Photodegradation of organic micropollutants in aquatic environment: Importance, factors and processes

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A B S T R A C T

Photochemical reactions widely occur in the aquatic environment and play fundamental roles in aquatic ecosystems. In particular, solar-induced photodegradation is efficient for many organic micropollutants (OMPs), especially those that cannot undergo hydrolysis or biodegradation, and thus can mitigate chemical pollution. Recent reports indicate that photodegradation may play a more important role than biodegradation in many OMP transformations in the aquatic environment. Photodegradation can be influenced by the water matrix such as pH, inorganic ions, and dissolved organic matter (DOM). The effect of the water matrix such as DOM on photodegradation is complex, and new insights concerning the disparate effects of DOM have recently been reported. In addition, the photodegradation process is also influenced by physical factors such as latitude, water depth, and temporal variations in sunlight as these factors determine the light conditions. However, it remains challenging to gain an overview of the importance of photodegradation in the aquatic environment because the reactions involved are diverse and complex. Therefore, this review provides a concise summary of the importance of photodegradation and the major processes related to the photodegradation of OMPs, with particular attention given to recent progress on the major reactions of DOM. In addition, major knowledge gaps in this field of environmental photochemistry are highlighted.

1. Introduction

Photochemistry is deeply integrated into the Earth's biological and ecological systems. In the atmosphere, the presence of oxygen and its photochemical product, ozone, screen out most ultraviolet radiation (UV) from the sun, making life on earth possible. Visible light, which is transmitted through the atmosphere, is intimately involved in various biological and chemical phenomena, such as vision of humans and animals, photosynthesis, and photodegradation. Those phenomena are explained by the sequential reactions caused by excited states of atoms and molecules (Wayne, 2005). As such, solar light and the induced photochemical processes are fundamental aspects of ecosystems and the environment. Consequently, photochemistry often appears as a dominant process in health and environmental problems as well. Nucleic acids and proteins are readily damaged by short-wavelength radiation (i.e., UV) and ecosystems can be disrupted by excess or unwanted light (i.e., light pollution) (Li et al., 2022). Such alterations of the light

environment have been shown to date mostly in relation to plant and animal physiology (Häder and Barnes, 2019; Li et al., 2022) as well as aquatic photochemistry and microbiology (Sulzberger et al., 2019).

Organic micropollutants (OMPs) are a serious concern due to their occurrence, persistence, and toxicity in aquatic environments. For instance, pharmaceuticals and personal care products (PPCPs) have been frequently detected worldwide in many water bodies including coastal seawaters, rivers, and lakes (Madikizela et al., 2020). Given their unexpected interaction with organisms, a certain portion of OMPs is detrimental to aquatic organisms (Rozas et al., 2017), including bacteria, algae, invertebrates (Brausch and Rand, 2011; Hernando et al., 2006; Michael et al., 2014) and fish (Crane et al., 2006; Schwaiger et al., 2004). The direct consequence of antibiotic residues is the development of antibiotic-resistant bacterial strains (Grenni et al., 2018), which can potentially cause severe disease, including urinary tract, lower respiratory tract, and bloodstream infections (Sanganyado and Gwenzi, 2019). In addition, even at low concentrations, long-term exposure to OMPs

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increases the ecological risk to aquatic organisms in the water environment (Kumar et al., 2019; Yang et al., 2020). Generally in aquatic ecosystems, each OMP can exhibit a wide range of concentrations (ng/L to µg/L level) (Kameda et al., 2011; Patel et al., 2019; Petrović et al., 2014; Vimalkumar et al., 2018; Zareitalabad et al., 2013). Relatively high OMP concentrations have commonly been observed in water bodies that receive treated wastewater because conventional wastewater treatment plants are not equipped to eliminate OMPs efficiently (Gruchlik et al., 2018; Knopp et al., 2016; Margot et al., 2013; Ribeiro et al., 2015; Sörengård et al., 2019).

Photodegradation plays an essential role in the fate of OMPs, particularly in the surface layer of water bodies, where solar irradiation (i.e., UV and visible light) are abundant during the daytime, thereby inducing direct and indirect photolysis of OMPs. In direct photolysis, OMPs undergo various photodegradation paths depending on their chemical structure, and the direct absorption of solar radiation is enhanced by the presence of light-absorbing functional groups such as aromatic rings (Boreen et al., 2003; Challis et al., 2013; Edhlund et al., 2006; Fatta-Kassinos et al., 2011). Indirect photodegradation in natural water involves photochemically produced reactive intermediates (PPRIs) such as singlet oxygen ($^1O_2$) and hydroxyl radical (HO·), which can initiate photodegradation of OMPs (Vione et al., 2014). Overall, the rate of photodegradation depends on the chemical structure of OMPs, the irradiance (determined by the photon flux in a particular wavelength band), and the water constituents present (e.g., DOM; Boreen et al. 2004, Fent et al. 2006).

Despite a growing number of studies on such underwater photolysis, a majority of them describe processes and mechanisms only under well-controlled conditions (e.g., in a photochemical reactor equipped with an artificial lamp). Thus, it is often difficult to place such knowledge in the context of photodegradation of OMPs in the natural aquatic environment. Compared with other pathways (e.g., biodegradation), the importance of photodegradation in the real environment is more largely unknown. Recently, several articles have been conducted to describe the *in situ* photochemical processes (Bouhala et al., 2020; Dimou et al., 2005; Shih and Wang, 2009). Nevertheless, the focus on irradiation conditions, processes, and target OMPs remain scarce and fragmented. These facts underscore the critical need to conduct comparative studies (e.g., Baena-Nogueras et al. 2017, Ossola et al. 2021) to obtain a comprehensive overview of the photodegradation as well as to undertake a quantitative assessment of OMPs in the aquatic environment.

Water matrix is widely regarded as an important factor in determining the photodegradation of OMPs due to its role in the production of PPRIs and the inhibition of photolysis (Challis et al., 2014; McNeill and Canonica, 2016; Sharpless and Blough, 2014; Vione et al., 2014; Vione and Scozzaro, 2019; Yan and Song, 2014). Nevertheless, limited knowledge of photodegradation processes in various water matrices, including the complex photoreactions of DOM, preclude us to obtain a comprehensive overview of such processes. In addition, photodegradation is also affected by various other physical environmental factors such as water depth, latitude, season, and time of day. These physical factors have received less attention than the water matrix, although many of the former are likely more important in defining the photodegradation kinetics of OMPs than the latter. Therefore, the impact of physical factors on photodegradation need to be elucidated as the basis for enhancing knowledge of environmental photochemistry in the broader sense.

Given these environmental processes that have yet to be revealed, we believe that it would be useful to update the existing knowledge in the field to achieve more effective management of aquatic photodegradation of OMPs. This review, therefore, aims to provide a concise overview of the importance of photochemical reactions in the fate of OMPs in the aquatic environment from a comprehensive viewpoint and addresses the basics of aquatic photochemistry and its relation to environmental factors including the water matrix and physical conditions.

2. Why photodegradation?

Solar energy is abundant on the surface layer of water bodies. Although approximately 72% of the solar energy reaches the Earth's surface (Valero et al., 2000), the short wavelengths (≤280 nm) are completely absorbed, due to atmospheric absorption and scattering. Consequently, direct solar irradiance is decreased from 1361 W m^{-2} at the top of the atmosphere to about 1000 W m^{-2} at the Earth's surface (Coddington et al., 2016; Myers, 2013). The total energy that reaches the Earth's surface is about 3×10^{24} J per year, which is equivalent to approximately 6500 times the annual energy consumption of humankind (4.6×10^{20} J per year) (Klan and Wirz, 2009). Within a water body, OMPs are mainly degraded and transformed by biological (e.g., biodegradation) and chemical (e.g., photolysis, hydrolysis) processes. Among them, hydrolysis is usually slow and requires the existence of hydrolytic functional groups in the OMP such as ester bonds (Xu et al., 2019, 2021) while photodegradation and biodegradation occur more extensively in the water environment. Owing to the abundant solar radiation and various photosensitizers (i.e., DOM) in the water, photodegradation may be a pivotal removal pathway for many OMPs, with possible interactions with other processes.

Baena-Nogueras et al. (2017) reported that the photodegradation and biodegradation rate constants of 33 frequently detected PPCPs, carried out following OECD guidelines No.316 (OECD, 2008) and No. 306 (OECD, 1992), were significantly larger than their hydrolysis rates. Furthermore, most of the studied PPCPs exhibited faster photodegradation (half-life, $t_{1/2}$ range 0.02–29 h) than biodegradation ($t_{1/2}$ range 4–2310 h) (Fig. 1), while we should note that this comparison depends on local physicochemical condition as well. In addition, typical PPCPs such as ibuprofen (IBP), diclofenac (DCF) and sulfamethoxazole (SMX) exhibited photodegradation rates of 0.03 h^{-1} ($t_{1/2}$ 23 h), 4.04 h^{-1} ($t_{1/2}$ 0.17 h), and 0.19 h^{-1} ($t_{1/2}$ 3.73 h), respectively, in spiked pure water under simulated solar light. In contrast, IBP exhibited a biodegradation rate of 0.0005 h^{-1} ($t_{1/2}$ 1386 h) in spiked freshwater, while DCF and SMX exhibited no biodegradation at all for 28 days (Baena-Nogueras et al., 2017). These studies suggested that photodegradation may play a more important role in many OMPs transformation processes than biodegradation.

