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Mechanisms of photochemical release of dissolved organic matter and iron from resuspended sediments

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ABSTRACT

Photochemical reactions can alter the transformation of sedimentary organic matter into dissolved organic matter (DOM) and affect its ultimate fate in water ecosystems. In the present study, the photorelease of DOM and Fe from resuspended lake sediments was investigated under different O₂ and NO₃⁻ concentration conditions to study the mechanisms of DOM and Fe photorelease. The amount of photoreleased Fe, which ranged from 0.22 to 0.70 μmol/L, was significantly linearly correlated with the amount of photoreleased DOM. O₂ and NO₃⁻ could promote the photochemical release of DOM and Fe, especially during the initial 4 h irradiation. In general, the order of the photorelease rates of DOM and Fe under different conditions was as follows: NO₃⁻/aerobic > aerobic ≈ NO₃⁻/anaerobic > anaerobic. The photorelease rates of DOM and Fe were higher for the initial 4 hr irradiation than these for the subsequent 8 hr irradiation. The photorelease of DOM and Fe is thought to proceed via direct photodissolution and indirect processes. The relative contributions of indirect processes (>60%) was much greater than that of direct photodissolution (<40%). The photoproducted H₂O₂ under aerobic and anaerobic conditions indicated that hydroxyl radicals (•OH) are involved in the photorelease of DOM. Using •OH scavengers, it was found that 38.7%, 53.7%, and 77.6% of photoreleased DOM was attributed to •OH under anaerobic, aerobic, and NO₃⁻/aerobic conditions, respectively. Our findings provide insights for understanding the mechanisms and the important role of •OH in the DOM and Fe photorelease from resuspended sediments.

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Introduction

Sediments operate as sinks and sources for natural organic carbon (OC) and anthropogenic contaminants in aquatic

ecosystems through the settling and release of large amounts of organic matter (He et al., 2016; Xu et al., 2016). Photo-induced dynamic exchanges (e.g., degradation, aggregation, and dissolution), which occur in the photic zone of the water column, play an important role in the transport and transformation of organic matter (Helms et al., 2013; Lee et al., 2019; Li et al., 2020). Recent studies have indicated that the photochemical release of dissolved organic matter (DOM) from re-

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suspended sediments is a potential source of dissolved organic carbon (DOC) in shallow water ecosystems (Hu et al., 2016; Liu and Shank, 2015). However, the mechanisms of DOM release from resuspended sediments upon sunlight irradiation are still not fully understood. Kieber et al. (2006) referred to the photorelease of DOM from irradiated resuspended sediments as photoproduction, Riggsbee et al. (2008) considered the mechanism to be photoassisted desorption, while others considered it to be photodissolution or solar-enhanced dissolution (Liu and Shank, 2015; Mayer et al., 2006; Shank et al., 2011). Moreover, our previous studies demonstrated the subsequent photodegradation of the photoreleased DOM (Hu et al., 2020; Hu et al., 2017). We also found that NO_3^- , ferric ions, and nano- TiO_2 can facilitate the photorelease of DOM through photoproduced hydroxyl radical ($\bullet\text{OH}$). Mayer et al. (2009a) and Estapa and Mayer (2010) found that dissolved oxygen can enhance the photodissolution of DOM with the production of peroxides. Appiani and McNeill (2015) reported the photoproduction of singlet oxygen from sediments and the sorbed molecules would be expected to undergo enhanced photodegradation. Guo et al. (2020) suggested that reactive oxygen free radicals are the driving force of photo-induced dissolved phosphate release. It is clear that photoproduced reactive oxygen species (ROS) play a critical role in the photorelease of DOM, however, the contribution of ROS oxidation to DOM photorelease remains unclear.

