

## **Aquatic photochemistry of sulfamethazine: Multivariate effects of main water constituents and mechanisms**

Yingjie Li, Xiangliang Liu, Biaojun Zhang, Qun Zhao, Ping Ning\*, Senlin Tian\*

Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, 650500, China

10 Pages, 3 Tables, 8 Figures

- Text S1** Chemicals
- Text S2** Quantum yields calculation.
- Text S3** Correction for light screening of DOM.
- Text S4** Laser flash photolysis experiment.
- Table S1** Factor definitions, coding levels, and design points for the four-factor central composite design
- Table S2** Experimental parameters and the observed photolytic rate constants for sulfamethazine photodegradation
- Table S3** Observed photodegradation constants and quantum yields for direct photodegradation of sulfamethazine under different conditions at pH = 6.
- Fig. S1** Irradiance spectrum of the simulated sunlight and ultraviolet absorption spectra of sulfamethazine in three pH solution (red line pH = 2, blue line pH = 5, violet line pH = 10).
- Fig. S2** Photolytic rate constants of sulfamethazine in the presence of DOM.
- Fig. S3** Degradation of sulfamethazine in the presence of H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub><sup>·-</sup> in the dark.
- Fig. S4** Observed photolytic rate constants of sulfamethazine under different conditions. 2-AN and BP represent 2-acetonaphthone and benzophenone, respectively.
- Fig. S5** Transient decay of triplet-excited 2-acetonaphthone and benzophenone monitored at λ = 440 nm and λ = 515 nm with different concentrations of DOM in the deoxygenated solutions, respectively.
- Fig. S6** Absorbance spectra of sulfamethazine solutions (20 μM) in the absence (black line)/presence (red line) of 50 μM Cu<sup>2+</sup>.
- Fig. S7** O<sub>2</sub><sup>·-</sup> generation kinetics in the presence of HA (10 mg C/L) and Cu<sup>2+</sup> (50 μM) with irradiation as shown by the reduction of XTT (400 μM) at pH = 6
- Fig. S8** Full-scan MS and MS/MS spectral of main photoproducts of sulfamethazine.

---

\*Corresponding author e-mail: ningping58@163.com; tiansenlin@outlook.com

**Text S1. Chemicals.**

Sulfamethazine (99%) and humic acid (HA, Cat no. 449752) were purchased from Sigma-Aldrich. Sodium nitrate (99%), sodium bicarbonate (99.5%), Sodium Peroxodisulfate (99%) and copper sulfate (98%) were from Tianjin Kemiou Chemical Reagent (China). 1,4-diazabicyclo[2.2.2]octane (DABCO), sorbic acid (99%), *p*-benzoquinone (98%), benzophenone (99%), and 2-acetonaphthone (98%), *p*-nitroanisole (97%) were obtained from J&K Scientific (China). Acetonitrile, isopropanol, and pyridine were of HPLC grade and from Sigma-Aldrich. Ultra pure water was obtained from a Millipore-Milli Q system. This water was used to prepare photolytic solutions and HPLC eluent. Other chemical reagents were of analytical grade and were used as received without further purification.

**Text S2. Quantum yields calculation.**

The quantum yields of sulfamethazine ( $\Phi_s$ ) was calculated using the chemical actinometer (*p*-nitroanisole/pyridine). For details on the calculation of  $\Phi_s$ , see the recently published paper by Laszakovits et al.<sup>1</sup>

**Text S3. Correction for light screening of humic acid (HA).**

The correction factor ( $f_c$ ) for light screening can be calculated as (Xie et al., 2013):

$$f_c = \frac{\sum L_\lambda \varepsilon_\lambda^s S_\lambda}{\sum L_\lambda \varepsilon_\lambda^s S_\lambda^0} \quad (\text{S1})$$

$$S_\lambda = \frac{1 - 10^{-(\varepsilon_\lambda^s C_s + \varepsilon_\lambda^c C_c)l}}{2.303(\varepsilon_\lambda^s C_s + \varepsilon_\lambda^c C_c)l} \quad (\text{S2})$$

