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The Limiting Factor to the Outbreak of Lake Black Bloom: Roles of Ferrous Iron and Sulfide Ions

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Algae-induced black bloom, a kind of black water phenomenon in some severe eutrophic lake areas, is characterized by a black color and offensive odor and is one of the most serious environmental problems in certain eutrophic shallow freshwater lakes in China. Ferrous iron (Fe^{2+}), soluble inorganic sulfides (ΣS^{2-}, $\Sigma S^{2-} = S^{2-} + HS^{-} + H_2S$), and dissolved oxygen (DO) in the overlying water are presumed to be directly related to the formation of black blooms. In this study, the algae-induced black bloom in Lake Taihu, China, is simulated in the laboratory by using a large-scale lake process simulation apparatus. Changes in the characteristics of Fe^{2+}, ΣS^{2-}, DO, pH, and oxidation reduction potential (ORP) are investigated during the entire black bloom formation period. Results show that black blooms occurr in water columns with high Fe^{2+} and ΣS^{2-}, but not in water columns with high Fe^{2+} and low ΣS^{2-}, or low Fe^{2+} and ΣS^{2-}. During the formation of black bloom, Fe^{2+} increases quickly as DO decreases but starts to decrease before the outbreak of black bloom. ΣS^{2-} concentrations only increase sharply 12 h before the outbreak. Both Fe^{2+} and ΣS^{2-}, affected by oxic and redox conditions, respectively, contribute to the formation of black bloom. However, ΣS^{2-} is confirmed to be the limiting factor directly controlling the outbreak of the black bloom.

1. Introduction

Black bloom, characterized by black color and offensive odor in water columns, is a severe environmental deterioration phenomenon that has been affecting several hyper eutrophic shallow lakes in China in the recent years. Water quality in zones with black bloom is very low with high levels nitrogen and phosphorus loadings, low dissolved oxygen (DO),[1] and high levels of volatile odor substances.[2,3] Disastrous environmental events were triggered by black bloom that not only induced massive mortality of benthos, fishes, and macrophytes in lakes, but also caused crises regarding drinking water supply to over one million people in a lakeside city.[2,4] Black bloom phenomenon has been considered a serious environmental disaster in lake ecosystems in China.[5]

The black water phenomenon has been reported in many lakes and rivers in the past several decades.[6–8] Massive production of black metal sulfides in stable reduced chemoclines was considered to be responsible for the black water in some North American lakes.[6,7] In addition, long-term input of humic substances from soil leaching,[8,9] and outbreaks of protozoacould lead to black or dark color water bodies.[10] However, black blooms in shallow eutrophic lakes showed remarkable physicochemical differences with the aforementioned black water phenomena although the color of water appeared to be the same. Field investigations on black blooms revealed that the bulk accumulation and degradation of cyanobacteria or dead macrophytes causing severe water hypoxia were important factors inducing black blooms.[5] This discovery was compared with the formation of the black spot phenomenon in Wadden Sea in the early researches on black blooms.[11,12] However, black bloom mainly occurred in water columns rather than the black surface sediment, showing that these two phenomena were obviously different from each other. The theory of the formation of hypoxia zones (or dead zones) in gulfs and giant river estuaries proposes a four-phase progression of hypoxia, summarizing that long-term eutrophication might lead to water hypoxia and even anoxia eventually.[13] The black bloom phenomenon was regarded as an extreme case of the fourth phase of hypoxia in shallow hyper eutrophic lakes.[5] In this phase, the water enters into an anoxic state and H_2S is generated by microbial activity.[14,15]

Major physicochemical characteristics of the water column experiencing black blooms were confirmed through field investigations and laboratory studies. The results showed that the water column had high concentrations of N (total nitrogen [TN] 4.55–26.4 mg L^{-1}) and P (total phosphorus [TP] 0.33–2.85 mg L^{-1}) nutrients, low DO levels,[1] abundant ferrous irons (Fe^{2+}, 0.18–0.37 mg L^{-1}) and soluble inorganic sulfides (ΣS^{2-}, $\Sigma S^{2-} = S^{2-} + HS^{-} + H_2S$, 0.25–0.46 mg L^{-1}).[5] In addition, volatile organic sulfur compounds, mainly dimethyl sulfides (DMSs), were found to be the major odor substances, which formed as a result of algae or macrophyte degradation.[2,5] Therefore, high

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concentrations of Fe^{2+}, ΣS^{2-}, and DMSs were considered the most significant chemical characteristic distinguished from normal lake water. Nevertheless, early studies mainly on black bloom focused on nutrients and eutrophication related changes or odor sources in the water column.[1,16] Although the emergence of the black color marked the outbreak of the black bloom, [17] only few studies considered the formation mechanism and pointed out that Fe^{2+} and ΣS^{2-} are the blackening substances and important to the formation of the black bloom.[14,18] Recent studies have demonstrated that black ferrous sulfide (FeS) is the main blackening substance.[19] Furthermore, high concentrations of Fe^{2+} and ΣS^{2-} were confirmed to promote blackening of water columns and surface sediments under severe hypoxic and anoxic conditions.[6,7,20] However, the developmental process and changes in the characteristics of these ions during the formation of black bloom are still unknown. The influence or even control of these changes on the outbreak of black blooms remains unclear. Therefore, these factors must be studied to reveal the formation mechanism of black blooms.

