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Characteristics of carbon source greenhouse gas flux in the water–air formation in the middle and upper reaches of the Three Gorges Reservoir

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ABSTRACT

This study selected five points in the middle and upper mainstream of the Three Gorges Reservoir area. Starting from May 2016, the greenhouse gases CO_2 and CH_4 from the water–air formation at the sampling points have been monitored month by month for 10 months. Using the headspace balance method and the thin boundary layer model estimation method, we obtained the CO_2 and CH_4 partial pressure ranges and the water–air formation diffusion flux at the mainstream point. It is found that the CH_4 partial pressure of water body is significantly positively correlated with water temperature, and significantly negatively correlated with DO; the CH_2 partial pressure of water body is positively correlated with water temperature, but negatively correlated with conductivity, DO, pH and wind speed. The diffusion fluxes of CH_4 and CO_2 at the water–air formation are positively correlated with CH_4 partial pressure and water temperature, and negatively correlated with ph, DO and conductivity. It is also found that the reservoir has a certain mitigation effect on the release of CO_2 from the river water body, and the CH_4 diffusion flux at the water–air formation is roughly equivalent.

Key words: CO_2, CH_4, mainstream of middle and upper reaches, Three Gorges Reservoir, water–air formation flux

HIGHLIGHTS

- This study adopts the headspace balance technology to establish a water body carbon source greenhouse gas monitoring method suitable for reservoirs in the upper reaches of the Yangtze River.
- This study monitors and analyzes the greenhouse gas concentrations of carbon sources in water bodies at typical points of upstream reservoirs in different seasons and different operating conditions.

1. INTRODUCTION

Relevant studies show that the main biogenic elements such as carbon, nitrogen, phosphorus and silicon are in a very nonconservative state in the ‘river-reservoir system’. The reservoir has significantly changed the transport flux and form composition of river biogenic substances, and it may even affect the global circulation, mass balance and marine ecosystem of some elements (Congqiang *et al.*, 2009). The carbon cycle in the reservoir is a complex process. After the biogeochemical process in the reservoir, the form of biogenic elements changes greatly in the vertical direction of water body. Moreover, the inundation of terrestrial vegetation and soil by river interception will also cause the regeneration and mineralization of biogenic elements and increase the nutrient load of water bodies in the reservoir area (Campo & Sancholuz 1998). After the dam is built, a large number of biogenic elements can be intercepted by the dam, and the sedimentation of the reservoir will also take away the biogenic elements,

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resulting in the decrease of river transport flux (Parks & Baker, 1997). The water flow is slow and the light transmittance is good after impounding the reservoir. The phytoplankton in the water grows vigorously. Primary productivity is improved, and DOC concentration in water is relatively high. Therefore, reservoirs play an important role in the carbon cycle. The Yangtze River, with huge input of terrestrial organic carbon, is the largest river in Asia and the third-largest river in the world. The construction of the Three Gorges Reservoir may change the original carbon cycle law of the Yangtze River and change the original carbon source-sink structure. After the impoundment of the Three Gorges Reservoir in 2003, the river section of the reservoir area has changed from a natural river course to a river course and seasonal reservoir. As a typical river-type reservoir, the hydrodynamic characteristics of the Three Gorges Reservoir are significantly different in space. The mainstream in the reservoir area has significant one-dimensional flow characteristics and still maintains the characteristics of a natural river. Water storage changes the hydrological and hydrodynamic conditions of the tributary bay and the river topography. It cannot be simply generalized into a one-dimensional feature. It has long-term complex layered and anisotropic flow characteristics in-depth (Daobin *et al.*, 2010). The physical and chemical properties and hydrological and hydrodynamic conditions of the mainstream of the Three Gorges Reservoir has obvious difference. The differences in conditions are obvious. Against the background of questioning the rights and interests of hydropower clean energy and carbon emission political negotiations at home and abroad, it is imperative to comprehensively and systematically observe and analyze the budget pattern of greenhouse gases in water bodies and river basins after the Three Gorges Reservoir is formed and compare the differences with those before the reservoir is formed.

Many related studies have been carried out by foreign scholars. Tremblay *et al.* (2004) conducted a comparative analysis on the carbon flux of natural lakes and reservoirs in North America. Dos Santos *et al.* (2006) estimated the total flux of several reservoirs in South America and compared the flux characteristics of reservoirs in different climate zones. Louis *et al.* (2000) also analyzed the differences in the carbon flux characteristics of reservoirs in different climate zones around the world. Barros *et al.* (2011) assume that climate zone and reservoir age are the key factors affecting global reservoir carbon flux levels. The monitoring and research of greenhouse gas emissions from reservoirs in China have just started, and it is far from forming systematic important achievements. At present, domestic research can only give qualitative answers to some important questions about the benefits of hydropower greenhouse gas emission reduction. There is neither enough quantitative scientific data support, nor systematic research on greenhouse gas sources and sinks under China's climatic conditions, geological background and reservoir types.

