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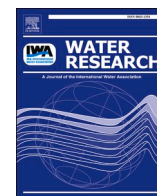
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Hydrophilicity-dependent photodegradation of antibiotics in ice: Freeze-concentration effects and dissolved organic matter interactions drive divergent kinetics, pathways and toxicity

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ABSTRACT

The photodegradation behavior of antibiotics with different hydrophilicity in ice and the synergistic effect of dissolved organic matter (DOM) remains unclear. This study unravels the dual role of DOM in driving divergent photodegradation pathways for five antibiotics (sulfamethoxazole (SMZ), oxytetracycline (OTC), levofloxacin (LFX), ciprofloxacin (CIP), and norfloxacin (NOR)) with different hydrophilicity in ice and compares the outcomes with a similar treatment in aqueous systems under simulated sunlight. The results showed that the photodegradation of hydrophilic antibiotics (SMZ, OTC, LFX) in ice is faster compared to water, which attributed to freeze-concentration effects that enhance light absorption in ice's liquid-like regions (LLRs). Conversely, hydrophobic antibiotics (CIP, NOR) degraded faster in water due to solvent cage effects. DOM amplified the photodegradation of hydrophilic antibiotics in ice by enriching humic-like substances in LLRs, which generated more reactive singlet oxygen (e.g. 77.1 % contribution to SMZ degradation), while inhibited the photodegradation of hydrophobic antibiotic via protein-like substances that quench excited states. Notably, DOM introduced ice-specific oxidative pathways of hydrophilic antibiotics, which altered their toxicity profiles and complicated toxicity trends toward *Vibrio fischeri*. These findings highlight the critical role of ice-phase photochemistry in cold regions, influencing antibiotic fate, transformation pathways, and ecological risks.

1. Introduction

The misuse of antibiotics has triggered a series of ecological and environmental issues, exacerbating risks to ecosystem and human health (Zhang et al., 2015). It has been reported that antibiotics are ubiquitously detected in various environmental media, with surface water bodies acting as their main sinks (Shao et al., 2018). Consequently, the pollution issues in watersheds caused by antibiotics cannot be overlooked. In surface waters exposed to sunlight, photochemical transformation is a significant pathway for the migration and transformation of antibiotics in aquatic systems (García-Galán et al., 2012; Lee et al., 2025; Ossola et al., 2021), in which the contribution of dissolved organic matter (DOM) is not negligible (Fede and Grannas, 2015; Zhang et al., 2022). After absorbing sunlight, DOM can generate various types of

photochemically produced reactive intermediates (PPRIs), such as its excited triplet state (³DOM*), singlet oxygen (¹O₂), and hydroxyl radicals (•OH), leading to the indirect photodegradation of antibiotics (Grannas et al., 2014; Liu et al., 2023).

In the Songliao Basin of the northeastern cold region in China, the optical characteristics and molecular composition of DOM are significantly different from the DOM characteristics and composition in tropical regions due to its high content of organic carbon and the influence of low-temperature environments (Wen et al., 2024). This difference could result in a higher degree of humification and different molecular weight distributions in the DOM of this cold area, thereby affecting its role and efficiency in the photodegradation processes (Guo et al., 2024). Besides, Northeastern China, being in a cold zone, experiences an average monthly temperature below 0 °C for five months each year. This leads to

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a prolonged ice-covered period. During this period, microbial metabolism in the watershed water is slow, and the water surface is covered by ice layers, hindering the volatilization, diffusion, and degradation of pollutants (Jiang et al., 2018; Kong et al., 2022; Zhang et al., 2020). Theoretically, the concentration of antibiotics in the watershed water during the ice-covered period would rise sharply. However, the actual detected concentrations of antibiotics have remained stable over time. Studies have indicated that this is attributed to the special contribution of temperature-insensitive photochemical processes to the migration and transformation of antibiotics in ice (Ge et al., 2016; Grannas et al., 2007; Klán and Holoubek, 2002).

The distribution of antibiotics in ice differs from that in water, with the freezing process causing local concentration of dissolved pollutants in the liquid-like regions (LLRs) around ice crystals, thereby altering their reactivity (Weber et al., 2009). Recent studies have revealed differences in the photochemical behavior of antibiotics in ice and water (Li et al., 2022b; Liu et al., 2023). It has been reported that the photodegradation rate of norfloxacin (NOR) in ice is 40.0 % higher than the rate in water due to the redshift of the absorption spectrum of NOR in ice, the enhancement of its absorption peaks, and the increase in its apparent quantum yield (Li et al., 2022a). Additionally, the photodegradation rates of sulfamethizole (SMT) and sulfachloropyridazine (SCP) in ice are 8.2 and 8.6 times faster than in water, respectively, whereas faster photodegradation rates of enrofloxacin (ENR) and difloxacin (DIF) were observed in water, with rate constants 1.8 and 2.0 times higher than in ice (Ge et al., 2024).

Furthermore, the generation of PPRIs from DOM in ice is significantly enhanced due to the freeze-concentration effect in LLRs. Under the same photon flux, the loss of furfuryl alcohol (FFA) caused by $^1\text{O}_2$ on ice is 11,000 times higher than in equivalent liquid samples (Bower and Anastasio, 2013). The steady-state concentration of $\bullet\text{OH}$ in LLRs is essentially the same as that in equivalent solutions. This has been suggested to be the result of an increase in both the sources and sinks of $\bullet\text{OH}$ in LLRs (Chen et al., 2016). Additionally, it was found that the triplet state of 3,4-dimethoxybenzaldehyde ($^3\text{DMB}^*$) in ice resulted in a 95 ± 50 -fold increase in phenol loss and a significant increase in concentration of phenol compared to an aqueous solution of similar composition (Chen and Anastasio, 2017).

As reported in a previous study, hydrophilic substances have strong interactions with water molecules and can form stable hydration structures. This allows them to be enriched in the pores of ice layers and in LLRs (Chen et al., 2023). As a result, the hydrophilicity of antibiotics could play an important role in the photodegradation of antibiotics in ice by dominating their distribution, as well as a study showed that differences in the hydrophilicity of antibiotics lead to different removal efficiencies (Yang et al., 2025). However, there is a lack of novel perspectives to investigate the similarities and differences in the photodegradation of antibiotics with different hydrophilic and hydrophobic properties in ice, especially in the presence of DOM that could induce the more uneven distribution of PPRIs in ice compared that in water.

To address these knowledge gaps, this study selected five antibiotics, sulfamethoxazole (SMZ), oxytetracycline (OTC), levofloxacin (LFX), ciprofloxacin (CIP) and NOR, which have a different hydrophilicity and which are frequently detected in rivers, to investigate the photodegradation behavior of antibiotics under frozen environmental conditions. Given the high organic carbon content and continuous freezing conditions in the surface waters of the Songliao Basin, we extracted DOM from the Songhua River (SRDOM) and the Liao River (LRDOM), as representatives of DOM. Furthermore, this study aims to elucidate the degradation pathways and the evolution of toxicity during the photodegradation of antibiotics with varying hydrophilicity in ice, thereby providing a comprehensive understanding of the environmental behavior and risks of antibiotics in surface water in cold regions.

2. Materials and methods

2.1. Materials

The reagents utilized in this research were of analytical reagent grade and the organic solvents used were of chromatographic purity, with their specifications comprehensively listed in Text S1 in the Supporting Materials.

Water samples were collected from the Songhua River and the Liao River located in Northeast China. Solid-phase extraction (SPE) was used to separate and enrich the DOM in the water samples. Specific information about the sampling sites is provided in Table S2 and the extraction procedures are detailed in Text S3.