Many OMPs are toxic to microorganisms (Ebert et al., 2011; Larsson et al., 2007; Le Page et al., 2017; Patel et al., 2019; Rubasinghege et al., 2018) partly because of the intended uses of the OMPs, for example, as antimicrobial agents. This toxicity poses significant challenges in terms of biodegradability in the environment. Hence, among the potential degradation and transformation processes, photodegradation possibly plays a rather important role in deciding the fate of OMPs in aquatic environments. It is also noteworthy that photochemical transformation of OMPs, including photodegradation in some cases, may result in photo-induced toxicity and generate more persistent products, which possibly increases the ecological risk (Buth et al., 2007; Latch et al., 2003a; Plumlee et al., 2009; Robert et al., 2017). For instance, the photodegradation of fenoxaprop-*p*-ethyl forms higher toxic and more persistent products such as 4-[(6-chloro-2-benzoxazolyl)oxy] phenol (48 h EC$_{50}$ of 1.49–1.64 mg/L) (Lin et al., 2008). Simulated solar irradiation can enhance the acute toxicity of fluoroquinolones and anthraquinones to *Daphnia magna* (Luo et al., 2018; Wang et al., 2009).

3. Overview of aquatic photodegradation

The photodegradation process is active only during daytime when light is abundant and the corresponding rate of photodegradation is highly affected by the light intensity imposed on the OMPs or photosensitizers. In addition, the extent of light attenuation increases with the depth of the water column and varies seasonally (Mathon et al., 2019). Against this backdrop, the influence of natural solar light on the degradation of OMPs remains largely unknown and has been scarcely studied despite that such information is essential for understanding the
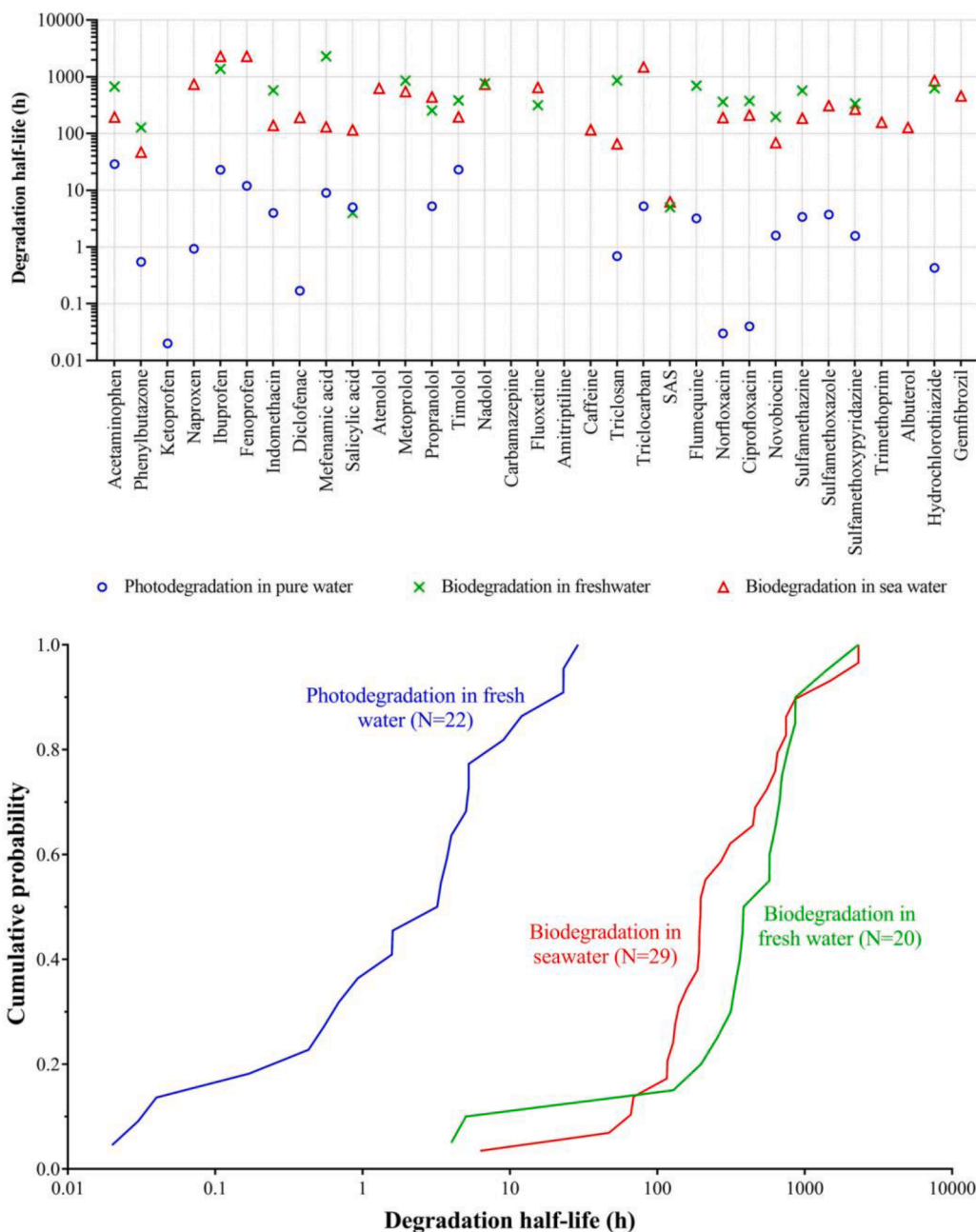
Fig. 1. Comparison and cumulative probability distributions of photodegradation and biodegradation (in fresh and sea waters) half-lives of commonly detected PPCPs, adapted from Baena-Nogueras et al. (2017).

attenuation process of OMPs and elucidating their fate in the environment (Wang et al., 2021b). Photodegradation processes can be either direct or indirect (Wang et al., 2017; Zhang et al., 2017; De la Cruz et al., 2013) as illustrated in Fig. 2.

Direct photolysis occurs when OMPs directly receive photon energy from an irradiation source and the OMP's electrons are excited to a higher energy level. This allows the molecule to undergo chemical transformations (i.e., fragmentation, intramolecular rearrangement, isomerization, hydrogen atom abstraction, dimerization, and electron transfer from/to the compound), ultimately causing the OMP to photodegrade (Schwarzenbach et al., 2002). An OMP's capability to undergo direct photolysis depends on two factors: the ability of the OMP to absorb photon energy as indicated by its molar absorption coefficient and the likelihood of the molecule to undergo a chemical transformation as indicated by its quantum yield (Ge et al., 2009; Yao et al., 2013).

Additionally, direct photolysis can be influenced by the water matrix *via* processes such as light screening caused by light-absorbing constituents as well as back reduction by DOM (Liu et al., 2020).

In indirect photodegradation, photons are received by photosensitizers to produce PPRIs, which ultimately degrade the target OMPs. Therefore, the composition of the water matrix in which the target OMPs occur can have a positive or negative influence on the efficiency of photodegradation (Lado Ribeiro et al., 2019). The indirect photodegradation is largely dependent on water matrix components such as NO_3^-/NO_2^- and DOM because these components can photo-generate PPRIs to degrade the OMPs (Ge et al., 2009). However, the impact of such components can also vary depending on the target OMPs (Wang et al., 2017; Zhang et al., 2017; Sun et al., 2014) as well as the source of DOM (Sun et al., 2014), which will be elaborated in the following section of this review.
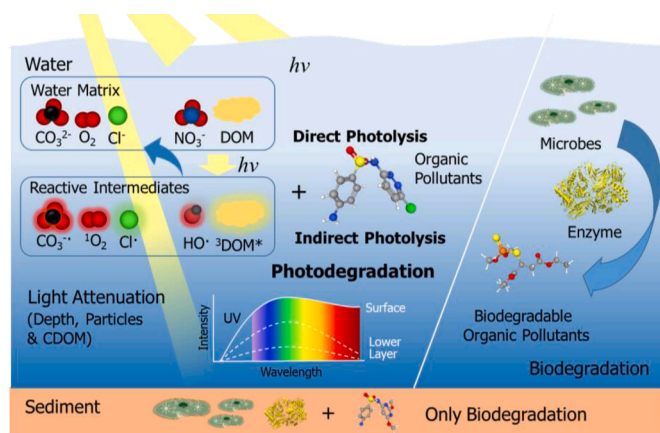
Fig. 2. Overview of photodegradation in aquatic environment.

Photodegradation studies are usually conducted under well-controlled conditions in the laboratory. The rates of photodegradation obtained from the laboratory experiments were then extrapolated to different environments, providing a great practical significance for the management of chemicals (precursors of OMPs). However, this strategy poses several challenges because laboratory conditions are often different from those in real water bodies (Mackay, 2001). In recent years, a kinetics-based and user-friendly model called APEX (Aqueous Photochemistry of Environmentally-occurring Xenobiotics) has been developed to predict the photo-transformation kinetics of OMPs (Bodrato and Vione, 2014; Vione, 2020). Zhou et al. (2018) have also developed a kinetics-based photodegradation rate prediction model, taking into account the variations in the intensity of underwater and hourly sunlight. These two models are useful in extrapolating photochemical persistence data determined in the laboratory to the real environment, although further development is needed to comprehensively study photodegradation in actual water environments.

