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# Increasing sulfate concentrations result in higher sulfide production and phosphorous mobilization in a shallow eutrophic freshwater lake

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ABSTRACT

Increasing sulfate input has been seen as an issue in management of aquatic ecosystems, but its influences on eutrophic freshwater lakes is not clear. In this study, it was observed that increasing sulfate concentration without additional cyanobacterial bloom biomass (CBB) addition did not have an obvious effect on element cycling during 1-year continuous flow mesocosm experiments in which water and sediments were taken from a shallow eutrophic lake with sulfate levels near 1 mM. However, following addition of CBB to mesocosms, sulfate-reducing bacteria (SRB) were observed in the water column, and increasing numbers of SRB in the water column were associated with higher sulfate input. Sulfate amendment (0–70 mg $L^{-1}$) also resulted in a larger amount of total dissolved sulfide (peak values of 5.90 ± 0.36 to 7.60 ± 0.12 mg $L^{-1}$) in the water column and acid volatile sulfide (1081.71 ± 69.91 to 1557.98 ± 41.72 mg $kg^{-1}$) in 0–1 cm surface sediments due to sulfate reduction. During the period of CBB decomposition, increasing sulfate levels in the water column were positively correlated with increasing diffusive phosphate fluxes of 1.23 ± 0.32 to 2.17 ± 0.01 mg $m^{-2}$ $d^{-1}$ at the water-sediment interface. As increases in sulfide and phosphate release rates deteriorated the water quality/ecosystem and even spurred the occurrence of a black water problem in lakes, the control of sulfate input level should be considered for shallow eutrophic lake management, especially during cyanobacterial bloom periods.


## 1. Introduction

Increasing nutrient inputs associated with both population and economic growth have caused eutrophication in freshwater ecosystems. Since the 1980s, cyanobacterial blooms have occurred with increasing frequency and intensity in eutrophic lakes (Paerl and Paul, 2012; Paerl et al., 2011; Vonlanthen et al., 2012). Apart from increasing eutrophication, sulfate concentrations are increasing in freshwater environments throughout the world (Baldwin and Mitchell, 2012; Tao et al., 2013; Zak et al., 2009). For example, during the past six decades, sulfate concentration in Lake Taihu, China, has shown an increasing trend due to local $SO_2$ emission and energy consumption, with current levels near 1 mM (Tao et al., 2013).

It has been reported that sulfate reduction accounts for 12–81% of organic matter mineralization in freshwater sediments (Holmer and Storkholm, 2001). Sulfate reduction to sulfide can mobilize Fe-bound P, which consequently influences iron cycling and eutrophication of freshwater ecosystems (Chen et al., 2014). Furthermore, the accumulation of reduced sulfur in sediments can be toxic to aquatic plants and benthic fauna (Holmer and Storkholm, 2001; Simkin et al., 2013). Sulfate reduction has also been implicated in mercury methylation in freshwater sediments (Yu et al., 2012). As a result, increasing sulfate input has been seen as an issue in management of freshwater aquatic ecosystems (Baldwin and Mitchell, 2012; Dierberg et al., 2011; Lamers et al., 2002; Zak et al., 2006).

Although the influence of sulfate on biogeochemical cycling in freshwater sediments has been well documented, sulfate reduction in the water column of shallow freshwater lakes has not been well

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studied. Water column sulfate reduction has been shown to occur in marine and stratified lake environments (Karnachuk et al., 2006; Lin et al., 2006; Nakagawa et al., 2012) and is regulated by many factors, including the sulfate-reducing bacteria (SRB), dissolved oxygen (DO), organic matter (OM) and sulfate concentration (Leonov and Chicherina, 2008). SRB are principally believed to be strict anaerobes, but they are able to tolerate oxygen by cell aggregation, migration and particle association (Dolla et al., 2006; Heidelberg et al., 2004), and are therefore able to live in both oxic and anoxic zones of water column (Teske et al., 1996; Wakeham et al., 2007). In addition, decomposition of OM (like algae) by microorganisms can deplete DO creating 'Dead Zones' in water column, providing hypoxic conditions (Diaz and Rosenberg, 2008). In permanently stratified lakes with relatively high sulfate concentrations (>1 mM), the supply of organic matter controls sulfate reduction in the water column, while sulfate concentration often regulates sulfate reduction in monomictic lakes (Nakagawa et al., 2012). The effects of the increased sulfate input on biogeochemical cycling in eutrophic freshwater lakes are poorly studied.

In shallow freshwater hyper-eutrophic lakes, like Taihu in China, sustained hypoxia in the water column should seldom occur due to regular mixing and $O_2$ exchange with the atmosphere (Qin et al., 2007). However, as a result of decomposition of cyanobacterial bloom biomass (CBB) (Shen et al., 2013), periodic hypoxia does occur (Zhu et al., 2008). In fact, black hypoxic water has recently degraded the Taihu ecosystems (Shen et al., 2013). Settlement and decomposition of algae in sediments is thought to be the main cause of black water in Lake Taihu (Qin et al., 2010; Wang et al., 2014; Zhou et al., 2015). Previous studies have shown that SRB living in sediments contribute to decomposition of CBB and the formation of black water in shallow freshwater lakes (Feng et al., 2014; Wang et al., 2014). Water column sulfate reduction in shallow freshwater lakes has not been previously documented. After it occurs, black water can persist for several days or even longer periods, with areas covering several $Km^2$ (Qin et al., 2015). The decomposition of CBB and subsequent DO depletion also influence the chemistry and the bacterial community composition of lake sediments (Handley et al., 2012; He et al., 2013). As sulfate and iron reduction are stimulated, this leads to the release of iron-bound P (Chen et al., 2014; Gunnars and Blomqvist, 1997). It also seems reasonable to postulate that sulfate reduction associated with decomposition of organic matter would increase the risk for 'black water' and cause deterioration of water quality in eutrophic lakes.

