Science of the Total Environment 651 (2019) 466–474

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Cyanobacteria blooms: A neglected facilitator of CH_4 production in eutrophic lakes

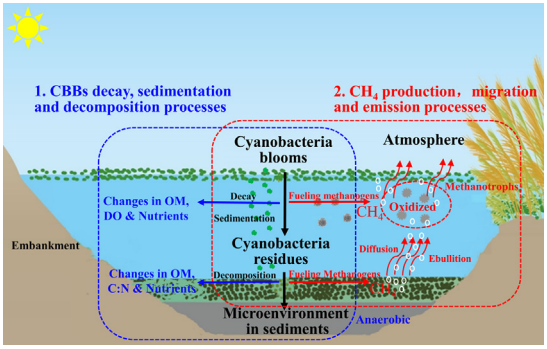
Xingcheng Yan [a,1], Xiaoguang Xu [a,1], Ming Ji [a], Zhongqian Zhang [a], Mingyue Wang [a], Songjun Wu [a], Guoxiang Wang [a,b,c,d,*], Chi Zhang [a], Huichao Liu [a]

[a] School of Environment, Nanjing Normal University, Nanjing 210023, PR China
[b] Jiangsu Center for Collaborative Innovation in Geographical Information Resource Development and Application, Nanjing 210023, PR China
[c] Jiangsu Key Laboratory of Environmental Change and Ecological Construction, Nanjing 210023, PR China
[d] Jiangsu Engineering Laboratory of Water and Soil Eco-remediation, Nanjing 210023, PR China

HIGHLIGHTS

- The high-resolution determinations of CH_4 concentrations in Taihu lake were conducted.
- CH_4 concentrations were influenced by the physiochemical parameters in surface water and sediments.
- CH_4 production in sediment was consistent with that in surface water.
- CBBs act as a neglected facilitator of CH_4 production in eutrophic lakes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 July 2018
Received in revised form 11 September 2018
Accepted 16 September 2018
Available online 17 September 2018

Editor: Jay Gan

Keywords:
Methane
Cyanobacteria blooms
Eutrophic lakes
Surface water
Sediment

ABSTRACT

Lakes are regarded as one of the important sources of atmospheric CH_4. However, the role of cyanobacteria blooms (CBBs) play in the CH_4 production in eutrophic lakes is not fully clear. In this study, the spatial distribution characteristics of CH_4 concentrations in surface water and sediment columns were investigated in Zhushan Bay of Taihu lake, China. Results showed that CH_4 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_4 concentrations were strongly influenced by various factors. In surface water, the occurrence of CBBs greatly contributed to CH_4 productions, as evidenced by the well-predicting for CH_4 concentrations using Chl-*a* and NH_4^+ concentrations. In the sediments, the Ignition Loss and C:N ratio values were two indicators of CH_4 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_4 production and migration from sediments to the water column, resulting in the coherence in CH_4 concentrations between the sediments and the surface water. The high-resolution determinations of CH_4 concentrations in surface water and sediments clarified that the CBBs were a neglected facilitator of CH_4 productions, which should be considered in the future estimation of CH_4 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).
[1] These authors contributed equally to this manuscript.

https://doi.org/10.1016/j.scitotenv.2018.09.197
0048-9697/

1. Introduction

Methane (CH_4) is an important greenhouse gas in the atmosphere, responsible for approximately 20% of the Earth's warming since pre-industrial times (Kirschke et al., 2013). CH_4 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_4 in the global CH_4 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_4 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_4 productions in lakes is fundamental to predicting the responses of carbon cycle in lake ecosystems to future climate change.

CH_4 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_4 flux was 225.7 ± 626.2 mmol m^{-2} yr^{-1}, significantly smaller than other local region results, such as Taihu lake (2106.3 mmol m^{-2} yr^{-1}) and Donghu Lake (531.5 ± 424.3 mmol m^{-2} yr^{-1}) (Xing et al., 2005; Wang et al., 2006; Bastviken et al., 2011; Yang et al., 2011). CH_4 fluxes from lakes are largely influenced by the two key processes: the CH_4 production and migration process. CH_4 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_4 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_4 fluxes are ebullition fluxes, diffusive fluxes, storage fluxes, and fluxes mediated by aquatic vegetations (Bastviken et al., 2004). CH_4 fluxes are influenced by not only the biotic (e.g. *Chaoborus*), but also the abiotic factors (e.g. wind speed, water depth, CH_4 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_4 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_4 productions in eutrophic lakes.

In this study, the CH_4 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_4 production in eutrophic lakes, and CH_4 produced in sediments influences the CH_4 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_4 productions and emissions from eutrophic lakes, and contribute to a more accurate estimation for future CH_4 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_4 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_4 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_4 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_4^+) and nitrate nitrogen (NO_3^-) levels were determined using an auto-analyzer (Auto-analyzer 3, SEAL, Germany). Samples for PO_4^{3-} analysis were filtered with Whatman GF/F and measured by the colorimetry method. Samples for Chl-*a* analysis were conducted 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_4 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).

$$\ln C_w = \ln f_G + A_1 + A_2\,(100/T) + A_3 \ln (T/100) + A_4\,(T/100)^2 + S\left[B_1 + B_2\,(T/100) + B_3\,(T/100)^2\right] \quad (1)$$

The C_w was the CH_4 concentration in surface water, $\mu mol \cdot L^{-1}$; f_G was the CH_4 concentration in headspace after equilibrium between water and headspace with N_2 (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, ‰, 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.

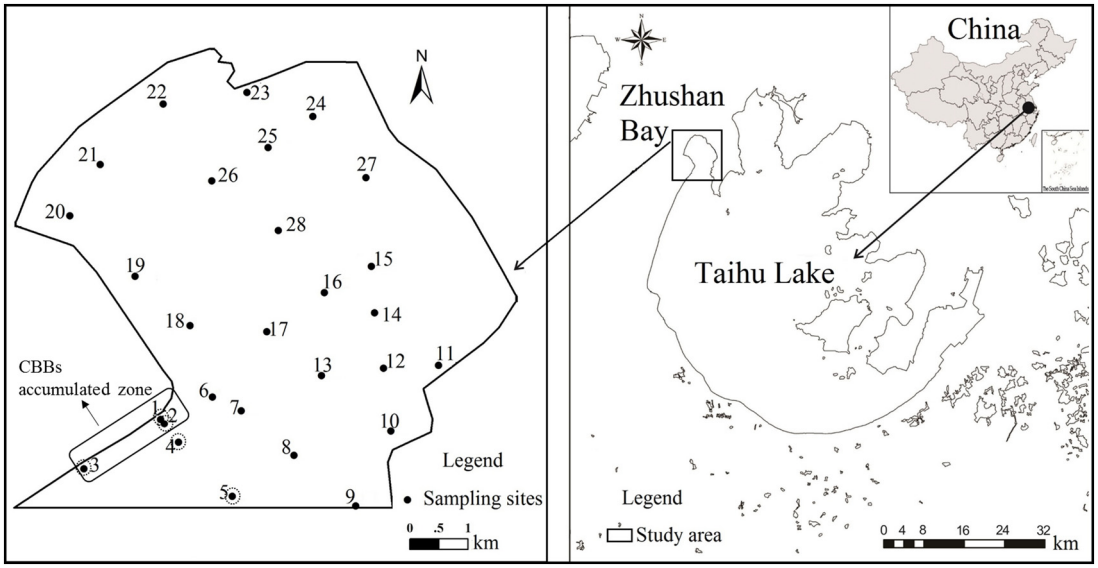


Fig. 1. The schematic diagram of study area and sampling sites. The CH_4 concentrations in the surface water of 28 sites were determined, while only S1–S5, surrounded by dotted circle, were determined for CH_4 contents in sediments. The CBBs accumulated zones (S1–S3) were marked with the full line.

