Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.
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Supplementary Information For

Disinfection of bromide-containing tryptophan water by UV/chlorine: Brominated halonitromethanes formation, impact factors, and pathways

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Text S1. Chemicals and reagents

Bromonitromethane (BNM), dibromonitromethane (DBNM), tribromonitromethane (TBNM), bromochloronitromethane (BCNM), bromochloronitromethane (BDCNM), and dibromochloronitromethane (BDCNM) were purchased from Quality Control Chemicals (USA). Methyl tert-butyl ether (MTBE) was purchased from Aladdin (China). Tryptophan, sodium bromide (NaBr), sodium thiosulfate ($Na_2S_2O_3$), disodium phosphate (Na_2HPO_4), and sodium dihydrogen phosphate (NaH_2PO_4) were purchased from Sinopharm (China). Sodium hypochlorite (NaOCl, 5%) purchased from Sigma-Aldrich (China) was used to prepare free chlorine solution.

Text S2. The average light intensity of the UV lamp

Photon fluence rate. The photon fluence rate (I_0) was measured by iodide/iodate chemical actinometry. The reaction solution (500 mL, pH 9.0) consisted of potassium iodide (0.6 M), potassium iodate (0.1 M) and sodium tetraborate (0.01 M). The value of I_0 was calculated by Eq. S1.

$$A_{352} = \Phi_{\mathrm{I_3^-}} \times I_0 \times \varepsilon_{\mathrm{I_3^-}} \times t \tag{S1}$$

where A_{352}, $\Phi_{\mathrm{I3-}}$ and $\varepsilon_{\mathrm{I3-}}$ are the absorbance of I_3^- at 352 nm, apparent quantum yield of I_3^- (M einstein^{-1}), and molar absorption coefficient of I_3^- (M^{-1} cm^{-1}), respectively; t is the radiation time (s). At 352 nm, the values of $\Phi_{\mathrm{I3-}}$ and $\varepsilon_{\mathrm{I3-}}$ were 0.74 mol einstein^{-1} and 26400 M^{-1} cm^{-1}, respectively. The time-dependent profile of I_3^- absorbance is shown in SI Fig. S2. Thus, the value of I_0 was determined to be 1.45×10^{-6} Einstein L^{-1} s^{-1}.

Effective path length. The effective path length (L) was measured by the photolysis kinetics of hydrogen peroxide (H_2O_2) with low concentrations and then calculated by Eq. S2.

$$\frac{dc_t}{dt} = -2.303 \times L \times \Phi_{H_2O_2} \times I_0 \times \varepsilon_{H_2O_2} \times c_t = -k_{obs} c_t \tag{S2}$$

where c_t is the concentration of H_2O_2 (M), ε_{H2O2} is the molar absorption coefficient of H_2O_2 (M^{-1} cm^{-1}), I_0 is the photon fluence rate (Einstein L^{-1} s^{-1}) and Φ_{H2O2} is the apparent quantum yield of H_2O_2 photolysis (mol Einstein $^{-1}$). At 254 nm, the values of Φ_{H2O2} and ε_{H2O2} were 1.0 mol einstein^{-1} and 19.6 M^{-1} cm^{-1}, respectively. The photolysis kinetics of H_2O_2 was shown in SI Fig. S3. The effective path length was measured to be 3.05 cm.

Average fluence rate. The average fluence rate (E_p^0) was calculated by Eq. S3.

$$E_p^0 = I_0 \times L \times u_\lambda \tag{S3}$$

where I_0 is the photon fluence rate (Einstein L^{-1} s^{-1}), L is the effective path length (cm), u_λ is the energy of 1 M photons (4.71×10^5 J Einstein^{-1} at 254 nm). The value of E_p^0 was 2.1 mW cm^{-2}.

Text S3. The analytical methods for Br-HNMs

The concentrations of Br-HNMs were measured using a gas chromatograph (Agilent HP6890, USA) equipped with an HP-1 chromatographic column (30.0 m × 0.32 mm × 5.0 μm). The temperature program consisted of an initial temperature of 50 °C for 5 min, followed by ramping to 140 °C at 10 °C min^{-1}, and then ramping to 280 °C at 20 °C min^{-1}. The temperature of the injection port was set at 235 °C, and the ECD detector temperature was set at 280 °C. The injection volume (1 μL) was carried by a high purity nitrogen (99.999%) gas with a constant flow rate of 1.0 mL min^{-1}.