The input photochemical parameters of OMPs in the aforementioned models such as quantum yield of direct photolysis and the second-order reaction rate constants are necessary for predicting the photochemical persistence. However, these parameters are not available for most of OMPs. Actually, thousands of chemicals have already been synthesized and used, and thus have entered the aquatic environment. Prediction of those photochemical parameters for OMPs is pertinent to persistence evaluation. Some pioneering studies employed quantitative structure-activity/property relationship (QSAR/QSPR) to predict these parameters including the quantum yield for OMPs (Chen et al., 2000, 2001a, 2001b; Niu et al., 2005; Shao et al., 2010; Yang et al., 2003) and the photochemical kinetics parameters (Li et al., 2014; Luo et al., 2017, 2019), which provide an opportunity for prediction given the lack of relevant data.

Nevertheless, this article cannot cover all the basics of environmental photochemistry and interested readers may refer relevant literature for further details about the basic mechanisms (Boule, 1999; Calza and Vione, 2015; Klan and Wirz, 2009; Schwarzenbach et al., 2002).

4. Effects of the water matrix on photodegradation

Photodegradation of OMPs can be influenced by the constituents in the water matrix such as ions (NO_3^-/NO_2^-, Fe^{2+}/Fe^{3+}, CO_3^{2-}/HCO_3^-, halide ions, etc.), DOM, and suspended solids (Ge et al., 2010a, 2010b, 2010c; Vione et al., 2014). Likewise, coexisting OMPs can be considered as water matrix components that can also affect photodegradation. The water matrix can either accelerate photodegradation or inhibit it. In addition, the water pH can influence the charge state of DOM and the presence of ionized OMPs in water, indicating a dependency of photodegradation upon the pH values of the water (Boreen et al., 2004; Ge

et al., 2010a; Wei et al., 2013; Werner et al., 2006). For example, ciprofloxacin (CIP) has five dissociated species and each of them had dissimilar photolytic kinetics and products (Wei et al., 2013). In the following sections, the effects of the water matrix on the photodegradation of OMPs are further elaborated.

4.1. Inorganic ions

Inorganic ions are ubiquitous in the aquatic environment and play various roles in the photodegradation of OMPs. The ions can interact with OMPs, thereby altering their photodegradation behaviors. For example, coordination with transition metals such as Cu(II) can alter the light absorption characteristic and photo-reactivity of OMPs (Wei et al., 2015). In addition, some inorganic ions can produce PPRIs (e.g., photolysis of NO_3^-/NO_2^- can produce HO·), which can provide additional opportunities for degradation of refractory OMPs. In this section, the focus is given mainly to inorganic ions that can produce PPRIs on the photodegradation of OMPs.

NO_3^-/NO_2^- are ubiquitous in natural waters and play important roles in the photodegradation of OMPs because NO_3^-/NO_2^- are important sources of HO·. The NO_3^-/NO_2^- are usually more abundant in freshwater than seawater (Boule, 1999; Takeda et al., 2004), indicating production of HO· by photolysis of NO_3^-/NO_2^- in freshwater can be more efficient than that in seawater. NO_3^-/NO_2^- can produce HO· through direct photolysis under the action of solar radiation ($\lambda > 280$ nm); the main reactions are shown below (Mack and Bolton, 1999; Wu et al., 2020):
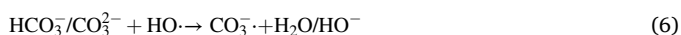
$$NO_2^- + hv \rightarrow \cdot NO + O^- \cdot \tag{1}$$

$$NO_3^- + hv \rightarrow [\cdot NO_2 + O^- \cdot]_{cage} \tag{2}$$

$$O^- \cdot + H^+ \rightleftharpoons HO \tag{3}$$

As shown in Eqs. (1)–(3), both NO_3^- and NO_2^- can directly absorb solar radiation and produce $O^- \cdot$, which is a precursor of HO·. The pKa of HO· is 11.9 (Eq. (3)), suggesting that reaction (3) favors the generation of HO· at environmental pH (Mack and Bolton, 1999). NO_2^- can be transformed to its conjugated acid HONO, which is more efficient in producing HO·, thereby increasing the production of HO· with decreasing the pH. However, this pH effect is obvious only in water with a pH < 5, which is not a common pH in surface waters (Arakaki et al., 1999). NO_3^- can photo-isomerize into OONO$^-$ and form its conjugated acid HOONO with pKa $\approx$ 6.5–7, where HOONO can produce HO· while OONO$^-$ cannot (Gligorovski et al., 2015; Mack and Bolton, 1999). Nevertheless, this pathway may also be insignificant in the natural environment because the quantum yield for photoproduction of OONO$^-$ under solar radiation is low (less than 0.26% at 313 nm irradiation) (Benedict et al., 2017). Although the concentration of NO_2^- is usually lower than that of NO_3^- in natural waters, NO_2^- absorbs solar radiation more effectively and produces HO· with a higher quantum yield ($\Phi_{NO_2^-}^{HO·} = 0.025$–0.065, depending on wavelength; $\Phi_{NO_3^-}^{HO·} \approx 0.01$) (Vione et al., 2014). Overall, comparable roles of NO_3^- and NO_2^- in producing HO· were commonly reported (Gligorovski et al., 2015; Minero et al., 2007; Takeda et al., 2004).

Fe ion species, particularly Fe(II)/Fe(III) complexes (mainly hydroxo and organic complexes), can participate in Fenton/Photo-Fenton reactions to generate HO· that causes OMPs degradation in sunlit aquatic environments. The photochemistry of Fe has been reviewed previously, and two representative equations (Eqs. (4) and (5)) concerning HO· production are shown below (Lueder et al., 2020; Vione et al., 2014). The importance of these reactions depends on specific water bodies where the pH is low enough and the concentrations of Fe(II)/Fe(III) are sufficiently high (Gligorovski et al., 2015). This is because Fenton/Photo-Fenton reactions are favored under low pH conditions (pH = 2~3) (Feng and Nansheng, 2000).

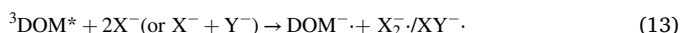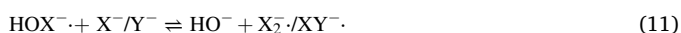$$FeOH^{2+} + hv \rightarrow Fe^{2+} + HO· \tag{4}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + HO^- \tag{5}$$
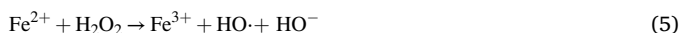
Photodegradation of OMPs can be influenced by CO_3^{2-}/HCO_3^-, mainly due to the generation of the carbonate radical ion ($CO_3^-\cdot$) that reacts with OMPs in sunlit water bodies. $CO_3^-\cdot$ is a selective oxidant with E_{NHE} ($CO_3^-\cdot/CO_3^{2-}$) = +1.59 V (Huie et al., 1991), which is lower than that of HO· while its steady-state concentration is estimated to be two orders of magnitude higher than that of HO· (Sulzberger et al., 1997). The reactions between $CO_3^-\cdot$ and OMPs mainly occur *via* electron transfer or a hydrogen abstraction mechanism (Liu et al., 2018). Thus, $CO_3^-\cdot$ plays an important role in photodegradation of some OMPs containing electron-rich structures such as nitrogen- and sulfur-containing compounds (thiols), and aromatic compounds (anilines and phenols) (Busset et al., 2007; De Laurentiis et al., 2014; Mazellier et al., 2007; Sun et al., 2020; Wu and Linden, 2010). $CO_3^-\cdot$ is a secondary radical because, as shown in Eqs. (6) and (7), the $CO_3^-\cdot$ is generated through either reaction between CO_3^{2-}/HCO_3^- and HO· or between CO_3^{2-} and excited species (i.e., excited triplet state of DOM and OMPs ($^3DOM^*/^3OMPs^*$)) (Yan et al., 2019).

$$HCO_3^-/CO_3^{2-} + HO\cdot \rightarrow CO_3^-\cdot + H_2O/HO^- \tag{6}$$

$$CO_3^{2-} + {}^3DOM^*/{}^3OMP^* \rightarrow CO_3^-\cdot \tag{7}$$

Reaction (6) is highly pH-dependent because of the dissociation of carbonic acid to CO_3^{2-} and HCO_3^- that occurs at different pH values (pKa_1= 6.3 and pKa_2= 10.3) (Vione et al., 2014). The generation of $CO_3^-\cdot$ is more strongly favored when pH increases from 6 to 9 (circumneutral pH) as CO_3^{2-} is more reactive than HCO_3^- toward HO· ($k_{HCO3}^{HO\cdot}$ = $8.5 \times 10^6\,M^{-1}\,s^{-1}$, k_{CO3}^{2-} = $3.9 \times 10^8\,M^{-1}\,s^{-1}$), and the proportion of CO_3^{2-} increases when the pH increases (Zhou et al., 2020). Eq. (7) is important only under specific conditions (waters with high DOC) (Canonica et al., 2005) and in most cases, Eq. (6) is the dominant reaction for generating $CO_3^-\cdot$ in natural water bodies.