2.2. Simulated sunlight irradiation experiments

The photolysis experiments were conducted in a GUV034-type photochemical reaction apparatus (Guangzhou Xingchuang Electronics Co., Ltd., China), utilizing a 400 W mercury lamp equipped with a 290 nm filter ($\lambda > 290$ nm) to mimic UV-A and UV-B portion of sunlight (N). The irradiation was divided into two parts: one part maintained the reaction temperature at 25 ± 1 °C, while in the other part the samples were placed in a freezer to freeze in the dark, and then subjected to photolysis experiments in a low temperature experiment box maintained at -15 ± 1 °C. In order to investigate whether the observed phenomenon is due to phase transition or temperature influence, experiments were further extended to -5 °C and 10 °C to deeply analyze its specific effect on related processes. To compare the photoreaction efficiency of the five antibiotics, the apparent quantum yields (Φ_T) of their photodegradation in ice and water were simultaneously measured (for detailed measurement methods, see Text S2) (Dulin and Mill, 1982; Laszakovits et al., 2017).

To investigate the impact of DOM on the photodegradation of antibiotics, different concentrations of six types of DOM were added to the antibiotic reaction solutions. Considering the high organic carbon content in the Songliao Basin, the effects of DOM concentrations of 5, 10, and 15 mgC L⁻¹ were examined. The solutions were then adjusted to pH 5.0, 7.0, and 9.0 using phosphate buffer to study the effects of DOM on antibiotic photodegradation under different pH conditions. Based on this, a detailed investigation was conducted into the underlying mechanisms behind the observed phenomena at pH 7.0 and DOM concentration of 5 mgC L⁻¹. The DOM used were three SRDOM (SRDOM-1, SRDOM-2, SRDOM-3), two LRDOM (LRDOM-1, LRDOM-2) and Suwannee River Natural Organic Matter (SRNOM) (detailed information is in Table S2). After mixing, both ice and water solutions were photolyzed in the reaction apparatus. Corrections were made for the photo-shielding effect caused by DOM, and the indirect photodegradation rate constants of the antibiotics (k_{ind} , with $k_{\text{ind-water}}$ for water and $k_{\text{ind-ice}}$ for ice) were calculated (the calculation formula is provided in Text S4).

Subsequently, quenching experiments were conducted with sorbic acid (SA, 0.1 mM) selected as a quencher for $^3\text{DOM}^*$ (Grebel et al., 2011), sodium azide (NaN_3 1 mM) as a quencher for $^1\text{O}_2$ (Boreen et al., 2004), and isopropanol (IPA, 1 mM) as a quencher for $\bullet\text{OH}$ (Latch et al., 2003).

To further validate the contribution of PPRIs produced by DOM to the photodegradation of antibiotics, a competitive kinetics method was employed to determine the second-order rate constants of the target antibiotics with $^1\text{O}_2$ and $\bullet\text{OH}$ in ice and water (Miller, 2005; Wang et al., 2019), with specific measurement steps detailed in Text S5. The second-order rate constants of antibiotics with $^3\text{DOM}^*$ were calculated according to Equation (S7).

2.3. Determination of the octanol-water partition coefficient ($\log K_{\text{ow}}$)

The $\log K_{\text{ow}}$ for the five antibiotics was quantified using a miniaturized shake-flask approach based on OECD 107 (Schönsee and Bucheli,

2020). To a glass vial, 200 μL of water-saturated octanol phase and 200 μL of octanol-saturated aqueous phase (with antibiotics) were added. The vial was sealed and shaken at 25 $^{\circ}\text{C}$ for 24 h in a constant - temperature shaker (ZWY - 240, Shanghai) at 200 rpm. After thorough shaking to reach partition equilibrium, the two phases were separated. The antibiotic concentrations in both phases were measured by high - performance liquid chromatography (HPLC), and $\log K_{\text{ow}}$ values were calculated using Eq. (1) (Port et al., 2018).

$$\log K_{\text{ow}} = \log \left(\frac{C_{\text{oct}}}{C_{\text{water}}} \right) \quad (1)$$

Where C_{oct} is the antibiotic concentration in the octanol phase ($\mu\text{g mL}^{-1}$); C_{water} is the antibiotic concentration in the water phase ($\mu\text{g mL}^{-1}$).

2.4. Determination of PPRIss generated by DOM

The [PPRIss] generated by SRDOM, LRDOM and SRNOM at a concentration of 5 mgC L^{-1} in ice and water were determined using the chemical probe method. FFA (0.1 mM) was used as a chemical probe for detecting $^1\text{O}_2$ ($^1\text{O}_2$ ss) (Haag and Hoigne, 1986), benzoic acid (BA, 0.1 mM) as a probe for detecting $\bullet\text{OH}$ ($\bullet\text{OH}$ ss), and 2,4,6-trimethylphenol (TMP, 0.1 mM) as a probe for detecting $^3\text{DOM}^*$ ($^3\text{DOM}^*$ ss) (Chu and Anastasio, 2003; Glover and Rosario-Ortiz, 2013). In the freezing experiments, the mixed solutions of the probes and DOM were frozen according to the method described in Section 2.2. Subsequently, the liquid and ice samples were irradiated at temperatures of 25 $^{\circ}\text{C}$ and -15°C , respectively, with further experimental details and calculation methods provided in Text S6.

2.5. Determination of antibiotic photolysis products

Photolysis experiments of solutions containing only the target antibiotics and mixtures of the target antibiotics with DOM were conducted in both ice and water. The photolyzed samples were analyzed using a high-resolution liquid chromatography-mass spectrometry (HPLC-MS, Orbitrap Exploris 120, Thermo Fisher Scientific, United States of America) to characterize and quantify the reaction products of the five antibiotics generated during the photodegradation experiments. Based on the identified products, potential degradation pathways of the target antibiotics during direct and indirect photolysis in ice and water were inferred.

2.6. Toxicity testing

This study utilized the bioluminescent bacterium *Vibrio fischeri* as a test organism to assess the acute toxicity of the five target antibiotics (5 mg L^{-1}) with and without DOM (5 mgC L^{-1}) during the photodegradation process at various sampling points. Prior to the toxicity assays, the pH of the antibiotic sample solutions was controlled at 7.0, after which the solutions were added to a diluted luminescent bacteria suspension containing 3 % sodium chloride (NaCl). The mixtures were exposed at room temperature for 15 min before being analyzed for fluorescence using a toxicity analyzer, with all experiments being repeated three times. Toxicity was expressed as the percentage inhibition of luminescence ($I\%$), calculated according to Eq. (2) (Zhou et al., 2019).

$$I\% = \frac{L_{\text{blank}} - L_{\text{sample}}}{L_{\text{blank}}} \times 100\% \quad (2)$$

Where L_{blank} is the luminous intensity of the blank sample; L_{sample} is the luminous intensity of the sample under test.

2.7. Methods of analysis

The ultraviolet-visible (UV/Vis) absorption spectra of the samples were obtained using a Hitachi U-2900 double-beam UV-

spectrophotometer.

Liquid samples were analysed immediately after the end of the light exposure, while frozen samples were first thawed at room temperature in the dark. An Agilent 1260II HPLC system (Agilent) with a UV-VIS detector and an Ultimate AQ-C18 column (250 mm $\times$ 4.6 mm, 5 mm, Welch Materials, Maryland) was used for the quantitative detection of the various samples, with the mobile phase composition, flow rate, detection wavelengths, and time to peak are shown in Table S3.

The distribution of antibiotics in ice was observed and imaged using cryogenic scanning electron microscope (cryo-SEM, Hitachi Regulus8100). The specific method is shown in Text S7.

The organic carbon content of the DOM was determined using a total organic carbon analyzer (Vario TOC, Elementar, Germany), and the three-dimensional fluorescence spectra of DOM were examined using a fluorescence spectrophotometer (Hitachi F-2700).

