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In situ enclosure experiments on the occurrence, development and decline of black bloom and the dynamics of its associated taste and odor compounds

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ABSTRACT

Black bloom has an offensive odor (caused by, e.g., dimethyl sulfide, DMS; dimethyl disulfide, DMDS; and dimethyl trisulfide, DMTS) and disastrous consequences for natural limnic ecosystems worldwide. However, research on black bloom and its taste and odor (T&O) compounds has been limited by the difficulty of predicting the time and location of black bloom events. Therefore, the occurrence, development and decline of black bloom and the dynamics of T&O compounds in each stage of black bloom were examined in Meiliang Bay, Lake Taihu, through an in situ enclosure (2.5 m × 2.5 m) simulation experiment with various levels of cyanobacterial biomass (0 g m^{-2}, 1500 g m^{-2}, 7500 g m^{-2} and 15,000 g m^{-2}, fresh weight). The principal odor-related substances and the physicochemical parameters were analyzed every two or three days. Black blooms occurred in the moderate (7500 g m^{-2}) and high (15,000 g m^{-2}) cyanobacterial biomass treatments concurrently on day 5 but did not occur in the low cyanobacterial biomass (1500 g m^{-2}) treatment or in the control group (0 g m^{-2}). Thus, black bloom could be induced by the decay of dense cyanobacterial populations under suitable meteorological and hydrographic conditions. As the extent of black bloom increased, the concentrations of nutrients (e.g., ammonium nitrogen and total phosphorus), odorous compounds, and total divalent anionic sulfur and the duration of low dissolved oxygen levels increased, whereas the pH decreased. In addition, linear regression analysis revealed that the concentrations of odorous compounds in the water column were significantly correlated with changes in certain physicochemical parameters (e.g., chlorophyll *a*, pH) and these changes were mainly induced by the breakdown of the cyanobacterial bloom. Overall, our study revealed that (i) the extent of black bloom (e.g., level of black water color, concentrations of offensive odor compounds and duration) is strongly influenced by cyanobacterial biomass; and (ii) extremely high concentrations of T&O compounds may originate from the decomposition of cyanobacteria.

1. Introduction

Black bloom, also known as black water agglomerate, is a serious natural ecosystem disaster that occurs worldwide in freshwater lakes and along seashores (Berthon and Zibordi, 2010; Pucciarelli et al., 2008). This phenomenon often occurs during the summer (Lu and Ma, 2009). Public concern about black bloom was triggered by the recent potable water crisis in the city of Wuxi. A black color and a strong offensive odor are the two most characteristic features of black bloom (Zhang et al., 2010). The offensive odorous compounds can lead to worse economic losses (Freuze et al., 2004). However, research on black bloom and its associated taste and odor (T&O) compounds has been limited by the difficulty of predicting the time and location of black bloom events (He et al., 2013).

Studies have suggested that β-cyclocitral, β-ionone and volatile organic sulfur compounds (VOSCs), such as dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS), are the major compounds responsible for the strong offensive odor of black bloom (Duval and Ludlam, 2001; Shen et al., 2014). Zhang et al. (2010) reported that DMS, DMDS, DMTS and β-cyclocitral reached the notably high concentrations of 93.9, 46.1, 17.2 and 21.0 μg L^{-1}, respectively, during the water crisis in Wuxi City, and Yang et al.

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Fig. 1. The black bloom that occurred in Lake Taihu.

(2008) reported that DMTS reached 11.7 and 1.8 $\mu g\,L^{-1}$ at two separate sampling sites on another sampling day. Additionally, a high concentration of DMS was also detected in black bloom induced by submerged plants (Shen et al., 2014). However, these reports were based on casual field follow-up investigations without continuous monitoring. Little is known about the dynamics of T&O compounds during the entire black bloom process.

Black bloom may be induced by algal blooms (Lu and Ma, 2009). Ma et al. (2013) showed that the decay of cyanobacterial blooms could induce anoxic water conditions, decrease pH, and increase nutrient loading in the lake water. The water in the enclosures was black and malodorous. Moreover, DMS, DMTS and β-cyclocitral simultaneously reached extremely high levels, with maxima of 62.33, 12.41 and 1.37 $\mu g\,L^{-1}$, respectively. Liu et al. (2015) suggested that sediment dredging at an appropriate depth could suppress the occurrence of black bloom but could not suppress the offensive odor. Feng et al. (2014) suggested that sulfide-reducing bacteria (SRB) and protein are the principal biological and organic factors, respectively, that contribute to the occurrence of black bloom. Most studies have primarily focused on the mechanism of black bloom occurrence. However, the development and decline of black bloom and the related T&O compounds in each stage remain unclear. Furthermore, little is known about how cyanobacterial biomass affects black bloom and T&O compounds.

