Supporting Information for

Evaluating Interferences in the External Calibration Method for Hydroxyl Radical Scavenging Capacity Measurement

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1. Collimated beam setup diagram

Figure S1 shows the diagram of collimated beam setup to generate radical species. The setup was used for •OH and non-•OH species generation and to measure OH radical scavenging capacity. The lamp enclosed was a 17-W low pressure mercury UV lamp (GPH357T5L/4, Atlantic Ultraviolet Corporation), and the fluence rate at the surface of the water was approximately 140 $\mu W/cm^2$.

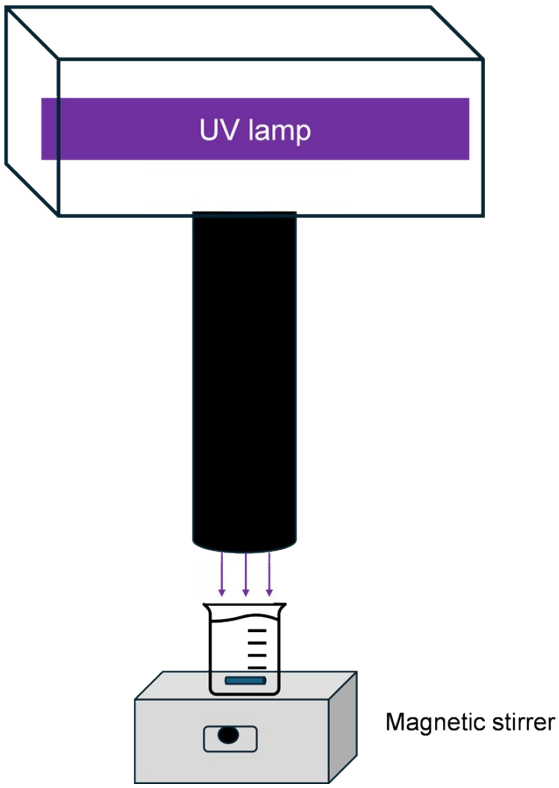

Fig. S1: Collimated beam setup diagram; a magnetic stirrer was used to continuously mix the sample while being exposed to UV light.

2. Quenching residual chloramines

A stock solution of chloramine was prepared by mixing NH_4Cl and NaOCl in Milli-Q water at a 1:1 molar ratio. This chloramine solution was then added to the synthetic water to create a range

of chloramine concentrations from 0 to 12 mg/L as Cl_2. After 30 minutes, the chloramine concentrations in the samples were measured using a HACH colorimeter (HACH 58700 Pocket Colorimeter Chlorine MR/HR). After chloramine addition, each sample was split in two: one part was measured for HRSC without quenching chloramines, while the other part's HRSC was measured after precisely chloramine quenching using sulfite or bisulfite. The scavenging capacity was determined using the external calibration method with a collimated beam apparatus (Fig. S1) as described by Wang et al.[1]

Excess addition of sulfite or bisulfite would result in an error in the measurement of scavenging capacity. It is therefore required to use the precise stoichiometric quantity of sulfite (or bisulfite) to completely quench chloramines. In this regard, sodium sulfite (or sodium bisulfite) was incrementally added to the sample and then the total residual chlorine concentration after each addition was measured. A curve demonstrating the residual chlorine concentration (as Cl_2) against the volume of Na_2SO_3 (or $NaHSO_3$) stock solution added was created. The dose of sulfite (or bisulfite) required to precisely quench the residual total chlorine is determined by extending the curve of residual total chlorine against sulfite (or bisulfite) dose to the point where the residual total chlorine reaches zero.

