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Increasing sulfate concentration and sedimentary decaying cyanobacteria co-affect organic carbon mineralization in eutrophic lake sediments

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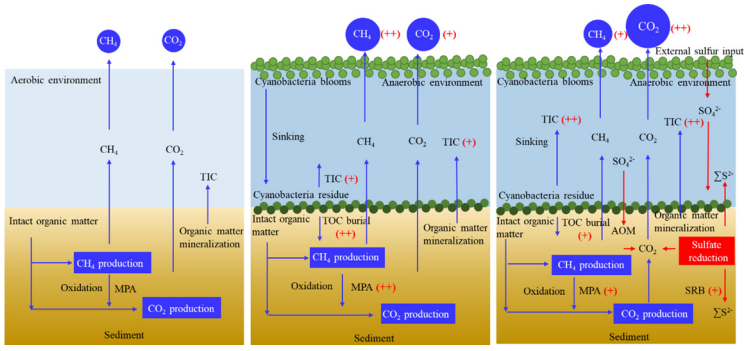
HIGHLIGHTS

- Cyanobacteria decomposition released a large amount of TIC from lake sediments.
- Cyanobacteria decomposition promoted the sulfate reduction reaction in sediments.
- The sulfate reduction enhanced organic carbon mineralization in sediments.
- Increasing sulfate concentration promoted CO_2 emission but inhibited CH_4 emission.
- Sulfate and cyanobacteria co-affected OC mineralization via MPA and SRB competition.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfate (SO_4^{2-}) concentrations in eutrophic lakes are continuously increasing; however, the effect of increasing SO_4^{2-} concentrations on organic carbon mineralization, especially the greenhouse gas emissions of sediments, remains unclear. Here, we constructed a series of microcosms with initial SO_4^{2-} concentrations of 0, 30, 60, 90, 120, 150, and 180 mg/L to study the effects of increased SO_4^{2-} concentrations, coupled with cyanobacterial blooms, on organic carbon mineralization in Lake Taihu. Cyanobacterial blooms promoted sulfate reduction and released a large amount of inorganic carbon. The SO_4^{2-} concentrations in cyanobacteria treatments significantly decreased and eventually reached close to 0. As the initial SO_4^{2-} concentration increased, the sulfate reduction rates significantly increased, with maximum values of 9.39, 9.44, 28.02, 30.89, 39.68, and 54.28 mg/L·d for 30, 60, 90, 120, 150, and 180 mg/L SO_4^{2-}, respectively. The total organic carbon content in sediments (51.16–52.70 g/kg) decreased with the initial SO_4^{2-} concentration ($R^2 = 0.97$), and the total inorganic carbon content in overlying water (159.97–182.73 mg/L) showed the opposite pattern ($R^2 = 0.91$). The initial SO_4^{2-} concentration was positively correlated with carbon dioxide (CO_2) emissions ($R^2 = 0.68$) and negatively correlated with methane (CH_4) emissions ($R^2 = 0.96$). The highest CO_2 concentration and lowest CH_4 concentration in the 180 mg/L SO_4^{2-} treatment were 1688.78 and 1903 μmol/L, respectively. These biogeochemical processes were related to competition for organic carbon sources between sulfate reduction bacteria (SRB) and methane production archaea (MPA) in sediments. The abundance of SRB was positively

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correlated with the initial SO_4^{2-} concentration and ranged from 6.65×10^7 to 2.98×10^8 copies/g; the abundance of MPA showed the opposite pattern and ranged from 1.99×10^8 to 3.35×10^8copies/g. These findings enhance our understanding of the effect of increasing SO_4^{2-} concentrations on organic carbon mineralization and could enhance the accuracy of assessments of greenhouse gas emissions in eutrophic lakes.

1. Introduction

Lakes connect several layers of in the earth's surface system and have an important impact on the circulation of carbon and other substances on the regional and global scale, among which, lake sediments are an important site of carbon storage (Mendonca et al., 2017; Davidson et al., 2018; Wang et al., 2018). Although the total area of global lakes is only 1.38% of the total area of ocean, the annual organic carbon fixed by sediments is equivalent to 50% of that fixed by the ocean (Tranvik et al., 2009). In recent years, frequent cyanobacterial blooms in eutrophic lakes have increased in shifts in sediment sources and sinks (Yan et al., 2017).

There is a general consensus that a bidirectional positive feedback occurs between global warming and cyanobacterial blooms (Mehnert et al., 2010; O'Reilly et al., 2015; Yan et al., 2017). Compared with the ocean and land ($0.012°Cyr^{-1}$ and $0.025°Cyr^{-1}$), lakes warm faster ($0.034°Cyr^{-1}$) (Gudasz et al., 2010). Rising temperatures enhance the growth rate of cyanobacteria by increasing the stability of the water column and lengthening the duration of thermal stratification, which is favorable for buoyant cyanobacteria. This, along with the increasing nutrient levels, might result in the frequent cyanobacterial blooms (Davis et al., 2009; Mehnert et al., 2010). Cyanobacterial blooms have damaged the ecological balance of lakes, and the carbon imbalance of the sedimentary carbon pool has become a major focus of current research (Yan et al., 2017; Davidson et al., 2018). The large input of cyanobacteria after their decay not only increases emissions of greenhouse gases such as CO_2 and CH_4, but also releases large amount biogenic organic matter to lake sediments, which affects organic carbon mineralization in eutrophic lakes (Yan et al., 2017; Tong et al., 2021). Recently, the easily biodegradable cyanobacteria-derived organic matter has been reported to have a co-metabolic effect that promotes the decomposition of intact sedimentary organic matter and the production of CO_2 and CH_4, thus facilitating the transformation of lake sediments from a carbon sink to a carbon source (Ma et al., 2020). The effect of cyanobacteria on the mineralization process of lake sediments is also reflected by the change in the physicochemical environments of overlying water (B. Li et al., 2021; J. Li et al., 2021; Wang et al., 2021). The growth and decay of cyanobacteria not only consumes a large amount of dissolved oxygen (DO) during decomposition processes but also hinders the deoxygenation process of water bodies, which results in an anaerobic state with strong reduction potential and alters the microbial community structure of water bodies (Shen et al., 2013). During cyanobacterial blooms, cyanobacteria residue on the surface sediment forms "Cyanobacterial detritus mat" (Qi et al., 2020). The organic matter produced during the decay of cyanobacteria is an important source of substrate for microorganisms (Xu et al., 2015; Zhu et al., 2021). The mineralization of organic carbon in lake sediments is the result of multiple processes, including the sulfate transformation processes. Cyanobacterial blooms have been reported to be an important factor driving sulfate reduction and methane production in eutrophic lakes (Yan et al., 2017; Zhao et al., 2019). Therefore, the impact of cyanobacteria blooms on the carbon output in eutrophic lakes requires a comprehensive consideration of variation in SO_4^{2-}, which has rarely been considered in previous studies.

