Sunlight Effects on Trichloronitromethane Formation Potential of Wastewater Effluents: Dependence on Nitrite Concentration

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Abstract

This study examined the effects of sunlight irradiation on the trichloronitromethane formation potential (TCNM-FP) of wastewater effluents, and the roles of nitrite and nitrate in this process. Using disinfected secondary effluents from four treatment plants, we observed that 8 h of sunlight irradiation (320 W/m^2) attenuated TCNM-FP by 17–47% for 9 out of 14 samples, but increased the TCNM-FP for two of the other samples. Longer time of irradiation (up to 36 h) further reduced TCNM-FP in a non-nitrified effluent with low nitrite and nitrate concentrations, but increased TCNM-FP in two nitrified effluents by 2- to 3-fold. When nitrite (0.1–2 mg N/L) was spiked into effluent samples, an increase in TCNM-FP after irradiation was observed. The higher the nitrite concentration, the greater the increase in TCNM-FP. In the presence of ~1 mg N/L of nitrite, 8 h of sunlight irradiation increased the TCNM-FP of four wastewater samples by 0.3–3.6 μg/mg C. In contrast, the spike of nitrate up to 20 mg N/L had no effect. The nitrite-sunlight effect was also observed for four model precursors (humic acid, tryptophan, tyrosine, and phenol). Humic acid and tryptophan featured higher increase in TCNM-FP than tyrosine and phenol after sunlight irradiation.

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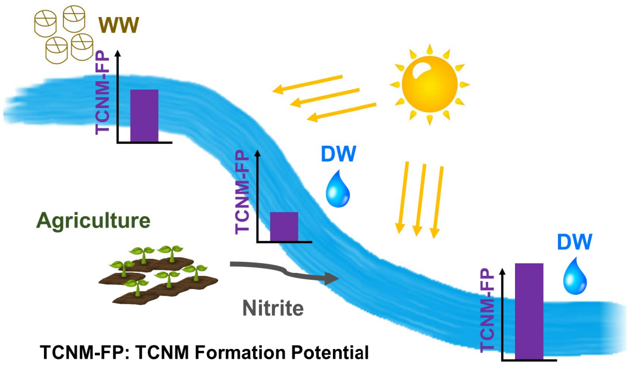


1. Introduction

Growing water scarcity around the globe is accompanied with increasing impacts of wastewater effluent and agricultural runoff on drinking water sources. For example, in the United States (U.S.), upstream wastewater effluent contributes to more than 10% of the surface water flow at the intake of 38 drinking water treatment plants that collectively serve over 10 million people.[1] Agricultural runoff can contribute up to 44% of total nitrogen and 58% of total phosphorous in the local surface water.[2] The concentration of dissolved organic nitrogen (DON) in wastewater effluents is 0.29–4.3 mg-N/L (5th to 95th percentile), much higher than that in pristine surface water (0.1–0.67 mg-N/L, 5th to 95th percentile).[3] Agricultural runoff can contain nitrite and nitrate concentrations as high as 1.2 mg/L and 20 mg/L, respectively.[4, 5] These organic and inorganic nitrogen constituents can promote the formation of nitrogenous disinfection byproducts (N-DBPs) in downstream water treatment plants.[6-9]

Trichloronitromethane (TCNM or chloropicrin) is a prevalent N-DBP featuring 10–100 times higher cytotoxicity and genotoxicity than trihalomethanes and haloacetic acids currently regulated by the U.S. Environmental Protection Agency (EPA).[10-12] A national survey in the U.S. from 1997 to 1998 reported that the range of TCNM concentration was <0.5–0.8 µg/L (25th to 90th percentile) in plant effluents and <0.5–0.9 µg/L (25th to 90th percentile) in distribution system samples,[13] but a more recent study reported 2.1 µg/L of TCNM concentration in plant effluent from a utility impacted by wastewater effluents.[6] Chlorination formed more TCNM than chloramination in a range of water matrices, including surface water,[14, 15] filter effluent,[14, 16] wastewater effluent,[17] and buffered solutions of nitrogenous model precursors[18]. TCNM formation positively correlates with the concentration of DON.[17, 19-21] Nitrogenous organic compounds such as amines[18, 22], amino acids/peptides[18, 23], amino sugars[23], nucleic acids[24], and pyrroles[18] can form

TCNM at yields ranging from 0.02% to 0.12% by chlorination or chloramination. The amino functional group has been shown to be a critical reaction site for TCNM formation: it can be oxidized by chlorine or chloramine to form a nitro group, which is then chlorinated to form TCNM.[20, 25, 26] Similarly, the amino group can be oxidized to a nitro group by ozone,[27] which was used to explain the enhanced TCNM formation when preozonation is employed prior to chlorination/chloramination.[14, 17, 20] Pre-ozonation (1 mg O_3/mg C, 5 min) was shown to increase the TCNM formation potential of wastewater effluents by 3–12 μg/mg C.[17] The presence of nitrite also promotes TCNM formation during chlorination.[23, 28-30] For example, the presence of 2 mg/L of nitrite increased TCNM formation by 6.7 times during chlorination of raw surface water at pH 6.[28] In addition, nitrite and nitrate were shown to promote TCNM formation when medium-pressure UV disinfection was used before chlorination or chloramination,[31-33] even when the solution only contained humic acid featuring low organic nitrogen (57 μg N/L).[31] Because wastewater effluents and agricultural runoff contribute to high concentrations of organic and inorganic nitrogen, utilities using source waters impacted by both are particularly at risk for elevated TCNM concentrations.

Sunlight irradiation can transform organic and inorganic nitrogen species as they travel from the discharge points to downstream water intakes,[34-38] but few studies have considered whether this process influences the formation potential of TCNM. The only two available studies reported opposite results. One of the studies reported 30% reduction in TCNM formation potential after 13 h sunlight irradiation for two wastewater effluents.[39] The other study, however, reported that the TCNM formation potential of activated sludge-derived soluble microbial products increased by 1.7 times after 8 h sunlight irradiation.[40] Additionally, nitrate and nitrite are known to generate reactive nitrogen species leading to the nitration of phenolic compounds,[41, 42] which may promote TCNM formation. However, this phenomenon has not been considered in the sunlight transformation of wastewater effluent organic matter regarding its impact on TCNM formation.

This study aims to evaluate whether sunlight irradiation alters the potential of wastewater effluents to form TCNM, and whether the presence of nitrite and nitrate influences this process. We first sampled four wastewater treatment plants multiple times over the course of 18 months, and measured TCNM formation potential before and after simulated sunlight irradiation in the laboratory. For selected samples, we also evaluated the effects of irradiation time. Second, we spiked varying concentrations of nitrite/nitrate into nitrified and non-nitrified effluents, respectively, to evaluate their effects on the change of TCNM formation potential upon sunlight irradiation. Lastly, because we observed that the presence of nitrite led to dramatic increases in TCNM formation potential after sunlight irradiation, we used five model precursors (tryptophan, tyrosine, asparagine, humic acid, and phenol) that are relevant to wastewater to explore the mechanisms.

2. Materials and Methods

2.1. Materials

Text S1 shows the detailed information of chemicals used in this study.

2.2. Wastewater Experiments

Wastewater samples were collected from the secondary clarifier of four wastewater treatment plants (WWTPs), stored in fluorinated high-density polyethylene containers, and transported to the University at Buffalo on ice within 2 h. Samples from WWTPs A and B are non-nitrified secondary effluents, while those from C and D are nitrified secondary effluents. The non-nitrified effluents featured high ammonia concentrations, while the nitrified effluents featured high nitrate concentrations (Table 1). Each WWTP was sampled 2–4 times over the course of 23 months. All samples were filtered by pre-combusted 0.7 μm glass fiber filters immediately upon receipt and stored at 4 °C before use. The analysis methods for water quality characteristics and their detection limits are shown in Text S2. Information on the WWTPs, sampling dates, and the water quality parameters of the samples are shown in Table 1. The filtered samples were used for experiments within 3 weeks after each sampling.

Table 1. Wastewater treatment plant information, sampling dates, and the water quality parameters of samples.

