

Formation of bromate and halogenated disinfection byproducts during chlorination of bromide-containing waters in the presence of dissolved organic matter and CuO

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Abstract

Previous studies showed that significant bromate (BrO_3^-) can be formed via the CuO-catalyzed disproportionation of hypobromous acid (HOBr) pathway. In this study, the influence of CuO on the formation of BrO_3^- and halogenated disinfection byproducts (DBPs) (e.g., trihalomethanes, THMs and haloacetic acids, HAAs) during chlorination of six dissolved organic matter (DOM) isolates was investigated. Only in the presence of slow reacting DOM (from treated Colorado River water, i.e., CRW-BF-HPO), significant BrO_3^- formation is observed, which competes with bromination of DOM (i.e., THM and HAA formation). Reactions between HOBr and 12 model compounds in the presence of CuO indicates that CuO-catalyzed HOBr disproportionation is completely inhibited by fast reacting phenols, while it predominates in the presence of practically unreactive compounds (acetone, butanol, propionic, and butyric acids). In the presence of slow reacting di- and tri-carboxylic acids (oxalic, malonic, succinic, and citric acids), BrO_3^- formation varies, depending on its competition with bromoform and dibromoacetic acid formation (i.e., bromination pathway). The latter pathway can be enhanced by CuO due to the activation of HOBr. Therefore, increasing CuO dose ($0\text{-}0.2 \text{ g L}^{-1}$) in a reaction system containing chlorine, bromide, and CRW-BF-HPO enhances the formation of BrO_3^- , total THMs and HAAs. Factors including pH and initial reactant concentrations influence the DBP formation. These novel findings have implications for elevated DBP formation during transportation of chlorinated waters in copper-containing distribution systems.

36 ▪ **Introduction**

37 Distribution systems are the final barriers for drinking water before delivery to the taps of
38 consumers. A generally used strategy to control microbial contaminants and bacterial growth and
39 to improve the hygienic drinking water quality in distribution systems is to maintain a residual
40 oxidant. Among various oxidants, chlorine is the most used chemical oxidant for residual
41 protection.¹

42 While chlorine disinfection provides hygienically safe drinking water, chlorine (in the form
43 of hypochlorous acid, i.e., HOCl, in water) also reacts with dissolved organic matter (DOM) to
44 produce potentially toxic chlorinated disinfection byproducts (DBPs). Among various DBPs, the
45 most recognized compounds are trihalomethanes (THMs) and haloacetic acids (HAAs).²⁻⁷ In the
46 presence of bromide (Br^-), HOCl can rapidly oxidize naturally occurring Br^- to hypobromous
47 acid (HOBr).⁸ Upon the reaction between HOCl/HOBr and DOM, four THMs (i.e., THM4, sum
48 of CHCl_3 , CHBrCl_2 , CHBr_2Cl , and CHBr_3) and nine HAAs (i.e., HAA9, sum of monochloro-,
49 dichloro-, trichloro-, monobromo-, dibromo-, bromochloro-, bromodichloro-, dibromochloro-,
50 and tribromo-acetic acids (MCAA, DCAA, TCAA, MBAA, DBAA, BCAA, BDCAA, DBCAA,
51 and TBAA, respectively)) can be formed.^{6, 9-11} THM4 and HAA5 (sum of MCAA, DCAA,
52 TCAA, MBAA, and DBAA) are currently regulated for drinking water at $80 \mu\text{g L}^{-1}$ and $60 \mu\text{g L}^{-1}$
53 by the U.S. Environmental Protection Agency (US EPA), respectively¹². These DBPs are also
54 fully or partly regulated in drinking water in other countries (e.g., European Union¹³, China¹⁴).

55 Unlike ozone which can further oxidize HOBr to potentially toxic bromate (BrO_3^-),¹⁵⁻¹⁷ the
56 rate constant for the reaction between HOCl and HOBr is low.¹⁸ Therefore, BrO_3^- formation
57 from chlorination of bromide-containing waters in water treatment is generally insignificant.

58 Recently we showed that CuO can catalyze HOX (X: Cl or Br) disproportionation to produce X⁻
59 and XO₃⁻ (eq 1 showing an example from HOBr).¹⁹



61 It was reported that CuO is one of the major corrosion products of copper pipes that are widely
62 used in municipal distribution systems and household plumbing.²⁰⁻²³ This disproportionation
63 pathway led to elevated BrO₃⁻ concentrations (e.g., 50 μg L⁻¹) exceeding the maximum
64 contaminant level (i.e., MCL, 10 μg L⁻¹ regulated by US EPA¹²) during chlorination of bromide-
65 containing waters in distribution systems.²⁴ In addition, previous studies showed that CuO can
66 enhance HOCl/HOBr reactions with iodate to periodate and activate the reactivity of the other
67 halogen-containing oxidant (e.g., ClO₂).^{25, 26}

68 In the presence of DOM, HOBr can react with organic moieties and thus CuO-catalyzed
69 disproportionation may be inhibited, shifting the DBP formation from inorganic (i.e., BrO₃⁻) to
70 halogenated organic species (e.g., THMs and HAAs). Previous studies showed that total THM
71 formation was enhanced and the speciation of HAA was affected by the presence of CuO.^{22, 23}
72 However, similar total HAA formation in the presence of CuO with that in the absence of CuO
73 was further observed.²⁷ Because of the variability of the results reported previously, it is still
74 unclear if the reaction between HOCl/HOBr and DOM can be enhanced by CuO, leading to the
75 elevated formation of both THM and HAA. Understanding how CuO will control the fate of
76 bromine (i.e., BrO₃⁻ versus brominated organics) during the transportation of chlorinated waters
77 containing various types of DOM in distribution systems is therefore of major importance.

78 In view of the potential toxicological significance of the formation of regulated DBPs in
79 drinking water, the objectives of this study were to investigate the formation and speciation of
80 BrO₃⁻, THMs and HAAs during chlorination of bromide-containing waters in the presence of

81 DOM isolates and CuO. Factors such as pH, initial concentrations of CuO, chlorine and Br⁻, as
82 well as the concentration and nature of DOM on DBP formation were studied. Furthermore, a
83 range of structurally diverse model compounds were selected to study the mechanism for the
84 formation of BrO₃⁻, THMs and HAAs in the presence of CuO.

85

86 ■ **Materials and methods**

87 **Reagents.** All chemical solutions were prepared from reagent grade chemicals or stock
88 solutions using deionized water (18.2 MΩ·cm, Millipore). A sodium hypochlorite (NaOCl)
89 solution was used as the source of chlorine (13% active chlorine, Acros Organics). CuO particles
90 were prepared according to a previously published method.¹⁹ The BET surface areas were
91 determined by a Micromeritics Tristar II to be 33.7 m² g⁻¹. The pH_{pzc} (pH at which CuO particles
92 have a zero charge) was determined to be 8.6.²⁸ HOBr solutions were prepared by reaction of
93 NaOCl with Br⁻.¹⁹ The descriptions of all other standards and reagents used in this study are
94 provided in Text S1 of the Supporting Information (SI).

95 **DOM Isolates and Selection of Model Compounds.** Six previously isolated DOM fractions
96 with the SUVA₂₅₄ values (i.e., UV absorbance at 254 nm divided by the corresponding dissolved
97 organic carbon concentration) ranging from 1.1 to 4.9 L m⁻¹ mg⁻¹ were used in this study (Table
98 S1, SI). Three hydrophobic DOM isolates, namely, CRW-PI1-HPO, CRW-F2E-HPO, and CRW-
99 BF-HPO were extracted from the influent of the water plant (Colorado River water, USA),
100 effluent after clarification (coagulation/flocculation/filtration) and biologically active filtration,
101 respectively.²⁹ RRW-HPO, LRW-HPO, and SRW-HPOA were isolated from the Ribou
102 Reservoir (France), Loire River (France), and Suwannee River (Georgia, USA), respectively. As

103 to better simulate drinking water distribution system condition, CRW-BF-HPO extracted from
104 plant effluent water was used as the DOM isolate throughout this study unless noted.