Halide ions can react mainly through an oxidation reaction with photochemically produced HO· or $^3DOM^*$ to form various halogen radical species (X·, $X_2^-\cdot$ and XY$^-\cdot$ where X and Y stand for Cl, Br, or I) (Parker and Mitch, 2016; Zhang and Parker, 2018; Zhang et al., 2018a):

$$HO\cdot + X^- \rightleftharpoons HOX^-\cdot \tag{8}$$

$$HOX^-\cdot \rightleftharpoons HO^- + X\cdot \tag{9}$$

$$HOX^-\cdot + H^+ \rightleftharpoons H_2O + X\cdot \tag{10}$$

$$HOX^-\cdot + X^-/Y^- \rightleftharpoons HO^- + X_2^-\cdot/XY^-\cdot \tag{11}$$

$${}^3DOM^* + X^- \rightarrow DOM^-\cdot + X\cdot \tag{12}$$

$${}^3DOM^* + 2X^- (\text{or } X^- + Y^-) \rightarrow DOM^-\cdot + X_2^-\cdot/XY^-\cdot \tag{13}$$

Compared with X·, $X_2^-\cdot$ and XY$^-\cdot$ are dominant in halide-containing sunlit waters (concentrations of all types of $X_2^-\cdot$ are estimated to be three orders of magnitude higher than all X·) because X$^-$, especially for Cl$^-$, are abundant, which can rapidly react with X· to form $X_2^-\cdot$/XY$^-\cdot$ (Ershov, 2004; Yang and Pignatello, 2017). In seawater, the steady-state concentrations of Br$^-\cdot$ and BrCl$^-\cdot$ are estimated to be 3–4 orders of magnitude higher than the concentration of HO· (Zhang and Parker, 2018). These halogen radicals can be quenched by HCO_3^-/CO_3^{2-} to form $CO_3^-\cdot$ and by DOM to form DOM radical. Halogen radicals can react with OMPs *via* halogenation (Cheng et al., 2021), and many polyhalogenated OMPs can be produced; these OMPs can exhibit serious ecological risks (Lallas, 2001). On the other hand, halogen radicals can also react with OMPs through oxidation reactions where halogen atoms are not introduced into the reaction products (Wang et al., 2021a). Since the reaction between halogen radicals and the OMPs is a redox reaction, the redox potential is pertinent to the reaction. The reduction potential of Cl· (E_{NHE} = 2.5 V) is the highest among all the halogen radicals (others range from 1.1 to 2.2 V) and is slightly lower than that of HO· (E_{NHE} = 2.7 V), indicating that Cl· has high reactivity toward many

OMPs (Wardman, 1989). Halogen radicals can react with saturated aliphatic compounds (*via* hydrogen abstraction), olefinic compounds (*via* addition reaction), aromatic compounds (*via* addition reaction, electron abstraction), and organosulfur species (adduct formation or sulfur oxidation) (Wang et al., 2021a; Zhang and Parker, 2018).

In addition to the generation of halogen radicals, Parker et al. (2013) have reported that an increase in ionic strength can slow down intra-organic matter electron transfer of $^3DOM^*$, resulting in higher steady-state concentrations of $^3DOM^*$ ($[^3DOM^*]_{ss}$). Elevation of $[^3DOM^*]_{ss}$ by halide ions has also been observed in further studies as well as the quenching of excited singlet-state DOM ($^1DOM^*$) (Glover and Rosario-Ortiz, 2013). Higher $[^3DOM^*]_{ss}$ can promote photodegradation when $^3DOM^*$ is critical to photodegradation (Chen et al., 2019; Li et al., 2016b). Suppression of photodegradation by halide ions was also observed for 17β-estradiol, a phenol, and this was attributed to the inhibition of electron transfer pathways between $^3DOM^*$ and 17β-estradiol (Grebel et al., 2012; Parker et al., 2013). Further research is needed to clarify the relative importance between the elevation of $[^3DOM^*]_{ss}$ and inhibition of the electron transfer pathways by halide ions in the photodegradation of OMPs. Regarding halide-specific effects, previous studies have found that Cl$^-$ and Br$^-$ can enhance photobleaching of DOM (Grebel et al., 2009; Grebel et al., 2012), thereby decreasing the sensitizing ability of DOM and inhibiting photodegradation. Halide ions like Br$^-$ may also exhibit a "heavy atom" effect on photodegradation, which can promote intersystem crossing from the excited singlet state to the excited triplet state and influence the photodegradation as a consequence (Koziar and Cowan, 1977; Li et al., 2016a).

4.2. Dissolved organic matter

DOM is ubiquitous in environmental water bodies, and it can widely absorb solar radiation up to 500 nm (Nebbioso and Piccolo, 2013). After absorbing light, DOM can produce various PPRIs such as $^1DOM^*$, aqueous electron (e_{aq}^-), superoxide ($O_2^-\cdot$), H_2O_2, $^3DOM^*$, $^1O_2$, and HO·, which contribute to photodegradation (Fig. 3). DOM can also inhibit photodegradation, for example, by competing for light with OMPs and quenching PPRIs generated during photodegradation.

4.2.1. Promotion effects

Carbonyl structures and aromatic compounds are the main chromophores of DOM. These chromophores absorb solar radiation and first produce $^1DOM^*$ with a short lifetime and low steady-state concentration in environmental waters (Boyle et al., 2009). $^1DOM^*$ has high reactivity

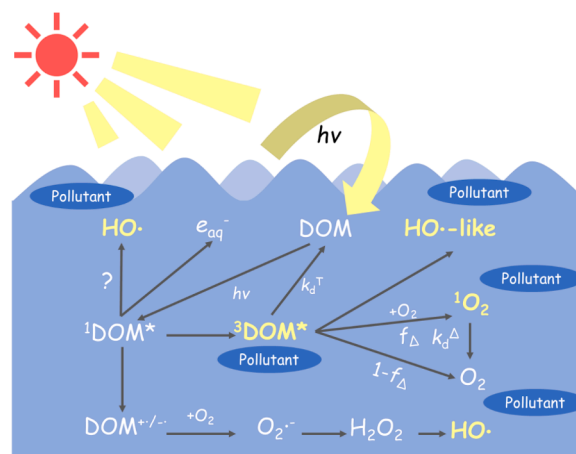**Fig. 3.** Production of photochemically produced reactive intermediates in DOM solution. (k_d^T is relaxation rate constant of $^3DOM^*$ by O_2-independent way; f_Δ is the proportion of $^3DOM^*$ reacting with O_2 that produces $^1O_2$; k_d^Δ is relaxation rate constant from $^1O_2$ to O_2) (Sharpless and Blough, 2014; McNeill and Canonica, 2016; Vione et al., 2014).

and has been shown to play a pivotal role in the formation of some PPRIs such as e_{aq}^- and charge-transfer-state DOM ($DOM^{+\cdot/-\cdot}$).

The excited singlet-state aromatic groups, mainly phenol and its derivatives (such as aromatic carboxylic acids (Köhler et al., 1985) and aromatic amino acids (Mossoba et al., 1982)) in $^1DOM^*$, can eject e_{aq}^-. The e_{aq}^- generated plays an insignificant role in OMPs attenuation in environmental waters because it is produced only inside the DOM microenvironment and mostly recombines with cations before escaping into the bulk solution (Zepp et al., 1987). Only hydrophobic OMPs with a very high octanol-water partition coefficient K_{OW}, such as Mirex ($K_{OW} \approx 10^{6.29}$; Burns et al. 1996, 1997), can bind with DOM so that e_{aq}^- can react to them.

$^1DOM^*$ can also produce $DOM^{+\cdot/-\cdot}$ through direct intramolecular electron transfer (McKay et al., 2016; Sharpless and Blough, 2014). These $DOM^{+\cdot/-\cdot}$ states are formed as a result of the transfer of an electron either partially or completely from an electron-rich donor (e.g., hydroxy- or alkoxy-benzenes) to an electron-poor acceptor (e.g., carbonyl-containing moieties like aromatic ketones and quinones) (McKay et al., 2016). To date, $DOM^{+\cdot/-\cdot}$ is widely regarded as the major PPRI responsible for the production of O_2^- (Ma et al., 2020; Zhang et al., 2012). Electron-rich phenolic moieties are precursors of $DOM^{+\cdot/-\cdot}$, which further verified that $DOM^{+\cdot/-\cdot}$ is the precursor of O_2^-. O_2^- often acts as a weak oxidant with E_{NHE} (O_2^-/ H_2O_2) = +0.91 V, playing an important role in the redox speciation of dissolved metals in natural water bodies (Ma et al., 2020). Catalyzed or uncatalyzed disproportionation of O_2^- can produce H_2O_2 (Cooper and Lean, 1989; Petasne and Zika, 1987; Scully et al., 1996), which is an important PPRI because it can further generate HO· through Fenton reactions (Southworth and Voelker, 2003). Although only about 12–35% of O_2^- is transformed to H_2O_2 *via* dismutation (Le Roux et al., 2021) where another portion of O_2^- undergoes photoinduced loss possibly by reacting with DOM^+· (Ma et al., 2020), O_2^- is still considered the most important PPRI for producing H_2O_2.