Text S4. The analytical methods for intermediates

The analysis of intermediates was performed using a gas chromatograph-quadrupole mass spectrometer (GC-MS, Agilent 7890A GC, 5975 MS) equipped with an HP-5m separation column (30 m × 0.25 mm, 0.25 μm). The temperature program consisted of an oven temperature of 40 °C for 2 min, followed by ramping to 300 °C at 40 °C min^{-1} and held for 5 min. The temperature of the injection port was set at 300 °C, and the detector temperature was set at 280 ℃. The injection volume (1 μL) was carried by a helium gas with a constant flow rate of 1.0 mL min^{-1}. The MS was operated in the total ion chromatogram mode and selected ion monitoring mode.

Text S5. Determination of chlorine and nitrogen

The concentrations of free chlorine and total chlorine were determined by the DPD-FAS method. The concentrations of total nitrogen (TN), ammonium nitrogen (NH_4^+-N), and nitrate nitrogen (NO_3^--N) were determined by alkaline potassium persulfate digestion-UV spectrophotometry, Nessler's reagent spectrophotometry, and UV spectrophotometry, respectively. The concentration of dissolved organic nitrogen (DON) was obtained by subtracting the concentrations of NH_4^+-N, nitrite nitrogen (NO_2^--N), and NO_3^--N from the concentration of TN, and the concentration of NO_2^--N was neligible because of the strong oxidative status of the reaction system.

Text S6. The calculation of bromine utilization factors (BUFs)

Bromine utilization factors (BUFs) represent the ratio of bromide ions used to form Br-HNMs to the initial concentration of bromide ions in the water samples, which can be calculated by Eq. S4.

$$\mathrm{BUF}=\frac{[\mathrm{BNM}]+[\mathrm{BCNM}]+[\mathrm{BDCNM}]+2[\mathrm{DBNM}]+2[\mathrm{DBCNM}]+3[\mathrm{TBNM}]}{[\mathrm{Br}^{-}]} \tag{S4}$$

where all concentrations are on a molar basis.

Table S1. Physical and chemical properties of nine HNMs

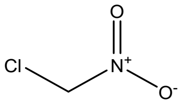
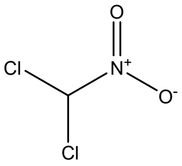
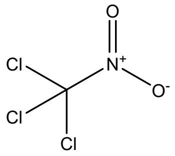
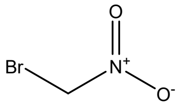
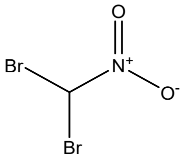
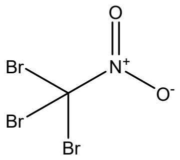
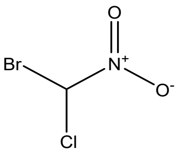
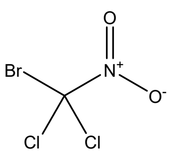
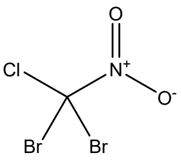
Compounds	Abbreviation	Structure	Weight	pKa	Boiling point （℃, 760 mm Hg）	Solubility （mg/L, 20℃）
Chloronitromethane	CNM		95.5	7.30	122.5	32020
Dichloronitromethane	DCNM		130	5.97	107	11750
Trichloronitromethane	TCNM		164.5	--	112	105800
Bromonitromethane	BNM		140.0	7.56	147.472	18680
Dibromonitromethane	DBNM		219.0	6.08	152.7	4577
Tribromonitromethane	TBNM		298.0	--	155.9	227.5
Bromochloronitromethane	BCNM		174.5	7.28	132.7	9163
Bromodichloronitromethane	BDCNM		209.0	--	115.5	1007
Dibromochloronitromethane	DBCNM		253.5	--	134.9	486.1

Table S2. Properties of tryptophan

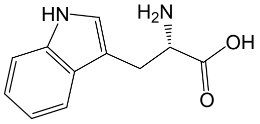
Amino acids	Formula weight	Molecular structure
Tryptophan	204.2	

