SUPPORTING INFORMATION

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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Text S1. Standards and description of reagents.

Acetone and n-butanol were purchased from Honeywell Burdick & Jackson, and Loba Chemie, respectively. Propionic acid sodium salt, butyric acid sodium salt, oxalic, malonic, succinic and citric acids, phenol, hydroquinone, catechol and resorcinol were provided by Sigma-Aldrich. Trihalomethanes (chloroform, dichlorobromomethane, dibromochloromethane and bromoform) (EPA 551B Halogenated Volatiles Mix), a mixed standard containing 9 haloacetic acids (EPA 552.2 Methyl Ester Calibration Mix), and surrogate standard decafluorobiphenyl were supplied from Supelco (Sigma-Aldrich).

Text S2. *Analytical methods*

Residual oxidants (the sum of concentrations of chlorine and bromine) were analyzed spectrophotometrically by the *N*,*N*-diethyl-p-phenylenediamine (DPD) method at 515 nm on a UV-visible spectrophotometer (Hach DR 5000).[1]

Bromate was quantified by a Dionex 1600 reagent free ion chromatograph (IC) with a potassium hydroxide (KOH) online eluent generator. Samples, injected via a 250 μL loop, were eluted (20 mM KOH) at a flow rate of 0.25 mL min^{-1} through an Ionpac AS19 column. The quantification limit for bromate is 1 μg L^{-1} and relative standard deviation is below 5%.

Total dissolved organic carbon (TOC) of DOM solutions was analyzed by a Shimadzu TOC-Vcsh Analyzer.

Total organic bromine (TOBr) was measured by pyrolysis and off-line ion chromatography. The sample (80 mL) was first quenched using sulfite, acidified, and enriched through adsorption onto an activated carbon column using a Mitsubishi TOX sample preparator (Model TX-3AA). The hydrogen halide gases produced by the combustion at 950ºC of the activated carbon sample were collected in 20 mL of MQ water in a closed flask using a Mitsubishi adsorbable halogen analyzer (AOX-200). Concentrations of bromide in the produced solutions were then analyzed by IC as the same method for bromate as described above. Bromide blank in the activated carbon column was subtracted, and then the bromide concentration (in μM) was used to calculate the

concentration of TOBr (as μM bromine), taking into account the concentration factor from the initial sample to the absorber solution.

A liquid chromatography coupled with an organic carbon detector (LC-OCD Model 8, DOC-LABOR, Germany) with a size exclusion chromatography column was used to compare DOM compositions.

THMs and HAAs were analyzed by EPA Method 551 and 552, respectively. Some modifications were made in our lab. For THM analyses, samples (40 mL) were spiked by 80 μL of decafluorobiphenyl solution (6 mg L^{-1} in acetone) as an internal standard, followed by the addition of 8 g of sodium chloride (NaCl) and 2.4 mL of Methyl tert-butyl ether (MTBE). The mixture was shaken for 2 min. After an additional 5 min phase separation, the MTBE layer was transferred to a 2 mL-amber bottle for the analyses by gas chromatograph (Agilent 7890A) equipped with an electron capture detector (GC-ECD). Separation of THMs was conducted by a DB-1701 capillary column (30 m × 250 μm × 0.25 μm). The column oven was held at 35 °C for 6 min, and then ramped to 125 °C at a rate of 10 °C min^{-1}, and further to 220 °C at a rate of 25 °C min^{-1} and held for 2 min.

For HAA analyses, 40 mL of samples were spiked by 40 μL of surrogate standard (2-bromopropionic acid, 10 mg L^{-1} in MTBE). Samples were then acidified by the addition of concentrated sulfuric acid (H_2SO_4), followed by the addition of 8 g of NaCl and 3.2 mL of MTBE. After 2 min vigorous shaking, followed by 5 min phase separation, the MTBE layer was transferred to a small vial using pasteur pipette, and 1 mL of H_2SO_4/CH_3OH (10% v/v) was introduced. The methylation was performed in a 50 °C water bath for 2 h. After neutralization with 4 mL of saturated sodium bicarbonate solution, the MTBE layer was transferred to a 2 mL-amber bottle for the analyses by gas chromatograph (Agilent 7890A) equipped with a mass spectrometry detector (Agilent 5975C). Separation of HAAs was conducted by a DB-1701 capillary column (30 m × 250 μm × 0.25 μm). The column oven was held at 35 °C for 6 min, and then ramped to 220 °C at a rate of 10 °C min^{-1}. The MS detector was operated in the electron

ionization (EI) mode with a potential of 70 eV. The quantification and confirmation of HAAs were operated in the selective ion mode (SIM).

Table S1. Sources and Characteristics of DOM Isolates

Source	Fraction	Abbreviation	$SUVA_{254}$ (m^{-1} L/mgC)*
Colorado River Water, USA	HPO**	CRW-BF-HPO	1.1
Colorado River Water, USA	HPO	CRW-F2E-HPO	1.7
Colorado River Water, USA	HPO	CRW-PI1-HPO	2.0
Ribou Reservoir water, France	HPO	RRW-HPO	3.1
Loire River Water, France	HPO	LRW-HPO	3.5
Suwannee River Water, USA	HPOA***	SRW-HPOA	4.9

*$SUVA_{254}$: Specific ultraviolet absorbance was calculated from UV absorbance at 254 nm (UV_{254}) divided by the corresponding DOC concentration.
**HPO: Hydrophobic fraction
***HPOA: Hydrophobic acids;

Six previously isolated hydrophobic DOM fractions (i.e., XAD-8 adsorption/desorption protocol) were used.[2] Hydrophobic acids (HPOA) were obtained from base desorption, whereas hydrophobic (HPO) were isolated with acetonitrile/water desorption. Three hydrophobic DOM fractions were previously extracted from the raw or treated Colorado River water at the Metropolitan Water District Southern California's Oxidation Demonstration plant (California, USA). The treatment trains of this water plant were preozonation (ozone dose 0.65 mg/L for virus inactivation) followed by conventional ferric chloride (2.0-2.2 mg L^{-1} as $FeCl_3$) and polydiallyldimethylammonium chloride (2.0-2.2 mg L^{-1}) treatment and biologically-active filters. CRW-PI1-HPO (HPO fraction) was collected from the influent of the water plant (raw water of Colorado River). CRW-F2E-HPO (HPO fraction) was extracted from the effluent of F2 at the water plant (after coagulation). CRW-BF-HPO (HPO fraction) was extracted from the outlet of the biologically active filters of the plant using XAD-8 resin. RRW-HPO and LRW-HPO were isolated from the Ribou Reservoir water and the Loire River water located in France. SRW-HPOA was isolated from the Suwannee River (Georgia, USA).