In this research, the formation process of algae-induced black bloom was simulated by using a large-scale simulation apparatus in the laboratory. Changes in the characteristics of Fe^{2+} and ΣS^{2-} as well as DO, oxidation-reduction potential (ORP), and pH were studied during the formation of the black bloom. Correlation analysis and principal component analysis (PCA) were employed to determine the potential relationship between these parameters and the black bloom. The present study is expected to fill the gaps between black bloom and the main influence or limiting factors, contributing to the understanding of its formation mechanism.

2. Experimental Section

2.1. Sampling

All samples used in the simulation were collected at one site (geographic coordinates: N 31°13′33″, E 119°54′41″) in the third largest freshwater lake in China,[21] Lake Taihu, which is a hyper eutrophic shallow lake and famous for severe cyanobacterial blooms.[22,23] The sampling site was at near-shore area west of the lake, where severe cyanobacterial bloom occurs every year and black blooms were reported several times by the local government in the last 5 years. The overlying water was sampled at the depth of 20 cm below the water surface and collected into 25 L polyethylene barrels, and then the sediment samples were collected using a gravity sediment core sampler (Rigo, Ø110 mm × L 500 mm, Japan). Algae were collected using a 25# phytoplankton net and then stored in a plastic barrel. The algae species were not identified, but during the algal bloom season in Lake Taihu, the dominant species are cyanobacteria, mainly *Microsystis aeruginosa* and *Aphanizomenon*.[4,14,17,22,23] The lake water was filtered using a 300 mesh nylon sieve for removing coarse suspended particles and algae before being injected into the simulation system. The algae sample was obtained through 6 h of filtering using the nylon sieve. Subsequently, the simulation was performed according to the method described in the following section.

2.2. Black Bloom Simulation Experiment

The black bloom simulation experiment was conducted in a Y-shaped sediment resuspension generation apparatus at the State Key Laboratory of Lake Science and Environment in Nanjing Institute of Geography and Limnology of Chinese Academy of Sciences.[24] The apparatus has six separate Plexiglass simulation columns (height: 200 cm, inner diameter: 11 cm) for simulation lacustrine sediment–water interface interactions. Each simulation column featured two frequency modulation electrical devices, in which one was connected to a rod with a wide spiral edge on the top and the other one was connected to a small fan at the side near the bottom of the column; these devices were used to simulate wind levels in the lake. The apparatus has been employed to study processes in sediment–water interfaces under mechanical disturbance, sediment resuspension,[25] and to simulate black bloom since its invention.[14,16,17,26]

The simulation of the treatment of black bloom comprised sediments, overlying water, and algae, all of which were sampled from the field. In the simulation column, a bar of in situ upper sediment core (20 cm in height) was sealed at the bottom and overlying lake water was then added without disturbing the core up to a height of 170 cm. Subsequently, 47.5 g algae (fresh wet, approx. 5 kg m^{-2}) were added to the column. The control check (CK) was set in the same manner as in the treatment simulation except for algae. Both the CK and treatments were done in triplicate and the simulation columns for CK and treatment were marked as CK 1#, CK 2#, and CK 3#, and treatment 1#, treatment 2#, and treatment 3#, respectively. CK and treatment simulations were performed in the Y-shaped apparatus simultaneously. In order to accurately simulate the actual environment in the lake, a 4 h long small wind condition (3.4 m s^{-1}) was induced in the simulation columns every afternoon. During the experiment period, temperature 28 ± 2 °C, which is favorable for black bloom formation, was maintained.

2.3. Monitoring and Analysis

In the simulation, physicochemical parameters including DO, ORP, pH, Fe^{2+}, and ΣS^{2-} were monitored regularly every morning. Moreover, in order to record the rapidly changing features of these parameters before the outbreak of the black bloom, a 1 h interval of monitoring was implemented for 12 h when the color of the water column started to turn dark. The overlying water at a depth of 1 m from the surface was sampled in each monitoring. Fe^{2+} and ΣS^{2-} concentrations in the water samples were determined immediately. Fe^{2+} was analyzed according to the ferrozine spectrophotometric method,[27] and ΣS^{2-} was analyzed using the methylene blue spectrophotometric method.[28] Both parameters were determined using spectrophotometry (Shimadzu UV-2550). Simultaneously, DO, ORP, and pH were measured by using a dissolved oxygen meter, a redox potential meter, and a pH meter, respectively.

2.4. Statistical Analysis

All regressions in the study were conducted using OriginLab 8.5 software. Correlation analyses were performed using SPSS 16.0

software and factor analysis was conducted using PCA followed by the Varimax rotation method in SPSS 16.0. Canonical correspondence analysis (CCA) was conducted using Canoco 4.5 software.

3. Results

3.1. Development of Black Bloom

Black color and offensive odor are the most significant sensory features of black blooms, but the black color was regarded as the indicator of the outbreak of black bloom owing to its visual recognizability.[14,17] In this study, changes in the color of water in the simulation columns of the CK and treatments were different. The overlying water in CK was colorless and a normal condition was maintained without black bloom. In contrast, the overlying water in the treatment columns was clear at the beginning of the experiment but turned turbid in the following days when the algae began to die. During afternoon and late afternoon at day 5 of the experiment, the color of the bottom water in two treatment columns (2# and 1#, respectively) turned light gray and then the water column gradually turned dark in the following evening; by the next morning it was black. As such, it could be confirmed that black bloom outbreak occurred at day 6 in these two simulation columns. However, in treatment 3#, the water was totally turbid and black bloom did not occur during the experimental period. According to previous studies,[14,17] not all black bloom outbreaks occurred simultaneously in a set of parallel simulations. It is common for outbreaks to lag by a few days in some simulation columns after the first outbreak of black bloom.