The photochemical reactions in aquatic systems can not only alter the quantity and quality of organic matter in sediments, but also affect the biogeochemical cycling of nutrients, trace metals, and other contaminants. Resuspended sediments can release dissolved nitrogen and phosphorus under sunlight irradiation (Hu et al., 2016; Li et al., 2017; Southwell et al., 2009), and these released nutrients could be utilized by bacteria or algae (Guo et al., 2020; Schiebel et al., 2014). The photochemical transformations can increase the bioavailability of photoreleased DOC and nitrogen (Mayer et al., 2011). Kieber et al. (2017) and Brooks Avery et al. (2017) reported the photochemical release of algal toxins from resuspended sediments. Skrabal et al. (2018) reported the photoproduction of dissolved Cu from suspensions of marine sediments. They also found that the photoreleased Cu was likely associated with organic matter and/or Fe oxyhydroxides, both of which are photoreactive. Meanwhile, the biogeochemical cycles of Fe and OC are strongly interlinked. The photochemical liberation of organically bound Fe by solar radiation is a significant natural source of ionic Fe for water and subsequent Fe oxyhydroxides for sediments (Kopacek et al., 2005; Kopacek et al., 2006). Variable, yet nonnegligible, amounts of OC were absorbed or complexed to dithionite-reducible Fe in sediments globally. Lalonde et al. (2012) suggested that 21.5% of the OC in sediments is directly bound to reactive Fe phases. Moreover, Estapa et al. (2012a) suggested that the DOC photoproduction rates are correlated well with sediment reducible Fe. Therefore, we assumed that DOM may be released from resuspended sediments during the photoreductive dissolution of Fe.

The main objectives of this study were to determine (1) whether Fe associated with resuspended sediments can be

released to the dissolved state after exposure to sunlight, (2) the mechanisms of photorelease of DOC and Fe from sediments, and (3) the role of ROS in DOC photorelease from resuspended sediments. For these purposes, surface sediments collected from shallow lakes were irradiated under various experimental conditions. Our results can help to improve the understanding of the photochemical release of DOM from resuspended sediments as well as the important role of ROS in the DOM photorelease.

1. Materials and methods

1.1. Materials

Surface sediments were collected from two large and shallow lakes, Taihu Lake and Hongze Lake, and stored at -80°C until further processing. Sediment resuspension frequently and continually occurred in these two lakes owing to natural or anthropogenic forces, thereby providing more opportunities for progressive and cumulative photochemical processes in sediments. The sampling sites in the two lakes and the particulate organic carbon (POC) content of the sediments are listed in Appendix A Table S1. Prior to the simulated irradiation experiments, the sediment samples were freeze-dried and then sieved through a 200-mesh sieve (about $75\ \mu\text{m}$ pore size) to exclude coarse sediment (Shank et al., 2011; Southwell et al., 2009).

1.2. Simulated irradiation experiments

Simulated irradiation experiments were conducted in an annular photoreactor, which uses a 500 W Xe lamp to provide an accurate simulation of the solar spectrum. The lamp was placed in the center of a cold hydro pump that circulated cooling water, and the temperature of the photo-reactor was maintained at $25\pm 1^\circ\text{C}$. The 100 mL suspension was placed into quartz sample tubes with magnetic stirrers to simulate sediment resuspension. The light intensity on the surface of quartz tube was measured with a miniature fiber optic spectrometer (FLA 4000A+, Flight, China). The light intensity was approximately $21\ \text{mW}/\text{cm}^2$, which was almost the same as that on the lake surface water on a midsummer day (Appendix A Fig. S1).

Two experiments were conducted to test the effects of oxygen on the photochemical release of DOC and Fe from resuspended sediments. In the first, two quartz tubes with 500 mg/L sediment suspensions were created; one was in contact with the air, which was considered as the aerobic condition. The other was bubbled with 0.08 L/min of N_2 for 30 min and then sealed with parafilm, which was defined as the anaerobic condition. Moreover, Milli-Q water used under anaerobic conditions was also bubbled with N_2 at 0.08 L/min for 30 min to remove the oxygen in pure water. The second experiment was conducted to determine the role of NO_3^- on the photochemical release of DOC and Fe. The NO_3^- concentration was set at $50\ \mu\text{mol}/\text{L}$ under both aerobic and anaerobic conditions based on our previous study (Hu et al., 2020). Sediment suspensions were irradiated for 0, 1, 2, 3, 4, 6, 8, 10, and 12 hr in these two ex-

periments. To determine the photochemical release of Fe from resuspended sediments, 500 mg/L sediment suspensions collected from Taihu Lake and Hongze Lake (Appendix A Table S1) were incubated under simulated solar irradiation for 8 hr. To determine the effect of $\bullet\text{OH}$ on the photochemical release of DOC, tert-butyl alcohol (TBA) was added to trap $\bullet\text{OH}$. 500 mg/L Hongze Lake sediment suspensions with and without this treatment were then subjected to irradiation and samples were collected after 0, 2, 4, 8, and 12 hr of irradiation. All the irradiated sediment suspensions were filtered through a 0.22 μm polyethersulfone membrane and stored in brown bottles at 4 °C for subsequent measurements.