Sediment samples were collected by the columnar dredge (PhenoSpex, China), containing a length of 100 cm acrylic tube with an internal diameter of 9 cm, which was pre-perforated in one side with the diameter of 10 cm and the interval of 3 cm, and sealed with tape around its ektexine before sampling. After retrieval, 5 mL of the sediment samples were extracted with 10 mL front-cut plastic syringes trough the pre-perforated holes, and extruded into a 43 mL brown glass serum vial containing 20 mL of 2.5% NaOH (Riedinger et al., 2010). The vial was immediately capped with a butyl septum and crimp cap, and subsequently shaken and finally kept in a storage box with ice bag. For porosity determination, other 43 mL brown glass serum vials were used. CH_4 contents in sediments of each interval were analyzed for three replicates, by gas chromatography. The CH_4 concentration in sediments was described as μmol CH_4 in per unit volume of pore water, and the volume of pore water was calculated based on the porosity.

2.2.3. Statistical analyses

The Statistical Package of the Social Science 18.0 (SPSS 18.0) was used for statistical analysis. The one-way analysis of variance (ANOVA) and correlation analysis were carried out using Bivariate Correlations Analysis. The relations of CH_4 between surface water and sediments were conducted by Spearman Correlations Analysis. Multiple regression analysis with a fully stepwise selection procedure was used to identify and model the strongest predictor variable (s) of CH_4 in surface water and sediments. The criteria of $p < 0.05$ and $p < 0.01$ were used to determine statistical significance at the 0.05 and 0.01 levels (two-tailed).

Parameters in sediments were performed by Origin 8.5, and by ArcMap 10.2 in surface water. The conceptual diagram was performed by Adobe Illustrator CS5.

3. Results

3.1. Vertical distributions of physicochemical parameters in sediments

The vertical distribution characteristics of Ignition loss, porosity, TN, TP, NH_4^+, NO_3^-, TOC, and C:N ratio were shown in Fig. 2. In general, the Ignition loss, porosity, TN, TP, NH_4^+, and TOC in sediments were decreased with the sediment depth, and were much higher in the CBBs accumulated zones than that in the open lake areas (Fig. 2a, b, c, d, e and g). The average TN and TP contents in the CBBs accumulated zones were 4027.36 ± 1977.82 mg·kg^{-1} and 2186.17 ± 743.17 mg·kg^{-1}, respectively. The highest values of TN and TP in the CBBs accumulated zones were 8712.15 ± 73.97 mg·kg^{-1} and 3936.24 ± 31.55 mg·kg^{-1}, respectively. In the open lake areas, the average TN and TP contents were 1355.36 ± 285.82 mg·kg^{-1} and 1336.65 ± 434.69 mg·kg^{-1}, respectively. The average NH_4^+ content in CBBs accumulated zones was 4 times of that in the open lake area. Contrarily, the NO_3^- contents in open lake areas were higher than that in the CBBs accumulated zones (Fig. 2f). The TOC contents in sediments of CBBs accumulated zones, especially in the first 10 cm of sediment column, were much higher than that in the open lake areas, with the values ranging from 37.14 ± 0.16 g·kg^{-1} to 53.42 ± 2.12 g·kg^{-1}. While in the open lake areas, the TOC contents ranged from 8.03 ± 0.11 mg·kg^{-1} to 12.79 ± 0.24 mg·kg^{-1}. The vertical distributions of C:N ratios in sediments were fluctuant, but displayed obvious differences between open lake areas (>7) and CBBs accumulated zones (<7) (Fig. 2h).

3.2. Physicochemical parameters in surface water

The spatial distribution characteristics of nutrient concentrations in surface water were shown in Fig. 3. In general, TN, TP, NH_4^+, DOC, and DTN concentrations in CBBs accumulated zones were much higher than that in the open lake areas, and the NO_3^- concentration was the highest in the northern area of Zhushan Bay. In CBBs accumulated zones, the TN and TP concentrations were 8.90 mg·L^{-1} and 1.90 mg·L^{-1}, respectively (Fig. 3a and b), and the NH_4^+ concentration was the highest of 5.98 mg·L^{-1}, occupying 67% of the TN. While in the open lake areas, the NH_4^+ concentrations ranged from 0.04 mg·L^{-1} to 1.51 mg·L^{-1}, <10% of TN (Fig. 3c). The NO_3^- concentrations in the northern shore was the highest, with the value of 1.75 ± 0.06 mg·L^{-1}, >50% of the TN. However, in CBBs accumulated areas, the NO_3^- concentrations were the lowest, even under 0.01 mg·L^{-1} (Fig. 3d). The DOC concentration in surface water was the highest with the value of 103.6 ± 0.06 mg·L^{-1} in S3 (Fig. 3h). In CBBs accumulated zones, the Chl-*a* concentrations in surface water were much higher than that in the open lake areas, with the highest value of 4253.08 μg·L^{-1} in S3 (Fig. 3i). In the open lake areas, the concentrations of Chl-*a* ranged from 30.88 μg·L^{-1} to 284.21 μg·L^{-1}.

3.3. Vertical distributions of CH_4 in sediments

The vertical contents of CH_4 in five columns of sediments were largely fluctuant, and there were no obvious patterns in vertical