Table S2. Physicochemical properties of model compounds

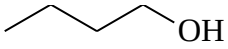
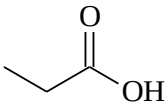
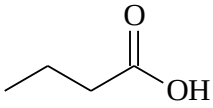
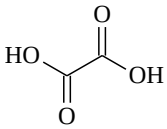
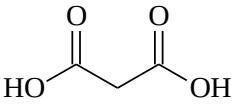
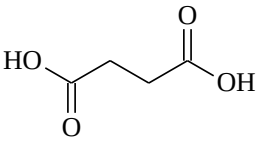
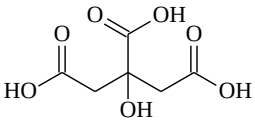
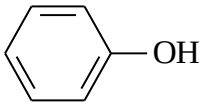
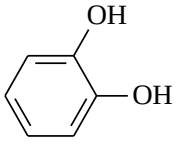
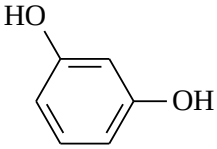
Model compound	Classification	Structure	Molar mass (g mol^{-1})	Log K_{OW}	pK_a
Acetone	ketone		58.08	-0.042	-
n-Butanol	alcohol		74.12	0.839	-
Propionic acid	monocarboxylic		74.08	0.33	4.88
Butyric acid	monocarboxylic		88.11	0.79	4.82
Oxalic acid	dicarboxylic		90.03	-1.19	1.25, 4.14
Malonic acid	dicarboxylic		104.06	-0.58	2.83, 5.69
Succinic acid	dicarboxylic		118.09	-0.59	4.2, 5.6
Citric acid	tricarboxylic		192.124	-1.7	3.14, 4.75, 6.39
Phenol	Phenolic		94.11	1.50	9.95
Hydroquinone	Phenolic		110.11	0.59	11.6
Catechol	Phenolic		110.11	0.88	9.48
Resorcinol	Phenolic		110.11	0.8	9.15

Table S3. Second-order rate constants for the reactions between bromine and model compounds

Model compound	Rate constants (M^{-1} s^{-1})	pH	Temperature (°C)	References
Acetone	<1	7	20	Estimated from the bromine consumption in this study and the rate constant for 2-butanone[3]
n-Butanol	<1	7	25	Estimated from the bromine consumption in this study and the rate constant for 2-propanol[4]
Propionic acid	<1	6	20	Estimated from the bromine consumption in this study and the rate constants for formic and acetic acids[3]
Butyric acid	<1	6	20	Estimated from the bromine consumption in this study and the rate constants for formic and acetic acids[3]
Oxalic acid	4×10^{1}	6	20	3
Malonic acid	3×10^{1}	4	20	3
Succinic acid	>1	6	20	Estimated from the bromine consumption in this study and the rate constants for oxalic and malonic acids[3]
Citric acid	>1	6	20	Estimated from the bromine consumption in this study and the rate constants for oxalic and malonic acids[3]
Phenol	$(6.5 \pm 1.5) \times 10^{5}$	7	24 ± 1	5
Hydroquinone	$(6.4 \pm 0.1) \times 10^{4}$	7	24 ± 1	5
Catechol	$(2.7 \pm 0.1) \times 10^{5}$	7	24 ± 1	5
Resorcinol	$(9.0 \pm 1.4) \times 10^{6}$	7	24 ± 1	5

Figure S1. Effect of CuO dose on formed bromate as well as bromine and chlorine in THMs and 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.

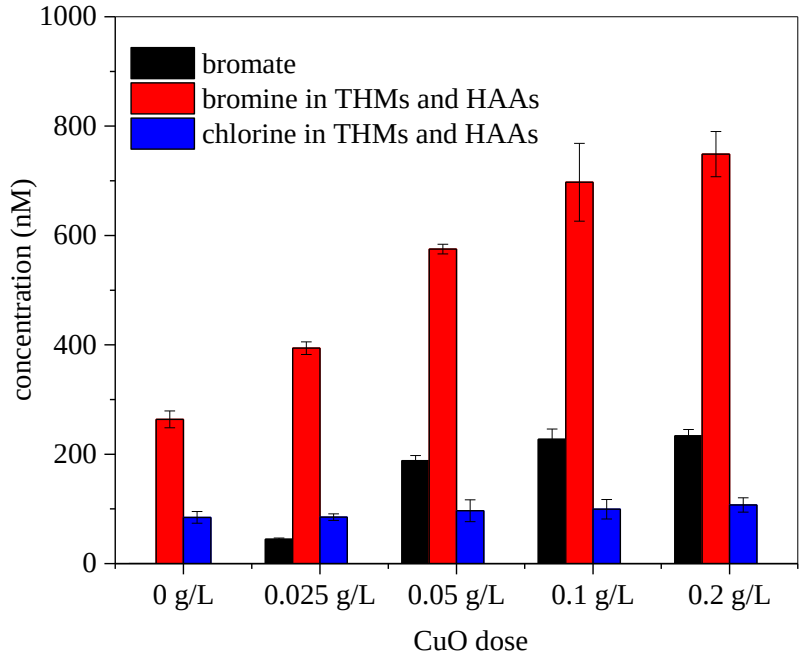


Figure S2. Adsorption of DOM (CRW-BF-HPO) on CuO. The inset shows the change of DOM concentration during the first 120 min. Experimental conditions: $[DOM]_0$ = 5 mg L^{-1}, [CuO] = 0.1 g L^{-1}, pH= 8.6, T =21±1 °C.