105 Three groups of model compounds representing functional moieties of DOM were selected,
106 including ketone, alcohol, mono-, di- and tri-carboxylic acids, and phenols. Structures and
107 physicochemical properties of model compounds are shown in Table S2 (SI).

108 **Analytical methods.** The analytical methods of residual oxidants, DOM characterization,
109 total organic carbon, total organic bromine (TOBr), BrO_3^- , THMs, and HAAs can be found in
110 detail in Text S2 (SI).

111 **Experimental setup and procedures.** The influence of various drinking water parameters
112 including CuO dose, initial chlorine and Br^- concentrations, pH and initial concentration and
113 type of DOM on the formation of BrO_3^- , THMs and HAAs was investigated. The CuO dose
114 ranged from 0 to 0.2 g L^{-1} , based on our previous study to be able to investigate the reaction
115 kinetics in a selected time frame.¹⁹ Initial chlorine concentrations ranged from 14 to $70 \text{ }\mu\text{M}$ (i.e.,
116 $1.0\text{-}4.9 \text{ mg L}^{-1}$ as Cl_2). Initial Br^- concentrations varied from 0 to $10 \text{ }\mu\text{M}$ (i.e., $0\text{-}800 \text{ }\mu\text{g L}^{-1}$),
117 covering the typical Br^- range in raw water.¹⁵ The pH was adjusted to 6.6, 7.6, 8.6 and 9.6 with
118 HNO_3 or NaOH solutions in the presence of a 2.5 mM tetraborate buffer. The pH changes were
119 less than 0.2 pH unit during the reaction. It should be noted that in most reaction conditions, a
120 pH value of 8.6 that approaches the optimum pH for HOBr disproportionation was adopted to
121 better observe the BrO_3^- formation.¹⁹ DOM concentrations ranged from 0 to 20 mg L^{-1} .

122 All experiments were conducted in the dark and under continuous agitation using a magnetic
123 stirrer in 250 mL capped amber bottles under headspace-free conditions at room temperature
124 ($21 \pm 1 \text{ }^\circ\text{C}$). Reactions were initiated by the injection of an aliquot of a HOCl/HOBr stock
125 solution, to the buffered solutions containing DOM or model compounds in the presence or

126 absence of CuO. Bromide was added when required. Samples were withdrawn at preselected
127 time points, filtered within 1-2 min through a 0.45- μm syringe filter (surfactant-free cellulose
128 acetate membrane). The filter was pre-treated with HOCl or HOBr solutions (1 mg L^{-1}) and then
129 rinsed with deionized water to avoid a potential oxidant demand. The filtered samples were
130 analyzed for residual oxidant concentrations. For the analyses of BrO_3^- , THMs and HAAs, the
131 samples were quenched immediately with sulfite. Each experiment was performed in duplicate.

132

133 ■ Results and discussion

134 **Effect of CuO dose and reaction time.** Figure 1 shows concentrations of the residual
135 oxidant and formed BrO_3^- , THMs and HAAs for various CuO doses ($0\text{-}0.2 \text{ g L}^{-1}$). In the absence
136 of CuO, HOCl and the formed HOBr react with DOM, and 25% of initial oxidant was consumed
137 after 2 h reaction, leading to 107.7 ± 6.5 and $11.9\pm 3.1 \text{ nM}$ for THM4 and total HAAs,
138 respectively. Because HOCl does not react with HOBr,¹⁸ BrO_3^- concentration is low ($< 1 \mu\text{g L}^{-1}$,
139 Figure 1a).

140 In the presence of CuO, higher chlorine demands were observed. Increasing the CuO dose
141 led to a lower residual oxidant after 2 h reaction, almost complete oxidant consumption was
142 obtained with 0.2 g L^{-1} CuO. This can be ascribed to potential heterogeneous reactions of
143 HOCl/HOBr on the CuO surface (e.g., HOCl/HOBr decay to oxygen, HOCl/HOBr
144 disproportionation, and halogenation of DOM).¹⁹ Along with the fast oxidant loss, enhanced
145 concentrations of BrO_3^- ($5.7\text{-}29.9\pm 1.5 \mu\text{g L}^{-1}$) were formed in the presence of increasing CuO
146 doses from 0.05 to 0.2 g L^{-1} , owing to the CuO-catalyzed disproportionation of HOBr.^{19,24}

147 Comparing with BrO_3^- , concentrations for bromine atom incorporated in THMs and HAAs
148 were higher (Figure S1, SI). This indicates that the HOBr reaction with DOM in the presence of

149 CuO is the major pathway, while disproportionation is minor. The formation of THMs and
150 HAAs was enhanced as compared with reactions conducted in absence of CuO (Figure 1b-c).
151 Increasing the CuO doses from 0 to 0.2 g L⁻¹ led to increasing total THM and HAA
152 concentrations, reaching 246.2±13.8 and 58.1±6.3 nM (i.e., 58.4±3.1 and 11.8±1.2 µg L⁻¹,
153 respectively) with 0.2 g L⁻¹ CuO, which were 2.3 and 4.9 times higher than those in the absence
154 of CuO, respectively.

155 Among the formed THMs and HAAs, CHBr₃ (70.1-198.6 nM) and DBAA (up to 43.1 nM)
156 were the main species, respectively. CHCl₃, CHBrCl₂ and CHBr₂Cl were detected at much lower
157 concentrations (<26.8 nM). Similarly, DCAA, TCAA, and BCAA were detected at low levels
158 (<10.4 nM). Tri-halogenated acetic acids (THAAs) were formed at much lower levels than di-
159 halogenated acetic acids (DHAAs). Only TCAA was detected (<1.5 nM), and due to the limited
160 initial bromide concentration other brominated THAAs were not detected. This may be ascribed
161 to the limited THAA precursor in the studied DOM. It has been proposed that THAAs and
162 DHAAs can have different precursors.³⁰

163 Figure S2 (SI) shows that the DOM concentration is stable in the presence of 0.1 g L⁻¹ CuO,
164 even for long reaction times (a few days), indicating that there is no significant adsorption of
165 DOM (i.e., CRW-BF-HPO) to CuO. Previous studies indicated that CuO can adsorb
166 HOCl/HOBr to form a CuO-HOCl/CuO-HOBr complex, thereby activating the reactivity of
167 HOCl/HOBr towards several inorganic species (e.g., chlorine, bromine, iodine, and iodate).^{19, 24,}
168 ²⁶ By analogy, it is proposed that in the presence of DOM the formed CuO-HOCl/CuO-HOBr
169 complex showed a higher reactivity towards the slow reacting moieties of DOM, thus enhancing
170 the formation of THMs and HAAs. Interestingly, increasing CuO dose from 0 to 0.2 g L⁻¹
171 significantly enhanced the formation of brominated species (e.g., CHBr₃ and DBAA) and

172 bromine atom incorporated in THMs and HAAs. However, the enhancement for the formation of
173 chlorinated species and chlorine atom incorporated in THMs and HAAs was less significant
174 (Figure 1b-c, Figure S1, SI). This might indicate that CuO is more prone to activate the reactivity
175 of HOBr than HOCl at pH 8.6, which was also observed for the HOCl/HOBr reactions with
176 iodate in the presence of CuO.²⁶ Our results agree with a previous investigation showing
177 enhanced THM formation in the presence of CuO.²³ However, the fact that another study
178 reported similar HAA formation in the presence and absence of CuO might be ascribed to the
179 low Br⁻ dose used (0.8±0.2 μM),²⁷ which minimized the enhancement of the reaction since
180 HOBr is more readily activated by CuO than HOCl.

181 During the chlorination process, bromine species includes Br⁻, HOBr, BrO₃⁻, and TOBr.
182 Concentrations of BrO₃⁻ and TOBr in the presence of 0.1 g L⁻¹ CuO were measured to be 0.2 and
183 1.5±0.2 μM, respectively. Due to analytical restrictions in measuring Br⁻ and residual HOBr in
184 tetraborate-buffered chlorinated solutions, the total mass balance of bromine species cannot be
185 calculated. However, if an initial Br⁻ concentration of 10 μM is considered, Br⁻ and HOBr were
186 the main bromine species (>83±2%) present at 2 h. Furthermore, based on residual oxidant
187 concentration and second-order rate constant between HOCl and Br⁻ ($k = 1550 \text{ M}^{-1} \text{ s}^{-1}$),⁸ it can be
188 estimated that HOBr predominates at 2 h. Since chlorine concentration tends to be lower, the
189 recycling of Br⁻ to HOBr becomes less important, leading to a lower yield of formation of BrO₃⁻
190 and brominated DBPs.

