Aqueous multivariate phototransformation kinetics of dissociated tetracycline: Implications for the photochemical fate in surface waters

Linke Ge[a,1], Qianqian Dong[b,1], Crispin Halsall[c], Chang-Er L. Chen[d], Jun Li[a], Degao Wang[b], Peng Zhang[a,]*, Ziwei Yao[a]

[a]Key Laboratory for Ecological Environment in Coastal Areas (SOA), National Marine Environmental Monitoring Center, Dalian 116023, China

[b]School of Environmental Science and Technology, Dalian Maritime University, Dalian 116023, China

[c]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[d]Department of Environmental Science and Analytical chemistry, Stockholm University, Stockholm 10691, Sweden

[1]These authors contributed equally to this work.

---

* Corresponding author. Tel.: +86 411 8478 2819; fax: +86 411 8478 2586.
E-mail address: pzhang@nmemc.org.cn (P. Zhang).

ABSTRACT

A~~Many a~~ntibiotics are ubiquitous pollutants in aquatic systems and can ~~they~~ exist as different dissociated species~~ion~~ depending on the pH of the system and the chemical in question.. ~~species in surface waters~~. New knowledge of their multivariate photochemical behavior (i.e. the photochemcial behaviour of different ionised forms) is needed to improve our understanding on the fate and possible remediation of these pharmaceuticals in surface and waste waters.~~better their risk assessment~~. In this study, the photochemical degradation of aqueous tetracycline (TC), one of the most widely ~~detected~~ used? antibiotics, and its dissociated forms (TCH$_2^0$, TCH$^-$ and TC^{2-})~~,~~ was investigated.~~one of the most widely detected antibiotics, was employed as a case to differentiate the distinct kinetics of apparent photolysis and ROS photooxidation for the dissociation forms (TCH~~$_2^0$~~, TCH~~$^-$ ~~and TC~~$^{2-}$). Simulated sunlight experiments and matrix calculations indicated that the three dissociated~~ion~~ species had dissimilar photolytic kinetics and photooxidation reactivities. TC^{2-} photodegraded the fastest due to direct ~~in the apparent~~ photolysis, followed by TCH$^-$ and TCH$_2^0$, whereas ~~. And~~ TCH$^-$ was found to be the most highly reactive towards •OH, while TC^{2-} reacted the fastest with $^1O_2$. Water with relatively high pH (e.g ~8-10) favours the dissociated forms of TCH$^-$ and TC^{2-} which are most susceptible to photochemical loss processes compared to neutral TC. The calculated corresponding environmental half-lives ($t_{1/2,E}$) in sunlit surface waters ranged from 0.05 h for pH = 9 in midsummer to 3.68 h for pH = 6 in midwinter at 45°N latitude. Adjusting the pH to slightly alkaline conditions prior to UV or solar UV light treatment may be an effective way of enhancing the photochemical removal of TC from contaminated water (e.g. wastewater). ~~The multivariate photochemical processes was dominated by apparent photolysis (especially in summer, 62% – 91%), followed by~~ ~~$^1O_2$~~ ~~and •OH oxidation. These results clarified the phototransformation kinetics of dissociated TC, which is significant for bettering the fate and risk assessment of ionizable emerging pollutants in the aqueous~~

Formatted: Strikethrough

Formatted: Not Superscript/ Subscript

Formatted: Not Superscript/ Subscript

Formatted: Not Superscript/ Subscript

~~environments.~~

Keywords: Tetracycline; Dissociation; Apparent photolysis; Hydroxyl radicals; Singlet oxygens; Environmental half-lives

1. Introduction

Antibiotics, the largest group of pharmaceuticals and personal care products (PPCPs), are ubiquitous in ~~the ~~aquatic environments~~s~~ (Schwarzenbach et al., 2006) (Luo et al., 2011) (Kolpin et al., 2002). They are of ~~acute ~~concern as they ~~as their pseudo-persistence and many of them ~~can promote environmental bacterial resistance which is recognized through the ~~,~~ spread of antibiotic-~~-~~resistant~~ce~~ genes that can~~and ~~subsequently threaten ~~the ~~human~~n’s~~ health if this resistance is present in bacterial pathogens (Shah et al., 2012) (Martinez, 2009). Recently, tetracycline antibiotics (TCs) have received growing ~~great ~~attention due to their wide spread use~~persisting~~ and increasing application in aquaculture, animal husbandry, and use in general medical treatments (Liu et al., 2017; Zhang et al., 2015) (Pulicharla et al., 2017). This~~e~~ extensive use results in the environmental occurrence of these compounds with ~~.~~ ~~To date, ~~increasing detection of TCs in ~~the ~~aquatic environments across many industrialised regions including countries like China where antibiotic use is extensive ~~ has been reported worldwide ~~(Kummerer, 2009) (Bu et al., 2013). ~~Particularly, the pollutants exist widely in China surface waters ~~(Fig. S1). To undertake an accurate risk assessment to protect human and environmental health then a more thorough understanding of the aquatic behaviour of ~~better the fate and risk assessment of ~~TCs is required, especially as these compounds are susceptible to photo-transformation/degradation under a variety of environmental conditions.~~in aquatic systems, understanding their pertinent environmental behavior is of vital importance.~~

