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# Cyanobacteria blooms: A neglected facilitator of CH<sub>4</sub> production in eutrophic lakes



Xingcheng Yan <sup>a,1</sup>, Xiaoguang Xu <sup>a,1</sup>, Ming Ji <sup>a</sup>, Zhongqian Zhang <sup>a</sup>, Mingyue Wang <sup>a</sup>, Songjun Wu <sup>a</sup>, Guoxiang Wang <sup>a,b,c,d,\*</sup>, Chi Zhang <sup>a</sup>, Huichao Liu <sup>a</sup>

<sup>a</sup> School of Environment, Nanjing Normal University, Nanjing 210023, PR China

<sup>b</sup> Jiangsu Center for Collaborative Innovation in Geographical Information Resource Development and Application, Nanjing 210023, PR China

<sup>c</sup> Jiangsu Key Laboratory of Environmental Change and Ecological Construction, Nanjing 210023, PR China

<sup>d</sup> Jiangsu Engineering Laboratory of Water and Soil Eco-remediation, Nanjing 210023, PR China

#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- The high-resolution determinations of CH<sub>4</sub> concentrations in Taihu lake were conducted.
- CH<sub>4</sub> concentrations were influenced by the physiochemical parameters in surface water and sediments.
- CH<sub>4</sub> production in sediment was consistent with that in surface water.
- CBBs act as a neglected facilitator of CH<sub>4</sub> production in eutrophic lakes.



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#### ABSTRACT

Lakes are regarded as one of the important sources of atmospheric CH<sub>4</sub>. However, the role of cyanobacteria blooms (CBBs) play in the CH<sub>4</sub> production in eutrophic lakes is not fully clear. In this study, the spatial distribution characteristics of CH<sub>4</sub> concentrations in surface water and sediment columns were investigated in Zhushan Bay of Taihu lake, China. Results showed that CH<sub>4</sub> concentrations in CBBs accumulated zones were much higher than that in the open lake areas, with the highest values of  $3.79 \ \mu mol \cdot L^{-1}$  and  $2261.88 \ \mu mol \cdot L^{-1}$  in surface water and sediment columns, respectively. CH<sub>4</sub> concentrations were strongly influenced by various factors. In surface water, the occurrence of CBBs greatly contributed to CH<sub>4</sub> productions, as evidenced by the well-predicting for CH<sub>4</sub> concentrations using Chl-a and NH<sub>4</sub><sup>+</sup> concentrations. In the sediments, the Ignition Loss and C:N ratio values were two indicators of CH<sub>4</sub> contents, suggesting that the methanogenesis processes were influenced by not only the quantities, but also the qualities of organic matter. The labile substrates produced during the CBBs decomposition processes promoted the CH<sub>4</sub> production and migration from sediments to the water column, resulting in the coherence in CH<sub>4</sub> concentrations between the sediments and the surface water. The high-resolution determinations of CH<sub>4</sub> concentrations in surface water and sediments clarified that the CBBs were a neglected facilitator of CH<sub>4</sub> productions, which should be considered in the future estimation of CH<sub>4</sub> emissions in eutrophic lakes.

\* Corresponding author at: 1, Wenyuan Road, Xianlin University District, Nanjing 210023, China.

- E-mail address: wangguoxiang@njnu.edu.cn (G. Wang).
- <sup>1</sup> These authors contributed equally to this manuscript.

#### 1. Introduction

Methane (CH<sub>4</sub>) is an important greenhouse gas in the atmosphere, responsible for approximately 20% of the Earth's warming since preindustrial times (Kirschke et al., 2013). CH<sub>4</sub> productions and emissions have been widely concerned due to its effects on climate warming and atmospheric chemistry (Wuebbles and Hayhoe, 2002). Freshwaters are considered as a particularly important source of CH<sub>4</sub> in the global CH<sub>4</sub> budgets, and can even offset 25% of the continental carbon sink (Louis et al., 2000; Bastviken et al., 2004; Bastviken et al., 2011). In terms of overall carbon budgets, the amount of CH<sub>4</sub> emissions from lakes represents 6–16% of total non-anthropogenic emissions, and even higher than that from the oceans (Bastviken et al., 2004; Tranvik et al., 2009). Thus, understanding the processes, mechanisms and responses to environmental changes of CH<sub>4</sub> productions in lakes is fundamental to predicting the responses of carbon cycle in lake ecosystems to future climate change.

