

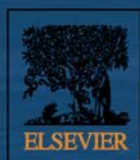
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Could wastewater analysis be a useful tool for China?



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Impact of dissolved organic matter on the photolysis of the ionizable antibiotic norfloxacin

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ABSTRACT

Norfloxacin (NOR), an ionizable antibiotic frequently used in the aquaculture industry, has aroused public concern due to its persistence, bacterial resistance, and environmental ubiquity. Therefore, we investigated the photolysis of different species of NOR and the impact of a ubiquitous component of natural water — dissolved organic matter (DOM), which has a special photochemical activity and normally acts as a sensitizer or inhibitor in the photolysis of diverse organics; furthermore, scavenging experiments combined with electron paramagnetic resonance (EPR) were performed to evaluate the transformation of NOR in water. The results demonstrated that NOR underwent direct photolysis and self-sensitized photolysis via hydroxyl radical ($\cdot\text{OH}$) and singlet oxygen ($^1\text{O}_2$) based on the scavenging experiments. In addition, DOM was found to influence the photolysis of different NOR species, and its impact was related to the concentration of DOM and type of NOR species. Photolysis of cationic NOR was photosensitized by DOM at low concentration, while zwitterionic and anionic NOR were photoinhibited by DOM, where quenching of $\cdot\text{OH}$ predominated according to EPR experiments, accompanied by possible participation of excited triplet-state NOR and $^1\text{O}_2$. Photo-intermediate identification of different NOR species in solutions with/without DOM indicated that NOR underwent different photodegradation pathways including dechlorination, cleavage of the piperazine side chain and photooxidation, and DOM had little impact on the distribution but influenced the concentration evolution of photolysis intermediates. The results implied that for accurate ecological risk assessment of emerging ionizable pollutants, the impact of DOM on the environmental photochemical behavior of all dissociated species should not be ignored.

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Introduction

Aquaculture industry has experienced an unprecedented increase in Asia during recent years, accounting for about 90% of the global aquaculture production (Naylor et al., 2000). Due to the widespread and unrestricted use of prophylactic antibiotics in this industry, a series of developments detrimental to the environment and human

health occurs (Martinez, 2008; Hvitendahl, 2012). The fluoroquinolone (FQ) group is one of the most important classes of antibiotics used worldwide in aquaculture industry (He et al., 2012; Quesada et al., 2013). Several recent studies have reported the presence of FQs in surface water in many countries, with detected concentrations up to a few $\mu\text{g/L}$ (Hirsch et al., 1998; Golet et al., 2002; Xu et al., 2007; Zou et al., 2011). It is reasonable to deduce that the concentration of

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FQs may be even higher in the aquaculture water due to the abuse of FQs.

Photolysis is an important transformation process for FQs in natural aqueous environments (Burhenne et al., 1999). Most of the FQs have two proton binding sites, resulting in a mixture of different dissociated species in the aqueous environment. Thus, the photochemical transformation of FQs at various pH conditions has attracted much interest. For example, Wammer et al. (2012) reported the difference of quantum yields of different dissociated species of norfloxacin, ofloxacin, and enrofloxacin, respectively. Wei et al. (2013) explained the distinct photolytic mechanisms for different dissociated species of ciprofloxacin in pure water based on computational methods. However, the influences of surface water components on photolytic transformation of different dissociated FQ species have been little reported.

Dissolved organic matter (DOM), which is widespread in natural aquatic environment (Kusari et al., 2009), is considered to be one of the important factors influencing the photolysis process of organic contaminants. Studies to date have already demonstrated the dual function of DOM on the photolysis of antibiotics, which includes the enhancement of photolysis kinetics through producing various reactive oxygen species (ROS, including $\cdot\text{OH}$ and $^1\text{O}_2$) (Andreozzi et al., 2004; Ge et al., 2009), and inhibition of photolysis kinetics by behaving as an inner filter to absorb solar light or as a sink for ROS and triplet excited states of pollutants (Chen et al., 2008; Prabhakaran et al., 2009; Vione et al., 2009; Wenk et al., 2011). Some experimental results have indicated mixed effects of DOM on the photodegradation of antibiotics. Ge et al. (2010) found inhibition by DOM through the reduction of $\cdot\text{OH}$ and $^1\text{O}_2$ produced in the self-sensitized photooxidation of FQs. Other researchers reported the promotion effect of DOM on sulfa drug photolysis through the formation of excited triplet-state DOM ($^3\text{DOM}^*$) to produce $\cdot\text{OH}$ and $^1\text{O}_2$ (Boren et al., 2005). To the best of our knowledge, however, few studies have focused on the impact of DOM on the photolysis of different dissociated species of ionizable antibiotics.

This article presents the photolysis results of different dissociated species of FQs in aqueous solution with DOM, using norfloxacin (NOR) as a model molecule. NOR is a widely used FQ antibiotic and is one of the environmental contaminants frequently detected in a variety of surface waters (Zou et al., 2011; Zhang et al., 2012). The influences of DOM from different sources on the photodegradation of NOR and its degradation intermediates were also investigated. The study is expected to be helpful for developing a full understanding of the influences of DOM on the photodegradation of ionizable antibiotics.