The design for the irradiation experiments is shown in Appendix A Fig. S2. Dark control experiments were conducted for the irradiation experiments. Quartz tubes containing samples were wrapped with layers of aluminum foil, and then suspended and sampled for the same irradiation time in darkness. In our study, the amount of photoreleased DOC and Fe were calculated from the difference between the irradiation experiments and the dark control.

1.3. Measurement of Fe and DOC

The total Fe concentration in the filtered samples from the irradiation experiments was measured using inductively coupled plasma mass spectrometry. These samples were acidified to pH 2 with analytical reagent HNO_3 before measurement. The DOC concentration was measured using the high-temperature catalytic combustion method with an Elementar Liqui-TOC analyzer. The organic matter content of sediment was determined using the loss on ignition method (LOI) at 450 °C for 3 hr, and the POC values were calculated by dividing the organic matter content obtained from LOI by the conversion factor of 1.7 as described by Kieber et al. (2006) and Hu et al. (2016).

Our experiments were designed with high initial POC and Fe content; therefore, the photochemical reactions under constant irradiance were described using apparent zero-order kinetics (Estapa et al., 2012b). The apparent zero-order rate constants of DOC and Fe were determined from the slope of the regression of the DOC and Fe concentrations over time.

1.4. Determination of H_2O_2

The H_2O_2 concentration was measured using a fluorescent H_2O_2 assay kit (Sigma-Aldrich, MAK165). A 3% H_2O_2 solution (0.88 mol/L) was used as the standard sample. 50 μL samples and standards were mixed with 50 μL of fluorescent chromogenic reagents, including red peroxidase substrate, horseradish peroxidase, and assay buffer. The mixed solutions were incubated in the dark at room temperature for 30 min. The fluorescence intensity of these mixed solutions was measured at an excitation wavelength with 540 nm and emission wavelength with 590 nm within 2 hr. H_2O_2 was measured with unfiltered water samples to reduce the negative impact of filtration (Mayer et al., 2009b). The trace suspended sediments could settle during the long incubation time, which could decrease the impact of suspended particles on the fluorescence measurements (Estapa and Mayer, 2010).

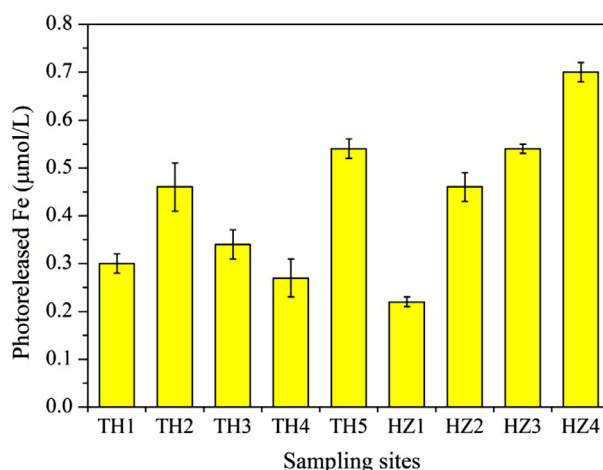


Fig. 1 – Photoreleased Fe contents from resuspended sediments in Taihu Lake and Hongze Lake.

2. Results

2.1. Photochemical release of Fe from resuspended sediments

The photochemical release of Fe from resuspended lake sediments after 8 hr of irradiation is shown in Fig. 1. Our results indicated that sunlight irradiation could promote the release of Fe from resuspended sediments, and the photoreleased Fe content ranged from 0.22 to 0.70 $\mu\text{mol/L}$. The highest photoreleased Fe contents were 0.54 and 0.70 $\mu\text{mol/L}$ for the Taihu Lake and Hongze Lake sediments, respectively, which were similar to those of photoreleased DOC (Appendix A Fig. S3a). The photoreleased DOC contents, ranging from 57.50 to 268.75 $\mu\text{mol/L}$, were significantly linearly correlated with those of the photoreleased Fe ($p < 0.05$; Appendix A Fig. S3b). This suggests that the photochemical release of Fe is closely related to the photochemical release of DOM from resuspended sediments.