CH₄ productions and fluxes from freshwater lakes have been intensively investigated, however, their results seem not to be coincident. A global estimation of the average CH<sub>4</sub> flux was 225.7  $\pm$  626.2 mmol m<sup>-2-</sup>  $vr^{-1}$ , significantly smaller than other local region results, such as Taihu lake (2106.3 mmol m<sup>-2</sup> yr<sup>-1</sup>) and Donghu Lake (531.5  $\pm$ 424.3 mmol  $m^{-2} vr^{-1}$ ) (Xing et al., 2005; Wang et al., 2006; Bastviken et al., 2011; Yang et al., 2011). CH<sub>4</sub> fluxes from lakes are largely influenced by the two key processes: the CH<sub>4</sub> production and migration process. CH<sub>4</sub> as the main product during the anaerobic mineralization of organic matter, is affected by various environmental factors in the water and sediments, e.g., temperature, organic matter, lake morphology (Bastviken et al., 2004; Gudasz et al., 2010; Marotta et al., 2014; Gruca-Rokosz and Tomaszek, 2015). CH<sub>4</sub> produced in the sediments and deep water can further migrate to the surface water, and subsequently emit to the atmosphere. The main pathways of CH<sub>4</sub> fluxes are ebullition fluxes, diffusive fluxes, storage fluxes, and fluxes mediated by aquatic vegetations (Bastviken et al., 2004). CH<sub>4</sub> fluxes are influenced by not only the biotic (e.g. Chaoborus), but also the abiotic factors (e.g. wind speed, water depth, CH<sub>4</sub> production and oxidation rates) (Bastviken et al., 2004; Hofmann et al., 2010; Carey et al., 2017). Essentially, the supply of accessible organic matter is the prerequisite for methanogenesis in the water as well as the sediments.

With the accelerating changes in large-scale land use and anthropogenic alternations of nutrients cycling, the freshwater eutrophication and CBBs occurrence have become the main concern in the freshwater management (Huisman et al., 2004; Carey et al., 2012; Michalak et al., 2013; Gkelis et al., 2014). When CBBs occur, they are easily driven and trapped by the macrophytes in the littoral zones, with subsequently forming dense scums (Xing et al., 2011). After their collapse, the intensive sedimentation and decomposition rapidly exhaust the dissolved oxygen (DO), and release a large amount of organic matter in the water as well as the sediments (Mann et al., 2013; Xu et al., 2015a, b; Yan et al., 2017). The environmental condition changes induced by the CBBs decomposition provide superior conditions for methanogenesis. Moreover, it is suggested that lake eutrophication may play an important role in CH<sub>4</sub> budgets in lake ecosystems, but the mechanisms are not fully clear (West et al., 2012, 2016). Hence, it's interesting to investigate the potential role of CBBs play in the CH<sub>4</sub> productions in eutrophic lakes.

In this study, the CH<sub>4</sub> concentrations with related physicochemical parameters in surface water and sediments were investigated during the occurrence of heavy CBBs in Zhushan Bay of Taihu lake. It is hypothesized that the occurrence of CBBs acts as a neglected facilitator of CH<sub>4</sub> production in eutrophic lakes, and CH<sub>4</sub> produced in sediments influences the CH<sub>4</sub> concentrations in the surface water, which subsequently emits to the atmosphere. These results will draw attentions to the role of CBBs playing in the CH<sub>4</sub> productions and emissions from eutrophic lakes, and contribute to a more accurate estimation for future CH<sub>4</sub> budget in eutrophic lakes.

