Environmental Science and Pollution Research
https://doi.org/10.1007/s11356-019-06098-7

SEDIMENT ENVIRONMENT, POLLUTION AND REMEDIATION

Methane distribution patterns along a transect of Lake Fuxian, a deep oligotrophic lake in China

Biao Li[1,2] · **Qiujin Gu**[3] · **Yuqing Miao**[1,4] · **Wenlei Luo**[1] · **Peng Xing**[1] · **Qinglong L. Wu**[1,5]

Received: 31 March 2019 / Accepted: 26 July 2019

Abstract

Freshwater ecosystems are recognized as one of the important natural methane (CH_4) sources, but little is known about the emission hotspots and the effects of algal blooms on CH_4 production in deep lakes. In this study, carried out from the littoral (S1), pelagic (S2-S4), and the deepest site (S5), water samples from different depths and sediment cores were collected along the transect of Lake Fuxian, a deep monomictic lake to investigate the spatial–temporal variations of CH_4. Dissolved methane concentration observed at the oxic metalimnion was 37.5% and 19.5% higher than that those observed at the epilimnion and at the layer between 80 and 100 m depth, respectively. During the overturn period, the vertical distribution of CH_4 in the water column was uniform, with an average concentration of 0.031 ± 0.007 μM in S2–S5. Statistical analysis indicated that the CH_4 concentration in the water column was significantly higher in S1 than other sites along the transect during both sampling periods. Sediment CH_4 concentration and methane production potential (MPP) were also significantly higher in S1 than in other sites. Along the sediment depth, the maximum MPP was observed at 6–8 cm in S1, but it moved up to the surface layer in S2–S5 in both sampling periods. In addition, stable carbon isotope analysis indicated that the surface sediments in the pelagic zone (S2–S5) mainly comprised autochthonous organic matters. In this zone, MPP had a significantly positive correlation with sediment total organic carbon (TOC) ($R^2 = 0.401$, $p < 0.01$). In summary, we described the spatial and temporal distributions of CH_4 in deep Lake Fuxian, littoral zones are CH_4 emission hotspots that can contribute to the CH_4 accumulation in the oxic metalimnion layer during the stratification period. In the pelagic zone, autochthonous organic matter was transported into the surface sediment after a massive algal bloom, representing another hotspot for CH_4 production.

Keywords Methane · Lake Fuxian · Hotspot · Littoral zone · Stratification · Overturn

Introduction

Methane (CH_4) is a powerful greenhouse gas that is 23 times more effective than carbon dioxide (CO_2) per molecule on a centennial time scale (Likens 2010) and contributes nearly 20% to global warming (West et al. 2016). Lakes cover only 3.7% of the Earth's surface (Verpoorter et al. 2014) but are considered a significant source of CH_4 to the atmosphere. In a

---

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11356-019-06098-7) contains supplementary material, which is available to authorized users.

✉ Peng Xing
pxing@niglas.ac.cn

✉ Qinglong L. Wu
qlwu@niglas.ac.cn

[1] State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, 73 East Beijing Road, Nanjing 210008, China

[2] University of Chinese Academy of Sciences, Beijing 100039, China

[3] Jiangsu Key Laboratory for Biodiversity and Biotechnology, School of Biological Sciences, Nanjing Normal University, Nanjing 210023, China

[4] Anhui Province Key Laboratory of Earth Surface Processes and Regional Response in the Yangtze-Huaihe River Basin, School of Geography and Tourism, Anhui Normal University, Wuhu 241000, Anhui, China

[5] Sino-Danish Centre for Education and Research, Beijing 100039, China

recent study, total CH_4 from freshwaters was estimated at 103 Tg CH_4/year, corresponding to 25% land greenhouse gas sink (Bastviken et al. 2011). According to overall carbon budgets, the amount of CH_4 emissions from lakes represents 6–16% of total natural source emissions (Bastviken et al. 2004), far higher than that recorded for oceans (only 3%) (EPA 2010).

In lake ecosystems, microbial methanogenesis represents a terminal step of organic matters (OM) degradation in sediment or anoxic waters (Reeburgh 2010). Hydrogenotrophic and acetotrophic methanogenesis are the two major pathways of CH_4 production (Conrad 1999; Liu et al. 2016). Some low molecular weight organic molecules, such as formate (Sparling and Daniels 1986), methanol (Conrad and Claus 2005), and dimethyl sulfide (Finster et al. 1992), can also be used for methanogenesis. Although the gross CH_4 production is extremely high, a large amount of CH_4 is biologically oxidized by aerobic or anaerobic CH_4 oxidation, which acts as an efficient filter of CH_4 before it reaches the atmosphere (Deutzmann et al. 2014; Egger et al. 2015; Knittel and Boetius 2009; Martinez-Cruz et al. 2018; Milucka et al. 2015). CH_4 that is not consumed is eventually transported to waters in shallow depths and can be released to the atmosphere by diffusive flux (Hofmann 2013), ebullition (Delsontro et al. 2016), or aquatic plants (Chanton et al. 1992). In several recent studies, CH_4 oversaturation was observed in oxygenated water columns (Grossart et al. 2011; Tang et al. 2016); this finding challenges the prevailing paradigm that microbial methanogenesis exclusively occurs in anoxic conditions. CH_4 transport from littoral zones (Fernández et al. 2016), in situ methanogenesis in oxic water (Grossart et al. 2011), and reduction of CH_4 oxidation (Tang et al. 2014) can be explained, but their conclusive mechanisms remain debatable.

The spatial–temporal heterogeneity of CH_4 concentration (Li et al. 2018; Zhou et al. 2018) and emission flux (Bastviken et al. 2010; Natchimuthu et al. 2016) in shallow lakes have been reported in previous studies, but only a few of them focused on deep lakes. Those few studies on deep-water lakes mainly explored the dynamics of CH_4 at the deepest point (Fernández et al. 2014; Grossart et al. 2011). For example, according to the CH_4 profile at the maximum depth near the center of Lake Mindelsee, CH_4 concentration when the lake was stably stratified was extremely low in the epilimnion, ranging from 0.5 to 1 μM, but it reached 1400 μM in the anoxic deep water. The near-surface CH_4 concentration substantially increased to 10–80 μM as the water column mixed, resulting in nearly 46% of stored CH_4 emission during the autumn overturn and contributing approximately 80% of the annual diffusive CH_4 emissions to the atmosphere in the deep dimictic lake (Fernández et al. 2014). In shallow lakes, typically littoral zones are usually the hotspots for CH_4 emission, and emission flux is usually higher in summer than in other seasons (Natchimuthu et al. 2016; Sun et al. 2018). A recent field study also demonstrated that phytoplankton blooms can facilitate CH_4 production in shallow eutrophic lakes (Yan et al. 2019). However, for deep lakes, issues such as coastal zones being possible hotspots for CH_4 production and emissions and the effects of algal blooms on CH_4 production and emission remain constrained.

In the present study, water samples from different depths and sediment cores were collected along a transect of Lake Fuxian, a deep lake in China to investigate the spatial–temporal variations of CH_4 in the area. Sample collection was carried out from the littoral zone, pelagic zone, and the deepest site. Moreover, we analyzed the source of organic carbon by using stable carbon isotopes and studied the effects of organic carbon on CH_4 production. On the basis of these data, we probed into the contribution of littoral zones to the overall budgets of lakes. In addition, we identified the relationships between organic carbon contents, especially autochthonous organic carbon, and methane production potential (MPP). We also discussed the potential implications of climate change and eutrophication on CH_4 accumulation in hypolimnion and metalimnion and on CH_4 emission to the atmosphere.

Materials and methods

Study area

Lake Fuxian, the second deepest freshwater lake in China, is located at Yuxi City, Yunnan Province, Southwest China. It has a maximum depth of 155 m, average depth of 95 m, and a surface area of 212 km^2 (Nanjing Institute of Geography and Limnology 1990). It also has one of the best water qualities in China and has thus been the guarantee of the sustained economic development of central Yunnan. Therefore, it contributes immensely to the local water supply and economic prosperity. However, intensive human activities and the rapid development of industries, agriculture, and tourism have aggravated the contamination problem of Lake Fuxian (Zeng and Wu 2009; Zhang et al. 2015a). In March 2018, a serious *Aphanizomenon flos-aquae* bloom was noted in the northern lake zones, posing a great threat to local drinking water safety.

In the present study, five sampling sites were chosen according to a transect from the littoral zone to the pelagic zone (Fig. 1). Specifically, S1 is located at Liangwang River Estuary, one of the main tributaries feeding into Lake Fuxian. S5 is near the deepest site of the lake. The other three sites, namely S2, S3, and S4, are between S1 and S5, with two adjacent points being 1.25 km apart. Water depths at S1–S5 were 29.4, 108.1, 125.2, 147.3, and 152.5 m, respectively.