where  $L_\lambda$  is the incident light intensity at a given wavelength  $\lambda$ ;  $\varepsilon_\lambda^s$  and  $\varepsilon_\lambda^c$  are the molar absorptivity of sulfamethazine and HA, respectively.  $C_s$  and  $C_c$  are the concentrations of sulfamethazine and HA, respectively.  $S_\lambda$  is the light screening factor in photolytic solutions, and  $S_0$  is the  $S_\lambda$  value when  $C_c = 0$ ;  $l$  is the average length of the optical paths. Dark controls were performed under the same conditions but without light irradiation, and all experiments

were performed in triplicate. The total organic carbon concentrations of HA were determined by a TOC analyzer after the water samples were acidified with 1 M HCl and purged with nitrogen.

***Text S4. Laser flash photolysis (LFP) experiment.***

To identify the triplet-excited state, a nanosecond LFP apparatus (LP920-S, Edinburgh Instruments Ltd.) was employed. The third harmonic (355 nm) oscillation of a Q-switched Nd<sup>3+</sup>:YAG laser (Quantel Brilliant, 64 mJ/pulse, 7 ns fwhm) was employed for the excitation of aromatic ketones. LFP was also employed to obtain CO<sub>3</sub><sup>·-</sup> by irradiation of the mixture of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> with HCO<sub>3</sub><sup>-</sup>.<sup>2</sup> Samples containing 0.4 M HCO<sub>3</sub><sup>-</sup> with 50 mM S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and various sulfamethazine concentrations were excited at 266 nm (HCO<sub>3</sub><sup>-</sup>+S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) of a Q-switched Nd<sup>3+</sup> : YAG laser. A 500 W xenon lamp was adopted as the probe light. The temporal profiles were recorded using a monochromator (TMS300) equipped with a photomultiplier (Hamamatsu R928) and a digital oscilloscope (Tektronix, TDS3012C). The transient absorption spectra were measured by an intensified charged-coupled device (CCD) with a gate time of 1.5 μs and a 0.2 μs time delay (Andor Technology, DH720). To prevent quenching of the triplet excited species by dissolved oxygen, nitrogen was bubbled to the solutions for 30 min.

Table S1. Factor definitions, coding levels, and design points for the four-factor central composite design

Factor	Factor concentration levels				
coded factor levels	-2	-1	0	1	2
X <sub>1</sub> : Cu <sup>2+</sup> (μmol/L)	0.00	5	10	15	20
X <sub>2</sub> : HA (mg C/L)	0.00	2.5	5	7.5	10
X <sub>3</sub> : NO <sub>3</sub> <sup>-</sup> (μmol/L)	0.00	25	50	75	100
X <sub>4</sub> : HCO <sub>3</sub> <sup>-</sup> (μmol/L)	0.00	50	100	150	200

Table S2. Experimental parameters and the observed photolytic rate constants for sulfamethazine photodegradation at pH = 6.

run	Cu <sup>2+</sup> ( $\mu$ M)	HA (mg C/L)	NO <sub>3</sub> <sup>-</sup> ( $\mu$ M)	HCO <sub>3</sub> <sup>-</sup> ( $\mu$ M)	$k_{\text{obs}}$ (h <sup>-1</sup> )	$R^2$
1	10	0	50	100	0.110 $\pm$ 0.006	0.995
2	5	2.5	25	50	0.130 $\pm$ 0.005	0.999
3	15	7.5	75	150	0.189 $\pm$ 0.015	0.996
4	10	5	50	100	0.174 $\pm$ 0.009	0.999
5	15	7.5	75	50	0.180 $\pm$ 0.005	0.999
6	20	5	50	100	0.177 $\pm$ 0.006	0.995
7	15	2.5	75	150	0.138 $\pm$ 0.012	0.999
8	15	7.5	25	50	0.176 $\pm$ 0.022	0.998
9	5	2.5	25	150	0.136 $\pm$ 0.011	0.998
10	15	2.5	25	50	0.143 $\pm$ 0.023	0.996
11	10	5	50	100	0.170 $\pm$ 0.010	0.996
12	10	5	50	200	0.160 $\pm$ 0.011	0.998
13	15	2.5	75	50	0.148 $\pm$ 0.002	0.998
14	10	5	50	100	0.162 $\pm$ 0.007	0.996
15	10	5	50	100	0.167 $\pm$ 0.011	0.997
16	10	5	100	100	0.161 $\pm$ 0.015	0.996
17	10	5	50	100	0.162 $\pm$ 0.025	0.999
18	10	5	50	0	0.079 $\pm$ 0.005	0.994
19	10	10	50	100	0.178 $\pm$ 0.013	0.999
20	15	7.5	25	150	0.175 $\pm$ 0.016	0.987
21	5	7.5	75	150	0.153 $\pm$ 0.011	0.998