The changes in the photoreleased Fe content along with the irradiation of Hongze Lake sediment under different NO_3^- and O_2 conditions are shown in Fig. 2. The photoreleased Fe content rapidly increased to 0.60 $\mu\text{mol/L}$ under aerobic conditions, and increased to approximately 0.31 $\mu\text{mol/L}$ under anaerobic conditions. There was no significant difference in the photoreleased Fe content between the aerobic and anaerobic treatment (t-test; $p = 0.22$). However, the amount of photoreleased Fe under aerobic conditions were significantly higher than that under anaerobic conditions during the last 8 h of irradiation (t-test; $p < 0.05$). This indicates that oxygen plays an important role in the photochemical release of Fe from resuspended sediments.

With the addition of 50 $\mu\text{mol/L}$ of NO_3^- , the amount of photoreleased Fe rapidly increased to 0.60 $\mu\text{mol/L}$ under anaerobic conditions. Under NO_3^- /aerobic conditions, the photoreleased Fe increased to 0.63 $\mu\text{mol/L}$ during the first 8 hr of irradiation, and then gradually increased to 0.68 $\mu\text{mol/L}$. The amount of photoreleased Fe was significantly higher with NO_3^- addition than that without NO_3^- addition under both

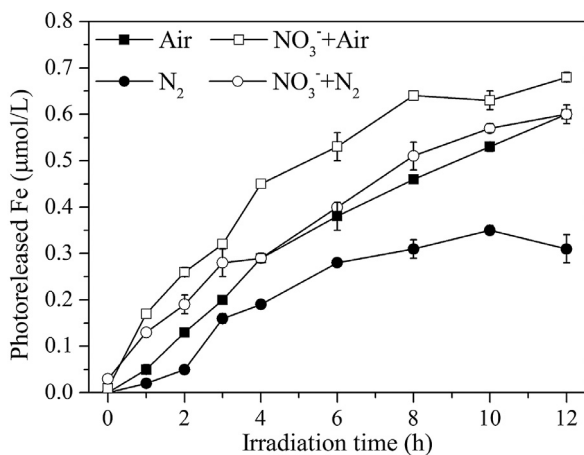


Fig. 2 – Changes in photoreleased Fe content during the 12 hr irradiation of resuspended sediment under different NO_3^- and O_2 conditions.

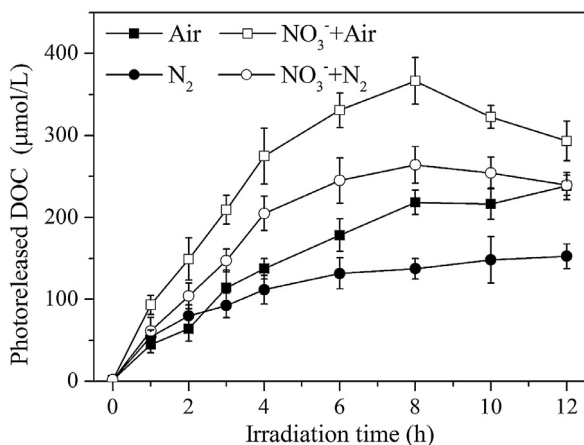


Fig. 3 – Changes in the photoreleased DOC content along with the irradiation of resuspended sediment under different NO_3^- and O_2 conditions.

aerobic and anaerobic conditions (t -test; $p < 0.05$). These results suggest that NO_3^- could also promote the photochemical release of Fe from resuspended sediments.