1. Materials and methods

1.1. Chemicals and reagents

NOR (98%) was obtained from Tokyo Chemical Industry Co. Ltd. (Japan), sorbic acid (SA, 99%) was purchased from J&K Scientific Ltd. (Beijing, China). High performance liquid chromatographic (HPLC)-grade acetonitrile (ACN) was purchased from Sigma-Aldrich (Waters-2695/FD 2475/UV 2996, Waters, USA). Three kinds of DOM, Suwannee River fulvic acid (SRFA), Elliott soil humic acid (ESHA), Leonardite humic acid (LHA), representing aquatic, terrestrial and coal-like DOM respectively, were obtained from the International Humic Substance Society. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Tokyo Chemical Industry Co. Ltd. (Japan). Other reagents were of analytical reagent grade and used without further purification. Ultrapure water was obtained with a Millipore-MilliQ system. For water pH-value adjustment, HCl (0.1 mol/L) and NaOH (0.1 mol/L) were used.

1.2. Photochemical experiments

All the photochemical experiments were carried out using a merry-go-round photochemical reactor (SGY-I, Stonetech Electric Equipment Co. Ltd., Nanjing, China) equipped with a water-cooled 350 W Xenon lamp surrounded by 290 nm cutoff filters to simulate sunlight. The emission spectrum of the light source was measured by a monochromator (Fig. 1).

Aqueous solutions of NOR (5 $\mu\text{mol/L}$) were adjusted to the desired pH with HCl/NaOH in order to avoid possible effects of buffers (Musa and Eriksson, 2009). The pH values changed slightly (<0.2) during the photolytic experiments. Photolytic quantum yields (Φ_{NOR}) were calculated by the following equation (Dulin and Mill, 1982):

$$\Phi_{\text{NOR}} = \frac{k_{\text{NOR}} \sum I_{\lambda} T_{\lambda} \varepsilon_{\lambda, \text{a}}}{k_{\text{a}} \sum I_{\lambda} T_{\lambda} \varepsilon_{\lambda, \text{NOR}}} \Phi_{\text{a}} \quad (1)$$

where, the subscript a stands for the chemical actinometer (*p*-nitroanisole/pyridine); I_{λ} and T_{λ} are the relative light irradiation intensity and the transmission ratio of the filter, respectively; $\varepsilon_{\lambda, \text{a}}$ and $\varepsilon_{\lambda, \text{NOR}}$ are the molar absorptivity of the actinometer and NOR at λ , respectively. The wavelength range was 290–400 nm. The chemical actinometer and NOR were placed in different tubes. Dark controls were performed under the same conditions. All the experiments were carried out at least in triplicate.

1.3. Analytical determinations

The concentration of NOR was determined by a 2695 Waters Alliance system equipped with a Waters 2475 Fluorescence Detector (FLD). The FLD excitation and emission wavelengths were at 278 nm and 445 nm, respectively. A SunFire ODS reverse-phase column (150 mm \times 4.6 mm, 5.0 μm) was coupled with a SunFire C18 guard cartridge (20 mm \times 4.6 mm, 5.0 μm). The column temperature was set at 40°C. The mobile phase was acetonitrile (A) and phosphoric acid in water (0.05%) (B) with the ratio of 10:90. The flow rate was set at 1 mL/min. The retention time for NOR was about 7.0 min.

The electron paramagnetic resonance (EPR) experiment was performed at room temperature using a Bruker model EPR 300E spectrometer equipped with an *in situ* irradiation source (500 W

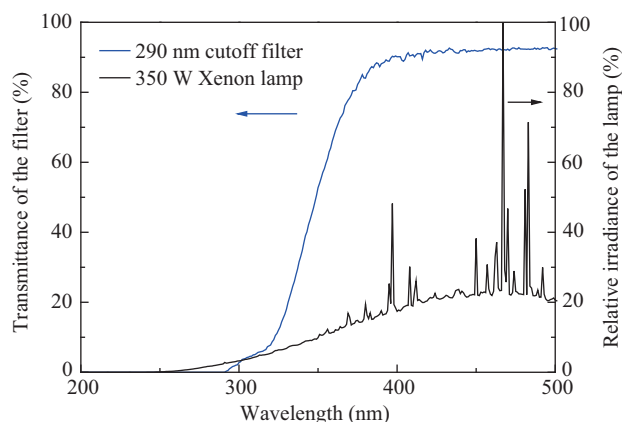


Fig. 1 – Relative irradiance of the 350 W Xenon lamps and transmittance of the 290 nm cutoff filters.

Xenon lamp, $\lambda > 290$ nm). Instrument parameters were as follows: center field = 3,360 G, sweep width = 100 G, microwave frequency = 9.78 GHz, microwave power = 12.7 mW and modulation frequency = 100 kHz. In order to ensure the comparability of the signal intensity of DMPO-OH adducts among different samples, solutions with different pH values were all strictly controlled at the same final concentrations of DMPO (100 mmol/L), NOR (5 μ mol/L) or SRFA (2 mg/L TOC), and in situ irradiation time of 3 min.

Photolytic intermediates were analyzed by an Agilent 1200 HPLC with an Agilent verified 6410 triple-quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source (HPLC-MS/MS). The column used for separation was a XTerra@MS C18 column (100 mm \times 2.1 mm, 3.5 μ m). The analysis was performed using 0.1% formic acid in MilliQ water as eluent A and acetonitrile as eluent B in gradient elution mode at flow rate of 0.2 mL/min. The elution gradient started with 90% A, linearly decreasing to 70% A over the first 7 min. The composition of the mobile phase was maintained for 13 min. At 20.06 min, the percentage of eluent A was increased to 100% and these conditions were held for 0.84 min before the initial mobile phase composition was restored at 23 min. After gradient elution, the column was equilibrated for 7 min before the next injection. The mass spectrometer conditions were: ionization mode: ESI, positive mode; scan range: m/z : 150–500; drying gas flow: 8 L/min; drying gas temperature: 300°C; fragmentor: 150 V; nebulizer pressure: 35 psi; capillary voltage: 4000 V.