## Supplementary Materials

22	5	7.5	75	50	$0.147 \pm 0.004$	0.999
23	15	2.5	25	150	$0.134 \pm 0.007$	0.998
24	5	7.5	25	50	$0.135 \pm 0.004$	0.999
25	10	5	50	100	$0.167 \pm 0.022$	0.998
26	5	2.5	75	150	$0.133 \pm 0.019$	0.999
27	5	2.5	75	50	$0.127 \pm 0.011$	0.999
28	5	7.5	25	150	$0.163 \pm 0.031$	0.998
29	0	5	50	100	$0.156 \pm 0.010$	0.997
30	10	5	0	100	$0.159 \pm 0.003$	0.998

Table S3. Observed photodegradation constants and quantum yields for direct photodegradation of sulfamethazine under different conditions at pH = 6.

	$k_{\text{obs}}$ ( $\text{h}^{-1}$ )	$\Phi/10^{-3}$
Sulfamethazine	$0.036 \pm 0.003$	0.15
Sulfamethazine+Cu <sup>2+</sup>	$0.046 \pm 0.004$	0.20

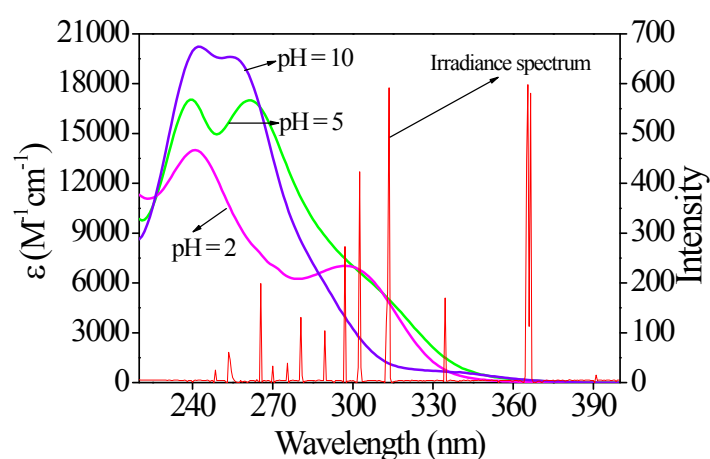


Fig. S1. Irradiance spectrum of the simulated sunlight and ultraviolet absorption spectra of sulfamethazine in three pH solution.

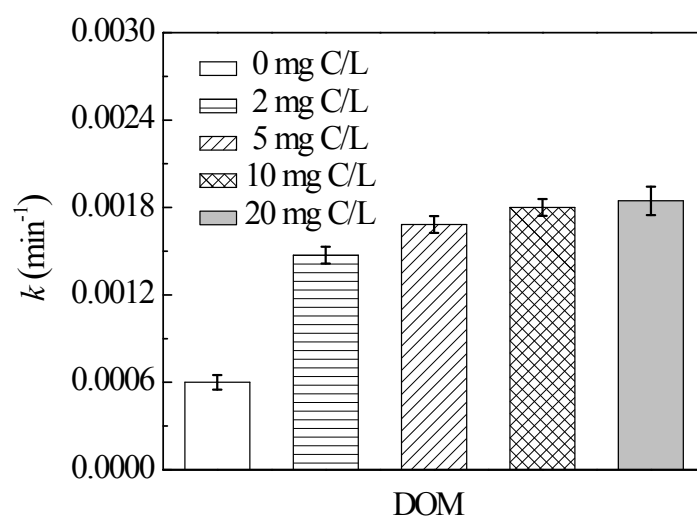


Fig. S2 Observed photolytic rate constants of sulfamethazine in the presence of HA.