Based on the above research, this study mainly focuses on the typical points in the upper and middle reaches of the Three Gorges Reservoir, and establishes a monitoring method of water carbon source greenhouse gas suitable for the upper reaches of the Yangtze River by using headspace balance technology. It monitors and analyzes the water carbon source greenhouse gas concentration at the typical points in the upper reaches of the reservoir in different seasons and under different operating conditions, grasps the different characteristics of water carbon source greenhouse gas concentration and its main environmental influencing factors, and estimates the greenhouse gas flux at the water–air formation. The useful basic data accumulation and scientific research method for further study and the evaluation of the greenhouse gas effect of reservoirs are expected to be provided by this research.

2. MATERIALS AND METHODS

2.1. Monitoring method of CO_2 and CH_4 at the water–air formation

Xiao *et al.* (2015) used the model estimation method and the static box method to monitor and compare the CO2 flux at the water–air formation of the Pengxi River, a typical tributary of the Three Gorges Reservoir. The difference between the two monitoring methods is smaller, and the water area has no effect on the difference between the two monitoring methods; it is also concluded that the thin boundary layer (TBL) model estimation method may be more appropriate for the canyon channel type reservoir, but the static box method – gas chromatography – will be affected by the flow pattern of water–air formation and be easily disturbed by water flow at the formation with rapid flow, thus affecting the monitoring results (Pumpanen *et al.*, 2004; Tremblay *et al.*, 2005). The monitoring area of greenhouse gas at the water–air formation is located in the middle and upper reaches of the Yangtze River, and the water flow on the river surface is more rapid than that in front of the dam, so the static box method is not suitable for this study area. Thus, this study adopted the headspace balance method (Pumpanen *et al.*, 2004; Tremblay *et al.*, 2005) and the TBL model estimation method (Jähne *et al.*, 1989; Tremblay *et al.*, 2005; Kolb & Ettre, 2006; Goldenfum, 2010; Richter & Jähne 2011) to monitor the greenhouse gas in the water–air formation area of this study.

2.2. Sampling and analysis method

From May 2016, sampling sites were monitored month by month for a period of 10 months. The monitoring time of all sampling points was controlled between 15 and 20 days in the middle of every month, and the daily monitoring time was from 10:00 am to 3:00 pm. The sampling tool was a 5-L water collector, and only 0.5 m surface water of each point was collected for the required water samples. Except for the indicators analyzed by hand-held instruments, other water samples were sent back to the laboratory immediately on the same day, and all testing and analysis work was completed within 48 h. The analysis indexes of field hand-held instruments include: water temperature, dissolved oxygen (DO), pH value, conductivity, air temperature, atmospheric pressure, wind speed, etc. (Jähne *et al.*, 1989). Chlorophyll content was measured by spectrophotometry. The diffusion fluxes of CO_2 and CH_4 in the water–air formation were calculated by the headspace balance method combined with the TBL model estimation method (Yu *et al.*, 2017). By shaking the water sample and the injected initial inert gas violently, the gas concentration of the water body was balanced with the gas concentration on the gas side. The gas partial pressure of the water sample before equilibrium was calculated by measuring the gas concentration on the gas side. The calculation method for the diffusion fluxes of CO_2 and CH_4 at the water–air formation is as follows (Matthews *et al.*, 2003):

$$Flux = k_x(C_{sur} - C_{eq})$$

In the formula, Flux is the diffusion fluxes of greenhouse gases (CO_2 and CH_4) (mmol/(m^2·h)); K_x is the gas exchange coefficient (cm/h); C_{sur} is the concentration of gas in the surface water (mmol/L) and C_{eq} is the saturation concentration of greenhouse gases in the atmosphere at the site temperature and pressure (mmol/L).

For the estimation of the exchange coefficient k_x, most of them use the mathematical empirical formula established by Jähne *et al.* (1989):

$$k_x = k_{600}\left(\frac{600}{S_c}\right)^{0.67}$$

In the formula, k_{600} is the exchange coefficient of sulfur hexafluoride (SF_6) gas (cm/h), and the S_c is the Schmidt constants of CO_2 and CH_4 at t °C.

This study adopts the exchange coefficient for the lake and reservoir ecosystem, and the CO_2 uses the empirical formula established by Cole and Caraco (1998):

$$k_{600} = 2.07 + 0.215U_{10}^{1.7}$$

CH_4 uses the empirical formula established by Macintyre *et al.* (2006):

$$k_{600} = 0.45U_{10}^{1.64}$$

In the formula, U_{10} is the wind speed at 10 m above the water surface (m/s).