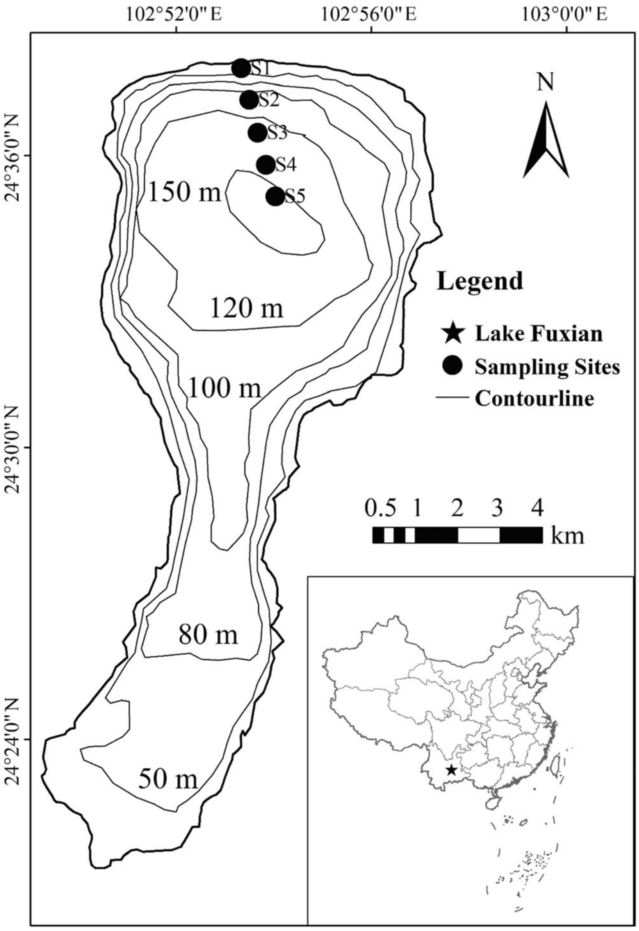


Fig. 1 Sampling sites of Lake Fuxian

Water and sediment sampling

We used the gradient standard of 0.2 °C/m for the temperature along the water column depth measured in Lake Fuxian to identify thermal stratification in the lake water; this standard is widely used in other lakes (Zhang et al. 2015b). According to a previous study, the thermal stratification in Lake Fuxian generally occurs between March and November, and overturn usually occurs between December and February in the next year (Nanjing Institute of Geography and Limnology 1990). Sampling was carried out on 13 October and 26 December 2018 at the stratification and overturn periods, respectively. Using a rosette sampler (Slimline, HYDRO-BIOS, Germany) equipped with 6 × 3.5 L Niskin bottles, water samples were collected at 10-m intervals from the surface to the bottom at S1. At S2, water samples were collected at 10-m intervals from the surface to depth 80 m and at 20-m intervals below 80 m. As for S3–S5, water samples were collected at 10-m intervals from the surface to depth 100 m and 20 m intervals below 100 m.

At each site, two sediment cores were retrieved using a gravity corer (Rigo Co., Japan) equipped with a plexiglass cylindrical tube (inner diameter of 110 mm, outer diameter of 120 mm, and length of 500 mm). In addition, three sediment cores for CH_4 measurement were collected with the same plexiglass tube but pre-drilled in one side. The diameter and interval of the pre-drilled holes were 10 and 20 mm, respectively, and the holes were sealed with a tape around the ektexine before sampling. After sediment collection, the cores were closed air-free with rubber stoppers at the bottom and the top and transported to the laboratory within 1 h.

Physicochemical parameters of water samples

During sampling campaigns, a multiparameter water quality probe (YSI 6600, Yellow Springs, Ohio) was deployed to measure water depth, temperature (T), dissolved oxygen (DO) concentration, conductivity, and pH at 1-m intervals along the depth. Water samples for the analyses of total nitrogen (TN) and total phosphorus (TP) were photometrically determined using a UV–VIS spectrophotometer (UV2700, Shimadzu, Japan) after digestion with alkaline potassium peroxodisulfate ($K_2S_2O_8$) (Ebina et al. 1983; Raveh and Avnimelech 1979). Chlorophyll-*a* (Chl-*a*) analysis was conducted via the hot ethanol extraction method (Jespersen and Christoffersen 1987). Water samples for the analyses of nitrate (NO_3-N), nitrite (NO_2-N), ammonium (NH_4-N), dissolved inorganic phosphorus (PO_4-P), and dissolved organic carbon (DOC) were filtered with Whatman GF/F membranes. Then, NO_3-N, NO_2-N, NH_4-N, and PO_4-P were measured using a continuous flow analyzer (San Plus, SKALAR, Netherlands). DOC was measured by high-temperature oxidation with a TOC analyzer (TOC-L CPH, Shimadzu, Japan).

Water content, TN, TOC, and stable carbon isotopes of TOC (δ^{13}C-TOC) in sediments

Sediment cores were sliced at 1-cm intervals down to a depth of 10 cm for the analyses of water contents, TN, TOC, and δ^{13}C-TOC under nitrogen protection. Water content from each interval was calculated as the weight loss from 5-mL wet sediment dried at 105 °C for 24 h. Sediment samples for TOC were acidified to remove carbonates with 1 HCl, rinsed with ultrapure water to remove chloride, dried at 45 °C, and then homogenized in a mortar (Chen et al. 2018). The concentrations of TN and TOC were measured by a CHNS elemental analyzer (EA 3000, EuroVector, Italy). The isotope composition of the TOC of S1 and S5 sediments was determined by a mass spectrometer (MAT 253 plus, Thermo Finnigan, USA) equipped with a Flash EA1112 elemental analyzer. The isotope ratios were reported as δ^{13}C-TOC, where δ values were denoted as ‰ deviation from the carbon isotopic composition of the Pee Dee Belemnite (PDB) standard.

$$\delta^{13}\mathrm{C}-\mathrm{TOC} = \left[\left(R_{sample}/R_{\mathrm{PDB}}\right)-1\right] \times 1000,$$

where R is the ratio of ^{13}C to ^{12}C; the precisions of δ^{13}C were higher than 0.2‰.

CH_4 measurement and analysis

For the water samples in each depth, triplicate 100-mL headspace bottles pre-added with 3.5 g potassium chloride (KCl) were completely filled with lake water on board and then quickly sealed with thick butyl rubber stoppers and aluminum cap. The dissolved CH_4 was measured using the headspace equilibration method (UNESCO/IHA 2010). As for the CH_4 in the sediment samples, 2 mL of the sediment samples was extracted with 2-mL front-cut plastic syringes through the pre-drilled holes and extruded into a 20-mL serum vial containing 6 mL of 1 M NaOH (Riedinger et al. 2010). The vials were immediately capped with butyl rubber stoppers and aluminum cap, subsequently shaken, and finally kept in a constant temperature incubator at 13 °C (in situ temperature of the bottom water in Lake Fuxian). CH_4 concentration was determined via gas chromatography (7890B, Agilent, America) equipped with a flame ionization detector (GC-FID) and a HayeSeq Q column (length 3.66 m and inner diameter 2 mm).

Airtightness tests, methane production potential (MPP), and methane oxidation potential (MOP) measurement

Airtightness tests were conducted by monitoring the CH_4 concentrations in the vials over time. Specifically, 1 mL 1% high purity CH_4 (99.99%) was injected into several 20-mL serum vials, which were pre-sealed with thick butyl rubber stoppers and aluminum cap. The CH_4 concentrations in the gas phase of all vials were measured after 0, 2, 5, 14, 21, and 28 days. At each time point, three sediment vials were sampled using a 2-mL gas-tight syringe and measured as mentioned above. Within 30 days, the CH_4 concentrations in the vials were stable with minimal fluctuations (Fig S1). This result suggests that serum vials can be used for incubation experiments over many days or even months.

For MPP measurement, 3.5-mL sediment or 10-mL metalimnion water was added to several 20-mL serum vials, after which purged with CH_4-free nitrogen for 2 min and quickly sealed with thick butyl rubber stoppers and aluminum cap. Vials were incubated at 13 °C (nearly in situ temperature in the lake's bottom) for sediments and 15 °C (nearly in situ temperature at metalimnion) for lake water, respectively. The CH_4 concentrations in the gas phase of all vials were measured after 0, 2, 5, 14, and 21 days. At each time point, three vials were autoclaved for sediments (Thomsen et al. 2004) or adding 200 μL 50% $ZnCl_2$ (w/v) for lake water to inhibit methanogenesis and sampled by 2-mL gas-tight syringe in the headspace. CH_4 concentration in sediment samples kept increasing linearly during the 3-week incubation without lag phase and MPP was calculated according to the slope of linear fit during the time courses of CH_4 concentrations (West et al. 2012). Due to the maximum CH_4 concentration of all vials was 10 000 ppm (only 1% v/v), headspace pressure change was negligible.