#### 2. Materials and methods

#### 2.1. Sampling sites

The study area, located in the Zhushan Bay of Taihu lake, was frequently influenced by the intense CBBs (Fig. 1). The CH<sub>4</sub> concentrations in surface water were determined in all 28 sites in August 2017. In this period, the accumulated CBBs contributed to the investigation of CH<sub>4</sub> distribution characteristics between the CBBs accumulated zones and the open lake areas. However, in consideration of in situ monitoring deviations caused by the time-cost determination of CH<sub>4</sub> concentrations in sediments, only five locations were selected, representing the influence of CBBs (Fig. 1, S1–S5). Herein, S1–S3 were located in the littoral zone with the intense CBBs, while S4 and S5 were located in the open lake area without observable CBBs.

#### 2.2. Analytical methods

#### 2.2.1. Physicochemical parameters

Total nitrogen (TN) and total phosphorus (TP) in surface water were photometrically determined using a UV–vis spectrophotometer (UV-6100, mapada, China) after digestion with  $K_2S_2O_8$  + NaOH (Raveh and Avnimelech, 1979; Ebina et al., 1983). Samples for the dissolved total nitrogen (DTN) and phosphorus (DTP) in the water were filtered and measured by the same methods with TN and TP. Samples for dissolved organic carbon (DOC) were acidified to pH < 2.0 and analyzed with a multi N/C analyzer (HT 1300, analytikjena, Germany). Ammonium nitrogen (NH<sub>4</sub><sup>+</sup>) and nitrate nitrogen (NO<sub>3</sub><sup>-</sup>) levels were determined using an auto-analyzer (Auto-analyzer 3, SEAL, Germany). Samples for PO<sub>4</sub><sup>3-</sup> analysis were filtered with Whatman GF/F and measured by the acetone extraction (Arar and Collins, 1997).

 $NH_4^+$  and  $NO_3^-$  levels in sediments were determined after being extracted by KCl solution (1 mol/L) using an auto-analyzer (Auto-analyzer 3, SEAL, Germany). The TN content in sediments was photometrically performed with a UV–vis spectrophotometer (UV-6100, mapada, China) (Raveh and Avnimelech, 1979). The TP content in sediments was analyzed by using the SMT method (Ruban et al., 2001). Samples for TOC analyses were freeze-dried and treated with 10% HCl overnight, dried at 60 °C for 12 h and then determined using a multi N/C analyzer (HT 1300, analytikjena, Germany). The porosity of the sediments was calculated by the water content of the sediments after drying at 80 °C until achieved constant weight (Riedinger et al., 2010). Drying sediment samples were calcined at 550 °C for 3 h, the Ignition loss was calculated from the difference in mass before and after (Heiri et al., 2001).

#### 2.2.2. CH<sub>4</sub> concentration

The dissolved  $CH_4$  concentrations in the water were measured using the headspace method (Casper et al., 2003; Hofmann et al., 2010), by gas chromatography with flame ionization detection (7890B Agilent, USA). The calculation method of  $CH_4$  concentrations in the water was as follows (Wiesenburg and Guinasso Jr, 1979).

$$\ln C_{w} = \ln f_{G} + A_{1} + A_{2} (100/T) + A_{3} \ln (T/100) + A_{4} (T/100)^{2} + S \left[ B_{1} + B_{2} (T/100) + B_{3} (T/100)^{2} \right]$$
(1)

The  $C_w$  was the CH<sub>4</sub> concentration in surface water,  $\mu$ mol·L<sup>-1</sup>;  $f_G$  was the CH<sub>4</sub> concentration in headspace after equilibrium between water and headspace with N<sub>2</sub> (99.9999%); *T* was the thermodynamic temperature, K, in this study, *T* was 298.15 K controlled by water bath; *S* was the salinity of lake water,  $\infty$ , here, it was 0 in freshwaters;  $A_i$  and  $B_i$  were constants, the values of  $A_1$ - $A_4$  were -415.2807, 596.8104, 379.2599, and -62.0757, respectively; the values of  $B_1$ - $B_3$  were -0.059160, 0.032174, and -0.004820, respectively.

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