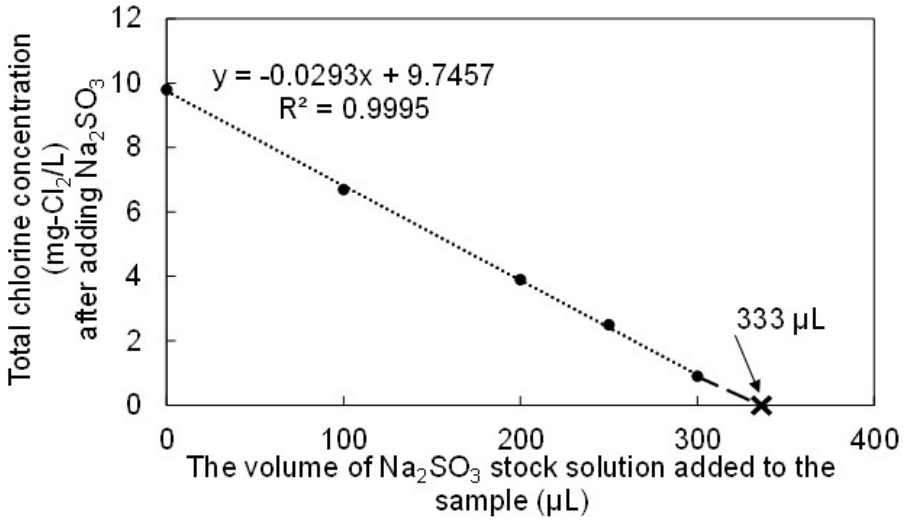

Fig. S2: Residual concentration of total chloramine (mg- Cl_2/L) in diluted tap water sample (TOC < 0.3 mg-C/L) after incrementally addition of Na_2SO_3 at room temperature. The intersection point represents zero total chloramine concentration, and 333 µL is the calculated volume of Na_2SO_3 stock solution, determined from the plot equation, which is required to completely consume all chloramines.

3. Effect of bromide on H_2O_2 decay

Fig. S3 shows the decay of H_2O_2 (initial concentration: 50 mg/L) in Milli-Q water in the presence of bromide (0, 2, and 10 mg/L) after 6 min of UV exposure. The extent of H_2O_2 decay was minimal and was not expected to affect the hydroxyl radical generation rate.

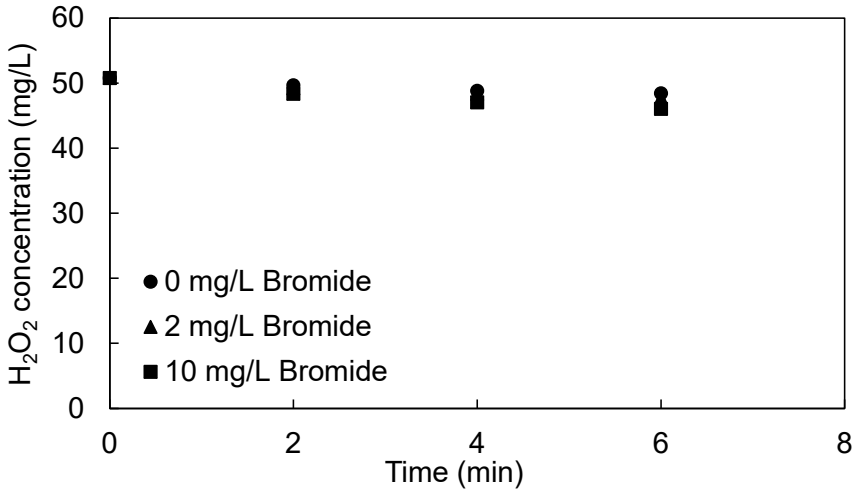

Fig. S3: Decay of H_2O_2 in the presence of different concentrations of bromide under the UV exposure over time in Milli-Q water and at the room temperature. Error bars indicate the min and max of the duplicated samples.

4. Chloramine species proportion in total chlorine

Fig. S4 indicates the proportion of monochloramine and dichloramine at different concentrations of total chlorine in synthetic water at pH = 5.5. Mono and dichloramine concentrations were measured by Indophenol method using the HACH Monochlor-F reagents. As shown in Fig. S4, both mono- and dichloramine were present in the sample (approximately 20–30% dichloramine and 70–80% monochloramine). The concentration of trichloramine and free chlorine were negligible.

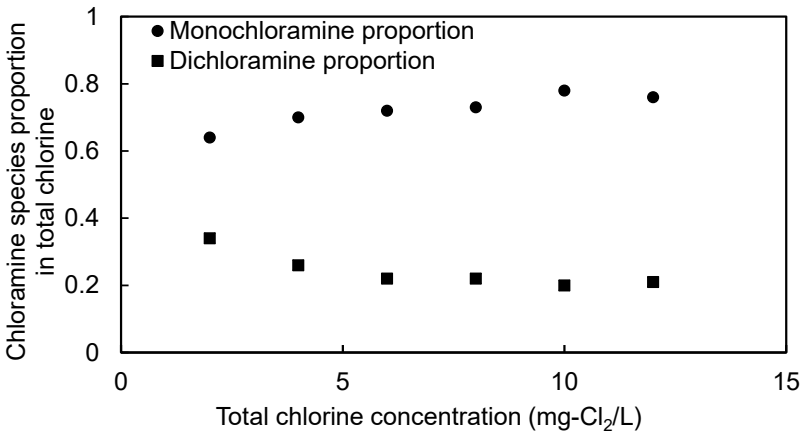

Fig. S4: The proportion of monochloramine and dichloramine at different concentrations of total chlorine at pH=5.5 and room temperature in diluted tap water (TOC < 0.3mg-C/L). The graph shows single experimental data.