191 Figure S3 (SI) shows concentrations of residual oxidant and formed BrO₃⁻, THMs, and
192 HAAs at different reaction times (i.e., ranging from 2 h to 12.7 h). Since the oxidant decays
193 faster at higher CuO doses (e.g., 0.2 g L⁻¹), a CuO dose of 0.025 g L⁻¹ was selected to allow the
194 reactions for longer time (> 12 h). After 12.7 h reaction, the residual oxidant concentration was

195 2.8±0.3 μM, corresponding to a 93% oxidant consumption. From 2 to 8 h, BrO₃⁻, THM4 and
196 total HAA concentrations increased by 217.6, 231.7, and 27.1 nM, respectively. However, from
197 8 to 12.7 h the increase was 194.1, 27.1, and 2.4 nM for BrO₃⁻, THM4 and total HAAs,
198 respectively. Comparable BrO₃⁻ formation but significantly less halogenated DBP formation in
199 the latter time range indicates that the disproportionation pathway outcompetes the halogenation
200 pathway. DOM consists of fast reacting and slow reacting/unreactive moieties, leading to the
201 two-stage reaction kinetics (i.e., rapid initial and slower consumption stages) for chlorination or
202 bromination of DOM isolates.⁶ After the degradation of fast reacting DOM moieties, the rate
203 constant for the reaction of HOBr disproportionation catalyzed by CuO was higher than that for
204 the reaction between HOBr and slow reacting DOM moieties. BrO₃⁻ formation becomes
205 important in the slower oxidant consumption stage.

206

207 **Effect of initial chlorine concentration.** Figure 2 shows concentrations of residual
208 oxidant and formed BrO₃⁻, THMs and HAAs for various initial chlorine concentrations (14-70
209 μM, i.e., 1.0-4.9 mg L⁻¹). Increasing the initial chlorine concentration led to an increasing
210 residual oxidant from 0 to 29.6±2.0 μM, with an increasing BrO₃⁻ formation (0 to 1.2±0.2 μM,
211 i.e., 0 to 146.5±20.5 μg L⁻¹). As above mentioned, the CuO-catalyzed disproportionation of
212 HOBr which is formed from the recycling of Br⁻ by HOCl will outcompete the HOBr reaction
213 with slow reacting/unreactive DOM moieties at higher Cl₂/DOM, leading to a significant BrO₃⁻
214 formation. Therefore, increasing initial chlorine concentration shifts the bromine from organic
215 (e.g., THMs and HAAs) to inorganic (i.e., BrO₃⁻) species (Figure S4, SI).

216 Increasing the initial chlorine concentrations from 14 to 40 μM increased THM4 from
217 194.9±6.5 to 379.9±86.4 nM (i.e., 47.6±1.6 to 90.9±20.5 μg L⁻¹), but further increasing chlorine

218 concentrations from 40 to 70 μM led to a decreasing THM4. Bromoform was the main THM
219 species (>74.2% among THM4), while CHCl_3 , CHBrCl_2 and CHBr_2Cl were the minor species.
220 In the presence of CuO, the reaction between HOBr and DOM (CHBr_3 formation) competes with
221 HOBr disproportionation (BrO_3^- formation). As above mentioned, in the second stage of reaction
222 (slow consumption kinetics), rate constant for HOBr disproportionation in the presence of CuO
223 is higher than HOBr reaction with slow reacting/unreactive DOM moieties, leading to the
224 preferential formation of BrO_3^- . As a consequence, a decreasing CHBr_3 formation was observed,
225 leading to a decreasing trend of THM4 since CHBr_3 is the main species of THM4.

226 Lower concentrations of HAAs (<43.6 \pm 3.1 nM, i.e., 8.6 \pm 0.6 $\mu\text{g L}^{-1}$) were produced than
227 THMs. However, a similar trend of HAA formation vs. initial chlorine concentration was
228 observed. Total HAA concentrations increased with increasing initial chlorine concentrations
229 from 14 to 40 μM , but then decreased for high doses. This can be ascribed to the decreasing
230 formation of DBAA which was the main HAA species due to elevated BrO_3^- formation at initial
231 chlorine concentrations of 40 to 70 μM . However, meanwhile, the formation of other minor
232 chlorinated HAA species increased because high concentrations of chlorine facilitate the
233 oxidation of DOM moieties/intermediates.

234

235 **Effect of initial bromide concentration.** The effect of initial Br^- concentration on
236 residual oxidant and DBP formation was investigated (Figures S5, SI). Significant oxidant
237 consumption (i.e., 39.3%-80%) was observed, which increased with increasing initial Br^-
238 concentration from 0.5 to 10 μM (i.e., 40-800 $\mu\text{g L}^{-1}$), since HOBr reacts with DOM and CuO
239 faster than HOCl at pH 8.6.^{6,19} Bromate was only observed at high Br^- concentration ($\geq 5 \mu\text{M}$),

240 because at low Br^- concentration ($< 5 \mu\text{M}$), the formed HOBr was mainly consumed by the
241 reactive DOM moieties.

242 An elevated THM formation was observed for an increasing initial Br^- concentration (Figure
243 S5b, SI), which is similar to previous studies performed in the absence of CuO.^{10, 31} In the
244 absence of Br^- , only CHCl_3 ($106.4 \pm 2.4 \text{ nM}$) was formed from the chlorination of DOM.
245 Increasing the Br^- concentration led to less CHCl_3 formation, but enhanced the formation of
246 brominated THMs. At an initial Br^- concentration of $2 \mu\text{M}$, chlorine concentration ($[\text{HOCl}]_0 = 40$
247 μM) was 10 times higher than bromine. However, the formed CHCl_3 was less than that of
248 CHBr_3 (36.8 nM vs 57.2 nM), indicating that the ability of bromine to produce THMs is at least
249 10 times higher than chlorine in the presence of CuO.

250 The formation of HAAs was significantly less than THMs. DCAA, TCAA, BCAA and
251 DBAA were detected (Figure S5c, SI). In a manner analogous to that observed for THMs,
252 increasing the initial Br^- concentration shifts the speciation of HAAs from chlorinated to
253 brominated species, which is similar to previous studies conducted in the absence of CuO.^{10, 32, 33}

254 Increasing the initial Br^- concentration leads to enhanced BrO_3^- formation and bromine
255 incorporated in THMs and HAAs. However, this reduces the incorporation of chlorine atom
256 (Figure S6, SI), since chlorine is consumed by the increasing Br^- in the solution, thus decreasing
257 available chlorine that can react with DOM. Increasing the initial Br^- concentration significantly
258 enhances the formation of THM4, but no significant enhancement of total HAA formation was
259 observed, leading to an increasing ratio of total THMs/HAAs with the increasing initial Br^-
260 concentration. This indicates that Br^- favours the formation of THMs in the presence of CuO,
261 comparing with HAAs, probably because more THM precursors are available than HAA

262 precursors in the studied DOM. It was reported that THM and HAA can be formed from
263 different precursors.³⁰

264

265 **Effect of pH.** During the chlorination of bromide-containing waters in the presence of
266 0.025 g L⁻¹ CuO and DOM, significant oxidant decay ($\geq 75.5\%$) was observed at a reaction time
267 of 8 h within the range of pH 6.6-9.6 (Figure 3). The corresponding BrO₃⁻ concentrations were
268 7.0 \pm 3.0, 13.2 \pm 0.4, 33.6 \pm 2.1 and 2.8 μ g L⁻¹ for pH 6.6, 7.6, 8.6, and 9.6, respectively. Maximum
269 BrO₃⁻ formation was at pH 8.6 near its *pK_a* (i.e., 8.8), since the CuO-catalyzed
270 disproportionation of HOBr occurs via the interaction between HOBr and OBr⁻.^{19, 24}

