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Environ. Sci. Technol., Just Accepted Manuscript • DOI: 10.1021/acs.est.5b03266 • Publication Date (Web): 02 Dec 2015

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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 (0-0.2 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.
**Introduction**

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

While chlorine disinfection provides hygienically safe drinking water, chlorine (in the form of hypochlorous acid, i.e., HOCl, in water) also reacts with dissolved organic matter (DOM) to produce potentially toxic chlorinated disinfection byproducts (DBPs). Among various DBPs, the most recognized compounds are trihalomethanes (THMs) and haloacetic acids (HAAs).\(^2\) In the presence of bromide (Br\(^-\)), HOCl can rapidly oxidize naturally occurring Br\(^-\) to hypobromous acid (HOBr).\(^8\) Upon the reaction between HOCl/HOBr and DOM, four THMs (i.e., THM4, sum of CHCl\(_3\), CHBrCl\(_2\), CHBr\(_2\)Cl, and CHBr\(_3\)) and nine HAAs (i.e., HAA9, sum of monochloro-, dichloro-, trichloro-, monobromo-, dibromo-, bromochloro-, bromodichloro-, dibromochloro-, and tribromo-acetic acids (MCAA, DCAA, TCAA, MBAA, DBAA, BCAA, BDCAA, DBCAA, and TBAA, respectively)) can be formed.\(^6\,9\) THM4 and HAA5 (sum of MCAA, DCAA, TCAA, MBAA, and DBAA) are currently regulated for drinking water at 80 µg L\(^-1\) and 60 µg L\(^-1\) by the U.S. Environmental Protection Agency (US EPA), respectively.\(^12\) These DBPs are also fully or partly regulated in drinking water in other countries (e.g., European Union\(^13\), China\(^14\)).

Unlike ozone which can further oxidize HOBr to potentially toxic bromate (BrO\(_3^-\)),\(^15\)-\(^17\) the rate constant for the reaction between HOCl and HOBr is low.\(^18\) Therefore, BrO\(_3^-\) formation from chlorination of bromide-containing waters in water treatment is generally insignificant.
Recently we showed that CuO can catalyze HOX (X: Cl or Br) disproportionation to produce $X^-$ and $XO_3^-$ (eq 1 showing an example from HOBr).\(^{19}\)

$$3\text{HOBr} \xrightleftharpoons[^{\text{CuO}}]{_{\text{CuO}}} \text{BrO}_3^- + 2\text{Br}^- + 3\text{H}^+$$  \hspace{1cm} (1)

It was reported that CuO is one of the major corrosion products of copper pipes that are widely used in municipal distribution systems and household plumbing.\(^{20-23}\) This disproportionation pathway led to elevated $\text{BrO}_3^-$ concentrations (e.g., 50 $\mu$g L\(^{-1}\)) exceeding the maximum contaminant level (i.e., MCL, 10 $\mu$g L\(^{-1}\) regulated by US EPA\(^{12}\)) during chlorination of bromide-containing waters in distribution systems.\(^{24}\) In addition, previous studies showed that CuO can enhance HOCl/HOBr reactions with iodate to periodate and activate the reactivity of the other halogen-containing oxidant (e.g, ClO\(_2\)).\(^{25,26}\)

In the presence of DOM, HOBr can react with organic moieties and thus CuO-catalyzed disproportionation may be inhibited, shifting the DBP formation from inorganic (i.e., $\text{BrO}_3^-$) to halogenated organic species (e.g., THMs and HAAs). Previous studies showed that total THM formation was enhanced and the speciation of HAA was affected by the presence of CuO.\(^{22,23}\) However, similar total HAA formation in the presence of CuO with that in the absence of CuO was further observed.\(^{27}\) Because of the variability of the results reported previously, it is still unclear if the reaction between HOCl/HOBr and DOM can be enhanced by CuO, leading to the elevated formation of both THM and HAA. Understanding how CuO will control the fate of bromine (i.e., $\text{BrO}_3^-$ versus brominated organics) during the transportation of chlorinated waters containing various types of DOM in distribution systems is therefore of major importance.

In view of the potential toxicological significance of the formation of regulated DBPs in drinking water, the objectives of this study were to investigate the formation and speciation of $\text{BrO}_3^-$, THMs and HAAs during chlorination of bromide-containing waters in the presence of...
DOM isolates and CuO. Factors such as pH, initial concentrations of CuO, chlorine and Br⁻, as well as the concentration and nature of DOM on DBP formation were studied. Furthermore, a range of structurally diverse model compounds were selected to study the mechanism for the formation of BrO₃⁻, THMs and HAAs in the presence of CuO.