~~The photochemical behavior of TCs is of concern, as photodegradation is a key factor in determining their environmental fate and ecological risk~~. TCs ~~They ~~can absorb sunlight directly and undergo apparent photolysis, including direct photolysis and self-sensitized photooxidation. The photolytic rate has been found to be ~~was ~~highly dependent on water chemistry parameters such as hardness and pH (Werner et al., 2006) (Wammer et al., 2011)

(Chen et al., 2011) (Jiao et al., 2008c) (Jiao et al., 2008b). Also, TCs may undergo indirect photodegradation or sensitized photooxidation mediated by the photogenerated reactive oxygen species (ROS) from dissolved organic matter (DOM), Fe(III) salts and nitrate present in surface waters~~.~~ Under solar and solar-simulated light (xenon lamp) irradiation (λ > 290 nm), ~~an~~ elevated TC photolysis efficiency was observed in the presence of ~~certain concentration~~ DOM, NO$_3^-$ and Fe(III). Radicals such as~~;~~ hydroxyl radicals (•OH) and ~~as well as~~ singlet oxygen~~s~~ ($^1O_2$) can ~~were found in the~~ mediate~~d~~ TC photodegradation. (Niu et al., 2013) (Jiao et al., 2008c) (Chen et al., 2008). Moreover, TCs can be phototransformed into more toxic intermediate products. For example, Niu et al. (Niu et al., 2013) and Jiao et al. (Jiao et al., 2008c) investigated the photomodified toxicities of TC to luminescent bacteria, and found that the phototransformed ~~more toxic~~ intermediates were more toxic than the parent TC~~generated~~. These studies ~~are constructive, and~~ indicate that photodegradation is an important transformation pathway that can give rise to degradation products that may be of ~~more~~ concern and rank alongside ~~than~~ the parent chemical~~s~~. Many antibiotics including TCs have a number of dissociated forms depending on the pH of the water ~~, affecting the aqueous fate and ecological risk of the antibiotics. However, new insights into photochemical behavior of TCs are necessary for their accurate persistence and risk assessment~~. These ~~.~~

In addition to apparent photolysis, ROS photooxidation may play a significant role in the phototransformation of organic pollutants. In sunlit surface waters with many coexisting photoreactive species such as DOM, Fe(III) and NO$_3^-$, the photoinduced ·OH and $^1O_2$ are most important transient oxidants. The •OH show less selectivity to oxidize most organic chemicals, while $^1O_2$ limit environmental reactions to compounds like polycyclic aromatics, pyrroles, and phenolate anions (Mill, 1999) (Keen and Linden, 2013) (Yao et al., 2013). Some previous studies indicated that photooxidation by •OH and $^1O_2$ was an important factor in determining the fate of antibiotics such as sulfa drugs (Boreen et al., 2004, 2005), nitrofurans

(Edhlund et al., 2006) and fluoroquinolones (Ge et al., 2015). However, reactivities of TCs towards the ROS and their corresponding environmental fate remain unknown. Furthermore, it is currently unclear how the bimolecular rate constants ($k_{\bullet \mathrm{OH}}$ and $k_{1\mathrm{O2}}$) differ for various dissociated species of TCs.

Commented [HC1]: All of this text is good but greatly lengthens the Introduction, plus we've already mentioned indirect photochemistry earlier on. I suggest that this is deleted or key points incorporated in the earlier paragraph re: indirect photochemistry

Here in this study, we employed tetracycline (TC, Fig. 1) as a model compound to study the multivariate photochemical behavior: apparent photolysis and ROS photooxidation. The molecular structure of TC has four ionizable moieties, and TC may exhibit five dominant dissociated~~ion~~ forms in water (Fig. 1). In the conditions of most fresh and sea waters (pH = 6 – 9), TC chiefly exists as ~~mainly presents in the~~ three species: TCH_2^0, TCH^- and TC^{2-}, which are the focus of ~~concerned in~~ this~~e~~ study. The objectives were~~are~~ to differentiate the phototransformation kinetics of the different species, calculate the corresponding environmental half-lives in sunlit surface waters, and assess ~~weigh~~ the relative contributions of individual photochemical reactions to the fate of TC in general ~~this antibiotics~~. To the best of our knowledge, this is the first comprehensive report on the aqueous multivariate phototransformation kinetics and fate of different dissociated TC.