Sulfate reduction processes have important effects on the mineralization of organic carbon, and these effects have been demonstrated in many ecosystems (Bowles et al., 2014; Fike et al., 2015). In marine ecosystems, the SO_4^{2-} content in the seawater is as high as 28 mM, which is far higher compared with freshwater lakes. Hence, sulfate reduction processes have important effects on the mineralization of organic carbon in sediments as well as their products of CH_4 and CO_2 (Chambers et al., 2011; Fike et al., 2015; Jorgensen et al., 2019). Anaerobic oxidation of methane (AOM) occurs in marine ecosystems (Maltby et al., 2016); it involves the oxidation of chemically inactive CH_4 to CO_2 catalyzed by microorganisms (Nordi et al., 2017). The SO_4^{2-} guided AOM process in marine sediments oxidizes approximately 90% of CH_4, which increases CO_2 emissions and net total carbon output (Reeburgh, 2007). Therefore, CH_4 is only be one of the main products of organic matter metabolism in sediments with low SO_4^{2-} content (Chen et al., 2016). Several previous studies have examined sulfate reduction in estuarine systems and coastal wetlands, and the results of these studies have shown that sulfate reduction has a significant effect on organic carbon mineralization (Sela-Adler et al., 2017). Continuous sulfate reduction is often not possible in freshwater lakes because of relatively low SO_4^{2-} concentrations (Chen et al., 2016; Hausmann et al., 2016). However, the impact of the sulfate reduction process on lacustrine ecosystems might be much greater than initially thought given that the concentration of SO_4^{2-} is continuously increasing (Holmer and Storkholm, 2001; Baldwin and Mitchell, 2012). A large amount of sulfur enters freshwater because of human activities including SO_4^{2-} and S^{2-}, which results in a significant increase in SO_4^{2-} in the global freshwater ecosystems (Baldwin and Mitchell, 2012; Yu et al., 2013). In eutrophic Lake Taihu, the concentration of SO_4^{2-} increased from 30 mg/L in the 1960s to 100 mg/L today, and the SO_4^{2-} concentration continues to increase (Yu et al., 2013; Zhao et al., 2021). Therefore, the effect of increasing SO_4^{2-} concentrations on organic carbon mineralization during the decay of cyanobacteria in eutrophic lakes requires increased attention.

In order to simulate the dramatical SO_4^{2-} increase of eutrophic lakes, in this study, a series of microcosmic systems, with initial SO_4^{2-} concentrations of 0, 30, 60, 90, 120, 150 and 180 mg/L, was constructed to explore the effect of increasing SO_4^{2-} concentrations and sedimentary decaying cyanobacteria on organic carbon mineralization processes especially the greenhouse gases emissions of eutrophic Lake Taihu. The findings of this study provide new insights into the dynamic changes in the sediment carbon pool and the response of the sediment carbon pool to global warming.

2. Materials and methods

2.1. Sample collection and preparation

Samples of sediments and cyanobacteria were collected from the eutrophic Lake Taihu (31°24′45″N, 120°0′42″E) in July 2020. Cyanobacteria were collected by a 64 μm mesh plankton net. Sediments from this site were collected using a gravity core sampler. The sediment samples were blended thoroughly, homogenized, and sieved (100 mesh), and then placed in a polyethylene bag. Cyanobacteria were collected and concentrated by sieving water through a fine plankton mesh (250 meshes) and stored in an incubator with ice packs, which was immediately taken to the laboratory. The cyanobacteria samples were flushed and centrifuged at 1500 r/min for 5 min by a CT15RT versatile refrigerated centrifuge (China) and freezed drying by Biosafer-10A. Different gradient sulfate concentrations were prepared from high purity water and Na_2SO_4.

2.2. Set-up of incubation experiment

A microcosm system was used to simulate the current conditions of Lake Taihu. The microcosm system was consisted of 51 anaerobic bottles for each SO_4^{2-} concentrations treatment (Φ 75 mm, length 180 mm, volume 500 ml), and there were three replicates for each system. According to the ratio of surface sediments and the average water depth in Lake Taihu and the cyanobacteria accumulation density during the cyanobacteria bloom (2500 g/m^2), 100 g of sediment, 200 ml of water and 0.11 g of cyanobacteria powder were added into each bottle (Zhang et al., 2021). Based on changes in SO_4^{2-} concentrations in Lake Taihu over the years (Yu et al., 2013), the SO_4^{2-} concentrations in the seven microcosms were set to 30, 60, 90, 120, 150, and 180 mg/L, as well as a control that lacked SO_4^{2-}. All the microcosm systems were placed in a biochemical incubator at a temperature of 25 °C. Each group was sampled 17 times on 1, 2, 3, 4, 5, 6, 7, 9, 11, 14, 18, 23, 28, 33, 38, 43 and 48d. Water, gas and soil samples were collected by destructive sampling. The gas was extracted by syringe from the microcosm systems, and one part of the sediment was used for microbe determination and kept in a refrigerator at −80 °C, the rest of the sediment and other samples were kept at 0–4 °C for less than 24 h before analysis.

2.3. Chemical analytical methods

Total nitrogen (TN) was determined photometrically using a UV–vis spectrophotometer (UV-6100, Mapada, China) (Raveh and Avnimelech, 1979). Total phosphorus (TP) was determined by colorimetry after digestion with $K_2S_2O_8$ + NaOH (Ebina et al., 1983). Water pH, DO, and oxidation reduction potential (ORP) were measured using calibrated probes (MP525, China). Soil samples for total organic carbon (TOC) analyses were acidified to pH < 2.0 and analyzed with a multi-N/C analyzer (HT 1300, Analytikjena, Germany). Water samples for dissolved total inorganic carbon (TIC) were analyzed with a multi-N/C analyzer (HT 1300, analytikjena, Germany). All water column and pore water samples were filtered through 0.45 μm Nylon filters prior to the measurements of SO_4^{2-} and $\sum S^{2-}$. They were detected using the turbidimetric (Tabatabai, 1974), methylene blue (Cline, 1969). The content of CH_4 was determined by gas chromatograph (Aglient,7890B).

2.4. Quantification of SRB and MPA in sediments

To confirm the changes in sediment MPA and SRB in the microcosm systems, the sequencing and real-time reverse-transcriptase quantitative polymerase chain reaction (RT-qPCR) technologies were used. The sediments from microcosm systems on 0, 7, and 38d were collected to characterize the abundance of MPA and SRB.

The sediment samples were collected and frozen at −80 °C in an ultra-low temperature freezer. The E.Z.N.A. ®Soil DNA Kit (Omega Bio-Tek, Norcross, GA, USA) was used to extract the total genomic DNA from each soil sample per the manufacturer's instructions. Nucleic acid quality and concentration were determined by 1% agarose gel electrophoresis and a NanoDrop 2000 UV spectrophotometer (Thermo Scientific, USA), respectively.

MPA and SRB in sediments were quantified using the quantitative polymerase chain reaction (qPCR) method. The primer pair for *dmpA* was 1106F/1378r, and the primer pair for *dsrB* was DSR1F+/DSR-R. The q-PCR experiments were performed on an ABI7300 qPCR instrument (Applied Bi osystems, USA) using ChamQ SYBR Color qPCR Master Mix as the signal dye. Each 20 μL reaction mixture contained 2 μL of the template DNA and 16.5 μL of ChamQ SYBR Color qPCR Master Mix. Standard curves for each gene were obtained by the tenfold serial dilution of standard plasmids containing the target functional gene. All procedures followed MIQE guidelines.

2.5. Statistical analysis

The Statistical Package for the Social Sciences 18.0 (SPSS 18.0) was used for statistical analysis. One-way analysis of variance (ANOVA) was used to analyze the significant differences in microbial abundance in different periods, and independent sample *t*-tests were used to determine the significance of the effect of cyanobacteria. The correlation analysis was carried out using bivariate correlation analysis.