Usually, the wind speed above the water body obtained by field monitoring can be converted by the following formula (Fed, 1982):

$$U_{10} = 1.22U_1$$

For freshwater, S_C can be calculated as follows (Matthews *et al.*, 2003):

$$S_c(CO_2) = 1911.1 - 118.11t + 3.4527t^2 - 0.04132t^3$$

$$S_c(CH_4) = 1897.8 - 114.28t + 3.2902t^2 - 0.03906t^3$$

Multiplying the monitored partial pressure of greenhouse gases in water by the Henry coefficient, we can get the saturation concentration C_{sur} of greenhouse gases in water. The calculation formula is as follows (Fed, 1982):

$$C_{sur} = K_0 \cdot p(\text{Gas})$$

In the formula, K_0 is the Henry coefficient, namely gas solubility (mol/(L·atm)); P (Gas) is the partial pressure of gas at the current water temperature (μatm).

The experimental analysis and calculation data were all entered into SPSS® or Origin® for statistical analysis. Spearman's correlation analysis is used to analyze p(CO_2), p(CH_4), CO_2 flux, CH_4 flux and various physical and chemical indexes (pH, TA, DO, water temperature, Chl-*a*, etc.), which shows the linear correlation between the data changes.

2.3. Study area

Based on hydrological characteristics and geographical form, this study selects five points to test and analyze the middle and upper reaches of the mainstream of the Three Gorges Reservoir. The locations are shown in Table 1. Among them, Zhutuo and Mudong points belong to the fluctuating backwater area of the Three Gorges Reservoir, while Fuling, Zhongxian and Wanzhou points belong to the perennial backwater area of the Three Gorges Reservoir.

Table 1. | Coordinates of each sampling point.

Sampling point	Coordinates*	Abbreviation
Zhutuo	N29°1′00″; E105°51′00″	ZT
Mudong	N30°30′15″; E106°02′48″	MD
Fuling	N29°48′00″; E107°27′00″	FL
Zhongxian county	N30°24′57.63″; E108°12′40.86″	ZX
Wanzhou	N30°46′26.66″; E108°24′46.74″	WZ

*The specific coordinate data come from Google China. Data quoted from: http://earth.google.com

3. RESULTS AND ANALYSIS

3.1. Characteristics of CO_2 and CH_4 flux in the water–air formation of the Three Gorges Reservoir

3.1.1. Partial pressures of CO_2 and CH_4 in surface water

See Figure 1 for partial pressure of CO_2 at each point in the mainstream of the Three Gorges Reservoir.

After a complete period of monitoring, it was found that the partial pressure of CO_2 in surface water at the mainstream points showed a similar law except ZX, and the partial pressure of surface water reached the maximum in July. The maximum CO_2 partial pressures at ZT, MD, FL and WZ are 4,484.07, 3,959.48, 4,216.47 and 3,724.60 μatm, respectively. Of course, the partial pressure of CO_2 at ZX point is also relatively high in July, and the trend of MD and FL is almost the same. Except for WZ point, the CO_2 partial pressure of surface water in the mainstream shows a decreasing trend with time, reaching the minimum in December, among which the minimum CO_2 partial pressures at ZT, MD, FL and WZ points are 1,246.99, 1,249.86, 1,256.00 and 1,292.09 μatm, respectively. The maximum CO_2 partial pressures at ZX and WZ points in the perennial backwater area are obviously smaller than those at ZT and MD points in the fluctuating backwater area, which indicates that the total carbon source does not increase obviously due to the increase of water capacity in the reservoir area after entering the perennial backwater area, and indirectly indicates the rationality of dividing fluctuating backwater area and perennial backwater area by FL point. However, after the impoundment of the Three Gorges Reservoir started in September, the partial pressure of CO_2 suddenly rose to the maximum value of 4,495.206 μatm in November, which suggested that ZT was located at the end of the reservoir area, so it was less affected by the reservoir area.

See Figure 2 for CH_4 partial pressure at the mainstream point of the Three Gorges Reservoir.

After a complete period of monitoring, the CH_4 partial pressure of the surface water appeared larger in May or June at the sampling points except at ZX, which may be due to the fact that the water level began to drop to the lowest water storage height after the mainstream entered May and June, and the CH_4 gas generated at the bottom of the river was not fully oxidized during the rising process, which made the CH partial pressure of the surface

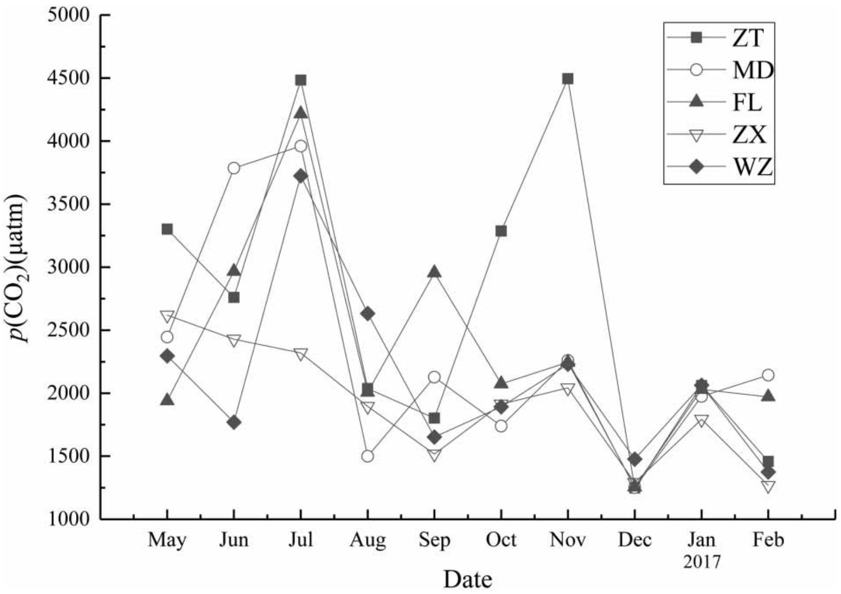

Fig. 1. | Results of the partial pressure of CO_2.