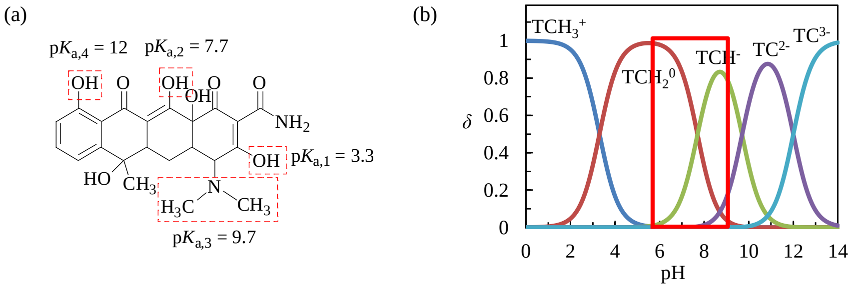

Fig. 1. Chemical structure (a) and dissociation species distribution (b) of tetracycline

2. Materials and Methods

2.1. Apparent photolysis experiments

Tetracycline (TC) with > 98% purity was provided by J&K Technology Co., Ltd.

Information of the other chemicals used are shown in Table S1. A merry-go-round photochemical reactor with a Pyrex-filtered and water-refrigerated high-pressure mercury lamp (500 W) was used to carry out the photochemical experiments. Pyrex-filtered mercury lamps were usually employed to simulate solar radiation ($\lambda > 290$ nm) (Dolinová et al., 2006; Matykiewiczová et al., 2007; Ziolli and Jardim, 2003). The emission spectrum of the light source was showed in our previous studies (Ge et al., 2009) (Ge et al., 2016). Reaction solutions (5 μmol L^{-1}) were added into quartz tubes and the reaction temperature was controlled at 25 ± 1 °C.

The absorption spectra (ε_{λ}) and apparent photolytic rate constants (k_{ap}) of TC were measured at the desired pH 6, 8 and 10, which were adjusted with HCl/NaOH. To determine quantum yields (Φ), a *p*-nitroanisole/pyridine actinometer was irradiated concurrently with TC photolysis (Dulln and Mill, 1982; Edhlund et al., 2006). Futhermore, to differentiate the $\varepsilon_{\lambda,i}$, $k_{ap,i}$ and Φ_i of the different dissociated~~ion~~ forms, matrix calculations were performed according to previous studies (Boreen et al., 2004) (Wei et al., 2013).

2.2. Determination of the ROS oxidation reactivities

To explore the •OH/$^1O_2$ reactivities, competition kinetics was used to determine the second-order rate constants k_{ROS} (i.e., $k_{\bullet OH}$ and k_{1O2}) for reactions of aqueous TC (pH = 6, 8 and 10) with •OH/$^1O_2$. The •OH and $^1O_2$ were photogenerated by 100 mM H_2O_2 and 20 μM perinaphthenone, respectively. The reference compounds were acetophenone (10 μM) and furfuryl alcohol (20 μM), respectively. Incident light was filtered~~trated~~ using~~by~~ 400 nm cut-off filters. Under the irradiation with $\lambda > 400$ nm, apparent photodegradation of the reference compounds can be avoided, while TC might suffer apparent photolysis. Therefore, ~~So,~~ to correct the interference of the TC apparent photolysis, control experiments without the photosensitizers (H_2O_2 and perinaphthenone) were performed, and the k_{AP} in the competition kinetic experiments was calculated according ~~referring~~ to Shemer et al. (Shemer et al., 2006).

The k_{ROS} values of TC were calculated with the following equation:

$$k_{\mathrm{ROS}} = \frac{(k_{\mathrm{CKE}} - k_{\mathrm{AP}})}{k_{\mathrm{CKE,R}}} k_{\mathrm{ROS,R}} \qquad (1)$$

where the $k_{\mathrm{CKE\ and}}$ $k_{\mathrm{CKE,R}}$ are apparent degradation rate constants of TC and the reference compounds in the competition kinetic experiments, respectively. And $k_{\mathrm{ROS,R}}$ represent the second-order rate constants of the reference compounds, $k_{\bullet\mathrm{OH,R}} = 5.9 \times 10^9$ M^{-1} s^{-1} and $k_{\mathrm{1O2,R}} = 1.2 \times 10^8$ M^{-1} s^{-1}。 Irradiation experiments and dark controls were carried out ~~at least~~ in triplicate.

Formatted: English (United Kingdom)

2.3. Analytical Determination~~s~~

A Waters UPLC coupled with a BEH C18 chromatographic column and a PDA eλ detector was employed to quantify TC, *p*-nitroanisole, acetophenone and furfuryl alcohol. UV−vis absorption spectra were recorded using a Hitachi U-2800 spectrophotometer. The analytical details are provided in Table S2.