5. Quenching chloramines with bisulfite

Fig. S5 shows the HRSC of samples before and after quenching chloramines using sodium bisulfite in the synthetic water sample. Sodium bisulfite decreased the pH level to a low as 3.8 at a dosage of 5.8 mg/L, potentially invalidating the calibration curve. The reason for this impact on the calibration curve is not clear, but one possible explanation could be related to the molecular structure of methylene blue which changes at low pH levels. This is supported by a slight increase in absorbance (6%) at the dye's signature wavelength of 664 nm when pH is reduced from higher levels to lower one (e.g., ≤4), as shown in Fig. S6.

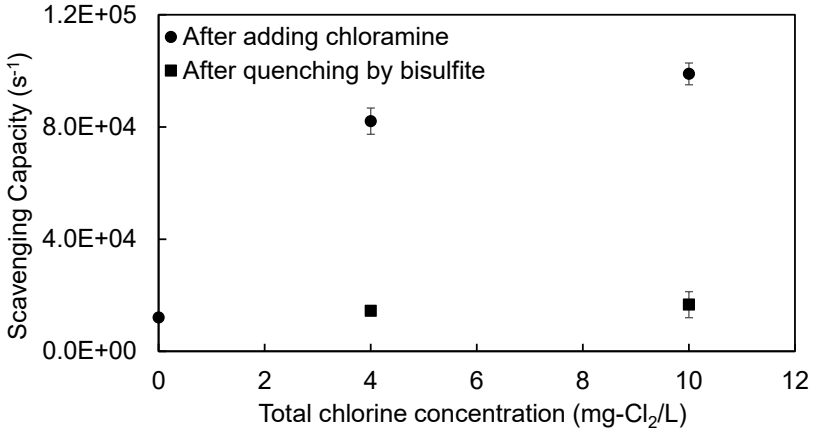

Fig. S5: Scavenging capacity of samples before and after quenching chloramine using sodium bisulfite in diluted tap water at room temperature (initial pH = 5.5 and TOC < 0.3 mg-C/L). Error bars indicate the min and max of the duplicated samples.

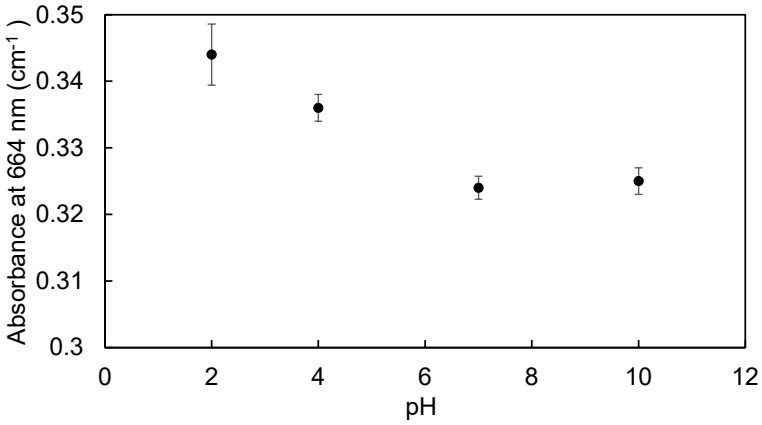

Fig. S6: Methylene blue (MB) absorbance (at 664 nm) at different pH levels in Milli-Q water at room temperature ([MB] = ~5 μM). Error bars indicate the min and max of the duplicated samples.

6. Statistical analysis result

Statistical analysis of the slopes of MB decay curves (Fig. 1 and Fig. 2) indicated that, in most cases, MB decay rates in the presence of radicals were not significantly different from those under direct photolysis ($p > 0.05$), suggesting negligible reactivity between MB and non-•OH radical species. A significant difference was observed only in the presence of humic acid ($p < 0.001$), likely attributable to its light-attenuating effect.

Table S1. Statistical analysis of Fig. 1: significance of MB decay rates under different conditions and direct photolysis using t-tests

Condition	p-Value	Significance
1.47 mM H_2O_2, 5 μM MB and 20 mM Carbonate	0.23	Not Significant
14.7 mM H_2O_2, 5 μM MB and 20 mM Carbonate	0.09	Not Significant

Table S2. Statistical analysis of Fig. 2: significance of MB decay rates under different conditions and direct photolysis using t-tests

Condition	p-Value	Significance
650 mM IPA	0.10	Not Significant
700 mM Methanol	0.42	Not Significant
113 mM Phenol	0.14	Not Significant
800 mM Acetone	0.44	Not Significant
10 mM Ethanol	0.11	Not Significant
250 mM Acetonitrile	0.10	Not Significant
100 mM Acetic Acid	0.20	Not Significant
~ 13 mM Humic Acid (as C)	<0.001	Significant

Reference

1. Wang, C.; Rosenfeldt, E.; Li, Y.; Hofmann, R., External Standard Calibration Method To Measure the Hydroxyl Radical Scavenging Capacity of Water Samples. *Environmental science & technology* **2020,** *54*, (3), 1929-1937.