WWTP	Treatment process	Sample number	Sampling date	pH	DOC[a] (mg C/L)	SUVA (L/mg·m)	NO_3^--N (mg N/L)	NO_2^--N (mg N/L)	NH_3-N (mg N/L)	TN (mg N/L)	DON (mg N/L)
A	Bar screening, secondary aeration, secondary clarification, sand filtration, and chlorination.	A1	3/10/2017	7.86	7.35	1.50	1.90	0.30	5.10	7.62	0.32
		A2	7/21/2017	7.64	10.20	1.31	1.00	0.39	16.33	17.50	NA[b]
		A3	1/22/2018	7.67	9.18	1.25	1.07	0.24	3.44	4.51	NA
		A4	5/2/2018	7.15	10.80	1.27	0.46	0.05	6.90	10.20	2.79
B	Bar screening, grit removal, primary settling, secondary aeration with addition of alum to remove phosphorus, secondary clarification, and chlorination.	B1	3/13/2017	7.35	12.00	1.08	0.60	0.20	6.90	7.83	0.13
		B2	4/30/2018	7.59	7.90	1.55	0.55	<0.02	12.00	15.30	2.74
		B3	12/7/2018	7.67	6.37	2.03	0.72	0.81	11.60	14.35	1.22
C	Screening, pre-chlorination, grit removal, primary settling, secondary aeration, nitrification, sand filtration, and chlorination.	C1	1/31/2017	7.47	8.24	2.18	15.20	0.80	1.90	18.20	0.30
		C2	8/23/2017	8.03	6.35	1.81	18.40	0.02	0.43	19.10	0.25
		C3	1/18/2018	6.99	7.81	2.01	14.10	0.10	0.07	13.60	NA
		C4	6/14/2018	6.54	6.12	2.28	26.70	0.11	0.15	28.50	1.54
		C5	12/7/2018	7.18	5.30	2.31	17.55	0.20	0.18	18.30	0.37
D	Bar screening, muffin grinding, secondary aeration, nitrification, secondary clarification, phosphorous removal by ferric chloride, sand filtration, UV disinfection, and reaeration.	D1	4/4/2018	7.21	4.20	2.43	3.42	0.10	0.08	4.93	1.33
		D2	6/14/2018	7.33	4.26	2.79	11.70	<0.02	<0.03	13.40	1.68

[a] DOC: dissolved organic carbon; SUVA: the specific UV absorbance at 254 nm; NO_3^--N: nitrate nitrogen; NO_2^--N: nitrite nitrogen; NH_3-N: ammonia nitrogen; TN: total nitrogen; DON: dissolved organic nitrogen.

[b] NA: not available due to the negative value calculated based on ammonia, nitrite, nitrate, and total nitrogen concentration.

The filtered secondary effluent samples were disinfected in the laboratory using sodium hypochlorite (2 mg/L as Cl_2, 30 min). Residual total chlorine (1–1.7 mg/L as Cl_2) was quenched by sodium thiosulfate using the molar ratio of 0.5:1 between thiosulfate and residual chlorine. The chlorine dose and contact time were selected to achieve exposure of 30–55 mg·min/L, similar to the disinfection conditions used in the treatment plants where samples were collected. This laboratory chlorination step was used to simulate wastewater disinfection at a consistent dose across different samples to obtain the final effluent that is exposed to sunlight in de facto reuse. For experiments evaluating the impacts of nitrite and nitrate, sodium nitrite or sodium nitrate was added after chlorine disinfection and quenching.

Each disinfected sample was separated into four 200 mL fractions. Two were placed in crystallization dishes, covered by quartz discs, and placed in a Q-SUN Xe-1 test chamber (Q-Lab Corporation, Westlake, OH). The other two were dark controls. The test chamber is equipped with a Xenon arc lamp to produce the full sunlight spectrum. Irradiation below 290 nm was removed by a daylight-Q filter (X-7460). The light intensity was set at 0.68 W/m^2 at 340 nm, and the total irradiation intensity was 320 W/m^2, determined using 2-nitrobenzaldehyde chemical actinometry as described previously.[43] Sample temperature was maintained at 20 ± 3 °C using a circulating water bath. After a set period of time, 30 mL of the irradiated or dark control sample was sampled to test TCNM formation potential (section 2.4 below). Water quality characteristics were measured again for both irradiated and dark control samples. It was verified that the fraction of incident photons absorbed at each wavelength within the sunlight spectrum was below 50% for all samples, despite the variation in their DOC concentrations (4.2–12 mg C/L). The absorbance results of four samples are shown in Figure S1 as examples. Therefore, samples were not diluted based on DOC prior to sunlight irradiation.

2.3. Model Precursor Experiments

TCNM model precursors phenol, tyrosine, tryptophan, asparagine, and humic acid were used to test the effects of nitrite on the change of TCNM formation potential by sunlight irradiation. Each precursor was dissolved in a 5 mM pH 7.2 phosphate buffer solution to achieve a dissolved organic carbon (DOC) concentration of 5 mg C/L. The solutions were spiked with sodium nitrite to achieve 0.1–2 mg N/L concentrations, and then subject to simulated sunlight or stored in the dark for 8 h. To evaluate the impacts of pre-chlorination, another group of precursor solutions were disinfected as describe in section 2.2 to simulate wastewater disinfection, spiked with 1 mg N/L of sodium nitrite, and then irradiated or kept in the dark for 8 h before analyzed for TCNM-FP. Lastly, to investigate the behavior of these model precursors in authentic wastewater matrix, phenol, tyrosine, tryptophan, and humic acid (5 mg C/L) were spiked into a nitrified effluent (C5). The spiked samples were disinfected, spiked with 1 mg N/L nitrite, irradiated or held in the dark, and then analyzed for TCNM-FP.

2.4. TCNM Formation Potential Test

The formation potential test procedure followed that of Krasner et al.[7], which was used in a previous survey of TCNM formation potential of wastewater effluents[17] and in the two previous studies on sunlight effects on TCNM formation[39, 40]. The TCNM formation potential test used chlorination, because chlorine forms more TCNM than chloramine for wastewater.[16, 17] Solutions were buffered at pH 7.2 with 10 mM phosphate buffer. The applied chlorine dose was calculated as NaOCl (mg/L as Cl_2) = 3 × DOC (mg C/L) + 8 × NH_3-N (mg N/L) + 10 (mg/L).[7] Thereafter, samples were kept in the dark at room temperature for 72 h. TCNM concentration was analyzed by gas chromatography-electron capture detector following solvent extraction using methyl *tert*-

butyl ether, as described previously[44] and summarized in Text S3. TCNM formation potential (TCNM-FP, µg/mg C) was calculated by the following equation:

$$\text{TCNM-FP} = C_{\text{After FP Test}} - C_{\text{Before FP Test}} \qquad \text{(Equation 1)}$$

where $C_{\text{After FP Test}}$ (µg/mg C) and $C_{\text{Before FP Test}}$ (µg/mg C) are the TCNM concentrations measured after and before formation potential test, respectively, after normalized by DOC.

3. Results and Discussion

3.1. Effect of Sunlight on the TCNM Formation Potential of Wastewater Effluents

The ratios of TCNM-FP between irradiated and dark control samples were used to evaluate whether sunlight alters the TCNM-FP of different wastewater effluents (Figure 1, top panel, and Table S1). After 8 h of irradiation, 9 out of the 14 samples showed reduced TCNM-FP, and the extent of reduction (17%–47%) is similar to that reported for two denitrified and UV-disinfected effluents in a previous study.[39] For the other 5 samples, however, TCNM-FP remained unchanged (A2, B1, and C2) or even increased by 1.5 times (B3) or 4.3 times (C1) after sunlight irradiation. B3 had high nitrite concentration (0.81 mg N/L), and C1 had high concentrations of both nitrate (15.2 mg N/L) and nitrite (0.8 mg N/L), which may play a role in their distinct behavior. Further discussion on the effects of nitrite and nitrate is included in sections 3.2 and 3.3 below. Non-nitrified and nitrified effluents did not show significant difference in the change of TCNM-FP by sunlight (Figure S2a).

Figure 1. Comparison of the TCNM formation potential between irradiated and dark control samples for different wastewater effluents. Secondary effluents collected from the WWTPs were disinfected with chlorine (2 mg/L as Cl_2, 30 min) in the laboratory, quenched with sodium thiosulfate (molar ratio of thiosulfate to residual chlorine = 0.5:1), and then irradiated under simulated sunlight (320 W/m^2) or kept in dark for 8 h. FP test: NaOCl (mg/L as Cl_2) = 3 × DOC + 8 × NH_3-N + 10; buffered by 10 mM phosphate at pH 7.2; contact time 72 h. Error bars represent the standard deviation from duplicate experiments.