3. Results and discussion

3.1. Apparent photolytic kinetics of the dissociation species

No significant loss of the target TC was observed in all dark controls, eliminating the possibilities of thermal and hydrolytic degradation or other losses. The UV~~−~~vis absorption spectra were run under different pH conditions, which indicated the light absorption of TC at $\lambda > 290$ nm (Fig. S2). As expected from the spectra, the target compound underwent apparent photolysis but at varying rates according to the ~~with the matrix~~ pH. As shown in Fig. 2 and Table S3, pseudo-first-order kinetics was followed with strong correlation coefficients ($R^2 > 0.95$). Furthermore, the rate constants (k_{ap}) were found to be elevated with increasing pH ~~increasing~~, which can be explained by its red shift in absorption spectra from pH 6 to pH 10. The pH dependence of k_{ap} was also found in previous studies (Werner et al., 2006) (Niu et al., 2013) (Jiao et al., 2008c), although~~. However,~~ these studies did not differentiate the distinct kinetics for each dissociated~~ion~~ species of TC.

The $k_{ap,i}$ and quantum yields of photodegradation (~~-~~Φ_i~~-~~) of the different dissociated~~ion~~ forms (i) are listed in Table 1, which shows that TC^{2-} photodegraded the fastest, followed by TCH^- and TCH_2^0. Theoretically, $k_{ap,i}$ can be expressed as Eq. 2,

Formatted: Font: Not Italic

Formatted: Font: Italic

$$k_{ap,i} \;=\; 2.303\Phi_i\sum(L_\lambda\varepsilon_{\lambda,i}) \qquad (2)$$

Formatted: English (United Kingdom)

Formatted: English (United Kingdom)

Formatted: Font: Not Italic, Not Superscript/ Subscript

Where L is the light irradiance and ε_λ is the molar extinction coefficient. Thus, the magnitude of $k_{ap,i}$ is dependent of Φ_i as well as the cumulative light absorption, $\sum(L_\lambda\varepsilon_{\lambda,i})$. As can be seen from Table 1, the Φ_i values varied significantly. The Φ_i ratio was calculated as 100:145:7094 for TC^{2-}, TCH^- and TCH_2^0. Their $\sum(L_\lambda\varepsilon_{\lambda,i})$ ratio was 100:106:105, suggesting that their light absorption was comparable. Therefore, it is Φ_i for the different dissociated~~ion~~ species that dominates their $k_{ap,i}$ values. Wei et al. (Wei et al., 2013) also found that the Φ_i plays a crucial role in determining the $k_{ap,i}$ of dissociated fluoroquinolone antibiotics.

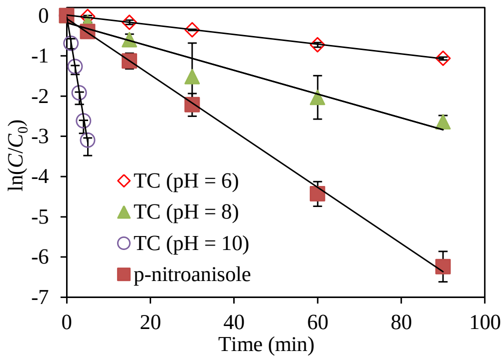

Fig. 2. Apparent photodegradation kinetics of TC and *p*-nitroanisole under different pH conditions

Table 1. Rate constants ($k_{ap,i}$), photolytic half-lives ($t_{1/2,ap,i}$) and quantum yields (Φ_i) for the apparent photolysis of different TC dissociation species under the lab condition

TC species	$k_{ap,i}$ (min^{-1})	$t_{1/2,ap,i}$ (min)	Φ_i
TCH_2^0	0.012 ± 0.001	58.16 ± 4.66	$(3.48 \pm 0.27) \times 10^{-4}$
TCH^-	0.020 ± 0.005	34.99 ± 7.87	$(5.87 \pm 1.33) \times 10^{-4}$
TC^{2-}	0.938 ± 0.021	0.74 ± 0.02	$(2.87 \pm 0.07) \times 10^{-2}$

3.2. ROS oxidation kinetics and reactivities

Aqueous TC disappeared very slowly in the control experiments (< 3%), ~~.~~whereas ~~However,~~ TC degraded faster in the competition kinetic experiments. As shown in Figs. S5 and S6, the ROS oxidation kinetics were fitted and exampled for different pH conditions. It was found that the compound was oxidated not only by •OH but also by $^1O_2$. The second-order reaction rate constants (k_{ROS}) are listed in Table 2, which shows that k_{ROS} values are highly pH dependent, especially for the $^1O_2$ oxidation kinetics. Under the studied pH conditions, the mean k_{ROS} values are equal to 4.63 × 10^{10} M^{-1} s^{-1} and 8.63 × 10^8 M^{-1} s^{-1} for $k_{\bullet OH}$ and k_{1O2}, respectively. The $k_{\bullet OH}$ value is greater than that of other antibiotics, such as sulfonamides (Boreen et al., 2004) (Boreen et al., 2005) and fluoroquinolones (Ge et al., 2015). Furthermore, the •OH oxidation kinetics of the two classes of antibiotics are also dependent of the ~~matrix~~ pH (Boreen et al., 2005) (Baeza and Knappe, 2011) (Ge et al., 2015).