3.2. DO

Black bloom is an extreme form of hypoxia, where DO depletion in the water column is a main characteristic.[1] The DO concentration in overlying water is shown in **Figure 1**a. In the CK columns, the DO concentration slightly decreased during the first several days but an aerobic level was maintained for the remaining experiment period. In the treatment columns, DO showed a decreasing trend throughout the study period and reached $<1\ \mathrm{mg\,L^{-1}}$. However, it was different between columns where black blooms occurred and the other column where it did not occur. In the overlying water of parallel treatments 1# and 2#, DO dropped quickly during the first 3 days and the water became hypoxic ($DO < 2\ \mathrm{mg\,L^{-1}}$) and DO continued to decline reaching anoxic levels. In contrast, an oxic condition was maintained in treatment 3# for as long as 5 days before it became hypoxic. It is clear that the degradation of dead algae in the water column was the reason for the decline of DO, which has also been considered the main cause for hypoxia in large water bodies.[13] The water columns remained in an anoxic condition for several days before black bloom finally occurred.

3.3. ORP

Changes in the ORP in the overlying water are shown in Figure 1b. ORP in the CK columns remained at relatively stable values around 300 mV and the overlying water remained in

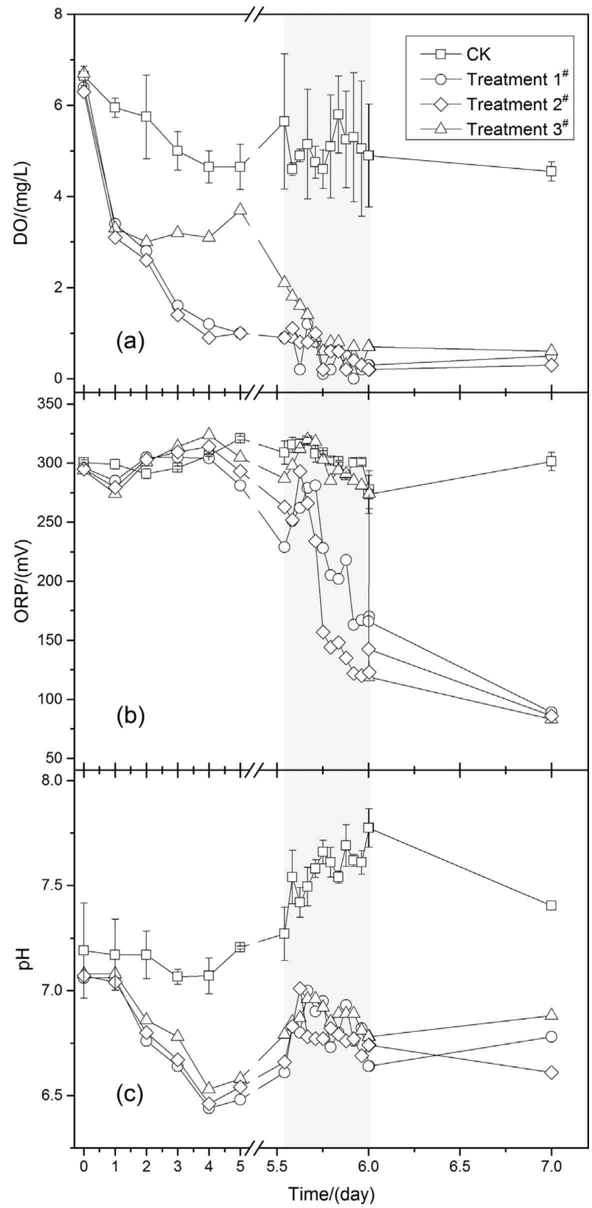

Figure 1. Changes of DO, ORP, and pH in water columns. No black bloom occurred in CK and treatment 3#; black blooms occurred in treatments 1# and 2#.

oxidized states. On the contrary, ORP in treatments 1# and 2# exhibited a declining trend until day 5 and dropped dramatically, changing to reduced conditions 12 h before the outbreak of black bloom. In treatment 3#, ORP also decreased although black bloom did not occur. Compared with the CK, overlying water in the treatment columns were in a significantly reduced condition (ORP 120–281 mV) before the outbreak of black bloom.

3.4. pH

As shown in Figure 1c, the pH in the overlying water of the CK and treatment columns showed different trends. In the CK, the pH levels (7.07–7.78) were neutral with an increasing trend and the overlying water was in a neutral–alkaline state. In the treatment columns, there was a remarkable decline in the pH value. Compared with the CK, the overlying water in the treatment columns were significantly acidic (pH 6.64–7.01) before the outbreak of black bloom.