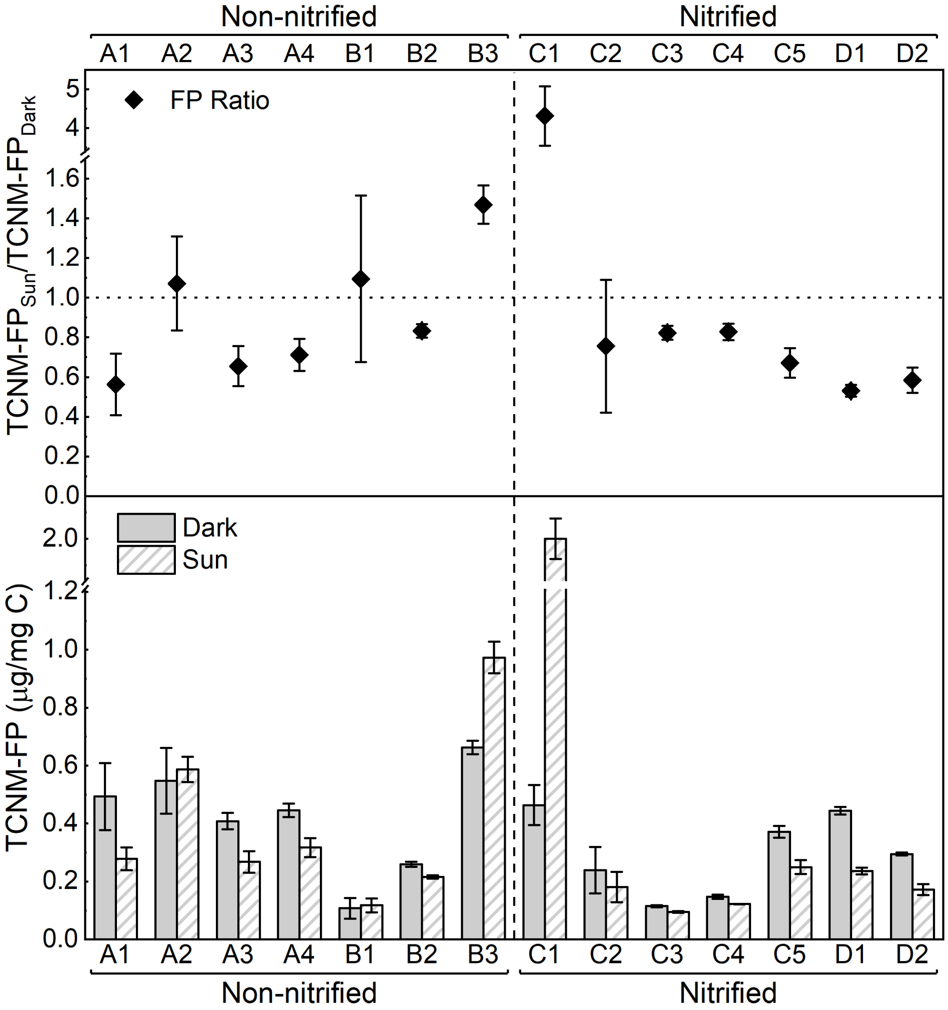
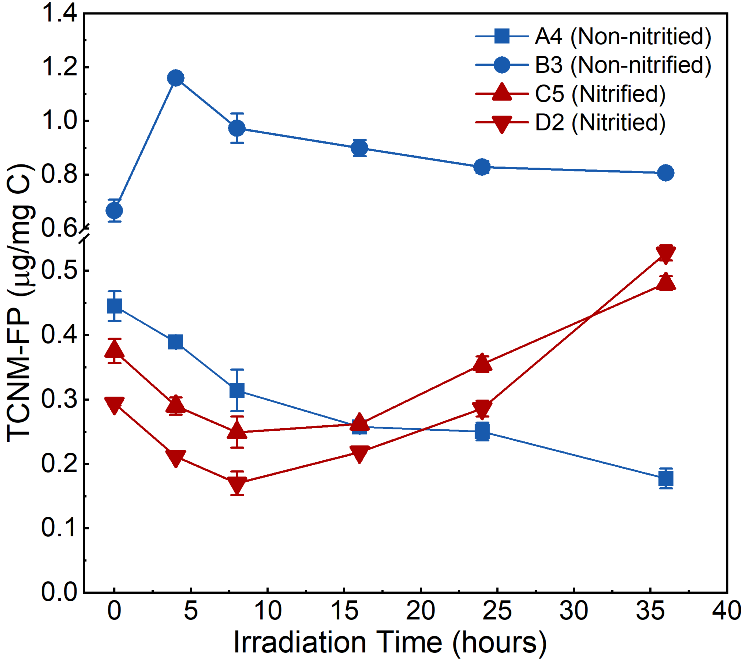


Figure 1 also shows the absolute TCNM-FP in irradiated and dark control samples (bottom panel). The TCNM-FP of dark control samples ranged from 0.11 to 0.66 µg/mg C, similar to that reported in a previous study (0.18–0.76 µg/mg C, 13 samples from 7 plants);[17] variations among samples from the same WWTP ranged from 1.3- to 6.2-fold. The formation potential of TCNM from non-nitrified and nitrified effluents were similar (Figure S2b), consistent with the finding from a previous study.[17] This is different from the trend for some other N-DBPs such as haloacetonitriles and *N*-nitrosodimethylamine, the formation potential of which is higher for non-nitrified effluents than nitrified effluents.[7]

The 8 h irradiation in the sunlight simulator (320 W/m^2) is equivalent to 2–3 days of natural sunlight irradiation (a midsummer day at 40° N latitude under clear sky).[45] To capture a wider range of travel time between wastewater discharge and downstream water supply, samples A4, B3, C5, and D2 were irradiated for up to 36 h (Figure 2 and Table S2). For the two nitrified effluents C5 and D2, TCNM-FP decreased by 0.12–0.13 μg/mg C in the first 8 h and then increased over the next 28 h to 0.48–0.53 μg/mg C, reaching a level higher than the non-irradiated sample. In contrast, different trends were observed for the non-nitrified effluents. The TCNM-FP of A4 decreased continuously from 0.45 to 0.18 μg/mg C as the irradiation time increased from 0 to 36 h, while the TCNM-FP of B3 increased from 0.67 to 1.16 μg/mg C in the first 4 h and then slowly decreased to 0.81 μg/mg C over the next 32 h. The TCNM-FP of dark control samples remained unchanged for all samples (Table S2).

Figure 2. Change of the TCNM formation potential by extended irradiation (up to 36 h) for wastewater effluents. Two non-nitrified effluents (A4 and B3) and two nitrified effluents (C5 and D2) collected from the WWTPs were disinfected with chlorine (2 mg/L as Cl_2, 30 min) in the laboratory, quenched with sodium thiosulfate (molar ratio of thiosulfate to residual chlorine = 0.5:1), and then irradiated under simulated sunlight (320 W/m^2) or kept in dark. FP test: NaOCl (mg/L as Cl_2) = 3 × DOC + 8 × NH_3-N + 10; buffered by 10 mM phosphate at pH 7.2; contact time 72 h. Error bars represent the standard deviation from duplicate experiments.



Two processes can occur simultaneously during sunlight irradiation that contribute to the decrease or increase of TCNM-FP, respectively: (1) a TCNM precursor is transformed to a product with much lower TCNM formation potential; (2) a non-precursor compound is transformed into a TCNM precursor. As shown in Table 2, for samples featuring TCNM-FP reduction after 8 h irradiation, their DON concentrations decreased by 0.01–0.34 mg N/L, with corresponding increase in ammonia concentration by 0.01–0.16 mg N/L; after 36 h irradiation, DON concentration in the non-nitrified effluent A4 decreased by 0.21 mg N/L, while ammonia concentration increased by 0.17 mg N/L. The transformation of DON to ammonia by sunlight can signify the decay of TCNM precursors.[35, 38] On the other hand, for the nitrified samples C5 and D2, DON concentration increased by 0.08–0.19 mg N/L after 36 h irradiation (Table 2), consistent with the increase in their TCNM-FP and indicating the formation of new TCNM precursors. The potential roles of nitrite and nitrate in forming new TCNM precursors are suggested by the different behavior of A4, B3, C5, and D2 over extended irradiation. For A4 with low concentrations of both nitrite (0.05 mg N/L) and nitrate (0.46 mg N/L), TCNM-FP continuously decreased upon exposure to sunlight. In contrast, C5 and D2, both of which had high nitrate concentration (11.7–17.6 mg N/L), showed significant increase in TCNM-FP after the initial decrease. Additionally, the nitrate concentrations in both C5 and D2 decreased by ~0.3 mg N/L over 36 h (Figure S3), accompanied by increase in nitrite concentration (by ~0.1 mg N/L). B3, which had high nitrite (0.81 mg N/L) but low nitrate (0.72 mg N/L), showed an initial surge in TCNM-FP followed by a slow decrease; in the meantime, its nitrite concentration decreased by 0.43 mg N/L. Further discussion on the nitrite/nitrate effects are included in sections 3.2 and 3.3 below.

Table 2. Water quality characteristics of irradiated and dark control samples.