2. Results and discussion

2.1. Direct and self-sensitized photolysis of different dissociated species of NOR

NOR, (with $pK_{a,1}$ of 6.30 and $pK_{a,2}$ of 8.38), has three dissociated species at varying pH, as shown in Fig. 2. Around neutral pH (7.5),

the carboxylic group of NOR is deprotonated and the peripheral piperazine nitrogen atom is protonated, leading NOR to be predominantly present as a zwitterion. The fractional distribution of the three dissociated species was calculated and shown in Fig. 3a. At pH 9.5 more than 90% of the NOR is in its anionic form due to the deprotonation of the carboxylic group, whereas at pH 4.5 the cationic species is prominent due to the protonation of the peripheral piperazine nitrogen atom. Therefore, pH 4.5, 7.5 and 9.5 were selected in the following work to investigate the phototransformation behaviors of different dissociated species of NOR.

The direct and self-sensitized photolysis experiments of different dissociated species of NOR were conducted first to enable the comparison between the absence and presence of some quenchers of reactive species. In the dark controls, no obvious loss of NOR was observed, indicating that the decay by microbiological, thermal, or hydrolytic means was negligible during the photolysis experiments. It is clearly shown in Table 1 that the photolysis rate constants of NOR (k_{NOR}) in pure water exhibited strong pH dependence due to changes in speciation, which is consistent with the previous reports on FQ photolysis (Ge et al., 2010). Quantum yields for each species of NOR (Table 1) were calculated according to Eq. (1) based on the rate constants, absorption spectra (Fig. 3b) and emission intensities of the lamp. The obvious difference among quantum yields of the three dissociated species explained the differences in their photodegradation activity, giving one primary reason that the observed photolysis rate constants (k_{NOR}) of the zwitterionic and anionic species were almost seven times faster than that of the cationic species. Another important explanation for this difference was exhibited by EPR spectra of cationic, zwitterionic and anionic NOR solutions in Fig. 7 (dash line). In the spectra, the 4-line characteristic of the DMPO-OH adduct was clearly observed, and the signal intensity of cationic NOR was much weaker than the others, indicating that the quantity of $\cdot\text{OH}$ generated from the

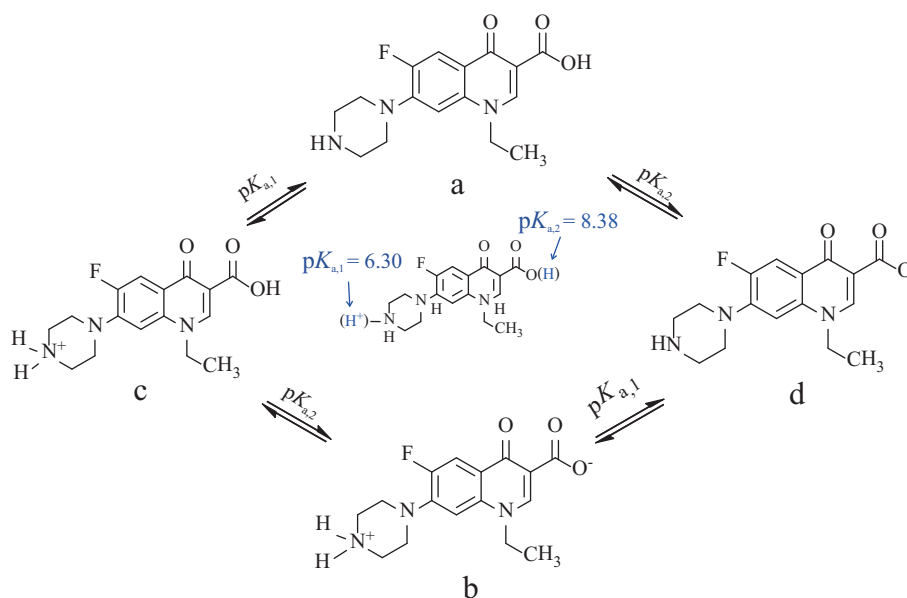


Fig. 2 – The different protonated states of norfloxacin depending on pH: (a) neutral NOR, (b) zwitterionic NOR, (c) cationic NOR, and (d) anionic NOR.

