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

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ABSTRACT

~~A~~Many ~~a~~ntibiotics are ubiquitous pollutants in aquatic systems and ~~can~~ they ~~ex~~ist as different dissociat~~ed 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 dissociat~~ion~~ed 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~~

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41 ~~environments.~~

42 *Keywords*: Tetracycline; Dissociation; Apparent photolysis; Hydroxyl radicals; Singlet

43 oxygens; Environmental half-lives

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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~~ huma~~nn's~~n 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 treatment~~s~~ (Liu et al., 2017; Zhang et al., 2015) (Pulicharla et al., 2017). Thi~~se~~s extensive use results in the environmental occurrence of these compounds with ~~.~~ ~~To date,~~ increasing detection of TCs in ~~the~~ aquatic environment~~s~~ 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)

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71 (Chen et al., 2011) (Jiao et al., 2008c) (Jiao et al., 2008b). Also, TCs may undergo indirect

72 photodegradation or sensitized photooxidation mediated by the photogenerated reactive

73 oxygen species (ROS) from dissolved organic matter (DOM), Fe(III) salts and nitrate present

74 in surface waters~~.~~ Under solar and solar-simulated light (xenon lamp) irradiation ($\lambda > 290$ nm),

75 ~~an~~ elevated TC photolysis efficiency was observed in the presence of ~~certain concentration~~

76 DOM, NO_3^- and Fe(III). Radicals such as~~,~~ hydroxyl radicals (•OH) and ~~as well as~~ singlet

77 oxygen~~s~~ ($^1O_2$) can ~~were found in the~~ mediated TC photodegradation. (Niu et al., 2013) (Jiao et

78 al., 2008c) (Chen et al., 2008). Moreover, TCs can be phototransformed into more toxic

79 intermediate products. For example, Niu et al. (Niu et al., 2013) and Jiao et al. (Jiao et al.,

80 2008c) investigated the photomodified toxicities of TC to luminescent bacteria, and found that

81 the phototransformed ~~more toxic~~ intermediates were more toxic than the parent TC~~generated~~.

82 These studies ~~are constructive, and~~ indicate that photodegradation is an important

83 transformation pathway that can give rise to degradation products that may be of ~~more~~

84 concern and rank alongside ~~than~~ the parent chemical~~s~~. Many antibiotics including TCs have a

85 number of dissociated forms depending on the pH of the water ~~, affecting the aqueous fate and~~

86 ~~ecological risk of the antibiotics. However, new insights into photochemical behavior of TCs~~

87 ~~are necessary for their accurate persistence and risk assessment.~~ These ~~.~~

88 In addition to apparent photolysis, ROS photooxidation may play a significant role in the

89 phototransformation of organic pollutants. In sunlit surface waters with many coexisting

90 photoreactive species such as DOM, Fe(III) and NO_3^-, the photoinduced ·OH and $^1O_2$ are

91 most important transient oxidants. The •OH show less selectivity to oxidize most organic

92 chemicals, while $^1O_2$ limit environmental reactions to compounds like polycyclic aromatics,

93 pyrroles, and phenolate anions (Mill, 1999) (Keen and Linden, 2013) (Yao et al., 2013). Some

94 previous studies indicated that photooxidation by •OH and $^1O_2$ was an important factor in

95 determining the fate of antibiotics such as sulfa drugs (Boreen et al., 2004, 2005), nitrofurans

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

100 Here in this study, we employed tetracycline (TC, Fig. 1) as a model compound to study the

101 multivariate photochemical behavior: apparent photolysis and ROS photooxidation. The

102 molecular structure of TC has four ionizable moieties, and TC may exhibit five dominant

103 dissociat~~ion~~ed forms in water (Fig. 1). In the conditions of most fresh and sea waters (pH = 6

104 – 9), TC chiefly exists as ~~mainly presents in the~~ three species: TCH_2^0, TCH^- and TC^{2-}, which

105 are the focus of ~~concerned in~~ th~~e~~is study. The objectives were~~are~~ to differentiate the

106 phototransformation kinetics of the different species, calculate the corresponding

107 environmental half-lives in sunlit surface waters, and assess ~~weigh~~ the relative contributions

108 of individual photochemical reactions to the fate of TC in general ~~this antibiotics~~. To the best of our

109 knowledge, this is the first comprehensive report on the aqueous multivariate