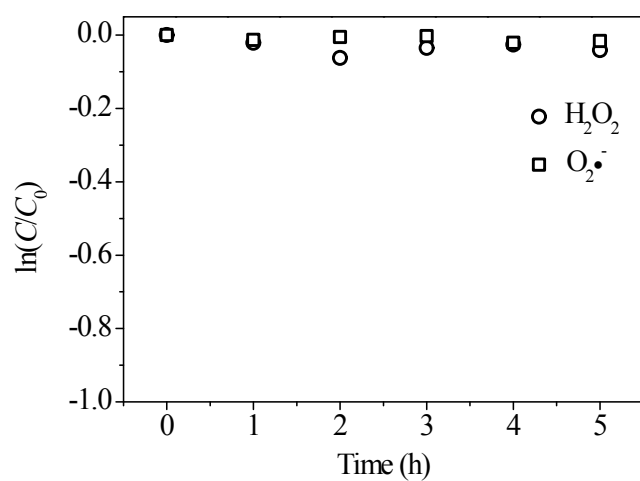


Fig. S3 Degradation of sulfamethazine in the presence of  $\text{H}_2\text{O}_2$  or  $\text{O}_2^{\cdot-}$  in the dark.

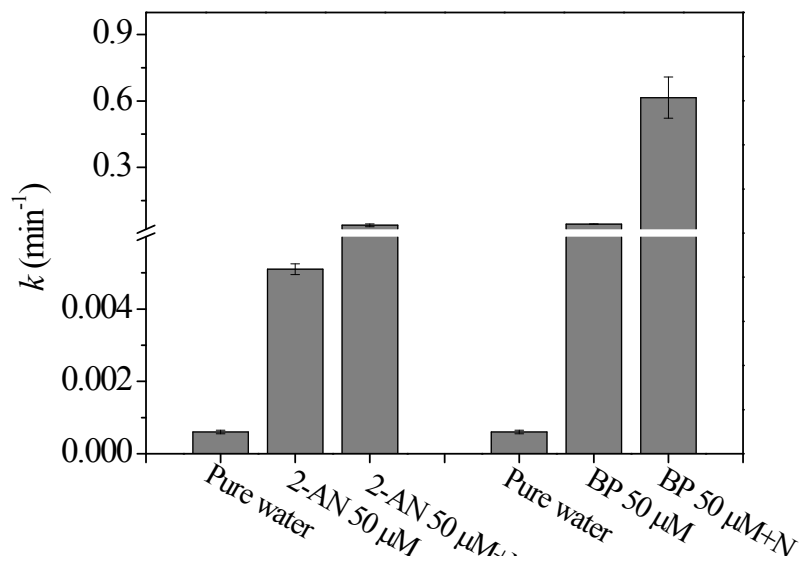


Fig. S4 Observed photolytic rate constants of sulfamethazine under different conditions. 2-AN and BP represent 2-acetonaphthone and benzophenone, respectively.

