Review

Photochemical behavior of dissolved organic matter in environmental surface waters: A review

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A B S T R A C T

As an important group of widespread organic substances in aquatic ecosystems, dissolved organic matter (DOM) plays an essential role in carbon recycling and transformation processes. The photochemical behavior of DOM is one of the main ways it participates in these processes, and it attracts extensive attention. However, due to a variety of sources and water conditions, including both freshwater and seawater environments, the photochemical properties of DOM exhibit great differences. Nowadays, a large number of studies have focused on the generation process of reactive species (RS) from sunlit DOM, while little effort has been made so far to provide a comprehensive summary of the photochemical behavior of DOM, especially in fresh and saline aquatic ecosystems. In this review, we analyzed the research hotspot on DOM photochemistry over the last 30 years, summarizing the generation of photoreactive species in natural water environments containing DOM (both freshwater and seawater) and listing the main factors affecting the rate, yield, and species of RS photoproduction. Compared with freshwater, seawater has unique characteristics such as high pH value, high ionic strength, and halide ions, which affect the photogeneration of RS, the photoconversion process, as well as the reaction pathways of various environmental substances. In general, DOM-induced surface water photochemistry has important impacts on the environmental transformation and toxic effects of aquatic pollutants and can even contribute significantly to the Earth's carbon cycle, which would have potential implications for both human and ecological health.

1. Introduction

Natural organic matter (NOM), a ubiquitous mixture of organic substances, is one of the most significant reactive carbon storage compartments in the natural environment [1]. On the one hand, NOM could connect living and non-living systems by participating in the food web as the energy source for heterotrophic microorganisms [2]. On the other hand, the solubility, bioavailability, as well as environmental fates of some organic/inorganic pollutants could also be strongly affected by the co-existing NOM [3,4]. In practice, NOM is often divided into particulate organic matter (POM) and dissolved organic matter (DOM), based on whether it can pass through 0.45-μm filters [5,6]. Among these two categories, DOM is considered a main reservoir of organic carbon in the aquatic ecosystem, with typical concentrations of 1–10 mg C/L [7]. It is estimated that there are approximately 6.62×10^{11} tons of dissolved organic carbon (DOC) in the ocean and 2.60×10^{8} tons/yr of total DOC flux transported by terrestrial rivers [8]. Therefore, it is of great significance to explore the effects of DOM on aquatic productivity and the global carbon budget, as well as the migration and transformation processes of other environmental pollutants [2,9].

Elementally, DOM is generally composed of C, H, O, N, P, and S. In terms of chemical structure, DOM usually contains various components, such as carboxyl, alcoholic/phenolic hydroxyl, ketone, aldehyde, quinone, and other chemical groups [5,10,11]. Due to the diversity of different functional groups, DOM exhibits unique physical and chemical properties, which could affect the environmental behavior of co-existing pollutants. For example, DOM could bind to some heavy metals, which would change their solubility and toxicity [5]. It can also interact with

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transition metals (e.g., Fe and Cu), thus influencing the metal speciation as well as the reactive oxygen species (ROS) generation [12–14]. In addition, some hydrophobic organic compounds could be enriched on the DOM surface as well as inside the DOM microphase, affecting their bioavailability and environmental fate [15,16]. Furthermore, DOM is also involved in the formation of colloids [17], cycling and availability of aqueous nutrients [18], and pH buffering [19]. In recent years, various studies have been focusing on DOM properties. Yang et al. [20] discovered that DOM could remarkably enhance the colloidal stability of CdS nanoparticles due to the increased electrostatic repulsion and the steric hindrance, which had a potential influence on the toxicity and bioavailability of CdS. Tang et al. [21] also reported that humic acid (HA) could serve as a natural surfactant, which would further increase the solubility of lignin by hydrophobic interactions. Therefore, these results directly demonstrate that DOM is an active component in the aquatic environment and has a significant influence on the environmental fates of both organic/inorganic contaminants and nanoparticles.

Moreover, as one of the main light-absorbing components in the natural water environment, DOM also plays an irreplaceable role in photochemical processes in aquatic systems [22]. Previous studies have revealed that DOM can produce a complex mixture of reactive species (RS) under natural light irradiation, including hydroxyl radical ($^{\bullet}OH$) [23–26], superoxide ($O_2^{\bullet-}$) [27–29], singlet oxygen ($^1O_2$) [16,30–32], hydrogen peroxide (H_2O_2) [33–36], excited triplet states ($^3DOM^*$) [37–40], and hydrated electrons (e_{aq}^-) [41–43]. Besides, Canonica et al. [44] have reported the occurrence of long-lived photooxidants that presumably exist as phenoxyl radicals generated from direct or indirect phototransformation of DOM phenolic moieties, and Garg et al. [45] also reported the generation of stable semiquinone-like and peroxyl-type radicals by irradiating DOM. All these photogenerated RS can further induce the transformation of numerous organic contaminants and affect the speciation of redox-active trace metals [46,47]. Chu et al. [16] reported that the photoreactivity of two typical amino acids (i.e., histidine and histamine) was significantly enhanced due to elevated $^1O_2$ concentration in the presence of DOM, especially when the amino acids were inside the DOM microphase. Xiao et al. [48] also observed that after the addition of 5 mg C/L DOM, the photodegradation rate constants of both sulfadimidine and sulfapyridine increased by ~10 times. Furthermore, partial degradation and photomineralization of DOM itself may also occur during irradiation, resulting in the release of smaller fragments such as amino acids, aldehydes, short-chain fatty acids, and carbon dioxide [49–51]. Due to the potential impacts on both ecosystems and the carbon cycle, investigating the photochemical behavior and the underlying mechanism of DOM is greatly needed.

The widespread presence of DOM in the aqueous environment, as well as the abundant RS photogeneration, have attracted much attention to the photochemistry of aquatic DOM [9,52]. However, currently, most researchers only studied the photochemical processes of DOM in freshwater systems, and thus, the knowledge of DOM photo-behavior in sea/saline water bodies is still limited. Meanwhile, there are also few relevant review articles available that focus on DOM in the marine environment. In fact, due to the huge volume of the ocean, seawater is considered the biggest DOM reservoir in nature [5,53]. Meanwhile, the large riverine discharge of terrestrial DOM to the ocean (0.4×10^{15}–0.9×10^{15} g/yr) makes it important to explore DOM behavior in saline water [54,55] (Fig. 1). However, the unique features of seawater (e.g., high pH value, high ionic strength, and the inclusion of halides) may cause some differences in DOM photochemical processes compared with the fresh water system. Therefore, to better summarize the photochemistry of DOM, this review mainly focuses on RS photogeneration and occurrence in fresh water and seawater in the presence of DOM. In addition, the impact on the translocation and transformation, as well as the potential toxicity and risks of co-existing contaminants, are also addressed. This review will provide valid information to predict the photochemical properties of surface water from different sources, the behavior of pollutants in aqueous systems, their ecological impacts, and the marine-terrestrial carbon cycle process.
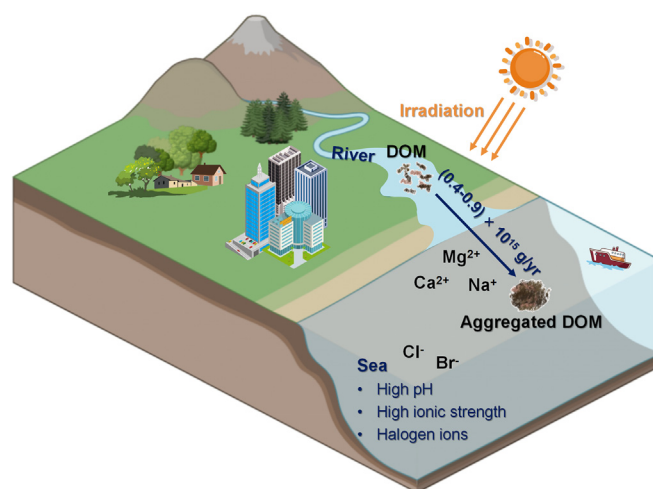

Fig. 1. The scheme of the DOM riverine discharge process. DOM, dissolved organic matter.

2. Bibliometric analysis

Previous researches have already made great progress on the intricate behavior of aquatic DOM under light irradiation conditions. To better understand the current status of relevant studies, a bibliometric analysis was performed based on the related literature (published year: 1991–2023) from Web of Science (WoS). The diagram of keywords co-occurring network is displayed in Fig. 2.