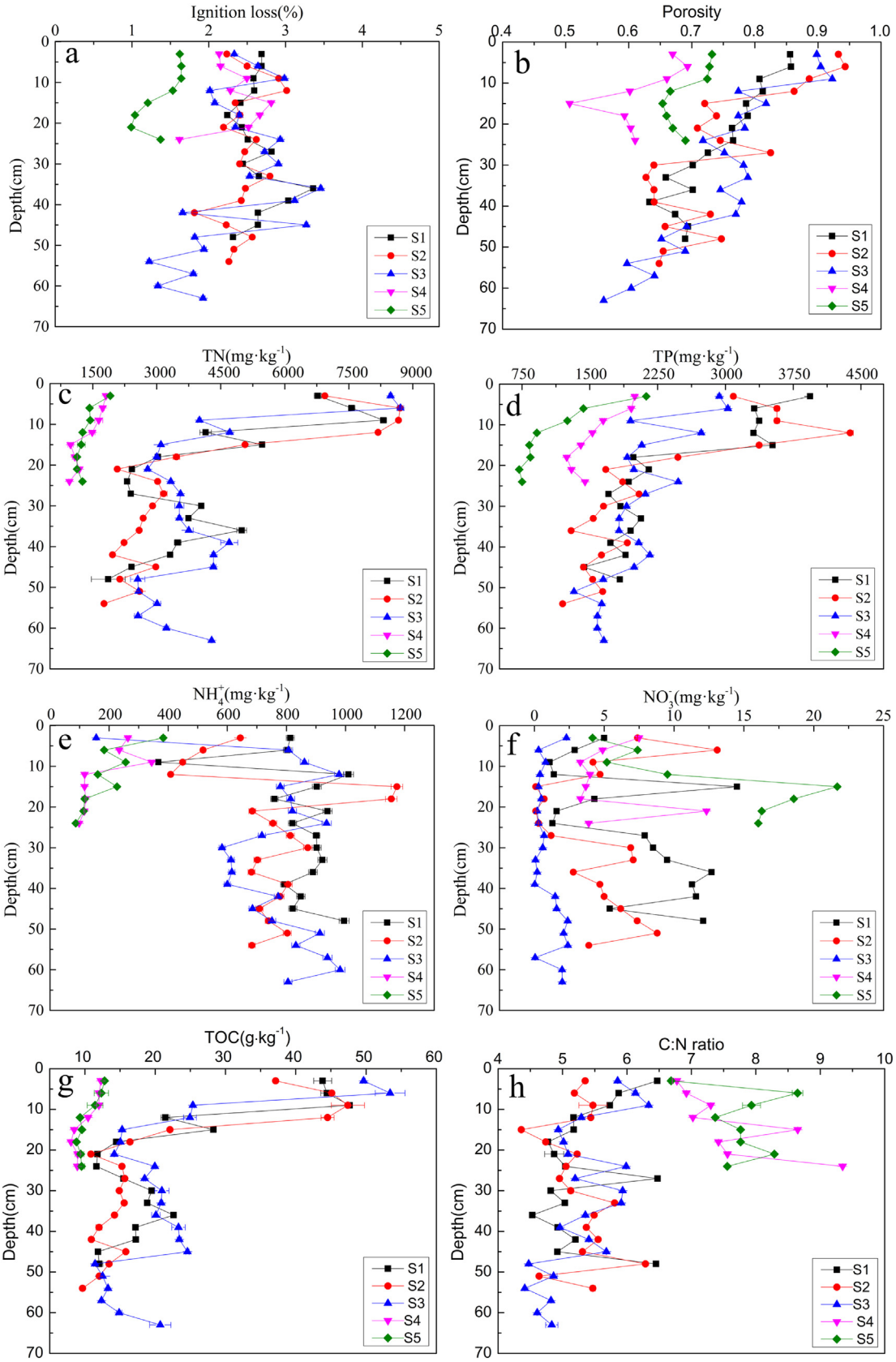


Fig. 2. Vertical distributions of physicochemical parameters in sediments.

sediment layers (Fig. 4). However, CH_4 contents in CBBs accumulated zones (S1–S3) were largely higher than that in the open lake areas (S4, S5). The average content of CH_4 in S1–S5 was 909.77 ± 257.92 μmol·L^{-1}, 1369.70 ± 395.41 μmol·L^{-1}, 947.57 ± 166.55 μmol·L^{-1}, 753.57 ± 264.67 μmol·L^{-1}, and 45.11 ± 13.63 μmol·L^{-1}, respectively. The average CH_4 content in CBBs accumulated zones was 1075.68 ±

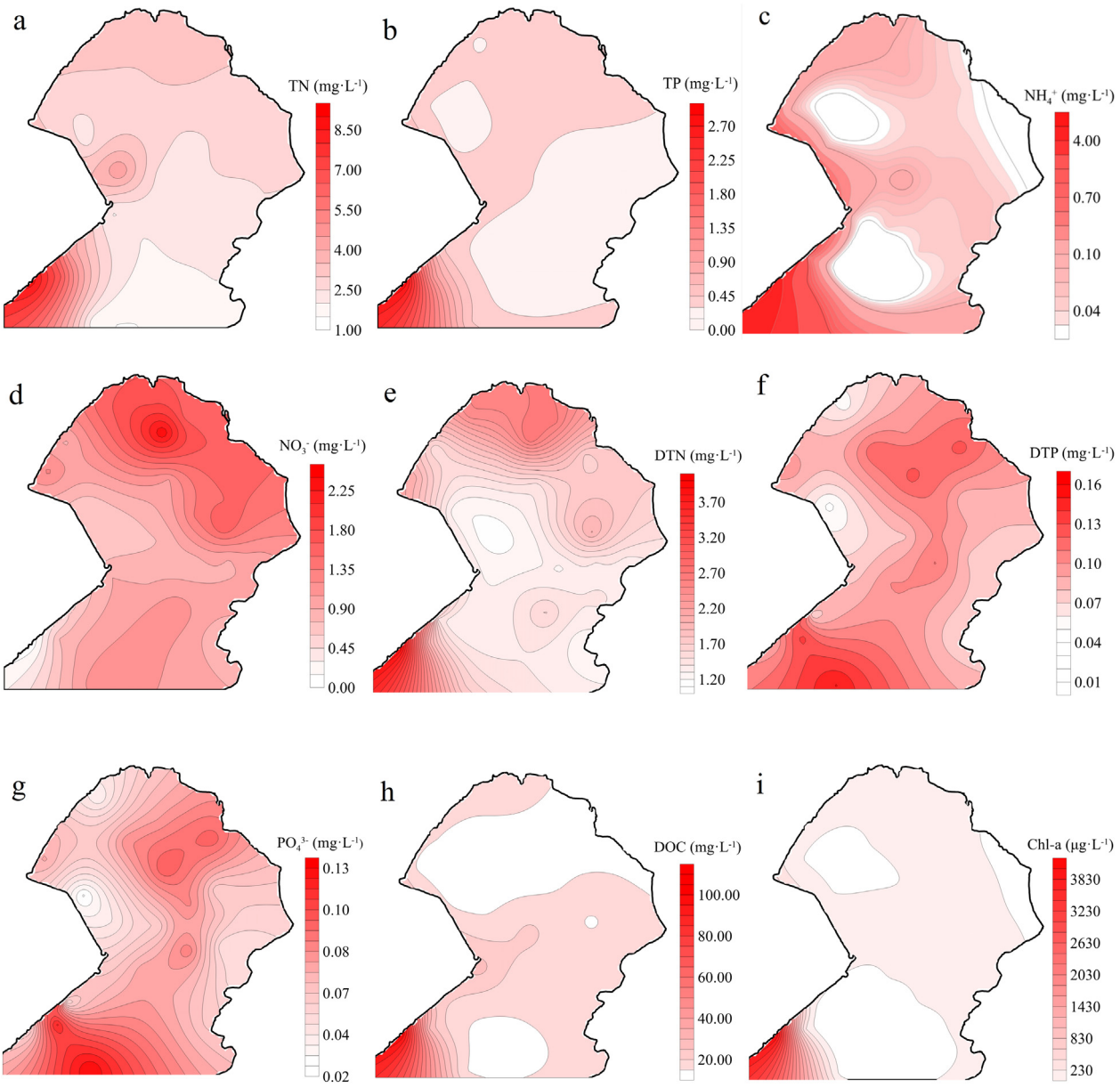


Fig. 3. Physicochemical parameters in surface water.