Sample number	Irradiation time (h)	pH		DOC (mg C/L)		SUVA (L/mg·m)		NO_3^--N (mg N/L)		NO_2^--N (mg N/L)		NH_3-N (mg N/L)		TN (mg N/L)		DON (mg N/L)	
		Dark[b]	Sun[c]	Dark	Sun	Dark	Sun	Dark	Sun	Dark	Sun	Dark	Sun	Dark	Sun	Dark	Sun
A1[a]	8	8.05	8.18	7.30	7.20	1.37	0.97	1.70	1.80	0.20	0.30	5.00	5.10	7.64	7.60	0.74	0.40
A2		7.66	8.12	10.11	10.30	1.26	1.15	0.97	1.05	0.38	0.27	16.15	16.23	17.49	17.39	NA[d]	NA
A3		7.71	8.08	9.17	9.17	1.21	1.05	1.06	1.08	0.24	0.24	3.40	3.41	4.45	4.48	NA	NA
A4		7.56	7.98	10.80	10.70	1.08	0.96	0.46	0.45	0.05	0.03	6.90	6.90	10.10	10.04	2.69	2.66
B1	8	7.62	8.15	12.10	11.90	0.99	0.92	0.50	0.50	0.18	0.15	6.84	6.92	7.86	7.88	0.34	0.31
B2		7.70	8.14	7.85	7.87	1.51	1.41	0.55	0.36	<0.02	<0.02	11.58	11.74	15.25	15.29	3.11	3.18
B3		7.83	8.06	6.38	6.36	1.92	1.76	0.77	0.79	0.83	0.64	11.47	11.56	14.32	14.35	1.25	1.36
C1	8	7.77	8.21	8.20	8.10	1.95	1.60	15.10	14.90	0.80	0.90	1.90	1.80	18.40	18.35	0.60	0.75
C2		8.07	8.17	6.35	6.37	1.62	1.42	18.40	18.20	0.02	0.04	0.32	0.41	19.02	18.97	0.29	0.32
C3		7.20	7.90	7.83	7.78	1.80	1.57	14.10	14.00	0.10	0.10	0.06	0.07	13.54	13.48	NA	NA
C4		7.11	7.95	6.10	6.10	2.03	1.79	26.70	26.64	0.06	0.09	0.15	0.20	28.45	28.32	1.54	1.39
C5		7.20	7.72	5.30	5.30	2.17	1.98	17.58	17.59	0.21	0.20	0.19	0.20	18.30	18.30	0.32	0.31
D1	8	7.31	7.90	4.21	4.24	2.22	2.03	3.42	3.41	0.10	0.10	0.07	0.08	5.10	5.10	1.51	1.51
D2		7.49	8.08	4.24	4.21	2.09	1.83	11.75	11.72	<0.02	0.04	<0.03	<0.03	13.47	13.29	1.70	1.52
A4	4	7.66	8.03	10.84	10.82	1.08	1.05	0.46	0.46	0.05	0.04	6.92	6.90	10.15	10.09	2.72	2.69
	16	7.60	7.95	10.90	10.87	1.08	0.94	0.47	0.45	0.05	0.05	6.92	6.95	10.20	10.10	2.76	2.65
	24	7.53	7.87	10.82	10.85	1.09	0.89	0.45	0.47	0.05	0.04	6.85	6.98	10.20	10.16	2.85	2.67
	36	7.59	8.05	10.85	10.75	1.08	0.79	0.46	0.46	0.05	0.04	6.88	7.05	10.25	10.20	2.86	2.65
B3	4	7.78	7.97	6.40	6.37	1.92	1.86	0.76	0.72	0.81	0.70	11.50	11.55	14.38	14.33	1.31	1.36
	16	7.72	8.10	6.38	6.36	1.92	1.62	0.75	0.87	0.82	0.58	11.52	11.50	14.30	14.32	1.21	1.37
	24	7.91	8.04	6.35	6.35	1.91	1.58	0.77	1.05	0.80	0.46	11.59	11.54	14.28	14.36	1.12	1.31
	36	7.81	8.08	6.37	6.39	1.93	1.42	0.75	1.14	0.81	0.38	11.55	11.50	14.40	14.38	1.29	1.36
C5	4	7.25	7.62	5.32	5.30	2.18	2.03	17.58	17.60	0.20	0.21	0.19	0.19	18.31	18.31	0.34	0.31
	16	7.28	7.57	5.34	5.31	2.17	1.79	17.57	17.54	0.20	0.23	0.18	0.18	18.30	18.32	0.35	0.37
	24	7.32	7.71	5.34	5.32	2.17	1.68	17.54	17.43	0.20	0.27	0.18	0.20	18.29	18.30	0.37	0.40
	36	7.31	7.65	5.31	5.30	2.17	1.47	17.55	17.35	0.21	0.32	0.17	0.18	18.32	18.32	0.39	0.47
D2	4	7.41	8.15	4.26	4.25	2.08	1.89	11.74	11.74	<0.02	0.03	<0.03	<0.03	13.54	13.38	1.78	1.60
	16	7.57	8.23	4.24	4.21	2.07	1.69	11.78	11.60	<0.02	0.05	<0.03	<0.03	13.46	13.42	1.66	1.76
	24	7.32	8.18	4.27	4.23	2.08	1.48	11.75	11.53	<0.02	0.08	<0.03	<0.03	13.59	13.55	1.82	1.93
	36	7.51	8.04	4.24	4.23	2.07	1.41	11.79	11.42	<0.02	0.10	<0.03	<0.03	13.55	13.46	1.74	1.93

[a] Samples from treatment plants A and B were non-nitrified; samples from treatment plants C and D were nitrified.

[b] Dark: dark control samples.

[c] Sun: irradiated samples.

[d] NA: not available due to the negative value calculated based on ammonia, nitrite, nitrate, and total nitrogen concentration.

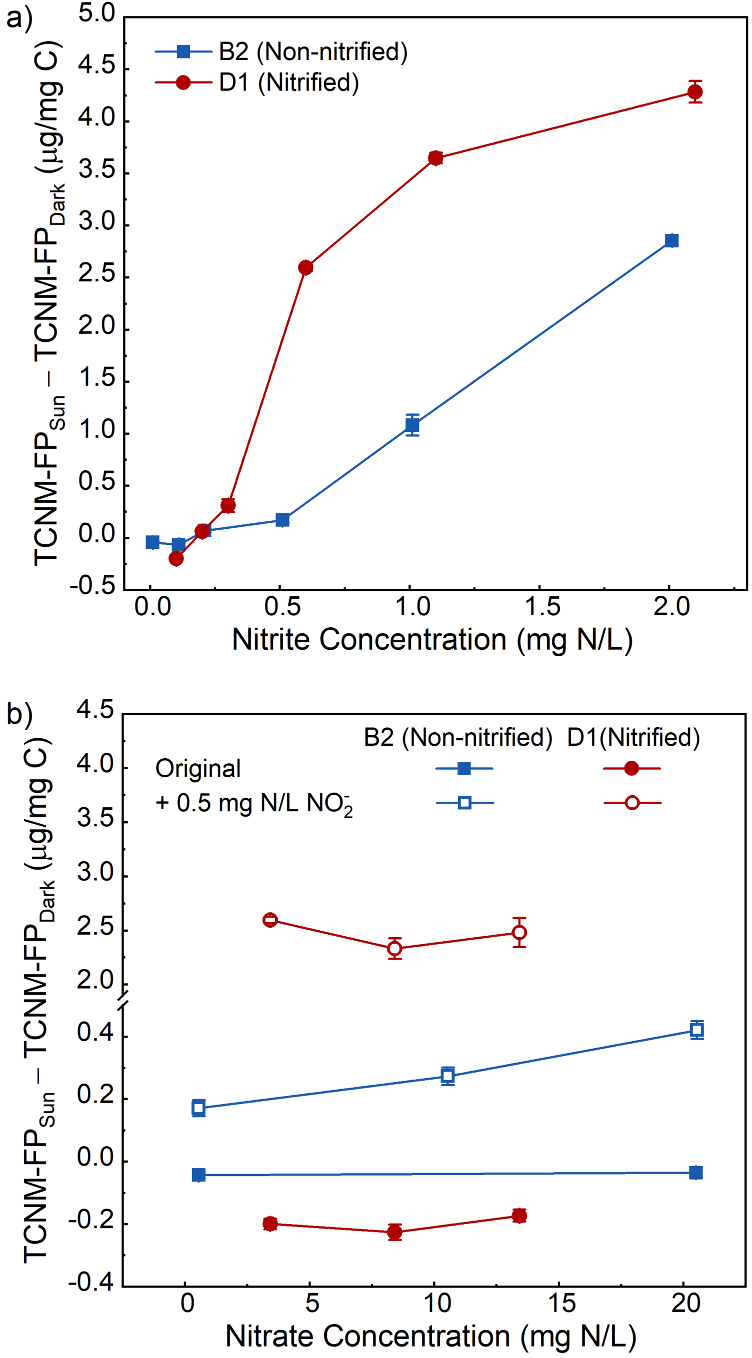
The specific UV absorbance at 254 nm (SUVA, L/(mg·m)) of irradiated and dark control samples are summarized in Table 2. SUVA decreased by 7%–29% after 8 h of sunlight irradiation. Extended irradiation (36 h) of A4, B3, C5, and D2 reduced SUVA by 26–32% from 1.08–2.17 L/(mg·m) to 0.79–1.47 L/(mg·m) (Figure S3c). SUVA was reported to be correlated with the formation of trihalomethanes, haloacetic acids, and haloacetonitriles.[46] However, statistical analysis using irradiated and dark control samples showed that a positive correlation between SUVA and TCNM-FP was only observed for non-nitrified effluents (Figure S4). A previous survey of 13 secondary effluents (4 non-nitrified and 7 nitrified) also concluded that SUVA was not a good indicator for TCNM-FP.[17] Neither was the change of TCNM-FP by sunlight, expressed as ratios between irradiated and dark control samples, correlated with the change of SUVA (Figure S5).

3.2. Combined Effects of Sunlight and Nitrite/Nitrate on the TCNM Formation Potential of Wastewater Effluents

Figure 3 shows the difference of TCNM-FP between irradiated (8 h) and dark control samples with varying nitrite and nitrate concentrations. Samples spiked with higher concentrations of nitrite showed greater increase in TCNM-FP after sunlight irradiation (Figure 3a and Table S3). In the absence of added nitrite, B2 and D1 lost 0.04 and 0.20 μg/mg C of their respective TCNM-FP after irradiation. However, when nitrite concentration reached 0.2 mg N/L, sunlight irradiation started to increase TCNM-FP. In the presence of 1 mg N/L of nitrite, which is the maximum contaminant level for drinking water in the U.S.,[47] the TCNM-FP of B2 and D1 increased by 1.1 and 3.6 μg/mg C, respectively, after 8 h irradiation. Similar increase in TCNM-FP was observed in four more wastewater samples (A4, B3, C5, and D1) spiked with nitrite (Table S3), which showed increase in TCNM-FP by 0.3–2.5 and 2.5–4.5 μg/mg C in the presence of ~1 and ~2 mg

N/L of nitrite, respectively. With comparable concentrations of nitrite, nitrified effluents (C4, C5, and D1) showed greater increase in TCNM-FP than non-nitrified effluents (A4, B2, and B3) (Figure S6). Results from dark control samples showed that increasing nitrite concentrations also increased TCNM formation during chlorination of wastewater effluents (Table S3), similar to that previously reported for surface water and filtered effluent.[28, 29] However, this increase is much smaller compared to that with sunlight irradiation prior to chlorination. For example, in the presence of ~2 mg N/L, TCNM-FP of the dark control samples increased to 0.5–1.2 µg/mg C, but that of the irradiated samples increased to 3.5–5.0 µg/mg C (Table S3).