Generally, the co-occurring keywords can be roughly categorized into four groups: (I) organic matter, (II) water matrix, (III) photoinduced RS, and (IV) the environmental behavior/toxicity/risk of coexisting contaminants. It can be inferred from the size of the circles that humic substances, aqueous solution, hydroxyl radical, and photodegradation are the most studied topics in each group. Besides, inferred from the color of the circles, the research topics concerning the photogeneration of RS from DOM were initiated in the early 1990s and have continued for the past three decades. In recent years, with the development of novel analytical methods and advanced instruments, new research hotspots such as the migration/transformation/toxicity/risk assessment of pollutants in irradiated DOM systems have drawn more attention [56–58]. However, the diversity of DOM structure and natural water compositions make the photochemical process more complicated. Therefore, to date, there is still limited information available for the photochemistry of DOM despite extensive relevant studies.

3. Reactive species generation in irradiated aquatic dissolved organic matter systems

DOM is the initiator of various reactions in aquatic systems, and for this reason, it is a key determinant in surface water chemistry [11,22]. Due to complex chemical composition combined with sunlight absorption spanning over several hundred nanometers, DOM exhibits multiple reactivities and takes part in different reactions. Phenol and quinone structures are considered as the most reactive functional groups of DOM, which can directly or indirectly produce a variety of RS under sunlight [23,59–61]. Fig. 3 summarizes the photoproduction/transformation processes of RS from DOM in surface water, and the main parameters of these RS are listed in Table 1.

3.1. Excited triplet states

It is generally recognized that under solar radiation, DOM eventually generates $^3DOM^*$ that encompasses several transient species with high reactivity [41,80]. Previous studies have proposed the formation
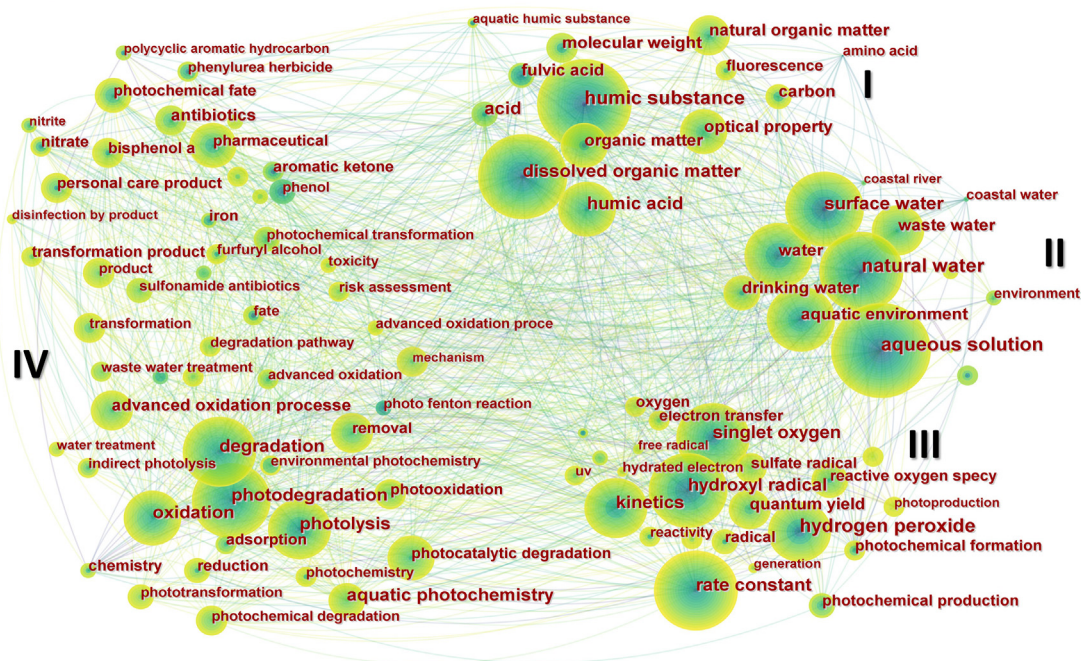
Fig. 2. The keywords co-occurring network diagram of literature concerning "natural organic matter under irradiation in aquatic environments" since 1991. CiteSpace (version 6.1 R4) was used for the bibliometric analysis based on the data exported from WoS. The syntax used for topic search on WoS was "TS = [("dissolved organic matter*" OR DOM OR "natural organic matter*" OR NOM) AND (water OR aquatic*) AND (photo*) AND (radical* OR "reactive species")]". The size of the circles is proportional to the article numbers, and the darker the circle color, the earlier the publishing year of the first relevant papers.

pathway of $^3DOM^*$ as shown in Eqs. 1 and 4. After absorbing light, DOM is excited to form singlet states $^1DOM^*$, then $^3DOM^*$ is generated via a further low-probability spin flip that is known as intersystem crossing (ISC) [22,81]. Besides, the charge-transfer complex might also be formed through an electron transfer process between the donor and acceptor moieties of DOM (Eq. 2) [11]. The lifetime of $^3DOM^*$ was assessed using laser flash photolysis, revealing a range of 10^{-6}–10^{-4} s. Multiple factors contributed to the change in $^3DOM^*$ lifetime, with dissolved oxygen concentration being the primary factor [38,40,64]. Generally, $^3DOM^*$ can further transform through several pathways. The

first one is internal conversion (vibrational deactivation) that prevails in anoxic waters [82]. Moreover, with a redox potential of ~1.7 V [65], $^3DOM^*$ can directly oxidize various environmental pollutants, most notably phenols, anilines, thiols, mercaptans, and sulfonamides, causing their degradation and transformation [11,81]. In addition, $^3DOM^*$ can also act as an electron donor, contributing to the reduction of some oxidants [83]. On the other hand, the annihilation of $^3DOM^*$ (dissolved O_2 being its main quencher) could subsequently produce various secondary ROS, e.g., $^1O_2$, $O_2^{\bullet-}$, and $^\bullet OH$ [80,84]. Therefore, $^3DOM^*$ is regarded as an important energy carrier and a very important
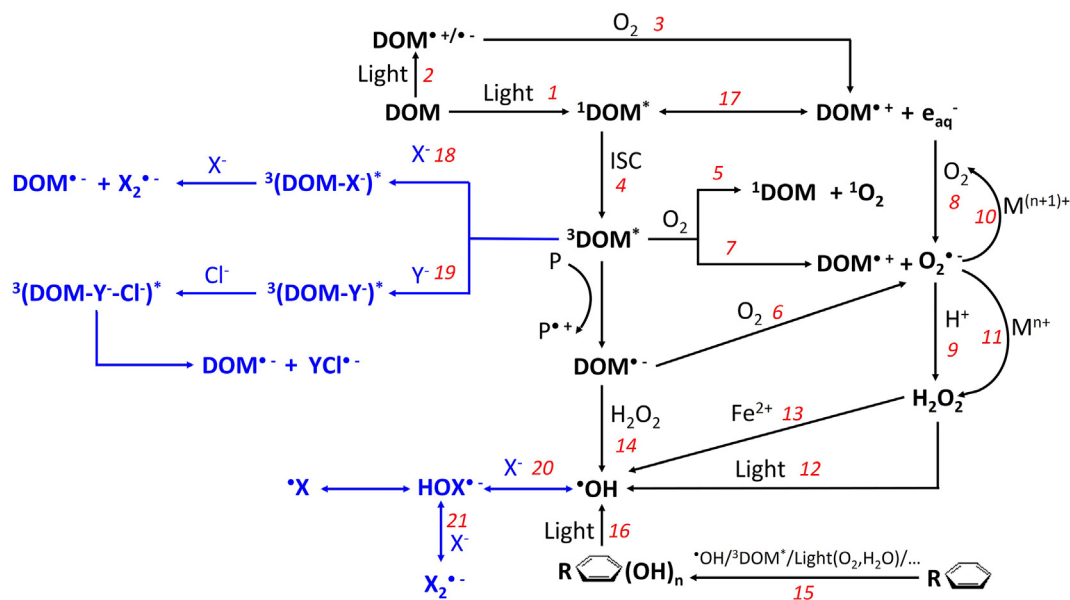

Fig. 3. The scheme of aquatic DOM photochemistry. Photochemical processes that occur only in seawater are marked in blue color. X and Y both present halogens, where X = Cl, Br, I, and Y = Br or I. P stands for an exogenous electron donor, and M stands for metals.

Table 1
Redox potential and half-life time of some typical DOM-related RS.

