

Removal of volatile organic sulfur compounds by aeration during algae-induced black blooms in shallow lakes

Cheng Liu, Shiguang Shao, Chengxin Fan and Qiushi Shen

ABSTRACT

High levels of volatile organic sulfur compounds (VOSCs) have frequently been detected during algae-induced black blooms, which pose an ecological threat to water bodies and their surrounding residents. In this study, aeration was applied to remove the VOSCs after the outbreak of a black bloom. The removal efficiencies under different aeration rates (A1 (0.06 m³-air min⁻¹ m⁻³), A2 (0.18 m³-air min⁻¹ m⁻³), and A3 (0.54 m³-air min⁻¹ m⁻³)) were compared. For treatments A2 and A3, the level of dissolved oxygen (DO) and the oxidation-reduction potential (Eh) increased sharply after 1 h of aeration, and about 70% of the VOSCs were removed from the water columns; however, for treatment A1, the increases in DO and Eh and the rate of removal of VOSCs were slower. The ultimate removal rate of VOSCs was >99% for all the aerated treatments after 24 h. The alteration of the oxidation-reduction conditions, induced by the aeration, could be the primary reason for the removal of the VOSCs. Thus, aeration treatment might be a feasible technique for the removal of VOSCs after the outbreak of black blooms in waterworks and some shallow lakes.

Key words | aeration, black bloom, dissolved oxygen, removal, volatile organic sulfur compounds

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INTRODUCTION

Black blooms, also known as 'black spots', 'black aggregations', and 'black water agglomerates' (Rusch *et al.* 1998; Lu 2012), have been observed in many lakes and bays (Duval & Ludlam 2009; Yang *et al.* 2008). Black-blooming waters pose a considerable ecological threat to water ecosystems and their surrounding residents. In 2007, a potable water crisis occurred in the city of Wuxi in China, when water supplied from the water plants became discolored and had a foul odor (Yang *et al.* 2008; Zhang *et al.* 2010). An algae-induced black bloom in Lake Taihu, the city's source of potable water, was responsible for the problem, which caused approximately two million inhabitants to suffer a drinking water shortage.

Algae-induced black blooms are now common phenomena in large shallow lakes, such as Lake Taihu and Lake Chaohu in China, during the algal bloom season (Paerl *et al.* 2011; Duan *et al.* 2014; Jiang *et al.* 2014). Black coloration and foul odor are the two characteristics most

typical of affected water during black-bloom events. High concentrations of metal sulfides (typically FeS) generated under conditions of low dissolved oxygen (DO; close to 0 mg L⁻¹) and low oxidation-reduction potential (Eh) are the factors that predominantly induce the black coloration (Stahl 1979; Shen *et al.* 2013). However, high concentrations of volatile organic sulfur compounds (VOSCs), including methanethiol (MTL), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS) are most responsible for the foul odor of the water, and they have frequently been detected during algae-induced black blooms (Yang *et al.* 2008; Lu 2012; Lu *et al.* 2013). Therefore, in the control of black blooms, it is important to consider both the black coloration and the foul odor of the affected water.

Most measures for controlling black blooms focus on the sediment because the black coloration is induced mainly by high levels of Fe²⁺ and ΣH₂S (H₂S, HS⁻, and S²⁻) accumulated in surface sediments and pore waters (Shen *et al.*

2013). Sediment dredging (He *et al.* 2013; Liu *et al.* 2015) and plow tillage (He 2013) have both proved suitable for controlling the black coloration. However, the foul odor induced by the VOSCs, which was the primary cause of the potable water crisis in Wuxi (Zhang *et al.* 2010), cannot be controlled by such measures (Liu *et al.* 2015). Thus, VOSCs continue to pose a significant threat to the aquatic environment during black blooms. These compounds have been studied for decades because of their low odor-threshold concentrations (OTCs) (Kiene & Visscher 1987; Watson 2004), which cause them to affect the smell and taste of drinking water. They generally originate from sulfur-containing amino acids like methionine and cysteine, as well as their derivatives *S*-methylmethionine and *S*-methylcysteine, in anoxic environments (Smet *et al.* 1998; Lomans *et al.* 2002a; Higgins *et al.* 2006). However, algae in large shallow lakes in China (e.g., Lake Taihu) contain many sulfur-containing amino acids (Li 2009), which are the primary sources of VOSCs during black blooms (Lu *et al.* 2013). In the past decade, despite the implementation of various measures (e.g., salvage and pollutant interception) to control algal blooms in China, the elimination of the origin of VOSCs has proven problematic and the bloom status has remained severe (Duan *et al.* 2014). There are still no effective measures to control VOSCs after the outbreak of an algae-induced black bloom. Therefore, effective measures are required for the removal of VOSCs to protect lake ecosystems and drinking water for local inhabitants. In this study, aeration experiments were used to investigate the removal of VOSCs because they are usually formed in anoxic environments (Lomans *et al.* 2002a; Higgins *et al.* 2006; Hu *et al.* 2007). Pilot studies were performed in a laboratory to compare and evaluate removal efficiency across various treatments.