The overlying water above sediment was used to measure MOP. Specifically, 10-mL overlying water was added to 20-mL serum vials and vortexed for 1 min to supply sufficient amount of air. The vials were sealed with thick butyl rubber stoppers and aluminum cap, after which 1-mL 1% high purity CH_4 (99.99%) was added and incubated at 13 °C. The experiment started after 2 h pre-incubation. CH_4 concentrations in the gas phase was measured at 0, 6, 12, 24, and 48 h, and MOP was calculated according to the slope of linear fit during the time courses of decreasing CH_4 concentrations.

Estimation of emission flux and storage CH_4

The diffusive flux of CH_4 to the atmosphere was calculated according to Liss and Slater (1974):

$$F_{CH_4} = K_{CH_4} \bullet M_{CH_4} \bullet \left(C_w - C_{eq}\right),$$

where F_{CH4}, K_{CH4}, and M_{CH4} are the air–water flux, transfer velocity, and the molar mass of CH_4, respectively; C_w is the measured surface water molar concentration of CH_4, and C_{eq} is the concentration of CH_4 in the surface water that is in equilibrium with the atmospheric concentration at in situ surface water temperatures (Wiesenburg 1979). K_{CH4} was estimated from K_{600} which denotes the transfer velocity of CO_2 under standard conditions (a Schmidt number of 600) by using the following equation (Fernández et al. 2014; UNESCO/IHA 2010):

$$K_{CH4} = K_{600} \bullet (Sc/600)^n,$$

where Sc is the Schmidt number of CH_4 at water surface temperatures and n is − 2/3 for $U_{10} \leq 3.7$ m/s and − 1/2 for $U_{10} > 3.7$ m/s, with U_{10} being the wind speed monitored 10-m above ground level according to the data of the automatic weather station of the Research Station of Lake Fuxian, Chinese Academy of Sciences (Fig. S4). The gas transfer velocity K_{600} was calculated using the equation of Cole and Caraco (1998):

$$K_{600} = 2.07 + 0.215 \bullet {U_{10}}^{1.7}$$

The mean flux of the littoral zone was calculated from S1, and that of the pelagic zone was calculated from S2 to S5. We have plotted hypsographic curves (Fig S2) according to the depth and corresponding area and volume (data kindly provided by Research Station of Lake Fuxian). CH_4 storage mass was calculated by multiplying average CH_4 concentration in certain depth with the corresponding water volume.

Data analysis

Statistical calculations were performed using Excel 2007. Correlation analysis and corresponding figure was performed by R 3.5.2; other statistical analyses were performed using the SPSS 22.0 software. Linear fitting, regression, and other figures were performed by Origin 2017. Data in the present study are presented as mean ± SD and homogeneity of variance among groups was tested by Levene's test. Intergroup differences of methane concentration, TOC, δ^{13}C-TOC at different sites during the same sampling period and the same site during different sampling period were examined with one-way analysis of variance (ANOVA) with the Tukey test. The significance levels were set when $p < 0.05$.

Results

Temperature, DO, and CH_4 in the water column

As shown in Fig. 2, in October, the water column was strongly thermally stratified with surface temperature of 21.8 °C down to 16.6 °C at nearly 30 m where the thermocline was located. Then, it steadily declined to the bottom at 13.5 °C. Temperature gradient in the metalimnion (25–35 m) was 0.48 °C/m, verifying that the water column was at the stratification period. Similarly, DO was stratified with surface water of 9.14 mg/L down to 4.68 mg/L at the depth of 30 m, stably decreasing to 0.27 mg/L from 120 m to the bottom. The dissolved methane concentration observed at the oxic metalimnion was 37.5% and 19.5% higher than that those observed at the epilimnion and at the layer between 80 and 100 m depth, respectively. Moreover, a decreasing gradient of CH_4 concentration was observed from S1 with 0.076 μM to S5 with 0.033 μM at the metalimnion layer along the transect.

In December, the water column was cooled down with surface water temperature of 15.6 °C, which decreased to 13.6 °C at approximately 45 m and then stabilized at the bottom. Temperature gradient between the depths of 25–35 m was 0.07 °C/m, verifying that the water column was at the overturn period. Similar to the observations in October, DO decreased from 8.22 mg/L at the surface water down to 4.56 mg/L at the depth of 30 m and then stably decreased to 0.27 mg/L at 120 m to the bottom. As for the CH_4, its vertical distribution in the water column was uniform with an average concentration of 0.031 ± 0.007 μM in S2–S5, but its concentration in S1 (0.056 ± 0.005 μM) was still significantly higher than that in S2–S5 ($p < 0.01$). CH_4 flux from water to atmosphere was calculated as 0.88 in S1 and 0.6 mg/m^2/day in S2–S5 during the stratification period. During the overturn period,

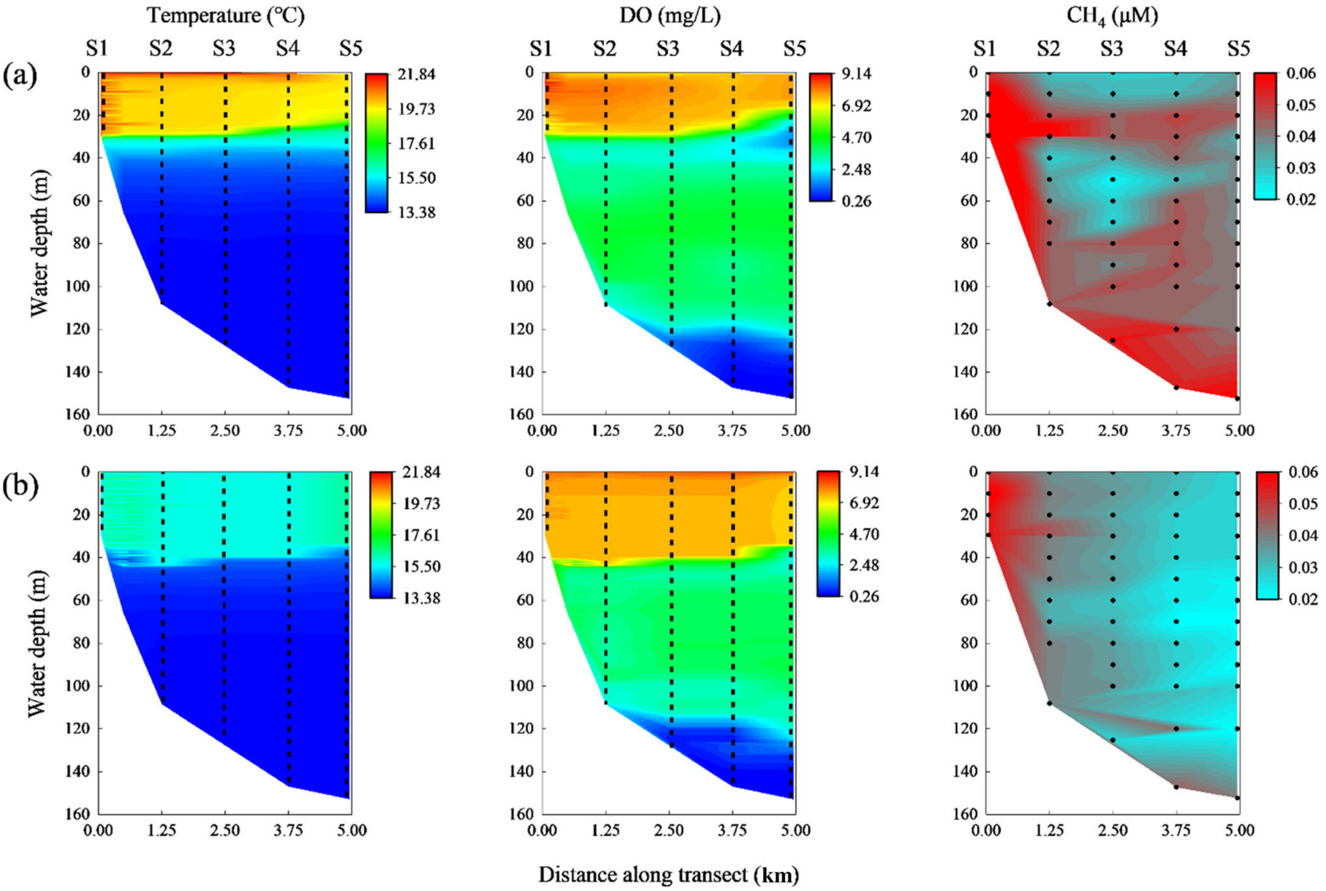


Fig. 2 Distribution patterns of water temperature (T), dissolved oxygen (DO), and methane (CH_4) along the transect during **a** stratification and **b** overturn period

CH_4 flux was stabilized at 0.85 mg/m^2/day in the littoral zone but decreased to 0.43 mg/m^2/day in the pelagic zone, which was 28.3% lower than that observed at S2–S5 during the stratification period (Table 1).

