Supplementary information

Combined effects of dissolved organic matter, pH, ionic strength and halides on photodegradation of oxytetracycline in simulated estuarine waters

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Number of texts: 1; Number of figures: 6; Number of tables: 3; Number of pages: 9

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Text S1. Calculation of photolysis rate constant and molar absorptivity for different species of OTC.

OTC photolysis followed pseudo-first order kinetics. The apparent degradation rate contributes by each component in the system:

$$-\frac{\mathrm{d}c}{dt} = k_{\mathrm{obs}} \bullet c = k_1 \bullet c_1 + k_2 \bullet c_2 + \cdots + k_i \bullet c_i \quad (1)$$

where c is the concentration of different species, k_{obs} (min^{-1}) is the observed first order rate constant of OTC in different pH solutions, k_{i} (min^{-1}) is the first order rate constant of each individual species. The equation can be changed to:

$$k_{\mathrm{obs}} = \alpha_1 \bullet k_1 + \alpha_2 \bullet k_2 + \cdots + \alpha_i \bullet k_i \quad (2)$$

where α_{i} is the fraction of each species at different pH and at different time during the irradiation. The α_{i} values can be calculated with the pKa (3.22, 7.46, and 8.94) of OTC as the time tends to be zero at the initial time.

Set A, K_{obs}, K_{i} as the matrix of $\alpha_1 \sim \alpha_{\mathrm{ij}}$, $k_{\mathrm{obs}}{}^{1} \sim k_{\mathrm{obs}}{}^{\mathrm{j}}$, and $k^1 \sim k^{\mathrm{i}}$. i represents the total number of species (4 in this study). j represents the total pH conditions (6 in this study). The independent rate constant of each species was then derived with:

$$K_{\mathrm{i}} = (A^{-1} \bullet A)^{\mathrm{T}} \bullet A^{-1} \bullet K_{\mathrm{obs}} \quad (3)$$

While calculating the molar absorptivity for different species of OTC, K_{obs} and K_{i} were replaced by E_{j} and E_{i}, which are the matrix of molar absorptivity for OTC at different pH and for each species of OTC, respectively.

The quantum yield of each OTC species was calculated from the individual rate constant and the molar absorption coefficient with the following equation:[1]

$$\Phi = \frac{-k_i}{2.303\Sigma(I_\lambda \cdot \varepsilon_\lambda)(S/V)l} \quad (4)$$

Where I_λ is the incident light intensity at wavelength λ (Einstein cm^{-2} s^{-1}); ε_λ is the molar absorption coefficient of OTC (cm^{-1} L mol^{-1}); S is the exposed area (cm^2); V is the volume of solution (mL); l is the light path length (cm).

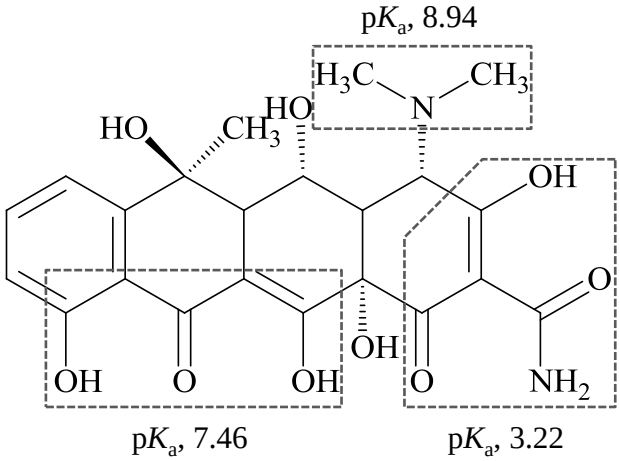

Fig. S1 Molecular structure and dissociation positions of ciprofloxacin.