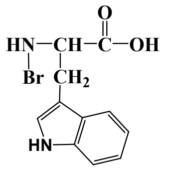
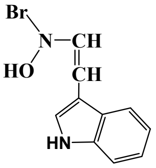
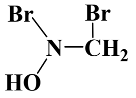
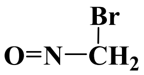
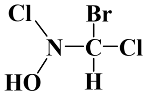
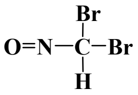
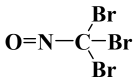
Table S3. The degradation of Br-HNMs by LP-UV irradiation and HO•

HNMs	ε_{254} (M^{-1} cm^{-1})	Φ_{254}	k_f ($\times 10^{-4}$ cm^2 mJ^{-1})	$k_{HO\bullet}$ ($\times 10^8$ M^{-1} s^{-1})
BNM	136	0.109	N.A.	0.84
BCNM	N.A.	N.A.	N.A.	4.2
DBNM	1570	0.146	N.A.	4.75
BDCNM	228	0.52	5.8	1.16
DBCNM	525	0.54	13.7	1.65
TBNM	729	0.59	20.8	2.38

N.A. represents not available.

ε is the molar absorption coefficient for HNMs (M^{-1} cm^{-1}), Φ is the quantum yield, k_f is the photolysis rate constant, and $k_{HO\bullet}$ is the second-order rate constant of the reaction of HO• and HNMs [1-5].

Table S4. The information on the possible intermediates

Molecular formulas	Structure	Weight	m/z	Ions
$C_{11}H_{11}N_2O_2Br$		283	283	
$C_{10}H_9N_2OBr$		253	252.9	
CH_3NOBr_2		205	205.1	
CH_2NOBr	 $O{=}N-\overset{Br}{CH_2}$	124	125	$(M+H)^+$
$CH_2NOBrCl_2$		195	194.9	
$CHNOBr_2$	 $O{=}N-\overset{Br}{\underset{H}{C}}-Br$	203	203.1	
$CNOBr_3$		282	283	$(M+H)^+$