The present study sought to address these knowledge gaps by conducting black bloom simulation experiments in Meiliang Bay, Lake Taihu, China, using various levels of cyanobacterial biomass. The dynamics of the T&O compounds, as well as those of water quality parameters, were continuously monitored in all enclosures until the black bloom disappeared. We also compared these findings to results that were previously collected from a natural black bloom (Fig. 1) in the mid- to late stage in June 2013 in Gonghu Bay, Lake Taihu. Fortunately, the development and decline of black bloom and the related T&O compounds in the in situ simulation experiment were consistent with the survey results from the natural black bloom. These results provide new insights that may help clarify the relationship between T&O compounds and factors relevant for better incident prediction, warning and prevention in the future.

2. Materials and methods

2.1. Study site

Lake Taihu (30°55′40″-31°32′58″N, 119°52′32″-120°36′10″E), the third largest freshwater lake in China, is a typical large and shallow eutrophic subtropical lake (surface area: 2338 km^2, mean depth: 1.9 m). Many serious black bloom incidents have recently occurred in Lake Taihu, particularly along the western and northern shorelines (Duan et al., 2014). In Meiliang Bay, in the northern part of Lake Taihu, enclosures have been deployed approximately 200 m away from the eastern shoreline. As a result of nutrient pollution, Meiliang Bay is eutrophic and experiences intensive blooms of algae (mostly cyanobacteria) during summer (Tang et al., 2014).

2.2. Experimental design

Twelve enclosures (2.5 m × 2.5 m) were constructed from waterproof polyvinyl chloride. The enclosures were open to the atmosphere and to the bottom sediment and were supported by four rigid horizontal hoops. The mean water depth in all enclosures was approximately 1.5 m. To prevent waves and rising water from entering, the enclosure walls were extended approximately 1 m above the mean water level. To minimize the artificial disturbances of the enclosure construction, the enclosures were left untreated for two weeks before the addition of cyanobacteria. Samples were collected from each enclosure on July 31, 2014, one day before adding cyanobacteria as a reference. The bloom cyanobacteria used in this work were collected from a cove on Meiliang Bay. The fresh cyanobacteria were centrifuged at 1500 r/min for 5 min, yielding a water content of approximately 65%, calculated according to previously reported methods (Liu et al., 2010). The cyanobacteria were alive when they were added to the enclosures. Four treatments with different levels of cyanobacterial biomass were applied: control (0 $g\,m^{-2}$, C), low cyanobacterial biomass (1500 $g\,m^{-2}$, L), moderate cyanobacterial biomass (7500 $g\,m^{-2}$, M), and high cyanobacterial biomass (15,000 $g\,m^{-2}$, H). Each treatment was performed in triplicate. Immediately after the addition of the cyanobacteria, the water in the enclosures was mixed by stirring with an oar. Experiments were terminated when the water column became colorless in all enclosures. Samples were collected every two or three days based on the changes in water quality parameters during the study period, beginning on day 1 (1 August, 2014).

2.3. Sampling and analyses

Samples were obtained between 10:00 AM and 1:00 PM at a single depth (0.5 m below the water surface) in the center of each enclosure. Samples for the analysis of total divalent anionic sulfur ($\sum S^{2-}$) were immediately transferred into bottles containing zinc acetate to prevent oxidation. Samples for evaluating T&O compounds and inorganic nutrients were collected in 1-L narrow-neck PE bottles with no headspace and stored immediately in a portable refrigerator at approximately 4 °C before transport to the laboratory. Upon arrival in the laboratory, all samples for the analysis of off-flavor were stored at −20 °C for no more than 5 days before analysis.

Water temperature, dissolved oxygen (DO), pH and total dissolved solid (TDS) were measured in situ using a HORIBA water quality monitor (HORIBA, Ltd. Kyoto Japan). Total nitrogen (TN), ammonium nitrogen (NH_4-N), total phosphorus (TP), $\sum S^{2-}$ ($\Sigma S^{2-} = H_2S + HS^- + S^{2-}$) and chlorophyll *a* were analyzed according to standard methods (Jin and Tu, 1990).

To estimate the T&O compounds, a 300-mL water sample was filtered through a Whatman GF/C fiberglass filter. The filtrate was analyzed for dissolved T&O compounds in water. The T&O compounds were analyzed with a P&T extraction device coupled with GC–MS according to Chen et al. (2010a) and Deng et al. (2011).

2.4. Statistical analysis

Correlations between water quality variables and T&O compounds were identified using Pearson's correlation coefficient

method implemented with SPSS 19.0 software. All data except pH were log(x + 1) transformed to meet homogeneity and normalization (He et al., 2015). Significance levels are marked as * (significant, $0.01 < p < 0.05$) or ** (highly significant, $p < 0.01$). All graphs were plotted using Origin 8.5 software.