Materials and methods

Reagents. All chemical solutions were prepared from reagent grade chemicals or stock solutions using deionized water (18.2 MΩ·cm, Millipore). A sodium hypochlorite (NaOCl) solution was used as the source of chlorine (13% active chlorine, Acros Organics). CuO particles were prepared according to a previously published method. The BET surface areas were determined by a Micromeritics Tristar II to be 33.7 m² g⁻¹. The pHₚᵢᵢ (pH at which CuO particles have a zero charge) was determined to be 8.6. HOBr solutions were prepared by reaction of NaOCl with Br⁻. The descriptions of all other standards and reagents used in this study are provided in Text S1 of the Supporting Information (SI).

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

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

**Analytical methods.** The analytical methods of residual oxidants, DOM characterization, total organic carbon, total organic bromine (TOBr), BrO$_3^-$, THMs, and HAAs can be found in detail in Text S2 (SI).

**Experimental setup and procedures.** The influence of various drinking water parameters including CuO dose, initial chlorine and Br$^-$ concentrations, pH and initial concentration and type of DOM on the formation of BrO$_3^-$, THMs and HAAs was investigated. The CuO dose ranged from 0 to 0.2 g L$^{-1}$, based on our previous study to be able to investigate the reaction kinetics in a selected time frame.$^{19}$ Initial chlorine concentrations ranged from 14 to 70 µM (i.e., 1.0-4.9 mg L$^{-1}$ as Cl$_2$). Initial Br$^-$ concentrations varied from 0 to 10 µM (i.e., 0-800 µg L$^{-1}$), covering the typical Br$^-$ range in raw water.$^{15}$ The pH was adjusted to 6.6, 7.6, 8.6 and 9.6 with HNO$_3$ or NaOH solutions in the presence of a 2.5 mM tetraborate buffer. The pH changes were less than 0.2 pH unit during the reaction. It should be noted that in most reaction conditions, a pH value of 8.6 that approaches the optimum pH for HOBr disproportionation was adopted to better observe the BrO$_3^-$ formation.$^{19}$ DOM concentrations ranged from 0 to 20 mg L$^{-1}$.

All experiments were conducted in the dark and under continuous agitation using a magnetic stirrer in 250 mL capped amber bottles under headspace-free conditions at room temperature (21±1 °C). Reactions were initiated by the injection of an aliquot of a HOCl/HOBr stock solution, to the buffered solutions containing DOM or model compounds in the presence or
absence of CuO. Bromide was added when required. Samples were withdrawn at preselected
time points, filtered within 1-2 min through a 0.45-µm syringe filter (surfactant-free cellulose
acetate membrane). The filter was pre-treated with HOCl or HOBr solutions (1 mg L\(^{-1}\)) and then
rinsed with deionized water to avoid a potential oxidant demand. The filtered samples were
analyzed for residual oxidant concentrations. For the analyses of BrO\(_3^-\), THMs and HAAs, the
samples were quenched immediately with sulfite. Each experiment was performed in duplicate.

- **Results and discussion**

  **Effect of CuO dose and reaction time.** Figure 1 shows concentrations of the residual
oxidant and formed BrO\(_3^-\), THMs and HAAs for various CuO doses (0-0.2 g L\(^{-1}\)). In the absence
of CuO, HOCl and the formed HOBr react with DOM, and 25% of initial oxidant was consumed
after 2 h reaction, leading to 107.7±6.5 and 11.9±3.1 nM for THM4 and total HAAs,
respectively. Because HOCl does not react with HOBr,\(^{18}\) BrO\(_3^-\) concentration is low (< 1 µg L\(^{-1}\),
Figure 1a).

In the presence of CuO, higher chlorine demands were observed. Increasing the CuO dose
led to a lower residual oxidant after 2 h reaction, almost complete oxidant consumption was
obtained with 0.2 g L\(^{-1}\) CuO. This can be ascribed to potential heterogeneous reactions of
HOCl/HOBr on the CuO surface (e.g., HOCl/HOBr decay to oxygen, HOCl/HOBr
disproportionation, and halogenation of DOM).\(^{19}\) Along with the fast oxidant loss, enhanced
concentrations of BrO\(_3^-\) (5.7-29.9±1.5 µg L\(^{-1}\)) were formed in the presence of increasing CuO
doses from 0.05 to 0.2 g L\(^{-1}\), owning to the CuO-catalyzed disproportionation of HOBr.\(^{19,24}\)

Comparing with BrO\(_3^-\), concentrations for bromine atom incorporated in THMs and HAAs
were higher (Figure S1, SI). This indicates that the HOBr reaction with DOM in the presence of
CuO is the major pathway, while disproportionation is minor. The formation of THMs and HAAs was enhanced as compared with reactions conducted in absence of CuO (Figure 1b-c). Increasing the CuO doses from 0 to 0.2 g L\(^{-1}\) led to increasing total THM and HAA 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\(^{-1}\), respectively) with 0.2 g L\(^{-1}\) CuO, which were 2.3 and 4.9 times higher than those in the absence of CuO, respectively.