MATERIALS AND METHODS

Sediment, water, and algae used in the study

Lake Taihu, which is the third largest freshwater lake in China, has a serious pollution problem because of the development of surrounding industrialized cities (Qin *et al.* 2007). Since the 1980s, large areas of algal bloom have occurred annually in the lake (Duan *et al.* 2014), with occasional

discoveries of resultant algae-induced black blooms (Lu & Ma 2009; Zhang *et al.* 2010), which pose a considerable threat to both the lake ecosystem and the inhabitants in the surrounding areas. In this study, prior to the experimental treatments, black blooms were simulated in a laboratory using raw sediment, water, and algae samples from Moon Bay in Lake Taihu, which is an area known to be prone to black blooms. The latitude and longitude of the sampling site are 31°24'37.7"N and 120°6'9.7"E, respectively. In July 2013, 15 sediment cores were sampled using a gravity corer (Rigo Co. Ltd, Japan; Ø110 mm × L500 mm) and were stored anaerobically in Plexiglas® tubes (Ø110 mm × L500 mm). The overlying water and algae used during the experiments were also sampled from the same site and stored anaerobically in plastic buckets. All sediment cores, together with the overlying water and algae, were transferred immediately to the laboratory without disturbance and treated within 24 h. The sediment cores and water were stored at normal temperatures, while the algae were stored at 4 °C to reduce degradation during transportation.

Experimental design

Black blooms were simulated using a group of Y-shaped sediment re-suspension generation apparatuses (Figure 1) before the aeration treatment (Fan 2006). Each sediment

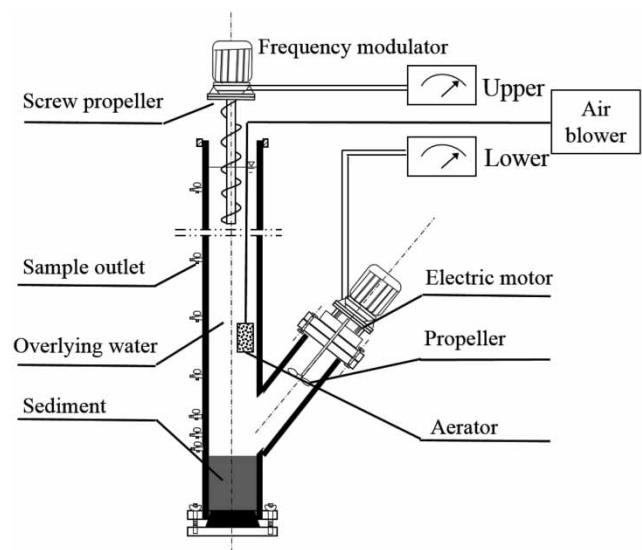


Figure 1 | Y-shaped sediment re-suspension generation apparatus.

core was placed in an apparatus with a 1.8-m overlying water column (lake water filtered through a medium-speed qualitative filter to remove large particles). The overlying water depth was approximated to the mean depth of Lake Taihu (Qin *et al.* 2007). Then, 47.5 g of drained algae (approximately $5,000 \text{ g m}^{-2}$; these were obtained by filtration through a $20\text{-}\mu\text{m}$ plankton net to remove water) were added to each water column for the simulations of the black blooms (Liu *et al.* 2010). The algae were mostly (>99% during the bloom seasons) composed of cyanobacteria (Xu *et al.* 2013). Wind disturbance was simulated by the rotation of propellers at the top and bottom of the apparatus (Figure 1). It required about 4 days for the outbreaks of black blooms to develop in all the columns. Propeller rotation was stopped after the outbreaks developed because field observations suggest that black blooms in lakes usually occur without wind disturbance. The systems were stabilized for another 24 h to allow the blooms to reach their peaks, following which the aeration treatment was performed.