RS	Redox potential	Half-life	References
e_{aq}^-	-2.77 V [E^0 (e^-/e_{aq}^-)]	10^{-8} s	[62,63]
$^3DOM^*$	1.3–1.9 V (vs. NHE[a])[b]	10^{-6}–10^{-4} s	[40,64–66]
$^\bullet OH$	2.8 V (vs. NHE)	10^{-9} s	[67,68]
$O_2^{\bullet-}$	-0.33 V [E^0 ($O_2/O_2^{\bullet-}$)]	5 s	[69,70]
$^1O_2$	1.1 eV	10^{-5} s	[70,71]
H_2O_2	1.76 V [E^0 (H_2O_2/H_2O)]	8.3 d	[70,72]
$CO_3^{\bullet-}$	1.78 V	0.01–0.025 s	[73,74]
$SO_4^{\bullet-}$	2.6 V	4×10^{-5} s	[68,75]
$Cl^\bullet$	2.5 V	10^{-9} s	[76–78]
$Cl_2^{\bullet-}$	2.1 V	10^{-8} s	[76,78]
$Br^\bullet$	2.0 V	10^{-9} s	[66,77]
$Br_2^{\bullet-}$	1.7 V	4×10^{-7} s	[79]
$I^\bullet$	1.4 V	–	[76]
$I_2^{\bullet-}$	1.1 V	–	[76]
$BrCl^{\bullet-}$	1.95 V	5×10^{-8} s	[66]

RS, reactive species.
[a] NHE stands for "normal hydrogen electrode".
[b] As $^3DOM^*$ is known as a mixture of multiple excited triplet states, the redox potential is not a univocal value [40].

species in direct/indirect photolytic processes in surface waters [40, 81].

$$DOM \xrightarrow{Light} {}^1DOM^* \tag{1}$$

$$DOM \xrightarrow{Light, charge transfer} DOM^{\bullet+/\bullet-} \tag{2}$$

$$DOM^{\bullet+/\bullet-} \xrightarrow{O_2} DOM^{\bullet+} \tag{3}$$

$$^1DOM^* \xrightarrow{ISC} {}^3DOM^* \tag{4}$$

3.2. Singlet oxygen

$^1O_2$ is an important ROS in natural waters. Due to its relatively low redox potential compared with other RS, it can selectively participate in the conversion reactions of various easily oxidized contaminants, including some organic compounds, environmental bacteria and viruses, and especially methylmercury (MeHg) [25,85,86]. Energy transfer between $^3DOM^*$ and dissolved oxygen is the major pathway for $^1O_2$ generation (Eq. 5) [36,87]. It is generally accepted that $^1O_2$ is the major secondary species derived from $^3DOM^*$ in aquatic systems, due to the high energy transformation efficiency from $^3DOM^*$ to O_2 and the relatively low energy required for the $O_2 \rightarrow {}^1O_2$ transition (~94 kJ/mol) [22]. It was estimated that 30–50% $^3DOM^*$ would eventually produce $^1O_2$ via O_2 reaction under natural water conditions [88]. Previous studies have also monitored the steady-state concentration of $^1O_2$ ([$^1O_2$]$_{ss}$) in natural surface waters, which is in the range of (0.4–94) $\times 10^{-14}$ mol/L [87,89]. Moreover, research has shown a significant increase in the $^1O_2$ concentration within the DOM micro-phase compared with the bulk solution by several orders of magnitude [16,30,32]. According to calculations by Latch and McNeill [30], the $^1O_2$ concentration profiles inside and near DOM particles would be controlled by mass-transfer kinetics, and the trapping of $^1O_2$ inside DOM during its diffusion into solution could partially explain these results [90]. Therefore, hydrophobic organic pollutants that can be captured into the DOM micro-phase are more susceptible to being degraded by $^1O_2$.
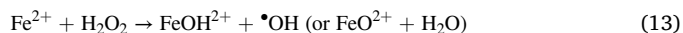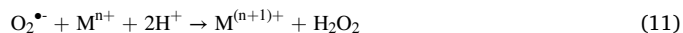
$$^3DOM^* + O_2 \rightarrow {}^1DOM + {}^1O_2 \tag{5}$$

3.3. Superoxide and hydrogen peroxide

The formation of $O_2^{\bullet-}$ mainly occurs through the reaction between O_2 and e_{aq}^- (Eq. 6). On the other hand, $O_2^{\bullet-}$ can also be produced by electron transfer from excited DOM to dissolved oxygen, as shown in Eqs. 7 and 8 [11,22]. With a rate constant of (1.9–2.2) $\times 10^{10}$ L/(mol·s), Eq. 6 is believed to be the dominant $O_2^{\bullet-}$ generation process in aerated surface waters [22]. Moreover, biological reactions might also be key sources of $O_2^{\bullet-}$, especially in seawater [91]. It has in fact been shown that microorganisms (including fungi, bacteria, and phytoplankton) produce $O_2^{\bullet-}$ to a significant extent, which was speculated to be deeply relevant to photosynthesis [92,93]. Specifically, $O_2^{\bullet-}$ can be generated during photosynthesis upon auto-oxidation of an electron acceptor of photosystem I, and some of the generated $O_2^{\bullet-}$ can be further disproportionated by superoxide dismutase (SOD) to produce H_2O_2 [94].

It was reported that approximately half of the generated $O_2^{\bullet-}$ would transform into H_2O_2 (Eq. 9) [36,95], which is also the major formation pathway for H_2O_2 in the natural aquatic environment [28]. A large part of the disproportionation of $O_2^{\bullet-}$ into H_2O_2 was catalyzed by metal ions (M^{n+}), most notably Fe, Mn, and Cu species (Eqs. 10 and 11) [96], and DOM itself could also induce the $O_2^{\bullet-}$ decay [97]. H_2O_2 is an important secondary product of sunlight-induced photoreactions with potential chemical and biological reactivities [22,98]. In the aquatic environment, the concentrations of H_2O_2 vary with both water depth and irradiation intensity, indicating the major role of sunlight irradiation in H_2O_2 generation [99]. Compared with other ROS, H_2O_2 is relatively stable in aquatic systems with a half-life of a few days (Table 1) and a higher cumulative concentration reaching up to µmol/L levels [28,98,100]. Due to its high oxidation ability, high cumulative concentration, and capability to act as $^\bullet OH$ precursors via direct photolysis and/or the Fenton(-like) reaction (Eqs. 12 and 13) [101], it is necessary to further explore the photochemical generation and reactive behavior of H_2O_2 in natural environments.
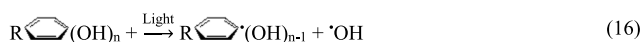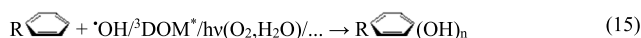
$$O_2 + e_{aq}^- \rightarrow O_2^{\bullet-} \tag{6}$$

$$^3DOM^* + O_2 \rightarrow DOM^{\bullet+} + O_2^{\bullet-} \tag{7}$$

$$DOM^{\bullet-} + O_2 \rightarrow DOM + O_2^{\bullet-} \tag{8}$$

$$2O_2^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2 \tag{9}$$

$$O_2^{\bullet-} + M^{(n+1)+} \rightarrow O_2 + M^{n+} \tag{10}$$

$$O_2^{\bullet-} + M^{n+} + 2H^+ \rightarrow M^{(n+1)+} + H_2O_2 \tag{11}$$

$$H_2O_2 \xrightarrow{Light} 2^\bullet OH \tag{12}$$

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + {}^\bullet OH \text{ (or } FeO^{2+} + H_2O) \tag{13}$$

3.4. Hydroxyl radical

$^\bullet OH$ is a powerful oxidant with a standard oxidation potential of 2.7 V in acidic solutions and 1.8 V under neutral conditions [62]. Due to its unselective and instantaneous oxidation ability, it has significant impacts on the environmental fates of various organic pollutants [67,102]. However, the photogeneration mechanism of $^\bullet OH$ from DOM is complicated and still not clear. The direct photolysis of H_2O_2 is one of the possible pathways for $^\bullet OH$ production (Eq. 12). However, due to the slight absorption of sunlight by H_2O_2, its photolysis is insignificant for $^\bullet OH$ photoformation [22,103]. It was also reported that the Fenton-like transformation process involving a reductive $DOM^{\bullet-}$ species and H_2O_2 (Eq. 14) would be another potential $^\bullet OH$ source [22,104,105], which was supported by the results of Sha et al. [106]. In their study, Sha et al. added phenol/aniline to the irradiated photosensitizers (i.e., benzoquinone, benzophenone, acetophenone, and 3-methoxyacetophenone) to generate $DOM^{\bullet-}$ [40,107] and found that the transformation of H_2O_2 to $^\bullet OH$ was significantly enhanced after $DOM^{\bullet-}$ generation [106]. This

phenomenon could further confirm the importance of Eq. 14 in $^\bullet$OH production from H_2O_2.

$$H_2O_2 + DOM^{\bullet-} \rightarrow DOM + OH^- + {}^\bullet OH \tag{14}$$

Other pathways leading to the formation of $^\bullet$OH include the Fenton reaction (Eq. 13), which involves photogenerated H_2O_2, and the photolysis of polyhydroxylated organic compounds (Eq. 16) as the photoactive DOM components. In the latter case, previous hydroxylation processes triggered by $^\bullet$OH, ^{3}DOM*, and/or other oxidants are required (Eq. 15) [108].