3. Results

3.1. Changes in SO_4^{2-} and $\sum S^{2-}$ in overlying water

The sulfate reduction reaction was observed in the treatment with cyanobacteria, and the SO_4^{2-} concentrations decreased substantially, eventually reaching close to 0. In the treatment with the initial SO_4^{2-} concentration of 30 mg/L, the lowest concentration was 2.93 mg/L on the 5th day. The lowest concentration of SO_4^{2-} in the treatment with initial SO_4^{2-} concentrations of 60 mg/L and 90 mg/L was observed on the 9th day, and the lowest concentrations were 2.56 mg/L and 6.25 mg/L, respectively. The lowest SO_4^{2-} concentration in the treatment with an initial SO_4^{2-} concentration of 120 mg/L was observed one day later and was 5.33 mg/L on the 10th day. The treatment with initial SO_4^{2-} concentrations of 150 mg/L and 180 mg/L decreased and remained at stable values for a long time, and the lowest concentrations were observed on the 23rd day, which were 1.18 mg/L and 0.24 mg/L, respectively. No significant change in the SO_4^{2-}concentration was observed in the cyanobacteria-free system.

The maximum $\sum S^{2-}$ concentration was positively correlated with the initial SO_4^{2-} concentration in the overlying water. Higher initial SO_4^{2-} concentrations were associated with higher maximum $\sum S^{2-}$ concentrations. The maximum $\sum S^{2-}$ concentration in the treatment with an initial SO_4^{2-} concentration of 180 mg/L was 5.85 times the maximum concentration of $\sum S^{2-}$ in the treatment with an initial SO_4^{2-} concentration of 30 mg/L, which was 3.59 mg/L and 0.61 mg/L, respectively. There was a positive correlation between the reduction rate of sulfate and the initial SO_4^{2-} concentration on the 1st day of incubation. The sulfate reduction rate in the highest initial SO_4^{2-} concentration treatment of 180 mg/L was 54.28 mg/L, which was 5.85 times higher than that in the lowest initial SO_4^{2-} concentration treatment of 30 mg/L. The sulfate reduction rates were 9.44, 28.02, 30.89, 39.68, and 54.28 mg/L·d in the treatments with initial SO_4^{2-} concentrations of 60, 90, 120, and 150 mg/L, respectively.

3.2. Variation in TIC in the overlying water

During the decay of cyanobacteria, a large amount of TIC was released. In the early stage, TIC in the overlying water significantly increased and then remained relatively stable. A similar trend was observed for the overlying water in the non-cyanobacteria treatment. The maximum concentration and final concentration of TIC in the overlying water were positively correlated with the initial SO_4^{2-} concentrations. In the treatment without SO_4^{2-}, TIC in the overlying water was the lowest, and the final concentration was 159.97 mg/L. When the initial concentration of SO_4^{2-} was 180 mg/L the final concentration was 182.73 mg/L, which was the highest of all treatments. In the treatment with initial SO_4^{2-}concentrations of 30, 60, 90, 120, and 180 mg/L, the final concentrations of TIC in the overlying water were 165.53, 166.63, 166.33, 170.8, and 177.8 mg/L, respectively.

3.3. Changes in TOC in the sediments

Changes in TOC in the sediment and the overlying water showed the same pattern: rising in the early stage, decreasing gradually in the later stage, and remaining stable thereafter (Fig. S3). However, TOC in the sediment decreased gradually in the treatment lacking cyanobacteria.

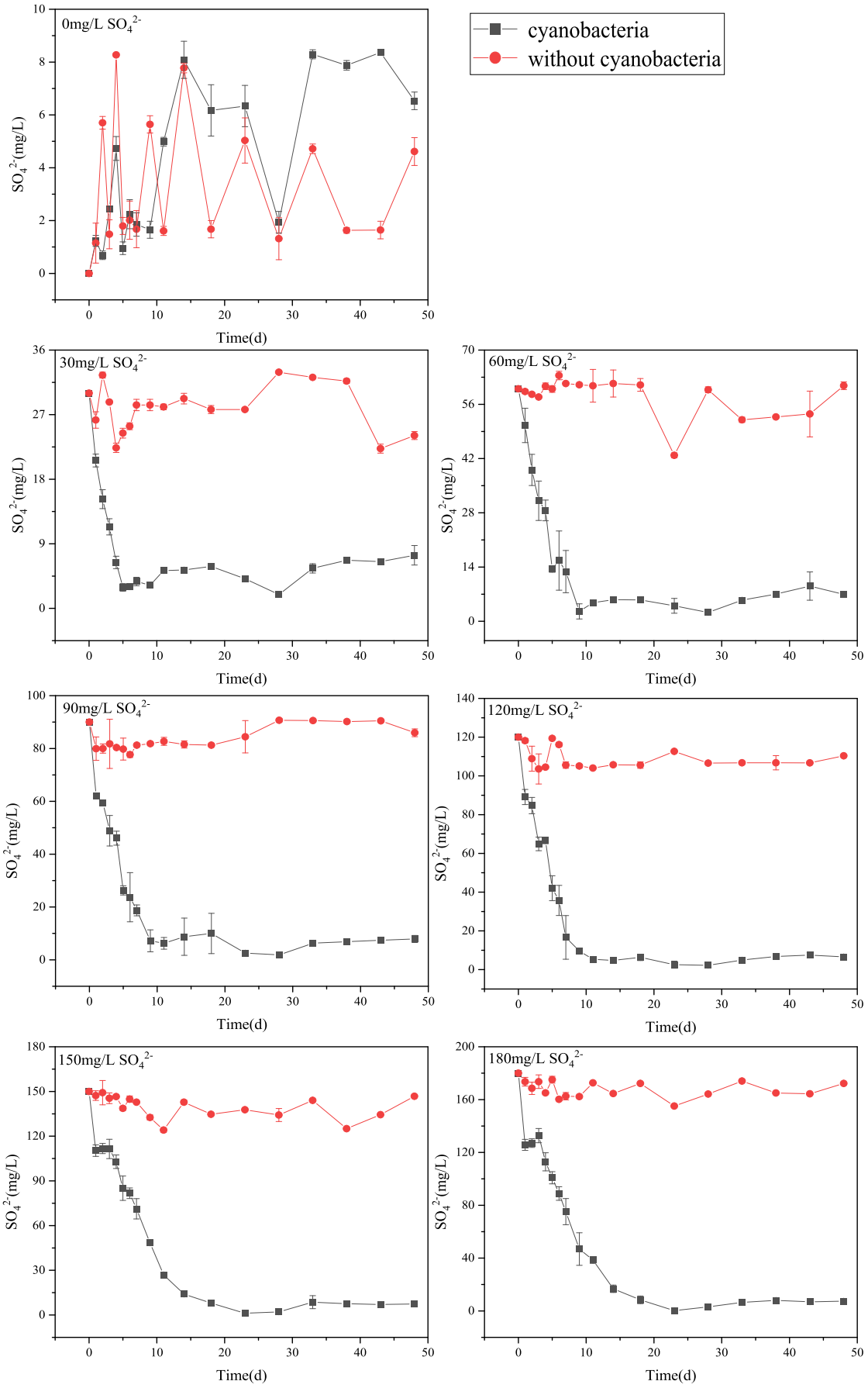

Fig. 1. Changes of SO_4^{2-} concentrations with different initial concentrations in overlying water with and without cyanobacteria.