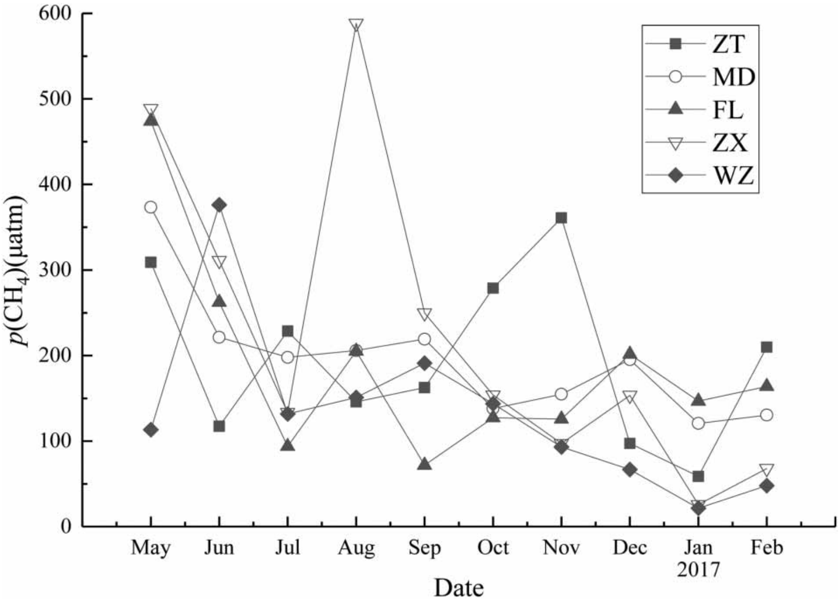

Fig. 2. | CH_4 partial pressure results of the mainstream points of the Three Gorges Reservoir.

water increase during this period. The change of CH_4 partial pressure at ZT point has no obvious law, which is obviously different from the other four points. Considering that ZT point is in a natural river state with little influence from the reservoir area, CH_4 partial pressure may be greatly influenced by the local environment. Except for the CH4 partial pressure at ZX point in August, MD, FL, ZX and WZ points showed a decreasing trend after May and June. However, due to the small CH_4 content in water, the difference of CH_4 partial pressure at each point was not obvious. Considering that the model method was greatly influenced by field factors, it needed to be further studied and analyzed by other methods.

3.1.2. Annual average partial pressures of CO_2 and CH_4

See Figure 3 for annual average partial pressures of CO_2 and CH_4 in surface water at the mainstream point of the Three Gorges Reservoir.

The average value calculated from a complete period of monitoring results represents the annual average level of CO_2 and CH_4 partial pressure in surface water at this point. The annual average CO_2 partial pressure at ZT point is 2,693.48 μatm, the annual average minimum is 1,908.78 μatm, while the annual average CO_2 partial pressures at MD, FL and WZ points are 2,365.89, 2,365.89 and 2,110.79 μatm. It is possible that after the river water enters the transition zone from the river area, the phytoplankton in the water gradually increases and the photosynthesis intensity obviously increases. The absorption of carbon in this process leads to the decrease of CO_2 partial pressure in the water. However, there is no obvious trend among the annual average CH_4 partial pressure values at every point in the mainstream. The annual average CH_4 partial pressure values at ZX point are 226.87 μatm, followed by ZT point 196.87 μatm, WZ point 133.61 μatm, MD and FL points 195.68 and 187.24 μatm, respectively.

3.1.3. Diffusion fluxes of CO_2 and CH_4 in the water–air formation

See Figure 4 for the annual average diffusion fluxes of CO_2 and CH_4 in surface water at the mainstream point of the Three Gorges Reservoir.