Figure 3. Change of TCNM formation potential by sunlight irradiation in samples with varying (a) nitrite and (b) nitrate concentrations. B2 (non-nitrified effluent) and D1 (nitrified effluent) collected from the WWTPs were disinfected with chlorine (2 mg/L as Cl_2, 30 min) in the laboratory, and quenched with sodium thiosulfate (molar ratio of thiosulfate to residual chlorine = 0.5:1). The disinfected samples were spiked with nitrite or/and nitrate, and irradiated under simulated sunlight (320 W/m^2) or kept in dark for 8 h. FP test: NaOCl (mg/L as Cl_2) = 3 × DOC + 8 × NH_3-N + 10; buffered by 10 mM phosphate at pH 7.2; contact time 72 h. Error bars represent the standard deviation from duplicate experiments. Nitrite and nitrate concentrations were summarized in Table S3 and Table S4, respectively.



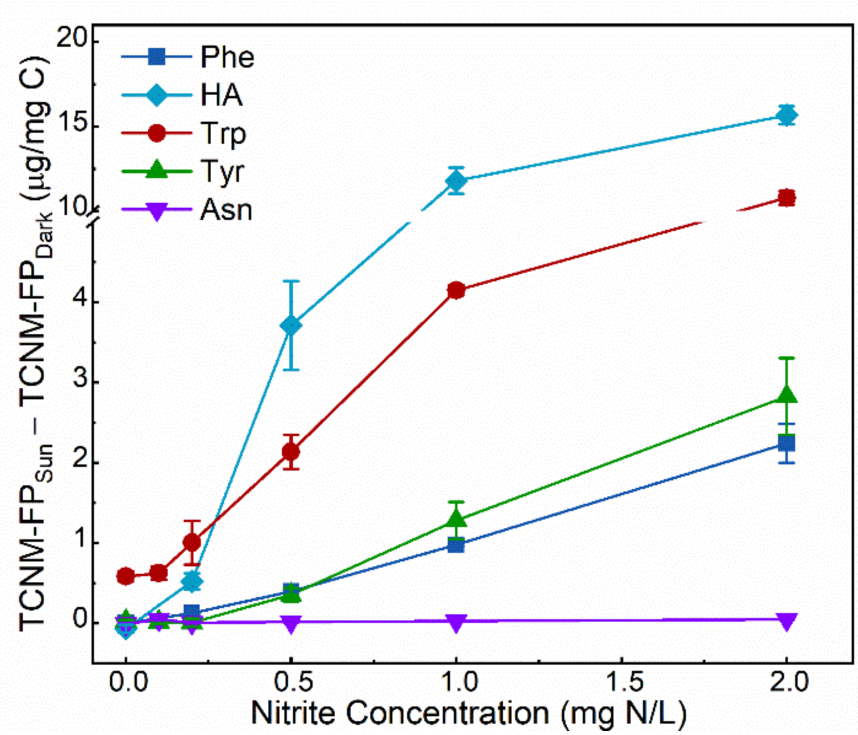
In contrast to nitrite, varying nitrate concentrations showed little effect on the change of TCNM-FP by sunlight irradiation (Figure 3b and Table S4). Non-nitrified effluent B2 and nitrified effluent D1 had 0.04 μg/mg C and 0.17–0.23 μg/mg C lower TCNM-FP after 8 h irradiation, respectively; their change in TCNM-FP was not affected by spiking nitrate up to 20 mg N/L (Figure 3b, solid symbols). Nitrate absorbs less light than nitrite within the sunlight spectrum (Figure S7). Previous studies reported that TCNM formation from humic acid or surface water increased by 3–6 times after irradiation by medium pressure UV (140–280 mJ/cm^2) in the presence of 1 mg N/L nitrate,[31, 33] which can be explained by the more significant light absorption by nitrate in the UV range. When B2 and D1 were spiked with 0.5 mg N/L nitrite (Figure 3b, open symbols, and Table S4), increasing nitrate from 0.55 mg N/L to 20.6 mg N/L resulted in 2.5 times greater increase in the TCNM-FP of B2, but did not change the TCNM-FP of D1. Overall, the effect of nitrate was much smaller than nitrite, even after taking into consideration of its higher concentrations than nitrite in typical surface waters.

The augmentation of TCNM-FP by nitrite after sunlight irradiation suggests that nitrite may contribute to the formation of new TCNM precursors, while sunlight deactivates some existing TCNM precursors in the meantime. This would account for some of the results observed in the initial survey (Figure 1). Seven of the 14 samples surveyed in Figure 1 (A1, A2, A3, B1, B3, C1, and C5) contained 0.2 mg N/L or more nitrite (Table 1), among which B3 and C1 had the highest nitrite concentrations (~0.8 mg N/L). For B3 and C1, which showed 1.5–4.3 times higher TCNM-FP after 8 h irradiation, the enhancement by nitrite likely dominated over the attenuation of precursors by sunlight. For the other five samples, the enhancement by nitrite was less due to the lower nitrite concentration (0.2–0.38 mg N/L), resulting in no net change or a reduction in TCNM-FP after irradiation.

3.3. Mechanistic Investigation into the Combined Effects of Sunlight and Nitrite on TCNM Formation Potential

Five TCNM model precursors relevant to wastewater effluents[18, 48-51] were evaluated, including phenol and humic acid that are non-nitrogenous and low in nitrogenous content (~ 0.01 mg/mg for DON/DOC[52]), respectively, and three amino acids tryptophan, tyrosine, and asparagine. In the presence of nitrite (0.1–2 mg N/L), sunlight irradiation increased TCNM-FP for all model precursors except for asparagine (Figure 4 and Table S5). The higher the nitrite concentration, the greater the increase in TCNM-FP, similar to that observed for wastewater effluents (Figure 3a). Humic acid and tryptophan featured the greatest increase in TCNM-FP, followed by tyrosine and phenol. The increase of TCNM-FP from humic acid was the highest at nitrite concentrations above 0.5 mg N/L, while that from tryptophan was the highest at nitrite concentrations below 0.5 mg N/L. Tyrosine and phenol showed similar increase in TCNM-FP. In the presence of 1 mg N/L nitrite, 8 h of sunlight irradiation increased the TCNM-FP of humic acid, tryptophan, tyrosine, and phenol by 11.8, 4.1, 1.3, and 1.0 μg/mg C, respectively. TCNM-FP of asparagine remained constant after sunlight irradiation regardless whether nitrite was present.

Figure 4. Change of TCNM formation potential of model precursors by sunlight irradiation with varying nitrite concentrations. Precursor compound concentration 5 mg C/L; solutions were buffered by 5 mM phosphate at pH 7.2. Solutions were subject to simulated sunlight (320 W/m^2) or kept in dark for 8 h. FP test: NaOCl (mg/L as Cl_2) = 3 × DOC + 8 × NH_3-N + 10; buffered by 10 mM phosphate at pH 7.2; contact time 72 h. Error bars represent the standard deviation from duplicate experiments. Phe = phenol; HA = humic acid; Trp = tryptophan; Tyr = tyrosine; Asn = asparagine.



In the absence of nitrite, humic acid lost 13% of its TCNM-FP after 8 h irradiation (Table S5), in contrast to a recent study observing no change in TCNM formation from natural organic matter rich in humic acid after 48 h irradiation.[40] Tryptophan exhibited enhanced TCNM formation (by 0.58 μg/mg C) after 8 h irradiation even in the absence of nitrite. The photolysis products of tryptophan include *N*-formylkynurenine, kynurenine, and tryptamine.[53] Our results suggest that some of these intermediates may be more potent TCNM precursors than tryptophan, warranting further investigation in future studies.