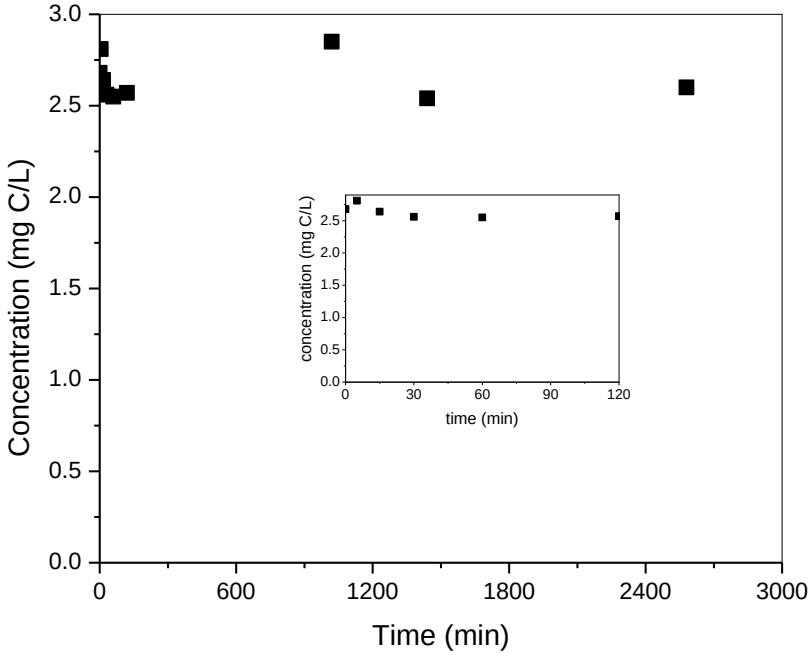


Figure S3. Effect of reaction time on (a) residual oxidant and formed BrO_3^-, (b) THMs and (c) HAAs. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 10 μM, [DOM] = 2.5 mg L^{-1}, [CuO] = 0.025 g L^{-1}, pH= 8.6, T =21±1 °C.

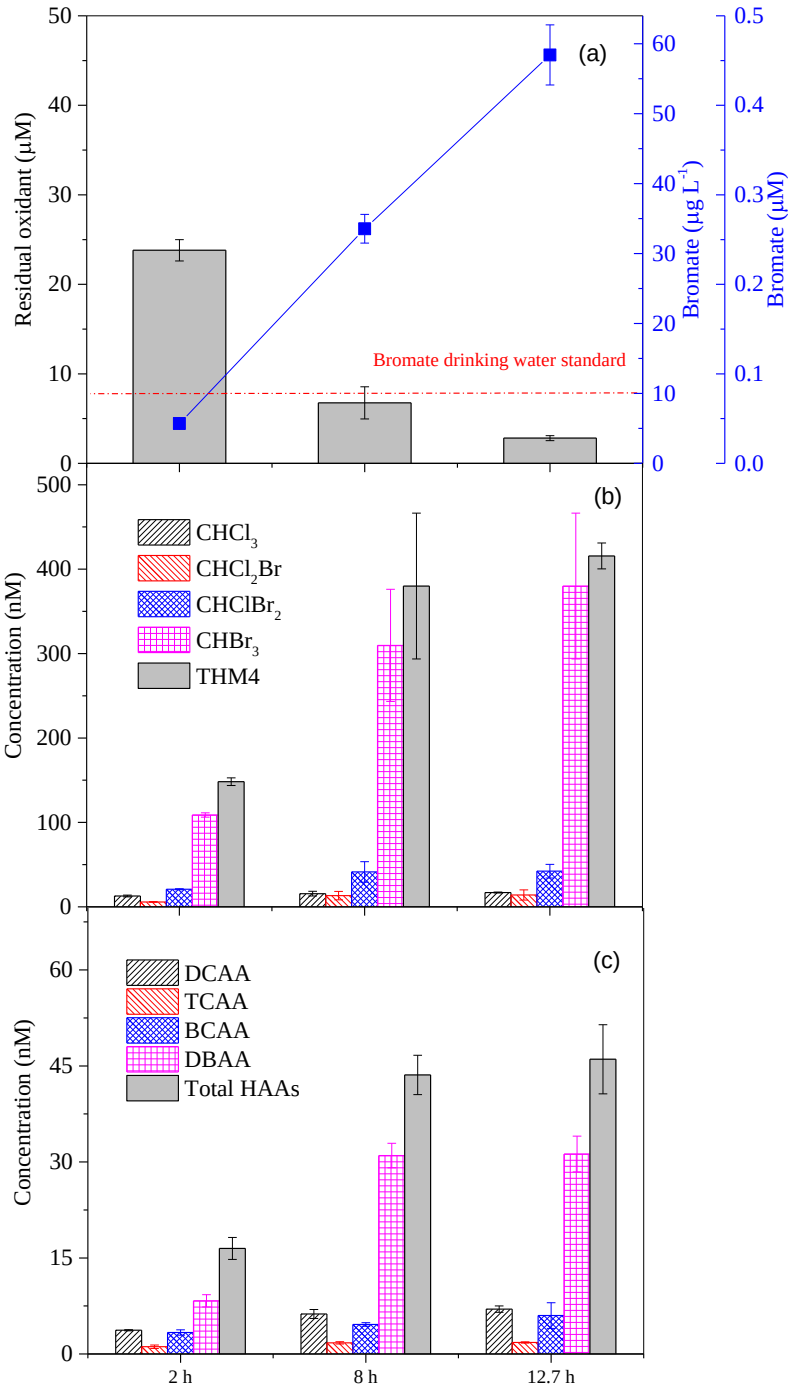


Figure S4. Effect of initial chlorine concentration on formed bromate as well as bromine and chlorine in THMs and HAAs. Experimental conditions: $[HOCl]_0$ = 14-70 μM, $[Br^-]_0$ = 10 μM, [DOM] = 2.5 mg L^{-1}, [CuO] = 0.025 g L^{-1}, pH= 8.6, T =21±1 °C, reaction time = 8 h.