$$R\bigcirc + {}^\bullet OH/{}^3DOM^*/h\nu(O_2,H_2O)/... \rightarrow R\bigcirc(OH)_n \tag{15}$$

$$R\bigcirc(OH)_n + \xrightarrow{\text{Light}} R\bigcirc{}^\bullet(OH)_{n-1} + {}^\bullet OH \tag{16}$$

3.5. Hydrated electron

Hydrated electron (e_{aq}^-) is a strong reducing species with high reactivity [43]. The generation of e_{aq}^- from DOM under solar light irradiation has been demonstrated (Eqs. 1 and 17) [42,43]. In this process, DOM is initially excited to produce ^{1}DOM*, from which e_{aq}^- can be further ejected. It has been shown that aromatic functional groups are the main active source for e_{aq}^- generation in DOM, while additional contribution could come from the excited singlet states of phenols and their derivatives [11,109]. Therefore, the yield of e_{aq}^- is closely related to the source and the structural composition of DOM [110], but it is also affected by the light source and the pH value of the solution. Thomas-Smith et al. [43] investigated the wavelength dependence of e_{aq}^- production using a probe method that detected the generated methyl radical, revealing a negative correlation between e_{aq}^- production and the irradiation wavelength. According to their results, the calculated yield of e_{aq}^- was reported to be ~100 times higher at 254 nm than at 350 nm [43]. At the same time, it has been shown that the photoproduction of e_{aq}^- is enhanced with the increase of solution pH [11].

Due to the low formation quantum yields under sunlight (10^{-5}–10^{-4} at wavelengths from 300 to 400 nm) [42,43], the environmental significance of DOM-derived e_{aq}^- is limited [11]. However, in the DOM microphase, there is potential to have an elevated local concentration of e_{aq}^-, which is of great significance for the transformation of DOM-bound hydrophobic pollutants and especially halogenated compounds [111].

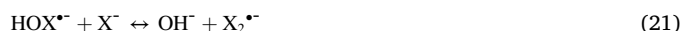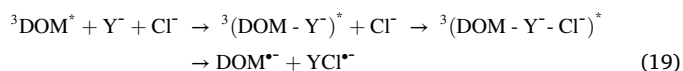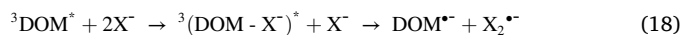$$^1DOM^* \leftrightarrow DOM^{\bullet+} + e_{aq}^- \tag{17}$$

3.6. Reactive halogen species

Oceans make up more than 70% of the Earth's water, and the average salt content of ocean water is about 3.5% (about 0.54 mol/of Cl$^-$, 0.84 mmol/L of Br$^-$, and 0.46 μmol/L of I$^-$) [112,113]. Therefore, the influence of halogen ions must be considered when studying the photochemical behavior of DOM in seawater. Previous studies have demonstrated that halogen ions in seawater could influence the production of multiple ROS [25,48,114]. Meanwhile, halogen ions can be converted to halogen radicals, which further affect the transformation of various environmental contaminants [66,115,116]. Especially, halogen ions can react with both ^{3}DOM* and $^\bullet$OH to produce the corresponding reactive halogen species (RHS), e.g., Cl$^\bullet$ Cl$_2^{\bullet-}$, Br$^\bullet$, I$^\bullet$, BrCl$^{\bullet-}$, and ICl$^{\bullet-}$ [66,77,80, 117,118] as shown in Eqs. 18–21, where X in the equation stands for Cl, Br, and I and Y stands for Br or I. Direct oxidation of halides by ^{3}DOM* plays the dominant role in the production of RHS [77]. In this process, ^{3}DOM* can firstly form a charge-transfer complex with halides [^{3}(DOM-X$^-$)*] and then be quenched to the ground state, which is accompanied by the release of RHS (Eqs. 18 and 19) [77,119]. Due to the high redox potential of chlorine radicals [E^0(Cl$^-$/Cl$^\bullet$) = 2.5 V; E^0(2Cl$^-$/Cl$_2^{\bullet-}$) = 2.1 V] and bromide radicals [E^0(Br$^-$/Br$^\bullet$) = 2.0 V;

E^0(2Br$^-$/Br$_2^{\bullet-}$) = 1.7 V, Table 1] [76], the generated halogen radicals can participate in the halogenation of DOM as well as the degradation of other organic contaminants, including phenol, benzoates, personal care products, and antibiotics [115,120]. Interestingly, while Cl$_2^{\bullet-}$ mostly acts as an oxidizing agent, the radical Br$_2^{\bullet-}$ has high bromination potential, especially toward phenols [121,122].

However, currently, most research on halogen radicals has focused on drinking water disinfection, but studies about the impact of halogen radicals on the transformation of contaminants in the natural environment are still limited.

$$^3DOM^* + 2X^- \rightarrow {}^3(DOM\text{-}X^-)^* + X^- \rightarrow DOM^{\bullet-} + X_2^{\bullet-} \tag{18}$$

$$^3DOM^* + Y^- + Cl^- \rightarrow {}^3(DOM\text{-}Y^-)^* + Cl^- \rightarrow {}^3(DOM\text{-}Y^-\text{-}Cl^-)^*$$
$$\rightarrow DOM^{\bullet-} + YCl^{\bullet-} \tag{19}$$

$$^\bullet OH + X^- \leftrightarrow HOX^{\bullet-} \leftrightarrow OH^- + {}^\bullet X \tag{20}$$

$$HOX^{\bullet-} + X^- \leftrightarrow OH^- + X_2^{\bullet-} \tag{21}$$

4. Factors influencing reactive species photogeneration from dissolved organic matter: Species and concentrations

The photogeneration of RS can be influenced by multiple factors, e.g., the structures of DOM [37,123,124], halide ions [81,116,125], as well as the co-existing metal ions [123] in the natural aquatic environment. Generally, due to the various origins as well as the diversity of environmental factors, DOM normally exhibits different RS photoproduction capabilities. Herein, we not only summarize the possible influencing factors of DOM photochemistry on RS generation but also discuss the underlying mechanisms for the different processes.

4.1. The effect of dissolved organic matter

4.1.1. Dissolved organic matter origin and structures
Multiple studies have reported that the origin of DOM could influence RS photogeneration. Compared to marine DOM, terrestrial-sourced DOM has higher C/N ratios, more aromatic carbon, and lignin structures [54], further influencing the photoactivity. Wang et al. [124] collected DOM samples around coastal mariculture areas and evaluated their photoreactivity. The results revealed that the DOM samples extracted from mariculture-impacted areas produced higher [^{3}DOM*]$_{ss}$ during irradiation [124]. Other studies also reported that the DOM of marine/estuarine origin exhibited higher quantum yields for ^{3}DOM* under natural irradiation [24,126]. Similarly, Wenk et al. [127] observed a pronounced inhibitory effect of terrestrial DOM on ^{3}DOM*-induced contaminant transformation compared to aquatic DOM. All these studies demonstrate that the DOM source would significantly affect its photochemical activity. Further studies proved that the influence of DOM sources on ROS photogeneration capability is directly related to DOM composition [11,65,124, 126]. Wang et al. [124] revealed that owing to the terrestrial inputs and biological excretions, DOM from mariculture areas had a higher degree of humification and more aromatic ketones, resulting in more effective production toward ^{3}DOM* [54,128,129]. Silva et al. [126] demonstrated that DOM samples collected from estuarine water were rich in fulvic acid (FA) and XAD-4 fractions (i.e., hydrophilic organic acids retained on a XAD-4 styrene-divinylbenzene column [130]), which might enhance the photoreactivity of DOM in coastal areas.

In addition to the origin of DOM, its average molecular weight (MW) can also result in different structural compositions, thus affecting the RS yield [37]. For example, it has been reported that FA with higher MW exhibits a lower yield of ROS and ^{3}FA*, possibly due to lower content of lignin-like structures. Fewer lignin-like components lead to lower amounts of hydroxyl and carbonyl groups, as well as lower electron-cloud densities, which all result in the inhibition of ROS/^{3}FA* generation [58,131]. In

addition to FA, similar results were also confirmed for other types of DOM, including Suwannee River humic acid, algae-derived DOM, and macrophyte-derived DOM [31,37]. Moreover, DOM with less aromatic and more saturated components can increase the ^{3}DOM* quantum yield, further promoting ^{1}O$_2$ production [39,132]. Higher O$_2^{\bullet-}$ and H$_2$O$_2$ yields can also be obtained for DOM with lower MW and less aromatic content [28,34]. In similar cases, it is likely that complex high-MW DOM molecules undergo rather strong intra-molecular interactions that enhance internal conversion processes (vibrational energy relaxation, without luminescence or chemical reactivity) at the expense of photosensitization activity. This issue decreases the quantum yields of RS generation [133], which can, however, be offset to variable degrees by the ability of high-MW DOM to absorb sunlight more efficiently than low-MW DOM.