Among the formed THMs and HAAs, CHBr\(_3\) (70.1-198.6 nM) and DBAA (up to 43.1 nM) were the main species, respectively. CHCl\(_3\), CHBrCl\(_2\) and CHBr\(_2\)Cl were detected at much lower concentrations (<26.8 nM). Similarly, DCAA, TCAA, and BCAA were detected at low levels (<10.4 nM). Tri-halogenated acetic acids (THAAs) were formed at much lower levels than di-halogenated acetic acids (DHAAs). Only TCAA was detected (<1.5 nM), and due to the limited initial bromide concentration other brominated THAAs were not detected. This may be ascribed to the limited THAA precursor in the studied DOM. It has been proposed that THAAs and DHAAs can have different precursors.\(^3\)

Figure S2 (SI) shows that the DOM concentration is stable in the presence of 0.1 g L\(^{-1}\) CuO, even for long reaction times (a few days), indicating that there is no significant adsorption of DOM (i.e., CRW-BF-HPO) to CuO. Previous studies indicated that CuO can adsorb HOCl/HOBr to form a CuO-HOCl/CuO-HOBr complex, thereby activating the reactivity of HOCl/HOBr towards several inorganic species (e.g., chlorine, bromine, iodine, and iodate).\(^{19,24}\)

By analogy, it is proposed that in the presence of DOM the formed CuO-HOCl/CuO-HOBr complex showed a higher reactivity towards the slow reacting moieties of DOM, thus enhancing the formation of THMs and HAAs. Interestingly, increasing CuO dose from 0 to 0.2 g L\(^{-1}\) significantly enhanced the formation of brominated species (e.g., CHBr\(_3\) and DBAA) and
bromine atom incorporated in THMs and HAAs. However, the enhancement for the formation of chlorinated species and chlorine atom incorporated in THMs and HAAs was less significant (Figure 1b-c, Figure S1, SI). This might indicate that CuO is more prone to activate the reactivity of HOBr than HOCl at pH 8.6, which was also observed for the HOCl/HOBr reactions with iodate in the presence of CuO.26 Our results agree with a previous investigation showing enhanced THM formation in the presence of CuO.23 However, the fact that another study reported similar HAA formation in the presence and absence of CuO might be ascribed to the low Br− dose used (0.8±0.2 µM),27 which minimized the enhancement of the reaction since HOBr is more readily activated by CuO than HOCl.

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

Figure S3 (SI) shows concentrations of residual oxidant and formed BrO3−, THMs, and HAAs at different reaction times (i.e., ranging from 2 h to 12.7 h). Since the oxidant decays 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 reactions for longer time (> 12 h). After 12.7 h reaction, the residual oxidant concentration was
2.8±0.3 μM, corresponding to a 93% oxidant consumption. From 2 to 8 h, BrO₃⁻, THM4 and total HAA concentrations increased by 217.6, 231.7, and 27.1 nM, respectively. However, from 8 to 12.7 h the increase was 194.1, 27.1, and 2.4 nM for BrO₃⁻, THM4 and total HAAs, respectively. Comparable BrO₃⁻ formation but significantly less halogenated DBP formation in the latter time range indicates that the disproportionation pathway outcompetes the halogenation pathway. DOM consists of fast reacting and slow reacting/unreactive moieties, leading to the two-stage reaction kinetics (i.e., rapid initial and slower consumption stages) for chlorination or bromination of DOM isolates. After the degradation of fast reacting DOM moieties, the rate constant for the reaction of HOBr disproportionation catalyzed by CuO was higher than that for the reaction between HOBr and slow reacting DOM moieties. BrO₃⁻ formation becomes important in the slower oxidant consumption stage.

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

Increasing the initial chlorine concentrations from 14 to 40 μM increased THM4 from 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
concentrations from 40 to 70 µM led to a decreasing THM4. Bromoform was the main THM species (>74.2% among THM4), while CHCl₃, CHBrCl₂ and CHBr₂Cl were the minor species. In the presence of CuO, the reaction between HOBr and DOM (CHBr₃ formation) competes with HOBr disproportionation (BrO₃⁻ formation). As above mentioned, in the second stage of reaction (slow consumption kinetics), rate constant for HOBr disproportionation in the presence of CuO is higher than HOBr reaction with slow reacting/unreactive DOM moieties, leading to the preferential formation of BrO₃⁻. As a consequence, a decreasing CHBr₃ formation was observed, leading to a decreasing trend of THM4 since CHBr₃ is the main species of THM4.