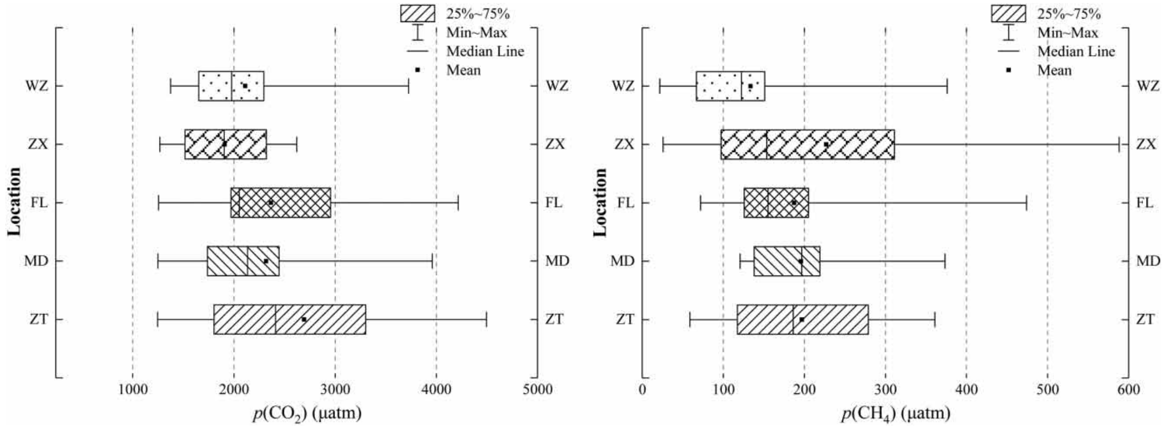

Fig. 3. | Annual average partial pressures of CO_2 and CH_4 in the mainstream.

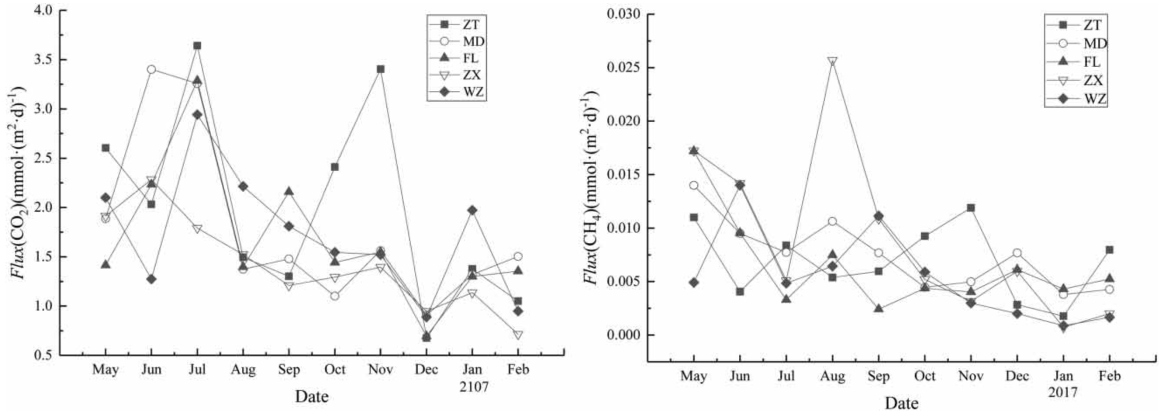

Fig. 4. | Results of the air–water CO_2 and CH_4 fluxes in the mainstream (TBL).

According to the partial pressures of CO_2 and CH_4 in surface water at each point, the diffusion fluxes of CO_2 and CH_4 in the water–air formation at each point in the mainstream of the Three Gorges Reservoir are obtained by the TBL model estimation method. The trend of CO_2 and CH_4 diffusion fluxes in the water–air formation at each point is roughly equal to the trend of partial pressures of CO_2 and CH_4, and all values are positive. It shows the 'source' of CO_2 and CH_4 release. Except for the ZT point, the CO_2 diffusion flux at the other four points gradually decreases with time after reaching the maximum value in June and July, and reaches the lowest value around December, which may be due to the gradual increase of carbon absorption by phytoplankton photosynthesis in the reservoir area, resulting in CO_2 in the water–air formation. However, except for the abnormal value of ZX in August, the CH_4 diffusion flux in the water–air formation showed a downward trend as a whole, reaching the maximum value in May and June and the lowest value around January. This may be because the CH_4 gas produced at the bottom of the river was not fully oxidized during the rising process after the water level decreased in May and June, but the CH_4 gas was fully oxidized during the rising process after the water storage began. As a result, the CH_4 diffusion flux gradually decreased when the water level began to drop in January. See Figure 4 for diffusion fluxes of CO_2 and CH_4 in water–air formation at various points in the mainstream.

3.1.4. Annual average diffusion fluxes of CO_2 and CH_4 at the water–air formation

See Figure 5 for the annual average diffusion fluxes of CO_2 and CH_4 in the water–air formation at the mainstream point of the Three Gorges Reservoir.