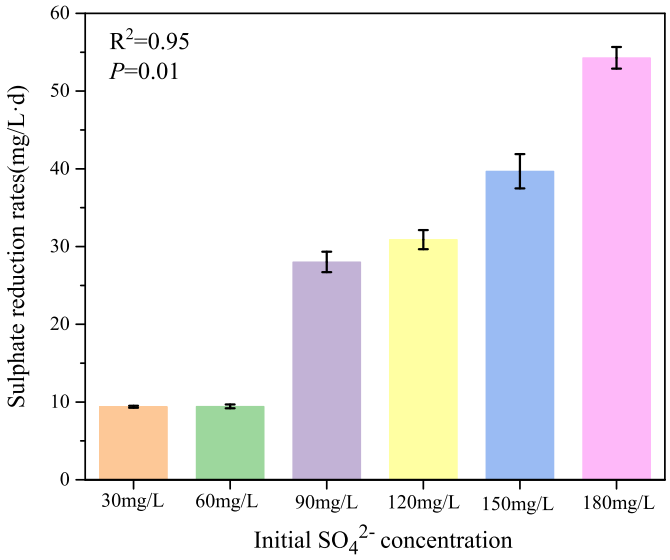

Fig. 2. The sulfate reduction rate of treatments under different initial SO_4^{2-} concentrations on the 1st day of incubation.

In the treatment with cyanobacteria, TOC in the sediment was negatively correlated with SO_4^{2-} in the overlying water. In the SO_4^{2-}-free treatment, the TOC in the sediment was 52.7 g/kg, which was only 1.54 g/kg higher than that in the original SO_4^{2-} treatment of 180 mg/L.

3.4. Dynamic changes in CO_2 and CH_4

A large amount of CH_4 and CO_2 was produced during the decomposition of cyanobacteria, and virtually no CH_4 and CO_2 were produced without cyanobacteria (Figs. 3, 4). As the SO_4^{2-}concentration increased, the final concentration of CH_4 decreased gradually. After 38 days, the CH_4 content was stable for all treatments. In the treatment without SO_4^{2-} addition, the CH_4 content was the highest, and it reached 3852.7 μmol/L after stabilization; the final concentration of CH_4 was 1903 μmol/L in the treatment with an initial SO_4^{2-} concentration of 180 mg/L. The final concentrations of CH_4 were 3279.29, 3227.75, 3156.63, 3098.81, and 2348.9 μmol/L in treatments with initial SO_4^{2-} concentrations of 30, 60, 90, 120, and 150 mg/L, respectively. After 18 days of incubation, the amount of CO_2 production was stable and positively correlated with the initial SO_4^{2-} concentration, and the highest values were 1688.78 μmol/L in the initial SO_4^{2-} concentration of the 180 mg/L treatment. The lowest CO_2 concentration was observed in the treatment lacking SO_4^{2-}, and the final concentration was 988.38 μmol/L. In other treatments, the final CO_2 concentration was also positively correlated with the initial SO_4^{2-} concentration. When the initial SO_4^{2-} concentrations were 30, 60, 90, 120, and 150 mg/L, the final CO_2 concentrations were 1123.22, 1127.76, 1161.74, 1216.58, and 1349.25 μmol/L, respectively. The concentration of CO_2 in the treatment without cyanobacteria increased slightly and then remained stable.

3.5. SRB and MPA in the sediments

In the presence of cyanobacteria, the abundance of MPA and SRB with different initial SO_4^{2-} concentrations was higher than when cyanobacteria were absent. The final abundance of SRB increased as the initial SO_4^{2-} concentrations increased, and MPA showed the opposite trend. Among treatments with cyanobacteria, the final abundance of SRB in the treatments with initial SO_4^{2-} concentrations of 0, 30, and 60 mg/L was less than the initial abundance, and the abundance of SRB was higher in the rest of the treatments. The highest abundance of SRB (2.98×10^8 copies/g) was observed in the treatment with an initial SO_4^{2-} concentration of 180 mg/L, which was 3.86 times higher than the treatment with an initial SO_4^{2-} concentration of 30 mg/L. With the exception of the treatment lacking SO_4^{2-}, the abundance of MPA in all the treatments decreased. In the treatment with an initial SO_4^{2-} concentration of 180 mg/L, the abundance of MPA was only 1.99×10^8 copies/g. The treatment without SO_4^{2-} had the highest abundance of MPA (3.35×10^8 copies/g).

4. Discussion

Sulfate reduction is an important mode of organic metabolism in natural ecosystems, especially in water layers with low DO (Hausmann et al., 2016; Jorgensen et al., 2019). The strength of sulfate reduction was affected by various factors, such as the availability of organic matter, the concentration of electron acceptors and temperature (Holmer and Storkholm, 2001; Wu et al., 2019; Zhang et al., 2021). During sulfate reduction, SRB mainly uses SO_4^{2-} as electron acceptors for anaerobic absorption, hence, the SO_4^{2-} concentration affects the reduction intensity of sulfate (Holmer and Storkholm, 2001; Saxton et al., 2021). Higher SO_4^{2-} concentrations correspond to higher reduction intensities of sulfate (Fig. 2). The abundance of SRB was also positively correlated with the initial SO_4^{2-} concentration (Fig. 5), because the sulfate reduction process was driven by SRB, and the increase in the SO_4^{2-} concentration promoted the organic metabolism of SRB (Chen et al., 2016). The decomposition of cyanobacterial blooms promoted the reduction of sulfate, and the SO_4^{2-} concentration decreased sharply when cyanobacteria were present (Fig. 1), which was consistent with the result of previous studies (Zhao et al., 2019). On the one hand, the decomposition of cyanobacteria converts the physicochemical environments of the water body, from an aerobic state to an anaerobic state with strong reduction potential (Feng et al., 2020; Bartosiewicz et al., 2021). On the other hand, it releases a large amount of carbon, nitrogen, and phosphorus into the water body, which promotes the growth of anaerobic microorganisms including SRB and MPA. The abundance of SRB and MPA increased significantly with cyanobacteria decomposition (Figs. 5, 6). Therefore, sulfate reduction and the anaerobic metabolism of organic compounds were strengthened (Handley et al., 2012; Feng et al., 2020). SO_4^{2-} is an electron acceptor that results in the formation of a large amount of $\sum S^{2-}$ through its participation in the sulfate reduction reaction, and its concentration increased with the initial concentration of SO_4^{2-} (Fig. S1). After the formation of $\sum S^{2-}$, one part of $\sum S^{2-}$ diffuses outwards in the form of H_2S, and the other part sinks into the sediments and is fixed in the sediments by the combination of Fe^{2+}, Fe^{3+} and Mn^{2+} (Zhang et al., 2021).