271 The concentration of BrO₃⁻ was lower than that of total bromine in THMs and HAAs, which
272 increased with increasing pH (Figure S7, SI). Significant amounts of THMs were formed within
273 the range of pH 6.6-9.6, e.g., THM4 were 169.4 \pm 12.6, 283.7 \pm 64.7, 379.9 \pm 86.4 and 473.4 \pm 118.2
274 nM (i.e., 39.2 \pm 2.5, 65.8 \pm 15.0, 90.9 \pm 20.4 and 108.9 \pm 24.0 μ g L⁻¹) for pH 6.6, 7.6, 8.6 and 9.6,
275 respectively. The upward trend in THM formation with pH was also reported in previous studies
276 performed in the absence of CuO.^{34, 35} Hypohalous acid (HOCl/HOBr) that is present as non-
277 dissociating species at lower pH (e.g., ≤ 7.6) shows a higher reactivity than its hypohalite ion
278 towards DOM.^{11, 36} However, THM formation is a multi-step process. The enolization of
279 carbonyl moiety of DOM or the hydrolysis of intermediate (e.g., trihalocarbonyl) to THM could
280 be the rate-limiting step and both pathways can be catalyzed by hydroxide ion.³⁷ It is likely that
281 these reactions play much more important roles in determining the pH effect on the THM
282 formation. Again, less HAAs ($\leq 43.6\pm 3.1$ nM, i.e., 8.6 ± 0.6 μ g L⁻¹) were formed than THMs
283 within the range of pH 6.6-9.6. HAA formation increased as the pH increased from 6.6 to 8.6 and

284 then slightly decrease within pH range of 8.6-9.6. DBAA were the main HAA species, while
285 DCAA, TCAA and BCAA were minor species.

286

287 **Effect of the initial DOM concentration.** Figure S8 (SI) shows the influence of initial
288 DOM concentration (1.25-20 mg L⁻¹) on the oxidant demand and DBP formation. In the absence
289 of DOM, the residual oxidant and BrO₃⁻ at a reaction time of 8 h were 7.0±0.1 and 7.5 ±0.1 μM,
290 respectively (Figure S9, SI). Increasing the initial DOM concentration decreases the residual
291 oxidant concentration and BrO₃⁻ formation due to the reaction between bromine and DOM. The
292 presence of 1.25 mg L⁻¹ DOM significantly reduced BrO₃⁻ concentrations from 957.7±13 to
293 58.3±11.7 μg L⁻¹. When DOM concentration is higher than 5 mg L⁻¹, BrO₃⁻ concentration is < 5
294 μg L⁻¹, indicating that the HOBr reaction with DOM will predominate in the presence of higher
295 concentrations of DOM.

296 Increasing initial DOM concentrations (0-20 mg L⁻¹) shifts bromine speciation from BrO₃⁻ to
297 organic brominated byproducts (e.g., THMs and HAAs) (Figure S10, SI). THM4 (64.0±15.5-
298 138.9±2.1 μg L⁻¹) increased with increasing DOM concentrations from 1.25 to 20 mg L⁻¹. Again,
299 CHBr₃ was the main THM species, whereas CHCl₃, CHBrCl₂ and CHBr₂Cl were the minor
300 species.

301 Increasing the DOM concentration only slightly increased the HAAs formation from
302 48.0±2.1 to 63.9±1.5 nM (i.e., 8.1±0.4 to 11.2±0.3 μg L⁻¹) (Figure S8c, SI). DCAA, TCAA,
303 BCAA and DBAA were detected. At lower initial DOM concentration (1.25-2.5 mg L⁻¹), the
304 heterogeneous HOBr involved reactions on the CuO surface predominate, since HOBr is much
305 more readily activated by CuO than HOCl. Increasing the initial DOM concentration increased
306 the DBAA formation. At higher DOM concentration (>2.5 mg L⁻¹), the direct homogeneous

307 reactions between HOCl and fast reacting DOM moiety becomes significant, leading to the
308 enhanced formation of chlorinated HAAs. Elevated BCAA formation even led to a slight
309 decreasing DBAA formation with the increasing DOM concentration from 2.5 to 20 mg L⁻¹.

310

311 **Effect of the type of DOM.** Oxidant decay and DBP formation in the presence of six
312 types of DOM isolates were studied (Figure 4, Figures S11-13, SI). The six DOM isolates
313 exhibited a wide range of SUVA₂₅₄ values (Table S1, SI). SRW-HPOA showed the highest
314 SUVA₂₅₄ (4.9 L mg⁻¹ m⁻¹), indicating a high aromatic character (i.e., high reactivity toward
315 oxidants), followed by LRW-HPO, RRW-HPO and CRW-PI1-HPO, with SUVA₂₅₄ values of 3.5,
316 3.1 and 2.0 L mg⁻¹ m⁻¹, respectively. CRW-F2E-HPO and CRW-BF-HPO are extracted from
317 treated Colorado River water (CRW-PI1-HPO), showing lower SUVA₂₅₄ values of 1.7 and 1.1 L
318 mg⁻¹ m⁻¹, respectively.

319 After 2 h chlorination of these DOM isolates in the presence of Br⁻, residual oxidant varied
320 from 20.5 to 30.0 μM (Figure S11, SI). Increasing the aromaticity of DOM (i.e., SUVA₂₅₄) led to
321 decreased residual oxidant but enhanced formation of total THMs and HAAs (Figure 4). For
322 example, CRW-BF-HPO isolated after advanced treatment of raw water for CRW-PI1-HPO is
323 the lowest reactive fraction, producing lowest total THMs and HAAs. SRW-HPOA, humic
324 substances with the highest SUVA₂₅₄ value among the six DOM isolates form 161.6±8.6 and
325 26.2±1.2 μg L⁻¹ for total THMs and HAAs, respectively. This trend agrees well with the
326 percentage of humic substances in DOM characterized in Figure S14 (SI). Humic substances
327 with the high aromatic/phenolic carbon and carboxyl group contents are the fast reacting
328 THM/HAA precursors.²⁹

329 In the presence of CuO, less oxidant (7.9-10.3 μM) remained due to the interaction between
330 CuO and HOCl/HOBr.¹⁹ Bromate formation was only detected in the presence of two DOM
331 fractions isolated from treated waters (29.1 ± 2.4 and $2.8 \mu\text{g L}^{-1}$ for CRW-BF-HPO and CRW-
332 F2E-HPO, respectively) (Figure S12, SI). In the presence of DOM isolates collected from raw
333 waters with higher SUVA_{254} values, the formed HOBr was mainly consumed by its reaction with
334 fast reacting DOM moieties (e.g., humic substances) and disproportionation is insignificant.

335 The presence of CuO generally enhanced the formation of total THMs and HAAs and
336 bromine/chlorine atom in THMs and HAAs (except from SRW-HPOA). DOM with the highest
337 SUVA_{254} value (e.g., SRW-HPOA) exhibited the lowest enhancement (Figures 4 and S15, SI).
338 For example, an increase of 124% for the THM4 formed from CRW-BF-HPO by CuO was
339 observed, while this was only 21.8% for SRW-HPOA. For HAA formation, there is even no
340 enhancement for SRW-HPOA. This may indicate that CuO can enhance the reactions with
341 relatively low rate constants.

342 The speciation of THMs and HAAs in the presence of CuO was similar to that in the absence
343 of CuO. Among the formed THMs and HAAs, CHBr_3 and DBAA were the main species,
344 respectively. In contrast, CHCl_3 , CHBrCl_2 and CHBr_2Cl were minor THM species, and DCAA,
345 TCAA, BCAA and BDCAA were formed at lower concentrations than DBAA (Figures S13, SI).

346

347 **Formation of bromate, THMs and HAAs from bromination of model compounds.**

348 Because the structure of DOM moieties is ambiguous and variable, the investigation of
349 model compounds provides information on the kinetics and mechanisms responsible for DBP
350 formation. Table 1 summarizes the consumption of HOBr, formation of BrO_3^- , CHBr_3 and

351 DBAA from HOBr reactions with various model compounds and their reaction rate constants
352 with bromine are shown in Table S3 (SI).