As TC is ionizable and has different dissociated~~ion~~ forms under the studied pHs ~~conditions~~ (Fig. 1), the oxidation reactivities were differentiated for each ~~individual~~ dissociated~~ion~~ species. The corresponding bimolecular reaction rate constants $k_{ROS,i}$ (i.e., $k_{\bullet OH,i}$ and $k_{1O2,i}$) of TCH_2^0, TCH^- and TC^{2-} were calculated and listed in Table 3. Among the three forms, TCH^- was found to be the most highly reactive towards •OH, while TC^{2-} reacted the fastest with $^1O_2$. The $k_{\bullet OH,i}$ values were 1-3 orders of magnitude larger than $k_{1O2,i}$, indictive of the higher reactivity of •OH. However, compared with •OH oxidation, the $^1O_2$ reaction activities varied by more orders of magnitude from TCH_2^0 to TC^{2-} (Table 3). This can be attributed to the higher selectivity of $^1O_2$ than that of •OH to oxidize organic chemicals (Larson and Weber, 1996; Mill, 1999). $^1O_2$ are more sensitive to deprotonation of ionizable chemicals that can increase the electron donating ability and decrease the steric hinerance (Jiao et al., 2008a) (Wei et al., 2013). For some other chemicals, •OH oxidation reactivities were also studied. Neutral forms of fluoroquinolones showed higher reactivities than protonated and anionic forms (Ge et al., 2015), while anionic

HO-PBDEs were oxidated faster than the neutral forms (Xie et al., 2013).

Table 2. The bimolecular rate constants k_{ROS} (i.e., $k_{\bullet OH}$ and $k_{^1O_2}$) for the reactions between TC and $\bullet OH/^1O_2$ under different pH conditions

k_{ROS}	pH = 6	pH = 8	pH = 10
$k_{\bullet OH} \times 10^{-9}$ ($L\cdot mol^{-1}\cdot s^{-1}$)	8.30 ± 0.52	72.10 ± 2.40	58.35 ± 1.91
$k_{^1O_2} \times 10^{-7}$ ($L\cdot mol^{-1}\cdot s^{-1}$)	0.77 ± 0.15	21.70 ± 4.67	236.50 ± 31.82

Table 3. The bimolecular reaction rate constants $k_{ROS,i}$ (i.e., $k_{\bullet OH,i}$ and $k_{^1O_2,i}$) of the different dissociation species of TC with $\bullet OH/^1O_2$

$k_{ROS,i}$	TCH_2^0	TCH^-	TC^{2-}
$k_{\bullet OH,i} \times 10^{-9}$ ($L\cdot mol^{-1}\cdot s^{-1}$)	6.37 ± 0.47	105.78 ± 3.40	35.29 ± 1.19
$k_{^1O_2,i} \times 10^{-7}$ ($L\cdot mol^{-1}\cdot s^{-1}$)	0.26 ± 0.03	25.99 ± 6.18	344.96 ± 45.07

3.4. Multivariate photochemical fate in sunlit surface waters

In the euphotic zone of surface waters, ·OH and $^1O_2$ are ubiquitous and are the most important transient photooxidants, leading to the oxidative degradation of aqueous organic micropollutants. Therefore, TC is expected to show the multivariate photochemical behavior, which mainly involves apparent photolysis as well as photooxidation by ·OH and $^1O_2$. Based on the determined kinetic parameters and related conditions of surface waters, the total environmental half-lives ($t_{1/2,E}$) for these phototransformation pathways were calculated according to Eqs. 3 – 5:

$$k_E = k_{ap} + [\bullet OH]k_{\bullet OH} + [^1O_2]k_{^1O_2} \quad (3)$$

$$k_E = \sum\delta_i[2.303\Phi_i\sum(Z_\lambda\varepsilon_{\lambda,i})] + [\bullet OH]\sum(\delta_i k_{\bullet OH,i}) + [^1O_2]\sum(\delta_i k_{^1O_2,i}) \quad (4)$$

$$t_{1/2,E} = \frac{\ln 2}{k_E} \quad (5)$$

Formatted: English (United States)

Formatted: English (United States)