Lake eutrophication is increasing because of human activities and climate warming, and this has resulted in increases in the frequency of cyanobacterial blooms (Davis et al., 2009; Yan et al., 2017). This in turn promotes the transfer and transformation of algal-derived carbon and ultimately affects the composition of sediment carbon pools (Li et al., 2018). During the decomposition process of cyanobacteria, TIC is released to the overlying water, and the deposition of cyanobacteia residues results in increased TOC input to sediments. Given that the TIC content of the overlying water and the TOC content of the sediments are continuously increasing (Figs. S2, S3). Therefore, the sedimentary decaying cyanobacteria has a significant effect on the carbon pool in eutrophic lakes. The sedimentary carbon pool is central to the carbon cycle in lake ecosystems, and it not only plays a role as a source/sink in the process of carbon balance but also provides a site for the production, consumption, and conversion of lake carbon (Wang et al., 2018). In freshwater lakes, most of organic carbon mineralization takes place in sediments, and CO_2 and CH_4 are important products of organic carbon mineralization mediated by microbes participation (Figs. 3, 4) (Tranvik et al., 2009). Emissions of CO_2 and CH_4 exacerbate the greenhouse effect and affect the carbon composition of the lakes (Bartosiewicz et al., 2021). The products of organic carbon mineralization are affected by many factors, and SO_4^{2-} is a particularly

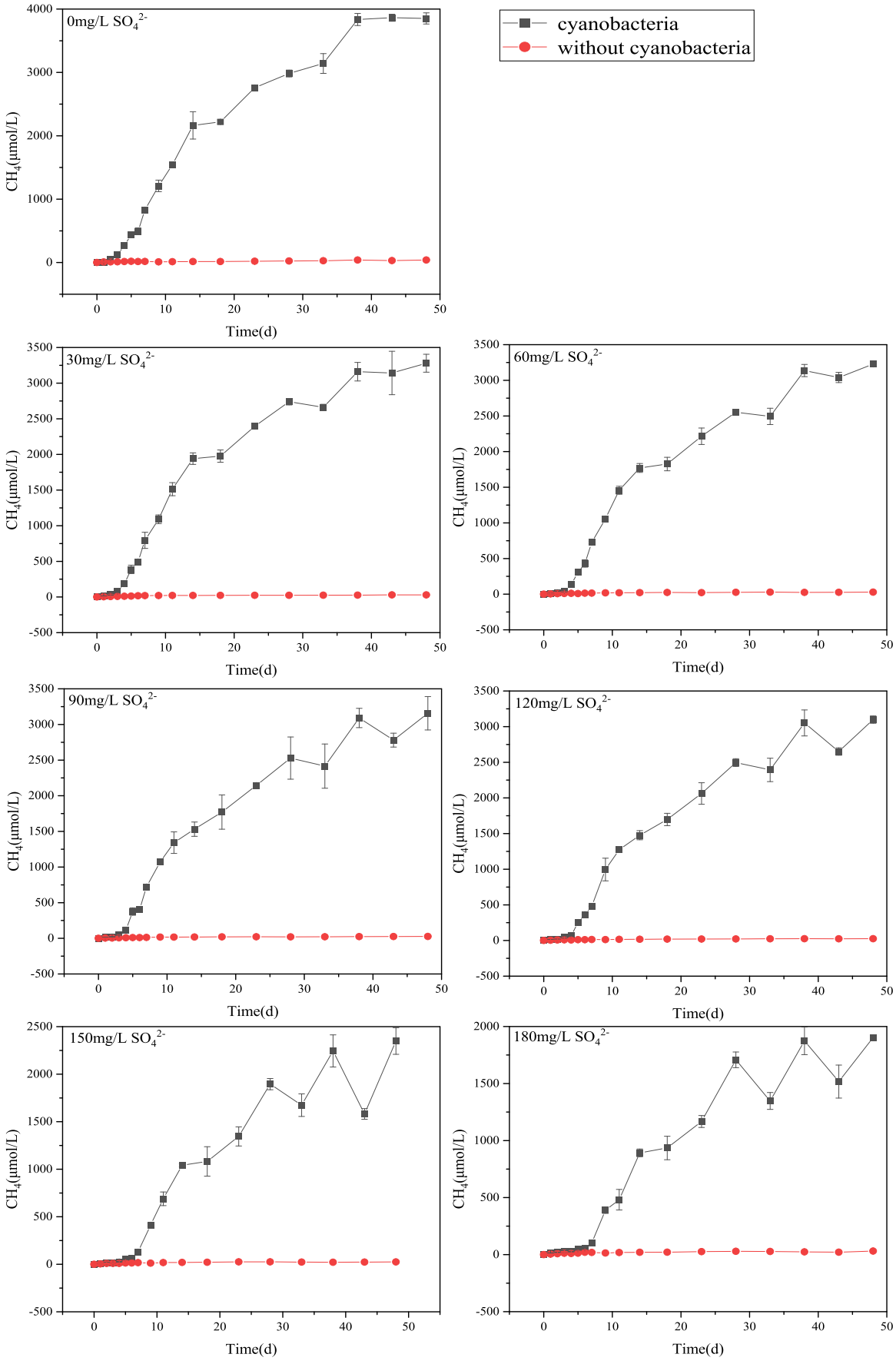

Fig. 3. Changes of CH_4 concentrations with different initial SO_4^{2-} concentrations in treatments with and without cyanobacteria.