2.2. Photochemical release of DOC from resuspended sediments

The photoreleased DOC content rapidly increased to 137.5 $\mu\text{mol/L}$ after 4 hr of irradiation under aerobic conditions, and then increased to 238.3 $\mu\text{mol/L}$ during the following 8 h of irradiation (Fig. 3). Under anaerobic conditions, the photoreleased DOC content increased to 111.7 $\mu\text{mol/L}$ during the first 4 hr of irradiation, and then gradually increased to 152.5 $\mu\text{mol/L}$. There was no significant difference in the photoreleased DOC content between the aerobic and anaerobic treatments during the first 4 hr of irradiation (t -test; $p = 0.89$). However, the photoreleased DOC content under anaerobic conditions was significantly lower than that under aerobic conditions (t -test; $p < 0.005$). These results indicate that oxygen plays an impor-

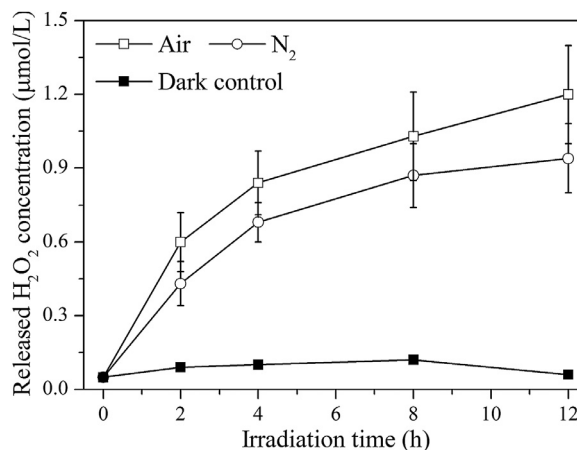


Fig. 4 – Changes in the H_2O_2 concentration under aerobic and anaerobic conditions.

tant role in the photochemical release of DOM from resuspended sediments.

With the addition of 50 $\mu\text{mol/L}$ NO_3^- , the photoreleased DOC increased to 205.0 $\mu\text{mol/L}$ after 4 hr of irradiation, and then increased to about 250.0 $\mu\text{mol/L}$ under anaerobic conditions. Under aerobic conditions, the photoreleased DOC increased sharply to 366.7 $\mu\text{mol/L}$ after 8 hr of irradiation, and then decreased to 293.3 $\mu\text{mol/L}$ during the subsequent 4 hr irradiation. Meanwhile, the photoreleased DOC were higher with NO_3^- addition than those without NO_3^- addition under both aerobic and anaerobic conditions (t -test; $p < 0.05$). These results suggested that NO_3^- could also promote the photochemical release of DOM from resuspended sediments, which was similar to the photorelease of Fe.

After the initial 4 hr irradiation, the photoreleased DOC and Fe increased almost linearly over time. Based on these results and previous studies (Estapa et al., 2012b; Hu et al., 2020; Hu et al., 2016), we assumed that few DOC was photodegraded during the first 4 hr irradiation. The photorelease rates of DOC and Fe were calculated under different O_2 and NO_3^- conditions (Table 1). The rates of DOC and Fe photorelease ranged from 25.83 to 70.63 $\mu\text{mol}/(\text{L}\cdot\text{hr})$ and from 0.045 to 0.115 $\mu\text{mol}/(\text{L}\cdot\text{hr})$, respectively.

2.3. Photochemical release of H_2O_2 from resuspended sediments

The changes in the H_2O_2 concentration during the 12 h irradiation of resuspended sediment are shown in Fig. 4. No obvious change in the H_2O_2 concentration was observed under the dark control. The H_2O_2 concentration sharply increased to 0.84 $\mu\text{mol/L}$ in the first 4 hr irradiation, and then gradually increased to 1.20 $\mu\text{mol/L}$ in the last 8 hr irradiation under aerobic condition. The significant difference between irradiation and the dark control indicated that sunlight irradiation could promote the release of H_2O_2 from resuspended sediments. Meanwhile, the photoreleased H_2O_2 under anaerobic conditions was significantly lower than that under aerobic conditions (t -test; $p < 0.05$), indicating the important role of oxygen.

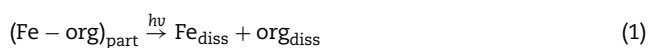
Table 1 – The photorelease rates (R^2) of DOC and Fe during the initial 4 hr irradiation under different O_2 and NO_3^- conditions.