3. Results

3.1. Black bloom profile

Microscopic determination revealed that the cyanobacteria *Microcystis* spp. accounted for more than 95% of the total phytoplankton used in the present study. No significant differences in water quality parameters (e.g., TN, chlorophyll *a* and DO) and T&O compounds (e.g., DMS and DMTS) were observed among the twelve enclosures prior to the addition of cyanobacteria ($p > 0.05$). The salient features of algae-caused black bloom are the black color and the odor of the water. However, odor alone is not sufficient to identify a black bloom because the causes of odors in natural waters are complicated and diverse. Therefore, the beginning and end of black bloom were defined as the appearance and disappearance of light black color. Previous studies described a classification method that defined artificial levels to describe the water color (He et al., 2013; Rusch et al., 1998). In the present study, the water color observed in our experiment was classified according to 5 levels, 0, 1, 2, 3 and 4, corresponding to colorless, gray, light black, black, and deep black, respectively. In groups C and L, the water remained colorless or gray throughout the study. Black bloom concurrently occurred on day 5 (level 2) and then disappeared after day 18 and day 24 in groups M and H, respectively. In addition, the level of the black color was deeper in group H than group M during the early stage of the experiment (Table 1).

3.2. Changes in chemical and physical water quality parameters

The mean water temperature was approximately 26.1–33.6 °C in all enclosures. Due to the addition of fresh cyanobacteria, the chlorophyll *a* concentrations reached extremely high levels (1.28, 4.04 and 4.90 mg L^{-1} in L, M and H, respectively) in those treatments, followed by a sharp decrease within a few days. TDS increased with increasing cyanobacterial biomass. The maximum TDS values reached 0.344, 0.439 and 0.560 mg L^{-1} concurrently on day 7 in groups L, M and H, respectively (Table 2).

Extremely low DO in the water column is another obvious feature of black bloom. As shown in Fig. 2A, DO decreased abruptly to zero on day 1 in M and H groups and on day 3 in group L, after which it remained at zero concentration. With the addition of more cyanobacterial biomass, extremely low DO was observed for longer periods of time. By contrast, the DO remained at a relatively high level in group C. The addition of greater cyanobacterial biomass was associated with lower pH (Fig. 2B); the pH values in group C never fell below 7.3. However, in the treatment groups, pH decreased sharply after the addition of cyanobacteria, with the minimum values concurrently observed on day 5 followed by gradual increases. As shown in Fig. 2C, the concentrations of $\sum S^{2-}$ remained low and never exceeded 0.4 mg L^{-1} in group C. However, the values in groups L, M and H peaked at 0.86, 9.9 and 12.2 mg L^{-1} on day 7 after a sharp increase and were nearly 100-, 1100- and 1400-fold greater, respectively, than that of group C at the same time point. Then, the concentrations declined steadily until day 27 and then remained at a low level.

The changes in TN, TP and NH_4-N are illustrated in Fig. 3. The initial increases in TN and TP were mainly due to the addition of fresh cyanobacteria. The concentrations of TN and TP peaked on day 3 and then gradually declined to low levels in all treatment groups.