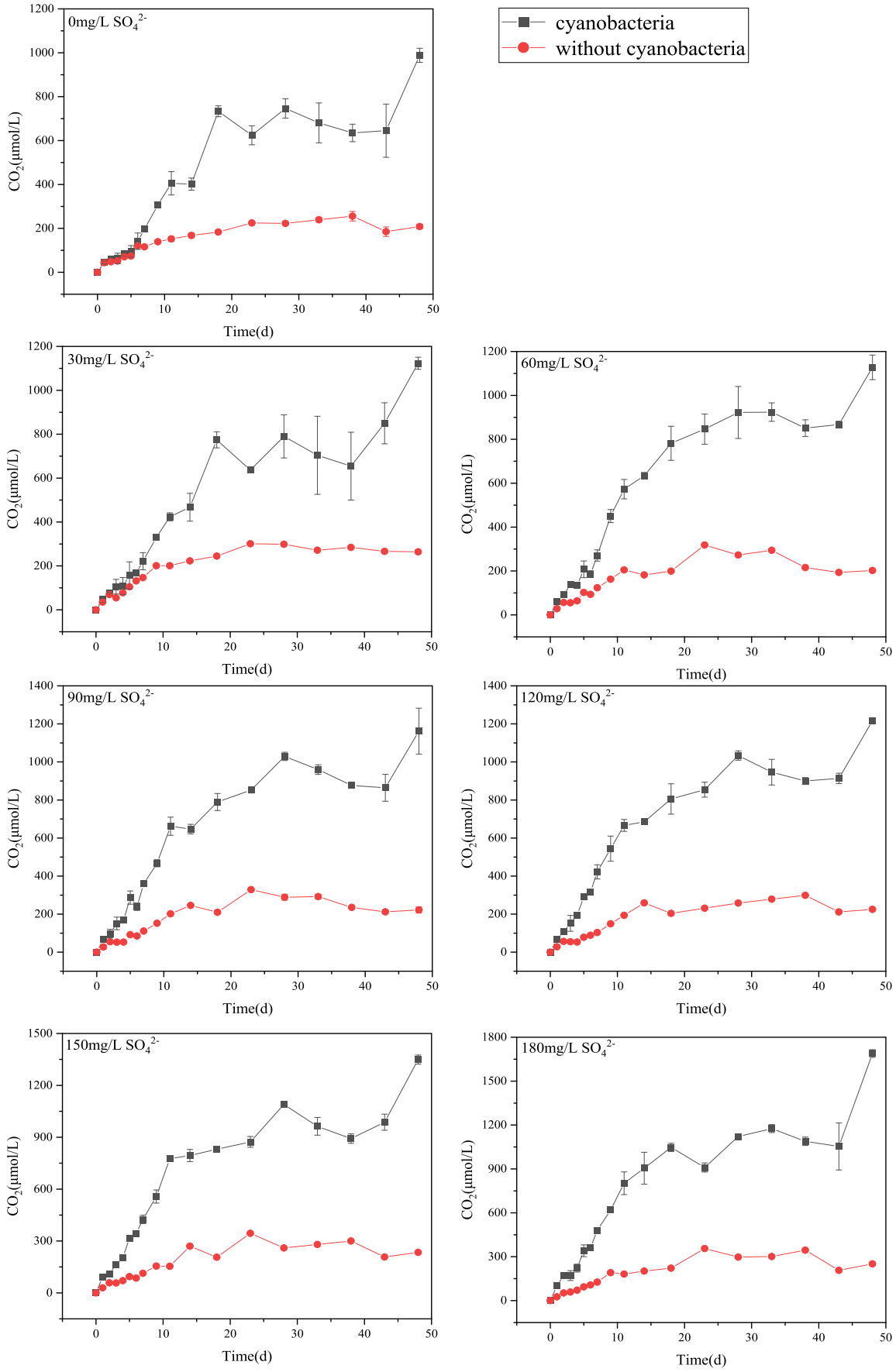

Fig. 4. Changes of CO_2 concentrations with different initial SO_4^{2-} concentrations in treatments with and without cyanobacteria.

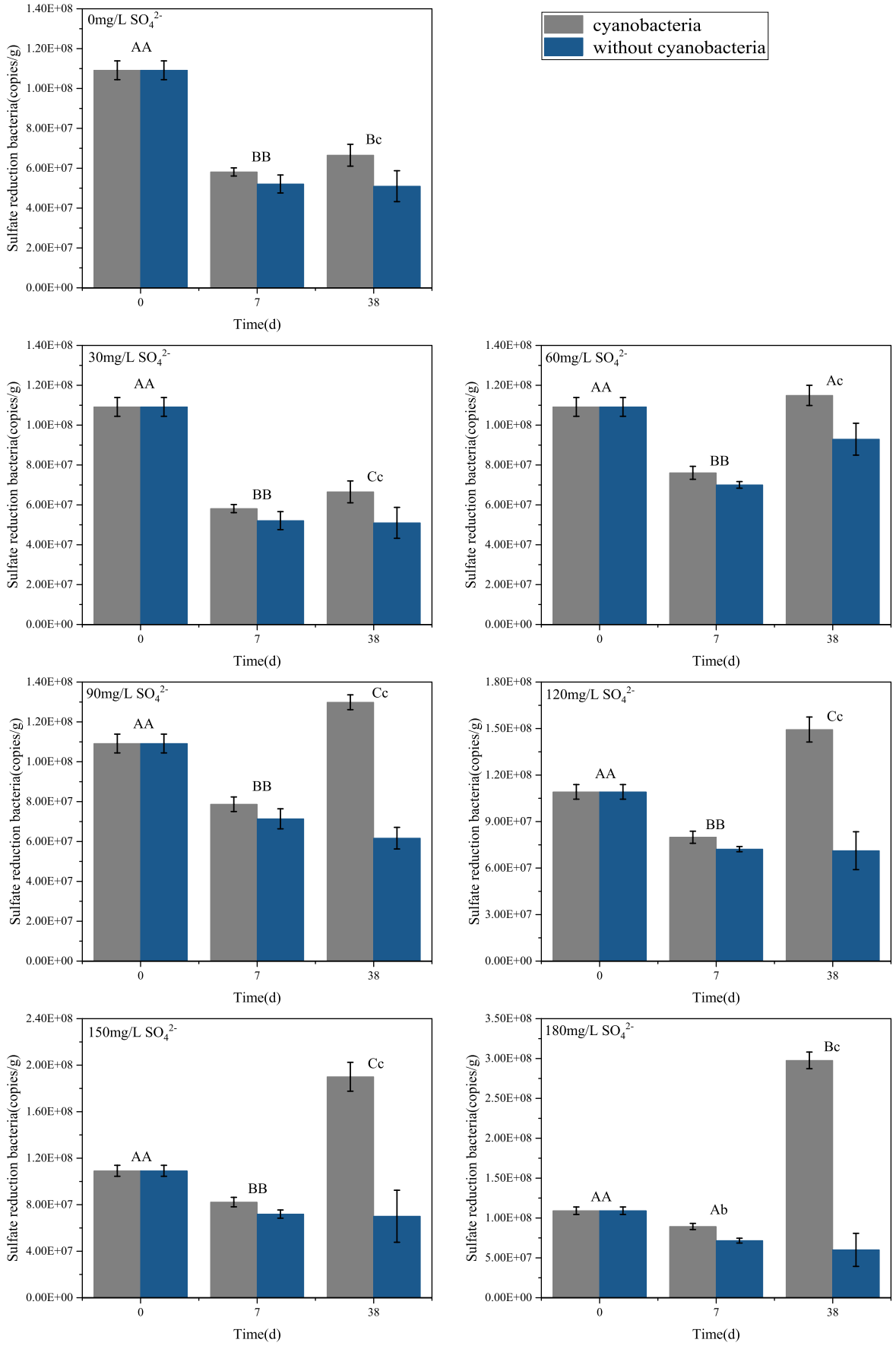

Fig. 5. Changes of SRB with different initial SO_4^{2-} concentrations in treatments with and without cyanobacteria. Different capital letters indicate the significant difference of microbial abundance, while differences upper- and lower-case letters indicate the significant influence of cyanobacteria.