Aromatic carbonyl and quinone groups in $^1DOM^*$ (about 4%−8%) can be transformed to $^3DOM^*$ through intersystem crossing (McKay, 2020). Although $^3DOM^*$ is less reactive than $^1DOM^*$, $^3DOM^*$ has a longer lifetime and higher steady-state concentration (10^{-14} to 10^{-12} M), thereby making it an important PPRI in environmental waters (McNeill and Canonica, 2016). $^3DOM^*$ can directly react with OMPs *via* oxidation (e.g., electron transfer, proton-coupled electron transfer, or other related mechanisms) or energy transfer (McNeill and Canonica, 2016) and is also the precursor of $^1O_2$ and HO· (mainly HO·-like species).

$^3DOM^*$ tends to react with aromatic anilines and electron-rich phenols *via* an oxidation mechanism. It mainly acts as an oxidant, and thus should have a higher reduction potential than the target compound. Plenty of examples of oxidation with $^3DOM^*$ were summarized by McNeill and Canonica (2016). For energy transfer reactions with $^3DOM^*$, a prerequisite is that the compound should have lower excited triplet energy (E_T) than that of $^3DOM^*$. The reaction between O_2 and $^3DOM^*$ that forms $^1O_2$ is a typical energy transfer reaction—it requires only 94 kJ mol^{-1} (Zepp et al., 1977). $^1O_2$ occurs in sunlit DOM solutions with steady-state concentrations ranging from 10^{-12} to 10^{-15} M, which is in the same range as $^3DOM^*$ (McNeill and Canonica, 2016; Peterson et al., 2012). $^1O_2$ is a selective oxidant and can react rapidly with only certain OMPs such as phenolates and furans (Ossola et al., 2019) as well as indoles, imidazoles, and some easily oxidized amino acids (Boreen et al., 2008; Latch et al., 2003b). It is notable that the distributions of $^1O_2$ exhibit a microheterogeneity because the species is produced in a microenvironment of DOM, and sometimes it reaches higher steady-state concentration in the hydrophobic sites of DOM compared with that in the bulk solution (Grandbois et al., 2008; Latch and McNeill, 2006). Therefore, hydrophobic OMPs that can bind to DOM are possibly susceptible to reaction with $^1O_2$.

In addition to $^1O_2$, it is often reported that only compounds containing dienes can react with $^3DOM^*$ through energy transfer *via* compounds such as sorbic acid (Grebel et al., 2011), isoprene, and sorbic

alcohol (Zhou et al., 2019a) and the corresponding products are their cis-/trans-isomers. Since dienes structures rarely occur in OMPs, oxidation of OMPs by $^3DOM^*$ is more common than energy transfer (Li et al., 2015, 2016a). $^3DOM^*$ are mixtures of different excited triplet-state species, which means the E_T is distribution rather than a definite value.

Zepp et al. (1985) employed diene probes and demonstrated that about 37% of $^3DOM^*$ had high E_T (≥ 250 kJ mol^{-1}), labeled as high-energy $^3DOM^*$ (Hi-$^3DOM^*$). The remainder was labeled as low-energy $^3DOM^*$ (94 kJ mol^{-1} $\leq E_T \leq 250$ kJ mol^{-1}). Recently, Zhou et al. (2019a) used sorbic alcohol ($E_T \approx 250$ kJ mol^{-1}) as a Hi-$^3DOM^*$ probe and found that the average proportion of Hi-$^3DOM^*$ in 15 different types of DOM was 33%, close to the 37% reported previously (Zepp et al., 1985). Further work by Wang et al. (2020a) confirmed the high reactivity of Hi-$^3DOM^*$ in the photodegradation of OMPs using 11 different types of DOMs. Notably, the proportion of Hi-$^3DOM^*$ depended on the source of DOM, with the proportion being higher in autochthonous freshwater DOM than allochthonous freshwater DOM (Zhou et al., 2019a). A more recent study indicated that about 58% of the Hi-$^3DOM^*$ generated from leaf litter, soil, stream water, and lake water samples, can react with 2,4,6-trimethylphenol (TMP, a widely used electron-transfer probe) verifying that Hi-$^3DOM^*$ is possibly important in oxidation of OMPs (Wasswa et al., 2022). They also reported the precursors of Hi-$^3DOM^*$ were photo-resistant and bio-refractory meaning that Hi-$^3DOM^*$ may be more important in reaction with OMPs and generating $^1O_2$ even after undergoing environmental processes like photobleaching and biodegradation.

Furthermore, Guo et al. (2021) found that maricultural seawater DOM (S-DOM) can generate more Hi-$^3DOM^*$ than S-DOM with less influence of mariculture, contributing to the high reactivity of $^3DOM^*$. This is the first time to quantify Hi-$^3DOM^*$ in S-DOM given that S-DOM is different from freshwater DOM in many aspects (detailed in Section 4.2.3). However, further study is needed to clarify whether Hi-$^3DOM^*$ plays an important role in the overall photodegradation of OMPs in the natural environment as has been assumed.

$^3DOM^*$ is a precursor of HO·, which is a highly reactive radical that reacts with OMPs at a near diffusion-controlled rate. HO· production by DOM also exhibits microheterogeneity similar to that of $^1O_2$, where more HO· is possibly produced inside the hydrophobic core of DOM (Yan et al., 2021). Hence, hydrophobic OMPs that can enter the DOM microenvironment are possibly specifically susceptible to photodegradation. However, in sunlit surface waters, the steady-state concentration of HO· (10^{-16}–10^{-18} M) is much lower than that of $^3DOM^*$ or $^1O_2$ even though direct photolysis of nitrite/nitrate or photo-Fenton reactions can elevate the steady-state concentration of HO· (Mack and Bolton, 1999; White et al., 2003; Zepp et al., 1992). Regarding the production of HO·, there is still a dispute as to whether HO· is produced by $^3DOM^*$ or other precursors like $DOM^{+\cdot/-\cdot}$ in DOM solutions exposed to sunlight (McKay and Rosario-Ortiz, 2015). In addition to free HO·, the generation of HO·-like species has also been reported, including lower-energy hydroxylation intermediates that react with OMPs at a slightly lower rate than free HO· reacts with them, and quinones are regarded as the precursors of these species (Gan et al., 2008; Liu et al., 2019; Page et al., 2011). Although studies usually do not distinguish between them in measurement, the presence of HO·-like species can be confirmed by using methane, which selectively quenches HO· rather than HO·-like species (Page et al., 2011).

Two pathways were proposed for the production of HO·, namely, H_2O_2-dependent and H_2O_2-independent pathways (McKay and Rosario-Ortiz, 2015). The percentage for the H_2O_2-dependent pathway varied among the DOM samples (Page et al., 2011). In the H_2O_2-independent pathway, it has been observed that the steady-state concentrations of $^3DOM^*$ and $^1O_2$ increased while the quantum yield of HO· decreased after quenching of $^1DOM^*$ (Glover and Rosario-Ortiz, 2013), implying that HO· and $^1O_2$ do not share the same precursor ($^3DOM^*$) and that $^1DOM^*$ may contribute to HO· production. Sun et al. (2015) found

that direct photolysis of substituted phenols, specifically carboxylate-substituted phenols, may be an important source of HO· in DOM. Two feasible pathways were proposed: (1) the carboxylate-substituted phenol generates an e_{aq}^- and a phenol cation radical. Then, the phenol cation radical either undergoes deprotonation and forms HO· or (2) is transformed to a dihydroxycyclohexadienyl radical intermediate that finally eliminates HO·. However, the importance of this mechanism is not clear because good correlation has not been observed between the quantum yield for HO· production and the DOM electron-donating capacity (EDC), which is mainly due to polyphenol moieties in DOM (McKay et al., 2017). This lack of good correlation could be due to the small experimental database, the heterogeneity in producing HO· from different substituted phenols (Sun et al., 2015), and the fact that some polyphenolic HO· precursors are formed only after DOM is irradiated (Berto et al., 2016). Thus, further studies are needed to clarify the production mechanism of HO· in DOM solutions and, in particular, the correlation between the quantum yield for HO· production and EDC should be investigated using irradiated DOM.

4.2.2. Inhibition effects of DOM

Light screening and quenching are the two main inhibition effects of DOM on the photodegradation of OMPs (Canonica and Laubscher, 2008; Chin et al., 2004). The light screening effect is based on the fact that DOM competes for light with the OMPs resulting in inhibition of the direct photolysis. The light screening effect is unavoidable for most OMPs because direct photolysis is induced mainly by short-wavelength light, which overlaps the absorption spectra of DOM under solar radiation. In addition to OMPs, DOM also screens and weakens radiation for other photosensitizers such as NO_3^-/NO_2^-, inhibiting their photolysis that yields HO· (Vione et al., 2014).