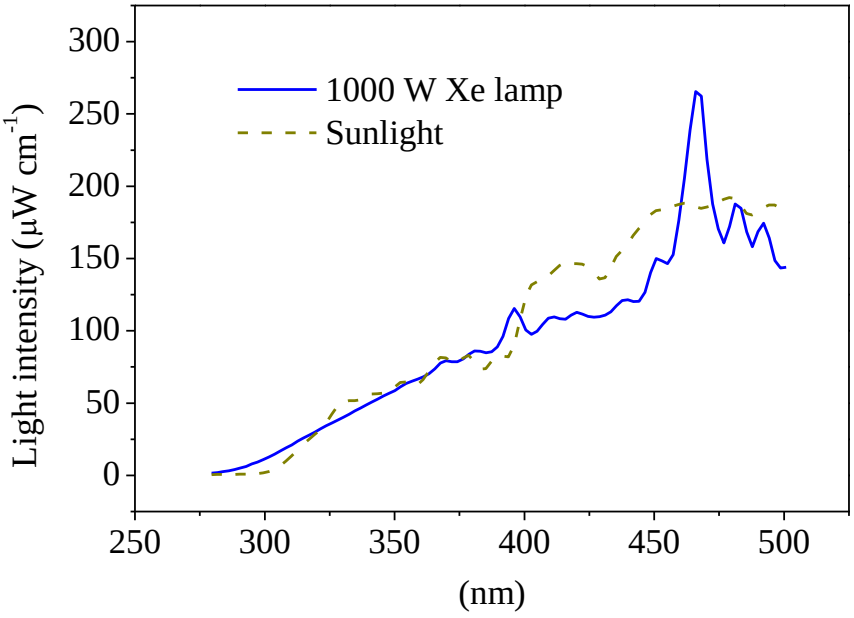

Fig. S2 The 1000 W Xe lamp and sunlight irradiation spectra (The sunlight irradiation spectrum was measured at midsummer in Dalian, China (38°53′29.9″N and 121°32′4.1″E)).

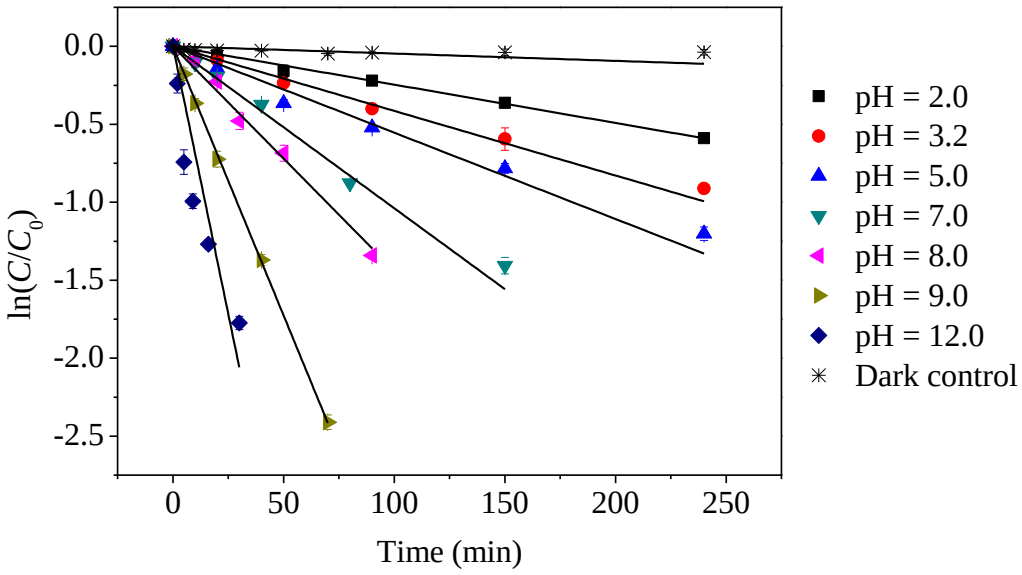

Fig. S3 Direct photolysis kinetics of OTC at different pH.

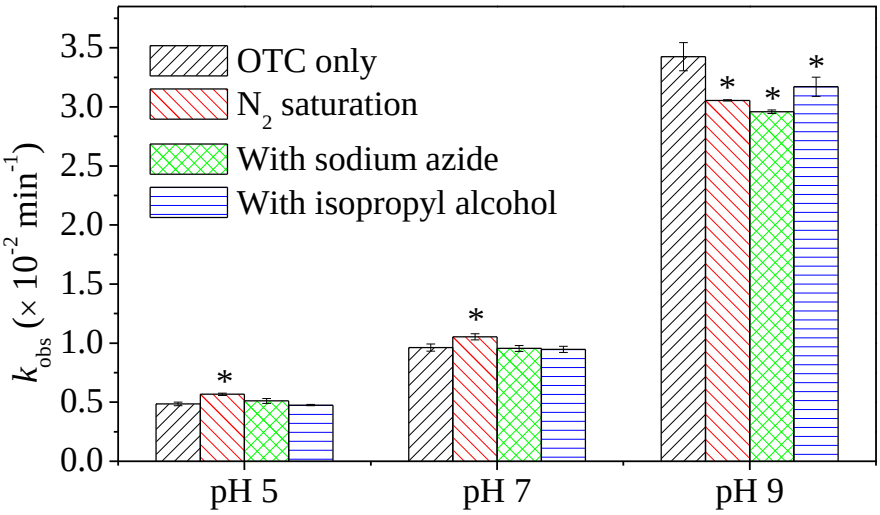

Fig. S4 Observed first-order photolysis rate constants (k_{obs}) OTC in different conditions (* stands for significant difference, $p < 0.05$, $n = 3$; the error bars represent the 95% confidence interval, $n = 3$).