The chemical parameters during the two sampling periods are shown in Fig. S3. The correlation analysis (Fig. 3) indicated that CH_4 had a significant positive correlation with the nutrient indices, such as Chl-*a*, NH_4-N, NO_2-N, TN, TP, and PO_4-P, during the stratification period. However, CH_4 only had a significant positive correlation with temperature, DO Chl-*a*, and DOC, as well as a significant negative correlation with NO_3-N.

CH_4 concentration and MPP in sediments

As shown in Fig. 4, during the stratification period, the CH_4 concentration in all the sediments generally increased from the surface (73.61–139.54 μM) downward along the depth profile to the bottom and ranged from 865.65 to 3010.61 μM. The concentration in S1 was 1487.11 ± 878.41 μM, which was significantly higher than that in the other sites ($p < 0.01$). Similar patterns were also noted during the overturn period as the CH_4 concentration increased along the depth profile at all sites. The concentration in S1 (1132.71 ± 769.08 μM) was still significantly higher than that in the other sites ($p < 0.01$). However, the CH_4 concentration during the overturn period was significantly lower than that during the stratification period for all sites except for S2 ($p < 0.05$).

During the stratification period, the MPP at S1 sediment was as low as 8.76 mmol/m^3/day in the surface and reached the maximum value of 226.73 mmol/m^3/day at 6–8 cm. The value then decreased to 43.85 mmol/m^3/day at 8–10 cm, with an average of 110.42 ± 86.16 mmol/m^3/day, which was significantly higher than that for the other sites ($p < 0.01$). However, the MPP decreased with depth at the other sites along the transect. Moreover, the MPP in the surface sediment increased from S1 to S5 and was as high as 81.02 mmol/m^3/day. Similar to the conditions in the stratification period, the MPP at S1 sediment during the overturn period also first increased from 9.14 mmol/m^3/day in the surface to 81.39 mmol/m^3/day at 6–8 cm; it then decreased along the sediment depth. In the other sites of the transect, the maximum MPP was observed in the surface layer. However, the MPP during the overturn period was significantly lower than that during the stratification period in general ($p < 0.05$).

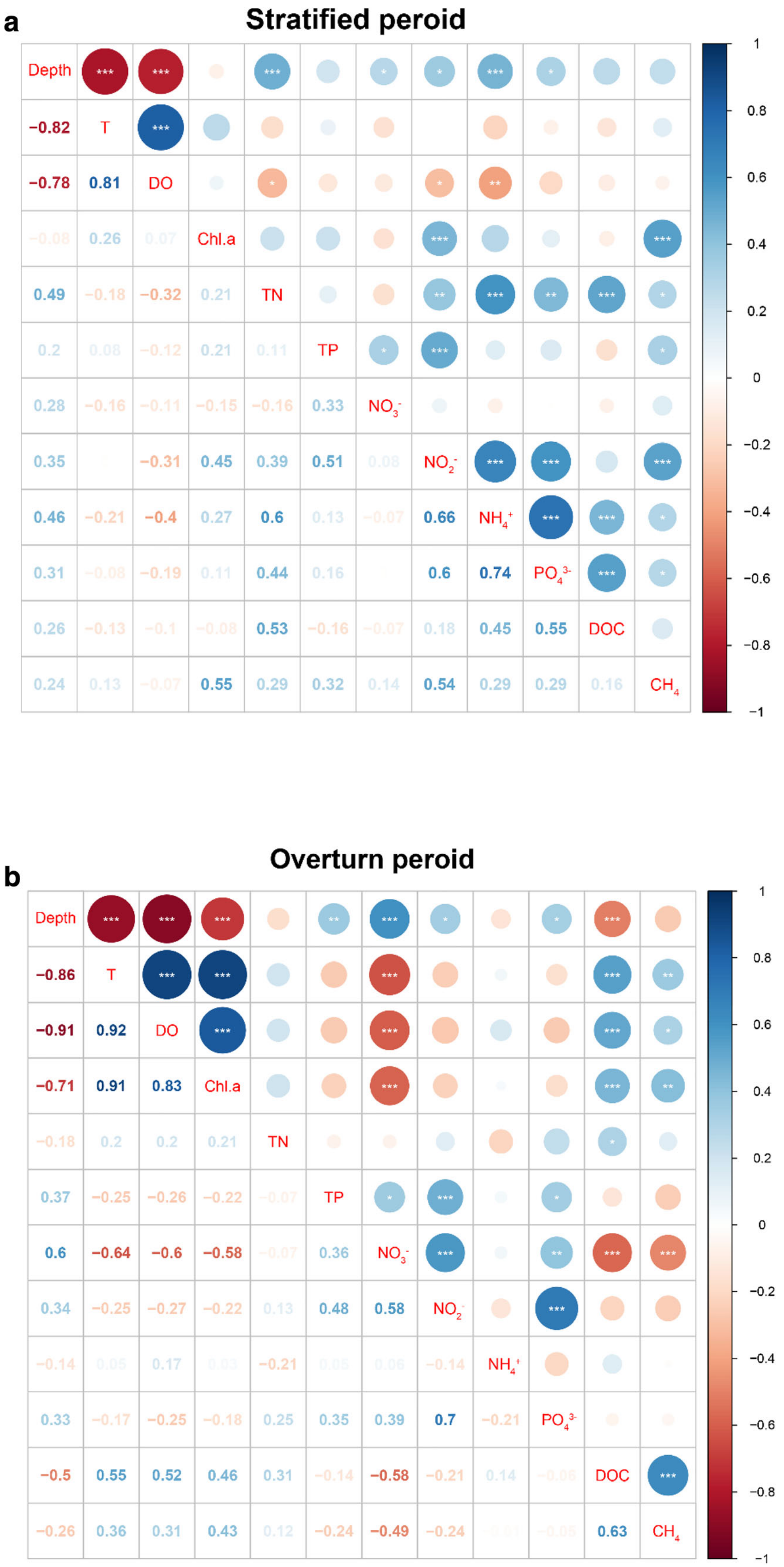
TOC and stable carbon isotope signature in sediments

TOC and its stable carbon isotope are shown in Fig. 5. Along the transect from the littoral zone to the pelagic zone, the TOC increased from S1 with a content of 3.690% to S5 with a content of 11.104% in the top layers of all sediment samples. Along the sediment depth, the TOC gradually decreased from the top layers to the depth of 10 cm with a content of 1.185% at S1. However, in S2–S5, a violent decrease was observed in the top 6-cm depth with the range of 1.623–2.446%, which then slowly decreased to nearly 1.2% (Fig. 5a). No significant difference was observed during the two sampling periods ($p > 0.05$). As for the stable carbon isotope of TOC, the δ^{13}C-TOC values ranged from − 26.70 to − 25.54‰ with an average

Table 1 Comparison of methane concentration, storage, and flux between Lake Fuxian and other deep lakes or bays

Lake	Maximum depth (m)	Period	CH_4 concentration (μM)		Flux (mg/m^2/d)		Storage CH_4 (kg)	References
			Littoral	Pelagic	Littoral	Pelagic		
Fuxian	158	Stratification	0.051–0.076	0.03–0.055	0.88	0.6	16092.12	This study
		Overturn	0.051–0.062	0.02–0.044	0.85	0.43	12389.34	
Mindelsee	13.5	Stratification		0.5~1400		10.1~23.5	18721	Fernández et al. 2014
		Overturn		10~80 at surface		202.1	17	
Stechlin	69.5	June		0.18~1.45				Grossart et al. 2011
Dendre stone pit	30	Spring		0.6~618		10.13		Roland et al. 2017
		Summer				16		
		Autumn				9.02		
		Winter		30~618		199.71		
Tanganyika	1470	Summer		0.1~120			10^9	Durischkaiser et al. 2015
Lugano	288	2008–2012		0.02~160				Blee et al. 2015
Constance	254	July, August	0.08~1.24	~0.3 at 1~5 m				Hofmann et al. 2010
Crampton	18.5	May~ August		0.28~0.33		0.416		West et al. 2016
Peter	18			0.2~387.23		0.432		
Chesapeake Bay	54	April	1 at bottom					Gelesh et al. 2016
		Mid-July	40 at bottom		3.2		1.9×10^{10}	

