which is

206 further oxidized by ozone to bromate (von Gunten and Hoigne, 1994).

207

208 Additional experiments were carried out with HR, DR and QR waters with addition of

209 iodide and bromide ([I$^-$] = 50 μg L^{-1}, [Br$^-$] = 500 μg L^{-1}, pH = 8) and with GB

210 containing naturally low iodide, a high bromide concentration and a low DOC

211 concentration (**Table 1**). Results are presented in the supporting information section

212 and show that the ozone demand for the complete oxidation of iodide increased with

213 the DOC concentration, with ≈ 50 μM of ozone required for 12 mgC L^{-1} in this

214 experiment **(Figure S3)**. For the highest NOM concentration (QR 20 mgC L^{-1}) the

215 iodide was not fully oxidized, even when the highest ozone dose was applied.

216 Moreover, for the high DOC values, bromate was formed at much lower

217 concentrations (< 10 µg L^{-1} for ≈ 65 µM O$_3$) **(Figure S4)**. This is due to the rapid

218 consumption of ozone by NOM as well as the scavenging effect of NOM for •OH

219 (Westerhoff et al., 1998). Conversely, it is noteworthy that bromate formation was

220 extremely high in HR and GB water (> 250 µg L^{-1} and > 500 µg L^{-1} for 64 µM O$_3$ and

221 78 µM O$_3$, respectively). This remarkable difference is attributable to the low DOC in

222 these waters leading to a higher stability of ozone. Consequently, the higher ozone

223 exposure enhances bromate formation.   Also, as GB has the lowest DOC

224 concentration and the highest bromide concentration, a high bromate formation was

225 expected.

226 To better understand iodate and bromate formation during ozonation of the various

227 water sources, **Figure 2a,b** shows iodate and bromate concentrations as a function of

228 the O$_3$/DOC ratio. This parameter was chosen to account for the varying DOC levels

229 in the selected waters.

230 The formation of iodate as a function of the normalized ozone dose (**Figure 2a)** was

231 similar for all waters. Iodide was fully oxidized to iodate with the exception of very

232 low O$_3$/DOC ratios.

233 In contrast, significant differences were observed for the formation of bromate

234 (**Figure 2b**). As expected, a low conversion of bromide to bromate was observed for

235 DR and QR due to the low O$_3$/DOC ratios that were achieved in the experiments (high

236 DOC concentration). For higher O$_3$/DOC ratios, the experiments with diluted GB and

237 diluted QR show a similar trend with a linear increase of bromate formation even

238 though the type of NOM and the initial bromide concentration (SUVA$_{254}$ = 1 and 4.9,

239 [Br-] = 870 and 100 µg L^{-1}, respectively) were different. For the experiments carried

240 out with HR a significantly higher bromate formation was observed for similar

241 O_3/DOC ratios compared to the other waters. In addition, the bromate formation

242 increased from the diluted to the non-diluted water, which was due to the higher

243 alkalinity of the non-diluted water (higher ozone stability and therefore higher ozone

244 exposure for the same O_3/DOC dose).

245

246 3.3.Formation of brominated by-products

247

248 Even though controlling bromate formation is the key prerequisite when using ozone,

249 the formation of bromoform and other brominated organic by-products also has to be

250 assessed. To illustrate the potential formation of other Br-DBPs, THMs were analyzed

251 during these experiments and the results from GB are presented in the SI (**Figure S5**).

252 During ozonation, iodate is formed instantaneously from HOI whereas HOBr is only

253 slowly oxidized to bromate and therefore has more time to react with NOM. In this

254 situation, HOBr is the only halogenating agent available, and therefore the main THM

255 formed was bromoform (**Figure S5**). A bromoform concentration up to 38 μg $L^{-1}$was

256 detected when the initial DOC concentration was only 1.1 mgC L^{-1}. The $CHBr_3$

257 concentration reached a maximum for an ozone dose of 49 μM and then decreased

258 with higher ozone exposure. HOBr/BrO^- and O_3 might compete for reaction with the

259 same activated structures in NOM (von Gunten, 2003b) and, above a critical O_3 dose

260 some reactive sites are oxidized by O_3 rather than halogenated, which may lead to

261 lower $CHBr_3$ concentrations. The highly brominated THMs, $CHBr_2Cl$ and $CHBr_2I$,

262 were also detected in trace amounts (**enlarged portion in Figure S5**) (see below for

263 explanation). The formation of THMs was monitored during a kinetic experiment

264 (results not shown) and only $CHBr_3$ was detected. It was then hypothesized that

265 $CHBr_2Cl$ and $CHBr_2I$ were not formed during the ozonation process but later on

266   through the reaction of HOBr with iodo- and chloro-organic precursors already

267   present in the raw water prior to ozonation. Such low concentrations (ng L^{-1} level) do

268   not constitute a health issue and are difficult to interpret.