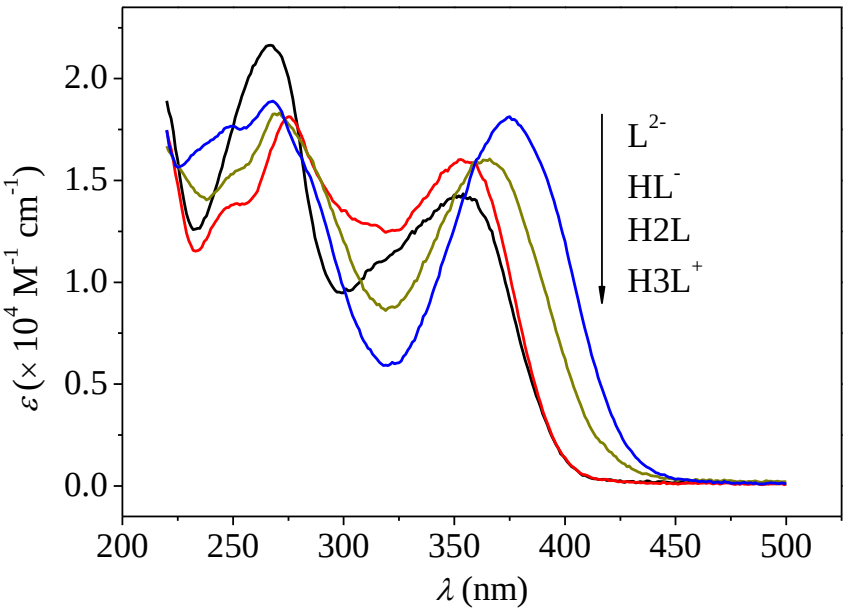

Fig. S5 Calculated molar absorptivity of different species of OTC.

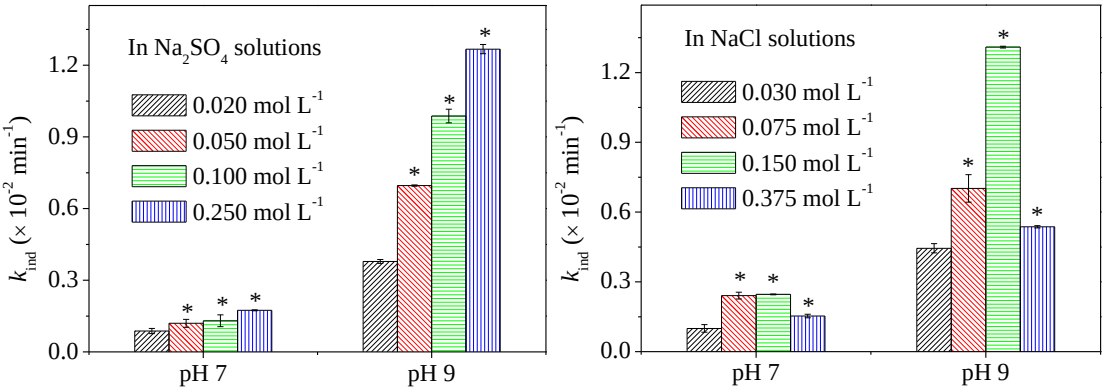

Fig. S6 SRNOM induced indirect photolysis rate constants (k_{ind}) of OTC in Na_2SO_4 and NaCl solutions at pH 7.0 and 9.0 (* stands for significant difference, $p < 0.05$, $n = 3$; the error bars represent the 95% confidence interval, $n = 3$).