Based on the mass-to-charge ratio (m/z) of the degradation products, the main transformation products (TPs) of the five antibiotics were identified using high-performance liquid chromatography-mass spectrometry (HPLC-MS) equipped with a quadrupole and an electrostatic field orbital trap, as well as electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) sources. The mobile phase and gradient elution conditions for the determination of the five antibiotic products are shown in Table S4. Compound Discoverer 3.3 SP3 software was utilized for m/z analysis, which facilitated the determination of the composition and structure of the TPs.

3. Results and discussion

3.1. Direct photolysis of antibiotics in ice

Under dark conditions, no significant degradation occurred for the five antibiotics in either ice or water (Fig. S2). Upon irradiation with simulated sunlight ($\lambda > 290 \text{ nm}$), all five antibiotics underwent photodegradation in both ice and water, which followed pseudo-first-order kinetics ($R^2 > 0.95$). A further comparison of the observed photolysis rate constants (k_{obs} , with $k_{\text{obs-water}}$ for water and $k_{\text{obs-ice}}$ for ice) for the five antibiotics revealed that LFX, OTC and SMZ photodegraded more rapidly in ice, with $k_{\text{obs-ice}}$ being 2.0, 1.4, and 1.2 times that of $k_{\text{obs-water}}$, respectively (Fig. 1). In contrast, CIP and NOR photodegraded more rapidly in water, with $k_{\text{obs-water}}$ being 1.9 and 1.4 times that of $k_{\text{obs-ice}}$, respectively (Fig. 1a). The five antibiotics differ in their degradation rates in water due to their structural diversity. The sulfonamide moiety and heterocyclic ring of SMZ undergo direct photolysis through N-S bond breaking (Boreen et al., 2004), while the tetracyclic structure of OTC contains a conjugated double bond, which contributes to light absorption but is susceptible to solvent quenching. In contrast, CIP and NOR contain piperazine rings whose flexible conformation promotes rapid photo-oxidation, while their fluorine substituents enhance photoreactivity through dielectric effects (Li et al., 2020).

The Φ_T for SMZ, OTC, LFX, CIP, and NOR were determined and all of them are greater in water than in ice, being 1.5, 1.4, 1.8, 3.6 and 2.5 times higher in water, respectively (Table S5). For CIP and NOR, the fold increase in $k_{\text{obs-water}}$ is less than the fold increase of Φ_T in water, and for LFX, OTC, and SMZ, the values of Φ_T in ice were lower than in water, but the $k_{\text{obs-ice}}$ values were higher, indicating that the light absorption capacity of these five antibiotics is higher in ice than in water. This is primarily due to the enhanced absorbance of the five antibiotics in the ice, such as CIP and NOR, which show a red shift of 3 nm and 7 nm respectively at peak absorbance, moving the absorbance to a wavelength with greater photon flux (Fig. S3). As well as the indication that the water molecules in the ice exist in a hexagonal, tightly packed crystal structure that provides a relatively flat surface at the microscopic level (Hong et al., 2024). When light is incident on the surface of the ice, it is reflected in an orderly fashion, enhancing the light absorption of the ice relative to the water (Hullar et al., 2020; Li et al., 2024; McNeill et al., 2012).

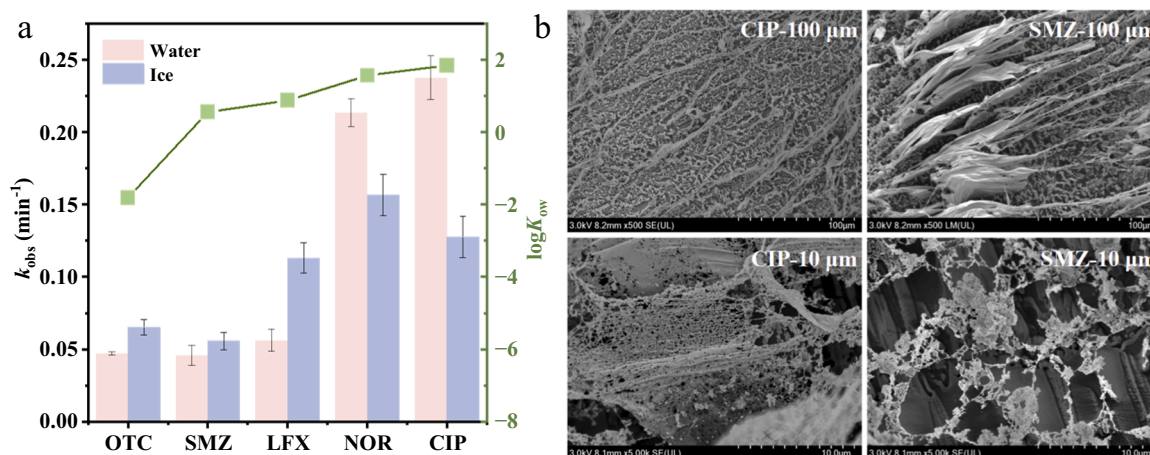


Fig. 1. (a) Observed pseudo-first order photolysis rate constants (k_{obs}) in ice and water and octanol-water partition coefficients of the five antibiotics; (b) The image of cryo-SEM of CIP and SMZ in pure ice (the white part is antibiotics).

The $\log K_{ow}$, which is an indicator for hydrophilicity/hydrophobicity (Woodburn et al., 1984), for the five antibiotics was determined based on the shake-flask method (OECD 107) (Schönsee and Bucheli, 2020). The values determined (shown in Fig. 1a) are consistent with those reported in literatures (Cheng et al., 2023; Fan et al., 2021; Lee et al., 2024). It was observed that the more hydrophilic antibiotics ($\log K_{ow} < 1$), LFX, OTC, and SMZ, photodegraded more rapidly in ice. This is attributed to the freeze-concentration effect, which has the greatest impact on the photodegradation of these three antibiotics. During the freezing process, hydrophilic antibiotic molecules are more locally concentrated in the LLRs around ice crystals (Barnes and Wolff, 2004), increasing their light absorption efficiency and enhancing the photo-reactivity of the antibiotics, thereby increasing their $k_{obs-ice}$. In contrast, the hydrophobic antibiotics ($\log K_{ow} > 1$), CIP and NOR have a higher value of k_{obs} in water (Fig. 1a), which is attributed to these hydrophobic chemicals being more prone to the solvent cage effect. The hydrophobic substances prefer to stay in the heterogeneous ice, in which the solvent cage effect is more pronounced, leading to slower reactions of the molecules in ice (McNeill et al., 2012). We have also confirmed the distribution of CIP and SMZ with different hydrophobicity in ice. As shown in Fig. 1b, compared with CIP, SMZ is more significantly aggregated and enriched in LLRs after freezing, while CIP is relatively more dispersed. Experimental results at different temperatures showed that liquid phase cooling (25 °C to 10 °C) only resulted in a slight decrease in the reaction rate, while freezing (10 °C to -15 °C) caused a significant difference in the degradation rate of hydrophilic antibiotics. This further proves that the above experimental results are caused by phase transition rather than temperature change (Fig. S4).

To assess the relevance in natural environments, we used Songhua River water samples for photolysis experiments in ice and water, and simulated partial freezing along with three freeze - thaw cycles. Results in Fig. S5 showed that in natural ice, the $k_{obs-ice}$ of hydrophilic antibiotics (SMZ, OTC, LFX) is faster than in natural water but slower than in pure water ice. For hydrophobic antibiotics (CIP, NOR), the trend is opposite. This is mainly due to a decrease in the absorbance of the five antibiotics in natural water and ice (Fig. S3) as well as impurities and bubbles in natural ice weakened but didn't fully offset the freeze-concentration effects, and partially disrupted the solvent cage effect for hydrophobic antibiotics. In the ice - water mixture state, the k_{obs} is between $k_{obs-water}$ and $k_{obs-ice}$, showing the continuous freeze-concentration and solvent cage effects during phase transition. Moreover, freeze - thaw cycles promoted hydrophilic antibiotic photolysis and reduced inhibition of hydrophobic antibiotic photolysis due to cumulative effects.