Photorelease rate($\mu\text{mol}/(\text{L}\cdot\text{hr})$)	Aerobic	Anaerobic	NO_3^- /aerobic	NO_3^- /anaerobic	10 mmol/LTBA
DOC	34.17 (0.98)	25.83 (0.90)	70.63 (0.99)	51.08 (0.99)	15.83 (0.99)
Fe	0.070 (0.99)	0.045 (0.94)	0.115 (0.98)	0.067 (0.94)	/

3. Discussion

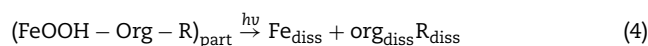
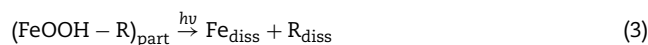
3.1. Photorelease of Fe from resuspended sediments

Our results suggested that sunlight irradiation could promote the release of DOM from suspended lake sediments, which is consistent with previous studies demonstrating the photochemical release of DOM from various suspended particles, including sediments, soil, algal detritus, and litter leaves (Helms et al., 2014; Mayer et al., 2012; Pisani et al., 2011). Lalonde et al. (2012) determined that 21.5% of the total organic carbon is directly associated with Fe, especially in surface sediments. Estapa et al. (2012b) suggested that the content of reducible Fe oxides and organic-bound Fe in sediments is positively correlated with the photorelease of DOC during the first hour of irradiation. In this study, the photoreleased Fe was significantly correlated with the photoreleased DOC (Appendix A Fig. S3). For Fe associated with organic matter, a possible mechanism for Fe and DOC photorelease may be involved in either an inorganic form (Reaction (1)) or as an organic complex (Reaction (2)).



Previous studies have reported that the organically bound Fe can be rapidly photochemically liberated to inorganic species (Kopacek et al., 2006; Porcal et al., 2010; Porcal et al., 2009). It is likely that Reaction (1) is the dominant mechanism, whereby Fe is photoreleased as an inorganic form or is rapidly converted to one after being released as an organic complex. However, Estapa and Mayer (2010) observed no significant differences between total dissolved Fe in the filtrate of the 24 hr irradiated and non-irradiated suspensions. They found a 0.4 $\mu\text{mol}/\text{L}$ increase of total Fe in the 0.7–8.0 μm fraction of irradiated sediment suspensions. Previous studies have observed the reoxidation and precipitation of photoreduced Fe during the photodegradation of dissolved organic-metal complexes (Porcal et al., 2020; Porcal et al., 2017). Porcal et al. (2017) reported that the concentration of particulate Fe increased by up to 3.0 $\mu\text{mol}/\text{L}$ after 24 h irradiation of filtered water samples. Helms et al. (2013) found that the net Fe particle formation occurred between 10 days and 20 days of irradiation, while no particulate Fe was detected during the first 10 days. From these findings, we inferred that Fe could be photoreleased during the primary irradiation of sediments, but this photoreleased Fe could precipitate as particulate forms over longer timescales. The dynamic transformation process of Fe during the photodissolution of resuspended sediments appears to be complex, which requires further study and investigation.

It has been reported that Fe oxyhydroxides and Fe-organic complexes are generally associated with phosphorus, heavy metals, and other materials (Froelich et al., 1982). Previous studies have also demonstrated that the photoreduction of Fe oxyhydroxides and photodecomposition of Fe-organic complexes (Oleinikova et al., 2019; Waite, 2005). Skrabal et al. (2018) suggested that the photoreduction of the Fe oxyhydroxide can be a potential factor for Cu photorelease from resuspended sediments. Therefore, the photoreduction of the Fe oxyhydroxide could be a potential mechanism for the photorelease of Fe, nutrients, heavy metals, and other pollutants.



Moreover, Fe can participate in a series of photochemically initiated reactions to produce radical species, including peroxy radicals and $\bullet\text{OH}$ (Guo et al., 2020; Mostofa and Sakugawa, 2016). Our previous study demonstrated that Fe^{3+} (5–20 $\mu\text{mol}/\text{L}$) can promote the photorelease and photodegradation of DOM from resuspended sediments through the production of radical species (Hu et al., 2020). In our study, the photoreleased Fe concentration was about 0.70 $\mu\text{mol}/\text{L}$, which might have had very little impact on the photochemical release of DOM.