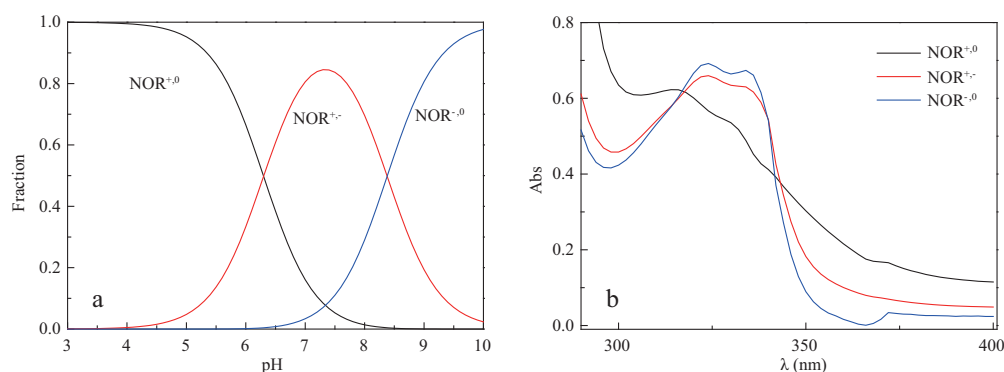


Fig. 3 – Fraction distribution (a) and UV-vis absorbance spectra (b) of the three dissociated species of norfloxacin (NOR).

photolysis of cationic NOR was less than that of zwitterionic and anionic NOR. Thus $\cdot\text{OH}$ was presumably another principal element inducing the tremendous difference of k_{NOR} between cationic species and zwitterionic and anionic species. Furthermore, the generation of $\cdot\text{OH}$ would probably accelerate the self-sensitized photolysis of NOR.

The addition of isopropanol (IPA, $\cdot\text{OH}$ quencher) in pure water induced a pronounced retardation of the photolysis rate for the three NOR species (Fig. 4), indicating that their photoreactions involved self-sensitized photooxidation via $\cdot\text{OH}$. The addition of NaN_3 ($\cdot\text{OH}$ and $^1\text{O}_2$ quencher) in pure water markedly inhibited the photodegradation of zwitterionic and anionic NOR. The more significant inhibitive effect of NaN_3 than that of isopropanol suggested that the zwitterionic and anionic forms of NOR also underwent $^1\text{O}_2$ -mediated self-sensitized photolysis. The contribution of $\cdot\text{OH}$ and $^1\text{O}_2$ was calculated by the following equations:

$$R_{\text{OH}} = \frac{k_{\text{OH}}}{k_{\text{NOR}}} \approx \frac{k_{\text{NOR}} - k_{\text{IPA}}}{k_{\text{NOR}}} \quad (2)$$

$$R_{^1\text{O}_2} = \frac{k_{^1\text{O}_2}}{k_{\text{NOR}}} \approx \frac{k_{\text{IPA}} - k_{\text{NaN}_3}}{k_{\text{NOR}}} \quad (3)$$

where, R_{OH} and $R_{^1\text{O}_2}$ are the contribution ratio of $\cdot\text{OH}$ and $^1\text{O}_2$, respectively, k_{OH} and $k_{^1\text{O}_2}$ are the self-sensitized photolysis kinetics rate constants of $\cdot\text{OH}$ and $^1\text{O}_2$, k_{NOR} , k_{IPA} , and k_{NaN_3} are the photolysis kinetics rate constants of NOR in pure water and with the presence of IPA or NaN_3 , respectively. The calculated R_{OH} for cationic, zwitterionic and anionic NOR was 27%, 22%, and 17%, respectively, indicating that the effect of $\cdot\text{OH}$ decreased with increasing pH. The calculated $R_{^1\text{O}_2}$ for cationic, zwitterionic and anionic NOR was approximately 0, 5% and 39%, respectively, indicating the effect of $^1\text{O}_2$ rose with

the increase of pH. As the effects of $\cdot\text{OH}$ and $^1\text{O}_2$ on the photolysis of NOR species were opposite, and DOM is considered a sink both for $\cdot\text{OH}$ and $^1\text{O}_2$, it was reasonable to hypothesize that DOM would produce different impacts on the photolysis of NOR species.

Considering that the formation of $\cdot\text{OH}$ and $^1\text{O}_2$ in pure water is caused by the reaction of triplet excited states of NOR ($^3\text{NOR}^*$) with water molecules and ground state oxygen, the influence of triplet excited states of NOR species on photolysis was investigated. The addition of sorbic acid (SA, a triplet quencher, Velosa et al., 2007) in pure water indeed induced a significant inhibition on the photolysis of all three NOR species (Fig. 5), moreover, the inhibition of triplet excited states increased with the increase of pH. These results indicated that at pH 7.5 and 9.5, NOR species were easily transformed to $^3\text{NOR}^*$ under the irradiation of simulated solar light. The $^3\text{NOR}^*$ will further influence the photodegradation of NOR either by forming $\cdot\text{OH}$ and $^1\text{O}_2$, or by fragmenting. The clear existence of kinetic constant difference among the three NOR species with the addition of SA, meant differences in their behavior in direct and self-sensitized photolysis in pure water. Therefore, it is logical to deduce that the effects of DOM on the degradation of NOR include the influences on direct photolysis of NOR and fragmenting of NOR caused by $^3\text{NOR}^*$, in addition to the quenching of $\cdot\text{OH}$ and $^1\text{O}_2$ (as mentioned above).

2.2. Effects of DOM on NOR photolysis

The effect of DOM on the photolysis of NOR was investigated by the calculation of the light screening factor (S_λ) of DOM and k_{DOM} , wherein k_{DOM} is the rate constant reflecting the effect of DOM on NOR photolysis, and S_λ of DOM was calculated as follows (Miller and Chin, 2002):

$$S_\lambda = \frac{1 - 10^{-\alpha_\lambda l}}{2.303 \alpha_\lambda l} \quad (4)$$

where, S_λ is the screening factor, the smaller the S_λ value, the heavier the screening effect; α_λ (cm^{-1}) is the wavelength specific attenuation coefficient of DOM; l (cm) is the path length of the tubes used in photochemical experiments.