Formatted: English (United States)

Formatted: English (United States)

Formatted: English (United Kingdom)

Formatted: English (United Kingdom)

where k_E is the total first-order rate constant; $[\bullet OH]$ and $[^1O_2]$ represent the environmental levels of 10^{-15} M and 10^{-12} M for •OH and $^1O_2$, respectively (Cooper et al., 1989; Mill, 1999); δ_i represents ~~stands for~~ the fraction of each dissociated~~ion~~ form and the values are referred to Fig. 1; Z_λ is tabulated~~r~~ solar photon flux at noon of summer and winter (Northern

Formatted: Font: (Default) Times New Roman, 12 pt

Hemisphere), assuming continuous irradiation (Leifer, 1988; OECD, 1997). Important variables~~ value~~s in the calculations ~~calculating process~~ are provided in Tables S4 and S5, and the $t_{1/2,\mathrm{E}}$ results for 45°N latitude are listed in Table 4.

As shown in Table 4, the $t_{1/2,\mathrm{E}}$ values range from 0.05 h for pH = 9 in midsummer to 3.68 h for pH = 6 in midwinter, suggesting the high dependence of $t_{1/2,\mathrm{E}}$ on the water pH and seasonal solar irradiance~~s~~. Referring to previous studies (Edhlund et al., 2006) (Boreen et al., 2004, 2005), the $t_{1/2,\mathrm{E}}$ of some other antibiotics were estimated (Table S6). In direct comparison~~s~~, the values of TC are comparable to those of nitrofuran antibiotics, but ~~and~~ less than those of sulfonamides. As for the multivariate photochemical fate of TC in sunlit surface waters, the relative contributions of the three pathways are ~~were~~ shown in Table 4 and Fig. S3, which indicated that apparent photolysis is usually ~~(especially in summer, 62% – 91%)~~ the dominant process (especially in summer, accounting for 62 – 91% loss?), followed by $^1O_2$ and •OH oxidation.

Apart from the three pathways, aqueous organic pollutants may undergo solar photosensitized degradation by excited DOM. Furthermore, the kinetics and contributions of these pathways can be affected by water depth andother~~,~~ aqueous constituents that may attenuate or absorb sunlight respectively~~, screen~~. To better understand the associated kinetics, further studies are needed to select specific water bodies and calculate the corresponding field values of $t_{1/2,\mathrm{E}}$ for TC.

Table 4. Contributions of apparent photolysis and oxidation degradation to the photochemical transformation (% loss) of TC and the corresponding total half-lives ($t_{1/2,\mathrm{E}}$) in surface waters at 45°N latitude

Seasons	pH	Apparent photolysis	Oxidation degradation		$t_{1/2,\mathrm{E}}$ (h)
			•OH	$^1O_2$	
Summer	6	90.69%	4.84%	4.47%	1.12
	7	72.62%	9.03%	18.35%	0.76

	8	62.06%	9.46%	28.48%	0.25
	9	77.98%	2.35%	19.67%	0.05
Winter	6	69.49%	15.86%	14.65%	3.68
	7	38.47%	20.29%	41.24%	1.71
	8	28.29%	17.88%	53.83%	0.48
	9	46.40%	5.71%	47.88%	0.12

4. Conclusion and environmental implications

This is the first study to comprehensively report~~ed~~ the aqueous multivariate phototransformation kinetics and fate of different dissociated forms of TC. Distinct kinetics of apparent photolysis and photooxidation~~s~~ by •OH and $^1O_2$ were observed for the three main species, TCH_2^0, TCH^- and TC^{2-} under~~in~~ typical surface water conditions, indicating acid-base dissociation and the corresponding pH-dependent behavior should be considered in the risk assessment of these ionizable micropollutants. TC^{2-} can photodegrade the fastest, followed by TCH^- and TCH_2^0. On the other hand ~~And~~ TCH^- shows the highest reactivity towards •OH, while TC^{2-} reacts the fastest with $^1O_2$. The multivariate phototransformation half-lives in sunlit surface waters are highly dependent on the ~~matrix~~ pH of the water and seasonal solar irradiance~~s~~, ~~usually~~ with apparent photolysis serving as the most dominant degradation pathway~~,~~ followed by $^1O_2$ and •OH oxidation. The findings in this study indicate that TC removal can be enhanced by controlling the pH to favour TC^{2-} as the dominant ionized form of the chemical, prior to solar or artificial UV-light treatment during tertiary wastewater treatment for example. ~~Based on the pH variations, the transport of ionizable organic pollutants from freshwater to estuaries and sea areas may result in the varying degradation rates.~~

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21577029 and 41476084), and the Key Laboratory for Ecological Environment in Coastal Areas (201602) and the Marine Science Foundation (2012501) of SOA, China.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.12.087.