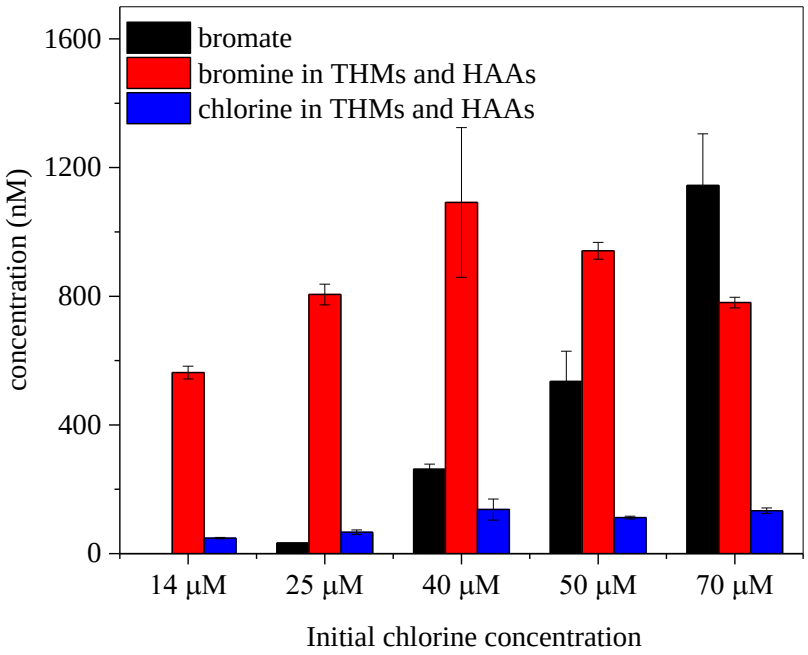


Figure S5. Effect of initial bromide concentration on (a) residual oxidant and formed BrO_3^-, (b) THMs and (c) HAAs. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 0-10 μM, [DOM] = 2.5 mg L^{-1}, [CuO] = 0.025 g L^{-1}, pH= 8.6, T =21±1 °C, reaction time = 8 h.

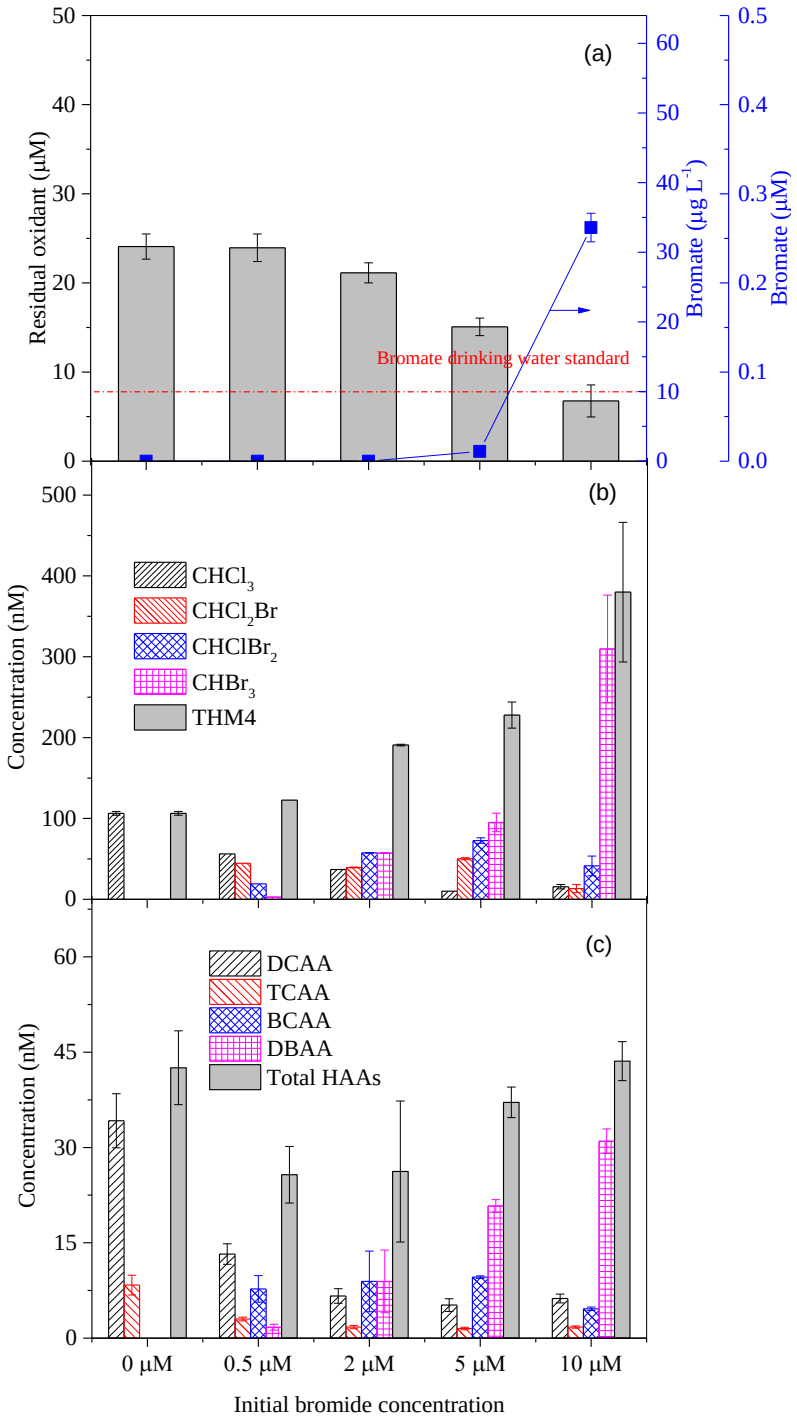


Figure S6. Effect of initial bromide concentration on formed bromate as well as bromine and chlorine in THMs and HAAs. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 0-10 μM, [DOM] = 2.5 mg L^{-1}, [CuO] = 0.025 g L^{-1}, pH= 8.6, T =21±1 °C, reaction time = 8 h.

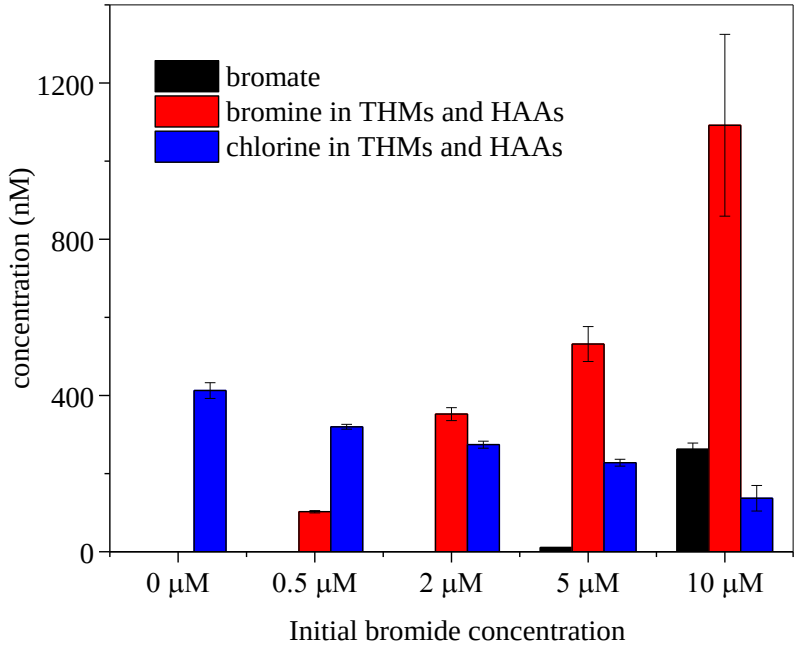


Figure S7. Effect of pH on formed bromate as well as bromine and chlorine in THMs and HAAs. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 10 μM, [DOM] = 2.5 mg L^{-1}, [CuO] = 0.025 g L^{-1}, pH= 6.6-9.6, T =21±1 °C, reaction time = 8 h.