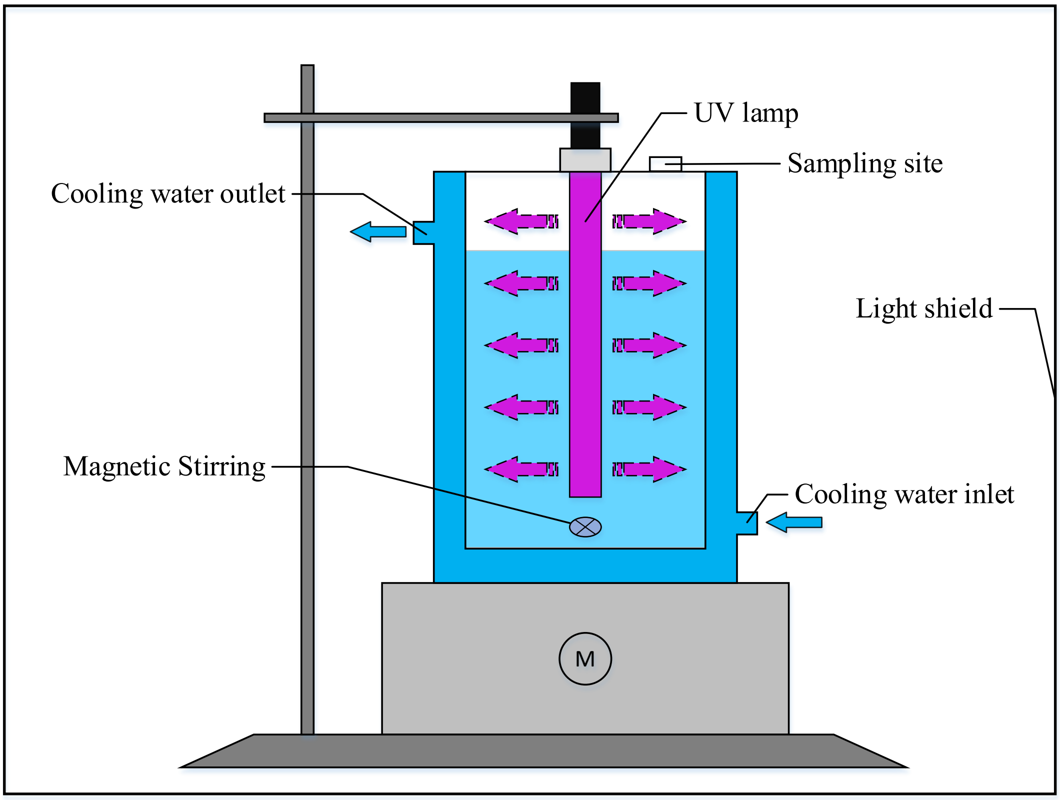


Fig. S1. Illustration of experimental set-up. The 500 mL cylindrical quartz reactor has double layers with an inner diameter of 10.0 cm, a height of 20.0 cm, and a thickness of 1.0 cm. A low-pressure UV mercury lamp (254 nm) was used to supply UV irradiation. The average fluence rate (E_p^0) of this UV lamp was determined to be 2.1 mW cm^{-2} (Text S2).