References

1) Baeza, C., Knappe, D.R.U., 2011. Transformation kinetics of biochemically active compounds in low-pressure UV Photolysis and UV/H_2O_2 advanced oxidation processes. Water Research 45, 4531-4543.
2) Bodrato, M., Vione, D., 2014. APEX (Aqueous Photochemistry of Environmentally occurring Xenobiotics): a free software tool to predict the kinetics of photochemical processes in surface waters. Environmental Science: Processes & Impacts 16, 732-740.
3) Boreen, A.L., Arnold, W.A., McNeill, K., 2004. Photochemical fate of sulfa drugs in the aquatic environment: Sulfa drugs containing five-membered heterocyclic groups. Environmental Science & Technology 38, 3933-3940.
4) Boreen, A.L., Arnold, W.A., McNeill, K., 2005. Triplet-sensitized photodegradation of sulfa drugs containing six-membered heterocyclic groups: Identification of an SO_2 extrusion photoproduct. Environmental Science & Technology 39, 3630-3638.
5) Bu, Q., Wang, B., Huang, J., Deng, S., Yu, G., 2013. Pharmaceuticals and personal care products in the aquatic environment in China: A review. Journal of hazardous materials 262, 189-211.
6) Chen, Y., Hu, C., Qu, J.H., Yang, M., 2008. Photodegradation of tetracycline and formation of reactive oxygen species in aqueous tetracycline solution under simulated sunlight irradiation. Journal of Photochemistry and Photobiology A: Chemistry 197, 81-87.
7) Chen, Y., Li, H., Wang, Z., Tao, T., Hu, C., 2011. Photoproducts of tetracycline and oxytetracycline involving self-sensitized oxidation in aqueous solutions: Effects of Ca^{2+} and 2+. Journal of Environmental Sciences 23, 1634-1639.
8) Cooper, W.J., Zika, R.G., Petasne, R.G., Fischer, A.M., 1989. Sunlight-induced photochemistry of humic substances in natural waters: major reactive species; Suffet, I. H., MacCarthy, P., Eds.; American Chemical Society: Washington, DC; pp 333-62.
9) Dolinová, J., Růžička, R., Kurková, R., Klánová, J., Klán, P., 2006. Oxidation of aromatic and aliphatic hydrocarbons by OH radicals photochemically generated from H_2O_2 in ice. Environmental Science & Technology 40, 7668-7674.
10) Dulln, D., Mill, T., 1982. Development and evaluation of sunlight actinometers. Environmental Science & Technology 16, 815-820.
11) Edhlund, B.L., Arnold, W.A., McNeill, K., 2006. Aquatic photochemistry of nitrofuran antibiotics. Environmental Science & Technology 40, 5422-5427.
12) Ge, L.K., Chen, J.W., Qiao, X.L., Lin, J., Cai, X.Y., 2009. Light-source-dependent effects of main water

constituents on photodegradation of phenicol antibiotics: Mechanism and kinetics. Environmental Science & Technology 43, 3101-3107.

13) Ge, L.K., Li, J., Na, G.S., Chen, C.E., Huo, C., Zhang, P., Yao, Z.W., 2016. Photochemical degradation of hydroxy PAHs in ice: Implications for the polar areas. Chemosphere 155, 375-379.

14) Ge, L.K., Na, G.S., Zhang, S.Y., Li, K., Zhang, P., Ren, H.L., Yao, Z.W., 2015. New insights into the aquatic photochemistry of fluoroquinolone antibiotics: Direct photodegradation, hydroxyl-radical oxidation, and antibacterial activity changes. Science of the Total Environment 527-528C, 12-17.

15) Jiao, S., Zheng, S., Yin, D., Wang, L., Chen, L., 2008a. Aqueous oxytetracycline degradation and the toxicity change of degradation compounds in photoirradiation process. Journal of Environmental Sciences 20, 806-813.

16) Jiao, S.J., Zheng, S.R., YIn, D.Q., Wang, L.H., Chen, L.Y., 2008b. Aqueous oxytetracycline degradation and the toxicity change of degradation compounds in photoirradiation process. Journal of Environmental Sciences 20, 806-813.

17) Jiao, S.J., Zheng, S.R., Yin, D.Q., Wang, L.H., Chen, L.Y., 2008c. Aqueous photolysis of tetracycline and toxicity of photolytic products to *luminescent bacteria*. Chemosphere 73, 377-382.

18) Keen, O.S., Linden, K.G., 2013. Degradation of antibiotic activity during UV/H_2O_2 advanced oxidation and photolysis in wastewater effluent. Environmental Science & Technology 47, 13020-13030.

19) Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.T., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999-2000: A national reconnaissance. Environmental Science & Technology 36, 1202-1211.