3.2. Effect of DOM on photodegradation of antibiotics in ice

3.2.1. Effects of freeze-concentration mediated DOM on antibiotic photolysis

As illustrated in Fig. 2, the addition of SRDOM, LRDOM, and SRNOM consistently enhanced the photodegradation of hydrophilic antibiotics (SMZ, OTC, and LFX) in ice, while their effects on the photolysis in water exhibited variability. In water, all the selected DOM inhibited the photodegradation of LFX while they promoted the photodegradation of SMZ and OTC, and the promotional effect was significantly weaker compared with the impact observed in ice. Also, the introduction of DOM consistently reduced the k_{obs} of hydrophobic antibiotics (CIP and NOR) in ice, exhibiting inhibitory effects on their photodegradation. Specifically, SRDOM and LRDOM demonstrated stronger inhibition in ice compared to their effects in water. Differently and divergent effects were observed in water. Especially for NOR, the addition of SRDOM-1, SRDOM-3, and LRDOM-2 increased the $k_{obs-water}$, thereby promoting NOR photodegradation in water. Additionally, compared to SRNOM, SRDOM and LRDOM exhibited higher photochemical activity (Table S5). The addition of SRDOM and LRDOM thus resulted in significantly higher k_{obs} values for both hydrophilic and hydrophobic antibiotic in ice and in aqueous environments as compared to the observations in the case of SRNOM addition.

To investigate and compare the impact of SRDOM, LRDOM and SRNOM on the photodegradation of different hydrophilic antibiotics, k_{ind} values induced by these DOM were calculated with the method described in Text S4 (Guerard et al., 2009). As can be seen in Fig. 2 and Fig. S6, the values of k_{ind} of hydrophilic SMZ and OTC are both greater than 0 in ice, and the k_{ind} of hydrophilic LFX in ice increases significantly in comparison to the rate constant in water, while the k_{ind} of hydrophobic CIP and NOR are both less than 0 in ice. Reports indicate that protein-like substances in DOM tend to migrate towards the ice layer, while humic-like substances predominantly remain in the LLRs (Feng et al., 2024; Pan et al., 2024). We analyzed the composition of the six DOM, and it can be observed from the three-dimensional fluorescence spectra that the main components of the six DOM are primarily humic-like, followed by protein-like substances (Fig. S7). Since SMZ, OTC and LFX are hydrophilic antibiotics, they are more concentrated in LLRs. Humic-like substances of DOM that also prefer to concentrate in LLRs contain a large amount of phenolic hydroxyl, carboxyl and other active functional groups (Lee et al., 2012). These functional groups are associated with high photochemical activity and promote the photodegradation of hydrophilic antibiotics in ice, leading to a k_{ind} greater than 0 (Cheng et al., 2022). On the contrary, CIP and NOR are more hydrophobic, which prefer a frozen in the ice as well as protein-like

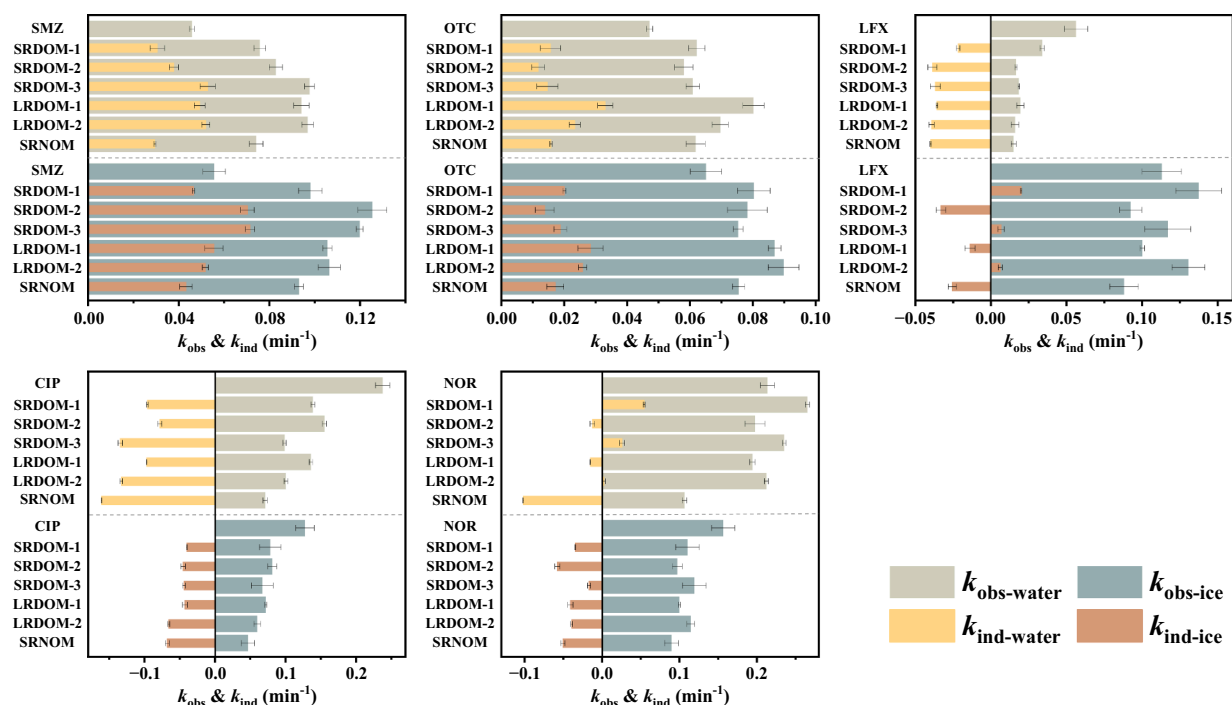


Fig. 2. The apparent first-order degradation rate constants (k_{obs}) of the five antibiotics studied and the degradation rate constants (k_{ind}) induced by the photosensitizing effect of DOM in the presence of DOM ($k_{\text{obs-water}}$ and $k_{\text{ind-water}}$ for water and $k_{\text{obs-ice}}$ and $k_{\text{ind-ice}}$ for ice).

substances of DOM (Guerard et al., 2009). The protein-like substances contain a large number of phenolics that quench the excited states of CIP and NOR molecules, exhibiting a dynamic quenching effect, leading to a k_{ind} less than 0.

3.2.2. Effects of different concentrations of DOM and different pH on antibiotic photolysis in ice

In view of the high organic carbon content (up to 17.02 mgC L^{-1}) in the Songliao Basin (Zhao et al., 2017), the effects of varying DOM concentrations in ice on the photodegradation of antibiotics were investigated. The results showed that for hydrophilic antibiotics, increased DOM concentrations exhibited distinct behaviors for LFX in ice and water: enhanced inhibition in water versus enhanced promotion in ice. Regarding OTC and SMZ, elevated DOM concentrations significantly amplified their photodegradation, particularly in ice where the promotional effects exceeded those in the aqueous phase. This indicates that the ice phase provides a more favorable environment for photodegradation of hydrophilic antibiotics. For hydrophobic antibiotics (CIP and NOR), the photodegradation inhibition rates in the ice and water exhibited a statistically significant positive correlation with DOM concentration (Fig. S8). Notably, the inhibitory intensity in the ice increased by 1.03 - 1.19 times and 1.27 - 1.31 times compared to the aqueous phase, respectively.