Lower concentrations of HAAs (<43.6±3.1 nM, i.e., 8.6±0.6 µg L⁻¹) were produced than THMs. However, a similar trend of HAA formation vs. initial chlorine concentration was observed. Total HAA concentrations increased with increasing initial chlorine concentrations from 14 to 40 µM, but then decreased for high doses. This can be ascribed to the decreasing formation of DBAA which was the main HAA species due to elevated BrO₃⁻ formation at initial chlorine concentrations of 40 to 70 µM. However, meanwhile, the formation of other minor chlorinated HAA species increased because high concentrations of chlorine facilitate the oxidation of DOM moieties/intermediates.

Effect of initial bromide concentration. The effect of initial Br⁻ concentration on residual oxidant and DBP formation was investigated (Figures S5, SI). Significant oxidant consumption (i.e., 39.3%-80%) was observed, which increased with increasing initial Br⁻ concentration from 0.5 to 10 µM (i.e., 40-800 µg L⁻¹), since HOBr reacts with DOM and CuO faster than HOCl at pH 8.6.6,19 Bromate was only observed at high Br⁻ concentration (≥ 5 µM),
because at low Br\(^-\) concentration (< 5 µM), the formed HOBr was mainly consumed by the
reactive DOM moieties.

An elevated THM formation was observed for an increasing initial Br\(^-\) concentration (Figure
S5b, SI), which is similar to previous studies performed in the absence of CuO.\(^{10,31}\) In the
absence of Br\(^-\), only CHCl\(_3\) (106.4±2.4 nM) was formed from the chlorination of DOM.
Increasing the Br\(^-\) concentration led to less CHCl\(_3\) formation, but enhanced the formation of
brominated THMs. At an initial Br\(^-\) concentration of 2 µM, chlorine concentration ([HOCl]\(_0\)= 40
µM) was 10 times higher than bromine. However, the formed CHCl\(_3\) was less than that of
CHBr\(_3\) (36.8 nM vs 57.2 nM), indicating that the ability of bromine to produce THMs is at least
10 times higher than chlorine in the presence of CuO.

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

Increasing the initial Br\(^-\) concentration leads to enhanced BrO\(_3^-\) formation and bromine
incorporated in THMs and HAAs. However, this reduces the incorporation of chlorine atom
(Figure S6, SI), since chlorine is consumed by the increasing Br\(^-\) in the solution, thus decreasing
available chlorine that can react with DOM. Increasing the initial Br\(^-\) concentration significantly
enhances the formation of THM4, but no significant enhancement of total HAA formation was
observed, leading to an increasing ratio of total THMs/HAAs with the increasing initial Br\(^-\)
concentration. This indicates that Br\(^-\) favours the formation of THMs in the presence of CuO,
comparing with HAAs, probably because more THM precursors are available than HAA
precursors in the studied DOM. It was reported that THM and HAA can be formed from different precursors.\textsuperscript{30}

\textbf{Effect of pH.} During the chlorination of bromide-containing waters in the presence of 0.025 g L\textsuperscript{-1} CuO and DOM, significant oxidant decay (≥75.5\%) was observed at a reaction time of 8 h within the range of pH 6.6-9.6 (Figure 3). The corresponding BrO\textsubscript{3}\textsuperscript{-} concentrations were 7.0±3.0, 13.2±0.4, 33.6±2.1 and 2.8 µg L\textsuperscript{-1} for pH 6.6, 7.6, 8.6, and 9.6, respectively. Maximum BrO\textsubscript{3}\textsuperscript{-} formation was at pH 8.6 near its \(pK\textsubscript{a}\) (i.e., 8.8), since the CuO-catalyzed disproportionation of HOBr occurs via the interaction between HOBr and OBr\textsuperscript{-}.\textsuperscript{19,24}

The concentration of BrO\textsubscript{3}\textsuperscript{-} was lower than that of total bromine in THMs and HAAs, which increased with increasing pH (Figure S7, SI). Significant amounts of THMs were formed within the range of pH 6.6-9.6, e.g., THM4 were 169.4±12.6, 283.7±64.7, 379.9±86.4 and 473.4±118.2 nM (i.e., 39.2±2.5, 65.8±15.0, 90.9±20.4 and 108.9±24.0 µg L\textsuperscript{-1}) for pH 6.6, 7.6, 8.6 and 9.6, respectively. The upward trend in THM formation with pH was also reported in previous studies performed in the absence of CuO.\textsuperscript{34,35} Hypohalous acid (HOCl/HOBr) that is present as non-dissociating species at lower pH (e.g., \(\leq 7.6\)) shows a higher reactivity than its hypohalite ion towards DOM.\textsuperscript{11,36} However, THM formation is a multi-step process. The enolization of carbonyl moiety of DOM or the hydrolysis of intermediate (e.g., trihalocarbonyl) to THM could be the rate-limiting step and both pathways can be catalyzed by hydroxide ion.\textsuperscript{37} It is likely that these reactions play much more important roles in determining the pH effect on the THM formation. Again, less HAAs (≤43.6±3.1 nM, i.e., 8.6±0.6 µg L\textsuperscript{-1}) were formed than THMs within the range of pH 6.6-9.6. HAA formation increased as the pH increased from 6.6 to 8.6 and
then slightly decrease within pH range of 8.6-9.6. DBAA were the main HAA species, while DCAA, TCAA and BCAA were minor species.