Three kinds of DOM from different sources (SRFA, ESHA, LHA), which were confirmed to be able to produce $\cdot\text{OH}$ by EPR

Table 1 – Photolytic rate constants (k_{NOR}) and quantum yields (Φ_{NOR}) of different dissociated species of NOR in pure water.

pH	Dissociated species	k_{NOR} (hr^{-1})	Φ_{NOR}
4.5	Cationic NOR	0.95 ± 0.02	$5.00 \times 10^{-3} \pm 0.10 \times 10^{-3}$
7.5	Zwitterionic NOR	6.98 ± 0.43	$4.00 \times 10^{-2} \pm 0.25 \times 10^{-2}$
9.5	Anionic NOR	6.53 ± 0.20	$3.96 \times 10^{-2} \pm 0.12 \times 10^{-2}$

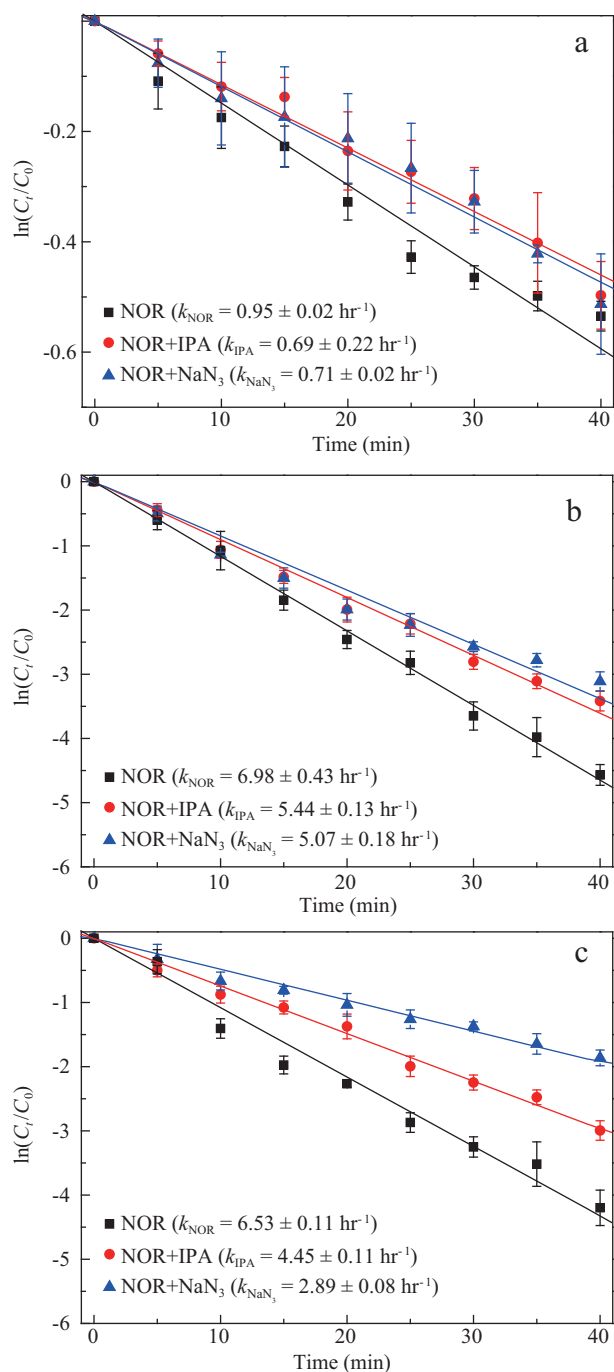


Fig. 4 – Effects of isopropanol (IPA) and NaN_3 on the photolysis kinetics of (a) cationic, (b) zwitterionic and (c) anionic species of NOR in pure water.

detection, were chosen to assess the effect of DOM on NOR photolysis. As shown in Table 2, the three kinds of DOM were found to have a light screening effect, without exception, since all the S_λ values were below 1.0 (Miller and Chin, 2002). The light screening effect of DOM became stronger with the increase of concentration. DOM from different sources showed similar tendencies, with no obvious differences. Thus, DOM competitively absorbed actinic photons ($\lambda = 290\text{--}400\text{ nm}$) in the presence

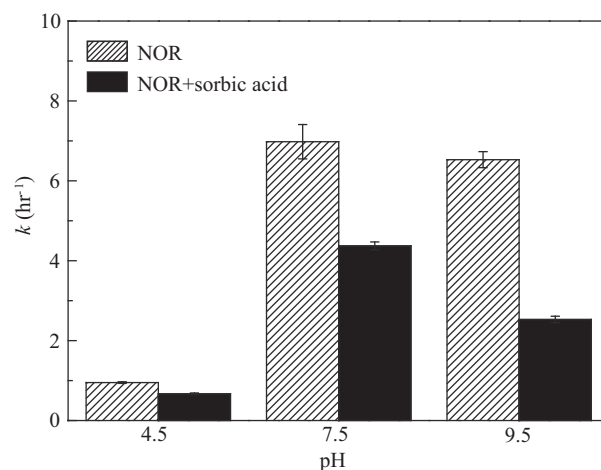


Fig. 5 – Effect of sorbic acid ($20\text{ }\mu\text{mol/L}$) on photolysis kinetic constants of NOR in pure water.

of NOR, resulting in the retardation of NOR direct and self-sensitized photolysis.