Fig. 3 Correlation analysis of physiochemical parameters in water column



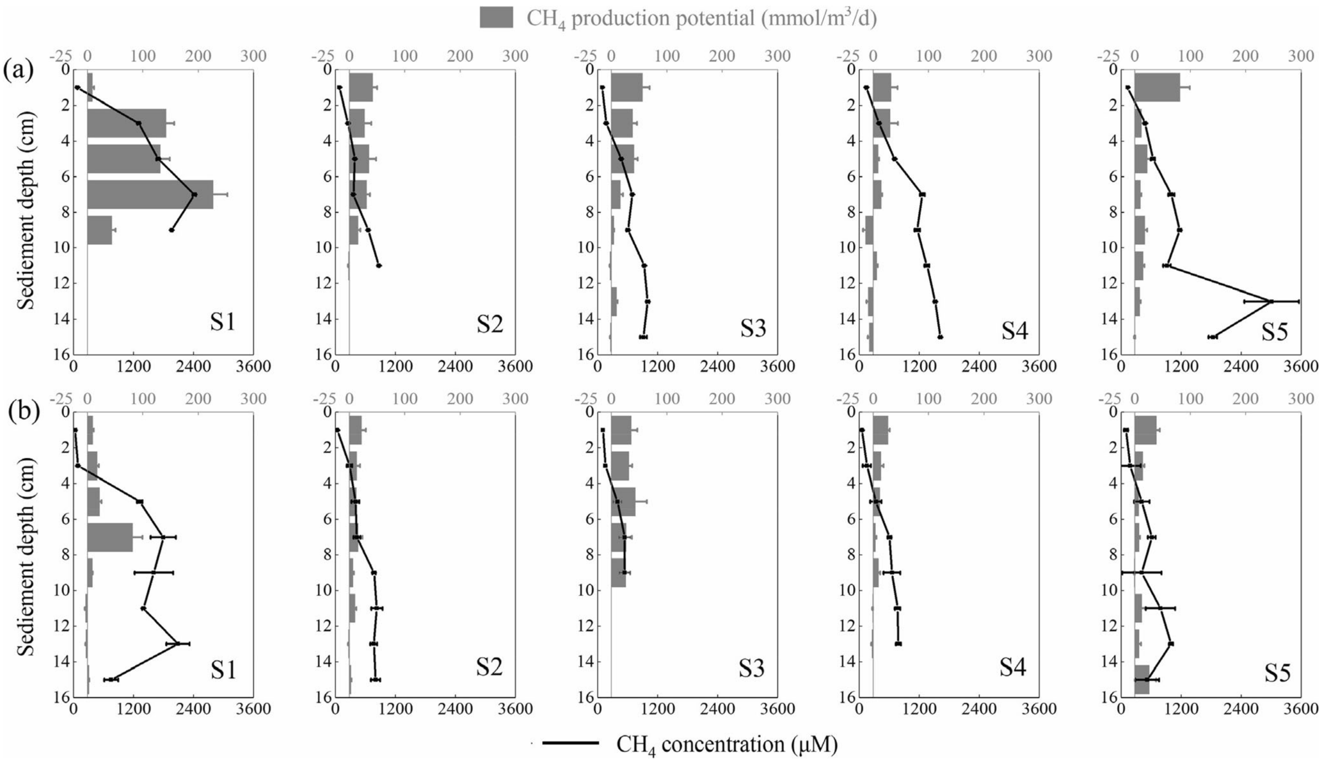


Fig. 4 Distribution patterns of methane concentration and methane production potential (MPP) in sediments during **a** stratification and **b** overturn period. Methane concentration was shown in line and MPP was shown in histogram

value of − 26.20 ± 0.37‰ in the S1 sediment and ranged from − 28.56 to − 27.08‰ with an average value of − 27.79 ± 0.0.53‰ in the S5 sediment during the stratification period. During the overturn period, the δ^{13}C-TOC values ranged from − 26.77 to − 25.12‰ with an average value of − 25.92 ± 0.56‰ in the S1 sediment and ranged from − 28.58 to − 27.29‰ with an average value of − 28.17 ± 0.47‰ in the S5 sediment (Fig. 5b). A significant difference of δ^{13}C-TOC was not observed in the S1 or S5 sediment between the two sampling periods ($p = 0.592$), but δ^{13}C-TOC in the S5 sediment was significantly lower than that in the S1 sediment during both periods.

Discussion

Patterns of CH$_4$ concentration in the water column

In this study, CH$_4$ was significantly accumulated at the oxic metalimnion and hypoxic hypolimnion during the stratification period. However, CH$_4$ concentration in the water column became uniform after the overwhelming mixture. In addition, the CH$_4$ concentration was significantly higher in the littoral zone than in the pelagic zone during both sampling periods (Fig. 2).

Aside from the different availabilities of organic carbon and redox conditions in the sediments, littoral zones are known to become warm quickly and are susceptible to waves (Hofmann 2013; Li et al. 2018). CH$_4$ concentrations are typically higher in littoral zones than in pelagic zones in shallow lakes (Hofmann 2013; Juutinen et al. 2003; Wang et al. 2006). Similar distribution patterns were also detected in the current study. In Lake Fuxian, the temperature of the bottom water at S2–S5 stabilized at 13.39 °C during both periods. This value was lower than that at S1, where the bottom water temperatures were 21.09 °C and 15.77 °C during the stratification and overturn periods, respectively. Incubation experiments indicated that MPP is more sensitive to temperature than methane oxidation potential (MOP) is as the temperature sensitivity (Q_{10} value) of the MPP varied from 1.7 to 24.5 in the range of 10 to 30 °C (Duc et al. 2010). According to that estimation, MPP in S1 was 1.5–11.7 and 1.1–2.1 times higher than S2–S5 during stratification and overturn period respectively, which is in accordance with our measurement of MPP that S1 was 4.4–14.7 and 0.5–1.7 times higher than S2–S5 during two sampling periods. Although the DO in the bottom water at S1 (4.51 and 7.47 mg/L during the stratified and overturn periods, respectively) was higher than that at the other sites (0.27–2.75 mg/L), the CH$_4$ concentration remained high in the littoral zones, where the bottom water was warmer than that in the pelagic zones in Lake Fuxian. The above result indicated that temperature had strong effect on the methane in the littoral zone of the lake.

Waves generally represent an important hydrodynamic process and cause stronger turbulence in the littoral zone than in the pelagic zone. Waves reduce the thickness of the