**Effect of the initial DOM concentration.** Figure S8 (SI) shows the influence of initial DOM concentration (1.25-20 mg L⁻¹) on the oxidant demand and DBP formation. In the absence 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, respectively (Figure S9, SI). Increasing the initial DOM concentration decreases the residual oxidant concentration and BrO₃⁻ formation due to the reaction between bromine and DOM. The presence of 1.25 mg L⁻¹ DOM significantly reduced BrO₃⁻ concentrations from 957.7±13 to 58.3±11.7 µg L⁻¹. When DOM concentration is higher than 5 mg L⁻¹, BrO₃⁻ concentration is < 5 µg L⁻¹, indicating that the HOBr reaction with DOM will predominate in the presence of higher concentrations of DOM.

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

Increasing the DOM concentration only slightly increased the HAAs formation from 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, BCAA and DBAA were detected. At lower initial DOM concentration (1.25-2.5 mg L⁻¹), the heterogeneous HOBr involved reactions on the CuO surface predominate, since HOBr is much more readily activated by CuO than HOCl. Increasing the initial DOM concentration increased the DBAA formation. At higher DOM concentration (>2.5 mg L⁻¹), the direct homogeneous
reactions between HOCl and fast reacting DOM moiety becomes significant, leading to the enhanced formation of chlorinated HAAs. Elevated BCAA formation even led to a slight decreasing DBAA formation with the increasing DOM concentration from 2.5 to 20 mg L\(^{-1}\).

**Effect of the type of DOM.** Oxidant decay and DBP formation in the presence of six types of DOM isolates were studied (Figure 4, Figures S11-13, SI). The six DOM isolates exhibited a wide range of SUVA\(_{254}\) values (Table S1, SI). SRW-HPOA showed the highest SUVA\(_{254}\) (4.9 L mg\(^{-1}\) m\(^{-1}\)), indicating a high aromatic character (i.e., high reactivity toward oxidants), followed by LRW-HPO, RRW-HPO and CRW-PI1-HPO, with SUVA\(_{254}\) values of 3.5, 3.1 and 2.0 L mg\(^{-1}\) m\(^{-1}\), respectively. CRW-F2E-HPO and CRW-BF-HPO are extracted from treated Colorado River water (CRW-PI1-HPO), showing lower SUVA\(_{254}\) values of 1.7 and 1.1 L mg\(^{-1}\) m\(^{-1}\), respectively.

After 2 h chlorination of these DOM isolates in the presence of Br\(^-\), residual oxidant varied from 20.5 to 30.0 µM (Figure S11, SI). Increasing the aromaticity of DOM (i.e., SUVA\(_{254}\)) led to decreased residual oxidant but enhanced formation of total THMs and HAAs (Figure 4). For example, CRW-BF-HPO isolated after advanced treatment of raw water for CRW-PI1-HPO is the lowest reactive fraction, producing lowest total THMs and HAAs. SRW-HPOA, humic substances with the highest SUVA\(_{254}\) value among the six DOM isolates form 161.6±8.6 and 26.2±1.2 µg L\(^{-1}\) for total THMs and HAAs, respectively. This trend agrees well with the percentage of humic substances in DOM characterized in Figure S14 (SI). Humic substances with the high aromatic/phenolic carbon and carboxyl group contents are the fast reacting THM/HAA precursors.\(^{29}\)
In the presence of CuO, less oxidant (7.9-10.3 μM) remained due to the interaction between CuO and HOCl/HOBr.\textsuperscript{19} Bromate formation was only detected in the presence of two DOM fractions isolated from treated waters (29.1±2.4 and 2.8 μg L\textsuperscript{-1} for CRW-BF-HPO and CRW-F2E-HPO, respectively) (Figure S12, SI). In the presence of DOM isolates collected from raw waters with higher SUVA\textsubscript{254} values, the formed HOBr was mainly consumed by its reaction with fast reacting DOM moieties (e.g., humic substances) and disproportionation is insignificant.

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

The speciation of THMs and HAAs in the presence of CuO was similar to that in the absence of CuO. Among the formed THMs and HAAs, CHBr\textsubscript{3} and DBAA were the main species, respectively. In contrast, CHCl\textsubscript{3}, CHBrCl\textsubscript{2} and CHBr\textsubscript{2}Cl were minor THM species, and DCAA, TCAA, BCAA and BDCAA were formed at lower concentrations than DBAA (Figures S13, SI).