3.2. Mechanisms of the photorelease of DOC from resuspended sediments

The photorelease rates of DOC during the initial 4 h irradiation were higher than those after longer irradiation (tens of hours) (Table 1) (Hu et al., 2016; Mayer et al., 2006). Estapa et al. (2012a) reported that the 1 hr photorelease rates ranged from 12.6 to 28.1 $\mu\text{mol}/(\text{L}\cdot\text{hr})$, which were higher than the 4 hr photorelease rates. In our study, a decrease in photoreleased DOC content was observed under NO_3^- /aerobic conditions (Fig. 3). Previous studies reported the decrease in CDOM abundance, fluorescence intensity of humic-like components, and DOC concentration during the irradiation of suspended sediments (Hu et al., 2020; Hu et al., 2017). These results suggested that the photoreleased DOM from sediments can be photodegraded subsequently under sunlight irradiation. The subsequent photodegradation could affect the release rates of DOC, especially over longer timescales. Therefore, the initial 4-hr release rates of DOC and Fe were used for further discussion.

Previous studies have demonstrated that the photodegradation of DOM is thought to proceed via two pathways, namely direct and indirect processes (Doane, 2017; Mostofa et al.,

Table 2 – Contributions of direct photodissolution and indirect processes to the photorelease of DOC and Fe under NO_3^- and aerobic conditions.

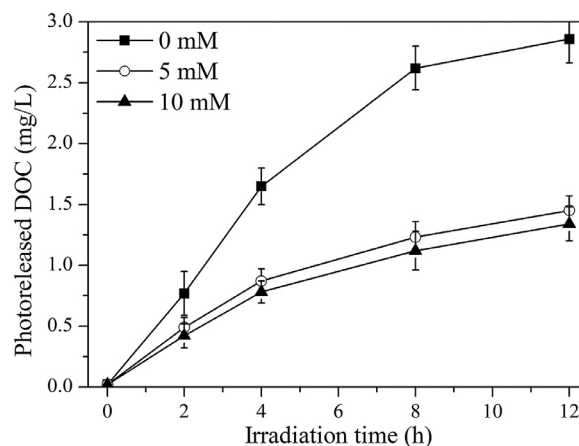
	Direct photodissolution	Indirect processes Role of O_2	Role of NO_3^-
DOC	25.83 (36.6%)	8.34 (11.8%)	36.46 (51.6%)
Fe	0.045 (39.1%)	0.025 (21.8%)	0.045 (39.1%)

2012). Direct process involves energy and electron transfer after light absorption by DOM, while DOM is oxidized by photochemically generated reactive oxygen species (ROS), such as $\bullet\text{OH}$, singlet oxygen, and H_2O_2 . Estapa and Mayer (2010) investigated the photoredox transformations of oxygen, carbon and peroxides that accompany the photodissolution of particulate organic matter (POM) and found that the photoreactions of marine POM include the same redox transformations that have been observed in DOM. In our study, purging nitrogen resulted in a very low concentration of DO in the sediment suspensions. Thus, we assumed that the formation of ROS was minimized and DOC/Fe was photoreleased primarily by direct photodissolution under anaerobic conditions.

It is thought that ROS under aerobic and NO_3^- addition conditions are mainly derived from the role of O_2 and NO_3^- (Hu et al., 2020; Mayer et al., 2009b). The relatively high photorelease rates of DOC and Fe under aerobic or NO_3^- addition conditions compared with those under anaerobic conditions were regarded as the results of indirect processes (Table 1). The increase in photoreleased DOC and Fe under aerobic condition compared with that under anaerobic condition was attributed to the role of O_2 . The increase in photoreleased DOC and Fe under NO_3^- /aerobic condition was regarded as the result of NO_3^- . The contributions of direct photodissolution and indirect processes to the photorelease of DOC and Fe under the NO_3^- +air condition were calculated based on the rate constants, which are listed in Table 2. The relative contributions of indirect processes to the photorelease of DOC and Fe (>60%) were much greater than those of direct photodissolution (<40%), indicating the important role of ROS. The relative contribution of direct photodissolution was similar among the photorelease of DOC (36.6%) and Fe (39.1%).