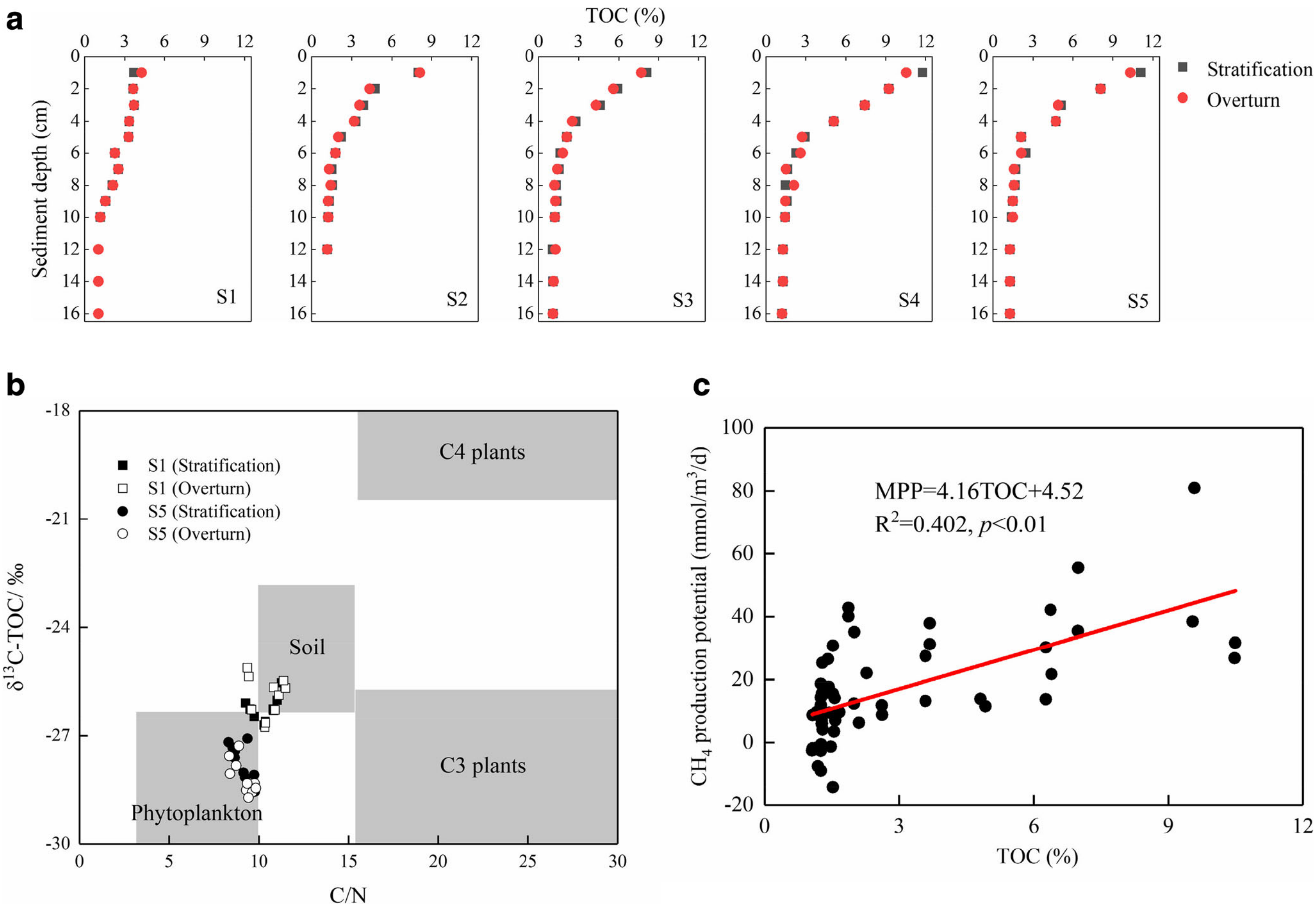


Fig. 5 **a** Distribution patterns of TOC along sediment depth. **b** Source of organic carbon in S1 and S5 sediment. **c** Correlation analysis between TOC and methane production potential (MPP) in surface sediment at S2–S5

diffusive boundary layer, resulting in an increase in diffusive flux from the sediment to the overlying water (Hofmann et al. 2010). However, in the present study, the depth of all five sites along the transect was over 30 m, at which point the wave disturbances exerted minimal effects on the sediments. Finally, the availability of organic carbon in sediments is an essential factor that determines CH_4 concentration. However, the TOC in S1 (1.19–3.61%) was significantly lower than that in the other sites along the transect (1.08–11.76%). Thus, organic matter might not have affected the heterogeneity of CH_4 in the water column along the sampling transect. A detailed analysis of the effects of organic matter on CH_4 can be found in the second part of the discussion below.

Apart from our observation of the CH_4 peak being nearly at the thermocline where DO was 4.51–5.68 mg/L during the stratification period, several recent studies also observed CH_4 peaks in upper oxic water (Grossart et al. 2011; Tang et al. 2014, 2016), contrary to the prevailing paradigm that CH_4 production only occurs in anoxic conditions (Reeburgh 2010). To date, three explanations are available. First is the CH_4 transport from the littoral zone to the pelagic zone. As mentioned previously, CH_4 concentration in the littoral zone was higher than that in the pelagic zone, and a decreasing gradient of CH_4 concentration was observed from 0.076 μM in S1 to 0.033 μM in S5 at a depth of 30 m; this result is a powerful evidence to verify CH_4 transport from shallow coastal zones (Fernández et al. 2016). Another explanation of CH_4 peak in oxygenated water is the reduction of CH_4 oxidation by photosynthesis that allowed the accumulation of CH_4 in the oxygen-rich upper layer (Tang et al. 2014). However, according to Zhou's field investigation results in the northern part of Lake Fuxian (Zhou et al. 2016), the depth of 1% photosynthetically active radiation (PAR) ranged from 11 to 16 m in autumn and 11.5–14 m in winter; all values were significantly lower than the thermocline depth. Thus, the possibility of CH_4 accumulation due to the weakening of CH_4 oxidation was low. The last explanation is the in situ methanogenesis in oxic waters. For example, several studies found that CH_4 production exists within micro-anoxic zones, such as detritus and animal gut (Oremland 1979). However, we did not find any CH_4 production by using waters from the metalimnion layer. Further investigation into micro-anoxic methanogenesis by using stable carbon isotope analysis, molecular microbiology, and in-lake incubation should be carried out in the future to verify the mechanism of the CH_4 peak at the thermocline depth and to identify the responsible organisms.

No CH_4 peak was observed during the overturn period, and the result of the correlation analysis was different from those obtained during stratification. These results may be attributed to the turbulence of the epilimnion and hypolimnion water exchange. According to the estimation of CH_4 storage and emission flux in Lake Fuxian, more CH_4 flux was emitted in the littoral zone than in the pelagic zone. Particularly during the overturn period, 0.85 mg/m^2/day CH_4 was emitted in the littoral zone, but only 0.43 mg/m^2/day was emitted in the pelagic zone. As for CH_4 storage, it was 30% higher during stratification than that during overturn period. Both the storage CH_4 and emission flux were lower during the overturn period than during the stratification period, indicating that most of the decreasing CH_4 was oxidized in water during the transition from the stratification period to the overturn period.

Sources of organic carbon and its effects on CH_4 production

Lakes receive a complex mixture of organic matters derived from autochthonous and allochthonous sources. Given that the macrophyte distribution occupies only 0.1% of the water surface area in Lake Fuxian (Nanjing Institute of Geography and Limnology 1990), autochthonous OM mainly consists of metabolites and residues of microbe and phytoplankton, whereas terrestrial (allochthonous) OM includes plant debris, soil erosion, and organic wastes from domestic and industrial sewage. Owing to the difference of δ^{13}C-TOC and TOC/TN values from different sources, they are widely used to evaluate the source of organic matter in sediments. However, the range of δ^{13}C-TOC and TOC/TN values from different sources sometimes overlaps and is influenced by seasonal changes, human activities, climate change, and geographical conditions. Thus, they tend to vary with different ecosystems, and an accurate analysis of the source of organic matter requires large-scale sampling and comprehensive analysis of specific ecosystem samples. According to the isotopes of organic carbon in water, sediment, soil, and river in previous studies on the catchment of Lake Fuxian (Chen et al. 2018; Ding et al. 2016; Song et al. 2016), combined with the sampling data in the current study, we established a classification unit to analyze the sources of organic carbon in littoral and pelagic sediments (Fig. 5b). The range of δ^{13}C-TOC (− 26.7 to − 25.12 ‰) in the S1 sediment was similar to that of soil organic carbon (− 27.2 to − 17.6 ‰, Ding et al. 2016) and higher than that of C3 (− 30.8 to − 27.4‰) and C4 plants (nearly − 13‰), indicating that the riverine transport of organic matter by S1 (Liangwang River) into the lake mainly derived from soil erosion instead of terrestrial plant debris. Meanwhile, although algae δ^{13}C-TOC showed seasonal variation, the range of δ^{13}C-TOC in the S5 sediment (− 28.58 to – 27.08 ‰) was close to that of algae, with an average of − 27.9‰ according to Xu (2005). Using a lipid biomarker, Zhang et al. (2015a) also found that the pelagic zone in Lake Fuxian was mainly affected by algal organic carbon. Overall, according to the carbon isotope composition and the ratio of TOC to TN, we can verify that allochthonous and autochthonous organic matter settled down in S1, whereas autochthonous organic matter was found in S5. This result was in accordance with a previous finding that the organic matter of Lake Fuxian was influenced partly by terrestrial sources and mainly by algal sources and that the site with a shallow water depth was affected by terrestrial sources (Chen et al. 2018).

In this field investigation, we also found that TOC presented a significant positive correlation with the MPP in the sediments from S2 to S5 (Fig. 5c, $R^2 = 0.401$, $p < 0.01$), where it was not greatly affected by terrestrial organic matter. Organic carbon addition can facilitate CH_4 production according to several incubation results in the laboratory. For example, Grasset et al. (2018) found significant but variable CH_4 production in anoxic freshwater sediments by adding allochthonous and autochthonous organic matter, and observed that the organic carbon from phytoplankton decomposes faster than the organic carbon from terrestrial plant leaves. West et al. (2012) found that methanogenesis rates are significantly raised following the addition of algal biomass. Terrestrial carbon addition also facilitates the increase of methanogenesis rates, but such increase is not statistically significant (West et al. 2012). Both studies indicated that autochthonous organic matter is labile and easily used by microorganisms. The surface sediment of S5 has a TOC of as high as 11.1% (Fig. 5a), which is significantly higher than that for many hypereutrophic lakes in China, such as Lake Taihu (with a maximum value of 5.34%, (Yan et al. 2019)) and Lake Chaohu (0.34–1.57%, (Zan et al. 2012)); and close to that for Lake Xingyun (0.73–13.2%, (Zhang et al. 2014)). It is also much higher than that for several similar deep lakes, such as Lake Lugano (1.1–3.2%, (Bechtel and Schubert 2009)), Lake Zug (1.2–6.3%, (Meckler and Schubert 2004)), and Lake Lonar (2.65 ± 1.47%, (Menzel et al. 2013)). As a result, the high TOC content with high bioavailability to microbials has a risk of promoting CH_4 emission from sediment pore water to overlying water. In this work, DO was only 0.27 mg/L, and the measured MOP in the overlying water was negligible. Consequently, a large amount of CH_4 accumulated at the bottom of the lake, greatly increasing the risk of CH_4 release to the atmosphere in the overturn period.