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

Because the structure of DOM moieties is ambiguous and variable, the investigation of model compounds provides information on the kinetics and mechanisms responsible for DBP formation. Table 1 summarizes the consumption of HOBr, formation of BrO\textsubscript{3}\textsuperscript{-}, CHBr\textsubscript{3} and
DBAA from HOBr reactions with various model compounds and their reaction rate constants with bromine are shown in Table S3 (SI).

Second-order rate constants (k) for bromine reactions with acetone, n-butanol, propionic and butyric acids are \(< 1 \text{ M}^{-1} \text{s}^{-1}\), which are considered as practically unreactive compounds.\(^\text{11}\) Slight HOBr consumption (\(\leq 4.6\%\)) was observed and CHBr\(_3\) was the only DBP formed at 2 h (Table 1). Among them, acetone shows the highest CHBr\(_3\) formation via the classical haloform formation pathway.\(^\text{11}\) Similar HOBr consumption and BrO\(_3^-\) formation comparing with that in the absence of model compounds indicates that the presence of practically unreactive compounds does not affect the disproportionation of HOBr. However, the presence of CuO changes the CHBr\(_3\) and DBAA formation. The CHBr\(_3\) formation from propionic and butyric acids was slightly enhanced, while its formation from acetone and n-butanol was inhibited by CuO. The reason is unknown, but it is likely that the structure of model compounds will also determine the extent for the enhancement of CHBr\(_3\) formation by CuO. Interestingly, DBAA were additionally formed, indicating that CuO can enhance the reactivity of HOBr via the electron transfer pathway to oxidize acetone and n-butanol to their acid forms.

Oxalic, malonic, succinic and citric acids are considered as slow reacting compounds which 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 and malonic acids, respectively\(^\text{38}\)). At 2 h, \(< 6.8\%\) of HOBr was consumed (Table 1). Citric acid is the strongest precursor of THM and HAA (375.7±36.7 nM and 31.6±6.8 nM, respectively). It was known as an important CHCl\(_3\) precursor during the analogous chlorination process through multi-steps (e.g., oxidative decarboxylation, halogenation of methylene groups and subsequent hydrolysis of intermediates).\(^\text{39-41}\) The formation of THM and HAA (i.e., \(\leq 4.2\pm0.3\) and \(\leq 2.2\pm0.1\)
nM, respectively) from oxalic, malonic, and succinic acids was lower, which agrees with previous studies.\textsuperscript{42,43}

The presence of CuO significantly enhanced the consumption of HOBr in the presence of these slow reacting compounds (≥93.2%). Bromate was not detected in the presence of oxalic and malonic acids but its concentrations in the presence of succinic and citric acids were 1.5±0.1 and 0.2 µM, respectively. CuO-catalyzed disproportionation of HOBr is in competition with the heterogeneous reactions between CuO-HOBr and slow reacting compounds. Therefore, the contribution for the latter pathway follows the sequence of oxalic ≅ malonic > citric > succinic acids. The enhanced formation of CHBr\textsubscript{3} and DBAA comparing with homogenous solutions indicates that the bromination pathway is enhanced by CuO. Citric acid showed the highest CHBr\textsubscript{3} and DBAA formation among slow reacting compounds. The rate-limiting step (i.e., decarboxylation of citric acid to 3-oxopentanedioic acid) seems to be significantly enhanced by CuO. Both brominated DBPs and BrO\textsuperscript{3−} formation are insignificant in the presence of oxalic acid, implying an oxidation of oxalic acid to carbon dioxide.

Rate constants for the reactions between HOBr and phenolic compounds are > 10\textsuperscript{4} M\textsuperscript{-1} s\textsuperscript{-1}, and thus they are included as fast reacting compounds,\textsuperscript{44-48} consuming > 84% of HOBr after 2 h. Resorcinol known as a fast CHCl\textsubscript{3} precursor,\textsuperscript{49-51} shows the highest CHBr\textsubscript{3} formation (6367.5±35.0 nM). In contrast, CHBr\textsubscript{3} formation from other phenolic compounds is significantly lower (< 49.1±2.3 nM). Phenol was known as a slow CHCl\textsubscript{3} precursor and the bromination of hydroquinone and catechol occurs predominately via the oxidation pathway.\textsuperscript{48-51} Phenolic compounds do not form significant amount of DBAA (< 7.1±0.9 nM). Because HOBr reacts quickly with phenolic compounds, heterogeneous reactions on the CuO surface tends to be less
significant, leading to the insignificant enhanced formation of BrO$_3^-$, CHBr$_3$ and DBAA. (Table 1).