208.48 μmol·L^{-1}, comparing to 422.51 ± 400.75 μmol·L^{-1} in the open lake areas.

3.4. CH_4 concentrations in surface water

CH_4 concentrations in surface water of CBBs accumulated zones were much higher than that in the open lake areas (Fig. 5), with the highest value of 3.79 ± 0.10 μmol·L^{-1} in S3. The average CH_4 concentration in the CBBs accumulated zones and open lake areas were 1.78 ± 1.43 μmol·L^{-1} and 0.14 ± 0.06 μmol·L^{-1}, respectively. In open lake areas, the CH_4 concentration ranged from 0.02 ± 0.003 μmol·L^{-1} to 0.25 ± 0.02 μmol·L^{-1}. The CH_4 concentration in the west littoral zones of Taihu lake was high, especially in CBBs accumulated areas (such as S1, S2, and S3), according to the spatial distribution characteristics of CH_4 concentrations in Zhushan Bay of Taihu lake (Fig. 5).

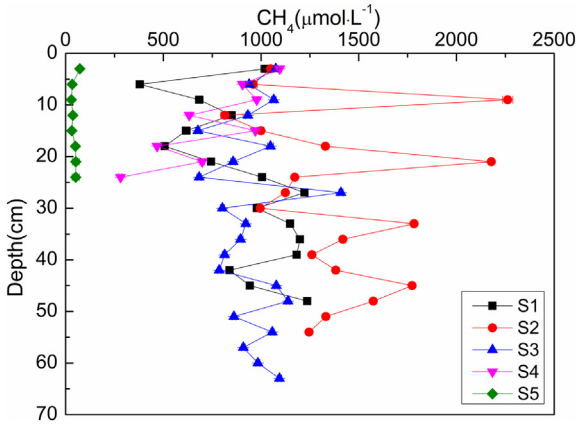


Fig. 4. Vertical distributions of CH_4 in sediments.

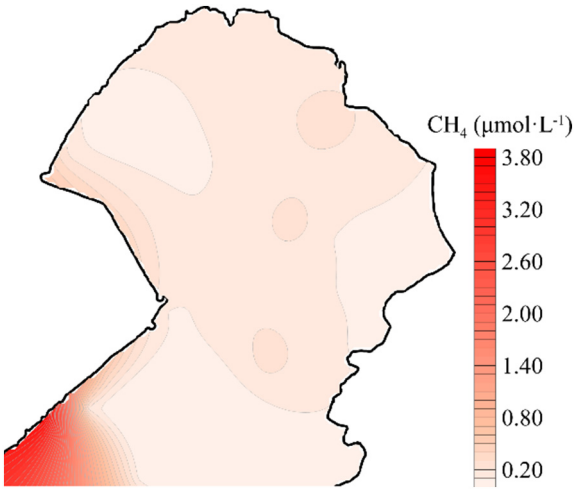


Fig. 5. CH_4 concentrations in surface water.

3.5. The relations between physicochemical parameters and CH_4 in sediments

In sediments, CH_4 content was positively related to the TN ($p < 0.05$), Ignition loss and NH_4^+ content ($p < 0.01$), and negatively related to the NO_3^- ($p < 0.05$) and C:N ratios ($p < 0.01$). The strongest correlation variable was C:N ratios (Fig. 6). In addition, the multiple regression analysis showed that the Ignition loss and C:N ratios can be used to predict the CH_4 contents in sediments (Adj. $R^2 = 0.373$, Table 1).

3.6. The relations between physicochemical parameters and CH_4 in surface water

The correlations between CH_4 and physicochemical variables in surface water were analyzed (Fig. 7). CH_4 concentration was significantly and positively related to TN, TP, NH_4^+, DOC, and Chl-*a* concentrations in surface water ($p < 0.01$), and negatively related to NO_3^- concentration ($p < 0.01$). The strongest correlation variable was Chl-*a* concentration.

The multiple regression analysis indicated that three models could be used to predict the CH_4 concentration in the water, that is, only Chl-*a*, or Chl-*a* and NH_4^+, or Chl-*a*, NH_4^+ and TP. Here, the Chl-*a* and NH_4^+ were chosen to fit the model (Adj. $R^2 = 0.971$, Table 2), since the TP concentrations in the water were strongly influenced by the primary production.

4. Discussion

In this study, CH_4 contents in sediments of CBBs accumulated zones were much higher than that in the open lake areas. CH_4 represents a major product of organic matter decomposition in lakes, and the majority of CH_4 production occurs in anoxic sediments (Rudd and Hamilton, 1978). Anaerobic carbon mineralization, in terms of methanogenesis in anaerobic sediments, can account for up to 50% of the overall carbon mineralization in freshwater lakes (Wetzel, 2001; Bastviken et al., 2004; Hofmann et al., 2010). In CBBs accumulated zones, the TOC contents and the Ignition loss values in sediments were higher than that in the open lake areas, due to the sedimentation of CBBs from water to sediments. In addition, the anoxic conditions were induced by the decay of CBBs in sediments, where the anaerobic biological degradation of organic carbon releases not only CO_2 but also a significant amount of CH_4 (Bastviken et al., 2011). The mineralization process of organic carbon in