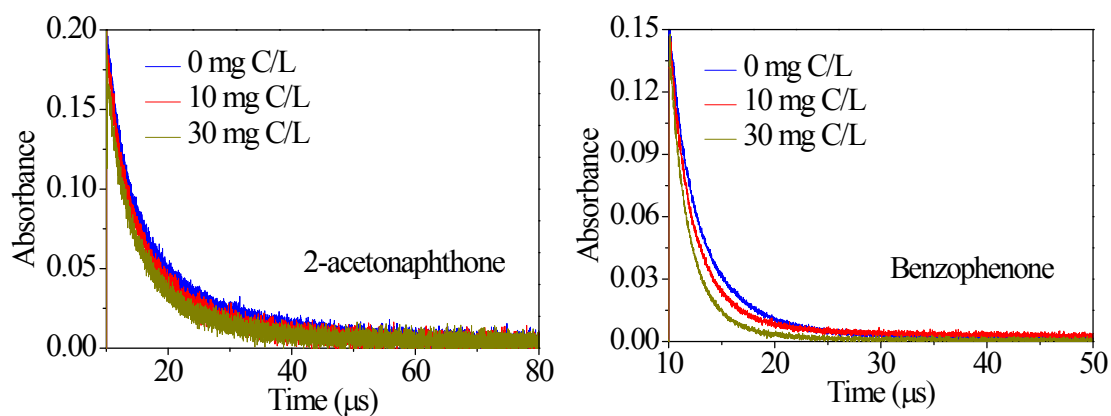


Fig. S5 Transient decay of triplet-excited 2-acetonaphthone and benzophenone monitored at  $\lambda = 440$  nm and  $\lambda = 515$  nm with different concentrations of HA in the deoxygenated solutions, respectively.

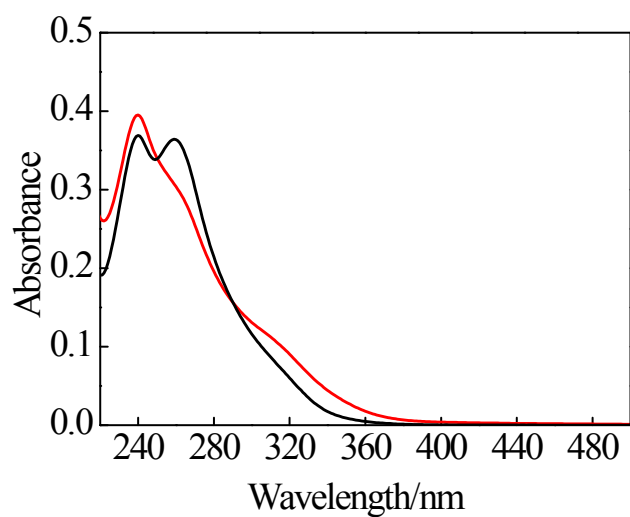


Fig. S6 Absorbance spectra of sulfamethazine solutions (20  $\mu\text{M}$ ) in the absence (black line)/presence (red line) of 50  $\mu\text{M}$   $\text{Cu}^{2+}$  at pH = 6.

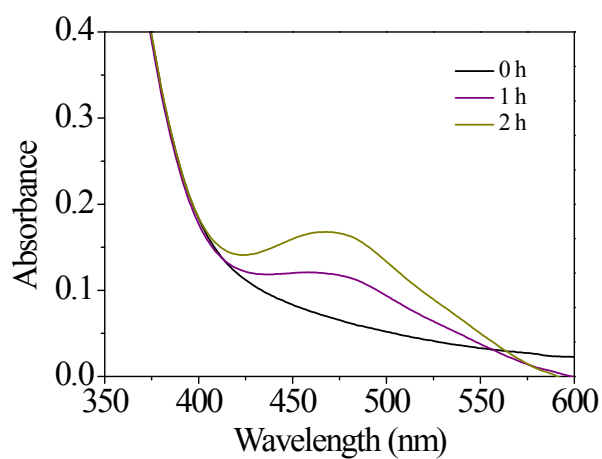


Fig. S7  $\text{O}_2^{\cdot-}$  generation kinetics in the presence of HA (10 mg C/L) and  $\text{Cu}^{2+}$  (50  $\mu\text{M}$ ) with irradiation as shown by the reduction of XTT (400  $\mu\text{M}$ ) at pH = 6.