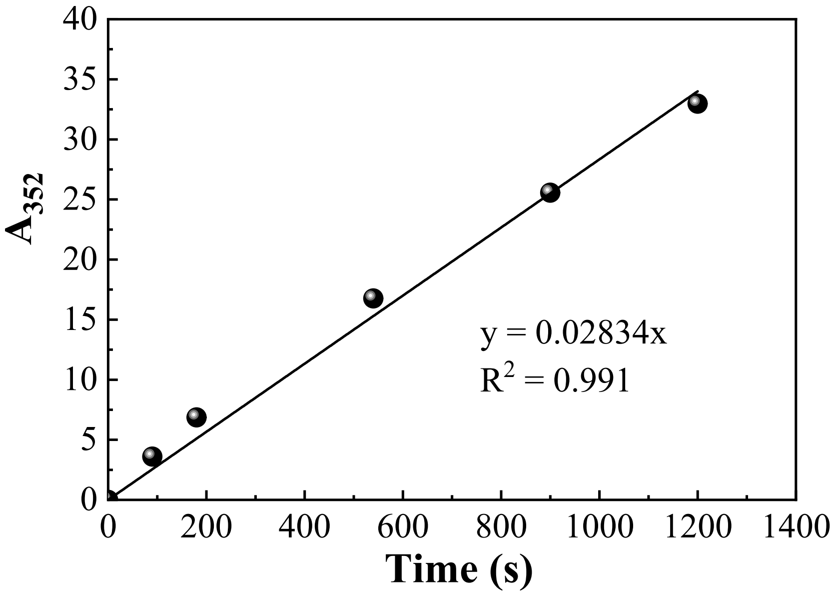


Fig. S2. Time-dependent profile of I_3^- absorbance at 352 nm

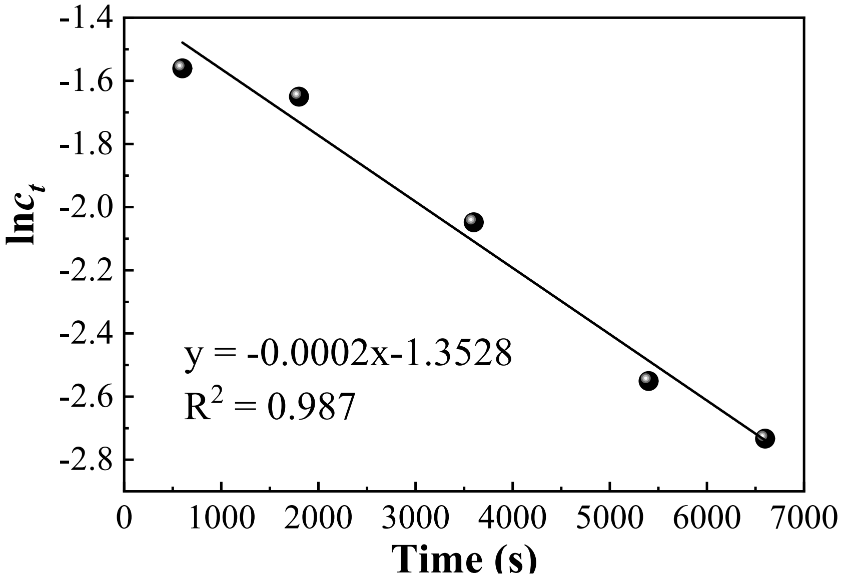


Fig. S3. Photolysis of H_2O_2 at 254 nm

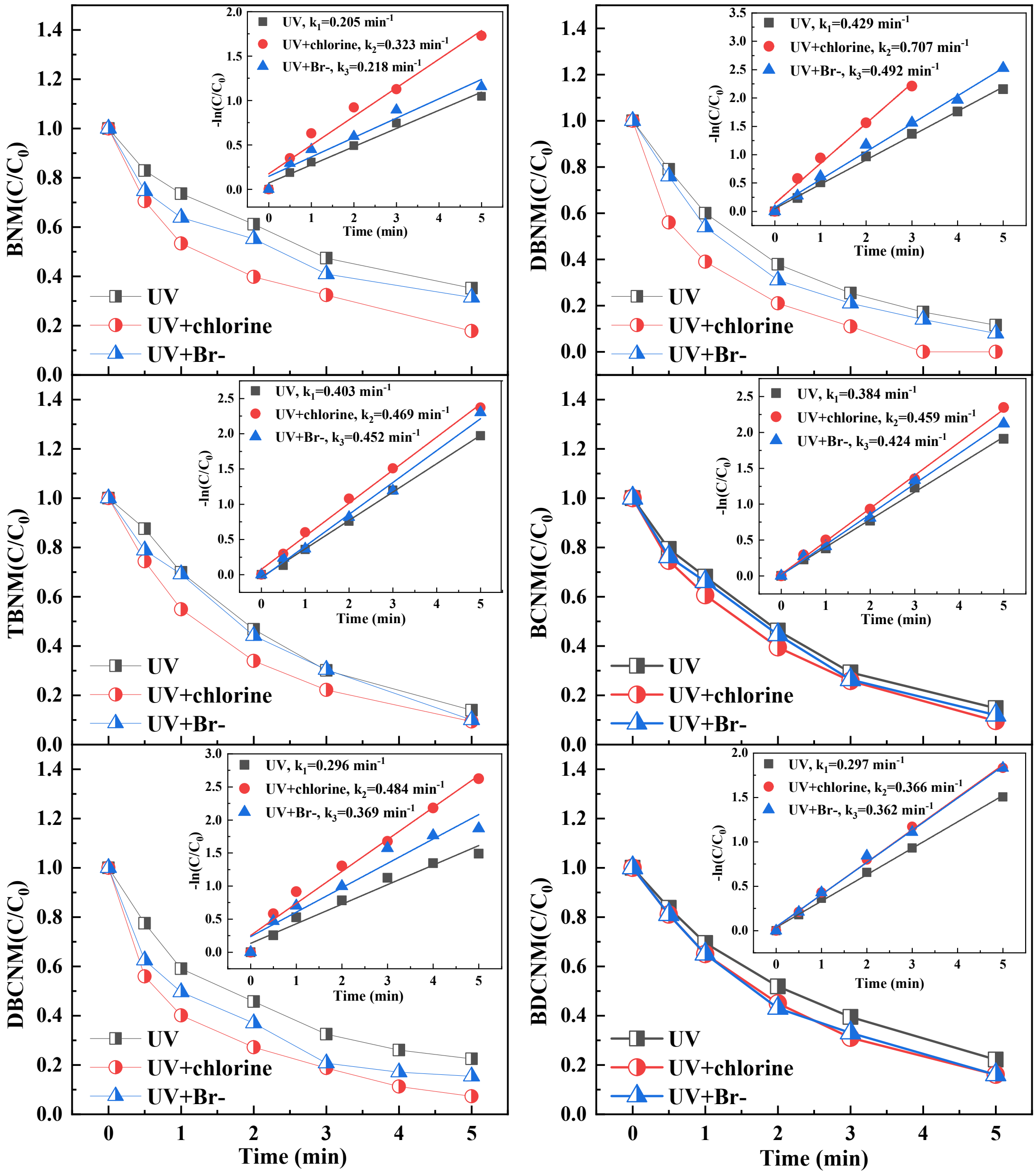


Fig. S4. Degradation efficiencies and kinetics of BNM, DBNM, TBNM, BCNM, DBCNM, and BDCNM under UV irradiation, UV+chlorine, and UV+Br^-, respectively. Experimental conditions: [BNM] = [DBNM] = [TBNM] = [BCNM] = [DBCNM] = [BDCNM] = 200 μg L^{-1}, [free chlorine] = 1.0 mg L^{-1}, [Br^-] = 1.0 mg L^{-1}, pH=7.0, UV intensity was 2.1 mW cm^{-2}.