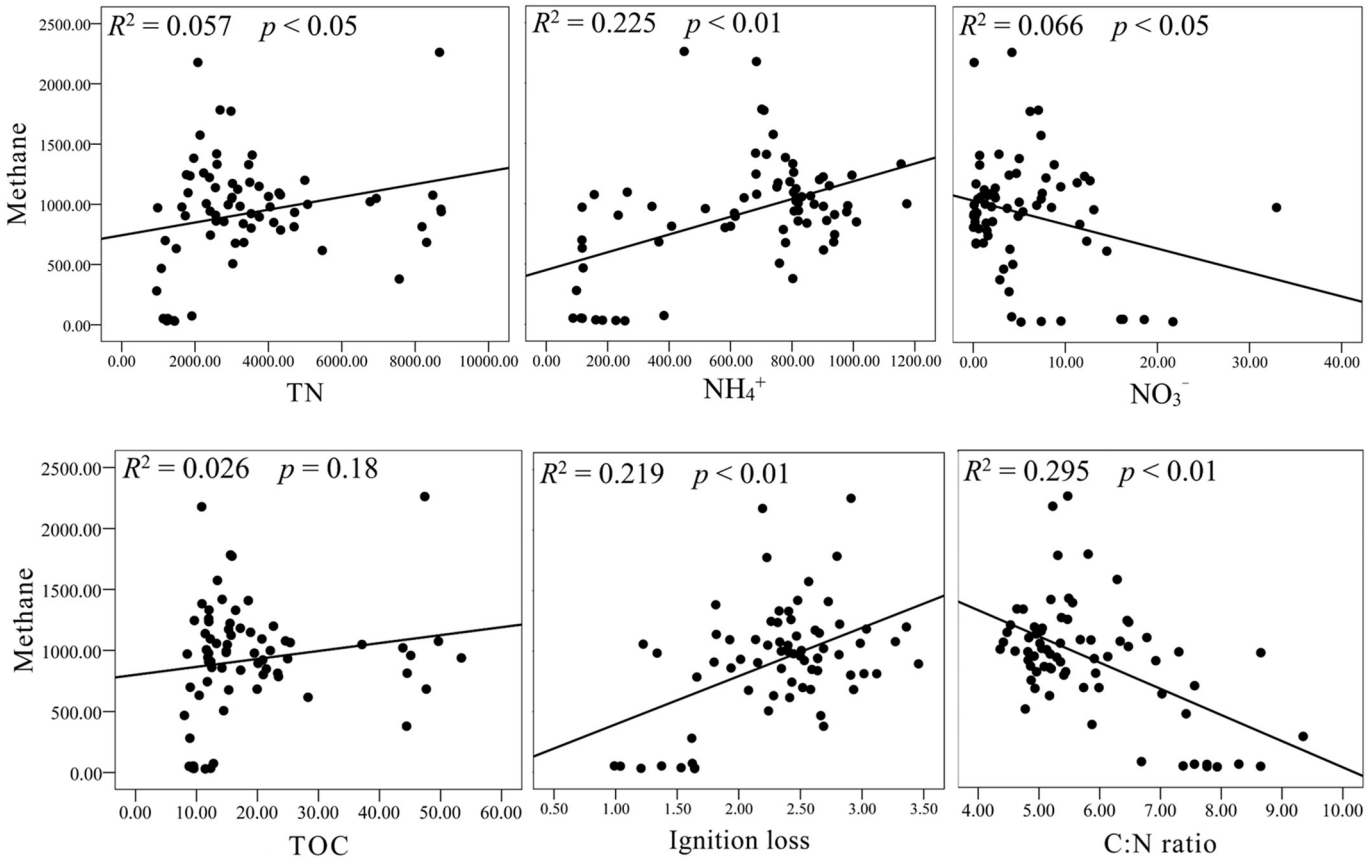


Fig. 6. The relations between physicochemical parameters and CH_4 in sediments.

Table 1
Multiple regression model with stepwise selection procedure displaying variables significantly correlated with measured CH_4 concentrations in the sediments (n = 71).

Equation	Adj. R^2	Significant level		
		F-test	*t*-Test	
		F	t_1	t_2
$CH_4 = 1291.511 - 173.929$ (C:N ratio) + 278.487 (Ignition loss) + β	0.373	21.823	−4.379	3.270

CH_4 (μmol·L^{-1}), Ignition loss (%); β residuals for the equation, also an indicator for unknown sources.

Table 2
Multiple regression model with stepwise selection procedure displaying variables significantly correlated with measured CH_4 concentrations in the surface water (n = 28).

Equation	Adj. R^2	Significant level		
		F-test	*t*-Test	
		F	t_1	t_2
$CH_4 = 0.092 + 0.01$ (Chl-*a*) + 0.174 (NH_4^+) + α	0.971	422.786	9.969	4.418

CH_4 (μmol·L^{-1}), Chl-*a* (μg·L^{-1}) and NH_4^+ (mg·L^{-1}); α residuals for the equation, also an indicator for unknown sources.

sediment is affected by temperature, lake depth, organic carbon quality, and lake trophic state (Heyer and kalff, 1998; Molot and Dillon, 1996; Gudasz et al., 2010; Marotta et al., 2014). Regressions based on all available data in sediments suggested that Ignition loss and C:N ratio values were most useful variables for predicting CH_4 contents in sediments (Table 2). The Ignition loss value is a reference for organic matter contents in sediments. The positive correlations between CH_4 content and Ignition loss value indicated that sufficient organic matter contributed greatly to the CH_4 production from sediments. The C:N ratio is an indicator of organic matter source. The C:N ratio < 8 indicates that the organic matter mainly derives from autochthonous, while the C:N ratio > 12 relates the dominant allochthonous organic matter (Martinotti et al., 1997; Gąsiorowski and Sienkiewicz, 2013). In this study, the C:N ratios were all below 12 with spatial heterogeneities, suggesting the compositions of sedimentary organic matter dominated by autochthonous sources. Considering that the Ignition loss and C:N ratio values were predictive for CH_4 contents in sediments, it was concluded that methanogenesis process was not only affected by the quantities, but also the qualities of sedimentary organic matter. It can be concluded that the CBBs are better substrates than the allochthonous organic matter for methanogenesis in lake sediments of eutrophic lakes (Schwarz et al., 2008; Davidson et al., 2015; West et al., 2015).

The CH_4 concentrations in surface water of CBBs accumulated zones were much higher than that in the open lake areas. On the one hand, CH_4 productions through the CBBs decomposition process were an important source of CH_4 concentration in the water. In this study, the west littoral zone of Taihu lake was frequently influenced by the intense CBBs, especially in the summer. These overwhelming CBBs are generally utilized by microorganisms in the water and sediments during their sedimentation from the water column to the surface sediments (Shao et al., 2013; Xu et al., 2014), resulting in anoxic environments with subsequently the release of organic matter in the water and sediments (Wang and Chen, 2008; Mann et al., 2013; Yan et al., 2017). It promotes an increase of the abundance of fermentative microorganisms and fuels the growth of heterotrophs in the water (Komada et al., 2013; Chen et al., 2016), which stimulates methanogenesis process in the water. On the other hand, CH_4 production in the sediments was another important source of CH_4 concentration in the water. CH_4 produced by the mineralization of CBBs residues, further migrates to the overlying water, as evidenced by the site-to-site symmetric phenomenon of CH_4