269   Even though the oxidation of iodide to iodate with minimal bromate formation was

270   achieved for waters containing high concentration of NOM, it is not a realistic

271   scenario due to the high cost and energy requirement related to the high ozone doses

272   required. In practice, when high DOC concentrations are encountered, ozone is

273   applied after a coagulation/flocculation process. The resulting decrease in NOM, due

274   to the pre-treatment, enables the use of lower ozone doses, with the same extent of

275   iodide oxidation and bromate formation.

276

277   3.4. Ozonation of pre-chlorinated/post-clarified water : influence of pH on formation

278   of iodate, bromate and THMs

279

280   To investigate the behavior of bromine and iodine species under more realistic

281   conditions, ozonation experiments were performed on plant samples (JG) collected

282   after a pre-chlorination step followed by coagulation, flocculation and clarification.

283   As shown in **Figure 3,** the bromate formation was consistent with the previous

284   experiments with an increase in bromate concentration with increasing O_3/DOC ratio.

285   Even though part of the iodide was already oxidized to iodate during the pre-

286   chlorination step ($[IO_3^-]_o = 4$ µg L^{-1}), the requirement of 100% iodide conversion to

287   iodate with a bromate concentration below the guideline value (<10 µg L^{-1}) was not

288   fulfilled in this experiment. However, according to **Figure 3**, 65 to 75% (for pH 7.5

289   and 6.5, respectively) of the initial iodide was oxidized to iodate for a bromate level

290   of 10 µg L^{-1}. Even if 25 to 35% of iodide remained after ozonation treatment, this still

291   leads to a significant decrease of I-DBP formation potential during final disinfection.

292   A higher degree of iodide oxidation can only be achieved by a higher ozone dose

293   which leads to higher bromate levels. Therefore, in this case, bromate has to be

294   minimized by an other method. It has been well established that bromate

295   minimization can be achieved by lowering the pH or by ammonia addition (Pinkernell

296   and von Gunten, 2001).

297

298   A decrease of pH from 7.5 to 6.5 reduced the bromate formation by more than a

299   factor of 2 (**Figure 3**). A decrease of pH reduces bromate formation by shifting the

300   equilibrium HOBr/BrO$^-$ towards HOBr, which does not react with ozone, as well as

301   lowering the •OH exposure (Pinkernell and von Gunten, 2001; von Gunten, 2003b).

302   Therefore, the addition of coagulant, which results in a decrease in DOC and a

303   decrease in pH, has multiple advantages related to minimization of bromate and halo-

304   organic compounds. Furthermore, iodate formation was not affected by the change in

305   pH, which is due to the fact that HOI is quickly oxidized to iodate by ozone (Bichsel

306   and von Gunten, 1999) and the speciation of HOI (pK_a = 10.4 (Bichsel and von

307   Gunten, 2000)) is not affected much in the pH range 6.5-7.5. Lowering the pH is

308   therefore an effective method for bromate minimization while maintaining the extent

309   and rate of iodate formation constant.

310   To illustrate the delicate balance between the formation of bromate and bromo-

311   organic compounds, the formation of bromoform and bromate at pH 6.5 and 7.5 are

312   presented in **Figure 4**.

313

314   In a previous study (Siddiqui et al., 1994), bromate formation decreased and

315   bromoform formation increased due to pH depression. In our case, while the bromate

316 mitigation was as expected, only a slight increase in bromoform concentrations was

317 measured at equivalent ozone doses with decreasing pH. The oxidation of bromide by

318 ozone is not pH dependent, thus the resulting transient concentration of $HOBr/OBr^-$ is

319 expected to be similar for both pHs. Bromate formation accounted for only 1 to 4% of

320 the initial bromide concentration and didn't significantly affect the amount of

321 $HOBr/BrO^-$ present in solution. Also, with a pK_a of 8.8 (Haag and Hoigne, 1983) the

322 partition between HOBr and BrO^- is not greatly affected by the decrease of pH from

323 7.5 to 6.5, HOBr being the dominant species by at least 2 orders of magnitude.