The photolysis rate constants (k_{DOM}) caused by the impact of DOM on NOR photolysis can be described by the following equation (Miller and Chin, 2002):

$$k_{\text{DOM}} = k_{\text{obs}} - k_{\text{NOR}}S_\lambda \quad (5)$$

where, k_{obs} is the rate constant of NOR photolysis in the presence of DOM, k_{NOR} is the direct and self-sensitized degradation rate constant in pure water. Apparently, a positive k_{DOM} value indicates that DOM has an enhancing effect on NOR photolysis, and a negative k_{DOM} value indicates DOM causes inhibition of NOR photolysis.

The impacts of DOM on sensitized photolysis of three NOR species were evaluated with different concentrations and kinds of DOM. A significant difference in DOM influence was observed on sensitized photolysis of the three NOR species (Fig. 6). For zwitterionic and anionic NOR, the three kinds of DOM caused obvious inhibition. Nevertheless, the impacts of DOM on cationic NOR photolysis varied with its concentration, facilitating cationic NOR photolysis at lower concentrations (from 2 to 5 mg/L TOC, approximating natural sea water (Jeong et al., 2014)), and restraining cationic NOR photolysis at higher concentrations (10 mg/L TOC, approximating natural estuarine water (Abril et al., 2002)). Because at pH 7.5 and 9.5, NOR species were more easily transformed to $^3\text{NOR}^*$ under simulated solar light irradiation compared with pH 4.5 (Fig. 5),

Table 2 – Light screening factor of three kinds of dissolved organic matter (DOM) for wavelengths 290–400 nm.

DOM concentration (mg/L TOC)	S_λ		
	SRFA	ESHA	LHA
2	0.98	0.91	0.90
5	0.89	0.80	0.79
10	0.76	0.63	0.64

SRFA: Suwannee River fulvic acid; ESHA: Elliott soil humic acid; LHA: Leonardite humic acid.

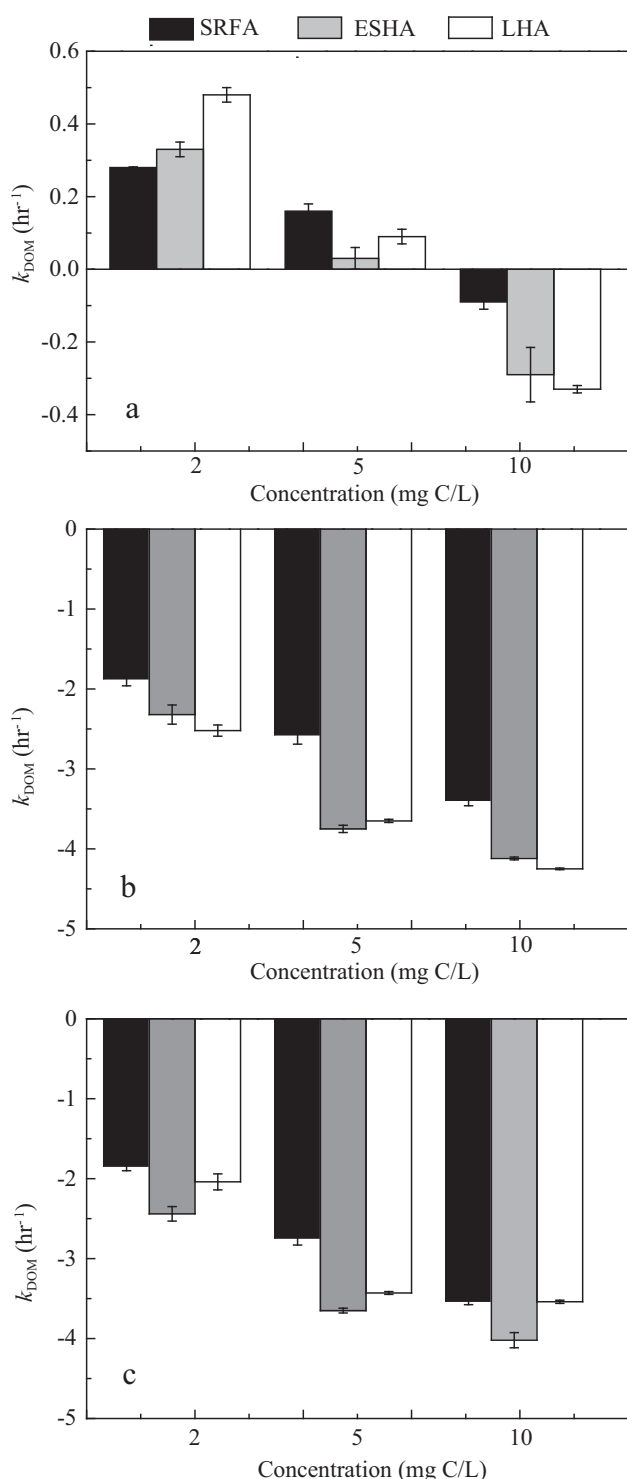


Fig. 6 – k_{DOM} values of three DOM for (a) cationic, (b) zwitterionic and (c) anionic species of NOR.