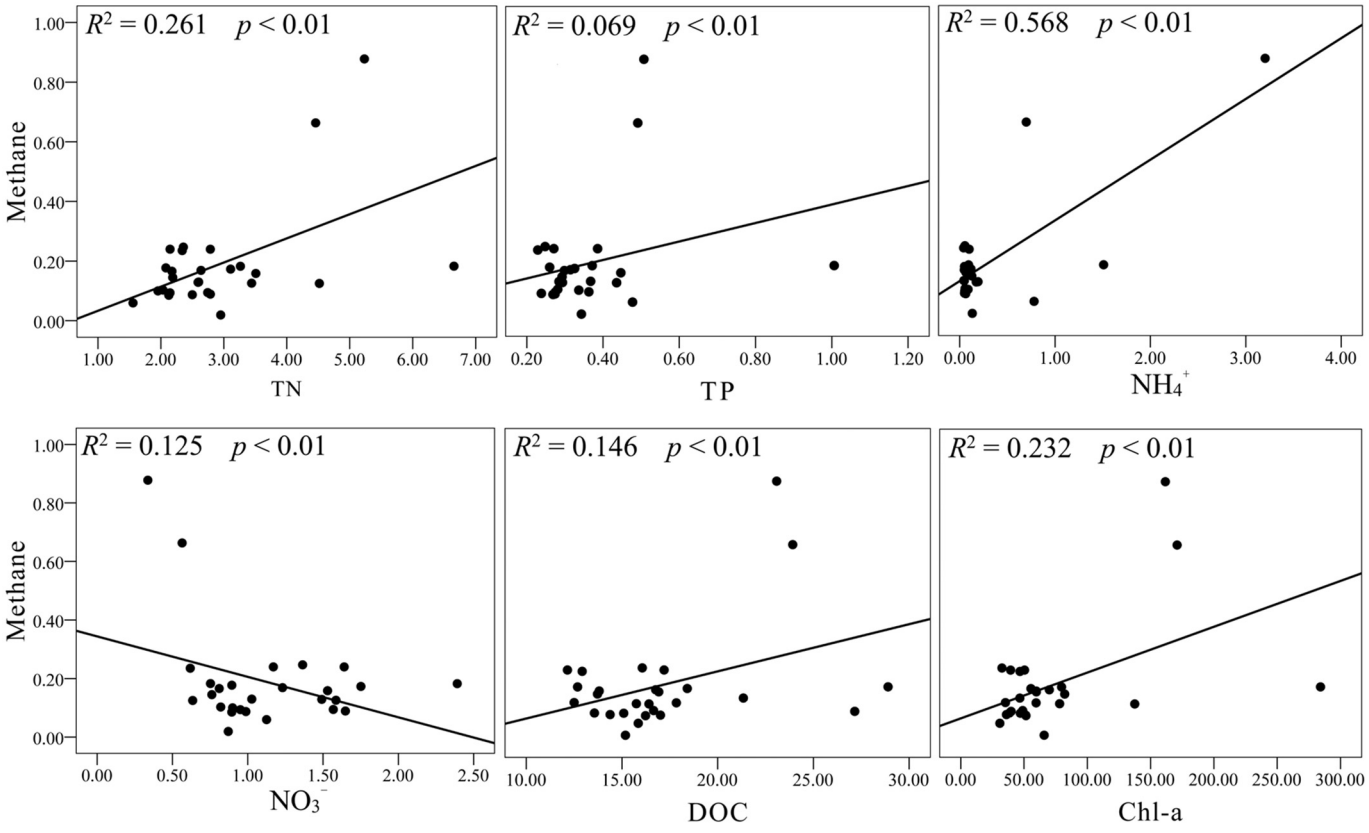


Fig. 7. The relations between physicochemical parameters and CH_4 in surface water (S3 site was excluded with its outliers).

contents between sediments and the surface water. Methanogenesis processes are influenced by various factors in the water. Regressions based on all available data suggested that Chl-*a* and NH_4^+ concentrations were most useful variables for predicting CH_4 concentrations in the water. Meanwhile, the relationships between CH_4 and Chl-*a* were generally found in accordance with the relationships with TP, supporting that autochthonous production stimulated CH_4 productions. A significantly positive relation was found between CH_4 and NH_4^+ ($p < 0.01$), indicating the indirect influence of NH_4^+ levels on CH_4 productions. It is related that NH_4^+ and CH_4 are both produced during the mineralization processes of organic matter. In addition, NH_4^+ concentrations are probably induced by a relative anoxic condition in the water, otherwise, it would be oxidized to NO_3^- under oxic conditions. This phenomenon has already been observed that NH_4^+ accumulation in the hypolimnion provides an overall measurement of organic matter mineralization (Bédard and Knowles, 1991). The anoxic conditions in the water column further contribute to CH_4 productions. Therefore, the accumulated NH_4^+ concentration may be along with the high CH_4 production in surface water.

Undoubtedly, not all of the CH_4 produced in sediments can migrate to the surface water, and subsequently to the atmosphere. It suggests that 51–81% of the CH_4 produced in the deep sediments is oxidized in the water column (Bastviken et al., 2004). In this study, the CH_4 concentrations of S1–S5 in the water-sediments interface were analyzed, with the values of 1.17, 8.09, 15.61, 0.59, and 0.16 $\mu mol \cdot L^{-1}$, respectively. Compared to the CH_4 concentration in the surface water of relevant sites, 24.79%–91% of the CH_4 in the water-sediment interface were oxidized, in the case of without considering the CH_4 diffusion in the water column. In addition, the emission potential of CH_4 in surface water was estimated in this study, based on the equilibrium with the atmospheric CH_4 concentration of 2.2 $nmol \cdot L^{-1}$ in the surface water (Wiesenburg and Guinasso Jr, 1979), wherein the atmospheric concentration of CH_4 being set up to 1.8 ppm (Encinas Fernández et al., 2014). CH_4 concentrations in surface water were all supersaturation, especially in the CBBs accumulated zones. Even though, the higher saturation of CH_4 in surface water may be not related to the higher emission fluxes, because gas flux in water-air interface is also related to the Schmidt number of gas and Transfer velocity (Cole and Caraco, 1998; Crusius and Wanninkhof, 2003). The difference between the CH_4 concentration in surface water and the equilibrated CH_4 with atmospheric concentration was the driving force for CH_4 migration at water-air interface. Therefore, the potential of CH_4 emission from surface water to atmosphere in CBBs accumulated zones was much higher than that in the open lake areas.

Combined with our previous findings of laboratory observations, the CH_4 production is increased with the addition of CBBs (Yan et al., 2017). It suggests that CBBs play a facilitator role in CH_4 production in eutrophic lakes, but largely neglected in numerous studies. The promoting effects of CBBs on CH_4 production were mainly through the following two aspects: 1) Sufficient labile organic matters, provided by CBBs, were the prerequisite substance for CH_4 production. It was clarified that a large amount of organic carbon released to the water column and sediments during the decay of CBBs (Xu and Jiang, 2013; Mann et al., 2013; Yan et al., 2017). 2) The anoxic environmental conditions in the water and sediments, induced by the decomposition of CBBs, were a key variable controlling the methanogens processes. Dense scum of CBBs prevent the reoxygenation processes in the water. In addition, the decay processes of CBBs also deplete the dissolved oxygen (He et al., 2013). In order to clearly illuminate the role of CBBs play in the CH_4 productions in eutrophic lakes, a conceptual diagram was put forward (Fig. 8). During the CBBs decay, i.e., the sedimentation and decomposition processes, the physicochemical parameters and environmental conditions are changed (e.g. organic matter, nutrients, C:N and anaerobic conditions), which is further to fuel the methanogens in the water as well as sediments. Therefore, CH_4 productions from eutrophic freshwater lakes need to be re-estimated due to the occurrence of CBBs.