324 Therefore, a similar extent of bromoform formation was observed at both pHs.

325 Furthermore, for a bromate concentration < 10 μg L^{-1}, the observed bromoform

326 concentration was < 1 μg L^{-1} (**Figure 4**) which is far below the drinking water

327 standards for THMs (US-EPA, 2006; EU, 1998).

328

329 3.5. Fate of THMs in pre-chlorinated/post-ozonated water (JG)

330

331 **Figure 5** shows the evolution of chloro-, bromo- and iodo-THMs during ozonation of

332 JG water. It should be noted that, for these experiments, THMs were already present

333 in the samples due to the pre-chlorination process. The concentration of $CHCl_3$,

334 $CHBrCl_2$ and $CHBr_2Cl$ remained fairly constant for increasing ozone doses, because

335 ozone and •OH do not react with these THMs (von Gunten, 2003a) (**Figure 5a**). In

336 contrast, $CHBr_3$ increased with increasing ozone dose, which is consistent with a

337 buildup of HOBr. However, the measured THM concentrations were far below the

338 drinking water guidelines (80 μg L^{-1} in US, 100 μg L^{-1} in EU for ΣTHMs). I-THMs

339 were also detected in the pre-chlorinated/post-clarified samples (**Figure 5b**). These

340 THMs were formed during pre-chlorination, likely also due to the presence of

ammonia (0.33 mg L^{-1}) and subsequent monochloramine formation. The I-THMs

were affected differently to the regulated THMs during ozonation. CHCl$_2$I and

CHBrClI concentrations decreased from 200 ng L^{-1} and 125 ng L^{-1} in the post-clarified

water to 45 ng L^{-1} and 30 ng L^{-1}, respectively, after treatment with an ozone dose of

104 μM (5 mg L^{-1}). CHBr$_2$I behaved differently, increasing from 65 ng L^{-1} to a

maximum of 165 ng L^{-1} for an ozone dose of 83 μM.

To better understand the fate of I-THMs during ozonation, a kinetic experiment was

carried out with the pre-chlorinated/post-clarified (JG) water, with each I-THM

(CHCl$_2$I, CHBrClI, CHBr$_2$I, CHClI$_2$, CHBrI$_2$, CHI$_3$) added to achieve a concentration

of 2 μg L^{-1} (ozone dose 62 μM). As illustrated in **Figure 6,** the I-THMs were all

oxidized with similar kinetics. This finding is consistent with a previous kinetic study

in which it was demonstrated that the I-THMs were poorly oxidized by ozone ($k_{O_3} < 2$

M^{-1}s^{-1}) and rapidly oxidized by •OH radicals ($k_{•OH} > 7\text{-}8 \ 10^9$ M^{-1}s^{-1}) (Bichsel, 2000).

In this experiment, the oxidation of CHBr$_2$I was similar to the other I-THMs,

seemingly in contradiction with the results in **Figure 5b**. The net formation of CHBr$_2$I

might be explained by the reaction of HOBr with I-NOM moieties formed during the

pre-chlorination step. The formation of CHBr$_2$I probably occurs after ozone depletion

because HOBr is much more stable in solution and can react with iodo- and chloro-

organic precursors. In practice, the ozonation process would be followed by a

granular activated carbon/ biological activated carbon (GAC/BAC) filter, where

HOBr would be quenched. Therefore, the phenomenon of formation of CHBr$_2$I would

only be expected to a limited extent.

365   4.Conclusion

366

367   The application of ozone is an efficient process for mitigating iodine-derived water

368   quality problems, whilst controlling the formation of bromate. Kinetic experiments in

369   raw waters showed that using the optimal water specific ozone exposure, iodide was

370   fully oxidized to iodate prior to bromate formation. Thus, this is an efficient way to

371   minimize iodinated disinfection by-products in post-chlorination or post-

372   chloramination. Ozone dose experiments for a wide range of waters also

373   demonstrated that complete conversion of iodide to iodate was achieved, while

374   keeping the bromate concentration below the guideline value of 10 µg L^{-1}. However,

375   for bromate formation, some significant differences were observed between different

376   water matrices and no clear trend could be found due to the complex mechanism of

377   bromate formation. Lowering the pH has shown to be a useful way to improve the