Four treatments were implemented after the outbreaks of the black blooms developed: control (CK, without treatment), A1, A2, and A3, for which, in the latter three experiments, 1, 3, and 9 L-air min^{-1} of aeration (corresponding to 0.06, 0.18, and $0.54 \text{ m}^3\text{-air min}^{-1} \text{ m}^{-3}$) was applied in the middle of the water columns. Air-blast aeration was used for the treatments using air blowers (Figure 1) through which the airflow rate was controlled using rotameters (Krohne DK800, Germany). Temperature in the laboratory was maintained at $27 \pm 2^\circ\text{C}$, approximating the normal temperature of Lake Taihu during the early summer (Hu *et al.* 2006). All treatments were applied for 24 h to study their effects in removing VOSCs during black blooms.

Chemical analyses

Water samples were collected from the outlets in the middle of the columns in the laboratory (Figure 1). The water samples were stored in 40 mL brown glass bottles, sealed immediately, and preserved at 4°C for the analyses of VOSCs and H_2S . Samples were collected successively at 0, 1, 2, 3, 5, 8, and 24 h during the aeration treatment. Concurrent with the sampling, the levels of DO and Eh were

analyzed using electrodes (Mettler Toledo SG68, Switzerland) placed in the middle of the water columns.

Concentrations of Fe^{2+} and Fe^{3+} in the water were analyzed immediately after the sampling using the ferrozine method (Stookey 1970). VOSCs and H_2S were analyzed using gas chromatography, which has been used by many other researchers for the detection of VOSCs (Hu *et al.* 2007; Chen *et al.* 2010; Lu *et al.* 2012). In this study, a headspace solid-phase micro-extraction (HS-SPME) procedure, coupled with an Agilent 7890A gas chromatograph (Agilent Technologies, USA), was used for the determination of VOSCs and H_2S . Twenty milliliters of water was extracted from each of the samples using a $50/30\text{-}\mu\text{m}$ DVB/carboxen-PDMS fiber (Supelco, No. 57348-U, USA) over 30 min at 65°C , with agitation at 150 rpm. Separation and determination of the VOSCs were achieved via gas chromatography using a GAS-PRO capillary PLOT column ($60 \text{ m} \times 0.32 \text{ mm}$; Agilent Technologies) and a flame photometric detector. The detector was fed with hydrogen, synthesis air, and helium as an auxiliary gas, at rates of 50, 65, and 30 mL min^{-1} , respectively, and maintained at 250°C . Helium was also used as the carrier gas at a flow rate of 3.0 mL min^{-1} . The gas chromatograph was programmed from 50 (held for 5 min) to 250°C ($25^\circ\text{C min}^{-1}$, held for 10 min). Standard curves were obtained using standard solutions purchased from Sigma-Aldrich (USA). The concentrations of VOSCs, with detection limits ranging from 2.2 to 4.0 ng L^{-1} , were determined by comparison with the standard curves.

Statistics

Pearson's correlation and analysis of variance (ANOVA) with Tukey's test (used to check the differences between the different treatments) were implemented using SPSS[®] software for Windows[®] (Version 19.0; IBM, USA). Graphics were generated from the data using Origin[®] software (Version 8.5; OriginLab, USA).

RESULTS AND DISCUSSION

Changes of DO and Eh

Alteration of the redox conditions is crucial for the formation and degradation of VOSCs (Lomans *et al.* 2002a, 2002b). DO

and Eh, which are both important indicators of the oxidation-reduction status of water, were analyzed and the results are shown in Figure 2. It can be seen that DO saturation and Eh improved significantly for treatments A1, A2, and A3 during the experiment, but they changed little for treatment CK. However, the trends in the development of DO saturation differed significantly ($P < 0.05$) between both the A1 and A2 treatments and the A3 treatment. DO saturation increased considerably for treatments A2 and A3 during the first hour of the experiment. Conversely, other than for a slight increase during the first hour (followed by a subsequent decrease shortly after), DO saturation in treatment A1 changed little until the fifth hour of the experiment. Moreover, DO saturation in the water samples of treatments A2 and A3, with non-significant ($P > 0.05$) differences in the experimental results, was greater than in A1. DO saturation stabilized after 8 h for all treatments and the final DO saturations were similar under treatments A2 (98.25%) and A3 (102.96%), but considerably lower under A1 (68.64%). In the development of Eh, the difference was non-significant ($P > 0.05$) between treatments A2 and A3, but it was significant between A2, A3, and A1. As in the development of DO, the increase of Eh under treatment A1 was slower than under both A2 and A3. However, the final Eh values for treatments A1 (271.4 mv), A2 (272.4 mv), and A3 (273.4 mv) were similar after 24 h.