However, the effect of aromaticity on the RS generation has not reached a definitive conclusion. Although research has reported that fewer aromatic components could enhance the RS quantum yields [37, 39,132], other studies have observed the opposite phenomenon. Tang et al. [134] found that DOM components with higher levels of aromatic groups had more pronounced photochemical properties, which could produce more ^{3}DOM*. In addition, Fujii and Otani [28] also observed that the photoproduction of H$_2$O$_2$ increased as the aromatic C content of the DOM increased. Thus, the impact of the DOM component on its photoactivity is complicated, and more in-depth studies are needed in the future.

As for $^{\bullet}$OH, Rosario-Ortiz and Canonica [82] found that the $^{\bullet}$OH quantum yield was higher for DOM with low MW and more fluorescence, implying that the DOM samples with fewer charge-transfer interactions could produce $^{\bullet}$OH more effectively [11]. However, the underlying mechanism for the influence of DOM structure on the apparent $^{\bullet}$OH quantum yield has not been clearly revealed. For instance, it is apparently counter-intuitive to observe a correlation between fluorescence (originating from singlet states) and $^{\bullet}$OH photoproduction that should involve some extent of triplet-state reactivity. This is certainly true for single molecules, where singlet- and triplet-induced processes are in mutual competition: photoactive quinones and aromatic ketones are hardly or not at all fluorescent, while fluorescent phenols are poor triplet sensitizers. However, within large classes of compounds, those groups of molecules showing low charge-transfer/internal conversion (e.g., low-MW DOM) have a high potential to include both efficient fluorophores and good photosensitizers [135].

Besides common ROS, it was also reported that the structure of DOM could affect the generation of RHS. Aromatic ketones and quinones are considered key functional groups for the photo-production of RHS. These moieties have been reported to primarily contribute to the photogeneration of ^{3}DOM* [136,137], which can further convert Cl$^-$/Br$^-$ into

RHS [77]. In conclusion, DOM origin and structure have a fundamental impact on the photogeneration of various RS.

4.1.2. Dissolved organic matter amount (dissolved organic carbon)

Other than the DOM origin, its total concentration can also affect the occurrence (photoproduction and/or scavenging) of RS. In particular, sunlit DOM is a source of ^{3}DOM*, ^{1}O$_2$, and $^{\bullet}$OH, but DOM is also the main scavenger of both $^{\bullet}$OH and Br$_2^{\bullet-}$. The effect of DOC at otherwise equal DOM features can be assessed by means of photochemical models where the DOM amount (DOC) is varied while optical and chemical properties of DOM are assumed to remain unchanged. In this framework, Fig. 4a reports the modeled steady-state concentrations of ^{3}DOM*/^{1}O$_2$, $^{\bullet}$OH, and Br$_2^{\bullet-}$ as a function of DOC concentrations in both freshwater (negligible Br$^-$) and seawater-like (0.84 mM Br$^-$) conditions [138]. Considering that increased DOC can induce ^{3}DOM*/^{1}O$_2$ production (Fig. 4a), and DOM does not scavenge either RS (^{3}DOM* is mainly quenched by O$_2$, while ^{1}O$_2$ is quenched by collisions with water [101]), the increase in both [^{3}DOM*] and [^{1}O$_2$] with elevated DOC amount is expected, assuming that the DOM optical/photochemical properties remain unchanged with varying DOC levels.

The reason for having [^{3}DOM*$_{sea}$] = 2[^{3}DOM*$_{frw}$] will be explained in *Section 4.2.3* [117]. Also, note that [^{3}DOM*]$_{frw}$ and [^{1}O$_2$]$_{frw}$ are approximately equal ([^{3}DOM*]$_{frw} \approx$ [^{1}O$_2$]$_{frw}$, Fig. 4a) because the reaction between ^{3}DOM* and O$_2$ gives ^{1}O$_2$ with ~50% yield, but the quenching rate constant of ^{1}O$_2$ is about one-half that of ^{3}DOM* in aerated solution [40].
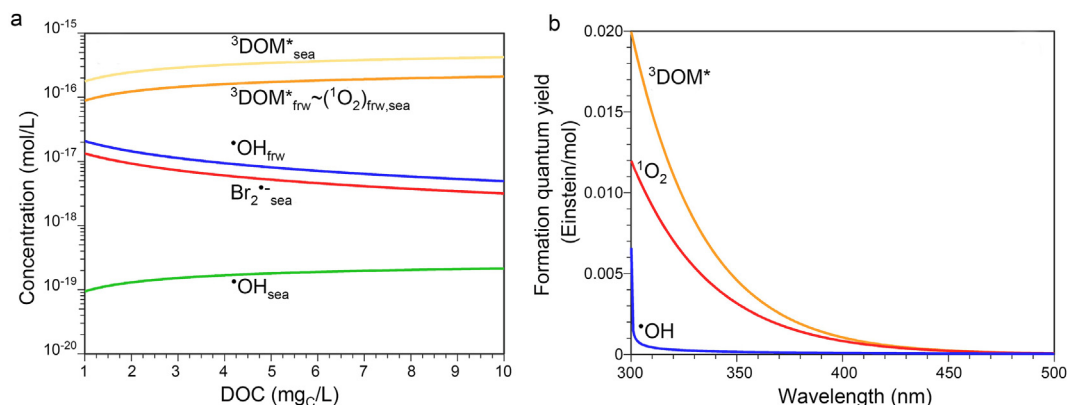
The orders of magnitude difference in [$^{\bullet}$OH] in the presence and absence of bromide is accounted for by the fact that Br$^-$ is by far the main $^{\bullet}$OH scavenger in conditions that are representative of seawater [62, 101]. Moreover, the fact that $^{\bullet}$OH$_{sea}$ is photogenerated by DOM and scavenged by Br$^-$ explains why [$^{\bullet}$OH$_{sea}$] increases with increasing DOC. In contrast, DOM is the main scavenger of both $^{\bullet}$OH in freshwaters (usually) and Br$_2^{\bullet-}$ [101], which explains why both [$^{\bullet}$OH$_{frw}$] and [Br$_2^{\bullet-}$$_{sea}$] decrease with increasing DOC.

4.2. The effect of environmental factors

4.2.1. Wavelength

In the case of ^{3}DOM*, ^{1}O$_2$, and $^{\bullet}$OH, it has been shown that the relevant formation quantum yields from irradiated DOM (specifically Suwannee River DOM and Mississippi River DOM) decrease with increasing wavelength (λ, nm). In particular, the average values read as follows (Eqs. 22–24) [139]:

$$\Phi_{3_{DOM^*}}(\lambda) = (0.020 \pm 0.002)\, e^{-\frac{\lambda - 300}{34 \pm 1}} \qquad (22)$$

Fig. 4. (a) Modeled (with the APEX software [138]) steady-state concentrations of ^{3}DOM*/^{1}O$_2$, $^{\bullet}$OH, and Br$_2^{\bullet-}$ in the presence of DOM alone ("frw", quantified as the DOC) and of DOM + 0.84 mM Br$^-$ ("sea"). Other conditions: 10 m water depth, absence of nitrate, nitrite, bicarbonate, or carbonate, sunlight irradiance as per noon, spring equinox. Note that [^{3}DOM*$_{sea}$] = 2[^{3}DOM*$_{frw}$] ([117], *vide infra*); (b) wavelength trends of the formation quantum yields of ^{3}DOM*, ^{1}O$_2$, and $^{\bullet}$OH. DOC, dissolved organic carbon; DOM, dissolved organic matter.

$$\Phi_{1_{O_2}}(\lambda) = (0.012 \pm 0.004) \, e^{\frac{\lambda-300}{37.5\pm2.5}} \tag{23}$$

$$\Phi_{\cdot_{OH}}(\lambda) = \left[(1.1 \pm 0.2) \times 10^{-4} \right] \sqrt{\frac{180 \pm 30}{\lambda - 300}} e^{-\sqrt{\frac{\lambda-300}{180\pm30}}} \tag{24}$$

The following Fig. 4b reports the wavelength trends of the quantum yields.