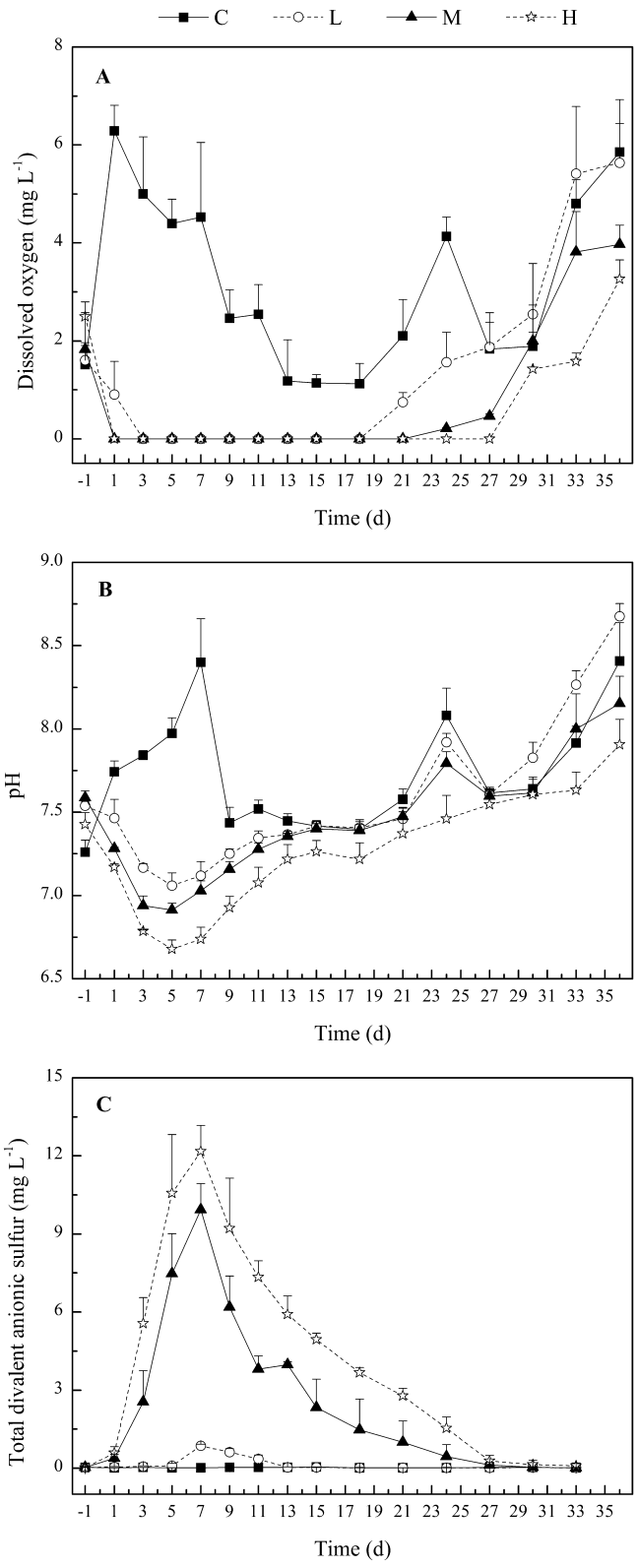

Fig. 2. Changes in dissolved oxygen, pH and total divalent anionic sulfur in the water column ($n = 3$). C: control group; L: low cyanobacteria biomass; M: moderate cyanobacteria biomass; H: high cyanobacteria biomass.

All groups had similar low concentrations of NH_4-N on day 1. However, after a sudden increase, the NH_4-N concentrations peaked on day 9 in groups M and H, reaching 16.6 and 37.0 mg L^{-1}, respectively, nearly 53 and 119 times the level in group C at the same

Table 1
Changes in water color during the experiment.

	Day −1	Day 1	Day 3	Day 5	Day 7	Day 9	Day 11	Day 13	Day 15	Day 18	Day 21	Day 24	Day 27	Day 30	Day 33	Day 36
C	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
L	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
M	0	1	1	2	3	3	3	2	2	2	1	0	0	0	0	0
H	0	1	1	2	4	4	4	3	3	2	2	2	1	1	0	0

Note: C: control group; L: low cyanobacteria biomass; M: moderate cyanobacteria biomass; H: high cyanobacteria biomass.

Table 2
Water quality parameters in the enclosures with different treatments.

Water quality parameters	C	L	M	H
Water temperature (°C)	26.1–33.4	26.3–33.6	26.1–33.5	26.1–33.4
chlorophyll *a* ($mg\,L^{-1}$)	0.02–0.18	0.03–1.28	0.03–4.04	0.02–4.90
TDS ($mg\,L^{-1}$)	0.305–0.335	0.307–0.344	0.311–0.439	0.321–0.560

Note: C: control group; L: low cyanobacteria biomass; M: moderate cyanobacteria biomass; H: high cyanobacteria biomass.

time point (Fig. 3C). By contrast, the values of TN, TP and NH_4-N remained relatively low and constant in the control treatment.

3.3. Dynamics of taste and odor compounds

The changes in the T&O compounds over time in the different cyanobacterial biomass treatment groups are presented in Fig. 4. DMS, DMDS and DMTS followed similar trends. The concentrations of DMS, DMDS and DMTS simultaneously reached extremely high levels on day 7 after a sharp increase in the early period of the experiment. In addition, the maximal values reached 44.7, 78.8, and 96.4 $\mu g\,L^{-1}$ for DMS; 4.5, 18.4, and 27.8 $\mu g\,L^{-1}$ for DMDS; and 6.5, 36.3, and 51.3 $\mu g\,L^{-1}$ for DMTS in groups L, M and H, respectively. The highest concentrations of β-cyclocitral and β-ionone in the treatment groups (6.6, 85.8, 144.6 for β-cyclocitral; and 0.2, 1.2, 2.1 $\mu g\,L^{-1}$ for β-ionone in groups L, M and H, respectively) occurred simultaneously on day 3. These values far exceeded their olfactory threshold concentrations. Then, these concentrations gradually decreased until the end of the experiment. However, in group C, concentrations of these T&O compounds remained low and relatively stable. In addition, the concentrations of these T&O compounds increased with increasing cyanobacterial biomass.

3.4. The relationships between taste and odor compounds and changes in the aquatic environment

Generally, no significant correlations (e.g., NH_4-N and ΣS^{2-}) or significant correlations with a low r^2 (e.g., TP and DO) were observed for T&O compounds release and water quality parameters in group C (Table 3). By contrast, highly significant ($p < 0.01$) positive correlations were observed between T&O compounds release

Table 3
Pearson's correlation matrix for various characteristics of the water samples.