378   process, since bromate formation significantly decreases, while iodate formation is

379   not affected by pH changes. The main THM formed was bromoform but traces of

380    $CHBr_2Cl$ and $CHBr_2I$ were also detected during ozonation of the raw waters. When

381   pre-chlorinated/post-clarified samples were ozonated, existing $CHCl_3$, $CHBrCl_2$ and

382    $CHBr_2Cl$ concentrations were unaffected, and, as expected the concentration of

383    $CHBr_3$ increased with increasing ozone doses. Conversely, ozone oxidized all I-

384   THMs to the same extent; however, $CHBr_2I$ might be formed after complete ozone

385   depletion by reaction of residual HOBr with iodo-organic THM precursors formed

386   during the pre-chlorination step. Under realistic water treatment conditions, HOBr

387   would be quenched by filtration through GAC/BAC, thus lowering the extent of

388    $CHBr_2I$ formation. Furthermore, the concentrations of regulated THMs analyzed

389   during this study were far below the drinking water standards and only traces of I-

390 THMs were detected. In summary, the use of ozone provides several benefits for

391 potable treatment of iodide-containing source waters: ozone selectively oxidizes

392 iodide to iodate, thereby reducing the potential formation of I-DBPs in a subsequent

393 disinfection step, and it also oxidizes I-THMs if they are already present in the water.

394 At the same time, it is possible to keep the concentration of bromate below the

395 drinking water standard, even for source waters with high bromide concentrations.

396

397 **Acknowledgments**

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Figure 1. Iodate and bromate formation as a function of the ozone doses for HR, DR and QR (see **Table 1**). Experimental conditions: 3.7 µM < [O$_3$] < 33 µM, [DOC] = 1.3 mgC L^{-1}, [I$^-$] = 50 µg L^{-1}, [Br$^-$] = 100 µg L^{-1}, pH 8 (1 mM phosphate buffer). Open symbols: bromate; filled symbols: iodate. Lines are shown to guide the eye.

Figure 2: Comparison of iodate and bromate formation during ozonation of natural waters (QR, HR, DR, GB, see **Table 1**): influence of the O$_3$/DOC ratio on (a) the formation of iodate, (b) the formation of bromate. Experimental conditions: 17 µM < [O$_3$] < 64 µM, [I$^-$] = 50 µg L^{-1} for QR diluted, HR diluted, HR, DR, QR and [I$^-$] = 30 µg L^{-1} for GB; [Br$^-$] = 100 µg L^{-1} for QR diluted, HR diluted, [Br$^-$] = 500 µg L^{-1} for HR, DR, QR and [Br$^-$] = 870 µg L^{-1} for GB; pH 8 (1 mM phosphate buffer). Lines are shown to guide the eye.

Figure 3: Influence of pH on bromate and iodate formation in pre-chlorinated/ post-clarified water (JG, **Table 1**). Experimental conditions: 0 µM < [O$_3$] < 104 µM, [DOC] = 3.5 mgC L^{-1}, [I$^-$] = 15 µg L^{-1}, [Br$^-$] = 940 µg L^{-1}. Lines are show to guide the eye.

Figure 4: Influence of pH on tradeoff between bromate and bromoform formation in JG water (**Table 1**). Experimental conditions: 21 µM < [O$_3$] < 104 µM, [DOC] = 3.5 mgC L^{-1}, [Br$^-$] = 940 µg L^{-1}.

Figure 5: Concentrations of (a) regulated THMs and (b) I-THMs for the ozonation of pre-chlorinated/ post-clarified water (JG, **Table 1**). Experimental conditions: 0 µM < [O$_3$] < 104 µM, [DOC] = 3.5 mgC L^{-1}, [I$^-$] = 15 µg L^{-1}, [Br$^-$] = 940 µg L^{-1}, pH 7.5.