4.2.2. pH

The pH value is one of the most important environmental factors, and various studies have reported that the environmental pH could affect the RS photogeneration yield. For example, Li et al. [140] found that as the initial pH increased from 3.8 to 8.2, the photo-sensitivity of DOM decreased, leading to decreased release of SO_4^{2-} from dissolved organic sulfur. Wasswa et al. [141] also reported that when pH increased from 6.5 to 8.5, the apparent quantum yield of $^1O_2$ decreased by ~15%, consistent with other studies [36,142,143]. Apart from $^1O_2$, the apparent quantum yield of $^\bullet OH$ is also pH-dependent, and in neutral conditions, it is significantly lower than in acidic or alkaline conditions [141]. Similar phenomena of pH-dependent $^\bullet OH$ yield were also observed in other studies [140,144,145]. As for $O_2^{\bullet-}$, although there is less literature focusing on the effect of pH on its production, previous studies have reported a significant impact of pH on its decay rate [28,146]. While for H_2O_2 photoproduction, only a slight influence was observed under natural pH conditions (pH 6.0–8.0) [28]. Considering the different pH values in common fresh water (6.0–7.0) and seawater (7.5–8.2) [77,140], evaluating the effect of pH on RS production is meaningful in understanding the generation and transformation mechanism of RS in different water bodies.

The strong pH-dependent photogeneration of $^1O_2$ could be explained by the lower quantum yield of $^3DOM^*$ at high pH [11]. As the representative energy of $^3DOM^*$ (180–320 kJ/mol) is remarkably higher than the energy barrier between $^1O_2$ and O_2 (~94 kJ/mol), O_2 can easily act as an energy acceptor from $^3DOM^*$ to form $^1O_2$ [40] (Eq. 3) [11,88]. As reported, pH affects the steady-state concentration of $^3DOM^*$ ($[^3DOM^*]_{ss}$) significantly [147,148]. Lan et al. [149] demonstrated that under alkaline conditions, DOM would form a linear structure to maximize contact with water, which could inhibit intermolecular interactions and suppress the generation of $^3DOM^*$. Therefore, the $^3DOM^*$ quantum yield would decrease at higher pH, further preventing the production of $^1O_2$ [36]. Similarly, the pH-dependent $^\bullet OH$ quantum yield could also be explained by the change in DOM morphology at different pH values [26,141]. Sun et al. [26] proposed that substituted phenols, especially carboxylate-substituted ones, are important $^\bullet OH$ sources under solar irradiation. When alkalinity increases, the phenol-like structure would undergo deprotonation to phenolate and decrease $^\bullet OH$ photogeneration [150,151]. Interestingly, different pH effects have been observed on the quantum yields of $^3DOM^*/^1O_2$ and $^\bullet OH$, which can be attributed to the fact that $^\bullet OH$ and $^3DOM^*/^1O_2$ are generated from different DOM components [152].

4.2.3. Ionic strength

Compared to fresh water, sea/coastal water contains higher salinity (0.54 mol/L Na^+ and Cl^-, 0.055 mol/L Mg^{2+}, 0.026 mol/L SO_4^{2-}, 6.8 mmol/L Ca^{2+}, 2.5 mmol/L HCO_3^-, 0.84 mmol/L Br^-, and trace amounts of other ions), which might influence the RS photogeneration process [112,116,117]. Parker et al. [117] found that at higher ionic strength, regardless of the salt type, the probed $^3DOM^*$ decay rate by 2,4,6-trimethylphenol (TMP, a typical $^3DOM^*$ probe [25,123]) was significantly inhibited. This phenomenon could be explained by an electron-transfer mechanism. Specifically, high ionic strength could promote DOM aggregation [153,154] and further influence the interaction between the electron donor moieties, e.g., hydroxyl/phenolic groups [117,147]. This phenomenon would inhibit the charge-transfer process and prevent $^3DOM^*$ quenching, leading to a slower $^3DOM^*$ decay rate and higher $[^3DOM^*]_{ss}$ [117]. In addition, at the ionic strength of seawater, the concentration of dissolved oxygen declines by ~20% [117], which would also

contribute to a slower decay of $^3DOM^*$ [155]. Therefore, $[^3DOM^*]_{ss}$ in seawater is about twice as that in fresh water [117]. However, for $^1O_2$, since both $^3DOM^*$ and O_2 are the main $^1O_2$ precursors (Eq. (5)), higher $[^3DOM^*]_{ss}$ in seawater nearly balances the decreased dissolved oxygen concentration. Therefore, negligible change was observed for $[^1O_2]_{ss}$ under high ionic strength conditions [117,156]. In addition to $^3DOM^*$, salinity could also affect the generation of $O_2^{\bullet-}$ and H_2O_2. It has been demonstrated that at higher salinity, a higher yield of e_{aq}^- could be obtained, which might enhance the production of $O_2^{\bullet-}$, and could eventually promote the formation of H_2O_2 (Eqs. 6 and 9) [24,28,157].

High ionic strength could also induce structural changes in DOM, which might affect the photogeneration of ROS (Fig. 5). In fact, monovalent cations in seawater (i.e., Na^+, Li^+, and K^+) together with a divalent cation (i.e., Mg^{2+}) can make the structure of DOM more compact, resulting in a decrease in DOM size. Moreover, other divalent cations (such as Ca^{2+} and Ba^{2+}) can readily induce DOM aggregation, causing the merging of multiple particles [154,158]. Additionally, the microheterogenous distribution of ROS in illuminated DOM solutions has been reported. For example, Yan et al. [159] used a series of chlorinated paraffins as $^\bullet OH$ probes and demonstrated that the $[^\bullet OH]_{ss}$ inside the DOM microphase was ~210 fold higher than in the aqueous phase. The $^1O_2$ concentration inside the DOM microphase was also determined by a hydrophobic dioxetane precursor, and the measured intra-DOM concentration was an order of magnitude higher than that measured in the water bulk by the hydrophilic furfuryl alcohol probe [30]. Therefore, we could infer that the aggregation of DOM in seawater might enhance ROS photogeneration by providing a larger intra-DOM microphase. However, further studies are still needed to provide convincing evidence for this speculation.

4.2.4. Specific ions

As the main anions in seawater, halogen ions have been reported to affect RS conversion as well as their concentrations and occurring species. Glover and Rosario-Ortiz [160] found that the presence of Cl^- and Br^- could significantly increase the concentrations of $^3DOM^*$ and $^1O_2$, which could be attributed to enhanced ISC from $^1DOM^*$ to $^3DOM^*$ in the presence of halogenides. At the same time, the fluorescence of organic species was quenched by the halide ions, which would further increase the ISC rate and produce higher concentrations of $^3DOM^*$ [25,160]. Because $^3DOM^*$ is an important $^1O_2$ precursor (Eq. 3), enhanced $^1O_2$ concentration might also be expected under high salinity conditions (but see previous *caveat* about decreasing $[O_2]$ at high ionic strength in *section 4.2.3*). Wu et al. [161] observed decreased $O_2^{\bullet-}$ cumulative concentration (from 2.57 μmol/L to 1.04 μmol/L) within 48 h of UV irradiation in the presence of 0.6 mol/L Cl^-, thereby suggesting that seawater-level Cl^- could inhibit the generation of $O_2^{\bullet-}$.

In addition to halide ions, some metal ions could also affect the generation of RS, and the different binding sites of various metal ions onto the DOM matrix might explain this phenomenon [162]. Previous research has proven that Mg^{2+} played a pivotal role in the production of $^3DOM^*$ [123] as well as $^1O_2$ [163] as Mg^{2+} could induce a more tightly wrapped structure for DOM that would also be responsible for increased fluorescence [123]. Furthermore, Mg^{2+}/Ca^{2+} in seawater were also proven to compete with Fe(II) for the DOM ligand-binding sites [100,164]. As $^\bullet OH$ is formed in larger amounts when Fe(II) is organically complexed [104], impeded binding between Fe(II) and DOM in the presence of Mg^{2+} and Ca^{2+} might prevent the formation of $^\bullet OH$ in seawater.