Phenolic moieties are mainly responsible for the quenching effects in DOM solutions. These electron-rich compounds can transfer an electron to ^{3}DOM*, thereby consuming ^{3}DOM*, but this inhibition effect is not predominant in sunlit natural water bodies (Canonica et al., 2000). A recent study reported that quenching of Hi-^{3}DOM* is more apparent than that of low-energy ^{3}DOM* owing to the higher redox potential of Hi-^{3}DOM* (Zhou et al., 2019a). On the other hand, the phenolic moieties can reduce the reactive intermediates generated from the oxidation reaction between ^{3}DOM* and OMPs. For example, oxidation of aromatic anilines by ^{3}DOM* forms a cation radical (aromatic aniline after the loss of an electron). Electron-rich phenolic moieties can transfer an electron to the cation radical reducing it back to its parent compound, thus inhibiting the reaction (Wenk and Canonica, 2012). Previous studies have reported that the content of phenolic moieties in autochthonous DOM is lower than that in allochthonous DOM (Guo et al., 2021; Zhou et al., 2019a), and thus the quenching effects is less obvious in autochthonous DOM (Bahnmüller et al., 2014; Wang et al., 2019; Wenk and Canonica, 2012). Additionally, Canonica and Laubscher (2008) reported that the quenching effects were observed in the photodegradation of OMPs containing phenols, anilines, and the like and that the inhibition efficiencies were different for different compounds.

Photobleaching of DOM can be considered as an indirect inhibition effect of DOM. After photobleaching of DOM, its photo-reactivity is decreased (Helms et al., 2009, 2014; Moran et al., 2000; Niu et al., 2014). In photobleaching, the chromophores are photochemically destroyed either through direct destruction of the DOM molecules by light or reactions between DOM and PPRIs. After photobleaching of DOM, the rate of photodegradation of OMPs in the same solutions could decrease. The photodegradation rate of OMPs decreased as the length of irradiation time increased, and the decrease was highly dependent on the characteristics of both the DOM and OMPs (Niu et al., 2014). Using solid-state ^{13}C nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy, Helms et al. (2014) found that aromatic carbon was preferentially removed while carbohydrate-like and amide/peptide-like carbons remained after photobleaching for up to 110 days.

4.2.3. Seawater DOM vs freshwater DOM

Although seawater covers 71% of the Earth's surface and acts as an important sink of OMPs, less attention has been paid to the effects of S-DOM on the photodegradation of OMPs compared with freshwater DOM. This is due to the difficulty of extracting S-DOM from seawater that typically has high salinity and relatively low DOM content. S-DOM is mainly autochthonous DOM derived from cellular excretions of marine phytoplankton and bacteria. S-DOM normally undergoes photobleaching for a long time and can be influenced by anthropogenic sources such as mariculture in coastal regions. Hence, the effects of S-DOM on the photodegradation of OMPs can differ from those of freshwater DOM.

Reverse osmosis coupled with electrodialysis (RO/ED) technology is normally used to extract S-DOM due to its high recovery efficiency (Zhang et al., 2013). Wang et al. (2018) extracted S-DOM by RO/ED and found that S-DOM influenced by mariculture activities exhibited higher photo-reactivity (higher PPRIs production quantum yield, light absorption rate and ^{3}DOM* reactivity) than S-DOM extracted from more pristine seawater. Wang et al. (2019) also found that compared with reference freshwater DOM (Suwannee River Fulvic Acid and Suwannee River Natural Organic Matter (SRNOM)), S-DOM undergoes more photobleaching in which a lower content of C=C and C=O functional groups is observed. However, compared with freshwater DOM, S-DOM enhanced the photodegradation of both 2,4-dihydroxybenzophenone and nebivolol to a greater extent, which was attributed to the higher reactivity of ^{3}DOM* with the OMPs and fewer antioxidants in the S-DOM (Wang et al., 2020b, 2019). Further work by Guo et al. (2021) indicated that Hi-^{3}DOM* is not responsible for the higher reactivity of ^{3}DOM* from S-DOM than that from freshwater DOM. In contrast, a lower content of phenolic moieties that lessened inhibition explained the higher reactivity of ^{3}DOM* from S-DOM. However, the S-DOM was extracted only from coastal areas in the Bohai Sea and further studies concerning the photochemistry of S-DOM from other regions are needed.

4.3. Suspended solids and coexisting pollutants

Suspended solids such as sand, clay, particulate organic matter, and phytoplankton are also ubiquitous in surface waters. These components can influence the underwater light environment, adsorb OMPs, and affect photosensitizing processes (Kirk, 1985; Lund-Hansen, 2004; Rose et al., 2014; Shang et al., 2015), possibly altering the photodegradation of OMPs. For example, suspended solids can inhibit the photodegradation of sulfamethoxazole and the inhibition effects become stronger with increasing concentration of the suspended sediments (Niu et al., 2013). The inhibition effect was mainly due to the suppression of HO· generation while adsorption of sulfamethoxazole on solids played an insignificant role. Thirumavalavan et al. (2012) attributed the effect of suspended solids to turbidity and light attenuation, and their study showed that the photodegradation of microcystin-LR was impeded when the turbidity increased.

Notably, a variety of OMPs, rather than a single one, may coexist in the same water body and thus the photodegradation of an OMP can be influenced by the coexisting OMPs. Generally, the coexisting OMPs can have multifarious effects on the photodegradation processes (Jentzsch et al., 2019; Zhang et al., 2018b) depending on the intended functions of the coexisting OMPs. For example, UV absorbers (used in polymers) are designed to absorb photon energy and then to release the excitation energy in the form of heat, so they can compete for photons with the target OMP during photodegradation. Primary antioxidants are capable of reacting with PPRIs, thus preventing further propagation of oxidation reactions. The antioxidants can also consume the generated PPRIs and prevent further reactions with the target OMP (Hunt, 2000).

In addition, recent studies have reported that trace amounts of coexisting OMPs can also increase the photodegradation of other OMPs

in waters (Jentzsch et al., 2019; Zhang et al., 2018b; Zhou et al., 2019b). For example, bezafibrate (BZF) displayed faster photodegradation in the presence of fenofibrate acid (FNFA) in ultrapure water, wastewater treatment plant effluent water, and the receiving river water, despite the usual resistance of BZF to degradation. The promotional effect of FNFA was due to its ability to generate $^1O_2$ and e^-_{aq}. Further tests conducted with SRNOM (5.0 and 10.0 mg/L) and BZF (5.0 mg/L) in the presence and absence of FNFA (1.0 mg/L) revealed that the presence of FNFA induced much faster photodegradation of BZF than the presence of SRNOM (Zhou et al., 2019b).

Hence, the influence of co-existing OMPs on each other's degradation can be important in surface waters, despite their lower concentration compared with DOM. However, the influences of co-exposure of the OMPs on mutual photodegradation has hardly been studied in water environments. Given the increased detection of diverse OMPs in surface waters, further investigations are necessary to elucidate the influence of co-existing OMPs on their mutual persistence in environmental waters.

5. Major physical factors for photodegradation of OMPs

Photodegradation is also influenced by physical environmental factors, such as the depth of water, latitude, temporal variation (diurnal and seasonal) and temperature (Koumaki et al., 2015; McKay and Rosario-Ortiz, 2015; Zepp and Cline, 1977). Those physical effects have received less attention than the water matrix because the physical effects are caused by variation of the light intensity and the wavelength profile apart from the diversity of photochemical reactions. However, changes in physical factors cannot be ignored when aiming to understand the photochemical reactions and the overall fate of OMPs. For example, thermal lake stratification can determine the vertical distribution of OMP concentrations as a result of the vertical mixing process and photolysis in the surface layer (Rehrl et al., 2020). Assuming the same wavelength profile, the rate of photodegradation would be proportional to the photon influx. In fact, most studies involving *in situ* photodegradation experiments performed at different locations and different times (i.e., different latitudes and seasons), might be more readily comparable if the effects of physical factors on light conditions are better understood.

5.1. Latitude

Sunshine duration and cloud conditions vary depending on latitude. This would obviously influence the availability of underwater light and thus light absorption by photosensitizers or OMPs. Annual irradiance (measured over the period 1951–1960) shows a substantial change with latitude (Fig. 4) (Landsberg, 1961; Lewis, 1987).

The total annual irradiance on the Earth's surface is maximal at the equator. Theoretically, the tropical latitudes (0° to 25°) should have the

Fig. 4. Variation of annual irradiance with latitude. [Data was collected from Lewis 1987].

highest annual irradiance (Fig. 4, theoretical Earth surface) because the sun shines almost directly over these areas. However, the subtropical latitudes (25° to 40°) were observed to have the highest annual irradiance (Fig. 4, land masses). This is because cloud conditions can influence the amount of solar radiation that reaches the Earth's surface. Clouds can decrease the solar flux by up to 70% of the initial solar radiation that is transmitted through the atmosphere to the surface (Janjai et al., 2011). The effect of cloud cover on decreasing light transmission has been estimated to be between 31% for UVB radiation and 72% for photosynthetically active radiation (PAR) (Musiolková et al., 2021). In addition, the uneven distribution of moisture causes the transmissivity of the atmosphere to be unusually high over the subtropical land masses. Thus, more light can reach the Earth's surface at subtropical latitudes than in tropical regions (Lewis, 1987).

Given a constant attenuation coefficient, daily irradiance at latitudes between 10°N and 5°S shows peaks twice a year in March and September (Lewis, 1987). The annual minimum daily irradiance for a constant attenuation coefficient near the equator would be approximately 85% of the annual maximum daily irradiance. The range of minima on the tropical latitudes is significantly higher, and the minimum daily irradiance at 30° latitude is approximately 50% of the minimum at the equator (Fig. 4). The relative importance of shorter wavelengths also varies depending on the latitude, which possibly affects the absorption spectra and the rate of photodegradation of OMPs (Schmitt et al., 2021).