		DMS	DMDS	DMTS	β-Cyclocitral	β-Ionone
C	ΣS^{2-}					
	TN		0.14^{**}	0.18^{**}	0.14^{**}	
	NH_4-N					
	TP		0.25^{**}	0.28^{**}	0.34^{**}	
	Chlorophyll *a*		0.27^{**}	0.32^{**}	0.24^{**}	
	pH					
	DO	0.17^{**}			0.27^{**}	
L	ΣS^{2-}	0.51^{**}	0.42^{**}	0.43^{**}	0.27^{**}	0.24^{**}
	TN	0.56^{**}	0.66^{**}	0.71^{**}	0.71^{**}	0.65^{**}
	NH_4-N	0.32^{**}	0.29^{**}	0.22^{**}	0.27^{**}	0.27^{**}
	TP	0.29^{**}	0.35^{**}	0.36^{**}	0.51^{**}	0.52^{**}
	Chlorophyll *a*			0.09^{*}	0.15^{**}	
	pH	-0.44^{**}	-0.47^{**}	-0.50^{**}	-0.45^{**}	-0.49^{**}
	DO	-0.42^{**}	-0.40^{**}	-0.41^{**}	-0.38^{**}	-0.46^{**}
M	ΣS^{2-}	0.74^{**}	0.69^{**}	0.77^{**}	0.61^{**}	0.72^{**}
	TN	0.59^{**}	0.55^{**}	0.50^{**}	0.74^{**}	0.55^{**}
	NH_4-N	0.19^{**}	0.17^{**}	0.24^{**}	0.24^{**}	0.34^{**}
	TP	0.60^{**}	0.62^{**}	0.53^{**}	0.85^{**}	0.64^{**}
	Chlorophyll *a*	0.27^{**}	0.31^{**}	0.20^{**}	0.38^{**}	0.20^{**}
	pH	-0.70^{**}	-0.72^{**}	-0.71^{**}	-0.83^{**}	-0.69^{**}
	DO	-0.34^{**}	-0.31^{**}	-0.30^{**}	-0.52^{**}	-0.33^{**}
H	ΣS^{2-}	0.76^{**}	0.71^{**}	0.81^{**}	0.66^{**}	0.82^{**}
	TN	0.70^{**}	0.66^{**}	0.66^{**}	0.81^{**}	0.69^{**}
	NH_4-N	0.22^{**}	0.19^{**}	0.28^{**}	0.24^{**}	0.40^{**}
	TP	0.70^{**}	0.70^{**}	0.69^{**}	0.89^{**}	0.74^{**}
	Chlorophyll *a*	0.55^{**}	0.59^{**}	0.48^{**}	0.54^{**}	0.41^{**}
	pH	-0.76^{**}	-0.86^{**}	-0.84^{**}	-0.82^{**}	-0.81^{**}
	DO	-0.34^{**}	-0.31^{**}	-0.31^{**}	-0.57^{**}	-0.36^{**}

Note: Asterisks denote highly significance at the $p < 0.01$ (**) and significant, $0.01\ p < 0.05$ (*) levels. C: control group; L: low cyanobacteria biomass; M: moderate cyanobacteria biomass; H: high cyanobacteria biomass.