3.3. Role of hydroxyl radicals on the photorelease of DOM

The $\bullet\text{OH}$ can be produced photolytically from NO_3^- and NO_2^- , Fenton's reaction (Fe^{2+} and H_2O_2), and upon irradiation of DOM (Guo et al., 2020; Niu and Croue, 2019). Similar to Mayer et al. (2009b) and Estapa and Mayer (2010), a significant production of H_2O_2 was observed during the irradiation of suspended sediment under both aerobic and anaerobic conditions (Fig. 4). In addition, excited state transients and singlet oxygen have been observed upon irradiation of POM (Appiani and McNeill, 2015; Cottrell et al., 2013). Li et al. (2017) reported that $\bullet\text{OH}$ concentration in sediment suspensions was $0.33 \times 10^{-16} \pm 0.07 \times 10^{-16}$ mol/L, and $\bullet\text{OH}$ was directly correlated to the photorelease of phosphorus from sediments. These results indicated that ROS play an important role in the photorelease of DOC and Fe from resus-

**Fig. 5 – Changes in photoreleased DOC under different TBA concentrations.**

pended sediments (Table 2). Therefore, we attempted to use scavengers to probe the formation of ROS and understand its contribution to the photorelease of DOC from resuspended sediments. TBA is effective for specifically quenching $\bullet\text{OH}$ (Du et al., 2014), thus 5 and 10 mmol/L TBA were added to the irradiated sediment suspensions under aerobic conditions.

With the addition of 10 mmol/L TBA, the photoreleased DOC increased to $65.00 \mu\text{mol/L}$ in the first 4 hr irradiation and then gradually increased to $111.67 \mu\text{mol/L}$ after the subsequent 8 hr irradiation (Fig. 5). There was a significant difference in the photoreleased DOC between 5 and 10 mmol/L TBA (*t*-test; $p > 0.05$). By comparing the release rates, it could be observed that the photorelease of DOC was significantly decreased by the addition of TBA (Table 1). Although TBA was only added under aerobic conditions, we assumed that the high concentration of TBA (10 mmol/L) could also quench the photoproduced $\bullet\text{OH}$ under anaerobic and NO_3^- /aerobic conditions. Therefore, the reduced photorelease rate constant indicated that 53.7% and 77.6% of the photoreleased DOC was attributed to $\bullet\text{OH}$ under aerobic and NO_3^- addition conditions, respectively. Almost 38.7% of the photoreleased DOC decreased with the addition of TBA under anaerobic conditions. Previous studies reported that natural organic matter was found to be an efficient photosensitizer for $\bullet\text{OH}$ production (Niu and Croue, 2019; Xu et al., 2020). Appiani and McNeill (2015) demonstrated the photochemical production of singlet oxygen from particulate organic matter. Cottrell et al. (2013) indicated that particulate organic matter is a potential source of triplet excited-state of POM ($^3\text{POM}^*$). In our study, H_2O_2 production during the irradiation of suspended sediments under anaerobic conditions were observed. These results suggested that $\bullet\text{OH}$ may be photoproduced during the photosensitization of POM, and then plays an important role in the direct photorelease of DOM from resuspended sediments.

4. Conclusion

In the present study, the photorelease of Fe from resuspended sediments was observed along with the photorelease of DOC

upon irradiation. These photoreleased Fe, which ranged from 0.22 to 0.70 $\mu\text{mol/L}$, was significantly linearly correlated with the photoreleased DOC. The initial 4 hr photorelease rates of DOC and Fe under different O_2 and NO_3^- conditions ranged from 25.83 to 70.63 $\mu\text{mol}/(\text{L}\cdot\text{hr})$ and 0.045 to 0.115 $\mu\text{mol}/(\text{L}\cdot\text{hr})$, respectively. O_2 and NO_3^- could accelerate the photorelease of DOC and Fe, especially during the initial 4 hr of irradiation. Our results suggested that the photorelease of DOC and Fe from resuspended sediments proceeds via direct photodissolution and ROS-dominated indirect processes. Based on the photorelease rate constants, the relative contributions of indirect processes to the photorelease of DOC and Fe (>60%) was much greater than that of direct photodissolution (<40%). The results of $\bullet\text{OH}$ trapping analyses showed that $\bullet\text{OH}$ play an important role of in the photorelease of DOM. Together, these results benefit our understanding of the photorelease of DOM and Fe from resuspended sediments. Continued investigation is necessary to better understand the subsequent photodegradation of photoreleased DOM and to fully understand the fate and transport of POM in shallow ecosystems.

Acknowledgments

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