Figure 6: Kinetics of I-THMs oxidation during ozonation of pre-chlorinated/post-clarified water (JG, **Table 1**). Experimental conditions: [DOC] = 3.5 mgC L^{-1}, [I$^-$] = 15 µg L^{-1}, [Br$^-$] = 940 µg L^{-1}, [O$_3$] = 104 µM (5 mg L^{-1}), CHCl$_2$I, CHBrClI, CHBr$_2$I, CHClI$_2$, CHBrI$_2$, CHI$_3$ spiked at 2 µg L^{-1}.
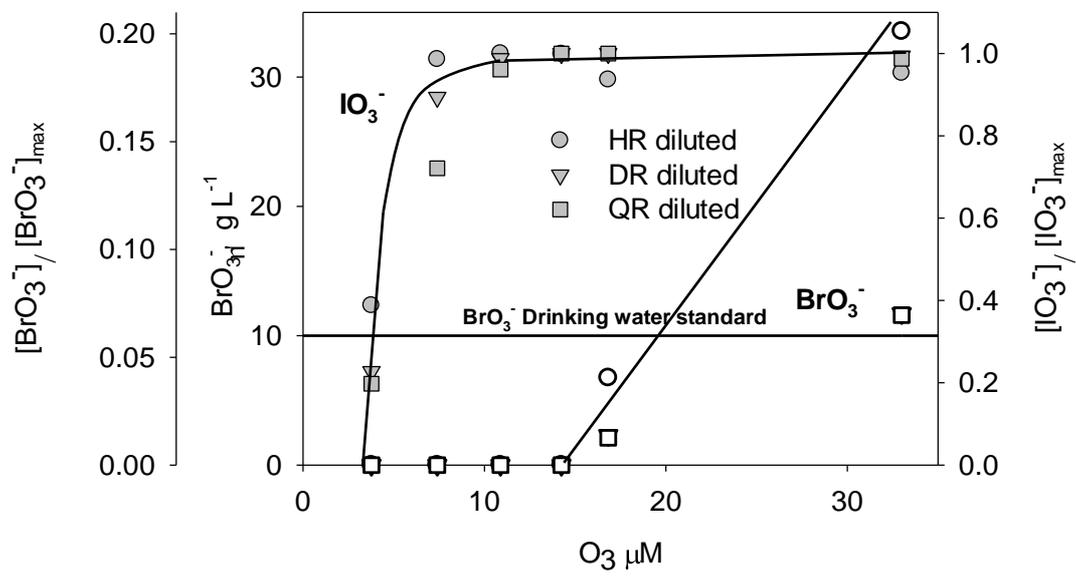
Figure 1.

533   **Figure 2**:

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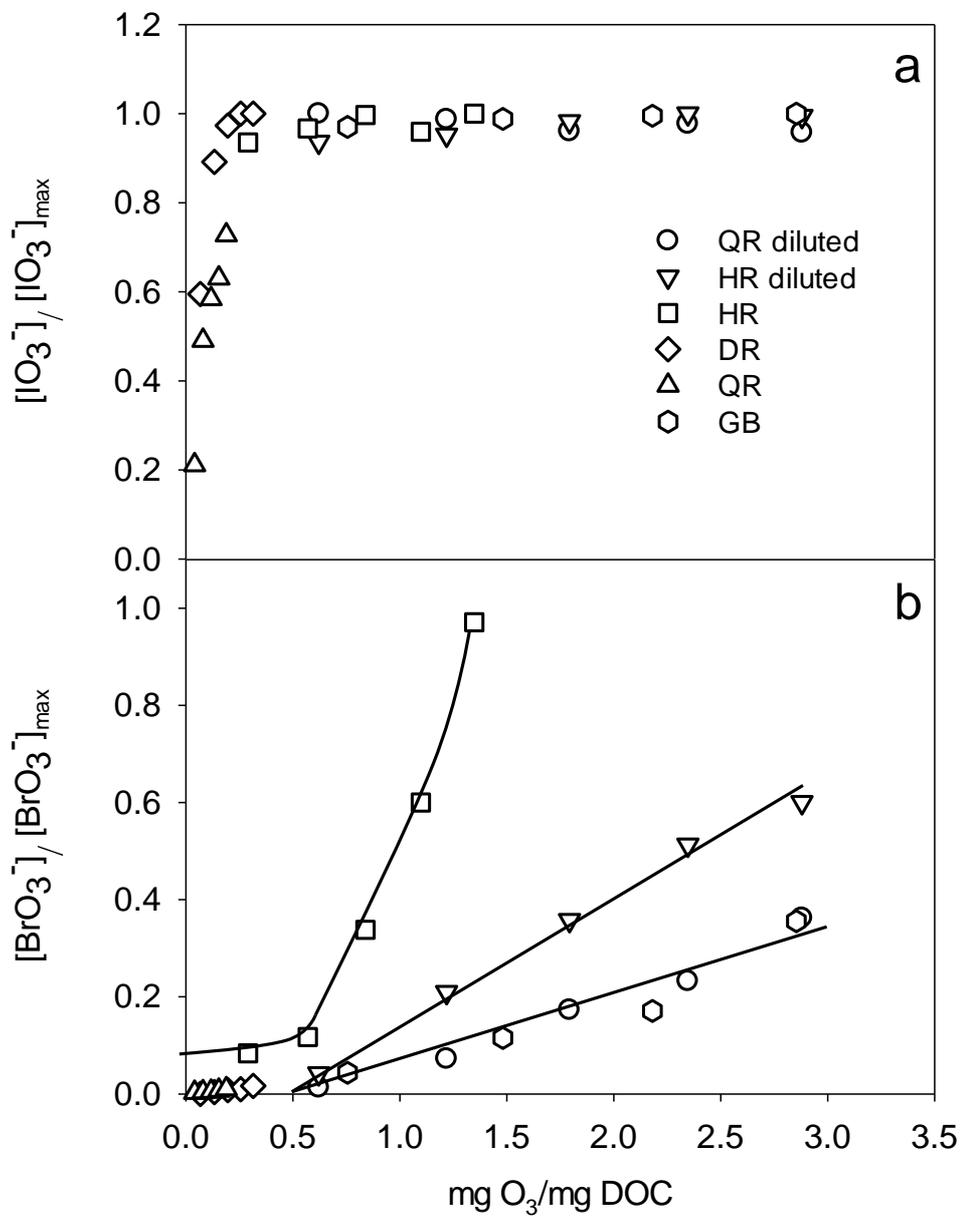
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The plot shows $BrO_{3,\eta}^{-}$ (g L^{-1}) on the y-axis (0–70) versus $CHBr_3$ μg L^{-1} on the x-axis (0–10). Two curves are shown: one labeled pH 7.5 (open circles) and one labeled pH 6.5 (filled circles). A horizontal line marks the BrO_3^{-} Drinking water standard at a value of 10.