In the Songliao Basin, river water pH ranges from 6.5 to 8.5 (mean 7.3 ± 0.6), with the lowest values occurring during spring meltwater pulses (April - May) due to organic acid release from thawing soils (Zhao et al., 2017). In light of this, two types of DOM (SRDOM-1 and LRDOM-2) with a concentration of 5 mgC L^{-1} were selected to further investigate the photodegradation behavior of five antibiotics in ice and water under pH 5.0, 7.0, and 9.0. The photolysis rate of antibiotics is dominated by the ionization state regulated by pH (Fig. S9). In water, the protonated state generally accelerates photolysis (Boreen et al. 2004). At pH 5.0, SMZ and OTC enhance photon capture efficiency through hydrophobic aggregation, while LFX, due to piperazine protonation expanding the conjugated system, achieves the fastest photolysis rate in water. CIP and NOR undergo carboxylate deprotonation at pH 9.0 and piperazine ring amine protonation, resulting in the fastest

photochemical transformation rates. In ice, hydrophilic SMZ (anionic state, pH 9.0) and OTC (zwitterionic state, pH 7.0) degrade fastest due to LLRs enrichment and conformational optimization; LFX due to the competitive effect between carboxylate protonation (pH 5.0) and piperazine deprotonation (pH 9.0), exhibits a rate change of $< 5\%$ and becomes the only antibiotic with weak pH dependence. The degradation trend of hydrophobic CIP and NOR is consistent with that in water, but the rate is lower than in water.

When DOM is present, pH amplifies phase differentiation by reshaping DOM functionality. In water, DOM promotes the degradation of SMZ and OTC but inhibits that of CIP, NOR, and LFX under different pH conditions, with a more pronounced effect in ice, mainly due to the enhanced acidity or alkalinity of pH caused by LLRs enrichment (Fig. S9). At pH 5.0, protonation of protein components enhances the quenching of hydrophobic antibiotics CIP and NOR, while at pH 9.0, humic substance deprotonation doubles the photolysis rate of hydrophilic antibiotic SMZ, and LFX due to the neutral state of piperazine weakening its binding with DOM, shows a smaller rate increase. This reveals that hydrophilicity exerts a pH-dependent dual-directional regulation on the photolysis of antibiotics in ice.

3.3. Different roles of PPRIs on photodegradation of antibiotics in ice

The degradation of antibiotics in ice and water is critically influenced by PPRIs generated from DOM upon photoexcitation. To investigate the contribution of different PPRIs to the photodegradation of antibiotics with different hydrophilicity, quenching experiments were conducted, and the contribution rates of $^3\text{DOM}^*$, $^1\text{O}_2$, and $\bullet\text{OH}$ to the photodegradation of antibiotics were calculated (Fig. S10). The calculations revealed for the hydrophilic antibiotics (SMZ, OTC, LFX) that $^3\text{DOM}^*$ contributed the most to their photolysis in water (46.9 %, 34.0 %, and 15.7 %, respectively), whereas $^1\text{O}_2$ showed the highest contribution in ice (77.1 %, 27.5 %, and 38.4 %, respectively) (Fig. 3a and S12a, b). Similarly, $^3\text{DOM}^*$ served as the primary PPRI promoting the photodegradation of hydrophobic antibiotics (CIP and NOR) in water (13.3 % and 23.3 %), while $^1\text{O}_2$ emerged as the dominant contributor in ice (26.6 % and 26.1 %) (Fig. 3b and S12c). Furthermore, it was observed that the

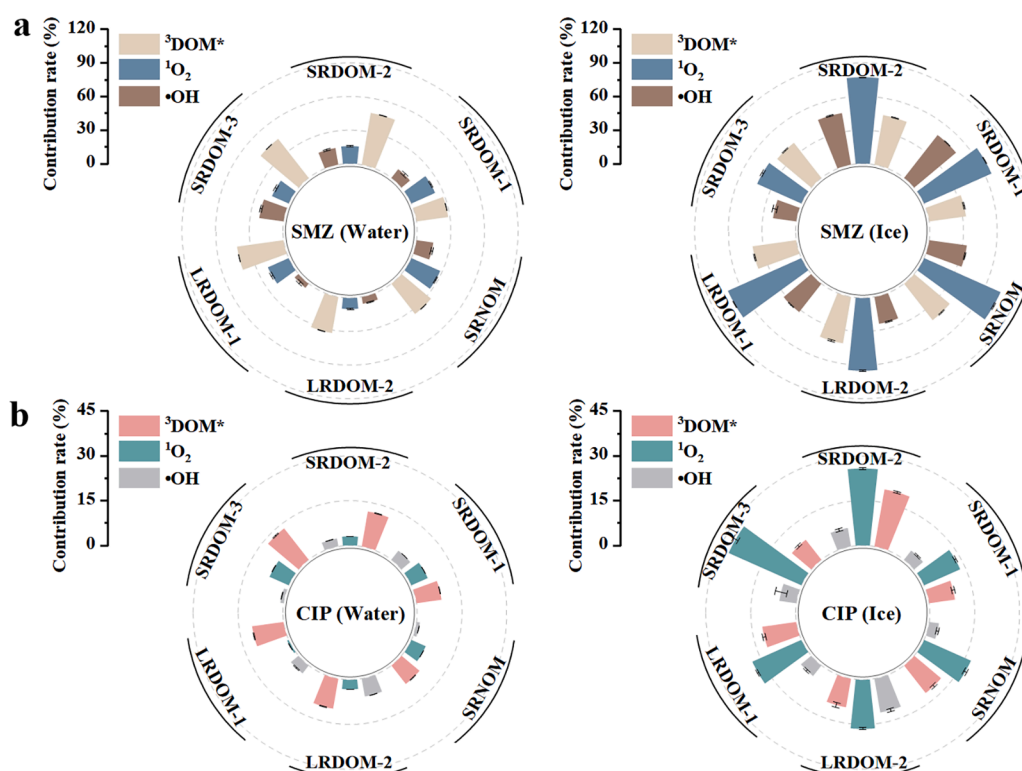


Fig. 3. The contribution of PPRIs to the photodegradation of SMZ (a) and CIP (b) in ice and water in the presence of DOM.

PPRIs exhibit a more pronounced role in initiating the degradation of hydrophilic antibiotics compared to hydrophobic antibiotics in both ice and water.

To further investigate the contribution of DOM-generated PPRIs to the photodegradation of antibiotics, the [PPRIs]_{ss} produced by the 6

DOM in ice and water (Fig. 4) and the rate constants for the secondary reactions of antibiotics with different PPRIs (Table 1) were determined, the values of the secondary reaction rate constants are in the same order of magnitude as those measured in previous studies (An et al., 2010; Boreen et al., 2004; Jeong et al., 2010; Lam and Mabury, 2005; Xu et al.,