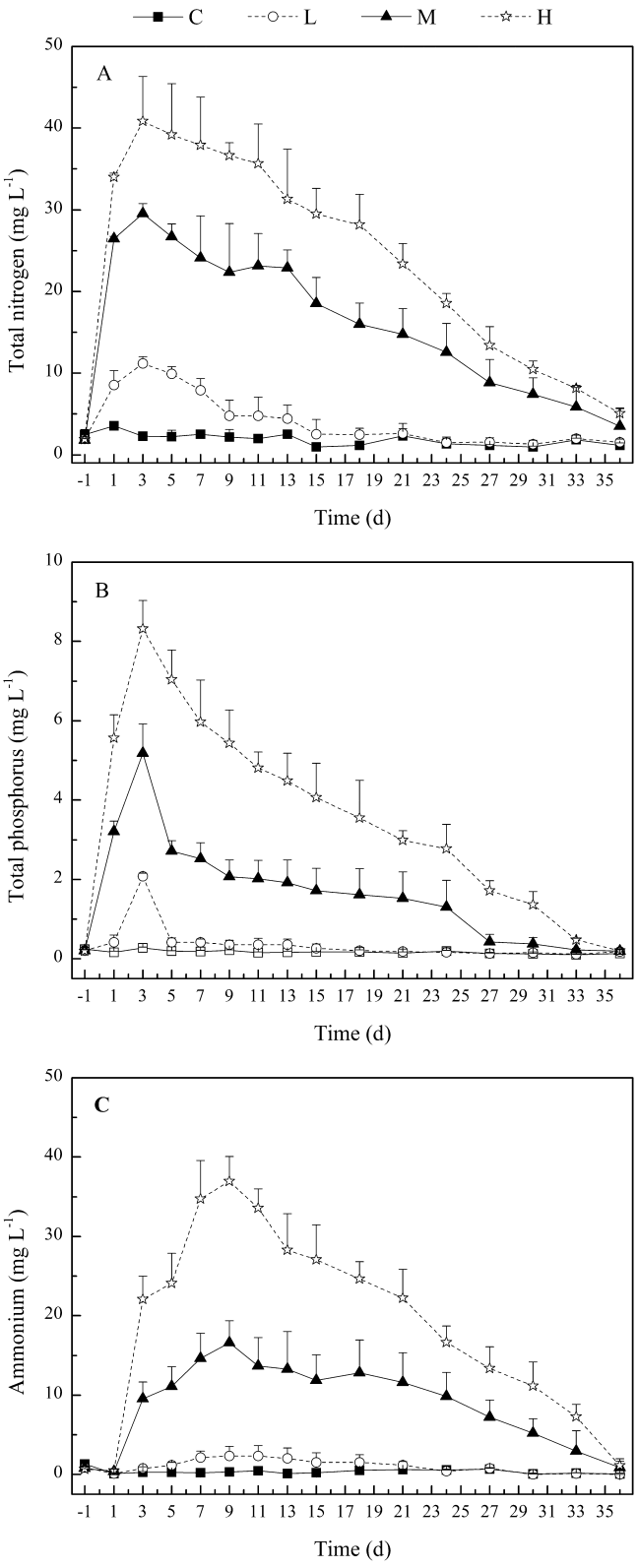

Fig. 3. Variations in total nitrogen, total phosphorus and ammonium in the water column ($n = 3$). C: control group; L: low cyanobacteria biomass; M: moderate cyanobacteria biomass; H: high cyanobacteria biomass.

and ΣS^{2-}, TP and TN, and highly significant ($p < 0.01$) negative correlations were observed for pH and DO in group L. Similarly, in groups M and H, which exhibited black bloom, the concentrations of the T&O compounds were highly negatively correlated ($p < 0.01$) with pH and DO but positively correlated ($p < 0.01$) with chlorophyll *a*, ΣS^{2-}, TN and TP. In addition, higher r^2 values were obtained for certain water quality parameters (TN, ΣS^{2-} and pH) at higher cyanobacterial biomass.

4. Discussion

4.1. Black bloom is affected by cyanobacterial biomass

In this study, an experiment was designed to study the occurrence, development and decline of black bloom and the variation in related T&O compounds during each stage. Our results demonstrated that black bloom can be induced by a dense cyanobacterial bloom. The only apparent difference among the four groups at beginning of the experiment was the cyanobacterial biomass. However, black blooms occurred in groups M and H, but not in groups L and C, indicating that the occurrence of black bloom was dependent on the addition of cyanobacterial biomass under suitable meteorological and hydrographic conditions. The rapid decay of dense cyanobacterial biomass can produce extremely low DO level, high nutrient release (Diaz and Rosenberg, 2008; He et al., 2009) and favorable concentrations of other factors, resulting in the occurrence of black bloom.

Our study indicated that the level of black bloom was significantly affected by the cyanobacterial biomass. The water color was deeper in group H than in group M during the early stages of the experiment, indicating that the black bloom was more severe in group H. Aqueous sulfides promote metal sulfide production, and the key factor responsible for the black color in natural waters is metal sulfides (particularly FeS) (Duval and Ludlam, 2001; Stahl, 1979). Significantly higher concentrations of ΣS^{2-} were observed as the cyanobacterial biomass in the water increased (Fig. 2C) in present study. Thus, a higher cyanobacterial biomass would cause the accumulation of more metal sulfides, thereby darkening the water color. In addition, black blooms are always accompanied by low DO, low pH, and a high concentration of nutrients (e.g., NH_4-N and TP). Thus, the severity of a black bloom could be indicated by the levels of these parameters. In this study, a lower pH and higher concentrations of nutrients (i.e., TN, TP and NH_4-N) (Figs. 2 and 3) were observed as the cyanobacterial biomass increased, consistent with the results of many studies of the process of cyanobacterial decay (Chuai et al., 2011). This result is an indirect indication that the severity of black blooms may increase with higher cyanobacterial biomass.

In addition, our results indicated that the time of occurrence of black bloom was not affected by the cyanobacterial biomass. Black blooms were observed on day 5 in groups M and H. Minimum values of pH and maximum concentrations of nutrients and ΣS^{2-} were observed on the same day in all cyanobacterial treatments, suggesting that a dense cyanobacteria load is essential for the occurrence of black bloom but that the timing of black bloom is related to as yet unidentified factors, such as the bacterial community composition and abundance (Feng et al., 2014; Li et al., 2011).