In this study, continuous flow mesocosms were operated for 1 year (phase I), followed by a CBB amendment and then 28 days further operation (phase II). The occurrence of sulfate reduction in the water column of shallow freshwater lakes during CBB decomposition and the impact of increasing levels of dissolved sulfate on sulfate reduction and sulfide production in the water column were investigated. In addition, P fluxes at the water-sediment interface (WSI) and P transformation in sediments were also studied with varied sulfate levels. This study will help to evaluate the influences of increased sulfate input on water quality and nutrient cycling in shallow eutrophic freshwater lakes.

## 2. Materials and methods

### 2.1. Water and sediments sampling

Samples of sediments and CBB as well as lake water were taken from eutrophic Lake Taihu. Lake Taihu (31°10′ N, 120°24′ E), one of the largest shallow freshwater lakes in China, is situated at the south of the Yangtze River delta with a mean depth of 1.9 m and an area of 2340 $km^2$ (Qin et al., 2007). Sediments were sampled using a gravity core sampler in Meiliang Bay in May, 2013, and CBB samples were harvested by sieving lake surface water through a fine mesh plankton net in May, 2014. CBB samples were immediately stored in polyethylene bottles. In addition, lake water, with sulfate concentration of 100 mg $L^{-1}$, was collected into several 50-L closed plastic barrels regularly. Sediments and CBB samples were placed on ice and transported to the laboratory within several hours of collection. Subsequent storage of all samples was at 4 °C for less than 24 h prior to usage.

### 2.2. Set-up of continuous flow mesocosms

Briefly, the experimental set-ups consisted of five perspex containers (50 cm long, 33 cm wide and 40 cm high). Six perspex columns (diameter 15 cm and height 30 cm) were placed in to each perspex container. Homogenized sediments were put separately into each column to a depth of approximately 20 cm.

Experiments included two phases. During Phase I, $Na_2SO_4$ was first dissolved in lake water and then transferred into closed plastic barrels (50 L) as follows: no addition (control, C), 10 mg $SO_4^{2-}$ $L^{-1}$ (10S), 30 mg $SO_4^{2-}$ $L^{-1}$ (30S), 50 mg $SO_4^{2-}$ $L^{-1}$ (50S), and 70 mg $SO_4^{2-}$ $L^{-1}$ (70S). Lake water without sulfate addition and sulfate-added lake water in barrels were separately pumped into the respective perspex containers by peristaltic pumps via an inlet located 5 cm above the bottom of the container at a rate of 1.5 L $d^{-1}$. The outlet was on the other side and 5 cm below the top of the container. The continuous flow mesocosms simulated current and continuous supply of nutrients to the water column. The incubation lasted for 1 yr, after which three perspex columns were removed for sediment analysis. The water samples in mesocosms in Phase I were taken monthly and analyzed to study the effect of increased sulfate without cyanobacterial bloom addition on water quality.

During Phase II, the remaining three perspex columns in each container were further incubated similarly to Phase I except that fresh CBB (1.5 L) was amended into each container. The amount of CBB added was calculated based on the density of the cyanobacterial blooms that occurred in Lake Taihu in May, 2014. The incubation lasted for 28 days in the dark. During this period, water samples from the water column were collected every 1–6 days at 5 cm below the water surface. To investigate the inorganic elements in overlying water (0–1.5 cm above the WSI) and pore-water in sediments, peepers (see below) were inserted into the each column on day 22 and removed to measure dissolved sulfide ($\sum H_2S$), $SO_4^{2-}$, Fe(II) and $PO_4^{3-}$ in pore-water on day 28. At the end of the incubation (day 28), sediments in each column were sectioned based on depth in an anaerobic glove box. Sediments at each depth were then analyzed as described below.

### 2.3. Chemical analytical methods

To determine the total phosphorous (TP) in water column (5 cm below the water surface), the water sample was autoclaved at 121 °C for 30 min after 4 mL $K_2S_2O_8$ was added. Then 10% ascorbic acid was added, followed by $PO_4^{3-}$ determination using the molybdenum blue method (APHA, 2005). Dissolved $PO_4^{3-}$ in water column was measured directly after filtering water sample with 0.45 μm pore size membranes. $\sum H_2S$ was analyzed using the methylene blue method (Cline, 1969), sulfate was analyzed using a turbidimetric method (Tabatabai, 1974) and concentration of Fe(II) was determined colorimetrically (Lovley and Phillips, 1987). Dissolved organic carbon (DOC) was analyzed using a Shimadzu TOC5000A. Dissolved oxygen (DO) in the water column were measured with a dissolved oxygen meter (YSI 550A) with a 0.01 mg $L^{-1}$ resolution during the sampling period.

The inorganic elements in overlying water just above sediments