Based on our results, it can be concluded that the BrO$_3^-$ formation decreases as the reactivity of models compounds with bromine increases. CuO can activate the reactivity of HOBr towards slow reacting compounds (e.g., di- and tri-carboxylic acids), leading to elevated CHBr$_3$ and DBAA formation. However, no significant effect was observed for practically unreactive or fast reacting phenolic compounds. These results confirm again the significant enhancement for slow reacting DOM isolates (e.g., CRW-BF-HPO, mainly comprising fulvic acid structures incorporating abundant polysaccharides moieties$^{29}$). However, DOM isolates such as SRW-HPOA (predominance of high aromatic/phenolic carbon and carboxyl group contents$^{29}$) exhibit less enhancement.

Mechanisms of CuO enhanced DBP formation during chlorination of bromide-containing waters in the presence of DOM. Scheme 1 shows a hypothetical formation mechanism of BrO$_3^-$ and halogenated DBPs during chlorination of bromide-containing waters in the presence of DOM and CuO. The reaction is initiated by the rapid oxidation of Br$^-$ by HOCl to HOBr/OBr$^-$ (reaction 1)$^8$. The formed HOBr/OBr$^-$ can compete with HOCl/OCl$^-$ to react with fast reacting DOM moieties (e.g., phenolic) via electrophilic substitutions (reaction 2a) and oxidation (reaction 2b) (k=500-5000 M$^{-1}$ s$^{-1}$)$^6,11$. Reaction 2a forms brominated DBPs, while reaction 2b produces oxidized DOM (DOM$_{ox}$) with the release of Br$^-$, which can be re-oxidized to HOBr in excess of HOCl (catalytic cycle). The latter one is the main pathway for bromination of most DOM.$^{52}$
In the presence of CuO, HOBr can combine with CuO to form a CuO-HOBr complex (reaction 3). Complexation of HOBr/OBr⁻ by the Lewis acid CuO polarizes the bromine molecule, thus increasing its electrophilicity and as a consequence its reactivity. The CuO-HOBr complex reacts with HOBr to generate oxygen and Br⁻ (reaction 4) or form BrO₃⁻ (i.e., disproportionation pathway, reaction 5). Moreover, this complex can react with slow reacting DOM moieties, leading to the formation of brominated DBPs (reaction 6a) or DOM₉ (reaction 6b). Estimated second-order rate constants for reactions 4 and 5 range between 1 and 500 M⁻¹ s⁻¹ according to previous kinetical model. Therefore, upon the complete degradation of fast reacting DOM moieties, in order to form both halogenated DBPs and BrO₃⁻ the rate constant for CuO-HOBr complex reaction with slow reacting DOM moieties (e.g., alcohol, ketone, carboxylic, etc) should be in the same order of magnitude with reaction 5 (k=1-500 M⁻¹ s⁻¹). Meanwhile, since the reaction between HOBr and slow reacting DOM is enhanced by CuO, elevated brominated DBPs can be formed.

HOCl will also react with fast reacting DOM moieties to produce chlorinated DBPs or DOM₉ (reactions 12a and 12b, respectively), approximately 10 times slower than the corresponding bromine reaction. Similarly, HOCl can combine with CuO to form a CuO-HOCl complex (reaction 13), which reacts with itself to produce oxygen and chlorate (ClO₃⁻) (reactions 14 and 15, respectively). Reaction 14 is the major pathway, while reaction 15 is a minor pathway. Therefore, even ClO₃⁻ can be formed in CuO-HOCl system, in the presence of DOM and Br⁻, the formation of ClO₃⁻ is insignificant since the rate constants for reactions 1, 12, and 14 are higher than reaction 15 (HOCl disproportionation). Because of the chemical similarity of HOCl with HOBr, it is expected that CuO can enhance the reactivity of HOCl towards the slow reacting DOM moieties, leading to elevated chlorinated DBPs or DOM₉ (reactions 16a and 16b,
respectively). However, rate constant for reaction 16 may be smaller than that of reaction 6 (i.e., bromination of DOM in the presence of CuO).

**Implications on water treatment.** Our results highlight that in the presence of DOM isolated from treated water that are representative of distributed drinking water, both BrO$_3^-$ and brominated DBP formation can be enhanced in the presence of CuO. CuO is present on the surface of copper pipes owing to the pipe corrosion.$^{21,23}$ This would raise a serious drinking water safety issue in distribution systems and household plumbing.