Due to the tilt of the Earth's axis of rotation, solar energy is received at a low angle at high latitudes; hence, the distribution of net energy per unit area is much less than that in the tropics. Also, higher latitudes (above 50°) often have the shortest sunshine duration annually and have more cloudy and rainy weather. At latitudes higher than 66.7° (the polar region), no direct energy is received at all from the sun for at least part of the year (Roots, 1989). Therefore, the degradation rate and the half-life times that are determined experimentally need to be corrected to estimate the actual degradation rate in the different regions. Furthermore, the attenuation of light by clouds has uncertainties with respect to the climatic reduction of light intensity at various geographical locations.

Indirect relationships of latitude with the water matrix and photochemistry can be identified based on the environmental conditions of the surface water. For instance, lakes located in high-latitude regions may be covered with ice for much of the year, so sunlight can barely reach the underlying water. Unless the ice melts, the photochemical process may likely cease to exist due to the efficient attenuation of light (Sommaruga, 2001). Moreover, several water bodies in high-latitude Nordic countries experience noticeable browning, a gradual increase in DOM concentration (Weyhenmeyer et al., 2016). Such browning could affect photoreactions by enhancing processes that are triggered by $^3DOM^*$ and $^1O_2$, over those induced by $HO\cdot$, $CO_3^-\cdot$ and direct photolysis (Calderaro and Vione, 2020). In addition to shifting the photodegradation pathways toward $^3DOM^*$, the increase in DOM could also lower the photodegradation rate constants and increase the photochemical persistence of OMPs (Vione and Scozzaro, 2019). Recent studies have updated the solar irradiance spectra between 70°S and 70°N at different times of the year, and these were validated against high-resolution spectroradiometer measurements (Apell and McNeill, 2019). Simulations of PPRI production using the updated solar irradiance spectra show that the spectrum of sunlight plays a role that is as important as the role of light intensity in determining PPRI production. Furthermore, the dependence of PPRI production on the solar irradiance spectra has recently been evaluated by designing reactors equipped with monochromatic LED lights for the experiments. The result show that the quantum yields of RIs decreased with an increasing wavelength from 375 to 490 nm and, notably, decreased to zero above 490 nm (Wu et al., 2021).
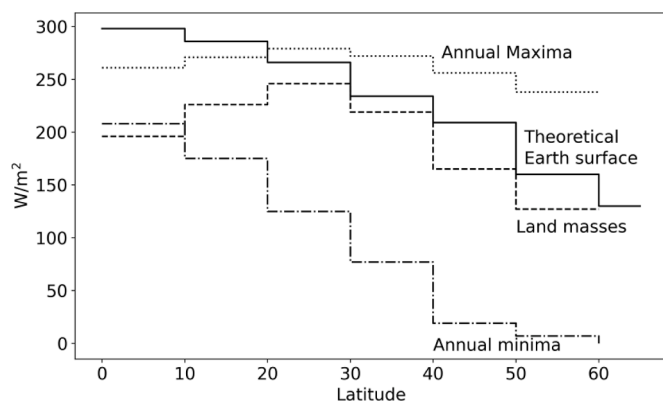
5.2. Seasonal and diurnal cycles

The solar irradiance varies daily and seasonally due to the rotation and revolution of the Earth, and the temporal variation of sunlight affects the photodegradation of OMPs. In terms of daily variation, the photochemical persistence of OMPs can be prolonged (for OMPs with photodegradation $t_{1/2}$ being over days) because no photodegradation occurs at nighttime. For example, recent studies indicated that the photodegradation $t_{1/2}$ of OMPs can be significantly underestimated if the variation of the intensity of sunlight with the time of day is not considered (Zhou et al., 2018; Chen et al., 2019; Guo et al., 2021). On the other hand, the variations (i.e., seasonal and diurnal) of the water matrix such as pH, NO_2^-, NO_3^-, and DOM together with the irradiance of sunlight, affected the photochemical processes including the overall kinetics of the OMP photo-transformations (Vione et al., 2018). Compared with freshwater and estuarine systems, the attenuation of sunlight in seawater is generally the weakest (Zhou et al., 2018), and thus such differences will also highly likely affect the photochemical rates and processes as a whole.

The diurnal solar light variations in Nigeria (tropic) (Soneye et al., 2019) and Northeast China (mid-latitude) (Zhou et al., 2018) are presented in Fig. 5A and 5B, respectively. The solar intensity increases from 7 am, reaching a maximum at around noon, and decreases to 0 Wm^{-2} at around 6 pm. The variation in the intensity of solar light suggested that the photodegradation rate of OMPs should likewise show a variation, although photodegradation studies usually simulate a solar intensity at noon which could largely overestimate the degradation rate of the OMPs. In addition, as shown in Fig. 5A, variation of the diurnal pattern of light intensity over the seasons can also be observed. Such differences in light intensity are caused by the attenuation of light by aerosol particles in the dry season and increased cloudiness and humidity in the wet season.

Stratification is also a seasonal phenomenon that commonly occurs in lakes and reservoirs, which also influences the photochemical processes in waters. For example, lake water typically undergoes stratification in summer in temperate climates. The epilimnion is the surface layer of water and thus receives more illumination, meaning that photodegradation processes will be more active there. In contrast, the hypolimnion is poorly illuminated due to light screening by the overlying water column, so photochemical processes are limited or negligible (Vione, 2020). The epilimnion and hypolimnion evolve differently, and thus a depth profile gradient is generated with respect to the concentration of photodegradable OMPs (Avetta et al., 2016). If the OMP is completely photodegraded in the epilimnion, the stratification phase considerably slows down the overall degradation kinetics (Vione and Scozzaro, 2019).

A recent study investigated the photodegradation of 23 OMPs in the free-water surface constructed wetland during the summer and winter in southern France (43.85°N). For the 23 OMPs studied, direct photolysis was the predominant process in summer, while indirect photodegradation was more significant in winter. Although the light intensity was higher in summer, the NO_3^- concentration was higher in winter enhancing the formation of HO· that promoted the wintertime indirect photodegradation (Mathon et al., 2019). In addition, a 7-year survey in a stream in the USA observed seasonal variation of NO_3^- in which NO_3^- concentrations were high during summer while low from mid-autumn to late spring. The low NO_3^- concentrations were attributable to the maximum availability of sunlight irradiance in late spring and the seasonal input of leaves to the stream in autumn (Mulholland and Hill, 1997). Another study conducted in the Guadiana River, Spain, has also shown that photodegradation is more important in summer than in winter (Vione et al., 2018). In the months with the highest clear-sky sunlight irradiance (i.e., June and July), the river water showed low NO_3^- concentrations and high DOM levels. This phenomenon may be quite typical of the surface water bodies as the minima for NO_3^- and the maxima for DOC concentrations occur frequently in summer in several surface-water environments (Vione et al., 2018).

5.3. Water depth

Underwater light intensity is generally attenuated with increasing water depth due to various components in the water column such as phytoplankton, particles, DOM, ions, and water itself. H_2O absorbs mainly red light (around 700 nm), which is one of the reasons for the color of the sea (Hale and Querry, 1973). Sunlight attenuation underwater alters the availability of light and affects the photochemical reactions of OMPs and photosensitizers (Zhou et al., 2018). Light absorption and scattering are the main causes of light attenuation in the water bodies (Kirk, 1977). In general, the intensity of light decreases exponentially with depth as described by Eq. (14).

$$I_Z = I_0 e^{-Ez} \quad (14)$$

where, I_z and I_0 are the intensities of light (Wm^{-2} or quanta $m^{-2}s^{-1}$) at depth z (m) and just below the surface, respectively, and E is the vertical attenuation coefficient (m^{-1}) for downward irradiance (Scheffer, 2004), which is affected by water matrix components such as DOM and inorganic ions. The depth of this photic environment varies depending on the water matrix and the wavelength of light (Avetta et al., 2016; Boreen et al., 2003; Vione and Scozzaro, 2019). The depth of light penetration generally refers to the depth at which the light has been attenuated by 99% (Zepp and Cline, 1977). Turbid lakes and estuaries show a light penetration depth of < 0.3 m, while the clearest oceans have a
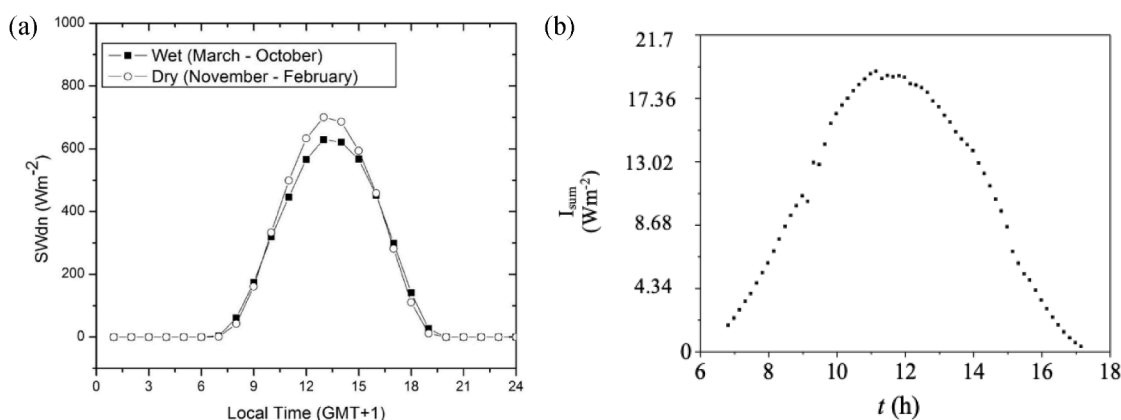

Fig. 5. (A) Diurnal and seasonal variation of the incoming solar radiation flux (SWdn) at Ile-Ife, Nigeria for the wet (March–October) and dry (November–February) seasons, during period of January 2016 to December 2017 (Soneye et al., 2019). (B) Diurnal solar radiation variation (referred to a cloudless day October 22, 2015, in Dalian, 38.9° N latitude, range 280 nm–500 nm) (Zhou et al., 2018).

penetration depth up to 150 m (Gons et al., 1997). In terms of wavelength, the depth of light penetration in freshwater is low for UV, blue, and red light, whereas green and yellow transmit to deeper water (Levine and MacNichol, 1982).