Effect of aeration on H₂S

Metal sulfides (largely FeS), formed by the reactions between hydrogen sulfide (H₂S, HS⁻, and S²⁻) and Fe²⁺,

have been found to be the main cause of the blackness for black-blooming waters (Shen *et al.* 2013; Feng *et al.* 2014; Liu *et al.* 2015). However, the methylation of H₂S in anoxic environments is one of the key reactions that form MTL, which might then form other VOSCs (Lomans *et al.* 2002a; Higgins *et al.* 2006). Therefore, the removal of H₂S from water is of considerable importance for the control of VOSCs and for the suppression of black blooms. Figure 3 shows that the development of the H₂S concentration in the water columns during the experiments decreased sharply for the aerated water columns after 24 h, but it remained high ($220.61 \pm 20.55 \mu\text{g L}^{-1}$) for treatment CK. As in the development of DO and Eh, the decrease in H₂S concentration under treatment A1 was slower than under both A2 and A3. A considerable decrease was detected during the first hour of the experiment for treatments A2 and A3, whereas the decrease was at a slower rate and mainly during the second to eighth hours for treatment A1.

Effect of aeration on VOSCs

In the simulated black-blooming water columns of this study, the highest concentrations of MTL, DMS, DMDS, and DMTS reached $18.91 \mu\text{g L}^{-1}$, $128.24 \mu\text{g L}^{-1}$, $12.36 \mu\text{g L}^{-1}$, and $26.85 \mu\text{g L}^{-1}$, respectively, before the treatments (Figure 4), which were close to those found in a previous study (Yang *et al.* 2008). All these values are much higher than the corresponding OTC for each VOSC, i.e., 2.1, 1.0, 4.0, and $0.01 \mu\text{g L}^{-1}$ for MTL, DMS, DMDS, and DMTS, respectively (Watson 2004). All the VOSCs remained stable at high levels under treatment CK but decreased sharply under treatments

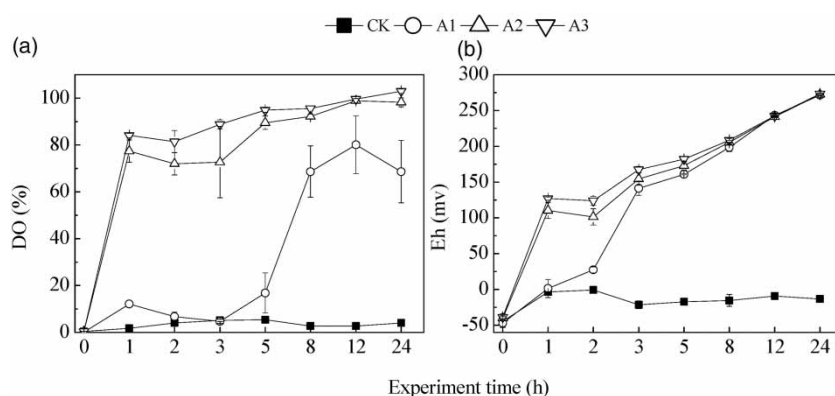


Figure 2 | Changes of DO saturation and Eh in water samples: (a) DO, (b) Eh.

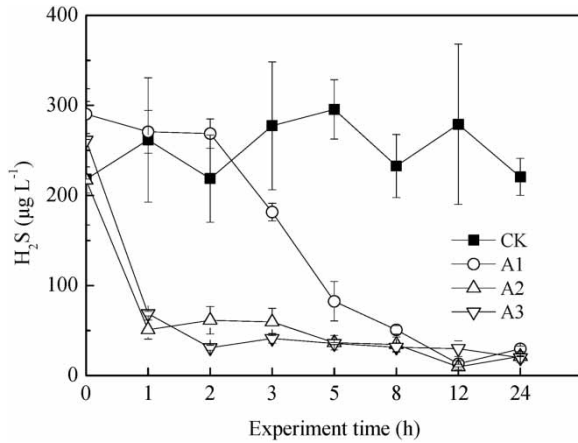


Figure 3 | Variation of H₂S in water samples during the treatments.