3.5. Fe^{2+} in Water Column

In addition to the high levels of N and P nutrients pollution (TN 4.55–26.4 mg L^{-1}, NH_4^+-N 2.99–15.1 mg L^{-1}, TP 0.33–2.85 mg L^{-1}) in the water column,[1] high Fe^{2+} (0.18–0.37 mg L^{-1}) and ΣS^{2-} (0.25–0.46 mg L^{-1}) levels were detected in the field investigation.[5] These high levels of chemicals in water distinguished from ordinary eutrophic lake water were considered as typical characteristics of black bloom.[5] Changes in Fe^{2+} concentration in the overlying water during the formation of black bloom are shown in **Figure 2**a. In the CK columns, Fe^{2+} concentration was very low of about 0.059 mg L^{-1}, whereas in the treatment columns, with high deviation and showed an increase-peak-decrease trend. In treatments 1# and 2#, Fe^{2+} reached its peak (1.51 and 0.82 mg L^{-1}, respectively) about 12 h before the black bloom outbreak and then decreased gradually. During these 12 h, Fe^{2+} concentration in these two simulation columns was 6.03–43.43 times higher compared to CK (0.033–0.085 mg L^{-1}).

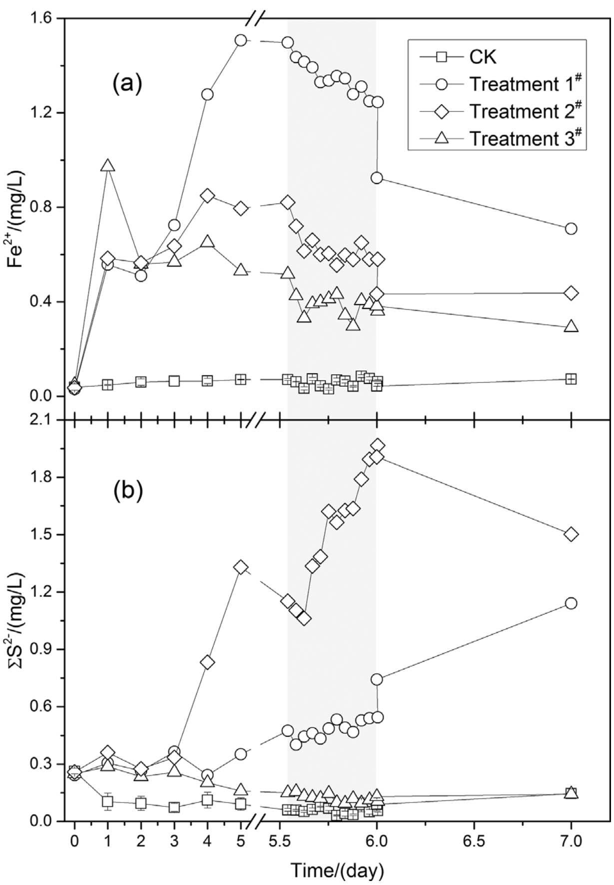

Figure 2. Changes of Fe^{2+} and ΣS^{2-} in water columns. No black bloom occurred in CK and treatment 3#; black blooms occurred in treatments 1# and 2#.

3.6. ΣS^{2-} in Water Column

Changes in ΣS^{2-} are shown in Figure 2b. In the water columns of CK and parallel treatment 3#, the ΣS^{2-} concentrations were relatively low although there was a little fluctuation at the beginning of the experiment. However, the ΣS^{2-} concentrations increased sharply at days 4 and 5 in treatments 1# and 2#, respectively. Unlike the decline of Fe^{2+} in the 12 h before the black bloom outbreak, ΣS^{2-} concentrations kept increasing rapidly until the outbreak and showed no significant decrease after the formation of black bloom. During the period before and after the outbreak, ΣS^{2-} concentrations in treatments 1# (1.06–1.97 mg L^{-1}) and 2# (0.40–1.14 mg L^{-1}) were 5.62–52.37 times higher compared with the CK columns (0.05–0.15 mg L^{-1}).

4. Discussion

4.1. Roles of Fe^{2+} and ΣS^{2-} in the Formation of Black Bloom

Because black blooms mainly occur in hyper-eutrophic lake zones with bulk algae accumulation, studies on this phenomenon pertained to eutrophication related fields, mainly focusing on N and P in water.[1,4] Induced by severe cyanobacterial bloom or massive deaths of other aquatic plants, black blooms are far more serious than common eutrophication from the water quality viewpoint. High Fe^{2+} and ΣS^{2-} concentrations were confirmed as two typical chemical features of black bloom water columns.[5] These characteristics appeared to be more important as FeS was identified to be the major blackening substance.[19] Abundant accumulation of Fe^{2+} and ΣS^{2-} in water columns directly lead to the formation of blackening substances.