353 Second-order rate constants (k) for bromine reactions with acetone, n-butanol, propionic and
354 butyric acids are $< 1 \text{ M}^{-1} \text{ s}^{-1}$, which are considered as practically unreactive compounds.¹¹ Slight
355 HOBr consumption ($\leq 4.6\%$) was observed and CHBr_3 was the only DBP formed at 2 h (Table
356 1). Among them, acetone shows the highest CHBr_3 formation via the classical haloform
357 formation pathway.¹¹ Similar HOBr consumption and BrO_3^- formation comparing with that in
358 the absence of model compounds indicates that the presence of practically unreactive compounds
359 does not affect the disproportionation of HOBr. However, the presence of CuO changes the
360 CHBr_3 and DBAA formation. The CHBr_3 formation from propionic and butyric acids was
361 slightly enhanced, while its formation from acetone and n-butanol was inhibited by CuO. The
362 reason is unknown, but it is likely that the structure of model compounds will also determine the
363 extent for the enhancement of CHBr_3 formation by CuO. Interestingly, DBAA were additionally
364 formed, indicating that CuO can enhance the reactivity of HOBr via the electron transfer
365 pathway to oxidize acetone and n-butanol to their acid forms.

366 Oxalic, malonic, succinic and citric acids are considered as slow reacting compounds which
367 react with bromine with second-order rate constants $> 1 \text{ M}^{-1} \text{ s}^{-1}$ ($k= 40$ and $30 \text{ M}^{-1} \text{ s}^{-1}$ for oxalic
368 and malonic acids, respectively³⁸). At 2 h, $<6.8\%$ of HOBr was consumed (Table 1). Citric acid
369 is the strongest precursor of THM and HAA ($375.7\pm 36.7 \text{ nM}$ and $31.6\pm 6.8 \text{ nM}$, respectively). It
370 was known as an important CHCl_3 precursor during the analogous chlorination process through
371 multi-steps (e.g., oxidative decarboxylation, halogenation of methylene groups and subsequent
372 hydrolysis of intermediates).³⁹⁻⁴¹ The formation of THM and HAA (i.e., $\leq 4.2\pm 0.3$ and $\leq 2.2\pm 0.1$

373 nM, respectively) from oxalic, malonic, and succinic acids was lower, which agrees with
374 previous studies.^{42, 43}

375 The presence of CuO significantly enhanced the consumption of HOBr in the presence of
376 these slow reacting compounds ($\geq 93.2\%$). Bromate was not detected in the presence of oxalic
377 and malonic acids but its concentrations in the presence of succinic and citric acids were 1.5 ± 0.1
378 and $0.2 \mu\text{M}$, respectively. CuO-catalyzed disproportionation of HOBr is in competition with the
379 heterogeneous reactions between CuO-HOBr and slow reacting compounds. Therefore, the
380 contribution for the latter pathway follows the sequence of oxalic \cong malonic > citric > succinic
381 acids. The enhanced formation of CHBr_3 and DBAA comparing with homogenous solutions
382 indicates that the bromination pathway is enhanced by CuO. Citric acid showed the highest
383 CHBr_3 and DBAA formation among slow reacting compounds. The rate-limiting step (i.e.,
384 decarboxylation of citric acid to 3-oxopentanedioic acid) seems to be significantly enhanced by
385 CuO. Both brominated DBPs and BrO_3^- formation are insignificant in the presence of oxalic acid,
386 implying an oxidation of oxalic acid to carbon dioxide.

387 Rate constants for the reactions between HOBr and phenolic compounds are $> 10^4 \text{ M}^{-1} \text{ s}^{-1}$,
388 and thus they are included as fast reacting compounds,⁴⁴⁻⁴⁸ consuming $> 84\%$ of HOBr after 2 h.
389 Resorcinol known as a fast CHCl_3 precursor,⁴⁹⁻⁵¹ shows the highest CHBr_3 formation
390 ($6367.5 \pm 35.0 \text{ nM}$). In contrast, CHBr_3 formation from other phenolic compounds is significantly
391 lower ($< 49.1 \pm 2.3 \text{ nM}$). Phenol was known as a slow CHCl_3 precursor and the bromination of
392 hydroquinone and catechol occurs predominately via the oxidation pathway.⁴⁸⁻⁵¹ Phenolic
393 compounds do not form significant amount of DBAA ($< 7.1 \pm 0.9 \text{ nM}$). Because HOBr reacts
394 quickly with phenolic compounds, heterogeneous reactions on the CuO surface tends to be less

395 significant, leading to the insignificant enhanced formation of BrO_3^- , CHBr_3 and DBAA. (Table
396 1).

397 Based on our results, it can be concluded that the BrO_3^- formation decreases as the reactivity
398 of models compounds with bromine increases. CuO can activate the reactivity of HOBr towards
399 slow reacting compounds (e.g., di- and tri-carboxylic acids), leading to elevated CHBr_3 and
400 DBAA formation. However, no significant effect was observed for practically unreactive or fast
401 reacting phenolic compounds. These results confirm again the significant enhancement for slow
402 reacting DOM isolates (e.g., CRW-BF-HPO, mainly comprising fulvic acid structures
403 incorporating abundant polysaccharides moieties²⁹). However, DOM isolates such as SRW-
404 HPOA (predominance of high aromatic/phenolic carbon and carboxyl group contents²⁹) exhibit
405 less enhancement.

406

407 **Mechanisms of CuO enhanced DBP formation during chlorination of bromide-**
408 **containing waters in the presence of DOM.** Scheme 1 shows a hypothetical formation

409 mechanism of BrO_3^- and halogenated DBPs during chlorination of bromide-containing waters in
410 the presence of DOM and CuO. The reaction is initiated by the rapid oxidation of Br^- by HOCl to
411 HOBr/OBr⁻ (reaction 1).⁸ The formed HOBr/OBr⁻ can compete with HOCl/OCl⁻ to react with
412 fast reacting DOM moieties (e.g., phenolic) via electrophilic substitutions (reaction 2a) and
413 oxidation (reaction 2b) ($k=500-5000 \text{ M}^{-1} \text{ s}^{-1}$).^{6, 11} Reaction 2a forms brominated DBPs, while
414 reaction 2b produces oxidized DOM (DOM_{ox}) with the release of Br^- , which can be re-oxidized
415 to HOBr in excess of HOCl (catalytic cycle). The latter one is the main pathway for bromination
416 of most DOM.⁵²

417 In the presence of CuO, HOBr can combine with CuO to form a CuO-HOBr complex
418 (reaction 3). Complexation of HOBr/OBr⁻ by the Lewis acid CuO polarizes the bromine
419 molecule, thus increasing its electrophilicity and as a consequence its reactivity. The CuO-HOBr
420 complex reacts with HOBr to generate oxygen and Br⁻ (reaction 4) or form BrO₃⁻ (i.e.,
421 disproportionation pathway, reaction 5).¹⁹ Moreover, this complex can react with slow reacting
422 DOM moieties, leading to the formation of brominated DBPs (reaction 6a) or DOM_{ox} (reaction
423 6b). Estimated second-order rate constants for reactions 4 and 5 range between 1 and 500 M⁻¹ s⁻¹
424 according to previous kinetical model.¹⁹ Therefore, upon the complete degradation of fast
425 reacting DOM moieties, in order to form both halogenated DBPs and BrO₃⁻ the rate constant for
426 CuO-HOBr complex reaction with slow reacting DOM moieties (e.g., alcohol, ketone,
427 carboxylic, etc) should be in the same order of magnitude with reaction 5 (k=1-500 M⁻¹ s⁻¹).
428 Meanwhile, since the reaction between HOBr and slow reacting DOM is enhanced by CuO,
429 elevated brominated DBPs can be formed.