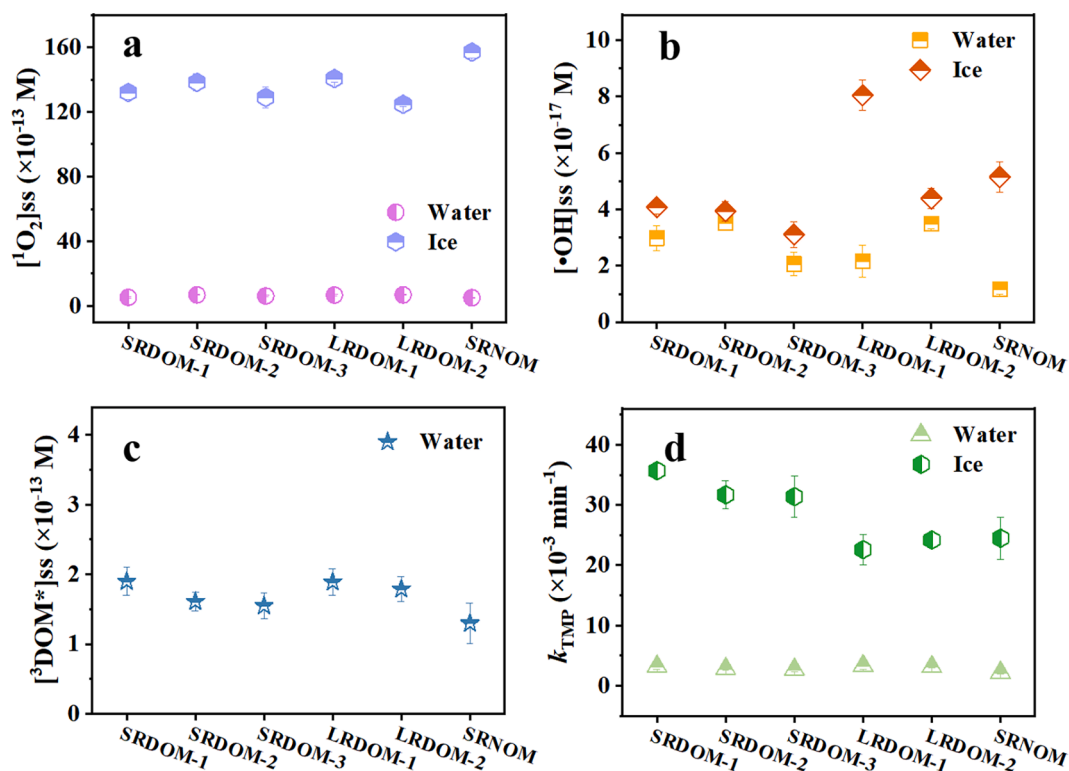


Fig. 4. Generation of [PPRIs]_{ss} (a, b, c) for six types of DOM in ice and water and rate constants for TMP loss (d) ([DOM] = 5 mgC L⁻¹).

Table 1

Secondary reaction rate constants for five antibiotics with $^1\text{O}_2$, $\bullet\text{OH}$ and $^3\text{DOM}^*$ in ice and water.

Antibiotic	$k_{A+^1\text{O}_2}$ ($\text{M}^{-1}\text{s}^{-1}$)		$k_{A+\bullet\text{OH}}$ ($\text{M}^{-1}\text{s}^{-1}$)		$k_{A+^3\text{DOM}^*}$ ($\text{M}^{-1}\text{s}^{-1}$)	
	Water	Ice	Water	Ice	Water	Ice
SMZ	2.5×10^5	9.5×10^5	4.8×10^9	8.1×10^9	1.7×10^{13}	2.2×10^{12}
OTC	1.5×10^6	7.2×10^6	8.4×10^9	5.8×10^9	7.1×10^{12}	3.8×10^{11}
LFX	3.9×10^7	1.5×10^7	1.8×10^{10}	1.2×10^{10}	/	3.7×10^{11}
CIP	3.0×10^6	2.1×10^6	2.0×10^{10}	3.2×10^{10}	/	/
NOR	2.5×10^6	1.3×10^6	7.3×10^{10}	1.1×10^{11}	9.3×10^{12}	/

2011). As shown in Fig. 4, the $[\text{O}_2]\text{ss}$ produced by the DOMs of different origins was similar, with SRDOM, LRDOM and SRNOM generating $[\text{O}_2]\text{ss}$ in ice which were 20.1 - 25.0, 18.1 - 20.9 and 30.7 times higher than in water, respectively. At the same concentration, the enrichment of $[\text{O}_2]\text{ss}$ produced by SRDOM and LRDOM in ice relative to water was less than that of SRNOM. The increase of $[\text{O}_2]\text{ss}$ in frozen environments is attributed to the freeze-concentration effect of DOM in ice. Compared to aqueous solutions, DOM is highly concentrated in the LLRs of ice (Bower and Anastasio, 2013). Studies also reported that the $[\text{O}_2]\text{ss}$ generated by Suwannee River fulvic acid and Elliott Soil humic acid in ice are 51.7 and 7.5 times higher than in water, respectively (Liu et al., 2023). This is similar to the results of this study and also indicates that $^1\text{O}_2$ plays a major role in ice, mainly due to the significant enrichment of $[\text{O}_2]\text{ss}$ from DOM in ice.

There were no significant differences in $[\bullet\text{OH}]\text{ss}$ in ice compared to water, except for an increase in LRDOM-1 and SRNOM (Fig. 4), mainly due to the concentrations of these two DOM and $\bullet\text{OH}$ precursors in LLRs, which enhances the photochemical production of $\bullet\text{OH}$. Especially in humus-rich DOM (Fig. S7), as was also observed in a previous study (Chen et al., 2016). Currently, there is no accurate method to evaluate the $[\text{DOM}^*]\text{ss}$ generated in ice, so the first-order rate constant of TMP loss (k_{TMP}) is used to assess the reactivity of DOM in ice. In ice, when the DOM concentration is 5 mgC L^{-1} , k_{TMP} is 6.8 to 11.6 times higher than in water, indicating that $^3\text{DOM}^*$ is produced in higher amounts in ice compared to water. However, the enrichment multiples in ice are much lower than the multiples reported for $^3\text{DMB}^*$ enrichment in ice (Chen and Anastasio, 2017), possibly due to the quenching effect of higher concentrations of DOM on the production of $^3\text{DOM}^*$.

The functional groups of antibiotics critically govern their reactivity with PPRIs. For hydrophilic SMZ and OTC, the aniline group ($-\text{NH}_2$) exhibits high susceptibility to $^1\text{O}_2$ attack via electron transfer, making $^1\text{O}_2$ the dominant contributor to their photodegradation in ice. This is directly evidenced by their 4.8 and 3.8 times higher second-order rate constants in ice versus water (Table 1), consistent with the results that freeze-concentration enhanced $^1\text{O}_2$ exposure in LLRs. Conversely, for hydrophobic antibiotics (CIP and NOR), the piperazine group ($-\text{N}_4\text{H}$) undergoes rapid oxidation by $^3\text{DOM}^*$ but suffers dynamic quenching by protein-like DOM in ice, aligning with their negative k_{ind} values (Fig. 2). Notably, the C-F bond in fluoroquinolones (CIP, NOR, LFX) resists direct photolysis, requiring $\bullet\text{OH}$ -mediated defluorination. However, $\bullet\text{OH}$ shows minimal ice and water differentiation in both abundance (Fig. 4) and antibiotic reactivity (Table 1), explaining its minor role in ice-phase kinetics.

3.4. Photodegradation products and pathways of antibiotics in ice

There is a distinct difference in the influence of DOM on the photodegradation process of the five antibiotics in ice and water as discussed above. This could further lead to differences in the photochemical transformation pathways of antibiotics in the presence of DOM. Based

on the retention times of degradation products, targeted m/z values, tandem MS fragmentation patterns, and references to previous studies, the structures of photodegradation products of the five antibiotics in the presence and absence of DOM in ice and water were formulated (Table S7 and Figs. S13 - S17 for details). Based on the identified intermediate compounds, potential reaction pathways for the antibiotics in ice and water were proposed. The results are shown in Fig. 5 with SMZ and CIP as representatives and Fig. S18 with other antibiotics.