110 phototransformation kinetics and fate of different dissociated TC.
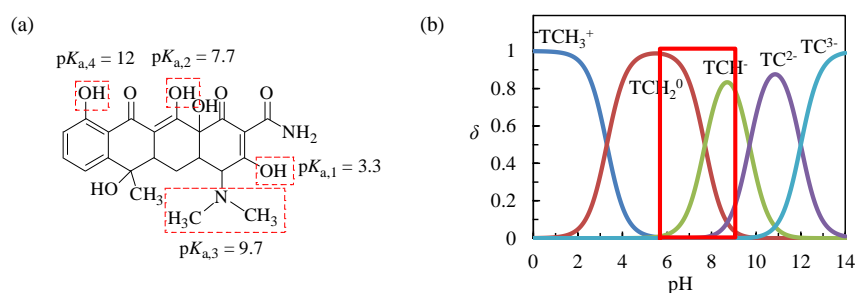
112 Fig. 1. Chemical structure (a) and dissociation species distribution (b) of tetracycline

2. Materials and Methods

2.1. Apparent photolysis experiments

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

117   Information of the other chemicals used are shown in Table S1. A merry-go-round

118   photochemical reactor with a Pyrex-filtered and water-refrigerated high-pressure mercury

119   lamp (500 W) was used to carry out the photochemical experiments. Pyrex-filtered mercury

120   lamps were usually employed to simulate solar radiation (λ > 290 nm) (Dolinová et al., 2006;

121   Matykiewiczová et al., 2007; Ziolli and Jardim, 2003). The emission spectrum of the light

122   source was showed in our previous studies (Ge et al., 2009) (Ge et al., 2016). Reaction

123   solutions (5 μmol L^{-1}) were added into quartz tubes and the reaction temperature was

124   controlled at 25 ± 1 °C.

125   The absorption spectra (ε_λ) and apparent photolytic rate constants (k_{ap}) of TC were

126   measured at the desired pH 6, 8 and 10, which were adjusted with HCl/NaOH. To determine

127   quantum yields (Φ), a *p*-nitroanisole/pyridine actinometer was irradiated concurrently with

128   TC photolysis (Dulln and Mill, 1982; Edhlund et al., 2006). Futhermore, to differentiate the

129    $\varepsilon_{\lambda,i}$, $k_{ap,i}$ and Φ_i of <u>the</u> different dissociat<u>ed</u>~~ion~~ forms, matrix calculations were performed

130   according to previous studies (Boreen et al., 2004) (Wei et al., 2013).

131   **2.2. Determination of the ROS oxidation reactivities**

132   To explore the •OH/^{1}O$_2$ reactivities, competition kinetics was used to determine the

133   second-order rate constants k_{ROS} (i.e., $k_{•OH}$ and k_{1O2}) for reactions of aqueous TC (pH = 6, 8

134   and 10) with •OH/^{1}O$_2$. The •OH and ^{1}O$_2$ were photogenerated by 100 mM H$_2$O$_2$ and 20 μM

135   perinaphthenone, respectively. The reference compounds were acetophenone (10 μM) and

136   furfuryl alcohol (20 μM), respectively. Incident light was fil<u>tered</u>~~trated~~ <u>using</u>~~by~~ 400 nm

137   cut-off filters. Under the irradiation with λ > 400 nm, apparent photodegradation of the

138   reference compounds can be avoided, while TC might suffer apparent photolysis. <u>Therefore,</u>

139   ~~So,~~ to correct the interference of the TC apparent photolysis, control experiments without the

140   photosensitizers (H$_2$O$_2$ and perinaphthenone) were performed, and the k_{AP} in the competition

141   kinetic experiments was calculated <u>according</u> ~~referring~~ to Shemer et al. (Shemer et al., 2006).

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

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

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

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

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kinetics for each dissociated species of TC.

The $k_{ap,i}$ and quantum yields of photodegradation (-Φ_i) of the different dissociated 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,

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

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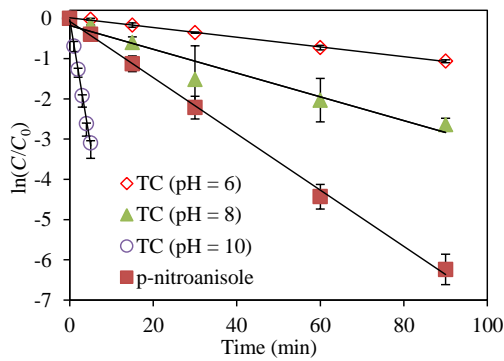
Fig. 2. Apparent photodegradation kinetics of TC and *p*-nitroanisole under different pH conditions

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 oxidized 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 $k_{•OH}$ and k_{1O2}, respectively. The $k_{•OH}$ 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 pH~~s 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., $k_{•OH,i}$ 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 $k_{•OH,i}$ 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

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

211

212 Table 2. The bimolecular rate constants k_{ROS} (i.e., $k_{\bullet OH}$ and k_{1O2}) for the reactions between TC and $\bullet OH/^1O_2$
213 under different pH conditions

k_{ROS}	pH = 6	pH = 8	pH = 10
$k_{\bullet OH} \times 10^{-9}$ (L·mol^{-1}·s^{-1})	8.30 ± 0.52	72.10 ± 2.40	58.35 ± 1.91
$k_{1O2} \times 10^{-7}$ (L·mol^{-1}·s^{-1})	0.77 ± 0.15	21.70 ± 4.67	236.50 ± 31.82

