Supporting Information For

Effects of Combined UV and Chlorine Treatment on the Formation of Trichloronitromethane from Amine Precursors

Lin Deng[1,2], Ching-Hua Huang[2,*], Yung-Li Wang[2]

[1] Department of Municipal Engineering, Southeast University, Nanjing, 210096, People Republic of China

[2] School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332, United States

* Corresponding Author. Phone: 404-894-7694. Fax: 404-385-7087.

E-mail: ching-hua.huang@ce.gatech.edu

Text S1. Chemicals and Reagents

Standard-grade trichloronitromethane (TCNM), dimethylamine (DMA) hydrochloride, methylamine (MA) hydrochloride, *N,N*-diethyl-*p*- phenylenediamine (DPD), ferrous ammonium sulfate (FAS), sodium hypochlorite (NaOCl), sodium thiosulfate ($Na_2S_2O_3$), methoxybenzene sulfonylchloride, phosphoric acid, acetone, methyl tertiary-butyl ether (MTBE), dichloromethane, ammonium chloride, *t*-butyl alcohol (TBA), sodium phosphate monobasic and dibasic, and sodium borate were obtained at >98% purity from Sigma-Aldrich (St. Louis, MO) or Fisher Scientific (Pittsburgh, PA). All reagents were used without further purification. Poly(dimethylamine epichlorohydrin) (referred to as polyamine in the main text at 50% by weight in water) was obtained from Sigma-Aldrich, stored at room temperature, and used without further purification. All aqueous solutions were prepared with ultra-pure water (conductivity >18 mΩ·cm) generated by a Milllipore Milli-Q water purification system (Billerica, MA). Prior to use, all glassware was cleaned with a laboratory detergent, rinsed with acetone and nanopure water, and baked at 300 °C for 3 h. Fresh stock solutions of free chlorine (NaOCl) and polyamine were made every time for the experiments. Concentration of free chlorine in the stock solution was quantified by the standard DPD-FAS method.[1]

Text S2. Experimental Methods and Analyses

Similar to the set-up described previously (Figure S1),[2] all experiments were performed in a magnetically stirred 60-mL cylindrical quartz reactor. UV irradiation was supplied from one side of the quartz reactor by up to three 4-W LP lamps (G4T5 Hg lamps, Philips TUV4W) peaking at 254 nm at ambient temperature (22°C). The photochamber was equipped with a fan for cooling during the experiments. The incident light irradiance in the active wavelength region was from

2.0 to 5.4 mW/cm^2 to the reactor center depending on the number of lamps used (corresponding to a photo fluence rate of 3.36 – 9.07 mEinstein/L-s) measured by a UVX (UVP, USA) radiometer.

The reaction solution pH (6 - 8) was maintained constant (±0.2) during the experiments by 2 mM phosphate buffer. The solution was continuously mixed using a magnetic stirrer. The top of the quartz reactor was capped by a rubber septum throughout the reaction except during sampling. Thus, volatilization of a small amount of TCNM could not be completely avoided. However, this volatilization loss was relative small during the early stage of reaction when the maximum TCNM formation occurred and was small compared to the loss of TCNM by photolysis at the later stage of reaction. The solution was first prepared with buffer and amine precursors, dosed with free chlorine (NaOCl) for 1 min, and then exposed to UV irradiation. Sample aliquots were drawn from the quartz reactor at pre-determined time intervals by a 5-mL pipette. The first sample taken was after free chlorine contact time of 1 min without UV irradiation. Upon collection, sample aliquots were immediately dosed with excess sodium thiosulfate to quench free chlorine. Afterwards, the samples were extracted with 1.7 mL of methyl tertiary-butyl ether (MTBE) for 2 min. One mL of the MTBE layer was transferred to a GC vial and analyzed for TCNM by an Agilent 6890 gas chromatography system equipped with a HP-5MS capillary column (30 m × 250 mm × 0.25 mm) and an electron capture detector (Palo Alto, CA). All experiments were conducted in triplicate or more. Calibration standards of TCNM (0.01 – 50 µg/L) yielded strong linear correlation (R^2 = 0.9992). The detection limit for TCNM was around 0.1 µg/L.