Effects of climate change and eutrophication on CH_4 emission in deep lakes

Similar to oxygen minimum zone in oceans (Stramma et al. 2008), many deep lakes, under the dual pressure of climate change and eutrophication, also show a trend of prolonged oxygen stratification, increased oxycline thickness, and shallowed oxycline depth, all of which exacerbate the anoxia of the bottom water (Zhang et al. 2015b). In the present study, the DO in the water column over a depth of 120 m was stably lower than 0.5 mg/L during the stratification and overturn periods and lower than the DO measured in 2016 (2.88 mg/L, (Li et al. 2019)). On the one hand, this hypoxic or even nearly anoxic condition in hypolimnion can facilitate CH_4 production and storage. On the other hand, although methanotrophs can survive in low oxygen environments (Roslev and King 1994), the fraction of CH_4–carbon incorporation into the bacterial biomass was up to 38-fold lower at hypoxic conditions (Steinle et al. 2017); this condition may weaken the aerobic oxidation of CH_4 under hypoxic or anoxic conditions. Some studies indicated that MOP can be enhanced under submicromolar oxygen conditions, but as to what extent the low-oxygen enhancement of MOP will counterbalance the elevated rates of methanogenesis in sediments remains unclear.

According to the China meteorological data sharing service system (http://cdc.cma.gov.cn/home.do) at the local site of Lake Fuxian, temperature significantly increased from 1952 to 2018 during winter (Fig. S5). Several studies found that increasing air temperature can lead to raised water temperature (Takeshige et al. 2013). As water temperature increases, overlying water and surface sediments will also have high temperature, especially in the littoral zone; this phenomenon can lead to a strong MPP (Duc et al. 2010). The shallow water depth in the littoral zone has a powerful risk for CH_4 emission to the atmosphere as a result of global warming. With the thermocline thickness increasing and thermocline depth shallowing, the CH_4 peak in the thermocline will become close to water–air interface, leading to a high CH_4 concentration difference between the surface water and the atmosphere. As a result, this phenomenon will cause a high diffusive flux of CH_4 from the lake and thereby exacerbate the greenhouse effect.

Conclusion

CH_4 production and storage concentration in the water column and sediments of Lake Fuxian during the stratified and overturn periods were studied, and the following conclusions were derived.

In the water column, the littoral zones are hotspots of CH_4 emission. CH_4 was significantly accumulated nearly at the oxic metalimnion and hypoxic hypolimnion during the stratification period. However, the CH_4 peak and storage disappeared during the overturn period.

Allochthonous and autochthonous organic matter settled down to the littoral zone, whereas mainly autochthonous organic matter was found in the pelagic zone. Maximum MPP was observed in the intermediate section of the S1 sediment but on the S2–S5 surface. Moreover, the MPP rose with increasing organic carbon contents in the surface sediments of S2–S5. This result indicates that the input of autochthonous organic carbon may lead to a high CH_4 production and emission risk.

Acknowledgments We would like to thank Jing Li, Jingya Xue, and Jianhua Luo for their help in the field work and figure modifications. We would also like to thank the two anonymous reviewers for their useful comments and constructive suggestions.

Funding information This study was jointly funded by the National Natural Science Foundation of China (91751111, 31730013), Chinese Academy of Sciences (QYZDJ-SSW-DQC030), and the Youth Innovation Promotion Association of CAS (2014273).

References

Bastviken D, Cole J, Pace M, Tranvik L (2004) Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate. Glob Biogeochem Cycles 18(4):1–12

Bastviken D, Santoro AL, Marotta H, Pinho L, Calheiros D, Crill P, Enrich-Prast A (2010) Methane emissions from Pantanal, South America, during the low water season: toward more comprehensive sampling. Environ Sci Technol 44(14):5450–5455

Bastviken D, Tranvik LJ, Downing JA, Crill PM, Enrichprast A (2011) Freshwater methane emissions offset the continental carbon sink. Science 331(6013):50

Bechtel A, Schubert CJ (2009) A biogeochemical study of sediments from the eutrophic Lake Lugano and the oligotrophic Lake Brienz, Switzerland. Org Geochem 40:1100–1114

Blee J, Niemann H, Erne M, Zopfi J, Schubert CJ, Lehmann MF (2015) Spatial ariations in surface water methane super-saturation and emission in Lake Lugano, southern Switzerland [J]. Aquat Sci 77(4): 535–545

Chanton JP, Martens CS, Kelley CA, Crill PM, Showers WJ (1992) Methane transport mechanisms and isotopic fractionation in emergent macrophytes of an Alaskan tundra lake. J Geophys Res-Atmos 97(D15):16681–16688

Chen X, Feng M, Ke F, Pan J, Fan F, Wang Y, Li W (2018) Source and biogeochemical distribution of organic matter in surface sediment in the deep oligotrophic Lake Fuxian, China. Aquat Geochem 24(1): 55–77

Cole JJ, Caraco NF (1998) Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF6. Limnol Oceanogr 43(4):647–656

Conrad R (1999) Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments. FEMS Microbiol Ecol 28(3):193–202

Conrad R, Claus P (2005) Contribution of methanol to the production of methane and its 13C-isotopic signature in anoxic rice field soil. Biogeochemistry 73(2):381–393

Delsontro T, Boutet L, St-Pierre A, Del Giorgio PA, Prairie YT (2016) Methane ebullition and diffusion from northern ponds and lakes regulated by the interaction between temperature and system productivity. Limnol Oceanogr 61:S62–S77

Deutzmann JS, Stief P, Brandes J, Schink B (2014) Anaerobic methane oxidation coupled to denitrification is the dominant methane sink in a deep lake. Proc Natl Acad Sci U S A 111(51):18273–18278

Ding W, Chen J, Yang H, Song Y, Tao H, Luo J (2016) Investigation on sources of organic carbon in major rivers in the catchment of Fuxian Lake, Yunnan Province. Earth Environ 44(3):290–296 (in Chinese)

Duc NT, Crill P, Bastviken D (2010) Implications of temperature and sediment characteristics on methane formation and oxidation in lake sediments. Biogeochemistry 100(1-3):185–196

Durischkaiser E, Schmid M, Peeters F et al (2015) What prevents outgassing of methane to the atmosphere in Lake Tanganyika?[J]. J Geophys Res Biogeosci 116(G2):1490–1492

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

Egger M, Rasigraf O, Sapart CJ, Jilbert T, Jetten MS, Röckmann T, Veen CVD, Bândă N, Kartal B, Ettwig KF, Slomp CP (2015) Iron-mediated anaerobic oxidation of methane in brackish coastal sediments. Environ Sci Technol 49(1):277–283

EPA U.S. Environmental Proctecion Agency (2010) Methane and nitrous oxide emissions from natural sources. Report No. EPA-43-R-10-001. EPA Office of Atmospheric Programs, Washington DC

Fernández JE, 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

Fernández JE, Peeters F, Hofmann H (2016) On the methane paradox : transport from shallow water zones rather than in situ methanogenesis is the major source of CH_4 in the open surface water of lakes. J Geophys Res Biogeosci 121:2717–2726

Finster K, Tanimoto Y, Bak F (1992) Fermentation of methanethiol and dimethylsulfide by a newly isolated methanogenic bacterium. Arch Microbiol 157(5):425–430

Gelesh L, Marshall K, Boicourt W, Lapham L (2016) Methane concentrations increase in bottom waters during summertime anoxia in the highly eutrophic estuary, Chesapeake Bay, U.S.A. Limnol Oceanogr 61:S253–S266

Grasset C, Mendonca R, Saucedo GV, Bastviken D, Roland F, Sobek S (2018) Large but variable methane production in anoxic freshwater sediment upon addition of allochthonous and autochthonous organic matter: methanogenic potential of different OC types. Limnol Oceanogr 63:1488–1501

Grossart HP, Frindte K, Dziallas C, Eckert W, Tang KW (2011) Microbial methane production in oxygenated water column of an oligotrophic lake. Proc Natl Acad Sci U S A 108(49):19657–19661

Hofmann H (2013) Spatiotemporal distribution patterns of dissolved methane in lakes: How accurate are the current estimations of the diffusive flux path? Geophys Res Lett 40(11):2779–2784