430 HOCl will also react with fast reacting DOM moieties to produce chlorinated DBPs or
431 DOM_{ox} (reactions 12a and 12b, respectively), approximately 10 times slower than the
432 corresponding bromine reaction.⁶ Similarly, HOCl can combine with CuO to form a CuO-HOCl
433 complex (reaction 13), which reacts with itself to produce oxygen and chlorate (ClO₃⁻) (reactions
434 14 and 15, respectively).¹⁹ Reaction 14 is the major pathway, while reaction 15 is a minor
435 pathway. Therefore, even ClO₃⁻ can be formed in CuO-HOCl system, in the presence of DOM
436 and Br⁻, the formation of ClO₃⁻ is insignificant since the rate constants for reactions 1, 12, and
437 14 are higher than reaction 15 (HOCl disproportionation). Because of the chemical similarity of
438 HOCl with HOBr, it is expected that CuO can enhance the reactivity of HOCl towards the slow
439 reacting DOM moieties, leading to elevated chlorinated DBPs or DOM_{ox} (reactions 16a and 16b,

440 respectively). However, rate constant for reaction 16 may be smaller than that of reaction 6 (i.e.,
441 bromination of DOM in the presence of CuO).

442 **Implications on water treatment.** Our results highlight that in the presence of DOM
443 isolated from treated water that are representative of distributed drinking water, both BrO_3^- and
444 brominated DBP formation can be enhanced in the presence of CuO. CuO is present on the
445 surface of copper pipes owing to the pipe corrosion.^{21, 23} This would raise a serious drinking
446 water safety issue in distribution systems and household plumbing.

447 Bromide levels in raw waters are highly variable in a range from <10 to $>1000 \mu\text{g L}^{-1}$.⁵³ A
448 survey over 23 water supplies in the USA and Canada showed that Br^- levels ranged from 24 to
449 $1120 \mu\text{g L}^{-1}$ (median of $109 \mu\text{g L}^{-1}$) in source waters.⁵⁴ Based on our results, it can be expected
450 that BrO_3^- formation should not be of concern when Br^- is present at concentration around 100
451 $\mu\text{g L}^{-1}$ (median level in natural waters in USA). However, when potable water is produced from
452 desalinated seawater,^{55, 56} groundwater⁵⁷ with high Br^- content (i.e., $> 400 \mu\text{g L}^{-1}$) and low DOC,
453 the risk of producing BrO_3^- exists. This may also apply to treated surface water in seasonal
454 seawater intrusion in coastal cities and some regions with Br^- enriched water (e.g., Australia,⁵⁷),
455 considering that Br^- is not removed in conventional treatment train while a large fraction of the
456 DOM incorporating the fast reacting moieties is generally eliminated. For treated water with high
457 concentrations of both Br^- and DOM moieties (e.g., blending desalinated seawater with other
458 source water), the possibility to produce BrO_3^- is reduced. However, elevated THMs and HAAs
459 can be expected, since CuO can activate the reactivity of HOBr towards hydrophilic carboxylic
460 acids leading to enhanced DBP formation from DOM moieties that are not originally expected to
461 form significant DBPs during disinfection. Accordingly, this will be a challenge to meet the

462 MCL for THM4 in drinking water (e.g., 80 $\mu\text{g L}^{-1}$ by US EPA, Figures 2-3, and Figures S5 and
463 S8, SI).

464 It should be noted that our data were obtained in a batch reactor which provides a different
465 hydraulic and operational condition from distribution systems. Therefore, additional studies will
466 be required in a long-term running copper-containing pilot-scale/full-scale distribution system to
467 assess the kinetics of oxidant decay and the formation of BrO_3^- , THMs, HAAs and emerging
468 DBPs (e.g., haloacetonitriles and haloketones)

469

470 **▪ Supporting Information**

471 Additional details of chemicals, methods, tables and figures. This material is available free of
472 charge via the Internet at <http://pubs.acs.org>.

473 **▪ Acknowledgements**

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Figure 1 Effect of CuO dose on (a) residual oxidant and formed BrO_3^- , (b) THMs and (c) HAAs. Experimental conditions: $[\text{HOCl}]_0 = 40 \mu\text{M}$, $[\text{Br}^-]_0 = 10 \mu\text{M}$, $[\text{DOM}] = 2.5 \text{ mg L}^{-1}$, $[\text{CuO}] = 0\text{-}0.2 \text{ g L}^{-1}$, $\text{pH} = 8.6$, $T = 21 \pm 1 \text{ }^\circ\text{C}$, reaction time = 2 h.

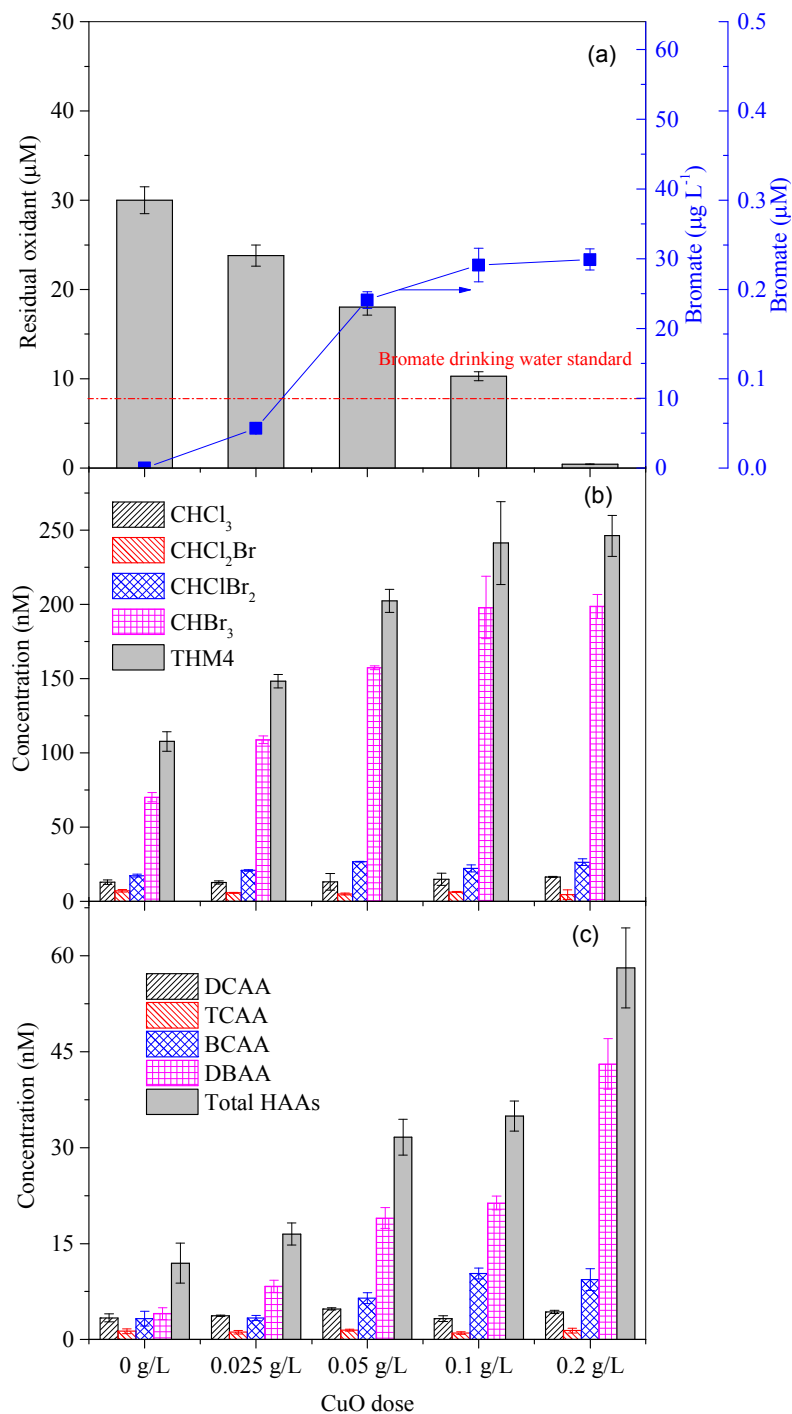


Figure 2 Effect of initial chlorine concentration on (a) residual oxidant and formed BrO_3^- , (b) THMs and (c) HAAs. Experimental conditions: $[\text{HOCl}]_0 = 14\text{-}70 \mu\text{M}$, $[\text{Br}^-]_0 = 10 \mu\text{M}$, $[\text{DOM}] = 2.5 \text{ mg L}^{-1}$, $[\text{CuO}] = 0.025 \text{ g L}^{-1}$, $\text{pH} = 8.6$, $T = 21 \pm 1 \text{ }^\circ\text{C}$, reaction time = 8 h.