5. Impacts of dissolved organic matter on the environmental fate and ecological effect of co-existing contaminants

5.1. Phototransformation of organic contaminants in the presence of dissolved organic matter

The photochemical behavior of DOM can affect the transformation of various organic pollutants in the environment and thus affect their ecological risks. As mentioned above, DOM can produce various RS
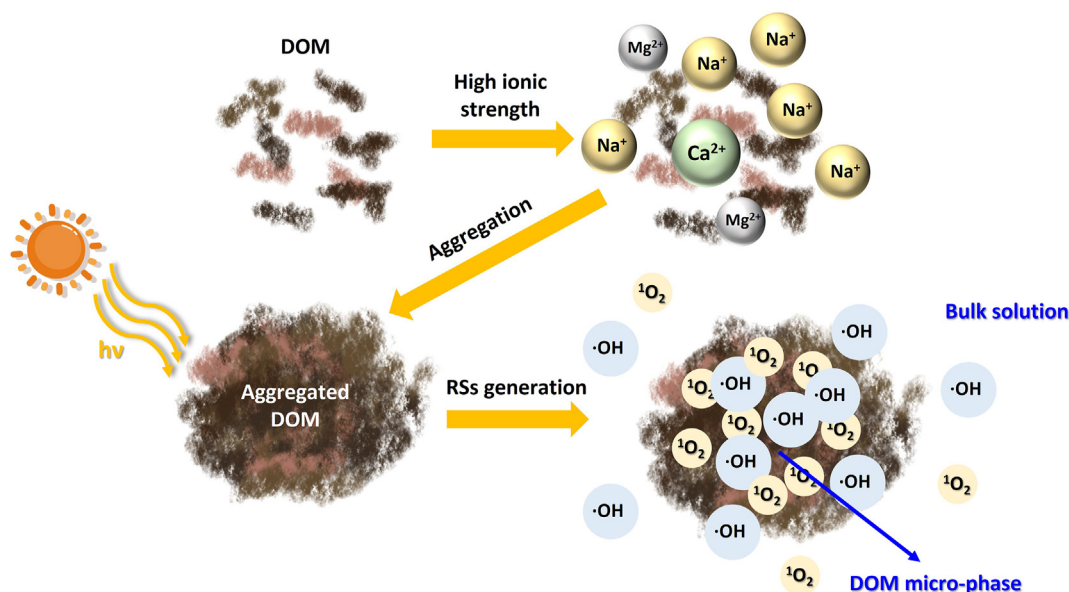
Fig. 5. The aggregation of DOM under high ionic strength conditions and its influence on RS photogeneration [32,154,159].

under natural irradiation, including $^{\bullet}OH$, $O_2^{\bullet-}$, $^1O_2$, and $^3DOM^*$ [126, 165]. Compared to direct photolysis, indirect photolysis can be more important for the environmental transformation of those organic pollutants that do not absorb sunlight, absorb poorly, or have low photolysis quantum yields. RS generated from DOM could play crucial roles during this process [56,81]. For example, Silva et al. [126] found that in the presence of 20 mg/L FA, the half-life of 17α-ethinylestradiol (EE2) and 17β-estradiol (E2) in freshwater decreased from 46 h and 94 h to 2.1 h and 2.9 h, respectively. Similar degradation enhancement effects were also observed for the photodegradation of other organic pollutants such as estriol (E3), estrone (E1), bisphenol A (BPA), sulfadiazine, acetaminophen, and naphthalene [116,125,166–168].

As the primary generated RS, $^3DOM^*$ plays an important role in the indirect photodegradation of contaminants. It is commonly believed that $^3DOM^*$ is especially responsible for the photolysis of aromatic anilines and electron-rich phenols [40,165]. Therefore, the transformation of pollutants containing these functional groups (e.g., acetaminophen) can be greatly promoted when DOM exists [168]. Although $O_2^{\bullet-}$ is a weak oxidant, it plays a significant role in trace-metal redox cycles. Zafiriou et al. [169] reported that the reaction with inorganically complexed Cu^{2+} is an important sink for $O_2^{\bullet-}$ in seawater. In addition to Cu, the redox cycles of Fe, Mn, Co, and Ag are also controlled by $O_2^{\bullet-}$ derived from DOM photolysis [170,171]. As far as $^1O_2$ is concerned, its relatively low oxidizing power ensures that its contribution to the indirect photodegradation of organic pollutants is limited to some categories, e.g., (chloro)phenolates, indoles, imidazoles, and furans [11]. However, several of these molecules are biologically significant, and this issue could account for the ability of $^1O_2$ to take part in the inactivation of bacteria and viruses [101]. Moreover, ROS such as $^1O_2$ and $^{\bullet}OH$ exhibit microheterogeneity within DOM [159,165,172]. As a consequence, the occurrence of substantial amounts of $^1O_2$ and $^{\bullet}OH$ in the DOM cores could be responsible for the accelerated degradation of various hydrophobic organic compounds, especially for the contaminants sensitive to $^1O_2$ and $^{\bullet}OH$ [159,172]. For example, Chu et al. [16] observed enhanced degradation of histidine and histamine in the presence of DOM due to elevated $^1O_2$ concentration inside the DOM microphase.

On the other hand, DOM could considerably inhibit the photodegradation of organic contaminants (Fig. 6). The main factors, as well as the photodegradation mechanisms of different contaminants in the presence of DOM, are listed in Table 2. For some compounds, the quenching effect of DOM on the production of ROS and the light shielding effect would play major roles [165]. For instance, the direct photolysis of both fluoroquinolone antibiotics and decabromobiphenyl ethers (BDE-209) is inhibited by DOM due to both ROS (especially $^{\bullet}OH$) scavenging and light shielding effects [173,174]. DOM is particularly effective in the inhibition of pollutant photodegradation under UV as it tends to attenuate UV irradiance [175,176], so the photolysis of contaminants that can be directly degraded under UV light (e.g., cytostatic drugs) is prevailingly inhibited by DOM [175]. Coherently, DOM could promote the photodegradation of thiamphenicol and florfenicol under solar irradiation through $^1O_2$ generation and inhibit it under UV irradiation due to UV attenuation [177]. DOM also contains some antioxidant components (e.g., phenolic groups) that can convert the radical intermediates back to their parent compounds, thus inhibiting the (especially $^3DOM^*$-sensitized) photolysis of pollutants [151,178].

In seawater, high ionic strength and the generated halide radicals might affect the transformation rates and products of organic contaminants in the presence of DOM. Moreover, the effect of halogen ions on the photoconversion of pollutants is also double-sided. Cheng et al. [174] found that with the coexistence of DOM, Cl⁻, and Br⁻, the photolysis rate
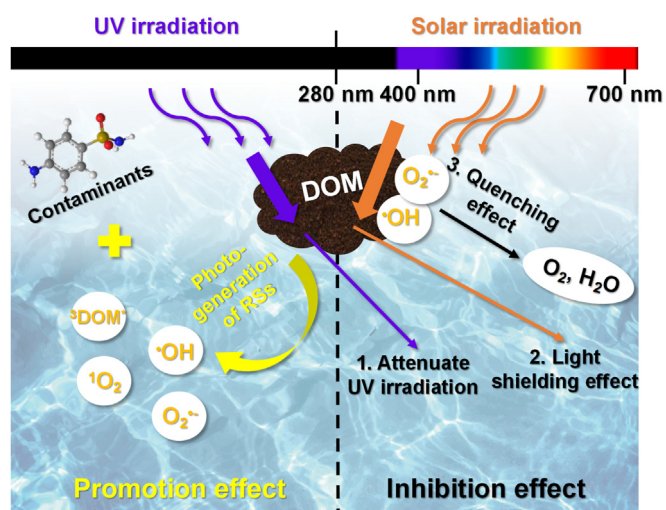

Fig. 6. The dual effects of DOM in the indirect photodegradation of organic contaminants.

Table 2
The dual effects of different DOM specimens on the indirect photodegradation of organic contaminants in aquatic systems.

Type of DOM	Concentration (mg C/L)	Contaminants	Light	Effect	Mechanisms	Ref.
HA	10	Amino acids	Solar	Promotion	Photogeneration of ^{3}DOM*, H_2O_2, $^1O_2$	[179]
HA	4–40	Florfenicol, thiamphenicol	Solar	Promotion	Photogeneration of $^1O_2$	[177]
NOM	10	Acetaminophen	Solar	Promotion	Photogeneration of ^{3}DOM*	[168]
DOM	5	Genistein	Solar	Promotion	Photogeneration of ^{3}DOM*	[180]
HA, FA	5	Mexiletine	Solar	Promotion	Photogeneration of ^{3}DOM*	[181]
HA, NOM	5	2,4,5-Trichlorobiphenyl	Solar	Promotion	Photogeneration of $^\bullet$OH, $^1O_2$	[182]
DOM	10	Decabromobiphenyl ethers	Solar	Inhibition	Light shielding and quenching effect	[174]
HA	2.5–10	Gatifloxacin, sarafloxacin	Solar	Inhibition	Quenching effect, competitive photoabsorption	[173]
HA, FA	15	Metoxuron	UV	Not obvious	Photogeneration of ^{3}DOM*, attenuate UV irradiation	[183]
HA	2–43	Florfenicol, thiamphenicol	UV	Inhibition	Attenuate UV irradiation, competitive photoabsorption	[177]
HA	1–10	Cytostatic drugs	UV	Inhibition	Attenuate UV irradiation	[175]

FA, fulvic acid; HA, humic acid; NOM, natural organic matter; UV, ultraviolet.

of BDE-209 was significantly promoted, most likely due to enhanced photogeneration of ^{3}DOM* that acted as a crucial RHS precursor [66,77] and directly promoted the photoreactions. In addition, Parker and Mitch [77] also observed that RHS took part in a 5-fold enhancement of the photodegradation rates of domoic acid and dimethyl sulfide. Furthermore, multiple studies have reported that increased Br$^-$ and Cl$^-$ concentrations could enhance phototransformation of sulfonamides in the aquatic environment, which is mainly linked to the formation of RHS [24,116]. However, as halide ions can also scavenge reactive intermediates, it is possible that the photolysis of organic compounds is inhibited in the presence of Cl$^-$ and Br$^-$ [24]. Grebel et al. [81] reported that the E2 photolysis rate was reduced by 90% when increasing the halide concentration to seawater levels; approximately 70% of this decrease was attributed to an ionic strength effect and the remaining 30% to halide-specific effects. Aside from the decline in photodegradation rates for contaminants, the photo-aging process of polypropylene microplastics also slowed down due to the quenching effect of Cl$^-$ on $O_2^{\bullet-}$ [161]. In conclusion, halogen ions have dual effects on the transformation of organic pollutants in the aqueous environment.