Table S1 Fractions of $H3L^{+}$, H2L, HL^{-}, and L^{2-} in different pH solutions.

pH	$H3L^{+}$	H2L	HL^{-}	L^{2-}
2.0	0.943	0.057	0.000	0.000
3.2	0.511	0.489	0.000	0.000
5.0	0.016	0.980	0.004	0.000
6.0	0.002	0.965	0.033	0.000
7.0	0.000	0.740	0.257	0.003
8.0	0.000	0.205	0.713	0.082
9.0	0.000	0.013	0.459	0.528
12.0	0.000	0.000	0.001	0.999

*The fractions were calculated with p*K*a of 3.22, 7.46, and 8.94 for OTC

Table S2 Observed first-order photolysis rate constants (k_{obs}) of OTC in the absence and presence of SRNOM, integrated light screening coefficient ($S_{290\text{-}455}$) of SRNOM, SRNOM induced indirect photolysis rate constants (k_{ind}) of OTC in different pH solutions, and the percentage of k_{ind} (P_{ind}) (The unit for k_{obs} and k_{ind} is $\times 10^{-2}$ min^{-1})

pH	k_{obs}	With 5 mg L^{-1} SRNOM				With 10 mg L^{-1} SRNOM			
		k_{obs}	$S_{290\text{-}455}$	k_{ind}	P_{ind} %	k_{obs}	$S_{290\text{-}455}$	k_{ind}	P_{ind} %
2.0	0.239 ± 0.007	0.233 ± 0.003	0.737	0.056 ± 0.005	24.2	0.146 ± 0.006	0.703	-0.022 ± 0.006	-15.2
3.2	0.378 ± 0.012	0.311 ± 0.006	0.716	0.040 ± 0.009	13.0	0.275 ± 0.010	0.682	0.017 ± 0.007	6.2
5.0	0.486 ± 0.013	0.414 ± 0.005	0.708	0.070 ± 0.009	16.9	0.405 ± 0.010	0.671	0.079 ± 0.008	19.5
7.0	0.963 ± 0.014	0.911 ± 0.03	0.721	0.216 ± 0.007	23.7	0.787 ± 0.026	0.693	0.120 ± 0.007	15.2
8.0	1.520 ± 0.021	1.433 ± 0.025	0.729	0.325 ± 0.008	22.7	1.340 ± 0.050	0.704	0.270 ± 0.007	20.2
9.0	3.425 ± 0.054	3.167 ± 0.067	0.716	0.714 ± 0.009	22.5	3.054 ± 0.040	0.695	0.674 ± 0.007	22.1
12.0	5.572 ± 0.078	5.027 ± 0.110	0.703	1.112 ± 0.007	22.1	5.011 ± 0.110	0.668	1.287 ± 0.007	25.7

*The errors of k_{obs} and k_{ind} represent 95% confidence levels, n = 3.

Table S3 Observed first-order photolysis rate constants (k_{obs}) of OTC in the absence and presence of SRNOM in Na_2SO_4, NaCl, and NaBr solutions with the same ionic strength at different pH (The unit for k_{obs} is $\times 10^{-2}$ min^{-1}).

Conditions		pH			
		6.0	7.0	8.0	9.0
Na_2SO_4	OTC	0.849 ± 0.041	0.963 ± 0.006	1.520 ± 0.001	3.425 ± 0.079
	OTC + SRNOM	0.648 ± 0.013	0.787 ± 0.006	1.340 ± 0.018	3.054 ± 0.097
NaCl 0.075 mol L^{-1}	OTC	0.864 ± 0.018	0.971 ± 0.015	1.526 ± 0.011	3.568 ± 0.013
	OTC + SRNOM	0.666 ± 0.012	0.914 ± 0.025	1.441 ± 0.015	3.173 ± 0.068
NaBr 0.075 mol L^{-1}	OTC	0.900 ± 0.018	1.025 ± 0.006	1.548 ± 0.007	3.820 ± 0.096
	OTC + SRNOM	0.711 ± 0.010	1.031 ± 0.025	1.506 ± 0.044	3.516 ± 0.035
NaBr (0.80 mmol L^{-1}) + Na_2SO_4	OTC	0.852 ± 0.021	0.965 ± 0.016	1.535 ± 0.015	3.597 ± 0.042
	OTC + SRNOM	0.651 ± 0.012	0.795 ± 0.010	1.402 ± 0.024	3.195 ± 0.114
NaCl (0.075 mol L^{-1}) + NaBr (0.80 mmol L^{-1})	OTC	0.858 ± 0.015	0.964 ± 0.012	1.515 ± 0.014	3.562 ± 0.019
	OTC + SRNOM	0.694 ± 0.013	1.013 ± 0.025	1.501 ± 0.015	3.453 ± 0.058

*The errors of k_{obs} represent 95% confidence levels, n = 3.

References

1. X. Jin, H. Xu, S. Qiu, M. Jia, F. Wang, A. Zhang and X. Jiang, Direct photolysis of oxytetracycline: Influence of initial concentration, pH and temperature, *J. Photochem. Photobiol. A– Chem.*, 2017, **332**, 224–231.