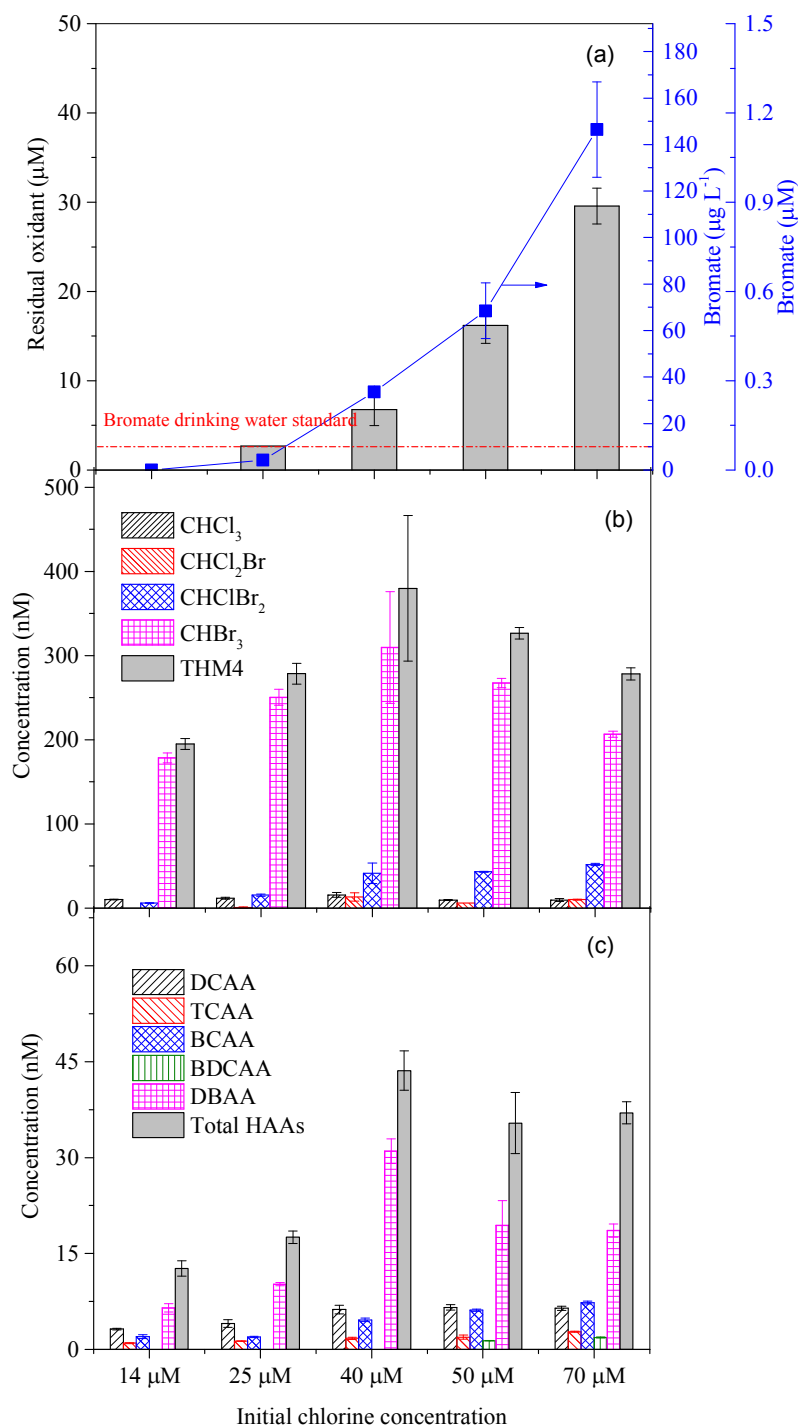


Figure 3 Effect of pH on (a) residual oxidant and formed BrO_3^- , (b) THMs and (c) HAAs. Experimental conditions: $[\text{HOCl}]_0 = 40 \mu\text{M}$, $[\text{Br}^-]_0 = 10 \mu\text{M}$, $[\text{DOM}] = 2.5 \text{ mg L}^{-1}$, $[\text{CuO}] = 0.025 \text{ g L}^{-1}$, $\text{pH} = 6.6\text{--}9.6$, $T = 21 \pm 1 \text{ }^\circ\text{C}$, reaction time = 8 h.

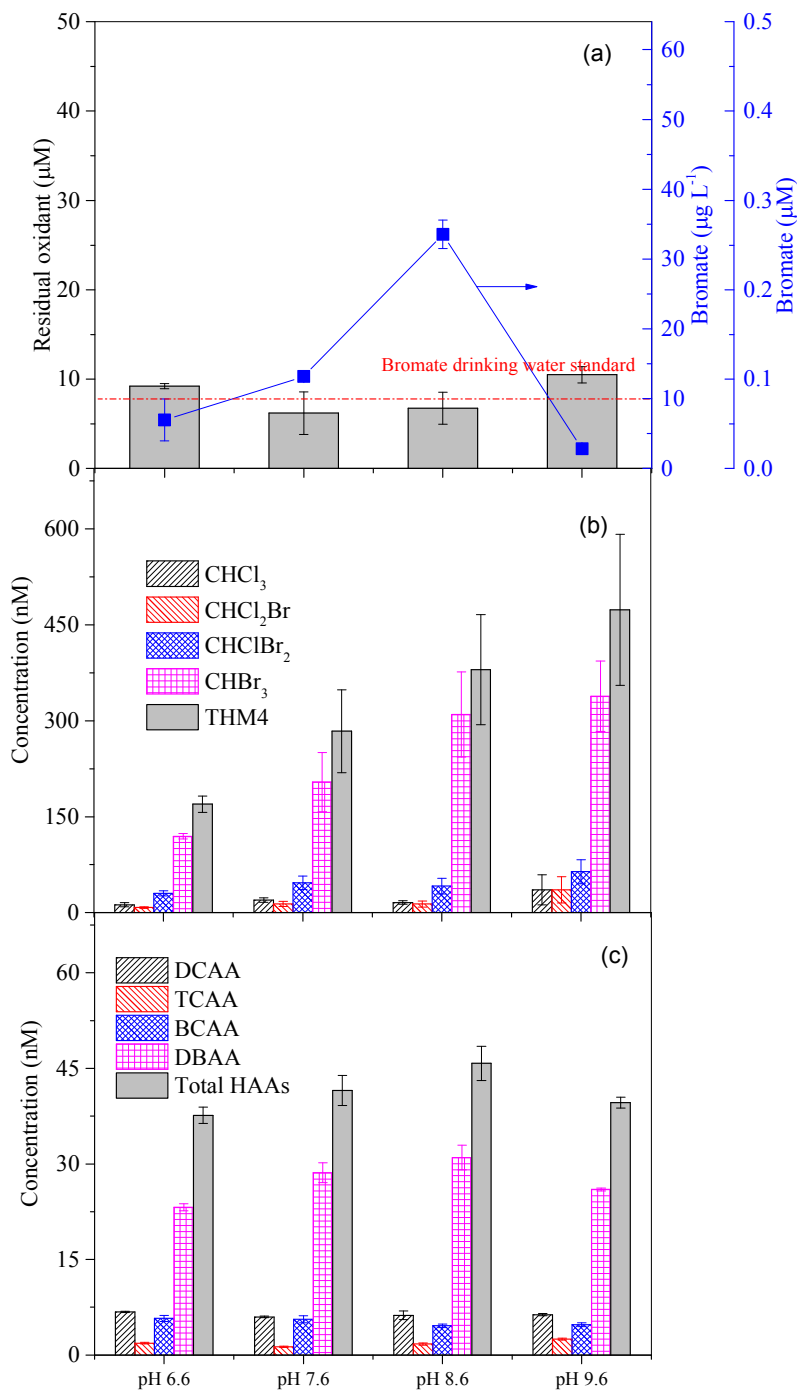
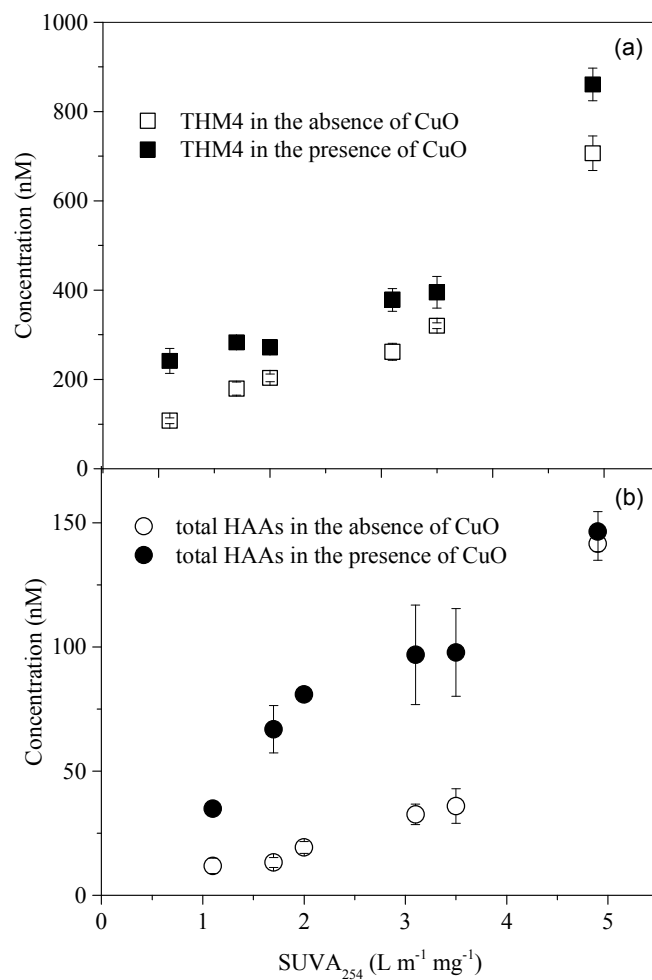