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

Jespersen AM, Christoffersen K (1987) measurement of chlorophyll-a from phytoplankton using ethanol as extraction solvent. Archiv Hydrobiol 109(3):445–454

Juutinen S, Alm J, Larmola T, Huttunen JT, Silvola J (2003) Major implication of the littoral zone for methane release from boreal lakes. Glob Biogeochem Cycles 17(4):1–28

Knittel K, Boetius A (2009) Anaerobic Oxidation of Methane: Progress with an Unknown Process. Annu Rev Microbiol 63(63):311–334

Li L, Xue B, Yao S, Tao Y, Yan R (2018) Spatial–temporal patterns of methane dynamics in Lake Taihu. Hydrobiologia:1–14

Li B, Xun F, Chen X, Ma S, Wang Y, Feng M (2019) Distribution characteristic and ecological risk assessment of AVS and SEM in surface sediments of Lake Fuxian. J Lake Sci 31(1):72–80 (in Chinese)

Likens GE (2010) Biogeochemistry of inland waters. Academic Press, NY, pp 480–502

Liss PS, Slater PG (1974) Flux of gases across the air-sea interface. Nature 247(5438):181–184

Liu Y, Conrad R, Yao T, Gleixner G, Claus P (2016) Change of methane production pathway with sediment depth in a lake on the Tibetan plateau. Palaeogeogr Palaeoclimatol Palaeoecol 474:279–248

Martinez-Cruz K, Sepulveda-Jauregui A, Casper P, Anthony KW, Smemo KA, Thalasso F (2018) Ubiquitous and significant anaerobic oxidation of methane in freshwater lake sediments. Water Res 144:279–286

Meckler AN, Schubert CJ (2004) New organic matter degradation proxies: valid in lake systems? Limnol Oceanogr 49:2023–2033

Menzel P, Gaye B, Wiesner MG, Prasad S, Stebich M, Das BK, Anoop A, Riedel N, Basavaiah N (2013) Influence of bottom water anoxia on nitrogen isotopic ratios and amino acid contributions of recent sediments from small eutrophic Lonar Lake, central India. Limnol Oceanogr 58:1061–1074

Milucka J, Kirf M, Lu L, Krupke A, Lam P, Littmann S, Kuypers MM, Schubert CJ (2015) Methane oxidation coupled to oxygenic photosynthesis in anoxic waters. ISME J 9(9):1991–2002

Nanjing Institute of Geography and Limnology (1990) Lake Fuxian. Ocean Press, Beijing

Natchimuthu S, Sundgren I, Gålfalk M, Klemedtsson L, Crill PM, Danielsson Å, Bastviken D (2016) Spatio-temporal variability of lake CH_4 fluxes and its influence on annual estimates. Limnol Oceanogr 61:1–14

Oremland RS (1979) Methanogenic activity in plankton samples and fish intestines: a mechanism for in situ methanogenesis in oceanic surface waters. Limnol Oceanogr 24(6):1136–1141

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

Reeburgh WS (2010) Oceanic methane biogeochemistry. Chem Rev 3107:486–513

Riedinger N, Brunner B, Lin YS, Voßmeyer A, Ferdelman TG, Jørgensen BB (2010) Methane at the sediment–water transition in Black Sea sediments. Chem Geol 274(1):29–37

Roland F, Darchambeau F, Morana C, Bouillon S, Borges AV (2017) Emission and oxidation of methane in a meromictic, eutrophic and temperate lake (Dendre, Belgium). Chemosphere 168:756–764

Roslev P, King GM (1994) Survival and recovery of methanotrophic bacteria starved under oxic and anoxic conditions. Appl Environ Microbiol 60(7):2602–2608

Song Y, Chen J, Yang H, Ding W, Tao H, Luo J, Wang J (2016) Distribution and source of the organic matter in the sediment of Fuxian Lake, Yunnan Province. Bull Mineral Petrol Geochem 35(4):618–624 (in Chinese)

Sparling R, Daniels L (1986) Source of carbon and hydrogen in methane produced from formate by Methanococcus thermolithotrophicus. J Bacteriol 168(3):1402–1407

Steinle L, Maltby J, Treude T, Kock A, Bange HW, Engbersen N, Zopfi J, Lehmann MF, Niemann H (2017) Effects of low oxygen concentrations on aerobic methane oxidation in seasonally hypoxic coastal waters. Biogeosciences 14(6):1631–1645

Stramma L, Johnson GC, Sprintall J, Mohrholz V (2008) Expanding oxygen-minimum zones in the tropical oceans. Science 320(5876): 655–658

Sun M, Zhang G, Ma X, Cao X, Mao XY, Li J, Ye WW, Liu SM (2018) Dissolved methane in the East China Sea: distribution, seasonal variation and emission. Mar Chem 202:12–26

Takeshige A, Takahashi T, Nakata H, Kimura S (2013) Long-term trends in sea surface temperature in coastal water in relation to large-scale climate change: a case study in Omura Bay. Cont Shelf Res 66:73–82

Tang KW, McGinnis DF, Frindte K, Brüchert V, Grossart HP (2014) Paradox reconsidered: methane oversaturation in well-oxygenated lake waters. Limnol Oceanogr 59(1):275–284

Tang KW, Mcginnis DF, Ionescu D, Grossart HP (2016) Methane production in oxic lake waters potentially increases aquatic methane flux to air. Environ Sci Technol Lett 3:227–233

Thomsen U, Thamdrup B, Stahl DA, Canfield SDE (2004) Pathways of organic carbon oxidation in a deep lacustrine sediment, Lake Michigan. Limnol Oceanogr 49(6):2046–2057

UNESCO/IHA (2010) GHG Measurement Guidelines for Freshwater Reservoirs

Verpoorter C, Kutser T, Seekell DA, Tranvik LJ (2014) A global inventory of lakes based on high-resolution satellite imagery. Geophys Res Lett 41(18):6396–6402

Wang H, Lu J, Wang W, Yang L, Yin C (2006) Methane fluxes from the littoral zone of hypereutrophic Taihu Lake, China. J Geophys Res-Atmos 111(D17109)

West WE, Coloso JJ, Jones SE (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 WE, Creamer KP, Jones SE (2016) Productivity and depth regulate lake contributions to atmospheric methane. Limnol Oceanogr 61(S1):S51–S61

Wiesenburg DA (1979) Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. J Chem Eng Data 24(4): 356–360

Xu J (2005) Ecological studies on the food web structures and trophic relationships of freshwater lakes in China using stable carbon and nitrogen isotopes. Dissertation, Chinese Academy of Sciences. (in Chinese)

Yan X, Xu X, Ji M, Zhang Z, Wang M, Wu S, Wang G, Zhang C, Liu H (2019) Cyanobacteria blooms: a neglected facilitator of CH4 production in eutrophic lakes. Sci Total Environ 651(Pt 1):466–474

Zan F, Huo S, Xi B, Zhu C, Liao H, Zhang J, Kevin MY (2012) A 100-year sedimentary record of natural and anthropogenic impacts on a shallow eutrophic lake, Lake Chaohu, China. J Environ Monit 14(3):804–816

Zeng H, Wu J (2009) Sedimentary records of heavy metal pollution in Fuxian Lake, Yunnan Province, China: intensity, history, and sources. Pedosphere 19(5):562–569

Zhang W, Ming Q, Shi Z, Chen G, Niu J, Lei G, Chang F, Zhang H (2014) Lake sediment records on climate change and human activities in the Xingyun Lake catchment, SW China. PLoS One 9(7):e102167

Zhang Y, Su Y, Liu Z, Chen X, Yu J, Di X, Jin M (2015a) Sediment lipid biomarkers record increased eutrophication in Lake Fuxian (China) during the past 150 years. J Great Lakes Res 41(1):30–40

Zhang Y, Wu Z, Liu M, He J, Shi K, Zhou Y, Wang M, Liu X (2015b) Dissolved oxygen stratification and response to thermal structure and long-term climate change in a large and deep subtropical reservoir (Lake Qiandaohu, China). Water Res 75:249–258

Zhou Q, Zhang Y, Zhou Y, Chen Y, Qin J, Nie J (2016) Spectral attenuation of ultraviolet and visible radiation and its relationship with chromophoric dissolved organic matter in autumn/winter in Lake Fuxian, China. J Lake Sci 28(6):1316–1327 (in Chinese)

Zhou Y, Xiao Q, Yao X, Zhang Y, Zhang M, Shi K, Li X, Podgorski DC, Qin B, Spencer RGM (2018) Accumulation of terrestrial dissolved organic matter potentially enhances dissolved methane levels in eutrophic Lake Taihu, China. Environ Sci Technol 52(18):10297–10306