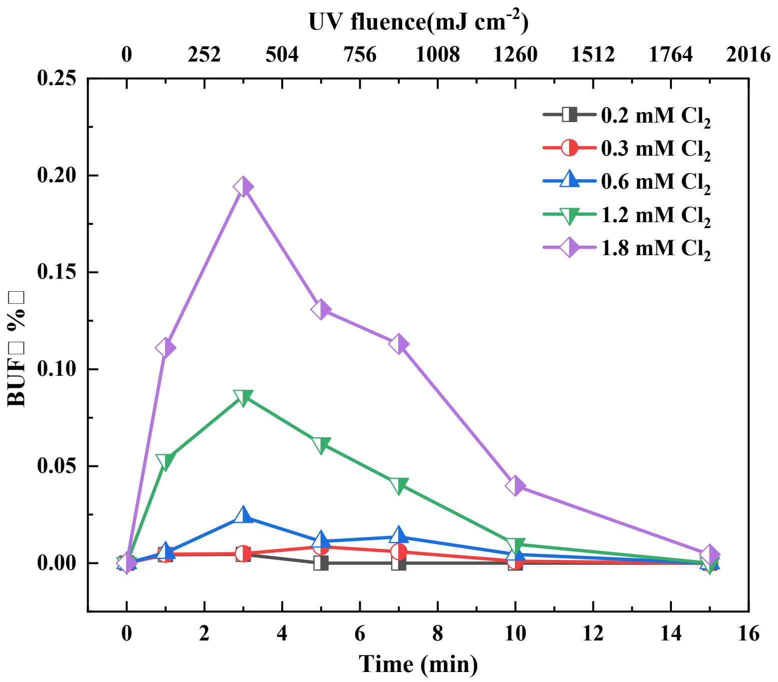


Fig. S5. Effects of free chlorine concentration on bromine utilization factors (BUFs) in the presence of Br$^-$ during UV/chlorine disinfection. [Tryptophan] = 2.0 mmol/L, [free chlorine] = 0.2, 0.3, 0.6, 1.2, 1.8 mmol/L, [Br$^-$] = 0.6 mmol/L, pH = 7.0.

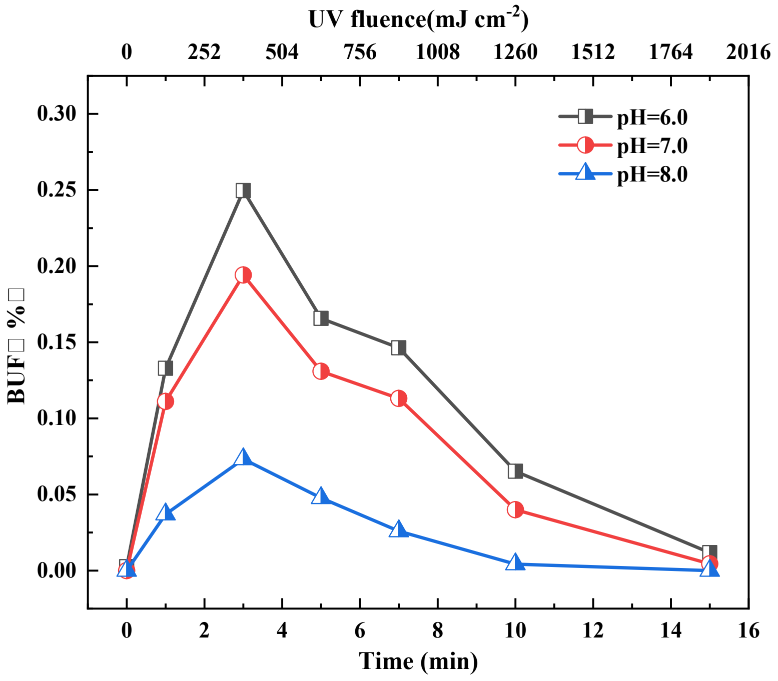


Fig. S6. Effects of pH on bromine utilization factors (BUFs) in the presence of Br$^-$ during UV/chlorine disinfection. Experimental conditions: [Tryptophan] = 2.0 mmol/L, [free chlorine] = 1.8 mmol/L, [Br$^-$] = 0.6 mmol/L, pH = 6.0, 7.0, 8.0.