Figure 4 Plot of $SUVA_{254}$ values vs. (a) THM4 and (b) total HAAs in the absence and presence of $0.1 \text{ g L}^{-1} \text{ CuO}$. Experimental conditions: $[\text{HOCl}]_0 = 40 \text{ } \mu\text{M}$, $[\text{Br}^-]_0 = 10 \text{ } \mu\text{M}$, $[\text{DOC}] = 1.3 \text{ mg C L}^{-1}$, $\text{pH} = 8.6$, $T = 21 \pm 1 \text{ } ^\circ\text{C}$, reaction time = 2 h.



Scheme 1 Potential reactions during chlorination of bromide-containing waters in the presence of dissolved organic matter and CuO. (Solid lines, main pathways; dashed lines, minor pathways.).

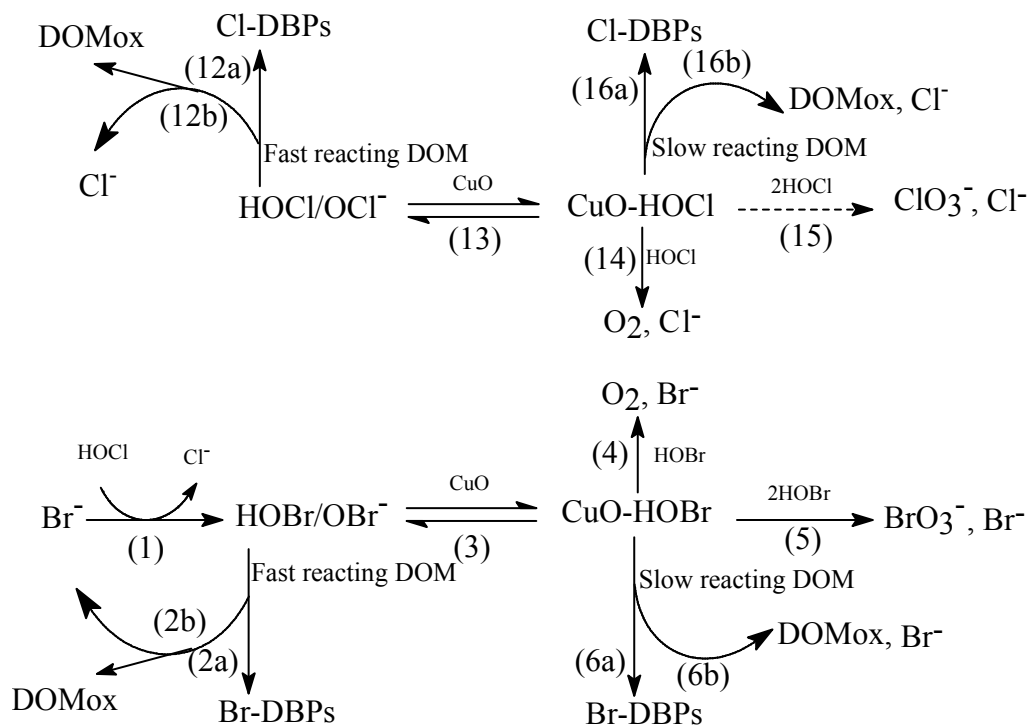


Table 1. Consumption of bromine and formation of byproducts during bromination of model compounds in the absence or presence of 0.1 g L⁻¹ CuO

Compounds	Consumed bromine μM		Bromate μM		CHBr ₃ nM		DBAA nM	
	-	+	-	+	-	+	-	+
blank	NA	40.0±0.6	NA	10.2±0.1	NA	NA	NA	NA
practically unreactive group								
Acetone	2.3±0.3	40.8±0.1	ND	10.1±0.4	219.4±4.4	144.2±6.8	ND	12.3±1.1
n-Butanol	1.9±0.8	40.2±0.1	ND	10.3±0.1	12.9±0.8	7.3±0.2	ND	15.0±0.8
Propionic acid	1.7±1.2	40.3±0.4	ND	10.2±0.1	3.3±0.2	5.7±0.2	ND	9.1±2.1
Butyric acid	1.7±0.1	39.9±0.1	ND	10.3±0.1	2.2±0.2	8.9±1.1	ND	12.9±0.8
slow reacting group								
Oxalic acid	1.6±0.5	47.3±0.8	ND	ND	2.2±0.3	4.1±2.1	0.9±0.1	3.1±1.5
Malonic acid	2.0±0.5	46.6±0.4	ND	ND	1.6±0.2	178.1±61.8	2.2±0.1	48.8±16.8
Succinic acid	1.8±0.8	48.8±0.5	ND	1.5±0.1	4.2±0.3	291.6±49.5	1.6±0.4	156.0±44.7
Citric acid	3.4±0.8	49.5±0.1	ND	0.2	375.7±36.7	8713.8±1821.0	31.6±6.8	1912.7±154.0
fast reacting group								
Phenol	49.6±0.1	49.6±0.1	ND	ND	49.1±2.3	31.5±1.0	1.6±0.3	1.2±0.2
Hydroquinone	42.1±0.2	43.5±0.3	ND	ND	10.2±0.6	18.3±0.6	2.3±0.4	2.3±1.0
Catechol	49.2±0.1	48.9±0.1	ND	ND	2.0±0.1	1.3±0.2	1.0±0.2	1.1±0.2
Resorcinol	49.6±0.1	49.6±0.1	ND	ND	6367.5±35.0	5357.5±103.8	7.1±0.9	7.8±0.3

Experimental conditions: [HOBr]₀ = 50 μM, [model compound]₀ = 50 μM, pH=8.6, T = 21±1 °C, reaction time = 2 h. -: In the absence of CuO; +: In the presence of CuO. NA: not available, ND: not detected.

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