Bromide levels in raw waters are highly variable in a range from $<10$ to $>1000$ µg L$^{-1}$. A survey over 23 water supplies in the USA and Canada showed that Br$^-$ levels ranged from 24 to 1120 µg L$^{-1}$ (median of 109 µg L$^{-1}$) in source waters.$^{54}$ Based on our results, it can be expected that BrO$_3^-$ formation should not be of concern when Br$^-$ is present at concentration around 100 µg L$^{-1}$ (median level in natural waters in USA). However, when potable water is produced from desalinated seawater,$^{55,56}$ groundwater$^{57}$ with high Br$^-$ content (i.e., $>400$ µg L$^{-1}$) and low DOC, the risk of producing BrO$_3^-$ exists. This may also apply to treated surface water in seasonal seawater intrusion in coastal cities and some regions with Br$^-$ enriched water (e.g., Australia,$^{57}$), considering that Br$^-$ is not removed in conventional treatment train while a large fraction of the DOM incorporating the fast reacting moieties is generally eliminated. For treated water with high concentrations of both Br$^-$ and DOM moieties (e.g., blending desalinated seawater with other source water), the possibility to produce BrO$_3^-$ is reduced. However, elevated THMs and HAAs can be expected, since CuO can activate the reactivity of HOBr towards hydrophilic carboxylic acids leading to enhanced DBP formation from DOM moieties that are not originally expected to form significant DBPs during disinfection. Accordingly, this will be a challenge to meet the
MCL for THM4 in drinking water (e.g., 80 µg L⁻¹ by US EPA, Figures 2-3, and Figures S5 and S8, SI).

It should be noted that our data were obtained in a batch reactor which provides a different hydraulic and operational condition from distribution systems. Therefore, additional studies will be required in a long-term running copper-containing pilot-scale/full-scale distribution system to assess the kinetics of oxidant decay and the formation of BrO₃⁻, THMs, HAAs and emerging DBPs (e.g., haloacetonitriles and haloketones).

- **Supporting Information**
  
  Additional details of chemicals, methods, tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

- **Acknowledgements**
  
  The authors would like to thank Julien Le Roux for the help on THM and HAA analyses. The authors acknowledge the funding and support from KAUST.
References


Figure 1 Effect of CuO dose on (a) residual oxidant and formed BrO₅⁻, (b) THMs and (c) HAAs. Experimental conditions: [HOCl]₀ = 40 µM, [Br⁻]₀ = 10 µM, [DOM] = 2.5 mg L⁻¹, [CuO] = 0-0.2 g L⁻¹, pH= 8.6, T =21±1 °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: [HOCl]$_0$ = 14-70 µM, [Br$^-$]$_0$ = 10 µM, [DOM] = 2.5 mg L$^{-1}$, [CuO] = 0.025 g L$^{-1}$, pH = 8.6, T = 21±1 °C, reaction time = 8 h.
Figure 3 Effect of pH on (a) residual oxidant and formed BrO\textsuperscript{3−}, (b) THMs and (c) HAAs. Experimental conditions: [HOCl]\textsubscript{0} = 40 µM, [Br\textsuperscript{−}]\textsubscript{0} = 10 µM, [DOM] = 2.5 mg L\textsuperscript{−1}, [CuO] = 0.025 g L\textsuperscript{−1}, pH = 6.6-9.6, T = 21±1 °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 g L\(^{-1}\) CuO. Experimental conditions: \([\text{HOCl}]_0 = 40 \mu\text{M}, [\text{Br}^-]_0 = 10 \mu\text{M}, [\text{DOC}] = 1.3 \text{ mg C L}^{-1}, \text{pH} = 8.6, T = 21 \pm 1 ^\circ\text{C}, \text{reaction time} = 2 \text{ h}.\)
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

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Consumed bromine (\mu M)</th>
<th>Bromate (\mu M)</th>
<th>CHBr(_3) nM</th>
<th>DBAA nM</th>
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<td>blank</td>
<td>NA</td>
<td>40.0±0.6</td>
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<td>NA</td>
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<td>practically unreactive group</td>
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<td>Acetone</td>
<td>2.3±0.3</td>
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<td>n-Butanol</td>
<td>1.9±0.8</td>
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<td>10.3±0.1</td>
<td>12.9±0.8</td>
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<td>Propionic acid</td>
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<td>Butyric acid</td>
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<td>39.9±0.1</td>
<td>10.3±0.1</td>
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<tr>
<td>slow reacting group</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Oxalic acid</td>
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<td>Malonic acid</td>
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<td>46.6±0.4</td>
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<td>1.6±0.2</td>
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<td>Succinic acid</td>
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<td>Citric acid</td>
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<td>0.2</td>
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<tr>
<td>fast reacting group</td>
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<tr>
<td>Phenol</td>
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<td>49.1±2.3</td>
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<tr>
<td>Hydroquinone</td>
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<td>10.2±0.6</td>
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<tr>
<td>Catechol</td>
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<td>48.9±0.1</td>
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<tr>
<td>Resorcinol</td>
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<td>49.6±0.1</td>
<td>ND</td>
<td>6367.5±35.0</td>
</tr>
</tbody>
</table>

Experimental conditions: \([\text{HOBr}]_0\) = 50 µM, \([\text{model compound}]_0\) = 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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