However, Fe^{2+} and ΣS^{2-} in overlying water did not increase simultaneously. Results (Figure 2a) showed that Fe^{2+} increased rapidly along with the decreases in DO and peaked at 12–24 h before the outbreak of black blooms. During the critical 12 h before the outbreak, Fe^{2+} concentrations began to decrease gradually in all three parallel treatment columns regardless of whether black bloom occurred or not. ΣS^{2-} concentration in the water columns remained at relative low levels in the first 4 days and began to increase at 24–48 h before the outbreak of black blooms in parallel treatments 1# and 2# (Figure 2b). In the parallel treatment 3#, ΣS^{2-} remained at low levels and showed no increase during the entire experiment. This might be because of the spatial heterogeneity of sediment cores. It was highly possible that the time for the outbreak of black bloom in treatment 3# was not sufficient because the simulations were terminated at day 2 after the outbreak of black bloom in treatments 1# and 2#. Nevertheless, the data obtained from treatment 3# were still meaningful to the study. Based on these results, three inferences can be deduced: first, increases in Fe^{2+} concentration is a common feature for hypoxic water columns; second, rapid increases in ΣS^{2-} concentration in water columns is an important indicator for black bloom outbreak; and third, accumulations of Fe^{2+} and ΣS^{2-} in water columns are both critical to the formation of black blooms, but ΣS^{2-} is a rather direct limiting factor controlling the outbreak.

The asynchronous increase of Fe^{2+} and ΣS^{2-} in the study can be attributed to the different reduction priorities of Fe^{3+} and SO_4^{2-}. In lake environments, the priority reduction sequence of oxidants is O_2, NO_3^-, NO_2^-, Mn^{4+}, Fe^{3+}, and SO_4^{2-}.[29] With the depletion of DO, the ions used for major electron acceptors in biochemical reactions are reduced according to this order. Therefore, it is reasonable that the increase of Fe^{2+} was prior to ΣS^{2-}. As the redox condition changed from a ferric iron controlled system to a sulfate controlled system, ΣS^{2-} began to increase. The relation between Fe^{2+} and ΣS^{2-} in this study is shown in **Figure 3**. Fe^{2+} concentrations reached a peak and began to decrease when the $Fe^{2+}/\Sigma S^{2-}$ (molar ratio) was ≤ 1, along with the increases in ΣS^{2-} concentration. The consumption of Fe^{2+} by S^{2-} was one of the reasons for this decrease. Absorption by increased dissolved organic matters in the development of hypoxia could be another reason for the decrease in Fe^{2+}.[30] In parallel treatments 1# and 2#, with the rapid substantial increase in ΣS^{2-} concentration, sufficient S^{2-} would react with Fe^{2+} and form massive black FeS precipitates. The newly formed bulk precipitates would then be absorbed by suspended substances or suspend by themselves in the water column, causing the black color and marking the outbreak of black bloom. In the CK columns, both Fe^{2+} and ΣS^{2-} showed low levels. In parallel treatment 3#, Fe^{2+} concentration was high but ΣS^{2-} concentration was low. No black bloom occurred in these water columns. Thus, it is obvious that the increase in ΣS^{2-} triggered the outbreak, indicating that ΣS^{2-} is a direct key limiting factor controlling the formation of black blooms.

4.2. Sources of Fe^{2+} and ΣS^{2-} in the Water Column

Fe and S are redox sensitive elements. In lakes, Fe^{2+} and ΣS^{2-} concentrations are closely related with the redox state of the water environment.[31,32] Fe^{2+} and ΣS^{2-} distributions in the pH–ORP field are mapped in **Figure 4**. In well-oxidized water with high ORP and weak alkaline conditions, both Fe^{2+} and ΣS^{2-} concentrations were very low. High levels of Fe^{2+} and ΣS^{2-} were found in relatively low pH and neutral to slightly acidic conditions. Correlation analyses showed that both Fe^{2+} and ΣS^{2-} had significantly negative correlations with pH and ORP (**Figure 5**). In oxic lake water with high ORP and pH, Fe, and S mainly existed in oxidation states of Fe^{3+} and SO_4^{2-}. The species of Fe^{2+} and ΣS^{2-} can be oxidized by plenty of oxidants and are suppressed at very low levels in the overlying water.[33,34] While DO depletion occurred and hypoxia and anoxia formed in the water column, a series change of electron acceptors of oxidation–reduction reactions could be triggered with decreasing in pH and ORP.[29] As the anoxia developed, Fe^{3+} and SO_4^{2-} were used as electrons acceptors in anaerobic respiration and were reduced to Fe^{2+} and ΣS^{2-} eventually.[29,35] As a consequence, sufficient oxidants were no more available for oxidizing the increasing Fe^{2+} and ΣS^{2-} concentrations in the water column. As such, Fe^{2+} and ΣS^{2-} could exist at this low pH and ORP reduced environment, which finally affected the accumulation of Fe^{2+} and ΣS^{2-} in the water columns.

Besides the physical conditions, the transportation and transformation of Fe^{2+} and ΣS^{2-} are closely associated with sediments in lake eco-systems.[20,33,36] The environmental

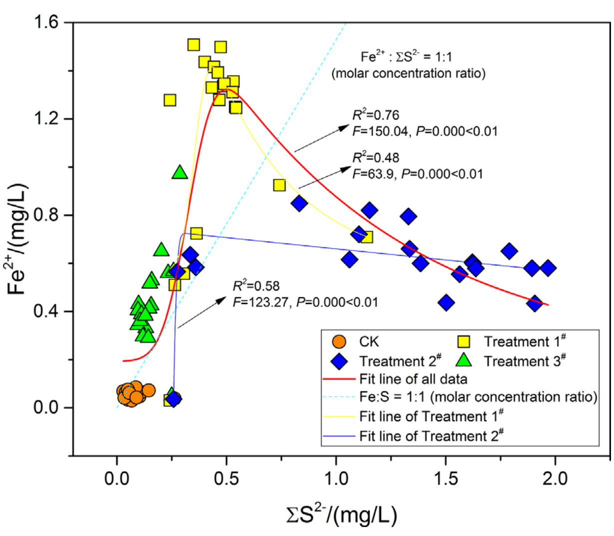

Figure 3. Regression of Fe^{2+} versus ΣS^{2-}. No black bloom occurred in CK and treatment 3#; black blooms occurred in treatments 1# and 2#.