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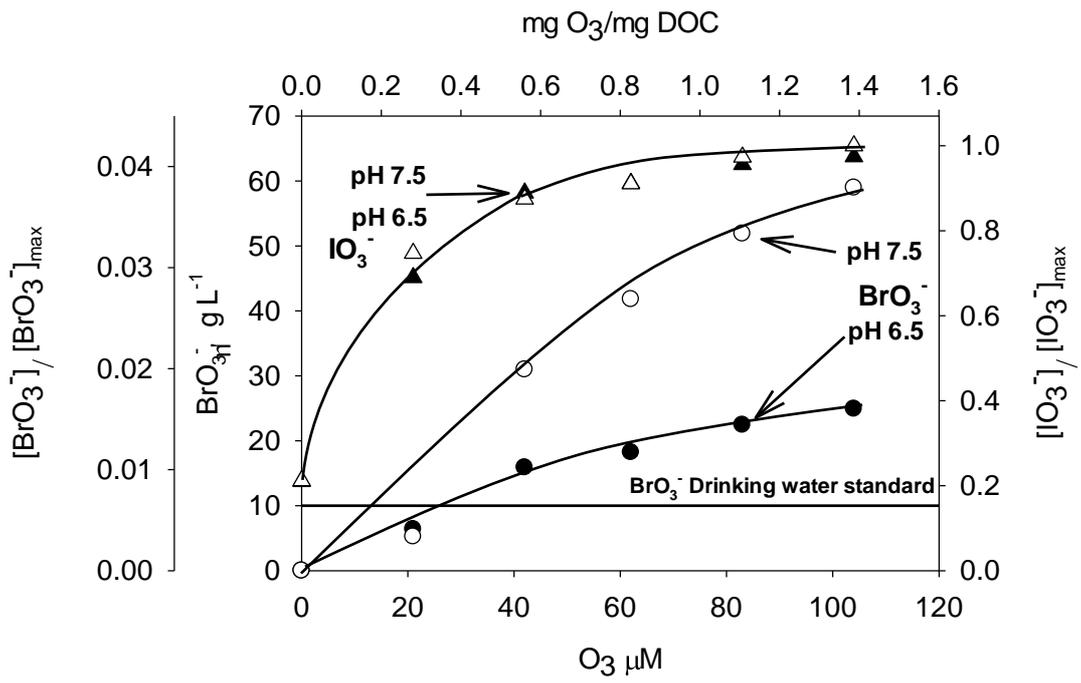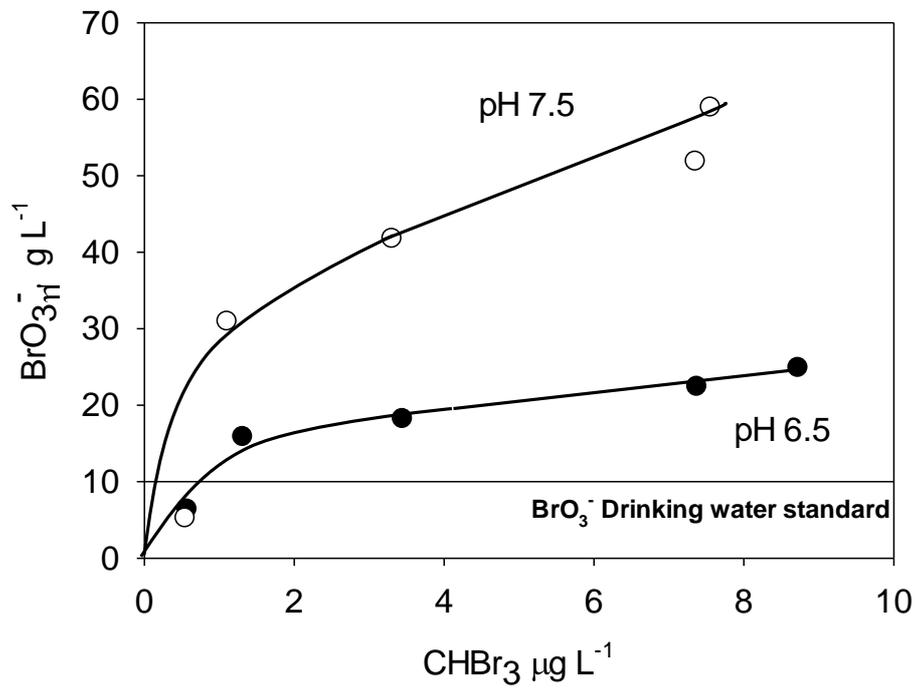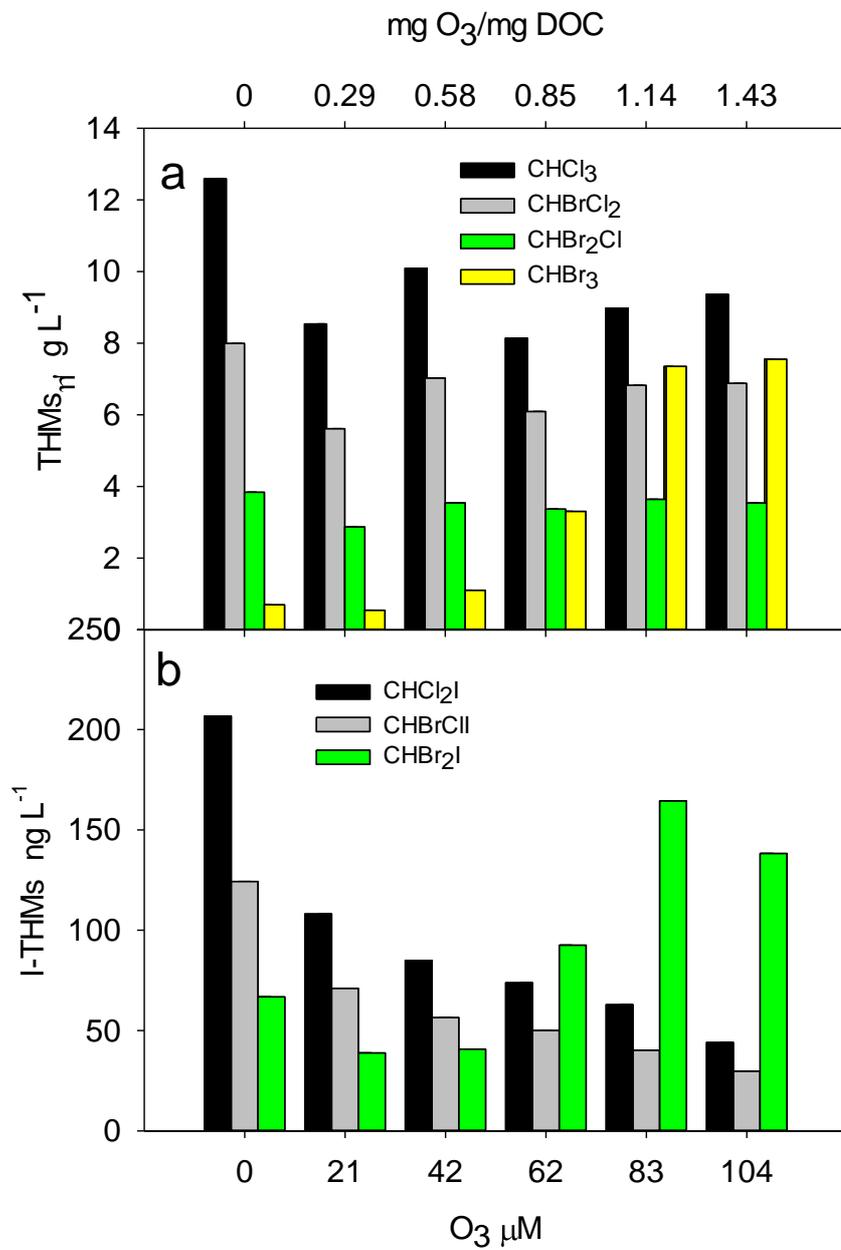
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547 **Figure 6:**
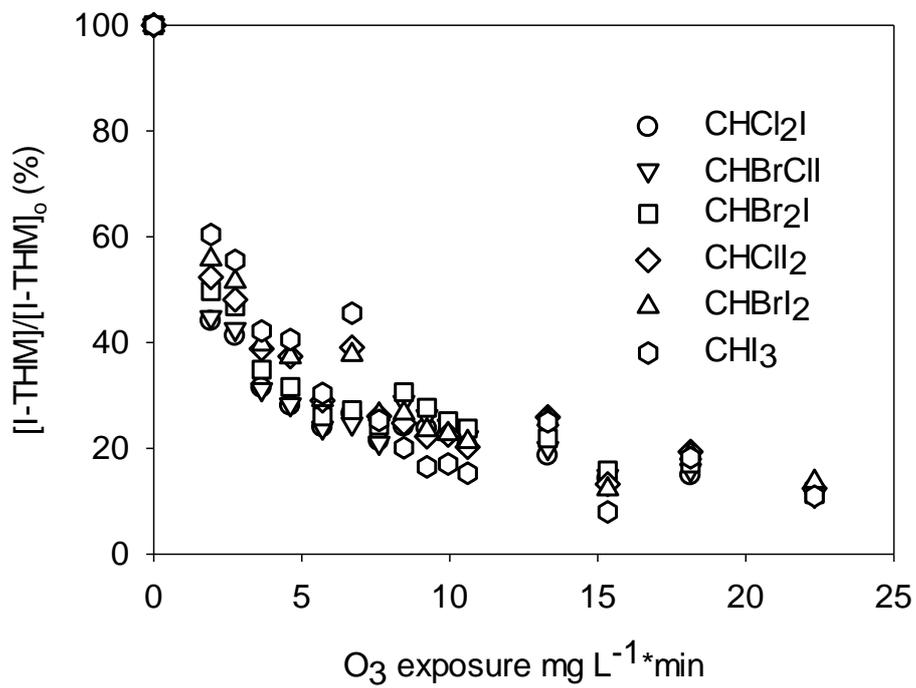
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550 **Table 1.** Main water quality parameters for the investigated waters

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	HR	DR	QR	GB	JG
DOC (mgC L^{-1})	2.8	12.0	20.0	1.1	3.5
SUVA (mgC^{-1}L m^{-1})	1.7	4.1	4.9	1.0	2.6
Br$^-$ (μg L^{-1})	170	410	400	870	940
I$^-$ (μg L^{-1})	<LOD	<LOD	<LOD	30	15
pH	8.6	7.5	6	6.6	6.7
SO$_4^{2-}$ (mg L^{-1})	12	20	17	61	82
Cl$^-$ (mg L^{-1})	50	330	160	180	255
Ca^{2+} (mg L^{-1})	25	8	3.4	1.8	43
Mg^{2+} (mg L^{-1})	21	24	10	6	16
Alkalinity (mg L^{-1} CaCO$_3$)	146	14	14	55	86

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