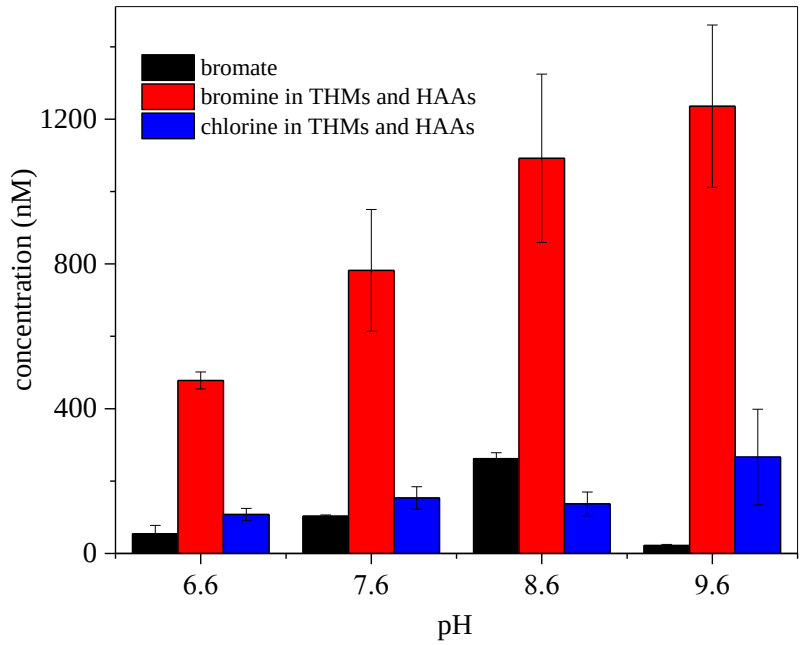


Figure S8. Effect of initial DOM concentration on (a) residual oxidant and formed BrO_3^-, (b) THMs and (c) HAAs. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 10 μM, [DOM] = 1.25-20 mg L^{-1}, [CuO] = 0.025 g L^{-1}, pH= 8.6, T =21±1 °C, reaction time = 8 h.

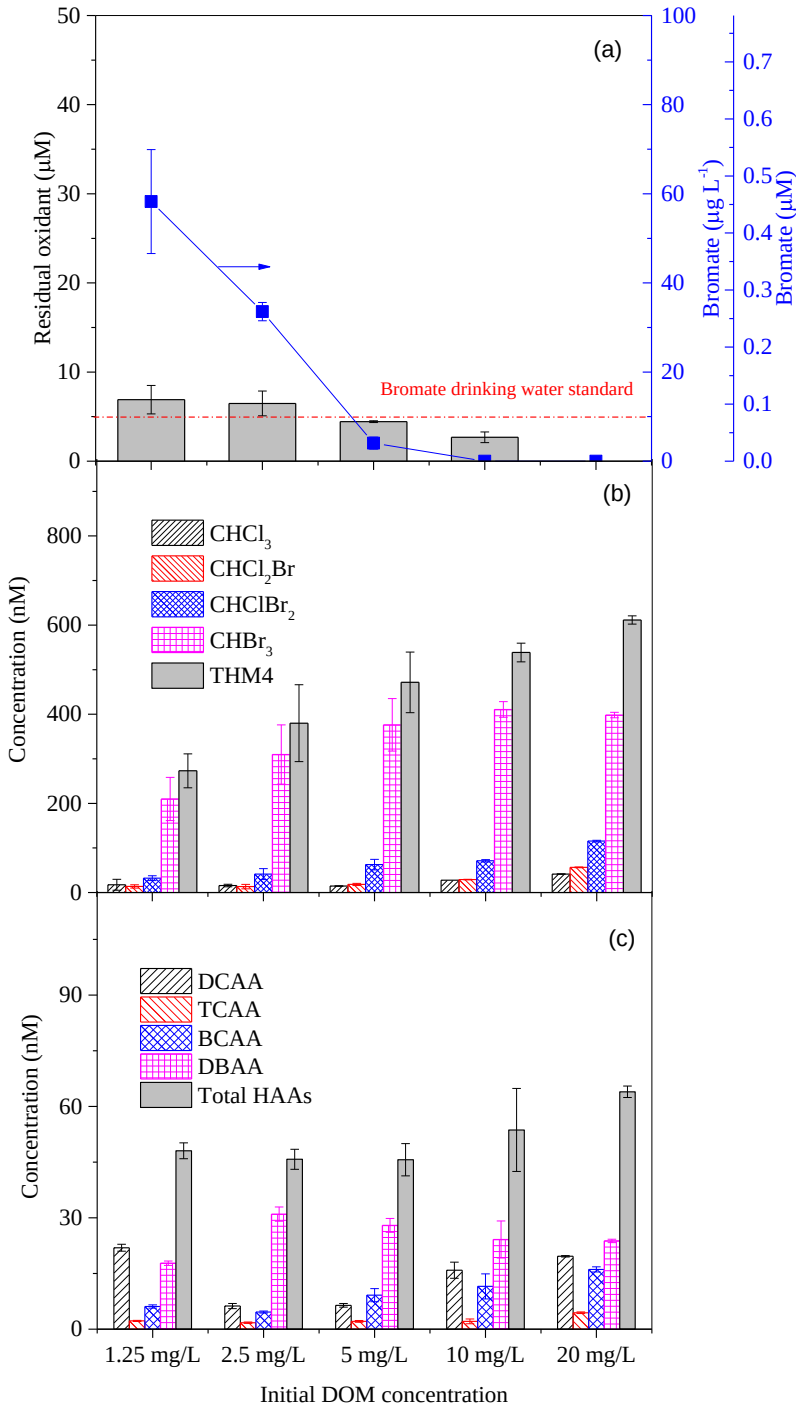


Figure S9. Oxidant decay (a) and bromate formation (b) during chlorination of bromide-containing waters in the absence of DOM. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 10 μM, [CuO] = 0.025 g L^{-1}, pH= 8.6, T =21±1 °C.