A1–A3. However, the development trends of the VOSCs differed between the three aerated treatments. Similar development trends were found between treatments A2 and A3, but the development under treatment A1 was quite different. Among the VOSCs, DMTS decreased at a faster rate than the others did under A1, although not as fast as under A2 and A3. MTL under A1 decreased quickly during the first hour, but it then slowed thereafter until stabilizing after 8 h. The decreases in DMS and DMDS were much slower for A1 (Figure 4) than for A2 and A3. It took

12 and 5 h for the DMS concentrations to decrease below the OTC in the water samples for treatments A2 and A3, respectively, while the final DMS concentration under treatment A1 (1.07 µg L⁻¹) remained above the OTC (Watson 2004). DMDS concentrations decreased to below the OTC after 1 h for treatments A2 and A3, but only decreased to this level after 8 h for treatment A1. In fact, the DMDS concentration even stabilized for a period during the second to fifth hours under treatment A1.

Alteration of oxidation-reduction conditions

Anaerobic degradation of sulfur-containing amino acids to form MTL and H₂S is the most important mechanism for the formation of VOSCs (Lomans *et al.* 2002a, 2002b; Higgins *et al.* 2006). Other VOSCs (i.e., DMS, DMDS, and DMTS) are formed subsequently through the methylation and oxidation of MTL (Chin & Lindsay 1994; Higgins *et al.* 2006; Lu 2012). Moreover, the formation of MTL via the anaerobic methylation of H₂S (Lomans *et al.* 2002b; Higgins *et al.* 2006) aggravates the formation of VOSCs. Furthermore, the formation of FeS by Fe²⁺ and S²⁻ under a reductive environment is the main reason for the black coloration of the water (Shen *et al.* 2013; Liu *et al.* 2015).

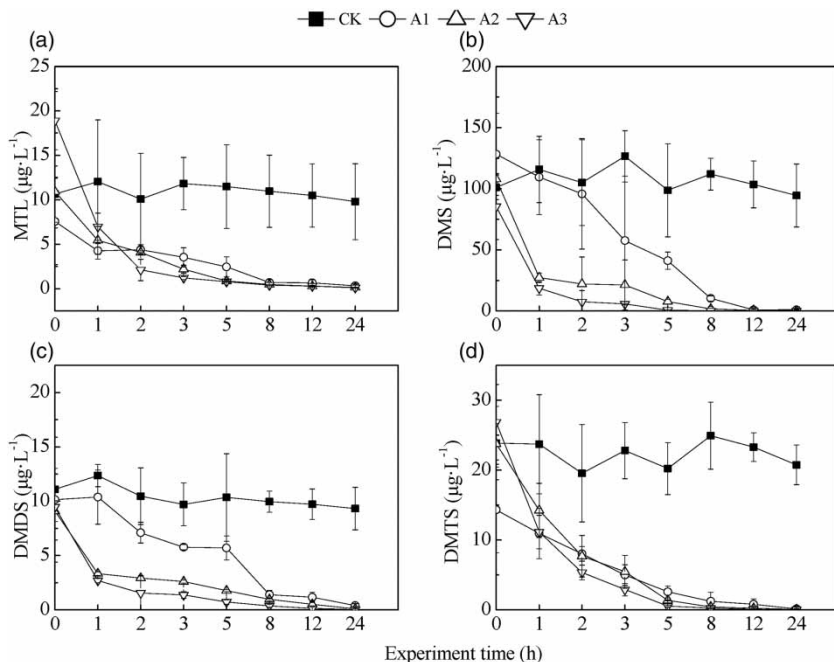


Figure 4 | Effects of aeration on VOSCs during the experiments: (a) MTL, (b) DMS, (c) DMDS, and (d) DMTS.

Therefore, the transition of oxidation-reduction conditions in water bodies is crucial for both the control of VOSCs and the elimination of odorous smells and black coloration.