20) Kummerer, K., 2009. Antibiotics in the aquatic environment - A review - Part I. Chemosphere 75, 417-434.

21) Larson, R.A., Weber, E.J., 1996. Reaction mechanisms in environmental organic chemistry Carbohydrate Polymers 29, 293-294.

22) Leifer, A., 1988. The Kinetics of Environmental Aquatic Photochemistry: Theory and Practice. American Chemical Society: Washington, DC.

23) Liu, X., Steele, J.C., Meng, X.Z., 2017. Usage, residue, and human health risk of antibiotics in Chinese aquaculture: A review. Environmental Pollution 223, 161-169.

24) Luo, Y., Xu, L.Q., Rysz, M., Wang, Y., Zhang, H., Alvarez, P.J.J., 2011. Occurrence and transport of tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the Haihe River Basin, China. Environmental Science & Technology 45, 1827-1833.

25) Martinez, J.L., 2009. Environmental pollution by antibiotics and by antibiotic resistance determinants. Environmental Pollution 157, 2893-2902.

26) Matykiewiczová, N., Klánová, J., Klán, P., 2007. Photochemical degradation of PCBs in snow. Environmental Science & Technology 41, 8308-8314.

27) Mill, T., 1999. Predicting photoreaction rates in surface waters. Chemosphere 38, 1379-1390.

28) Niu, J.F., Li, Y., Wang, W.L., 2013. Light-source-dependent role of nitrate and humic acid in tetracycline photolysis: kinetics and mechanism. Chemosphere 92, 1423-1429.

29) OECD, 1997. Guidance Document on Direct Phototransformation of Chemicals in Water. OECD Environmental Health and Safety Publication. Series on Testing and Assessment No.7, Paris, France.

30) Pulicharla, R., Hegde, K., Brar, S.K., Surampalli, R.Y., 2017. Tetracyclines metal complexation: Significance and fate of mutual existence in the environment. Environmental Pollution 221, 1-14.

31) Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., von Gunten, U., Wehrli, B., 2006. The challenge of micropollutants in aquatic systems. Science 313, 1072-1077.

32) Shah, S.Q., Colquhoun, D.J., Nikuli, H.L., Sørum, H., 2012. Prevalence of antibiotic resistance genes in the bacterial flora of integrated fish farming environments of Pakistan and Tanzania. Environmental Science &

Technology 46, 8672-8679.

33) Shemer, H., Sharpless, C.M., Elovitz, M.S., Linden, K.G., 2006. Relative rate constants of contaminant candidate list pesticides with hydroxyl radicals. Environmental Science & Technology 40, 4460-4466.

34) Vione, D., Minella, M., Maurino, V., Minero, C., 2014. Indirect photochemistry in sunlit surface waters: Photoinduced production of reactive transient species. Chemistry-A European Journal 20, 10590-10606.

35) Wammer, K.H., Slattery, M.T., Stemig, A.M., Ditty, J.L., 2011. Tetracycline photolysis in natural waters: Loss of antibacterial activity. Chemosphere 85, 1505-1510.

36) Wei, X.X., Chen, J.W., Xie, Q., Zhang, S.Y., Ge, L.K., Qiao, X.L., 2013. Distinct photolytic mechanisms and products for different dissociation species of ciprofloxacin. Environmental Science and Technology 47, 4284-4290.

37) Werner, J.J., Arnold, W.A., McNeill, K., 2006. Water hardness as a photochemical parameter: Tetracycline photolysis as a function of calcium concentration, magnesium concentration, and pH. Environmental Science & Technology 40, 7236-7241.

38) Xie, Q., Chen, J.W., Zhao, H.X., Qiao, X.L., Cai, X.Y., Li, X.H., 2013. Different photolysis kinetics and photooxidation reactivities of neutral and anionic hydroxylated polybrominated diphenyl ethers. Chemosphere 90, 188-194.

39) Yao, H., Sun, P., Minakata, D., Crittenden, J.C., Huang, C.H., 2013. Kinetics and modeling of degradation of ionophore antibiotics by UV and UV/H_2O_2. Environmental Science & Technology 47, 4581-4589.

40) Zhang, Q.Q., Ying, G.G., Pan, C.G., Liu, Y.S., Zhao, J.L., 2015. Comprehensive evaluation of antibiotics emission and fate in the river basins of China: source analysis, multimedia modeling, and linkage to bacterial resistance. Environmental Science & Technology 49, 6772-6782.

41) Ziolli, R.L., Jardim, W.F., 2003. Photochemical transformations of water-soluble fraction (WSF) of crude oil in marine waters: A comparison between photolysis and accelerated degradation with TiO_2 using GC–MS and UVF. Journal of Photochemistry and Photobiology A: Chemistry 155, 243-252.