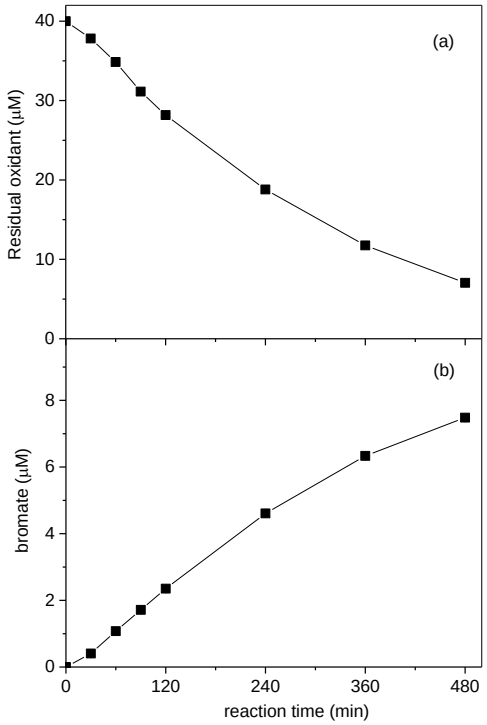


Figure S10. Effect of initial DOM concentration on formed bromate as well as bromine and chlorine in THMs and HAAs. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 10 μM, [DOM] = 1.25-20 mg L^{-1}, [CuO] = 0.025 g L^{-1}, pH= 8.6, T =21±1 °C, reaction time = 8 h.

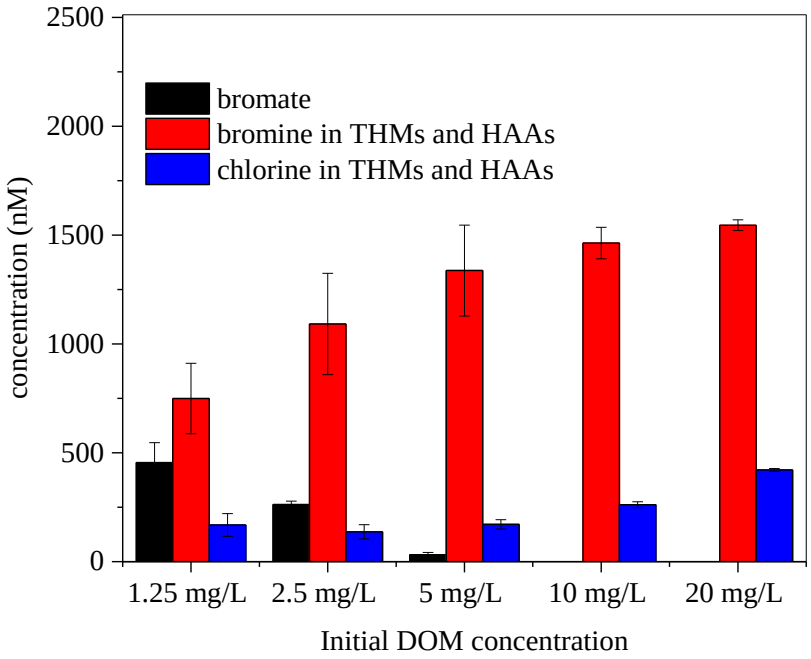


Figure S11. Effect of DOM type on oxidant decay in the absence of CuO. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 10 μM, [DOC] = 1.3 mg C L^{-1}, pH= 8.6, T =21±1 °C, reaction time = 2 h.

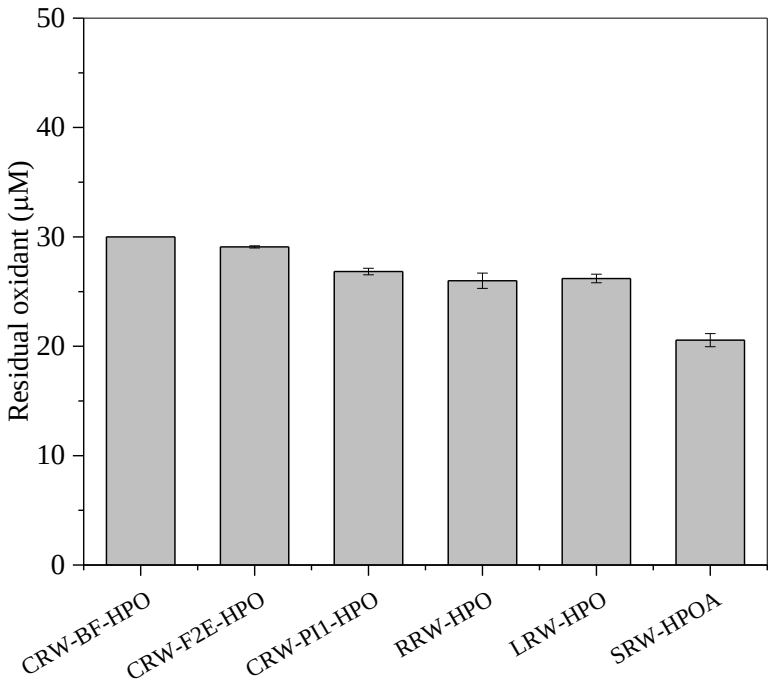


Figure S12. Effect of DOM type on oxidant decay and bromate formation in the presence of CuO. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 10 μM, [DOC] = 1.3 mg C L^{-1}, [CuO] = 0.1 g L^{-1}, pH= 8.6, T =21±1 °C, reaction time = 2 h.