214
215 Table 3. The bimolecular reaction rate constants $k_{ROS,i}$ (i.e., $k_{\bullet OH,i}$ and $k_{1O2,i}$) of the different dissociation
216 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·mol^{-1}·s^{-1})	6.37 ± 0.47	105.78 ± 3.40	35.29 ± 1.19
$k_{1O2,i} \times 10^{-7}$ (L·mol^{-1}·s^{-1})	0.26 ± 0.03	25.99 ± 6.18	344.96 ± 45.07

217

3.4. Multivariate photochemical fate in sunlit surface waters

219 In the euphotic zone of surface waters, $\cdot OH$ and $^1O_2$ are ubiquitous and are the most

220 important transient photooxidants, leading to the oxidative degradation of aqueous organic

221 micropollutants. Therefore, TC is expected to show the multivariate photochemical behavior,

222 which mainly involves apparent photolysis as well as photooxidation by $\cdot OH$ and $^1O_2$. Based

223 on the determined kinetic parameters and related conditions of surface waters, the total

224 environmental half-lives ($t_{1/2,E}$) for these phototransformation pathways were calculated

225 according to Eqs. 3 – 5:

$$k_E = k_{ap} + [\bullet OH]k_{\bullet OH} + [^1O_2]k_{1O2} \qquad (3)$$

$$k_E = \sum \delta_i [2.303\Phi_i \sum (Z_\lambda \varepsilon_{\lambda,i})] + [\bullet OH]\sum(\delta_i k_{\bullet OH,i}) + [^1O_2]\sum(\delta_i k_{1O2,i}) \qquad (4)$$

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

229 where k_E is the total first-order rate constant; $[\bullet OH]$ and $[^1O_2]$ represent the environmental

230 levels of 10^{-15} M and 10^{-12} M for $\bullet OH$ and $^1O_2$, respectively (Cooper et al., 1989; Mill, 1999);

231 δ_i represents stands for the fraction of each dissociateding form and the values are referred to

232 Fig. 1; Z_λ is tabulated, solar photon flux at noon of summer and winter (Northern

11

233 Hemisphere), assuming continuous irradiation (Leifer, 1988; OECD, 1997). Important

234 variables values in the calculations calculating process are provided in Tables S4 and S5, and

235 the $t_{1/2,E}$ results for 45°N latitude are listed in Table 4.

236   As shown in Table 4, the $t_{1/2,E}$ values range from 0.05 h for pH = 9 in midsummer to 3.68 h

237 for pH = 6 in midwinter, suggesting the high dependence of $t_{1/2,E}$ on the water pH and

238 seasonal solar irradiances. Referring to previous studies (Edhlund et al., 2006) (Boreen et al.,

239 2004, 2005), the $t_{1/2,E}$ of some other antibiotics were estimated (Table S6). In direct

240 comparisons, the values of TC are comparable to those of nitrofuran antibiotics, but and less

241 than those of sulfonamides. As for the multivariate photochemical fate of TC in sunlit surface

242 waters, the relative contributions of the three pathways are were shown in Table 4 and Fig. S3,

243 which indicated that apparent photolysis is usually (especially in summer, 62% – 91%) the

244 dominant process (especially in summer, accounting for 62 – 91% loss?), followed by $^1O_2$ and

245 •OH oxidation.

246   Apart from the three pathways, aqueous organic pollutants may undergo solar

247 photosensitized degradation by excited DOM. Furthermore, the kinetics and contributions of

248 these pathways can be affected by water depth andother, aqueous constituents that may

249 attenuate or absorb sunlight respectively, screen. To better understand the associated kinetics,

250 further studies are needed to select specific water bodies and calculate the corresponding field

251 values of $t_{1/2,E}$ for TC.

252

253 Table 4. Contributions of apparent photolysis and oxidation degradation to the photochemical

254 transformation (% loss) of TC and the corresponding total half-lives ($t_{1/2,E}$) in surface waters at 45°N

255 latitude

Seasons	pH	Apparent photolysis	Oxidation degradation		$t_{1/2,E}$ (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
	6	69.49%	15.86%	14.65%	3.68
Winter	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 reported the aqueous multivariate phototransformation kinetics and fate of different dissociated forms of TC. Distinct kinetics of apparent photolysis and photooxidations by •OH and $^1O_2$ were observed for the three main species, TCH_2^0, TCH^- and TC^{2-} underin 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 irradiances, 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.

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279

280 **Appendix A. Supplementary data**

281   Supplementary data to this article can be found online at

282 http://dx.doi.org/10.1016/j.scitotenv.2017.12.087.

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