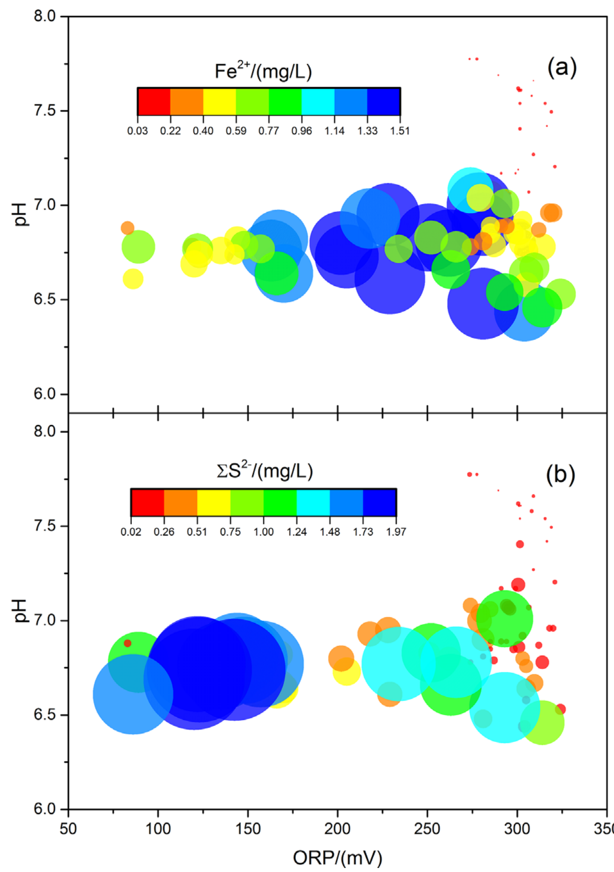

Figure 4. Distribution maps of Fe^{2+} and ΣS^{2-} in pH-ORP system.

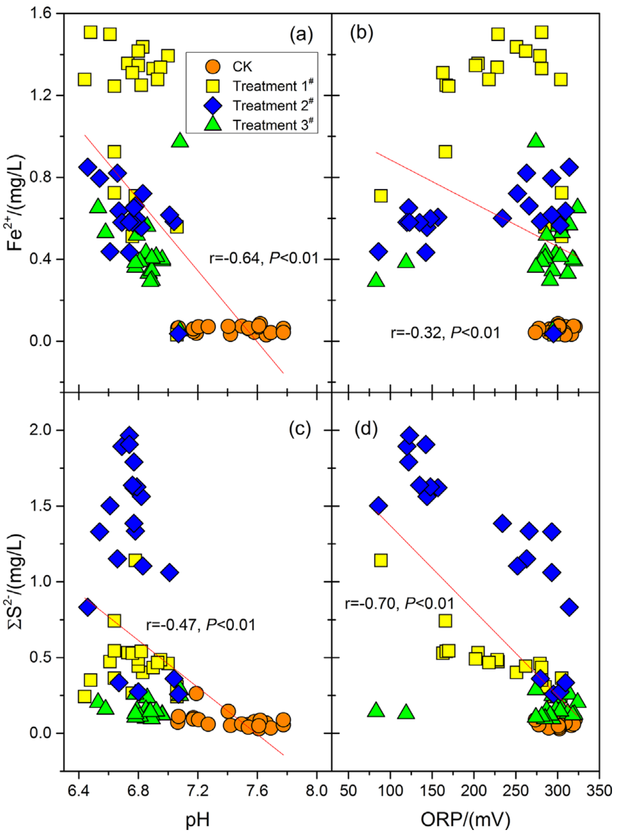

Figure 5. Correlations between Fe^{2+}, ΣS^{2-}, pH, and ORP. No black bloom occurred in CK and treatment 3#; black blooms occurred in treatments 1# and 2#.