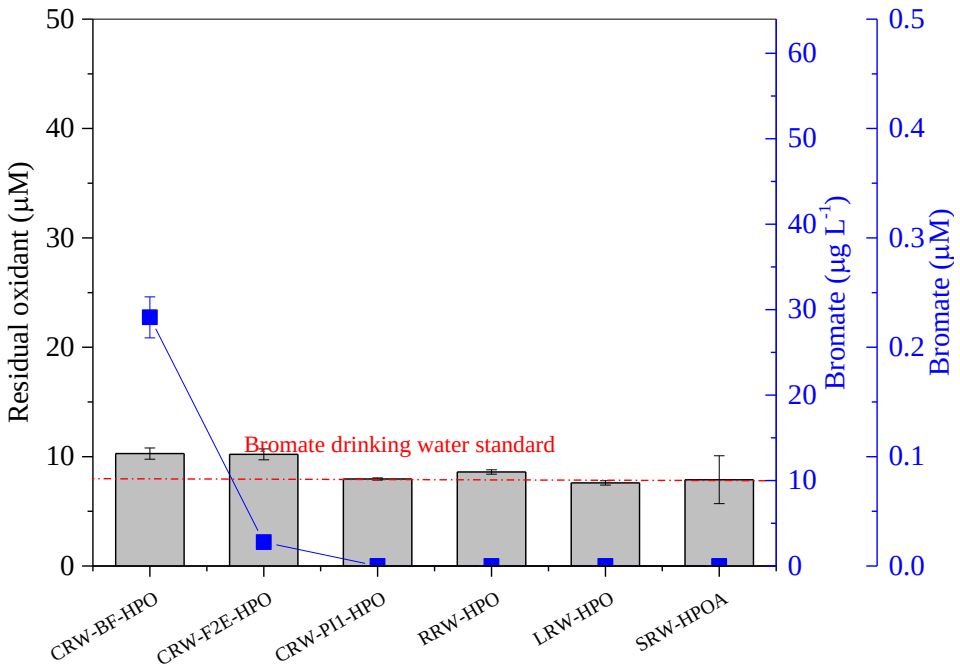


Figure S13. Effect of DOM type on the speciation and concentration of THMs and HAAs in the absence or presence of 0.1 g L^{-1}CuO. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 10 μM, [DOC] = 1.3 mg C L^{-1}, pH= 8.6, T =21±1 °C, reaction time = 2 h.

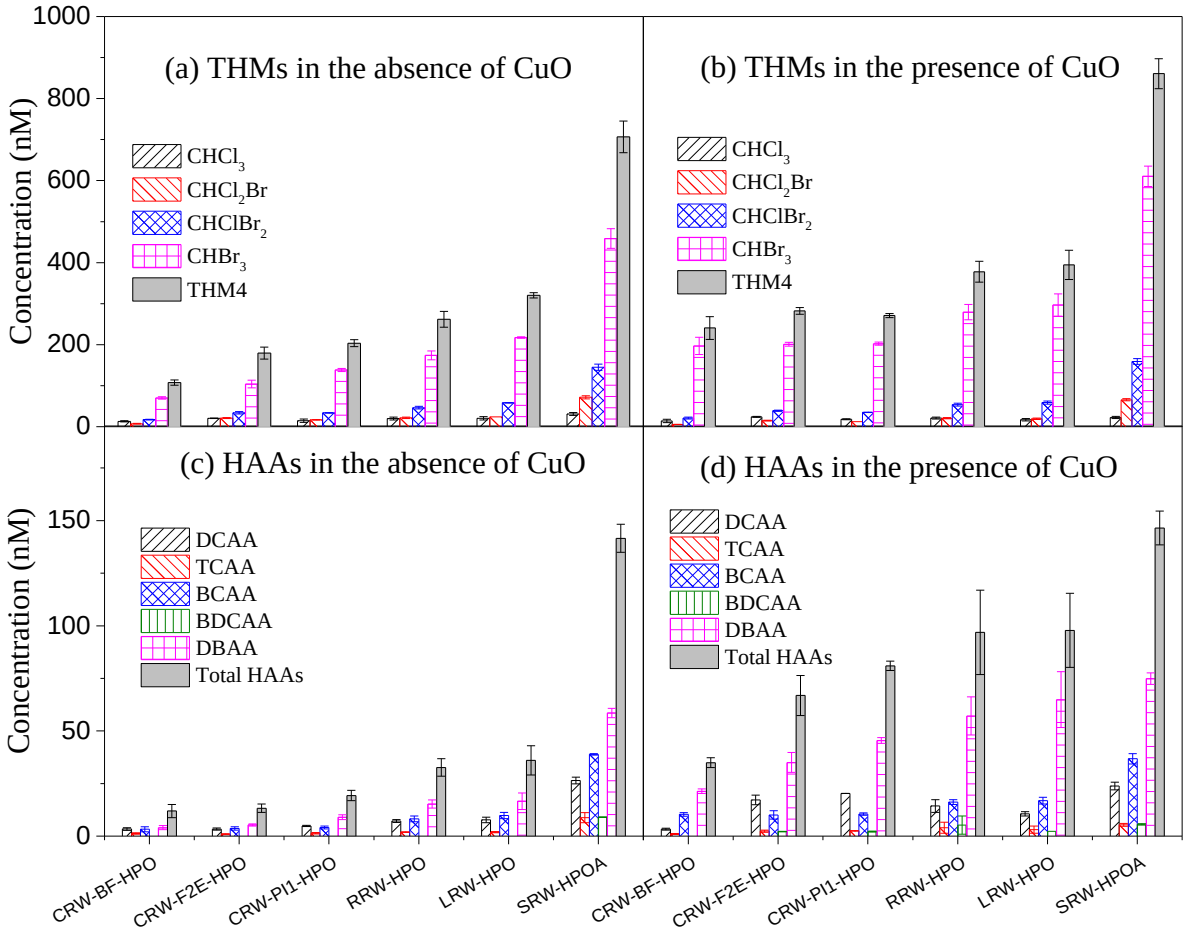
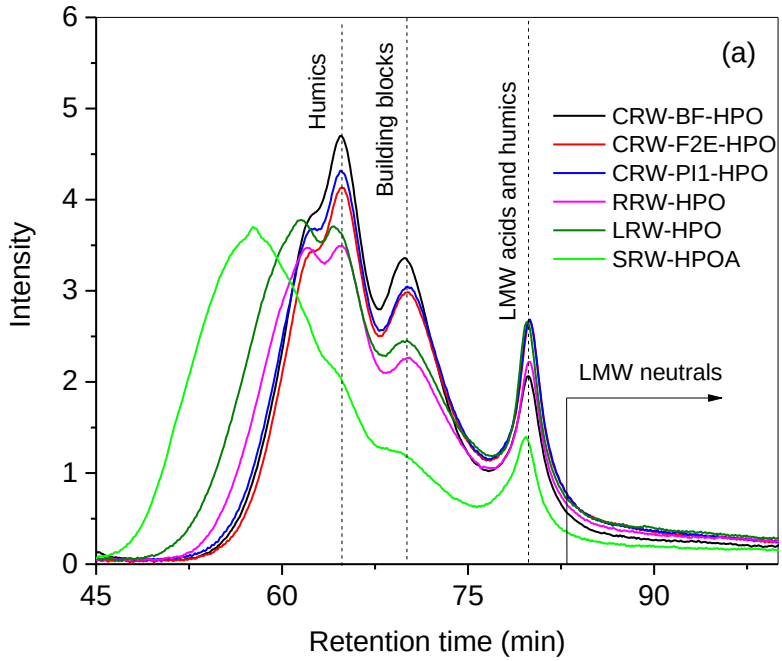