Upon sunlight irradiation, the direct photolysis of nitrite can form nitrating agents $^\bullet NO_2$, N_2O_4, and $ONOO^-$ (reactions 1–8).[41, 54-56] Additionally, sunlight irradiation of tryptophan[57, 58], tyrosine[57, 59], and humic acid[60, 61] can generate reactive oxygen species (e.g., $O_2^{\bullet-}$) that react with nitrite to form $ONOO^-$ (reaction 9).[56, 57] These nitrating agents can react with organic compounds to form TCNM precursors. For example, irradiation of nitrite-containing phenol solutions (1.1 mM phenol and 10 mM NO_2^- at pH 6.0) has been shown to form 2-nitrophenol and 4-nitrophenol at rates of 1.9×10^{-9} and 1.4×10^{-9} M/s, respectively.[42] These two nitrophenol compounds can form TCNM at 5.7%–7.2% molar yields (0.1 mM nitrophenol, 142 mg/L as Cl_2 and 112 h),[48] which are 50–360 time higher than other reported TCNM precursors (0.02%–0.12%).[18, 22-24] Moreover, $^{\bullet}NO_2$ and $ONOO^-$ were shown to react with tryptophan and tyrosine to form 6-nitrotryptophan and 3-nitrotyrosine,[62-64] respectively, which may be responsible for the increase in TCNM-FP after irradiating tryptophan/tyrosine in the presence of nitrite (Figure 4).

$$NO_2^- + hv \rightarrow {}^{\bullet}NO + {}^{\bullet}O^- \tag{1}$$

$$^{\bullet}O^- + H_2O \leftrightarrow {}^{\bullet}OH + OH^- \tag{2}$$

$$NO_2^- + {}^{\bullet}OH \rightarrow {}^{\bullet}NO_2 + OH^- \tag{3}$$

$$2\,{}^{\bullet}NO_2 \rightarrow N_2O_4 \tag{4}$$

$$2\,{}^{\bullet}NO + O_2 \rightarrow N_2O_4 \tag{5}$$

$$^{\bullet}NO_2 + {}^{\bullet}OH \rightarrow ONOOH \tag{6}$$

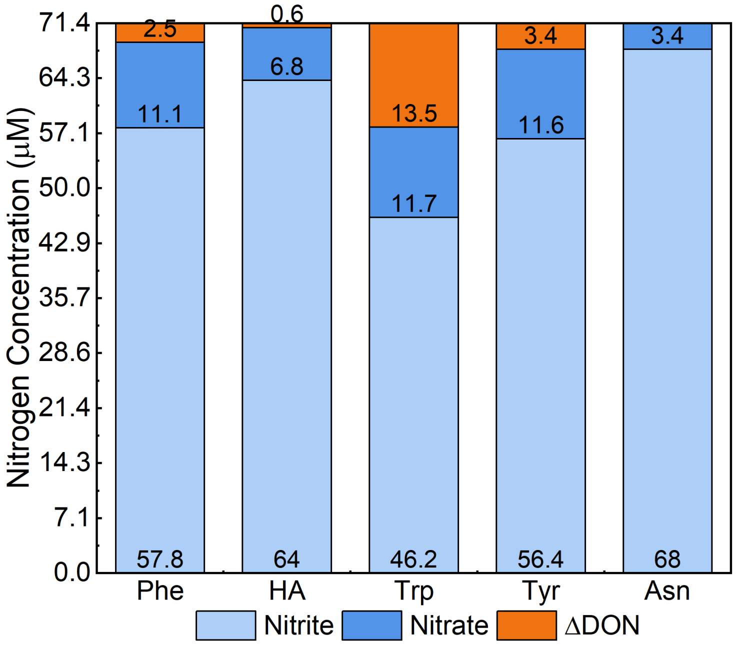
$$ONOOH \leftrightarrow ONOO^- + H^+ \tag{7}$$

$$^{\bullet}NO + ONOO^- \rightarrow {}^{\bullet}NO_2 + NO_2^- \tag{8}$$

$$^{\bullet}NO + O_2^{\bullet-} \rightarrow ONOO^- \tag{9}$$

In the precursor solutions with 1 mg N/L initial nitrite concentration, we observed the loss of nitrite and the formation of nitrate and DON upon exposure to sunlight (Figure 5). Ammonia was not detected (< 0.03 mg N/L or 2.1 μM). The greatest nitrite loss occurred in the tryptophan solution (35%), followed by tyrosine (21%) and phenol (19%), and then humic acid (10%) and asparagine (5%). Nitrate formation was comparable in phenol, tryptophan, and tyrosine (11.1–11.7 µM), which was greater than that in humic acid (6.8 µM) and asparagine (3.4 µM). Tryptophan solution had the largest increase in DON (13.5 µM), suggesting that some of the inorganic nitrogen was incorporated into tryptophan, likely as a nitro-functional group (e.g., 6-nitrotryptophan).[62] Similarly, DON increased by 2.5 and 3.4 µM in phenol and tyrosine solutions, respectively, most likely attributable to the formation of nitrophenol moieties. If nitrophenol moieties were the major component of the new DON, they would fully account for the increase in TCNM-FP in phenol and tyrosine solutions (0.98–1.3 µg/mg C), based on the previously reported TCNM yields of nitrophenols (5.7%–7.2%).[48]

Figure 5. Concentrations of nitrite and nitrate, and the change in DON concentration after sunlight irradiation. Precursor compound concentration 5 mg C/L, equivalent to phenol 69.4 µM, tryptophan 37.9 µM, tyrosine 46.3 µM, and asparagine 104.2 µM. Solutions were buffered by 5 mM phosphate at pH 7.2. Initial nitrite concentration 1 mg N/L (71.4 µM). Samples were subject to simulated sunlight (320 W/m^2) for 8 h. Phe = phenol; HA = humic acid; Trp = tryptophan; Tyr = tyrosine; Asn = asparagine. Detection limits were 1.4 µM and 1.4 µM for NO_3^--N and NO_2^--N, respectively.



To evaluate whether total phenolic compound measurement can provide a useful indicator for the tendency of wastewater effluents to increase TCNM formation after sunlight irradiation in the presence of nitrite, the increase in TCNM-FP in 4 wastewater samples was plotted against their measured total phenolic compound concentration (Figure S8). In the presence of 2 mg/L nitrite, the increase in TCNM-FP predicted by total phenolic concentration is much lower than that observed in wastewater effluents, suggesting other wastewater constituents played a crucial role.

Further experiments were conducted to evaluate whether the model precursors would behave similarly under scenarios more closely simulating wastewater treatment processes. First, the effect of pre-chlorination (simulating wastewater disinfection) was evaluated (Table S6 and Figure S9). With pre-chlorination (2 mg/L as Cl_2, 30 min), the TCNM-FP of all precursor solutions still increased after irradiation, but the increase was 15–67% smaller for precursors with phenolic groups (humic acid, tyrosine, and phenol) compared with that without pre-chlorination. This can be attributed to the lower nitration efficiency of chlorophenols than phenols, which resulted in less formation of new TCNM precursors. Bruice et al. reported that the nitration of 4-chlorophenol was 40% slower than that of phenol.[65] In contrast, pre-chlorinated tryptophan solution showed the same increase in TCNM-FP as that without pre-chlorination, while pre-chlorinated asparagine solution showed higher TCNM-FP after sunlight irradiation that was not observed in the absence of pre-chlorination.

Second, the influence of wastewater matrix, including solution conditions and the presence of other precursors, were evaluated. Four model precursors humic acid, tryptophan, tyrosine, and phenol were spiked into a nitrified effluent C5, and processed the same as the non-spiked C5 sample; the TCNM-FP of all samples were compared (Table S6 and Figure S10). The spike of humic acid, tryptophan, and tyrosine into wastewater increased TCNM formation in the dark control samples (Table S6), as expected from them being known TCNM precursors. After irradiation, all precursor-spiked wastewater samples showed increased TCNM-FP, but the increase was less than that of the corresponding precursor solutions (except for tyrosine) and the non-spiked wastewater (Figure S10). These results were not attributed to the competition for light absorption between wastewater and nitrite, because similar nitrite decay (0.24–0.29 mg N/L) was observed in all samples. Instead, these results may be the net outcome of three competing processes: (a) the formation of new TCNM precursors (e.g., nitrophenols and nitrotryptophan), and the photodegradation of (b) these new precursors and (c) their parent compounds (e.g., tryptophan). In the presence of wastewater, photodegradation of precursors (processes b and c) can be enhanced due to the sensitized reactions by effluent organic matter.[66-68] For example, tryptophan photolysis was 2.7 times faster in the presence of 5 mg C/L fulvic acid,[67] and fulvic acid can account for up to 40% of DOC in wastewater effluent.[69] Between precursor-spiked and non-spiked samples, the lower increase in TCNM-FP in the spiked samples may be attributable to their higher DOC that led to more scavenging of reactive intermediates, which limited the formation of new precursors (process a). Further studies are needed to quantify the contribution of each process.

4. Environmental Implication

The findings of this study suggest that the TCNM-FP of fresh wastewater effluents may not be an accurate indicator for downstream water utilities regarding their risk of TCNM disinfection byproduct. After 8 h irradiation under simulated sunlight (equivalent to approximately 2–3 d under natural sunlight), 9 out of 14 wastewater effluents lost 17%–47% of their TCNM-FP. Of the other five samples, however, three showed no change, and two even showed 1.5- and 4.3-fold increase in TCNM-FP. Extended irradiation of four wastewater samples (36 h under simulated sunlight) showed further complication. Continuous decrease in TCNM-FP was only observed in a non-nitrified effluent with low nitrite and nitrate concentration. For the two nitrified effluents tested, TCNM-FP decreased in the first 8 h and then increased to a level higher than that of the original sample by the end of 36 h.