The mean values of CO_2 diffusion flux in the water–air formation and CH_4 diffusion flux at the water–air formation of the Three Gorges Reservoir are 41.29 ± 4.46 mmol·m^{-2}·d^{-1} and 0.168 ± 0.028 mmol·m^{-2}·d^{-1}, respectively. The research river reach is preliminarily explored as the 'source' of greenhouse gas. The CO_2 diffusion flux in the water–air formation of the mainstream points first decreases with the flow direction from ZT to ZX, and the annual average CO_2 diffusion flux is 47.97 mmol·m^{-2}·d^{-1} at ZT point, 34.09 mmol·m^{-2}·d^{-1} at ZX point, 42.69 mmol·m^{-2}·d^{-1} at MD point and 40.38 mmol·m^{-2}·d^{-1} at FL point. It may be that after the water flow gradually enters the reservoir area, the water capacity increases, and the precipitation and utilization of carbon is enhanced, which leads to the decrease of CO_2 diffusion flux from ZT to ZX. Then, with the continuous intake of exogenous carbon, the carbon content in the reservoir increases obviously, which leads to the gradual increase of CO_2 diffusion flux. There is no obvious change rule of CH_4 diffusion flux in the water–air formation at the mainstream point. The maximum value is 0.22 mmol·m^{-2}·d^{-1} at ZX point. The minimum value is 0.13 mmol·m^{-2}·d^{-1} at WZ point. The diffusion fluxes at ZT, MD and FL points are 0.16 mmol·m^{-2}·d^{-1}, 0.18 mmol·m^{-2}·d^{-1} and 0.15 mmol·m^{-2}·d^{-1}, respectively.

3.2. Analysis of influencing factors of CH_4 and CO_2 diffusion fluxes at the water–air formation

3.2.1. Surface water temperature

See Figure 6 for water temperature distribution at mainstream points in the Three Gorges Reservoir area.

During the monitoring in October, the surface water temperature at each point in the mainstream showed a consistent change trend, which first increased and then decreased. In August, the surface water temperature reached the maximum value, including ZT point water temperature of 25.1 °C, MD point water temperature of 25.9 °C, FL point water temperature of 29.4 °C, ZX point water temperature of 31.8 °C and WZ point water temperature of 33.7 °C. The minimum water temperature appears in December or January in winter, among which ZT, MD, FL, ZX and WZ are 13.7, 14.1, 13.0, 13.5 and 13.6 °C, respectively. In the same month, there is no big difference between the water temperature at each point and no abnormal value.

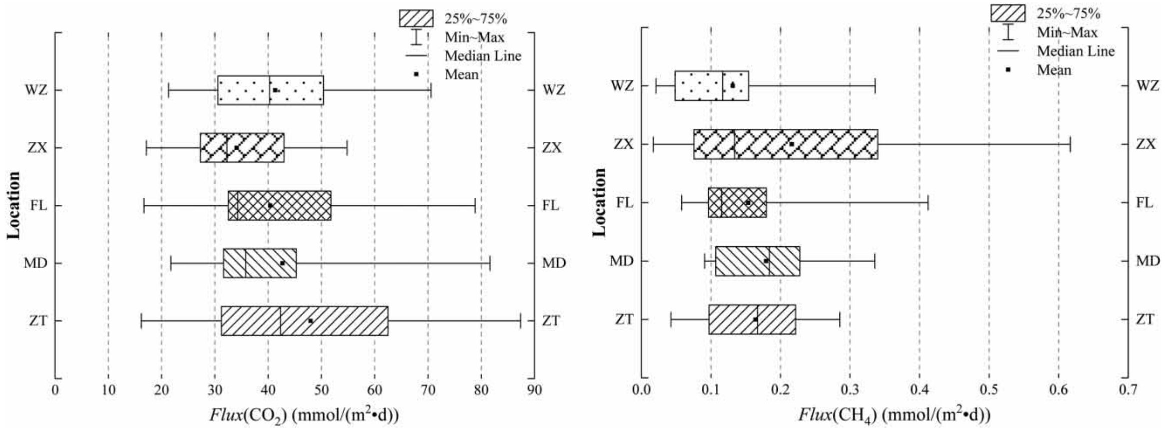

Fig. 5. | Results of the air–water CO_2 and CH_4 annual average fluxes in the mainstream (TBL).

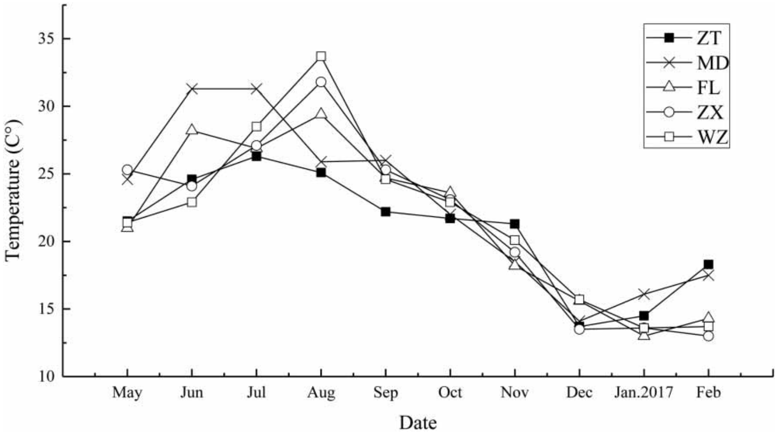

Fig. 6. | Distribution of water temperature at mainstream points.