For hydrophilic SMZ, four main degradation pathways were identified, involving ring opening and breaking of the oxazole ring, oxidation of the amino-N-position, desulfurization and acetylation at the -N-position (Fig. 5a). In pathway I, with or without DOM, SMZ undergoes ring-opening cleavage of the oxazole ring in both ice and water to form TP216 and TP100(2), followed by further methylation of the amino group to form TP215 and TP100(1) in water. In ice, TP216 is more stable than in water. In pathway II, under both conditions, SMZ undergoes photo-oxidation at the amino-N position on the benzene ring to form TP270. This is consistent with previous reports (Hu et al., 2007), and this photo-oxidation is followed by further photodegradation to the smaller molecular products TP110(1)/(2). In pathway III, in the presence of DOM, an additional methyl on the oxazole ring of SMZ is detected as TP268 in water, followed by hydroxylation after S-N bond cleavage in the sulfonyl group to form TP172, and further induction of C-S bond cleavage to form TP110(3) (Tang et al., 2022), with products TP172 and TP110(3) also detected in the absence of DOM in both ice and water. Pathway IV occurs only in ice, with or without DOM, where the amino-N position and the -N position on the S-N bond of SMZ undergo acetylation to form the carbonyl products TP296(1)/(2), and further demethylation to form the smaller molecular products TP165. For OTC, the primary degradation pathways include demethylation, hydroxylation, and methyl oxidation (Fig. S18a) (Delépée et al., 2000; Li et al., 2015). In the presence of DOM, distinct from direct photolysis, differences occur in the further oxidation of pathway I and the oxidation of methyl groups in pathway IV, which were also observed in previous studies (Chen and Huang, 2011; Han et al., 2020). For LFX, differences in the presence or absence of DOM occur mainly in processes such as hydroxylation reactions in pathway I and II and defluorination in pathway IV, which have also been reported in the literature (Fig. S18b) (Ge et al., 2015).

For hydrophobic CIP, four main degradation pathways were identified, involving the cleavage and oxidation of the piperazine ring, defluorination, and decarboxylation (Fig. 5b). In pathway I, in the presence of DOM, the piperazine ring of CIP undergoes acetylation to form TP360(1) in both ice and water, followed by further oxidation and ring cleavage to transform TP360(1) into TP334(1)/(2), a product also detected in another study (Paul et al., 2010). Eventually, this intermediate completely breaks down to form TP236(2). The transformation from TP334(1)/(2) to TP236(2) was also detected in the absence of DOM in both ice and water. In pathway II, with or without DOM, CIP primarily undergoes defluorination to form TP330, which is a common reaction pathway for CIP (Guo et al., 2013; Paul et al., 2010), followed by further cleavage of the piperazine ring and carboxyl group in ice to form the unique products TP177 and TP163. In pathway III, in the presence of DOM, CIP undergoes hydroxylation at different positions on the benzene ring as observed in previous study (Guo et al., 2013), with TP348(1) detected in ice and TP348(2) in water, followed by further cleavage of the piperazine and cyclopropyl groups to produce TP236(1)/(2) (Paul et al., 2007). In pathway IV, the cyclopropyl group of CIP is oxidized in the presence of DOM to form unique products in ice; TP348(3) and TP360(2), which are further oxidized to TP240 in both ice and water. For the other hydrophobic antibiotic NOR, pathway I primarily involves the initial formation of TP304 due to oxidation by $^1\text{O}_2$, as also detected in previous studies (Li et al., 2022a). In pathway II, in the presence of DOM, TP294 in water further breaks down into TP236(1), while in ice, it breaks down to form products with the same m/z but different structures, TP236(2)/TP236(3) (Fig. S18c).

Regarding the analysis of the photodegradation pathways for the five

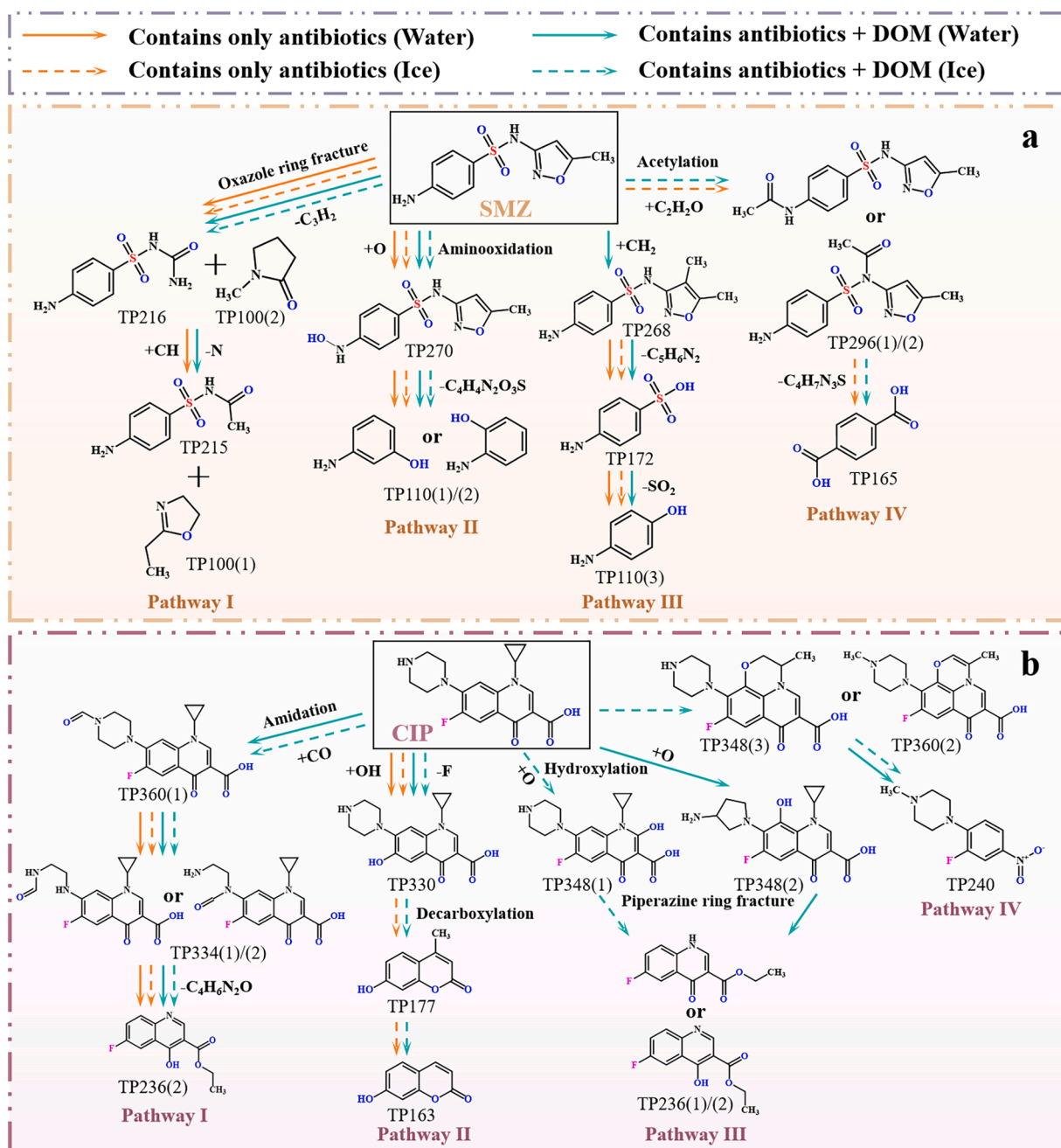


Fig. 5. Possible photodegradation transformation pathways for SMZ (a) and CIP (b) with and without DOM in ice and water (Orange lines indicate antibiotics only, green lines indicate DOM-containing antibiotics; solid lines indicate water, dashed lines indicate ice).

antibiotics with different hydrophilicity, it was found that the differences in pathways between ice and water during direct photodegradation are not significant. When DOM is present, the degradation pathways of the antibiotics differ in ice compared with the pathways in water. Thus, the uneven distribution of PPRIs from DOM in ice not only induces different photodegradation rates, but also results in different degradation pathways of these antibiotics.