Nitrite concentration plays an important role in the increase in TCNM-FP of wastewater upon sunlight irradiation. The two wastewater samples with the highest nitrite concentrations (~0.8 mg N/L) showed increases in TCNM-FP. When two wastewaters were spiked with various concentrations of nitrite, an increase in TCNM-FP after irradiation was observed at nitrite concentrations as low as 0.2 mg N/L, and more significant increases were observed at higher nitrite concentrations. In the presence of ~1 mg N/L nitrite, 8 h of simulated sunlight irradiation increased the TCNM-FP of four wastewater samples by 0.3–3.6 μg/mg C. This is similar in magnitude to the reported increase in TCNM-FP resulted from pre-ozonation,[14, 17, 20] the most significant cause of elevated TCNM formation in drinking water treatment considered so far. Previously, source water high in nitrite concentration was considered at risk for TCNM, but only due to the promotion of TCNM formation by nitrite during chlorination.[28, 29] Our results suggest that the increase due to nitrite alone (i.e., in dark controls) was much smaller than that resulted from sunlight irradiation in the presence of nitrite. In other words, source waters with high nitrite concentrations may be at greater risks for TCNM than previously considered.

The combined sunlight and nitrite effect was also observed in buffered (pH 7.2) solutions of model compounds humic acid, tryptophan, tyrosine, and phenol, but not in asparagine solution. In the presence of 1 mg N/L nitrite, TCNM-FP increased by 11.8 and 4.1 μg/mg C for humic acid and tryptophan, respectively, higher than the 1.0–1.3 μg/mg C increase observed for tyrosine and phenol. These increases were likely attributable to the nitrating agents generated by nitrite photolysis. When the precursors were spiked into wastewater, TCNM-FP still increased after sunlight irradiation in the presence of nitrite, but the increase was smaller than that in simple buffered solutions, suggesting other processes were competing with the formation of TCNM precursors by nitration. These processes need to be identified in future studies to provide a more accurate assessment of TCNM risks for source waters impacted by wastewater and nitrite (e.g., from agricultural runoff). It is also recommended to consider the overlaying influence of wastewater treatment processes (e.g., biological treatment and final disinfection) and drinking water disinfection conditions.

Supporting Information

Materials; analytical details; additional figures and tables.

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References

1. Rice, J.; Westerhoff, P., Spatial and temporal variation in de facto wastewater reuse in drinking water systems across the USA. *Environ. Sci. Technol.* **2015,** *49* (2), 982-989.
2. Pionke, H. B.; Gburek, W. J.; Sharpley, A. N., Critical source area controls on water quality in an agricultural watershed located in the Chesapeake Basin. *Ecol. Eng.* **2000,** *14* (4), 325-335.
3. Hu, H. Y.; Du, Y.; Wu, Q. Y.; Zhao, X.; Tang, X.; Chen, Z., Differences in dissolved organic matter between reclaimed water source and drinking water source. *Sci. Total. Environ.* **2016,** *551*, 133-142.
4. Olness, A.; Smith, S. J.; Rhoades, E. D.; Menzel, R. G., Nutrient and sediment discharge from agricultural watersheds in Oklahoma. *J. Environ. Qual.* **1975,** *4* (3), 331-336.
5. Tomer, M. D.; Wilson, C. G.; Moorman, T. B.; Cole, K. J.; Heer, D.; Isenhart, T. M., Source-pathway separation of multiple contaminants during a rainfall-runoff event in an artificially drained agricultural watershed. *J. Environ. Qual.* **2010,** *39* (3), 882-895.
6. Mitch, W. A.; Krasner, S. W.; Westerhoff, P.; Dotson, A., *Occurrence and formation of nitrogenous disinfection byproducts*. Water Research Foundation: Denver, CO, USA., 2009.
7. Krasner, S. W.; Westerhoff, P.; Chen, B. Y.; Rittmann, B. E.; Nam, S. N.; Amy, G., Impact of wastewater treatment processes on organic carbon, organic nitrogen, and DBP precursors in effluent organic matter. *Environ. Sci. Technol.* **2009,** *43* (8), 2911-2918.
8. Leavey-Roback, S. L.; Krasner, S. W.; Suffet, I. H., Veterinary antibiotics used in animal agriculture as NDMA precursors. *Chemosphere* **2016,** *164*, 330-338.
9. Chen, W.-H.; Young, T. M., NDMA formation during chlorination and chloramination of aqueous diuron solutions. *Environ. Sci. Technol.* **2008,** *42* (4), 1072-1077.
10. Muellner, M. G.; Wagner, E. D.; McCalla, K.; Richardson, S. D.; Woo, Y. T.; Plewa, M. J., Haloacetonitriles vs. regulated haloacetic acids: Are nitrogen-containing DBPs more toxic? *Environ. Sci. Technol.* **2007,** *41* (2), 645-651.
11. Plewa, M. J.; Wagner, E. D.; Jazwierska, P.; Richardson, S. D.; Chen, P. H.; McKague, A. B., Halonitromethane drinking water disinfection byproducts: Chemical characterization and mammalian cell cytotoxicity and genotoxicity. *Environ. Sci. Technol.* **2004,** *38* (1), 62-68.
12. Richardson, S. D.; Plewa, M. J.; Wagner, E. D.; Schoeny, R.; DeMarini, D. M., Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutat. Res.-Rev. Mutat.* **2007,** *636* (1-3), 178-242.
13. McGuire, M. J.; McLain, J. L.; Obolensky, A., *Information Collection Rule Data Analysis*. AWWA Research Foundation and American Water Works Association: Denver, CO, 2002.
14. Hu, J.; Song, H.; Addison, J. W.; Karanfil, T., Halonitromethane formation potentials in drinking waters. *Water. Res.* **2010,** *44* (1), 105-114.
15. Hua, G.; Reckhow, D. A., Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. *Water. Res.* **2007,** *41* (8), 1667-1678.
16. Bougeard, C. M. M.; Goslan, E. H.; Jefferson, B.; Parsons, S. A., Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine. *Water. Res.* **2010,** *44* (3), 729-740.
17. Song, H.; Addison, J. W.; Hu, J.; Karanfil, T., Halonitromethanes formation in wastewater treatment plant effluents. *Chemosphere* **2010,** *79* (2), 174-179.

18. Yang, X.; Shen, Q. Q.; Guo, W. H.; Peng, J. F.; Liang, Y. M., Precursors and nitrogen origins of trichloronitromethane and dichloroacetonitrile during chlorination/chloramination. *Chemosphere* **2012,** *88* (1), 25-32.

19. Lee, W.; Westerhoff, P.; Croué, J.-P., Dissolved organic nitrogen as a precursor for chloroform, dichloroacetonitrile, *N*-nitrosodimethylamine, and trichloronitromethane. *Environ. Sci. Technol.* **2007,** *41* (15), 5485-5490.

20. Yang, X.; Shang, C.; Shen, Q.; Chen, B.; Westerhoff, P.; Peng, J.; Guo, W., Nitrogen origins and the role of ozonation in the formation of haloacetonitriles and halonitromethanes in chlorine water treatment. *Environ. Sci. Technol.* **2012,** *46* (23), 12832-12838.

21. Chuang, Y.-H.; Tung, H.-h., Formation of trichloronitromethane and dichloroacetonitrile in natural waters: Precursor characterization, kinetics and interpretation. *J. Hazard. Mater.* **2015,** *283*, 218-226.

22. Deng, L.; Huang, C. H.; Wang, Y. L., Effects of combined UV and chlorine treatment on the formation of trichloronitromethane from amine precursors. *Environ. Sci. Technol.* **2014,** *48* (5), 2697-2705.

23. Shan, J.; Hu, J.; Sule Kaplan-Bekaroglu, S.; Song, H.; Karanfil, T., The effects of pH, bromide and nitrite on halonitromethane and trihalomethane formation from amino acids and amino sugars. *Chemosphere* **2012,** *86* (4), 323-328.

24. Yang, X.; Fan, C.; Shang, C.; Zhao, Q., Nitrogenous disinfection byproducts formation and nitrogen origin exploration during chloramination of nitrogenous organic compounds. *Water. Res.* **2010,** *44* (9), 2691-2702.

25. Joo, S. H.; Mitch, W. A., Nitrile, aldehyde, and halonitroalkane formation during chlorination/chloramination of primary amines. *Environ. Sci. Technol.* **2007,** *41* (4), 1288-1296.

26. Shah, A. D.; Mitch, W. A., Halonitroalkanes, halonitriles, haloamides, and *N*-nitrosamines: A critical review of nitrogenous disinfection byproduct formation pathways. *Environ. Sci. Technol.* **2012,** *46* (1), 119-131.

27. McCurry, D. L.; Quay, A. N.; Mitch, W. A., Ozone promotes chloropicrin formation by oxidizing amines to nitro compounds. *Environ. Sci. Technol.* **2016,** *50* (3), 1209-1217.

28. Hu, J.; Song, H.; Karanfil, T., Comparative analysis of halonitromethane and trihalomethane formation and speciation in drinking water: The effects of disinfectants, pH, bromide, and nitrite. *Environ. Sci. Technol.* **2010,** *44* (2), 794-799.

29. Hong, H.; Qian, L.; Xiao, Z.; Zhang, J.; Chen, J.; Lin, H.; Yu, H.; Shen, L.; Liang, Y., Effect of nitrite on the formation of halonitromethanes during chlorination of organic matter from different origin. *J. Hydrol* **2015,** *531*, 802-809.

30. Thibaud, H.; de Laat, J.; Merlet, N.; Doré, M., Chloropicrin formation in aqueous solution: Effect of nitrites on precursors formation during the oxidation of organic compounds. *Water. Res.* **1987,** *21* (7), 813-821.