5.2. Toxicology

DOM has been shown to affect the light conversion of many pollutants, and these changes would be further reflected in their toxicities. Sun et al. [58] demonstrated that under solar irradiation, FA (5 mg C/L) could induce the generation of ^{3}FA* and $^\bullet$OH that promote the degradation of microcystin-LR and convert it into less toxic products. You et al. [184] studied the toxicity of two antibiotics (roxithromycin and gatifloxacin) to the cyanobacterium *Synechocystis* sp., finding toxicity mitigation after 96 h of exposure (14:10 h light:dark cycle) in the presence of 10 mg/L HA. Besides, $^1O_2$ is known to be critical for the mercury (Hg) cycle in the environment, which could be affected by DOM that decreases the bioavailability of MeHg through generated $^1O_2$ [185,186]. Li et al. [187] also explored the acute toxicity of MeHg to embryonic zebrafish and proved that in the presence of both natural-DOM (Mississippi River, Yukon River, and Suwannee River NOM) and model-DOM (thiosalicylic acid, L-glutathione, dextran, alginic acid, and humic acid), the malformation rates induced by MeHg could be reduced to different extents.

On the other hand, contaminant toxicity can also increase, especially if RHS is involved. Thus, sunlight irradiation of DOM-containing seawater significantly increased the acute toxicity of BDE-209 on *Vibrio fischeri* compared to freshwater [174]. RHS can induce the formation of halogenated intermediates, which are generally more poisonous and persistent than their parent molecules [188] and can also react with the unsaturated bonds of DOM to produce halogen derivatives, which are more toxic than non-halogenated DOM [41,160,189]. Fan et al. [125] also reported that in simulated seawater, five out of six detected naphthalene intermediates showed higher acute toxicities, and all six intermediates exhibited higher developmental toxicities than the parent

compound. Furthermore, previous studies have reported that ^{3}DOM*-induced degradation reactions could also yield more toxic compounds. For example, triclosan could be transformed into 2,8-dichlorodibenzodioxin, and the highest yield was obtained in the presence of ^{3}DOM* [190].

In summary, the presence of DOM can promote the degradation of contaminants, sometimes resulting in the formation of less toxic byproducts. On the other hand, the presence of RHS and some ^{3}DOM*-induced dimerization reactions may lead to the formation of more toxic and persistent intermediates, thus increasing the toxicity of the irradiated mixtures. Therefore, the effects of DOM on the toxicity evolution of different pollutants under irradiation should be comprehensively considered with the change of reaction conditions and on a case-by-case basis until a general interpretation framework is developed.

6. Summary and future perspectives

This paper reviews the photogeneration of RS by DOM in different water bodies, highlighting its potential environmental significance. The factors influencing the photoformation of RS are also systematically summarized. Both DOM sources and environmental factors (e.g., pH value, ionic strength, and some specific ions) have significant impacts on the types and concentrations of RS generated from DOM. In particular, the free radicals and reactions under the influence of ionic strength are addressed as high salinity is common in seawater. In addition, due to the variations of DOM structure and RS yield induced by ionic strength, the photodegradation rates and product toxicities of some co-existing pollutants may also change under different salinities. In summary, this study lists the photochemical properties of DOM in natural water and summarizes the effects of various environmental factors on DOM photochemical behavior, which provides a reference for further exploring the ecological impact of DOM, e.g., the carbon cycle, drinking water safety, and the environmental transformation processes of various pollutants.

Nevertheless, the current research is still insufficient. Based on our analysis of existing work in the field, we recommend that future research on DOM photochemistry should follow the following guidelines:

(1) Effects of minor halides as well as mixed-halogen reactions. It has been demonstrated that although Br$^-$ concentration in natural seawater is much lower than Cl$^-$ concentration, the scavenging effect of Br$^-$ on ROS is even stronger than that of Cl$^-$ [77,191]. For instance, Br$^-$ is the main $^\bullet$OH scavenger in seawater and many brackish waters, while Cl$^-$ has negligible ability to consume $^\bullet$OH at seawater pH (Cl$^-$ is only able to scavenge $^\bullet$OH in acidic solution) [101]. In addition, despite the very low concentration of I$^-$, it might have a significant impact on the photochemical reactions induced by DOM [113,118]. Therefore, the effect of minor halides (i.e., Br$^-$ and I$^-$) on the phototransformation of DOM should raise more research attention, also because $Br_2^{\bullet-}$ is a much better halogenating agent than $Cl_2^{\bullet-}$ [121,122]. Furthermore, since natural water contains mixed halogens [77,192], future studies should focus more on the competitive

effect of different halides, and more sophisticated models should be developed to describe the complicated photochemical reactions occurring in saline water.

(2) In-depth investigation of ionic strength effects. When evaluating the halide-specific effect, the addition of halogen ions increases the ionic strength as well, which could possibly influence both radical [193] and non-radical [117] photochemical processes. However, effects arising from increased ionic strength are still insufficiently explored, especially regarding impacts on DOM morphology and structure. Therefore, it is necessary to conduct more comprehensive investigations into the effect of ionic strength on DOM morphology and aggregation and to further explore the consequent influence on DOM photochemical behavior in saline waters.

(3) A more comprehensive exploration of photogenerated organic radicals, such as phenoxyl, semiquinone, and organic peroxyl radicals, is also important [11,22,44,151]. Due to their relatively long lifetimes, organic radicals are generally more stable in the environment, which makes them more likely to interact with pollutants [44]. However, research concerning the generation mechanism and the environmental significance of organic radicals remains limited. Therefore, further studies focusing on the generation and reactivity of various organic radicals are needed to deepen our understanding of DOM photochemistry as well as the migration and transformation of contaminants in aquatic environments.

(4) Further exploration of degradation products and the corresponding environmental risk assessments. Considering the knowledge gaps concerning the degradation pathways of typical contaminants in saline waters, there is an urgent need for more thorough investigations into the degradation products formed in the presence of halogenides and their toxicity. In the meantime, to better understand the corresponding environmental risk, one should carry out an integrated risk assessment by considering factors such as DOM morphology, specific halogen ions, and ionic strength effects. This would enhance our understanding of the environmental behavior and impact of organic pollutants in natural waters, thereby providing scientific evidence that helps environmental management and protection.

(5) Exploration of the structural and photochemical property changes of DOM in natural water bodies, especially in estuarine areas. Indirect photodegradation of pollutants by DOM in freshwater and seawater has been well studied, and some studies have reported that salinity and halogen ions could influence the intermediates of irradiated DOM [174, 194]. However, how salinity and halogen ions can affect the transformation and mineralization processes of DOM is not clear, but it could be of great importance for understanding carbon sequestration and the global carbon budget. In estuarine regions, due to changes in salinity, the DOM structure may be modified when going from freshwater to seawater, and the subsequent photo-induced transformation of DOM may significantly differ in the transition. Although the relevant knowledge is still deficient, the development of computational chemistry (e.g., molecular dynamics) can help us reveal the morphology changes of DOM [195]. Moreover, more extensive use of modern analytical techniques, e.g., Fourier-transform ion cyclotron resonance mass spectrometry and radioisotope tracer technique, can provide more potential to characterize the structural transformation of DOM [196,197]. We suggest that future studies focus more in-depth on the changes in DOM three-dimensional structure, which is important to develop a DOM transformation model, to understand the DOM/contaminant interaction, and to reveal the mechanisms underlying DOM morphology changes in fresh to saline transition environments.

CRediT authorship contribution statement

Yichen Xu: Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Yutong Zhang:** Visualization, Investigation, Conceptualization. **Longlong Qiu:** Visualization, Investigation, Conceptualization. **Ming Zhang:** Investigation, Conceptualization.

Jiaojiao Yang: Writing – review & editing, Funding acquisition. **Rong Ji:** Writing – review & editing. **Davide Vione:** Writing – review & editing, Conceptualization. **Zhanghao Chen:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization. **Cheng Gu:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interests

The authors have declared no conflicts of interest.

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