The DMA and MA concentrations prior to and after the reaction were analyzed using a modified previous method.[3] Briefly, samples (5 mL) were spiked with the surrogate standard

DMA-d6 and derivatized with excess 4-methoxy-benzenesulfonyl chloride at pH 8.9 controlled by 10 mM borate buffer. Derivatized amines were extracted by 2 mL dichloromethane and analyzed by an Agilent 6890/5973 GC/MS system equipped with a Supelco Equity-1701 column (30 m × 250 μm × 0.25 μm) and a large volume injector (LVI). The GC oven temperature began at 100 °C for 1 min, then ramped at 8 °C/min to 250 °C and was finally held at 250 °C for 3 min. Derivatized DMA and MA were quantified by selected ion monitoring (SIM) mode. Calibration standards of DMA and MA in the range of 1.0 – 100 μg/L yielded strong linear correlation (R^2 = 0.9948 – 0.9997). The detection limit for DMA and MA was around 0.1 mg/L and 1.0 mg/L, respectively.

References:

(1) APHA, AWWA, WPCF. 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, American Water Works Association and Water Environment Federation, Washington, D.C., USA.

(2) Yao, H.; Sun, P. Z.; Minakata, D.; Crittenden, J. C.; Huang, C.-H. Kinetics and modeling of ionophore antibiotic degradation by UV and UV/H2O2. *Environ. Sci. Technol.* **2013**, *47* (19), 4581-4589.

(3) Park, S. H.; Wei, S.; Mizaikoff, B.; Taylor, A. E.; Favero, C.; Huang, C.-H. Degradation of amine-based water treatment polymers during chloramination as *N*-nitrosodimethylamine (NDMA) precursors. *Environ. Sci. Technol.* **2009**, *43* (5), 1360-1366.

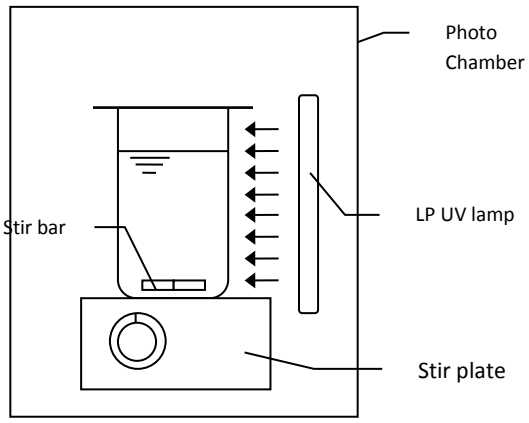

Figure S1. Illustration of experimental set-up. The 60-mL cylindrical quartz reactor has a diameter of 2.75 cm and a height of around 10.1 cm. Up to three LPUV lamps in parallel were used.

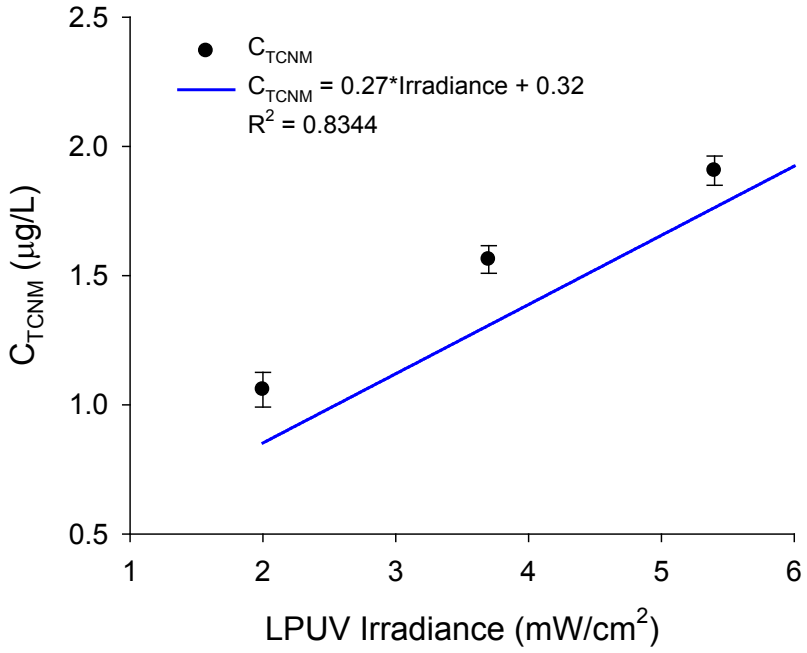

Figure S2. Relationship between the maximum TCNM formation (at ~5 min reaction time) and the applied LPUV irradiance under combined UV/chlorine conditions. Solutions contained 10 mg/L polyamine initially and were exposed to 7 mg/L of free chlorine and LPUV irradiance at 2-5.4 mW/cm^2 at pH 7.0 and 22 °C.