3.2.2. Dissolved oxygen

Figure 7 shows the distribution of DO at the mainstream points of the Three Gorges Reservoir.

It is found that the change of DO concentration on the surface of every point in the mainstream tends to increase gradually, and this similar change trend is just opposite to the changing trend of surface water temperature at every point in the mainstream. This is because the water temperature will affect the solubility of DO in water, and water with higher temperature will reduce the DO concentration in water. Moreover, due to the rapid flow velocity in the mainstream, the primary productivity such as algae at each point is not suitable for growth, so there will be no obvious photosynthesis and oxygen increase, and no obvious bloom and hypoxia will be formed. Therefore, the DO concentration at each point in the mainstream in winter will be significantly higher than that in summer. The DO in ZT, MD, FL, ZX and WZ points varied from 7.86 to 10.64, 7.51 to 9.60, 7.41 to 9.87, 6.71 to 9.83 and 6.97 to 9.24 mg·L^{-1}, respectively.

3.2.3. pH

See Figure 8 for pH distribution at the mainstream points of the Three Gorges Reservoir.

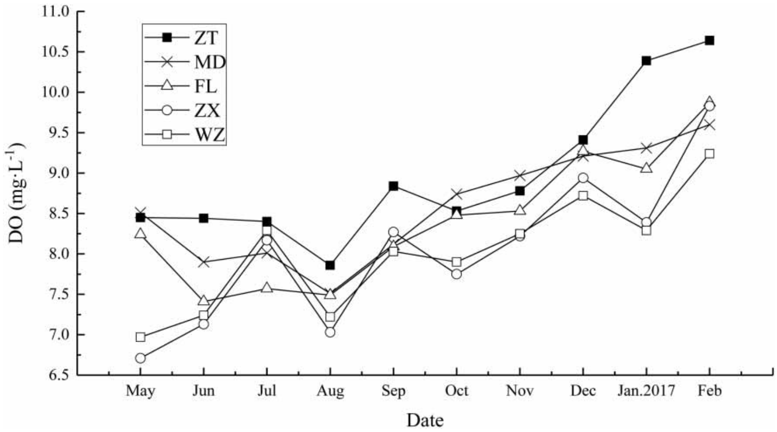

Fig. 7. | Distribution of DO at mainstream points.

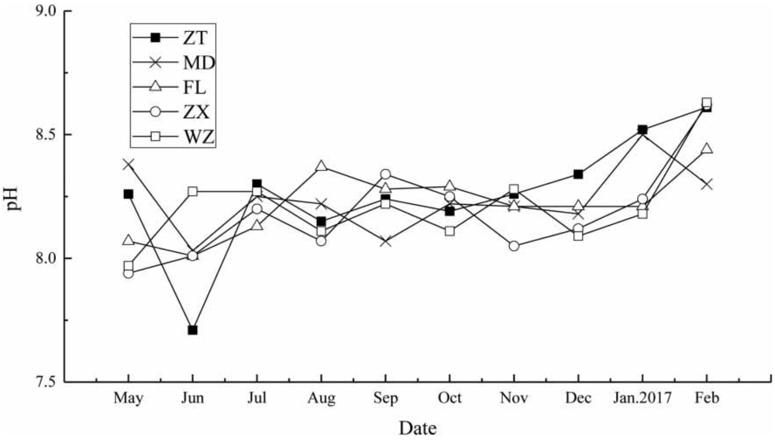

Fig. 8. | pH distribution at mainstream points.

The results show that the pH of water bodies in the mainstream of the Three Gorges Reservoir area fluctuates little along the whole course, among which the pH of ZT point varies from 7.71 to 8.61, MD point from 8.03 to 8.50, FL point from 8.01 to 8.61, ZX and FL points from 7.94 to 8.62, and WZ point from 7.97 to 8.62.

3.2.4. Chl-*a*

See Figure 9 for the distribution of Chl-*a* at the mainstream points of the Three Gorges Reservoir.

It is found that the distribution of Chl-*a* at ZT, MD and FL points in the mainstream of the Three Gorges Reservoir area is similar, which is relatively high in October and November, and reaches the maximum value in November, with the maximum Chl-*a* values of 5.42, 4.3 and 4.08 mg·L, respectively. This may be due to the fact that the Three Gorges Reservoir area entered the water storage period in October, and the water flow velocity of the mainstream decreased and the temperature was not low in autumn, which was beneficial to the growth of phytoplankton. In winter, after December, the chlorophyll content decreased obviously. However, there is a slight difference between ZX and WZ. The mass concentration of Chl-*a* at ZX is relatively large in January