Moreover, the wavelength profile of the irradiation shifts vertically in water depending on the water matrix (Minero et al., 2007). The absorption effects of DOM change depending on the wavelength profile, especially for light with wavelengths below 500 nm. Therefore, the penetration depth for sunlight is greater in waters containing lower concentrations of DOM and the corresponding rates of photo-transformation may be larger (Bracchini et al., 2007). In addition, the enhancement of photoreactions in shallow water is more conspicuous for processes triggered by UV absorbing species such as NO_3^-/NO_2^- (Vione and Scozzaro, 2019).

Previous studies concluded that UV light is attenuated by water within tens of centimeters of depth in lakes with a high DOM concentration and turbidity. In both cases, the photochemical reactions are significantly affected by the light attenuation (Huovinen et al., 2003; Leavitt et al., 1997; Markager and Vincent, 2000). It has also been reported that the steady-state concentration of $^1O_2$ in lake waters decreased by a factor of 8.8 when the depth increased from 0 m to 20 m, indicating that depth is an important factor in determining indirect photochemical processes (Partanen et al., 2021). Another study employing the APEX model demonstrated that the photochemical half-lives $t_{1/2}$ of three OMPs (ibuprofen, carbamazepine, and diclofenac) are almost linearly correlated with depth (Vione et al., 2018).

In addition to the variation of light attenuation with depth, photochemical reactions in the surface layer ($z = 0$ m) differ from those in bulk water, because the surface layer (air/water) creates a unique environment that can promote unique chemical reactions (George et al., 2015; Kappes et al., 2021). For example, interfaces covered with fatty acids are ubiquitous in the environment and fatty acids are believed to be photochemically inert in the actinic region; however, direct photolysis of fatty acids has been shown to occur, and complex volatile organic compounds are generated at an air-water interface coated solely with a monolayer of carboxylic acid (Rossignol et al., 2016). Likewise, photochemical reactions may also occur at the water/sediment interface in water bodies where the light is not completely attenuated at the bottom of the water column. These photochemical water/sediment interface reactions might determine the fate of many hydrophobic OMPs because sorption by sediments is an important removal pathway for OMPs (Golovko et al., 2020; Koba et al., 2018). Nevertheless, the photochemical reactions at interfaces have receive relatively little attention and further studies are needed.

5.4. Temperature

In general, the temperature is higher in summer than in winter and decreases with increasing water depth and latitude. Several photodegradation studies have highlighted the impact of temperature on the photodegradation process. For instance, McKay and Rosario-Ortiz (2015) studied the effect of temperature on HO· formation using five different types of DOM isolates at four or five different temperatures within the range of 10–40 °C. The apparent activation energies E_a for HO· formation from the DOMs (kJ mol^{-1}) were obtained using the Arrhenius equation (Eq. (15)).

$$\ln(\Phi_a) = -E_a/RT + \ln(A) \tag{15}$$

where, Φ_a is the apparent quantum yield of HO· through DOM photolysis, R is the universal gas constant (kJ K^{-1} mol^{-1}), T is the absolute temperature (K), and A is the pre-exponential factor. Plots of ln (Φ_a) vs (1/T) revealed significant slopes, indicating the temperature dependency of HO· formation through photolysis of the DOM isolates.

In addition, the photolysis of *p*-benzoquinone was studied by applying the Arrhenius equation to the production of phenol through *p*-benzoquinone photolysis and the loss of *p*-benzoquinone. It was revealed that Φ_a of formation of phenol through *p*-benzoquinone photolysis was temperature-independent while Φ_a of *p*-benzoquinone loss was temperature-independent when the temperature was over 23 °C and temperature-dependent when the temperature was less than 23 °C (McKay and Rosario-Ortiz, 2015).

Zhu and Kieber (2018) studied the photolysis of acetaldehyde, glyoxal, and methylglyoxal in North Pacific seawater under simulated solar radiation and revealed the apparent quantum yield of acetaldehyde was temperature-independent while those for glyoxal and methylglyoxal were temperature-dependent. Kieber et al. (2014) determined the impact of temperature on the apparent quantum yield for photochemically producing H_2O_2 in seawater samples collected from stations located in Antarctica, the Pacific Ocean, the Gulf of Mexico and the several other sites located on the East Coast of the United States. Their experimental results revealed that the apparent quantum yields for H_2O_2 production increased within the temperature range of 0–35 °C, with an average factor of 1.8 every 10 °C. The study indicated that the decrease of temperature and irradiation toward the polar region was mainly responsible for the decrease in H_2O_2 production in the seawater.

As indicated above, the temperature effects on the photochemical transformations in the aquatic environment are significant although the level of influence varies depending on the OMPs or the process of concern. Therefore, it is necessary to acknowledge temperature as an important physical factor influencing photochemical reactions in water.

6. Major knowledge gaps and challenges

- The DOM photochemistry is complex and has not been comprehensively explored. Further investigations are needed with a specific focus on topics such as the production mechanisms of HO·, the role of Hi-^{3}DOM* in photodegradation, and the photo-reactivity of less-studied DOM (e.g., S-DOM).

- Further research efforts are needed to develop prediction models for parameters necessary to describe the kinetics of OMP photodegradation (quantum yield, second-order rate constant, etc.). Thus, the model applicability can be improved in terms of domain and prediction accuracy (at present it is impossible to exhaustively determine the kinetics parameters of all OMPs experimentally).

- Given the recent development of computing performance and new calculating methods, research is encouraged to apply computational calculations (e.g., quantum chemical calculation, molecular dynamics simulation, and machine learning) to aquatic photochemical study as they can provide insights at a molecular level (Lereche et al., 2021; Vialykh et al., 2020; Westermayr and Marquetand, 2021; Xia et al., 2022).

- Modeling of photodegradation rates of OMPs in water bodies is required for their comprehensive understanding, which possibly supports sustainable application and discharge of organic chemicals in environment. Although the current models such as APEX is kinetics-based and practical, there is scope for further development, such as inclusion of the reactivity of actual ^{3}DOM*, quantum yields for the formation of PPRIs in different water matrix, and reactions involving halogen radicals.

- Photochemical and biological processes have close linkages in aquatic environment in terms of degradation and toxicity of OMPs and thus the comprehensive experimental studies elucidating actual environmental processes should also receive attention.

- Photodegradation has been shown to enhance the toxicity of OMPs in some cases, so researchers must also pay attention to degradation pathways and the potential toxicity of byproducts (Vione and Carena, 2020). Computational toxicology can be of great help in assessing the ecotoxicity of products as standard chemicals are not always available.

- The available photochemistry studies are biased toward temperate and subarctic regions, and thus more attention should be paid to

tropical regions where the incident solar radiation is more intense and many developing countries may have to deal with serious pollution caused by OMPs.

- A standard protocol for indirect photodegradation studies is needed to provide meaningful data to allow comparative research and ecological risk assessment. Recommendations for the determination of $^1O_2$ quantum yield is one such example (Ossola et al., 2021).
- In general, the increasing diversity of OMPs in water bodies is responsible for multifarious photodegradation, which poses challenges both in environmental science and environmental management for maintaining sustainable aquatic ecosystems.

7. Conclusions

Chemical pollution by OMPs has become a serious environmental issue and thus understanding the fate of OMPs is essential for ecological risk assessment. This review highlighted photodegradation as a major removal process of many OMPs in the aquatic environment. Its significance and processes depend on both physical and chemical conditions, which are pertinent to the persistence of OMPs. Physical condition basically determines overall energy input for photochemical reactions while water matrix (i.e., inorganic ions, DOM, suspended solids, and coexisting pollutants) determines reaction pathways and rates in both direct and indirect photolysis. In particular, S-DOM exhibits high photochemical reactivity on photodegradation of major types of OMPs such as sulfa drugs. Given that seawater is an important sink of OMPs, photochemical studies regarding S-DOM extracted from seawater should be supplemented for comprehensively understanding of the fate of OMPs in seawater. In addition to such experimental studies to elucidate each pathway, this review also pointed out the importance of integrating different approaches such as modeling based on theoretical and empirical equations and comprehensive experiment combining photochemical and biological processes. Those challenges support the design and implementation of reasonable and practical methods for the management of OMPs in aquatic environment. In this sense, we hope this review will stimulate further investigation of photodegradation processes and the fate of OMPs.

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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