5. Conclusion

The CH_4 concentrations and emission potential in CBBs accumulated zones were much higher than that in the open lake areas, because of the sufficient labile organic matter and anoxic environmental conditions induced by the decay processes of CCBs. CH_4 contents were influenced by various factors in the water and sediment columns. Chl-*a* and NH_4^+ were excellent predictors for CH_4 concentrations in surface water, and those were Ignition loss and C:N ratios in sediments. CH_4 produced in the sediments could migrate to the water, resulting in the coherence of CH_4 concentrations between sediments and the surface water. These findings suggested that CBBs were an important, yet largely neglected facilitator for CH_4 productions, which should be considered in the future estimation of CH_4 emissions in eutrophic lakes.

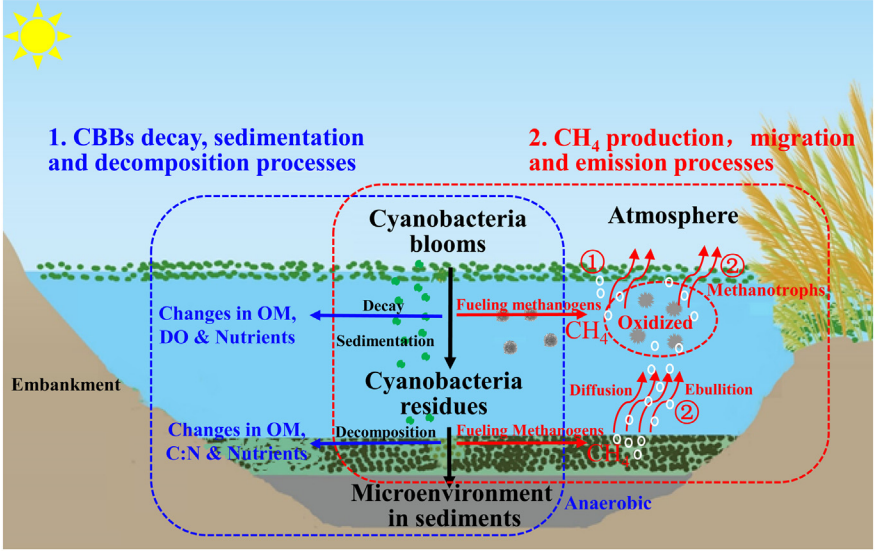


Fig. 8. A conceptual diagram of relationships between CBBs and CH_4 production in eutrophic lakes. Sufficient labile organic matters, provided by CBBs were the prerequisite substance for CH_4 production. The anoxic environmental condition in the water and sediments, induced by the decomposition of CBBs was the key variable controlling the methanogens process. The production, migration and emission processes: ① from the water, ② from the sediments.

Acknowledgements

This research was supported by the Major Science and Technology Program for Water Pollution Control and Treatment (No. 2017ZX07203-003), the National Natural Science Foundation of China (No. 41703105, No. 41573061 and No. 51679143), the Research Projects of Water Environment Comprehensive Management in Taihu Lake of Jiangsu Province (No. TH2014402, and No. TH2015202), and the Natural Science Foundation of the Higher Education Institutions of Jiangsu Province (17KJB170009). Finally, we would like to thank Yang Su for her encouragements and assistances in preparing this paper, and thank Jie Xu for his assistances in analyses greenhouse gases.

References

Arar, E.J., Collins, G.B., 1997. Method 445.0: In Vitro Determination of Chlorophyll *a* and Pheophytin a in Marine and Freshwater Algae by Fluorescence. United States Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Cincinnati.

Bastviken, D., Cole, J., Pace, M., et al., 2004. Methane emissions from lakes: dependence of lake characteristics, two regional assessments, and a global estimate. Glob. Biogeochem. Cycles 18 (4), GB4009.

Bastviken, D., Tranvik, L.J., Downing, J.A., et al., 2011. Freshwater methane emissions offset the continental carbon sink. Science 331 (6013), 50.

Bédard, C., Knowles, R., 1991. Hypolimnetic O_2 consumption, denitrification, and methanogenesis in a thermally stratified lake. Can. J. Fish. Aquat. Sci. 48 (6), 1048–1054.

Carey, C.C., Ibelings, B.W., Hoffmann, E.P., et al., 2012. Eco-physiological adaptations that favour freshwater cyanobacteria in a changing climate. Water Res. 46 (5), 1394–1407.

Carey, C.C., Mcclure, R.P., Doubek, J.P., et al., 2017. *Chaoborus* spp. transport CH_4 from the sediments to the surface waters of a eutrophic reservoir, but their contribution to water column CH_4 concentrations and diffusive efflux is minor. Environ. Sci. Technol. 52 (3), 1165–1173.

Casper, P., Furtado, A.L.S., Adams, D.D., 2003. Biogeochemistry and diffuse fluxes of greenhouse gases (methane and carbon dioxide) and dinitrogen from the sediments of oligotrophic Lake Stechlin, northern Germany. Adv. Limnol. 58, 53–71.

Chen, M., Li, X.H., He, Y.H., et al., 2016. Increasing sulfate concentrations result in higher sulfide production and phosphorous mobilization in a shallow eutrophic freshwater lake. Water Res. 96, 94–104.

Cole, J.J., Caraco, N.F., 1998. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF_6. Limnol. Oceanogr. 43 (4), 647–656.

Crusius, J., Wanninkhof, R., 2003. Gas transfer velocities measured at low wind speed over a lake. Limnol. Oceanogr. 48 (3), 1010–1017.

Davidson, T.A., Audet, J., Svenning, J., et al., 2015. Eutrophication effects on greenhouse gas fluxes from shallow-lake mesocosms override those of climate warming. Glob. Chang. Biol. 21 (12), 4449–4463.

Ebina, J., Tsutsui, T., Shirai, T., 1983. Simultaneous determination of total nitrogen and total phosphorus in water using peroxodisulfate oxidation. Water Res. 17 (12), 1721–1726.

Encinas Fernández, J., Peeters, F., Hofmann, H., 2014. Importance of the autumn overturn and anoxic conditions in the hypolimnion for the annual methane emissions from a temperate lake. Environ. Sci. Technol. 48 (13), 7297–7304.

Gąsiorowski, M., Sienkiewicz, E., 2013. The sources of carbon and nitrogen in mountain lakes and the role of human activity in their modification determined by tracking stable isotope composition. Water Air Soil Pollut. 224 (4), 1–9.

Gkelis, S., Papadimitriou, T., Zaoutsos, N., et al., 2014. Anthropogenic and climate-induced change favors toxic cyanobacteria blooms: evidence from monitoring a highly eutrophic, urban Mediterranean lake. Harmful Algae 39, 322–333.

Gruca-Rokosz, R., Tomaszek, J.A., 2015. Methane and carbon dioxide in the sediment of a eutrophic reservoir: production pathways and diffusion fluxes at the sediment–water Interface. Water Air Soil Pollut. 226 (2), 16.

Gudasz, C., Bastviken, D., Steger, K., et al., 2010. Temperature-controlled organic carbon mineralization in lake sediments. Nature 466 (7305), 478.

He, W., Shang, J., Lu, X., et al., 2013. Effects of sludge dredging on the prevention and control of algae-caused black bloom in Taihu lake, China. J. Environ. Sci. 25 (3), 430–440.

Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. J. Paleolimnol. 25 (1), 101–110.

Heyer, C.D., Kalff, J., 1998. Organic matter mineralization rates in sediments: a within- and among-lake study. Limnol. Oceanogr. 43 (4), 695–705.

Hofmann, H., Federwisch, L., Peeters, F., 2010. Wave-induced release of methane: Littoral zones as source of methane in lakes. Limnol. Oceanogr. 55 (5), 1990–2000.

Huisman, J., Sharples, J., Stroom, J.M., et al., 2004. Changes in turbulent mixing shift competition for light between phytoplankton species. Ecology 85 (11), 2960–2970.

Kirschke, S., Bousquet, P., Ciais, P., et al., 2013. Three decades of global methane sources and sinks. Nat. Geosci. 6 (10), 813–823.

Komada, T., Burdige, D.J., Crispo, S.M., et al., 2013. Dissolved organic carbon dynamics in anaerobic sediments of the Santa Monica Basin. Geochim. Cosmochim. Acta 110 (3), 253–273.

Louis, V.L.S., Kelly, C.A., Duchemin, Éric, et al., 2000. Reservoir surfaces as sources of greenhouse gases to the atmosphere: a global estimate. Bioscience 50 (9), 766–775.

Mann, A.J., Hahnke, R.L., Huang, S., et al., 2013. The genome of the alga-associated marine flavobacterium Formosa agariphila KMM 3901T reveals a broad potential for degradation of algal polysaccharides. Appl. Environ. Microbiol. 79 (21), 6813–6822.

Marotta, H., Pinho, L., Gudasz, C., Bastviken, D., Tranvik, L.J., Enrichprast, A., 2014. Greenhouse gas production in low-latitude lake sediments responds strongly to warming. Nat. Clim. Chang. 4 (6), 467–470.

Martinotti, W., Camusso, M., Guzzi, L., et al., 1997. C, N and their stable isotopes in suspended and sedimented matter from the PO estuary (Italy). Water Air Soil Pollut. 99 (1–4), 325–332.

Michalak, A.M., Anderson, E.J., Beletsky, D., et al., 2013. Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. Proc. Natl. Acad. Sci. U. S. A. 110 (16), 6448–6452.

Molot, L.A., Dillon, P.J., 1996. Storage of terrestrial carbon in boreal lake sediments and evasion to the atmosphere. Glob. Biogeochem. Cycles 10 (3), 483–492.

Raveh, A., Avnimelech, Y., 1979. Total nitrogen analysis in water, soil and plant material with persulphate oxidation. Water Res. 13 (9), 911–912.

Riedinger, N., Brunner, B., Lin, Y.S., et al., 2010. Methane at the sediment–water transition in Black Sea sediments. Chem. Geol. 274 (1), 29–37.

Ruban, V., López-Sánchez, J.F., Pardo, P., et al., 2001. Harmonized protocol and certified reference material for the determination of extractable contents of phosphorus in freshwater sediments–a synthesis of recent works. Fresenius J. Anal. Chem. 370 (2–3), 224.

Rudd, J.W.M., Hamilton, R.D., 1978. Methane cycling in a cutrophic shield lake and its effects on whole lake metabolism. Limnol. Oceanogr. 23 (2), 337–348.

Schwarz, J.I., Eckert, W., Conrad, R., 2008. Response of the methanogenic microbial community of a profundal lake sediment (Lake Kinneret, Israel) to algal deposition. Limnol. Oceanogr. 53 (1), 113–121.

Shao, K., Gao, G., Chi, K., et al., 2013. Decomposition of *Microcystis* blooms: implications for the structure of the sediment bacterial community, as assessed by a mesocosm experiment in Lake Taihu, China. J. Basic Microbiol. 53 (6), 549–554.

Tranvik, L.J., Downing, J.A., Cotner, J.B., et al., 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr. 54 (6part2), 2298–2314.

Wang, Y., Chen, F., 2008. Decomposition and phosphorus release from four different size fractions of *Microcystis* spp. taken from Lake Taihu, China. J. Environ. Sci. 20 (7), 891–896.

Wang, H., Lu, J., Wang, W., et al., 2006. Methane fluxes from the littoral zone of hypereutrophic Taihu Lake, China. J. Geophys. Res.-Atmos. 111 (D17), D17109.

West, W.E., Coloso, J.J., Jones, S.E., 2012. Effects of algal and terrestrial carbon on methane production rates and methanogen community structure in a temperate lake sediment. Freshw. Biol. 57 (5), 949–955.

West, W.E., Mccarthy, S.M., Jones, S.E., 2015. Phytoplankton lipid content influences freshwater lake methanogenesis. Freshw. Biol. 60 (11), 2261–2269.

West, W.E., Creamer, K.P., Jones, S.E., 2016. Productivity and depth regulate lake contributions to atmospheric methane. Limnol. Oceanogr. 61, S51–S61.

Wetzel, R.G., 2001. Limnology: lake and river ecosystems. EOS Trans. Am. Geophys. Union 21 (2), 1–9.

Wiesenburg, D.A., Guinasso Jr., N.L., 1979. Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. J. Chem. Eng. Data 24 (4), 356.

Wuebbles, D.J., Hayhoe, K., 2002. Atmospheric methane and global change. Earth Sci. Rev. 57 (3–4), 177–210.

Xing, Y., Yang, X.H., Ni, L., et al., 2005. Methane and carbon dioxide fluxes from a shallow hypereutrophic subtropical Lake in China. Atmos. Environ. 39 (30), 5532–5540.

Xing, P., Guo, L., Tian, W., et al., 2011. Novel Clostridium populations involved in the anaerobic degradation of *Microcystis* blooms. ISME J. 5 (5), 792–880.

Xu, H., Jiang, H., 2013. UV-induced photochemical heterogeneity of dissolved and attached organic matter associated with cyanobacterial blooms in a eutrophic freshwater lake. Water Res. 47 (17), 6506–6515.

Xu, X., Li, W., Fujibayashi, M., et al., 2014. Feedback of threshold via estimating sources and composition of sedimentary organic matter across trophic gradients in freshwater lakes. Sci. Total Environ. 500-501C, 373–382.

Xu, X., Li, W., Fujibayashi, M., et al., 2015a. Asymmetric response of sedimentary pool to surface water in organics from a shallow hypereutrophic lake: the role of animal consumption and microbial utilization. Ecol. Indic. 58, 346–355.

Xu, X., Li, W., Fujibayashi, M., et al., 2015b. Predominance of terrestrial organic matter in sediments from a cyanobacteria-blooming hypereutrophic lake. Ecol. Indic. 50, 35–43.

Yan, X., Xu, X., Wang, M., et al., 2017. Climate warming and cyanobacteria blooms: looks at their relationships from a new perspective. Water Res. 125, 449–457.

Yang, H., Xie, P., Ni, L., et al., 2011. Underestimation of CH_4 emission from freshwater lakes in China. Environ. Sci. Technol. 45 (10), 4203–4204.