31. Shah, A. D.; Dotson, A. D.; Linden, K. G.; Mitch, W. A., Impact of UV disinfection combined with chlorination/chloramination on the formation of halonitromethanes and haloacetonitriles in drinking water. *Environ. Sci. Technol.* **2011,** *45* (8), 3657-3664.

32. Lyon, B. A.; Dotson, A. D.; Linden, K. G.; Weinberg, H. S., The effect of inorganic precursors on disinfection byproduct formation during UV-chlorine/chloramine drinking water treatment. *Water. Res.* **2012,** *46* (15), 4653-4664.

33. Reckhow, D. A.; Linden, K. G.; Kim, J.; Shemer, H.; Makdissy, G., Effect of UV treatment on DBP formation. *J. Am. Water Works Ass.* **2010,** *102* (6), 100-113.

34. Chen, B. Y.; Nam, S. N.; Westerhoff, P. K.; Krasner, S. W.; Amy, G., Fate of effluent organic matter and DBP precursors in an effluent-dominated river: A case study of wastewater impact on downstream water quality. *Water. Res.* **2009,** *43* (6), 1755-1765.

35. Du, Y.; Zhang, X.; Li, C.; Wu, Q. Y.; Huang, H.; Hu, H. Y., Transformation of DON in reclaimed water under solar light irradiation leads to decreased haloacetamide formation potential during chloramination. *J. Hazard. Mater.* **2017,** *340*, 319-325.

36. Woods, G. C.; Dickenson, E. R. V., Natural attenuation of NDMA precursors in an urban, wastewater-dominated wash. *Water. Res.* **2016,** *89*, 293-300.

37. Wu, Q. Y.; Li, C.; Wang, W. L.; He, T.; Hu, H. Y.; Du, Y.; Wang, T., Removal of fluorescence and ultraviolet absorbance of dissolved organic matter in reclaimed water by solar light. *J. Environ. Sci.* **2016,** *43*, 118-127.

38. Bronk, D. A.; Roberts, Q. N.; Sanderson, M. P.; Canuel, E. A.; Hatcher, P. G.; Mesfioui, R.; Filippino, K. C.; Mulholland, M. R.; Love, N. G., Effluent organic nitrogen (EON): bioavailability and photochemical and salinity-mediated release. *Environ. Sci. Technol.* **2010,** *44* (15), 5830-5835.

39. Wu, Q. Y.; Li, C.; Du, Y.; Wang, W. L.; Huang, H.; Hu, H. Y., Elimination of disinfection byproduct formation potential in reclaimed water during solar light irradiation. *Water. Res.* **2016,** *95*, 260-267.

40. Wu, J.; Ye, J.; Peng, H. L.; Wu, M. R.; Shi, W. W.; Liang, Y. M.; Liu, W., Solar photolysis of soluble microbial products as precursors of disinfection by-products in surface water. *Chemosphere* **2018,** *201*, 66-76.

41. Mack, J.; Bolton, J. R., Photochemistry of nitrite and nitrate in aqueous solution: a review. *J. Photoch. Photobio. A* **1999,** *128* (1), 1-13.

42. Vione, D.; Maurino, V.; Minero, C.; Pelizzetti, E., New processes in the environmental chemistry of nitrite: nitration of phenol upon nitrite photoinduced oxidation. *Environ. Sci. Technol.* **2002,** *36* (4), 669-676.

43. Su, L.; Sivey, J. D.; Dai, N., Emerging investigator series: sunlight photolysis of 2,4-D herbicides in systems simulating leaf surfaces. *Environ. Sci.-Proc. Imp.* **2018,** *20* (8), 1123-1135.

44. Xu, J.; Tran, T. N.; Lin, H.; Dai, N., Removal of disinfection byproducts in forward osmosis for wastewater recycling. *J. Membrane Sci.* **2018,** *564*, 352-360.

45. Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental Organic Chemistry*. 2nd ed.; Wiley: Hoboken, NJ, 2003.

46. Chen, B.; Westerhoff, P., Predicting disinfection by-product formation potential in water. *Water. Res.* **2010,** *44* (13), 3755-3762.

47. EPA, U. S., National Primary Drinking Water Regulations. In.

48. Merlet, N.; Thibaud, H.; Dore, M., Chloropicrin formation during oxidative treatments in the preparation of drinking water. *Sci. Total Environ.* **1985,** *47*, 223-228.

49. Zhou, F.; Li, X.; Zeng, Z., Determination of phenolic compounds in wastewater samples using a novel fiber by solid-phase microextraction coupled to gas chromatography. *Anal. Chim. Acta* **2005,** *538* (1), 63-70.

50. Croue, J.-P.; Korshin, G. V.; Benjamin, M., *Characterization of Natural Organic Matter in Drinking Water* AwwaRF report 90780 ed.; AWWA: Denver, CO, 2000.

51. Confer, D. R.; Logan, B. E.; Aiken, B. S.; Kirchman, D. L., Measurement of dissolved free and combined amino acids in unconcentrated wastewaters using high performance liquid chromatography. *Water Environ. Res.* **1995,** *67* (1), 118-125.

52. Chapter 5 Elementary Composition of Humic Acids and Fulvic Acids. In *Developments in Soil Science*, Kumada, K., Ed. Elsevier: 1987; Vol. 17, pp 70-94.

53. Borkman, R. F.; Hibbard, L. B.; Dillon, J., The photolysis of tryptophan with 337.1 nm laser radiation. *Photochem. Photobiol.* **1986,** *43* (1), 13-19.

54. Fischer, M.; Warneck, P., Photodecomposition of nitrite and undissociated nitrous acid in aqueous solution. *J. Phys. Chem.* **1996,** *100* (48), 18749-18756.

55. Coddington, J. W.; Hurst, J. K.; Lymar, S. V., Hydroxyl radical formation during peroxynitrous acid decomposition. *J. Am. Chem. Soc.* **1999,** *121* (11), 2438-2443.

56. Koppenol, W. H., The basic chemistry of nitrogen monoxide and peroxynitrite. *Free Radical Bio. Med.* **1998,** *25* (4), 385-391.

57. Igarashi, N.; Onoue, S.; Tsuda, Y., Photoreactivity of amino acids: Tryptophan-induced photochemical events via reactive oxygen species generation. *Anal. Sci.* **2007,** *23* (8), 943-948.

58. Bent, D. V.; Hayon, E., Excited state chemistry of aromatic amino acids and related peptides. III. Tryptophan. *J. Am. Chem. Soc.* **1975,** *97* (10), 2612-2619.

59. Bent, D. V.; Hayon, E., Excited state chemistry of aromatic amino acids and related peptides. I. Tyrosine. *J. Am. Chem. Soc.* **1975,** *97* (10), 2599-2606.

60. Golanoski, K. S.; Fang, S.; Del Vecchio, R.; Blough, N. V., Investigating the mechanism of phenol photooxidation by humic substances. *Environ. Sci. Technol.* **2012,** *46* (7), 3912-3920.

61. Chu, C.; Erickson, P. R.; Lundeen, R. A.; Stamatelatos, D.; Alaimo, P. J.; Latch, D. E.; McNeill, K., Photochemical and nonphotochemical transformations of cysteine with dissolved organic matter. *Environ. Sci. Technol.* **2016,** *50* (12), 6363-6373.

62. Alvarez, B.; Rubbo, H.; Kirk, M.; Barnes, S.; Freeman, B. A.; Radi, R., Peroxynitrite-dependent tryptophan nitration. *Chem. Res. Toxicol.* **1996,** *9* (2), 390-396.

63. Goldstein, S.; Czapski, G.; Lind, J.; Merenyi, G., Tyrosine nitration by simultaneous generation of $^{\bullet}NO$ and $O_2^{\bullet-}$ under physiological conditions - How the radicals do the job. *J. Biol. Chem.* **2000,** *275* (5), 3031-3036.

64. Yamakura, F.; Ikeda, K., Modification of tryptophan and tryptophan residues in proteins by reactive nitrogen species. *Nitric Oxide* **2006,** *14* (2), 152-161.

65. Bruice, T. C.; Gregory, M. J.; Walters, S. L., Reactions of tetranitromethane. I. Kinetics and mechanism of nitration of phenols by tetranitromethane. *J. Am. Chem. Soc.* **1968,** *90* (6), 1612-1619.

66. Kawaguchi, H., Determination of direct and indirect photolysis rates of 2-chlorophenol in humic acid solution and natural waters. *Chemosphere* **1992,** *25* (5), 635-641.

67. Janssen, E. M. L.; Erickson, P. R.; McNeill, K., Dual roles of dissolved organic matter as sensitizer and quencher in the photooxidation of tryptophan. *Environ. Sci. Technol.* **2014,** *48* (9), 4916-4924.

68. Boreen, A. L.; Edhlund, B. L.; Cotner, J. B.; McNeill, K., Indirect photodegradation of dissolved free amino acids: The contribution of singlet oxygen and the differential reactivity of DOM from various sources. *Environ. Sci. Technol.* **2008,** *42* (15), 5492-5498.

69. Ma, H.; Allen, H. E.; Yin, Y., Characterization of isolated fractions of dissolved organic matter from natural waters and a wastewater effluent. *Water. Res.* **2001,** *35* (4), 985-996.