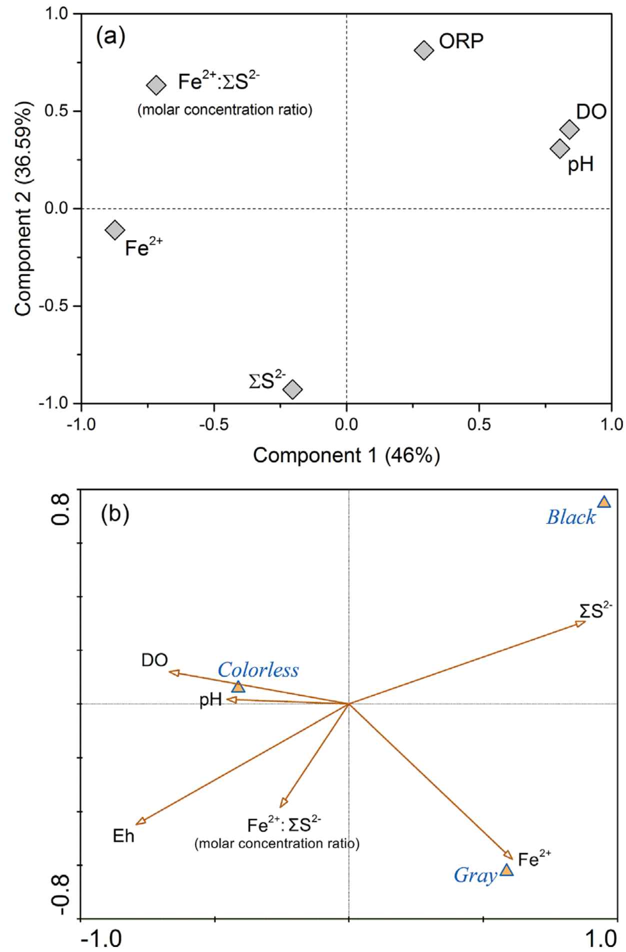

Figure 6. PCA (a) and CCA (b) analysis. Black, gray, and colorless are water colors in simulation columns at every water sampling time.

behavior of Fe^{2+} and ΣS^{2-} at the sediment–water interface is essential to the formation of black blooms.[14] Bulk iron related compounds or ions exist in sediments and pore water. Under hypoxic or anoxic conditions, these iron species in the form of Fe(III) can be reduced to Fe(II) by iron-reducing bacteria either in sediments or pore water.[20,32] During the formation of black bloom, Fe^{2+} concentrations in pore water in upper layers would increase significantly and be released into the overlying water under the concentration gradient. Therefore, Fe^{2+} in the overlying water was supplemented and increased eventually. The accumulation of ΣS^{2-} in water bodies is usually related to the sulfate reduction processes. Accompanied by the revival and proliferation of sulfate-reducing bacteria at the sediment–water interface in severe anoxic environments, SO_4^{2-} nearby the interface might get reduced to the terminal product ΣS^{2-}.[14,18] This is supposed to be the main source of ΣS^{2-} to the overlying water supporting the black bloom in treatments 1# and 2#.

4.3. Influences of Physicochemical Factors on Black Bloom

In order to understand the influence of different physicochemical factors on black bloom, principal factor analysis was employed to determine potential inner relationships. The result is shown in Figure 6a. Firstly, two components, explaining 82.59% of the total accumulated variance, with eigenvalues >1 were extracted. The first component explained 46% of the total variance. In the loading of this component, DO, pH, and Fe^{2+} were the major contributors. DO reflects the hypoxic/anoxic level of the water column; pH along with ORP represent the redox condition; and Fe^{2+} is one of the two direct factors influencing the blackening substance FeS. According to the results of this study, the decrease in DO and pH positively affected the increase in Fe^{2+}. Hence, component 1 shows that anoxic conditions affected Fe^{2+} concentrations leading to the black bloom. The second component explained 36.59% of the total variance. ΣS^{2-} and ORP contribute mostly to loading. Obviously, component 2 shows that redox conditions affected ΣS^{2-} concentrations leading to the black bloom. CCA (Figure 6b) also showed similar results with PCA that Fe^{2+} was greatly affected by DO and pH while ΣS^{2-} was more sensitive with ORP. Moreover, ΣS^{2-} concentration and the black color of water were positively correlated. In the biogeochemical reactions in sediments, electron acceptors (oxidants) are utilized in the order of oxygen, nitrate, metal oxides, and sulfate.[29] During the black bloom formation period, Fe^{2+} always starts to accumulate after the depletion of DO and nitrite. Along with the deepening of hypoxic, ORP decreased quickly and the water column became anoxic, which finally resulted in the accumulation of ΣS^{2-}. The analyses of PCA and CCA in this study coincide with the mechanism of the biogeochemical cycles of Fe and S in sediments. Therefore, the comprehensive results indicate that component 1 provides an anoxic and high Fe^{2+} precondition to the formation of black bloom, while component 2 controls the outbreak of black bloom by the ΣS^{2-} concentration during the formation stage.

5. Conclusions

This study revealed that two feature parameters Fe^{2+} and ΣS^{2-} changed under different conditions during the hypoxic/anoxic stage of the formation of black bloom. Fe^{2+} peaked and decreased before the outbreak of black bloom, whereas ΣS^{2-} increased rapidly during the 12 h before the outbreak. Results also implied that the formation of black blooms is mainly influenced by two components: Fe^{2+} concentrations affected by oxic conditions; and ΣS^{2-} concentrations affected by redox condition. Furthermore, ΣS^{2-} was proven to be the limiting factor controlling the formation of the black bloom. The results are of great importance to the formation mechanism of black bloom and the early warning and pre-control management. However, the biogeochemical transformation and transportation of Fe and S at sediment–water interface need to be further studied in order to uncover the whole formation mechanism of black blooms.

Abbreviations

CCA, canonical correspondence analysis; CK, control check; DMS, dimethyl sulfide; DO, dissolved oxygen; ORP, oxidation reduction potential; PCA, principal component analysis; TN, total nitrogen; TP, total phosphorus.

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Conflict of Interest

The authors have declared no conflict of interest.