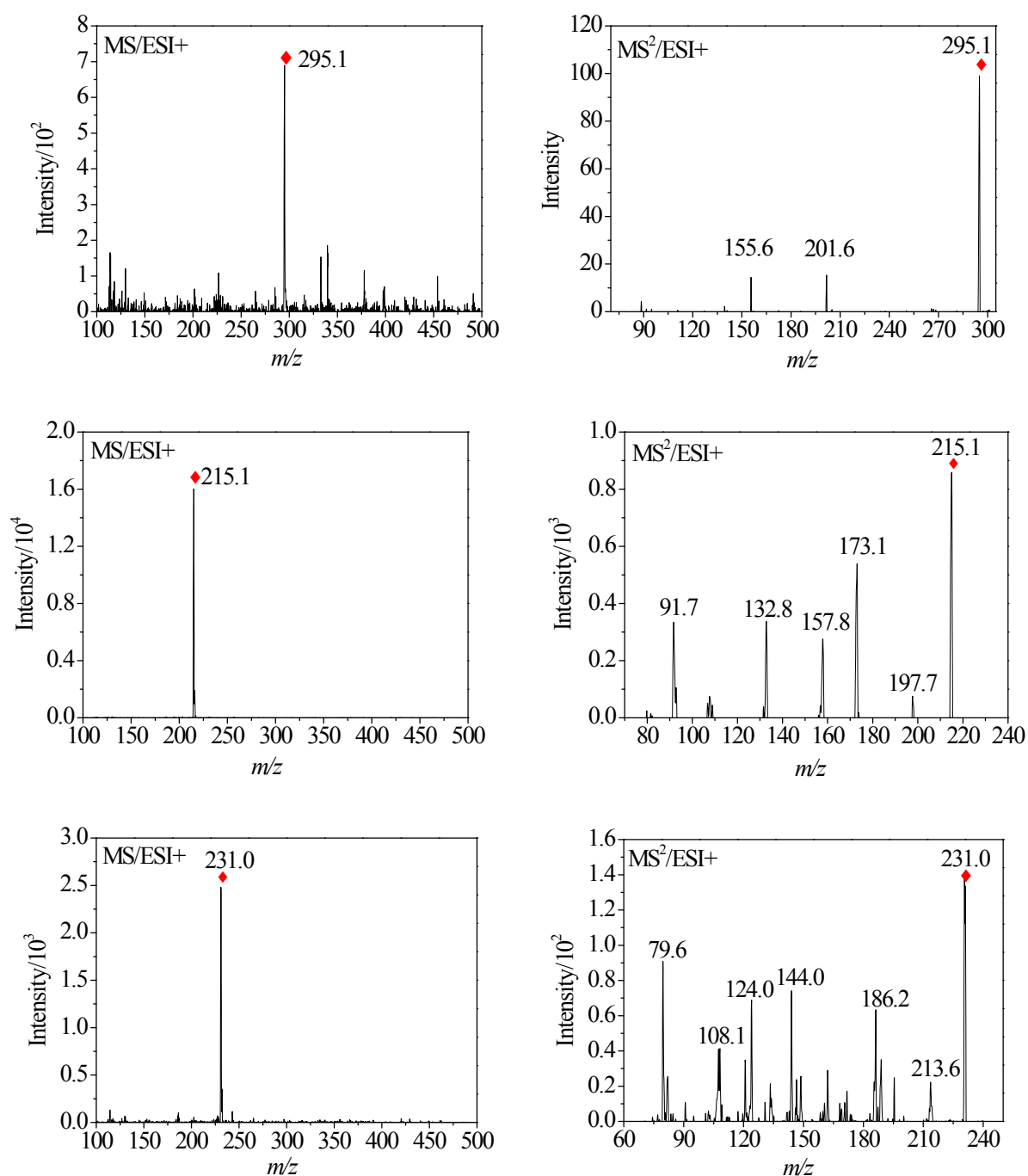


Fig. S8 Full-scan MS and MS/MS spectral of main photoproducts of sulfamethazine.

## References

- 1 J. R. Laszakovits, S. M. Berg, B. G. Anderson, J. E. O'Brien, K. H. Wammer, C. M. Sharpless, p-Nitroanisole/pyridine and p-nitroacetophenone/pyridine actinometers revisited: Quantum yield in comparison to ferrioxalate, *Environ. Sci. Technol. Lett.*, 2017, **4**, 11-14,

DOI: 10.1021/acs.estlett.6b00422, ISSN: 2328-8930

2 S. Canonica, T. Kohn, M. Mac, F. J. Real, J. Wirz, U. von Gunten, Photosensitizer method to determine rate constants for the reaction for carbonate radical with organic compounds, *Environ. Sci. Technol.*, 2005, **39**, 9182-9188, DOI: 10.1021/es051236b, ISSN: 0013-936X.