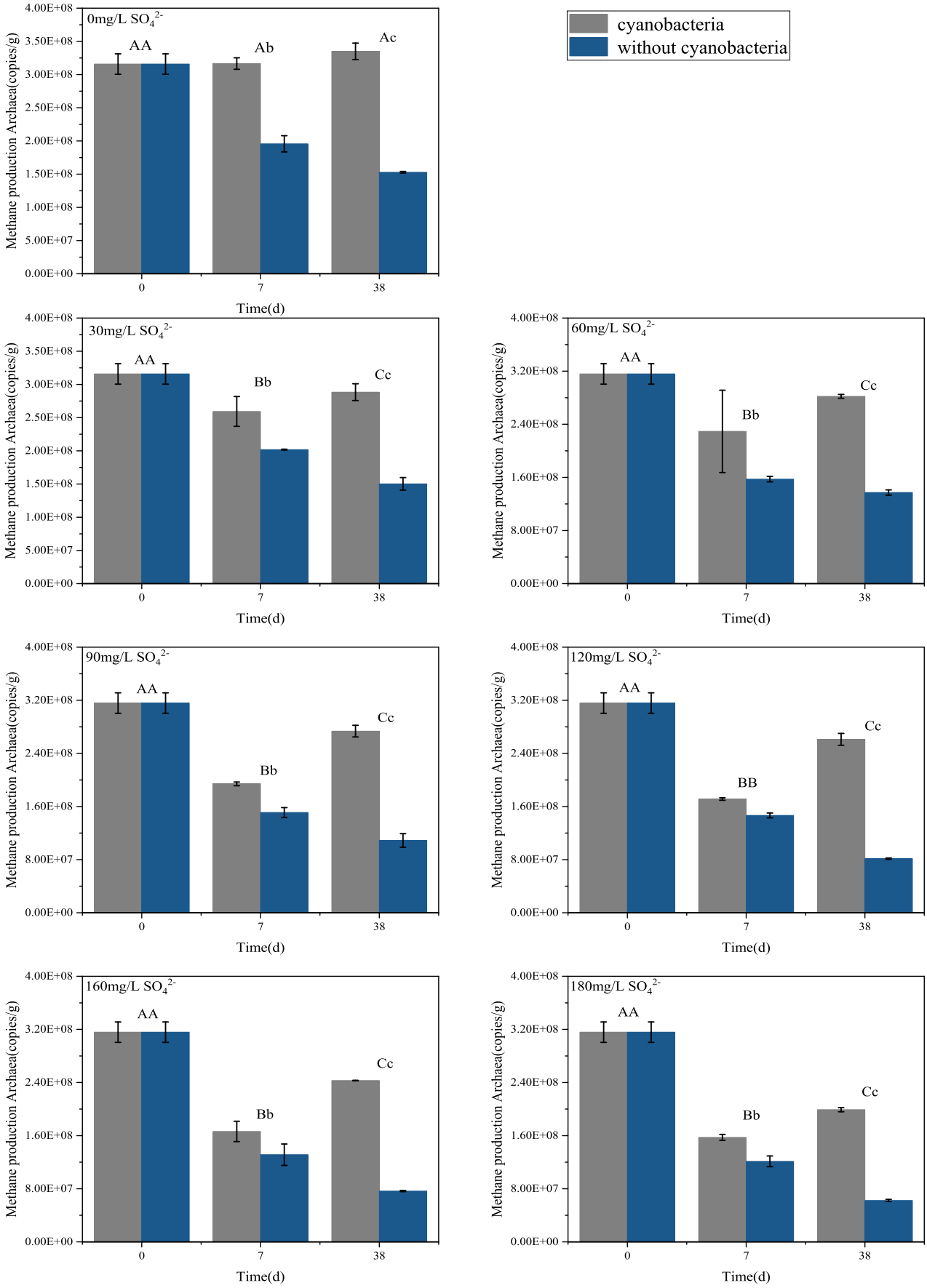

Fig. 6. Changes of MPA with different initial SO_4^{2-} concentrations in treatments with and without cyanobacteria. Different capital letters indicate the significant difference of microbial abundance, while differences upper- and lower-case letters indicate the significant influence of cyanobacteria.

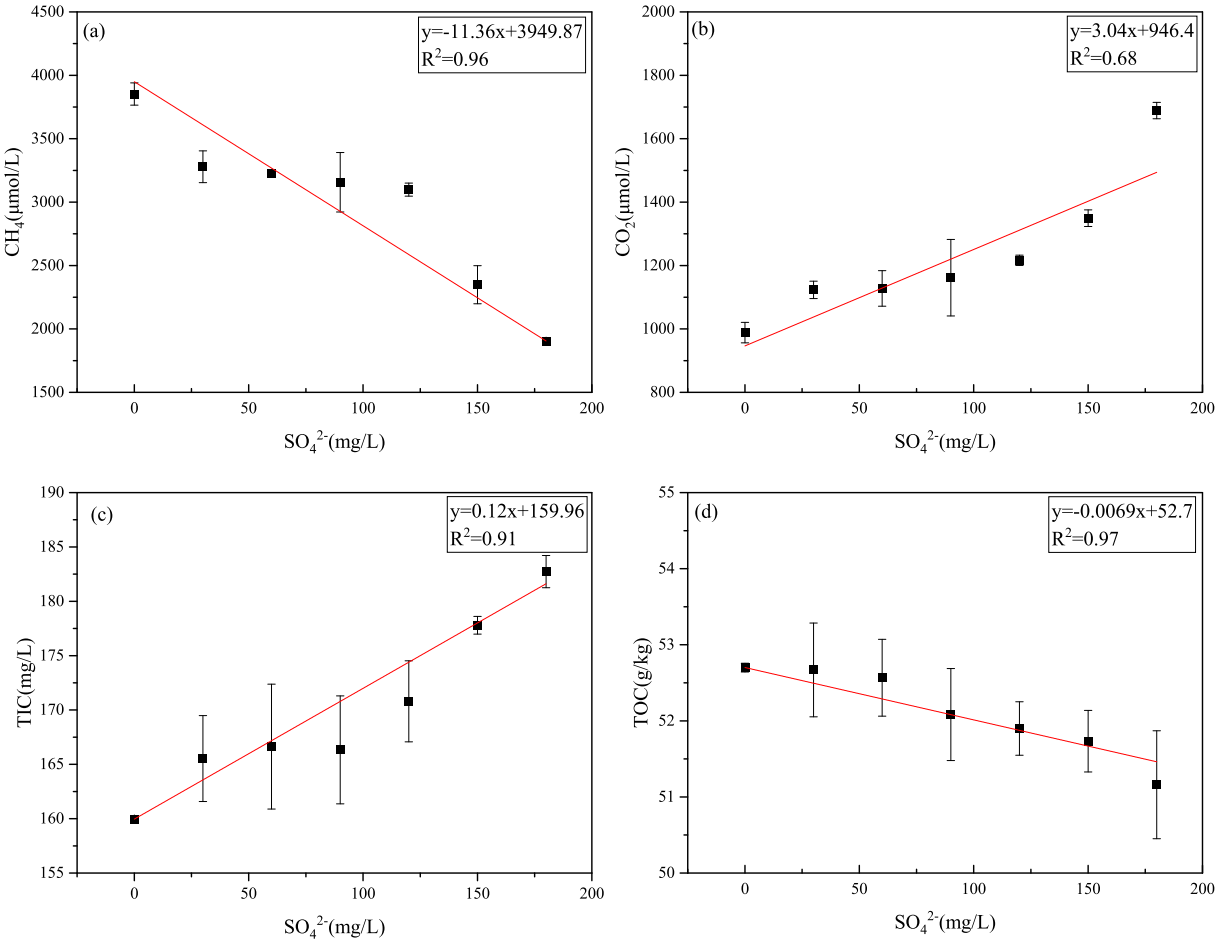

Fig. 7. Correlations of initial SO_4^{2-} concentration with (a) CH_4, (b) CO_2, (c) TIC in overlying water and (d) TOC in sediment, respectively.

important factors (Wu et al., 2019; Zhang et al., 2021). In marine ecosystems, high SO_4^{2-} concentrations result in CO_2 becoming one of the main products of organic metabolism and inhibit the production of CH_4 is inhibited (Zeng et al., 2019). AOM has also been observed in marine sediments since the 1970s (Beckmann et al., 2021). CH_4 produced in the methane-producing region of marine sediments is