Keywords

black bloom, hypoxia, lake, sediment, sulfide

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[1] G. H. Lu, Q. Ma, *J. Lake Sci*. **2010**, *22*, 481.
[2] M. Yang, J. W. Yu, Z. L. Li, Z. H. Guo, M. Burch, T. F. Lin, *Science* **2008**, *319*, 158.
[3] X. J. Zhang, C. Chen, J. Q. Ding, A. X. Hou, Y. Li, Z. B. Niu, X. Y. Su, Y. J. Xu, E. A. Laws, *J. Hazard. Mater.* **2010**, *182*, 130.
[4] B. Q. Qin, G. W. Zhu, G. Gao, Y. L. Zhang, W. Li, H. W. Paerl, W. W. Carmichael, *Environ. Manage*. **2010**, *45*, 105.
[5] Q. S. Shen, Q. L. Zhou, J. G. Shang, S. G. Shao, L. Zhang, C. X. Fan, *J. Environ. Sci*. **2014**, *26*, 281.
[6] J. B. Stahl, *Water Res*. **1979**, *13*, 467.
[7] B. Duval, S. D. Ludlam, *Int. Rev. Hydrobiol*. **2001**, *86*, 165.
[8] T. Rixen, A. Baum, T. Pohlmann, W. Balzer, J. Samiaji, C. Jose, *Biogeochemistry* **2008**, *90*, 129.
[9] H. Rai, G. Hill, *Int. Rev. Gesamten Hydrobiol*. **1981**, *66*, 37.
[10] S. Pucciarelli, F. Buonanno, G. Pellegrini, S. Pozzi, P. Ballarini, C. Miceli, *Environ. Res*. **2008**, *107*, 194.
[11] C. Neira, M. Rackemann, *J. Sea Res*. **1996**, *36*, 153.
[12] A. Rusch, H. Topken, M. E. Bottcher, T. Hopner, *J. Sea Res*. **1998**, *40*, 205.
[13] R. J. Diaz, R. Rosenberg, *Science* **2008**, *321*, 926.
[14] Q. S. Shen, C. Liu, Q. L. Zhou, J. G. Shang, L. Zhang, C. X. Fan, *J. Environ. Sci*. **2013**, *25*, 2353.
[15] X. F. Fan, P. Xing, *Archaea* **2016**, 8232135.
[16] W. He, J. G. Shang, X. Lu, C. X. Fan, *J. Environ. Sci*. **2013**, *25*, 430.
[17] Q. S. Shen, S. G. Shao, Z. D. Wang, L. Zhang, H. Y. Hu, C. X. Fan, *Chin. Sci. Bull*. **2012**, *57*, 1060.
[18] Z. Y. Feng, C. X. Fan, W. Y. Huang, S. M. Ding, *Sci. Total Environ*. **2014**, *470-471*, 1.
[19] Q. S. Shen, C. X. Fan, *J. Lake Sci*. **2015**, *27*, 591.
[20] V. Galman, J. Rydberg, A. Shchukarev, S. Sjoberg, *J. Paleolimnol*. **2009**, *42*, 141.
[21] B. Q. Qin, *J. Freshwater Ecol*. **2015**, *30*, 1.
[22] B. Q. Qin, W. Li, G. W. Zhu, Y. L. Zhang, T. F. Wu, G. Gao, *J. Hazard. Mater.* **2015**, *287*, 356.
[23] H. W. Paerl, H. Xu, M. J. McCarthy, G. W. Zhu, B. Q. Qin, Y. P. Li, W. S. Gardner, *Water Res*. **2011**, *45*.
[24] C. X. Fan, Chinese Patent **2004**, CN200410014329.X.
[25] B. S. You, J. C. Zhong, C. X. Fan, T. C. Wang, L. Zhang, S. M. Ding, *J. Environ. Sci*. **2007**, *19*, 1055.
[26] C. Liu, Q. S. Shen, Q. L. Zhou, C. X. Fan, S. G. Shao, *Ecol. Eng*. **2015**, *77*, 139.
[27] L. L. Stookey, *Anal. Chem*. **1970**, *42*, 779.
[28] J. D. Cline, *Limnol. Oceanogr.* **1969**, *14*, 454.
[29] J. J. Middelburg, L. A. Levin, *Biogeosciences* **2009**, *6*, 1273.
[30] H. T. Duan, R. H. Ma, S. A. Loiselle, Q. S. Shen, H. B. Yin, Y. C. Zhang, *Sci. Total Environ*. **2014**, *482*, 174.
[31] A. V. Leonov, O. V. Chicherina, *Water Resour.* **2008**, *35*, 417.
[32] B. Luef, S. C. Fakra, R. Csencsits, K. C. Wrighton, K. H. Williams, M. J. Wilkins, K. H. Downing, P. E. Long, L. R. Comolli, J. F. Banfield, *ISME J*. **2013**, *7*, 338.
[33] M. Holmer, P. Storkholm, *Freshwater Biol*. **2001**, *46*, 431.
[34] G. Jost, W. Martens-Habbena, F. Pollehne, B. Schnetger, M. Labrenz, *FEMS Microbiol. Ecol*. **2010**, *71*, 226.
[35] L. P. Nielsen, N. Risgaard-Petersen, H. Fossing, P. B. Christensen, M. Sayama, *Nature* **2010**, *463*, 1071.
[36] B. B. Jorgensen, *Limnol. Oceanogr.* **1977**, *22*, 814.