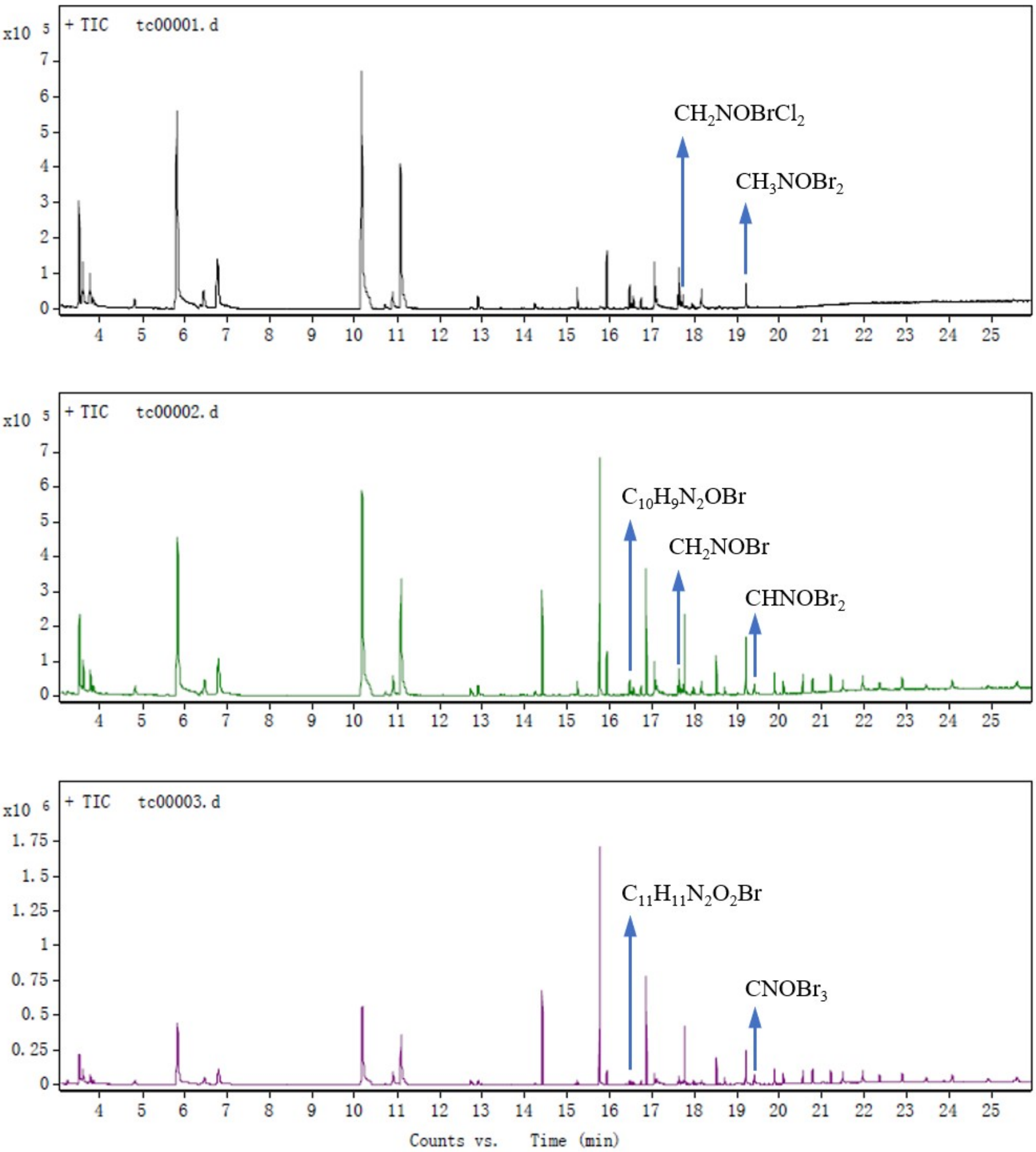


Fig. S7. GC/MS spectra for intermediate products during UV/chlorine disinfection in the presence of tryptophan and Br^-. Experimental conditions: [Tryptophan] = 2.0 mmol/L, [free chlorine] = 1.8 mmol/L, [Br^-] = 0.6 mmol/L, pH = 7.0.

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