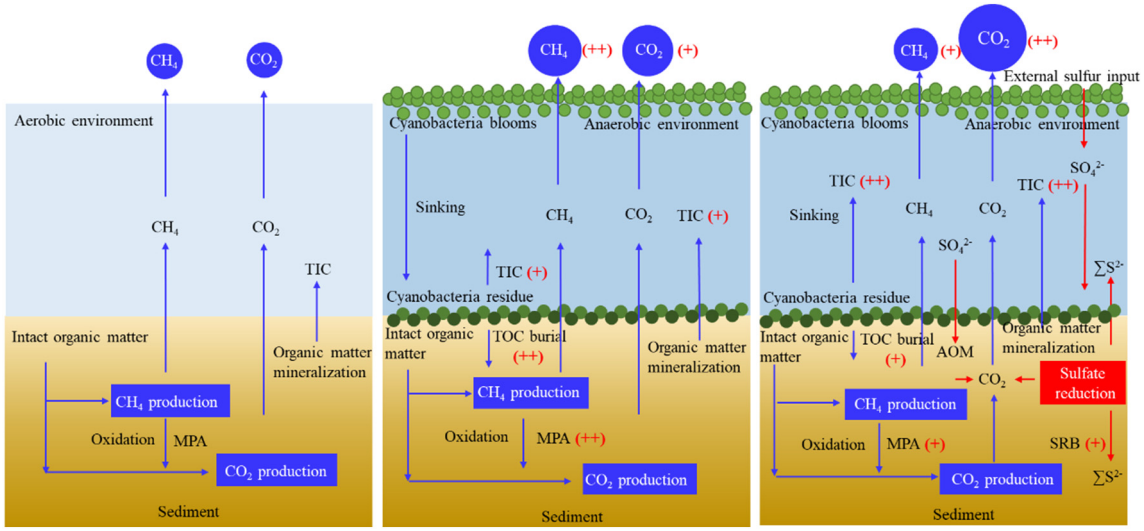

Fig. 8. A conceptual diagram of effects of cyanobacteria blooms and elevated SO_4^{2-} concentration on organic carbon mineralization in lakes. The accumulation and decay of cyanobacteria make the water become anaerobic, and the decomposition process of cyanobacteria releases a large amount of organic carbon in the overlying water and sediments, promoting the mineralization of organic carbon and increasing the emission of greenhouse gases CO_2 and CH_4. When the external sulfur input, the concentration of SO_4^{2-} increased significantly and the sulfate reduction process continues in the lake. The sulfate reduction reaction, on the one hand, intensizes the competition of carbon sources, on the other hand, promotes the oxidation of anaerobic methane, and ultimately inhibits the production of CH_4 and promotes the production of carbon dioxide. (+) indicates the relative increase, and (−) indicates the relative decrease of indexes with the influence of SO_4^{2-} or cyanobacteria.

diffuses upward and is oxidized at the bottom of the sulfur reduction region (Wang et al., 2021). Therefore, SO_4^{2-} has a major effect on the organic carbon mineralization products, and has a significant impact on the carbon output of lake sediments.

With the increasing SO_4^{2-} concentration up to 100 mg/L and a further upward trend in eutrophic lakes, the sulfate reduction mediated by SO_4^{2-} has a significant effect on TOC mineralization from cyanobacteria in eutrophic lakes (Craft et al., 2009; Yu et al., 2013). The increase in the SO_4^{2-}concentration in freshwater lakes results in a significant decrease in CH_4 production and a significant increase in CO_2 production during cyanobacteria decay processes (Figs. 3, 4). However, increases in the SO_4^{2-} concentration increased the abundance of SRB (Fig. 5), and thus promoting the sulfate reduction rate (Fig. 2). The effect of CH_4 emission is mainly mediated through the competition for organic carbon sources, which decreases the abundance of MPA (Fig. 6), as well as the coupling of anaerobic CH_4 with the sulfate reaction. The competition for carbon and the oxidation of CH_4 contribute to the emission of CO_2 emissions, because the products of CH_4 oxidation and the metabolites of sulfate reduction contain CO_2 (Vincent et al., 2021; Saxton et al., 2021). Anaerobic carbon mineralization in freshwater lakes has been shown to increase CO_2 emissions and thus increasing total net carbon output (Holmer and Storkholm, 2001). However, some studies have reported that the total CO_2 production does not increase as the SO_4^{2-} concentration increases in peatland and wetland systems, and the total carbon mineralization rate of peatland is not significantly affected by SO_4^{2-} concentrations (Vile et al., 2003). This may stem from the diversity of anaerobic mineralization pathways of organic carbon in wetland systems, including sulfate reduction, CH_4 production and oxidation of organic carbon compounds (Vile et al., 2003). Therefore, the increase in SO_4^{2-} may only change the pathway of carbon mineralization, and its effect on TOC output is not significant (Vile et al., 2003; Sihi et al., 2018). In the initial stage of this experiment, the reduction rate of sulfate increased with the SO_4^{2-} concentration (Fig. 2). When the reduction rate of sulfate increases to a certain level, the reduction rate of sulfate is affected by such factors as the availability of organic matter, which altered its contribution to CO_2 emissions (Holmer and Storkholm, 2001). Although a significant increase in CO_2 emissions from sulfate reduction has not been reported by previous studies, we observed a positive correlation between the initial SO_4^{2-}concentration and CO_2 emissions (Fig. 7; $R^2 = 0.68$), it was negatively correlated with CH_4 (Fig. 7; $R^2 = 0.96$) and TIC in overlying water and TOC in sediments (Fig. 7; $R^2 = 0.91$; $R^2 = 0.97$). This stems from the maintenance of sulfate reduction by a large amount of organic matter provided by cyanobacterial decay (Figs. S2, S3), and the relatively high level of SO_4^{2-} in eutrophic lakes, it also provides sufficient electron acceptors that permit continuous sulfate reduction (Zhao et al., 2019; B. Li et al., 2021; J. Li et al., 2021).

A conceptual diagram was made to clarify the effects of cyanobacterial blooms as well as the increase in the SO_4^{2-} concentration on TOC mineralization in lakes (Fig. 8). As indicated in the diagram, cyanobacterial blooms increase CO_2 and CH_4 emissions, and SO_4^{2-} input promotes the occurrence of the sulfate reduction reaction, which increases CO_2 emissions and reduces CH_4 emissions (Fig. 8). Cyanobacterial blooms significantly increased the TOC concentration in eutrophic lakes as well as CH_4 and CO_2 emissions and decreased TIC in the sediments. Following external sulfur input, the concentration of SO_4^{2-} increases significantly, and the sulfate reduction process in lakes continues. Sulfate reduction competed with the methane production and promotes the anaerobic oxidation of CH_4, which increases the CO_2 emissions. SRB and MPA play an important role in this process, and they compete for substrates for organic metabolism, and the abundance of SRB increased with the increase of initial SO_4^{2-} concentration, while the abundance of MPA showed an opposite trend. Therefore, when cyanobacterial blooms in eutrophic lakes are frequent and the SO_4^{2-} concentrations are high, the effect of SO_4^{2-} on lake TOC mineralization might increase the carbon output. The TOC content in the sediments at the end of the reaction was significantly lower than that at the initial stage (Fig. S3), which has a significant effect on the source/sink conversion and composition of the lake sediment carbon pool. Therefore, the effect of increasing SO_4^{2-} should be considered when assessing the carbon mineralization capacity of lake sediments.

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CRediT authorship contribution statement

Xu Xiaoguang: designed and led the study. Zhou Chuanqiao, Peng Yu, Yang Deng, Yu Miaotong, Chen Li, Zhang Lanqing, Zhao Fenjun, and Yan Yan: performed the investigation and analyzed the samples. Zhou Chuanqiao, Peng Yu: wrote the original draft with major edits and inputs from Xu Xiaoguang and Wang Guoxiang.

Declaration of competing interest

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

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