the quenching by DOM of $^3\text{NOR}^*$ (leading to the inhibition of fragmenting of NOR caused by $^3\text{NOR}^*$ and the quenching of $\cdot\text{OH}$ and $^1\text{O}_2$) was attributed to the inhibiting effect of DOM on sensitized photolysis of zwitterionic and anionic NOR. Moreover, with increased DOM concentration, the quenching of $^3\text{NOR}^*$ by DOM increased, leading to stronger suppression to zwitterionic and anionic NOR photolysis. Although the

inhibition effect of DOM was also present during photolysis of cationic NOR (pH 4.5), the enhancement of its photolysis by DOM outweighed its inhibition at lower concentrations of DOM, indicating that the cationic NOR photolysis underwent DOM-mediated sensitized photolysis in this case. At higher concentration of DOM (10 mg/L TOC), however, the inhibiting effect of DOM on cationic NOR photolysis outweighed its enhancement. In addition, DOM from different sources showed similar influencing tendencies on the photolysis of NOR species, but to different degrees. These differences were caused by the diversity of chromophoric functional units undergoing excitation on DOM from different sources (Nkhili et al., 2014).

Considering the similarity of DOM in natural water and the smaller difference among the influences of the three kinds of DOM on NOR photolysis (Fig. 6), SRFA (an aquatic DOM) was chosen as representative DOM to perform the EPR experiments to observe its influence on the concentration of $\cdot\text{OH}$ generated during photolysis of different NOR species. Comparing the signal intensity of the DMPO- $\cdot\text{OH}$ adduct generated in solutions of different NOR species with and without SRFA shown in Fig. 7, it was apparent that concentrations of $\cdot\text{OH}$ generated in zwitterionic and anionic NOR solutions were reduced to a great degree in the presence of SRFA, meaning the quenching of $\cdot\text{OH}$ by SRFA, which was attributed to the inhibiting effect of SRFA on sensitized photolysis of zwitterionic and anionic NOR. However, SRFA at the current concentration caused little inhibition of the photosensitization of cationic NOR, indicating that the facilitation of cationic NOR photolysis at lower DOM concentration was not caused by $\cdot\text{OH}$ enhancement. Nevertheless, DOM is composed of multiple chromophoric functional units, such as carboxyl and phenolic groups (Thurman and Malcolm, 1981), which can be influenced by the circumambient pH value. Therefore, the addition of SRFA with low concentration would give rise to enhancement of other reactive species ($^3\text{NOR}^*$, $^1\text{O}_2$) rather than $\cdot\text{OH}$ at pH 4.5, and thus induced the outweighing of sensitization compared to inhibition of SRFA. The results suggested that the impact of DOM on NOR photolysis was related to the direct and self-sensitive photolysis activity of NOR species and the concentration and components of DOM.

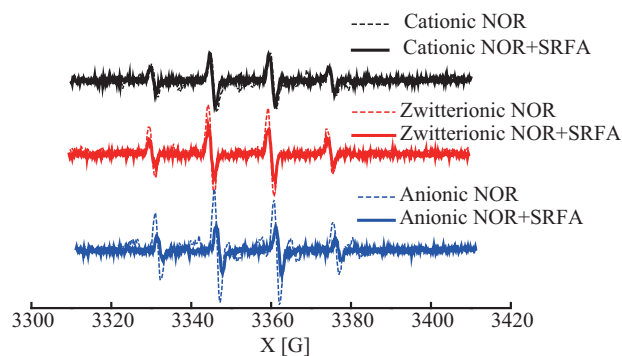


Fig. 7 – Comparison of the EPR signal intensity of the DMPO- $\cdot\text{OH}$ adduct in different NOR species containing solutions in the absence and presence of SRFA.

2.3. Identification of the intermediates of NOR photolysis

Some selected intermediates of different NOR species during the photolysis process in the presence or absence of DOM were identified and quantified by HPLC–MS/MS (Fig. 8), referring to the mechanism of FQ photolysis proposed in previous literature (Burhenne et al., 1997; Sturini et al., 2012). Considering the