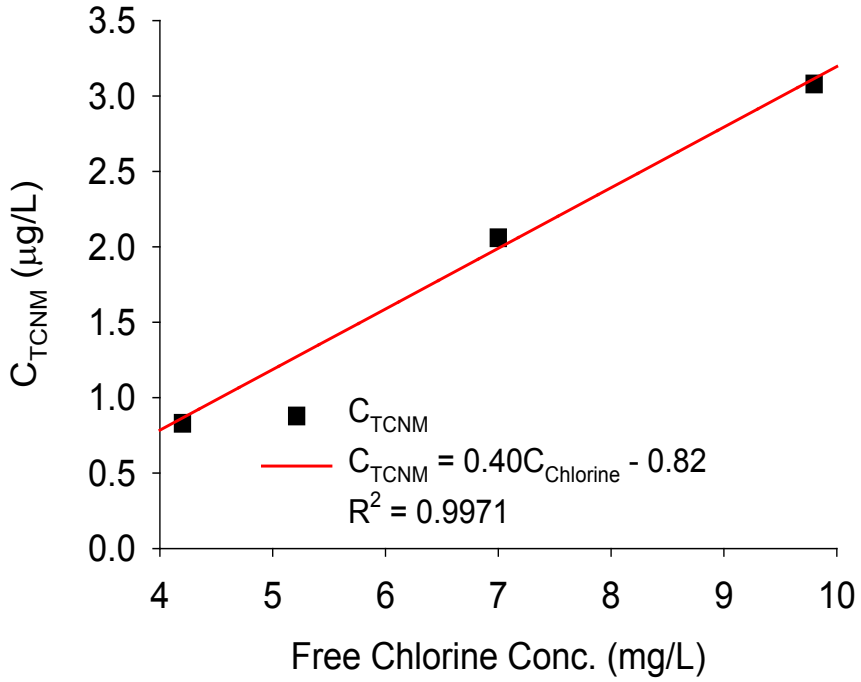

Figure S3. Relationship between the maximum TCNM formation (at ~5 min reaction time) and the applied free chlorine concentration from polyamine under combined UV/chlorine conditions. Solutions contained 10 mg/L polyamine initially and were maintained under LPUV (5.4 mW/cm^2) at pH 7.0 and 22 °C

Table S1. Comparison of the yield of TCNM formation from MA, DMA and polyamine under free chlorination only and combined LPUV/chlorine. All reactions were conducted at pH 7.0 and 22 °C.

[Oxidant] Dose	Precursors	$[Precursor]_0$ (μM)	$[TCNM]_{max}$ *	[TCNM]/[Precursor] % Yield	Comparison
Chlorine only:					
140 μM	MA	323	7.27 μg/L = 0.044 μM	0.014	7.0
140 μM	DMA	222	1.70 μg/L = 0.010 μM	0.005	2.5
100 μM	Polyamine	72.9**	0.33 μg/L = 0.002 μM	0.002	1
UV/chlorine:					
5.4 $mW \cdot cm^{-2}$/100 μM	MA	72.9	7.47 μg/L = 0.046 μM	0.063	3.9
5.4 $mW \cdot cm^{-2}$/100 μM	DMA	72.9	2.94 μg/L = 0.018 μM	0.025	1.6
5.4 $mW \cdot cm^{-2}$/100 μM	Polyamine	72.9**	1.97 μg/L = 0.012 μM	0.016	1
5.4 $mW \cdot cm^{-2}$/140 μM	MA	323	39.72 μg/L = 0.242 μM	0.075	3.4
5.4 $mW \cdot cm^{-2}$/140 μM	DMA	222	15.82 μg/L = 0.096 μM	0.043	2.0
5.4 $mW \cdot cm^{-2}$/140 μM	Polyamine	72.9**	2.67 μg/L = 0.016 μM	0.022	1

*: concentration at 30 min for chlorination alone and at 2-5 min for combined UV/chlorine conditions.
**: Estimated organic-N molar concentration based on the number of repeating unit in polyamine polymer.