As shown in Figure 2, levels of DO and Eh increased sharply after 1 h of aeration for treatments A2 and A3. Correspondingly, the H₂S concentration decreased sharply under these two treatments (Figure 3). However, large variations in the levels of DO and Eh occurred under treatment A1 until after 3–5 and 2–3 h of aeration, respectively. The decrease of H₂S under A1 occurred mainly between the second and eighth hours and it stabilized thereafter, concurrent with the stabilization of the DO level. Significant negative correlations ($P < 0.01$) were found between DO, Eh, and H₂S (Table 1). H₂S can be oxidized by molecular oxygen (O₂), which can be accelerated by catalysts such as Fe³⁺ (Mansfield *et al.* 1992). FeS is the main black compound during black blooms, and high levels of Fe²⁺ can be detected frequently in black-blooming waters (Shen *et al.* 2011; He *et al.* 2013; Feng *et al.* 2014). Fe²⁺ can be oxidized to Fe³⁺ and then become a catalyst for the oxidation of H₂S (Mansfield *et al.* 1992; Smet *et al.* 1998). In this study, the concentrations of Fe²⁺ and Fe³⁺ were also measured to verify both the alteration of the oxidation-reduction conditions and the effects on H₂S. The oxidation of Fe²⁺ to Fe³⁺ occurred mainly during the first hour of aeration under treatments A2 and A3, with concentrations of Fe²⁺ decreasing from 0.60 ± 0.01 mg L⁻¹ and 0.51 ± 0.02 mg L⁻¹ to 0.21 ± 0.05 mg L⁻¹ and 0.17 ± 0.01 mg L⁻¹, respectively (the concentrations of Fe³⁺ escalated accordingly). The corresponding change under treatment A1 occurred mainly between the second and

third hours of the experiment, with the concentration of Fe²⁺ changing from 0.42 to 0.26 mg L⁻¹. It is notable that the rate of decrease under A1 was slower than under A2 and A3. These variations are consistent with the changes of DO and Eh. The escalated Fe³⁺ became the catalyst for the oxidation of H₂S (Mansfield *et al.* 1992), which is why the concentrations of H₂S decreased quickly during the first hour of the experiment under treatments A2 and A3, but decreased at a slower rate after the second hour under A1. The decrease in H₂S acts to inhibit further formation of VOSCs (Lomans *et al.* 2002b; Higgins *et al.* 2006), and therefore the alteration of the oxidation-reduction conditions of the water columns by aeration might be important for the removal of VOSCs.

Mechanisms and effects of VOSC removal

It was stated in the previous subsection that the oxidation-reduction conditions in a water body could be changed under the aeration treatment. Under an oxidizing environment, MTL can be oxidized to DMDS and then oxidized further to sulfonic acid (Adewuyi & Carmichael 1986; Hwang *et al.* 1994), and DMS can be oxidized to dimethyl sulfoxide (DMSO) and other compounds (Arsene *et al.* 1999; Bentley & Chasteen 2004). Therefore, the alteration of the oxidation-reduction conditions (as demonstrated by the trends of development of DO and Eh in this study) is important for the removal of VOSCs. Moreover, significant negative ($P < 0.01$) correlations were discovered between the VOSCs and both DO and Eh (Table 1).

Table 1 | Pearson's correlation matrix for various characteristics in the water samples

	DO	Eh	H ₂ S	MTL	DMS	DMDS	DMTS	TVOSCs
DO	1	0.810**	-0.919**	-0.679**	-0.923**	-0.940**	-0.688**	-0.920**
Eh		1	-0.887**	-0.817**	-0.910**	-0.924**	-0.882**	-0.941**
H ₂ S			1	0.713**	0.976**	0.957**	0.733**	0.964**
MTL				1	0.698**	0.760**	0.959**	0.795**
DMS					1	0.978**	0.761**	0.988**
DMDS						1	0.802**	0.986**
DMTS							1	0.847**
TVOSCs								1

Significant at the ** $P < 0.01$ level.