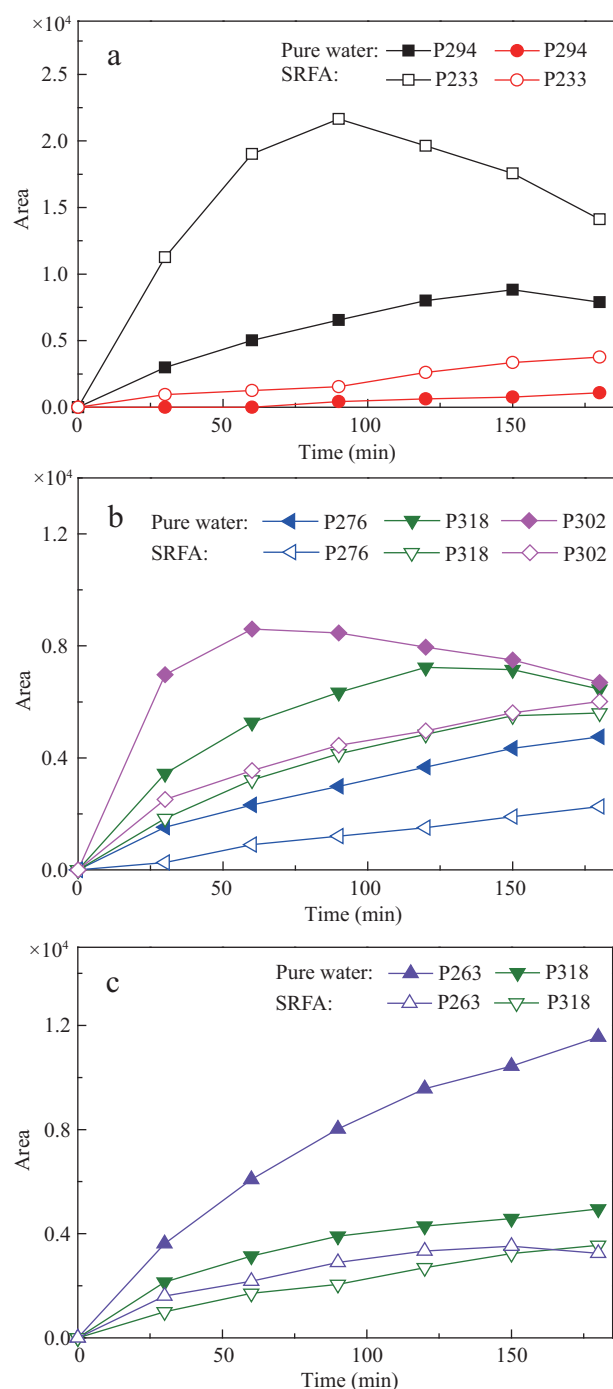


Fig. 8 – Evolution profiles of the photoproducts of cationic (a), zwitterionic (b) and anionic (c) species NOR in pure water and 5 mg/L TOC SRFA.

similarity of DOM in natural water and minor differences among the influences of three kinds of DOM on NOR photolysis (Fig. 6), SRFA (an aquatic DOM) was chosen as representative DOM to comparatively investigate the influence of DOM on the photolysis pathways of NOR species. SRFA had little impact on the distribution of photolysis intermediates, but showed its impact on the concentration evolution of intermediates. It should be noted that the photolysis intermediates of different NOR species and the influences of SRFA on the intermediate concentrations of different NOR species were quite different. For example, P294 and P233 (the chemical structures of all intermediates are shown in Fig. 8) were only detected during the photolysis of cationic NOR, P276, P318 and P302 were the intermediates detected during the photolysis of zwitterionic NOR, and P263 and P318 were the intermediates detected during the photolysis of anionic NOR. Comparing the intermediate concentrations with SRFA or not, it was found that SRFA facilitated the production of P294 and P233 as the intermediates of cationic NOR, however, it inhibited the production of P276, P318 and P302 as the intermediates of zwitterionic NOR and the production of P263 and P318 as the intermediates of anionic NOR. The results suggested that DOM had different influences on the photolysis of NOR species, which is consistent with the results from the comparison of k_{DOM} values of different NOR species (Fig. 6).

P294 and P233 were formed by cleavage of the piperazine side chain. P302 and P318 were generated by defluorination, and P276 was the further cleavage product of the piperazine ring of P302. P263 was formed by oxidation of the piperazine ring. According to the identified intermediates and the changes in their concentrations, and combined with the photolysis intermediates of NOR and the primary photolytic pathways for other FQs proposed by other researchers (Burhenne et al., 1997; Wei et al., 2013; Sturini et al., 2012), the primary photolytic pathways were inferred to include defluorination, cleavage of the piperazine side chain, and photooxidation (Fig. 9).

3. Conclusions

The present work demonstrates the impact of DOM on the photolysis of different dissociated species of NOR, and discusses the mechanism of the DOM effect on NOR photodegradation. The impact of DOM is related to the photolysis mechanisms of different NOR species and their concentration and components. Clearly the mechanism of DOM influence on the photolysis of NOR species in real natural water is more complicated than the one proposed in the present work, since the components in natural water are more complicated than in the experimental conditions. However, the results presented by this work are helpful for accurate risk assessment of ionizable organic chemicals, like many antibiotics.

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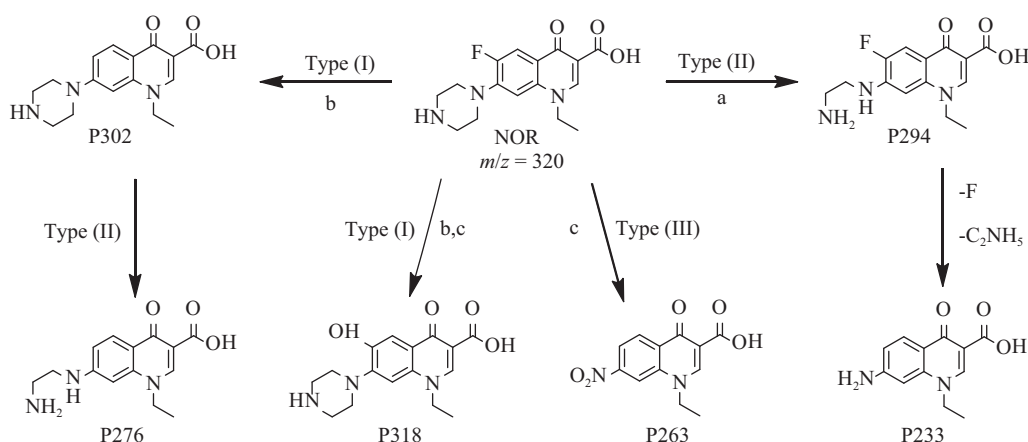


Fig. 9 – Primary photolysis pathways of cationic (a), zwitterionic (b) and anionic (c) species NOR in the presence of SRFA. The three photolytic pathway types (I), (II), and (III) stand for defluorination, cleavage of the piperazine side chain, and photooxidation, respectively.

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