Figure S14. (a) LC-OCD chromatograms of various DOM isolates; (b) Distribution of each LC-OCD fraction. Experimental conditions: [DOM] = 5.0 mg L^{-1}



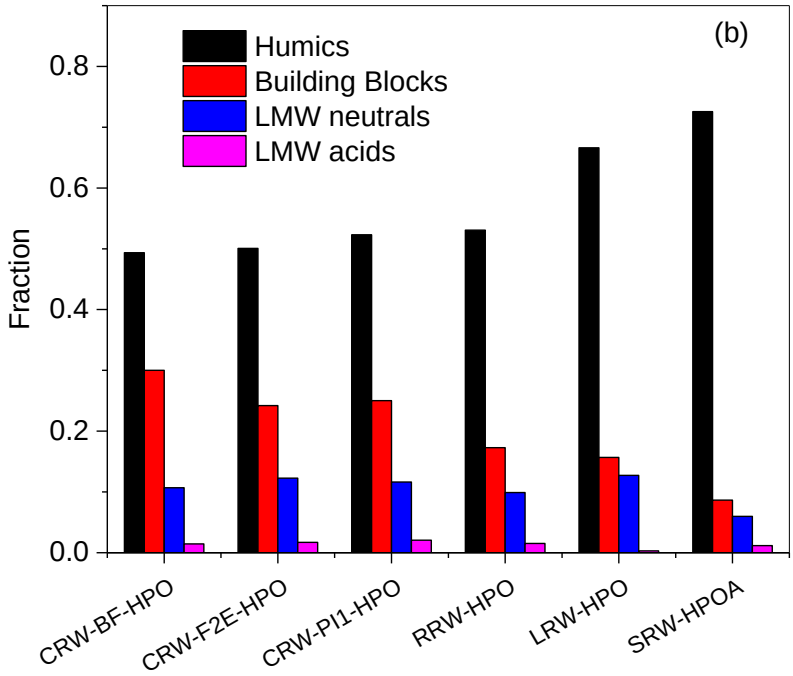
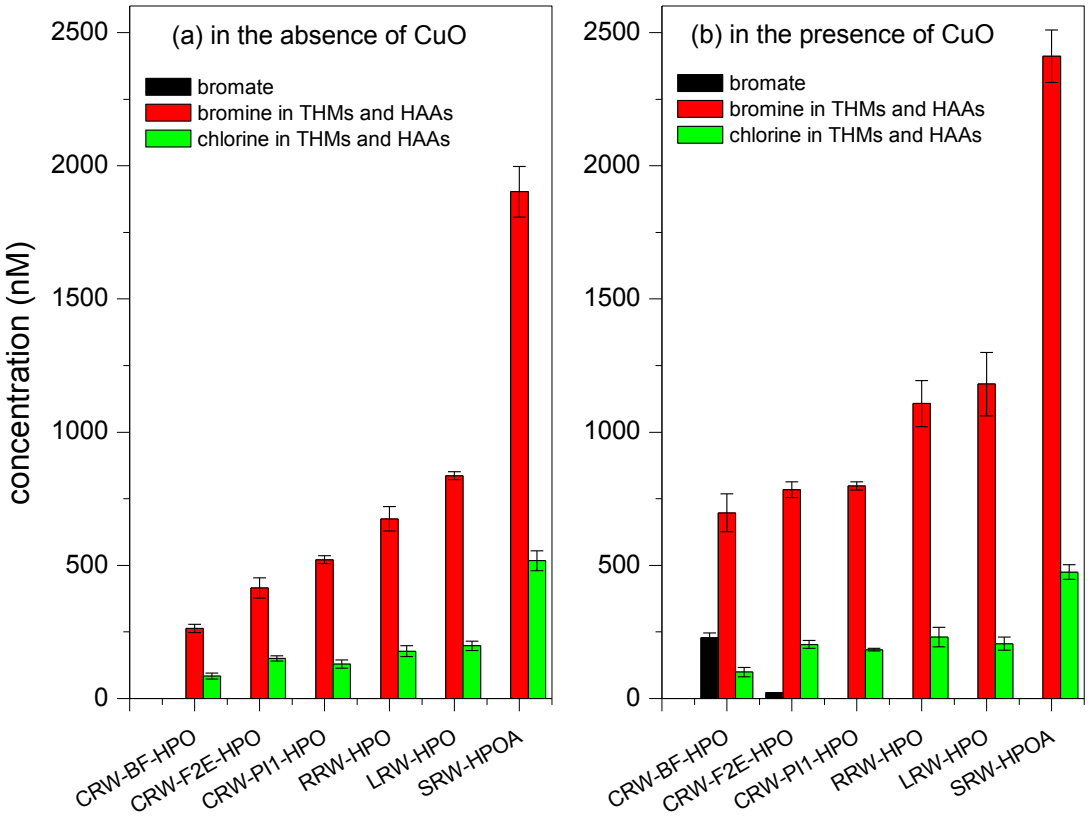


Figure S15. Effect of DOM type on formed bromate as well as bromine and chlorine in (a) the absence and (b) presence of 0.1 g L^{-1} CuO. Experimental conditions: $[HOCl]_0$ = 40 μM, $[Br^-]_0$ = 10 μM, [DOC] = 1.3 mg C L^{-1}, pH= 8.6, T =21±1 °C, reaction time = 2 h.



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2. Hwang, C. J.; Krasner, S. W.; Sclimenti, M. J.; Amy, G. L.; Dickenson, E.; Bruchet, A.; Prompsy, C.; Filippi, G.; Croué, J.-P.; Violleau, D., Polar NOM: Characterization, DBPs, and Treatment. Denver, Colorado: American Water Works Association Research Foundation and American Water Works Association. **2001**.
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