The removal rate of total VOSCs (TVOSCs) during the different periods (Figure 5) showed that most VOSCs (about 70%) were removed from the water for treatments A2 and A3 after 1 h of aeration, when the levels of both DO and Eh increased sharply (Figure 2). However, the removal of VOSCs was slower for treatment A1 than for A2 and A3. The largest rates of removal occurred during the periods 2–3 and 5–8 h after the commencement of the experiment (Figure 5), when the largest variations in Eh and DO occurred (Figure 2). This demonstrates the influence of both DO and Eh on the removal of VOSCs, whereby the increases in DO and Eh accelerate the oxidation of the VOSCs (Adewuyi & Carmichael 1986; Hwang *et al.* 1994; Bentley & Chasteen 2004). Under low aeration rates (treatment A1), MTL might decrease first and be oxidized to DMDS (Hwang *et al.* 1994). The DO saturation remained at a low level during the first to fifth hours of the experiment (Figure 2) because of the consumption of oxygen by H₂S and MTL oxidation (Mansfield *et al.* 1992; Higgins *et al.* 2006). Moreover, MTL and DMS might also be formed under the low DO and Eh levels by methylation of H₂S and MTL, respectively (Higgins *et al.* 2006). This could explain why the level of H₂S decreased after 2 h under treatment A1, while the level of MTL changed quite slowly between the second and eighth hours, when MTL might be formed by the methylation of H₂S on the one hand (Higgins *et al.* 2006), and be oxidized and methylated to DMDS and DMS, respectively, on the other (Hwang *et al.* 1994; Higgins *et al.* 2006). Moreover, the decreases in DMS and DMDS were slow because of their continuous formation during this period. These reasons caused the tardy

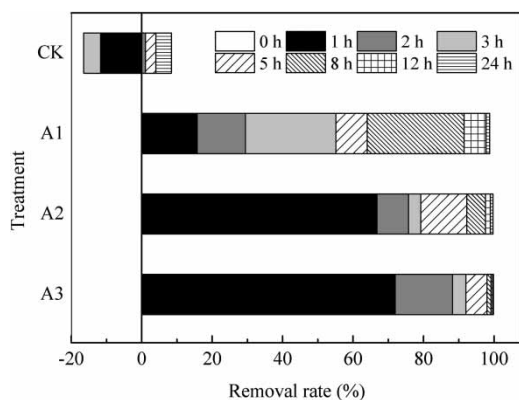


Figure 5 | Removal rate of total VOSCs during different periods of the experiments.

decrease of the TVOSCs under treatment A1 (Figure 5). The stripping effect during aeration might also be favorable for the removal of DMSs, except via the alteration of oxidation-reduction conditions, although this is not dominant and is even negligible for some volatile sulfur compounds according to previous studies (Fukuyama *et al.* 1986; Hwang *et al.* 1994). According to previous research, it is considered that it might have contributed to no more than 25% of the removal rate of sulfur compounds (Hwang *et al.* 1994).

The duration of a black bloom is usually no more than 2 days, according to our observations of black blooms in numerous shallow lakes. The emergency removal of VOSCs during the 24 h of a black bloom event might be crucial in avoiding a drinking water crisis for local inhabitants and other related ecological disasters. The final removal rate for all the aerated treatments was >99% after 24 h (Figure 5). Therefore, aeration is shown to be feasible for the removal of VOSCs during algae-induced black blooms. High aeration rates, such as those employed under treatments A2 and A3 (i.e., >0.06 m³-air min⁻¹ m⁻³), could be used in waterworks to overcome accidental malodorous problems associated with drinking water during black blooms. Lower aeration rates (i.e., <0.06 m³-air min⁻¹ m⁻³) could be used for the removal of VOSCs in black-blooming areas such as small bays in shallow lakes, where black blooms usually occur.

CONCLUSIONS

This study focused on the removal of VOSCs from water during algae-induced black blooms in shallow lakes. Air-blast aeration was used to eliminate VOSCs after the outbreak of black blooms. It was demonstrated that DO and Eh levels can be improved remarkably by aeration, leading to a decrease in H₂S, which is of considerable importance regarding the elimination of VOSCs and the suppression of black blooms. The alteration of oxidation-reduction conditions could be the most important factor in the removal of VOSCs. Aeration was found to be a feasible measure for the removal of VOSCs during black blooms. Different aeration rates could be used in waterworks and the small bays of shallow lakes to avoid future crises involving drinking water and other ecological disasters.

ACKNOWLEDGEMENTS

This study was supported financially by the One-Three-Five Project of Nanjing Institute of Geography and Limnology, CAS (No. Y213518090) and the Comprehensive Management Project for Taihu Water Environment of Jiangsu Province (No. JSZC-G2013-188).

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First received 24 April 2015; accepted in revised form 22 October 2015. Available online 18 November 2015