3.5. Toxicity changes during photodegradation of antibiotics in ice

To reveal the environmental risk of antibiotics during their transformation in ice, the acute toxicity of the five antibiotics and the photodegradation mixtures, with and without DOM, in ice and water, to *Vibrio fischeri* was measured. The results are shown in Fig. 6 with SMZ and CIP as representatives and Fig. S19 with other antibiotics.

For hydrophilic antibiotics (SMZ, OTC, and LFX), when containing only antibiotics, the inhibition rates in both ice and water slowly increased with irradiation time, and due to the faster photodegradation in ice, the maximum inhibition rate was reached in a shorter time period compared to the maximum rate of inhibition of samples irradiated in water (Fig. 6a and S19a, b). Divergent toxicity trends were observed between ice and water following DOM addition. A continuous increase of toxicity of samples of SMZ irradiated in water within 25 min was observed, while in samples of SMZ irradiated in ice the relative inhibition rate gradually increased within 20 min and then decreased between 20 - 25 min (Fig. 6a). The initial increase in the inhibition rate was associated with the accumulation of transient photoproducts, which are more toxic than the parent compound, and the subsequent decrease presumably due to the unique photodegradation pathways of SMZ in ice following further photodegradation to form less toxic TP296(1)/(2) and

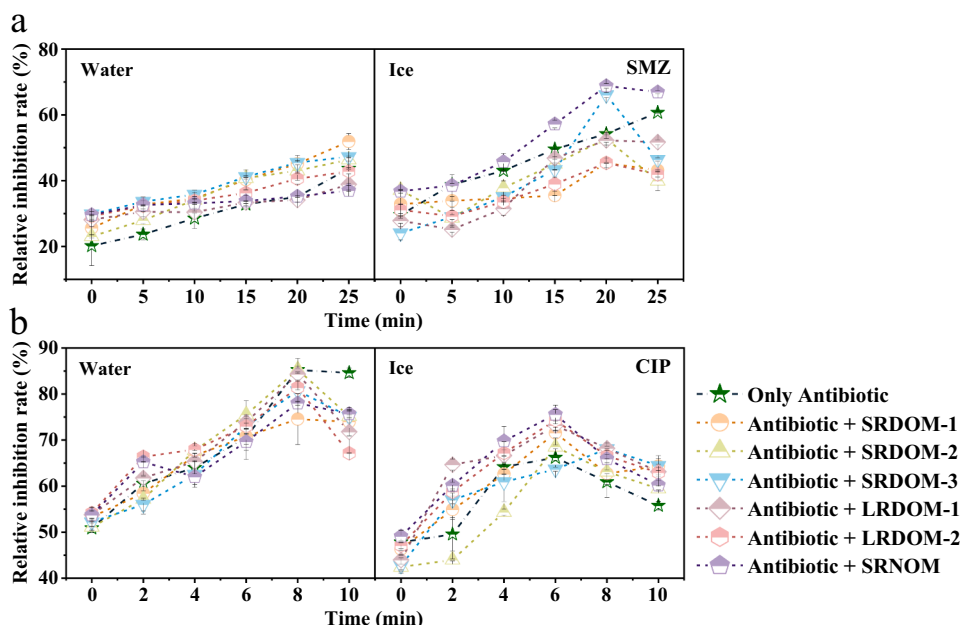


Fig. 6. The relative inhibition rates of *Vibrio fischeri* by SMZ (a) and CIP (b) as a function of irradiation time in the presence and absence of DOM in ice and water.

TP165 (Fu et al., 2018), leading to a decrease in relative inhibition rates. In case of OTC the acute toxicity of TP477(1)/(2) in Fig. S18a was significantly higher than the acute toxicity of doxycycline (Han et al., 2020), and the unique pathways present upon addition of DOM led to the transformation of TP477(1)/(2). This resulted in the relative inhibition rate of the luminescent bacteria by OTC containing DOM first increasing and then decreasing (Fig. S19a). The mixture of LFX and DOM in water also experienced a decrease in inhibition rates during the 15–20 min interval of photodegradation due to defluorination reactions as shown in Fig. S18b; in ice, the toxicity increased slowly, and at 20 min, the toxicity was greater than in samples irradiated in water (Fig. S19b). This biphasic toxicity trend is particularly evident in ice, as the hydrophilic antibiotics degrade more rapidly initially in ice ($k_{\text{obs-ice}} > k_{\text{obs-water}}$).

For hydrophobic antibiotics (CIP and NOR), degradation in ice is slower ($k_{\text{obs-ice}} < k_{\text{obs-water}}$), which results in a lower peak toxicity compared with that in water and a slower toxicity decline process. For instance, CIP-containing samples irradiated in water exhibited a peak relative inhibition rate of 85.23 % after 8-minute irradiation (Fig. 6b), while NOR-containing samples reached a maximum of 87.80 % following 6-minute irradiation in water (Fig. S19c). The lower photolytic toxicity observed in ice compared to water can be attributed to the further degradation of CIP and NOR intermediates in ice, leading to the formation of less toxic photoproducts. Following DOM addition, the relative inhibition rates in both ice and water aligned with the direct photodegradation trend, initially increasing and subsequently decreasing with prolonged irradiation time. This behavior primarily stems from defluorination and decarboxylation, both of which compromise the core structures of hydrophobic antibiotics CIP and NOR, thereby diminishing the antimicrobial activity and toxicity of their photodegradation products.

4. Conclusions

The seasonal ice formation in mid- to high-latitude regions constitutes a natural phenomenon, with seasonally ice-covered rivers accounting for approximately 15–20 % of the global river network length. The results in this study demonstrated that antibiotic residues in an ice environment undergo distinct photodegradation mechanisms compared to liquid water. The freeze-concentration effect in ice accelerated the

photodegradation of hydrophilic antibiotics. In contrast, hydrophobic antibiotics exhibited slower rates of direct photodegradation in ice than in water due to solvent cage effects. DOM, as a key factor affecting the photodegradation of antibiotics, with interactions with freeze-concentration effect, drives divergent photodegradation behaviors of antibiotics. However, quantitative characterization of these DOM-antibiotic interactions in ice (e.g., binding constants/the interaction among PPRs) remains technically challenging, necessitating future development of cryogenic-specific techniques. The distribution pattern of DOM in ice promotes the photolysis of hydrophilic antibiotics while inhibiting that of hydrophobic antibiotics. Additionally, the hydrophilicity modulation of photolysis in antibiotic ice was similarly bidirectional in terms of DOM concentration and pH dependence.

For hydrophilic and hydrophobic antibiotics, the interactions between freeze-concentration effects and DOM also alter their reaction pathways and toxicity profiles. Hydrophobic antibiotics, while degrading slower in ice, formed less toxic intermediates compared to water, while hydrophilic compounds maintained higher toxicity due to stabilizing by-products. These dynamics underscore the need to account for phase-dependent photochemistry, especially for contaminants with different hydrophilicity, in environmental risk assessments, particularly under climate change scenarios where ice cover dynamics are shifting. Future studies should be combined with on-site ice core sampling and post-melt toxicity testing to gain a deeper understanding of the migration process of TPs in ice.

CRedit authorship contribution statement

Jingshuang Cui: Writing – original draft, Data curation. **Yue Chen:** Writing – review & editing. **Fangyuan Cheng:** Writing – review & editing. **Hao Yang:** Writing – review & editing. **Jiao Qu:** Supervision, Project administration, Funding acquisition. **Ya-nan Zhang:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Willie J.G.M. Peijnenburg:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.watres.2025.124277](https://doi.org/10.1016/j.watres.2025.124277).

Data availability

Data will be made available on request.

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