However, the decline of black bloom was delayed with higher cyanobacterial biomass. In this study, the black bloom was sustained for 14 and 20 days in groups M and H, respectively. Moreover, a longer duration of low DO and high concentrations of NH_4-N and ΣS^{2-} were also observed in enclosures with higher cyanobacterial biomass. This relationship may be explained as follows. The addition of more cyanobacteria induced the accumulation of more cyanobacteria on the water surface. Thus, the organic matter in the water column would be constantly replenished as surface cyanobacteria were added until no more cyanobacteria accumulated on the water surface. In addition, under the same meteorological and hydrographic conditions, reducing a higher concentration of organic matter to a specified lower level requires

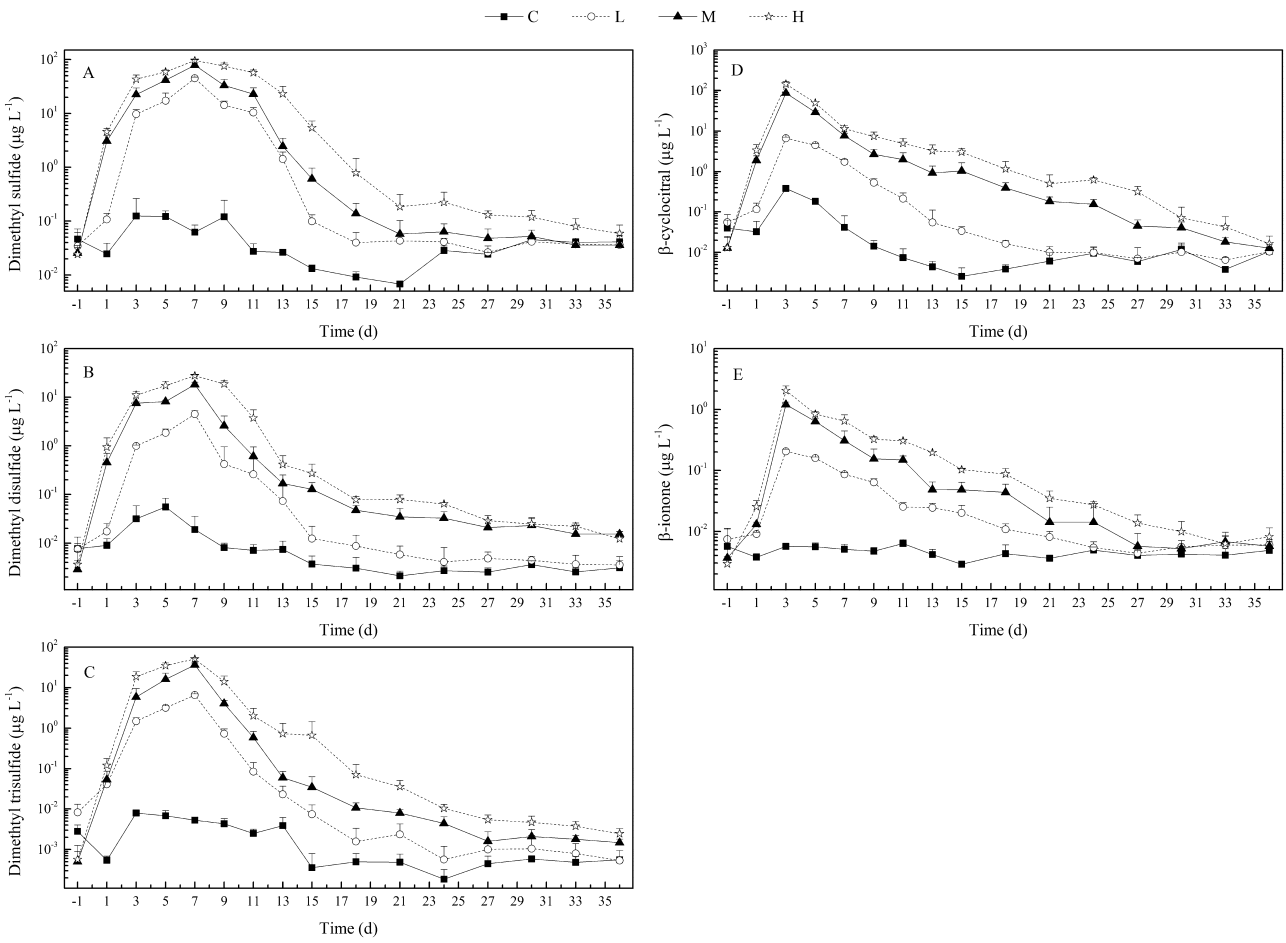

Fig. 4. Variations in taste and odor compounds in the water column ($n = 3$). C: control group; L: low cyanobacteria biomass; M: moderate cyanobacteria biomass; H: high cyanobacteria biomass.

additional time (Kirchman et al., 1991). Thus, the duration of black bloom is obviously affected by the cyanobacterial biomass.

4.2. Dynamics of taste and odor compounds in black bloom

A strong offensive odor is one of the two definitive characteristics of black bloom (Zhou et al., 2015). Our results indicated that the concentrations of T&O compounds (e.g., DMS, DMDS and DMTS) were correlated with the severity of black bloom. Certain water quality parameters (e.g., pH, TN and NH_4-N) could indicate the severity of black bloom, as discussed above. In this study, regression analysis demonstrated that T&O compounds were highly correlated with certain water quality parameters (e.g., TN, pH and ΣS^{2-}) in groups M and H, which exhibited black bloom. These strong relationships are also supported by several previous studies (Downing et al., 2010; Qi et al., 2012). In addition, the absolute value of r^2 was generally higher in group H than in group M. These results indirectly suggest that T&O compounds are strongly correlated with black bloom.

In addition, our results indicated that the variations in the T&O compounds were consistent with the variation in the black bloom. In this study, the extent of the black bloom initially increased rapidly and then progressively declined in the middle to late stages of the experiment. The concentrations of T&O compounds exhibited a similar pattern of variation, with a considerable increase during the early stages followed by a gradual decrease. Moreover, similar variations could be further confirmed by the highly significant correlations ($p < 0.01$) between the T&O compounds and certain water quality parameters (Table 3). These variations can be explained as follows. For the VOSCs, stored dimethylsulfoniopropionate (DMSP) in the algal cells could first be released into the ambient water column during the massive and rapid anaerobic algal decay (Ginzburg et al., 1998). Then, DMSP could lead to a rapid increase in DMS production by other microbes and via physicochemical degradation (Li et al., 2011). Second, microbial degradation of sulfur-containing organic compounds is another important mechanism of VOSC production (Drotar et al., 1987). The wild algae in this study were collected from Meiliang Bay in Lake Taihu, where crude protein accounts for more than 40% of the cyanobacterial dry weight (Fan, 1999; Villacorte et al., 2015). Sulfur-containing amino acids (i.e., methionine and cysteine) can provide copious available sulfur for SRB (Lu et al., 2013) and compensate for the lack of available sulfur in lake sediments.

As for β-cyclocitral and β-ionone, which have been identified as metabolites of *Microcystis* spp. (Watson, 2003; Watson et al., 2008), both can be released during the growth of *Microcystis* spp. and by the disruption of their cellular integrity (Suurnakki et al., 2015). In addition, because β-cyclocitral has lytic activity against cyanobacteria (Arii et al., 2015), a high concentration of β-cyclocitral would accelerate the decomposition of the cyanobacteria in the bloom, further increasing the release of β-cyclocitral and VOSCs.

In this study, the concentrations of these five T&O compounds in all of the cyanobacterial treatments far exceeded their OTCs. The water samples from all of these columns emitted a strong

offensive odor, while the water column in the control group was odorless throughout the simulation. Moreover, high correlations were observed between T&O compounds and certain water quality parameters (e.g., TN, pH and ΣS^{2-}) (Table 3) in all cyanobacterial treatments. These changes in chemical parameters were mainly induced by the decay of *Microcystis* (Chen et al., 2010b). Therefore, the decomposition of massive cyanobacterial blooms may be the primary source of the high concentrations of T&O compounds.

4.3. Field verification

In June 2013, we encountered a mid- to late-stage black bloom along the north shore of Gonghu Bay, Lake Taihu, that lasted approximately ten days with a maximum area of approximately 4.0 km^2. The strong offensive odor was apparent in a village near the shore. There was an obvious boundary line between the black bloom area and the normal area (Fig. 1). Large amounts of gas bubbled up continuously, and dead fish were observed in the black bloom area. In the black bloom area, the DO concentration in the water column was less than 1 $mg\,L^{-1}$, and this concentration persisted for at least six days. The major T&O compounds were dissolved DMS, DMDS, DMTS, and β-cyclocitral, with maximum values of 165.8, 25.5, 4.5 and 6.5 $\mu g\,L^{-1}$, respectively, on 21 June. These contaminants declined considerably over a few days. In addition, the concentrations of TN, TP and NH_4-N were obviously higher in the black bloom area than in the normal area, whereas the pH was lower in the black bloom area than in the normal area (Fig. 1S). The similar patterns of variation of the characteristic physical and chemical parameters and the concentrations of the major T&O compounds suggest that the results of the present simulation experiment will have practical value for the water resource managers of Taihu Lake in evaluating the probability of black bloom incidents.

5. Conclusions

This study was designed to investigate the occurrence, development and decline of a black bloom and the dynamics of T&O compounds during each stage of a black bloom. The black bloom was strongly affected by the cyanobacterial biomass. Although the time of the initial occurrence of black bloom was only slightly affected by the cyanobacterial biomass, the length of the black bloom event increased with higher cyanobacterial biomass. Furthermore, our results indicated that the concentrations of T&O compounds were closely correlated with the level of the black bloom, and the concentrations of these odorous compounds rapidly increased and peaked in the early stages, then gradually declined. These patterns of variation were very similar to those observed in a natural black bloom. The primary source of the extremely high concentrations of T&O compounds is likely the decomposition of the dense cyanobacterial bloom.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ecoleng.2015.11.039.

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