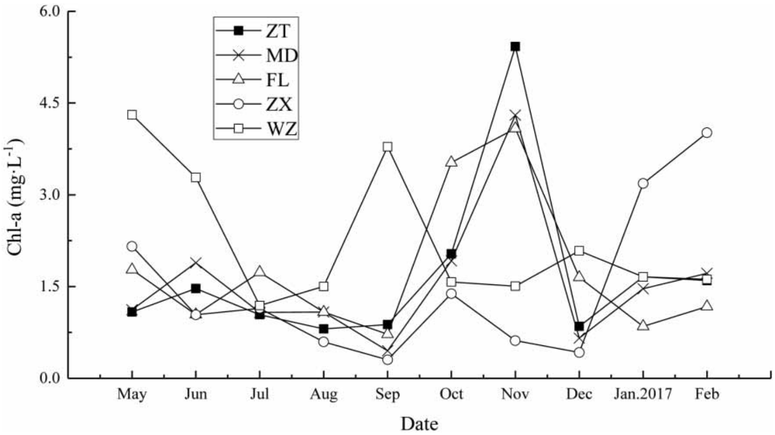

Fig. 9. | Distribution of Chl-*a* at mainstream points.

and February in winter, while that at WZ is relatively large in May and June in spring and summer, and the range of Chl-*a* is 0.30 ~ 4.0 and 1.5 ~ 4.3 mg·L^{-1}, respectively. Although there are differences in the changes of Chl-*a* at the mainstream points, the overall mass concentration of Chl-*a* at all points is very small, because the mainstream flow speed is fast and it is not suitable for the growth of primary productivity such as phytoplankton, so the mass concentration of Chl-*a* is low.

3.2.5. Correlation analysis between main environmental indicators and diffusion flux

The greenhouse gas diffusion flux at the water–air formation is determined by the concentration of the corresponding gas in the water body and the atmosphere and the gas exchange coefficient. The exchange coefficient K value has a crucial influence on the final result, but the value of K is often affected by surface water bodies. The turbulence mixing effect and the influence of wind speed, wind direction, rainfall and other environmental factors have become very complicated. Therefore, the results of the model estimation method may have large uncertainties. Studies have shown that when the surface water bodies such as reservoirs and oceans are affected by wind, The value of K can be expressed as a function of wind speed (Jonathan & Nina, 1998), but under weak wind conditions, the relational expression does not hold (Matthews *et al.*, 2003). In this study, the climate data of the field test was available at the time of sampling, but the water surface was under weak wind conditions at the time of sampling, so it was not used as a reference for the main environmental factors. The surface water temperature, DO, pH, Chl-*a*, conductivity and wind speed are correlated with the partial pressures of CO_2 and CH_4 in water and the diffusion fluxes of CO_2 and CH_4 in the water–air formation (headspace TBL model estimation method). The analysis results are shown in Table 2.

It is found that the CO_2 partial pressure and CH_4 partial pressure at each point have a strong correlation with the diffusion fluxes of CO_2 and CH_4 at the water–air formation and various environmental indicators except Chl-*a*:

1. CH_4 partial pressure in water body is positively correlated with water temperature, and negatively correlated with DO. Because the change of water temperature will affect the solubility of CH_4 gas in water, when the water temperature is higher, CH_4 gas will easily rise from the river bottom to the surface water body. At the same time, the appropriate water temperature is helpful for the activity of methanogenic bacteria at the river bottom. When the temperature is higher, more CH_4 gas will be produced by methanogenic bacteria.
2. CO_2 partial pressure is positively correlated with water temperature, but negatively correlated with conductivity, DO, pH and wind speed. Similarly, the change of water temperature will affect the solubility of CO_2

Table 2. | Correlation analysis between indicators and fluxes of CH_4, CO_2, pressures of CO_2 and CH_4 in the mainstream.

	CH_4 partial pressure	**CO_2 partial pressure**	**CH_4 flux**	**CO_2 flux**
CH_4 partial pressure	1	–	0.971**	–
CO_2 partial pressure	–	1	–	0.879**
Water temperature	0.448**	0.543**	0.515**	0.612**
Conductivity	–	–0.353*	–0.324*	–0.360
DO	–0.310**	–0.373*	–0.420**	–0.487**
pH	–	–0.280*	–	–0.317**
Wind speed	–	–0.344*	–	–
Chl-*a*	–	–	–	–

Note: *P≤ 0.01 indicates extremely significant correlation; **P ≤ 0.05 indicates significant correlation. (Cited from Hui *et al.* 2007.)

gas in water. The higher the water temperature, the more CO_2 gas escapes from the water surface. The conductivity of water reflects the total dissolved solids, and the negative correlation between CO_2 partial pressure and conductivity may be due to the decomposition and transformation of some dissolved carbon by microorganisms, which reduces the conductivity of water and increases the CO_2 partial pressure in water. The respiration and decomposition of microorganisms in water will consume oxygen and carbon in water, so the more DO consumed, the higher the partial pressure of CO_2 in water. There is an ion balance between hydrogen ions, bicarbonate ions and CO_2 in water. When the pH value of water is higher, the concentration of hydrogen ions decreases, and CO_2 gas tends to combine with water to generate bicarbonate ions, which leads to the decrease of CO_2 partial pressure in water. Wind disturbance on water surface will accelerate the diffusion of CO_2 gas in water body and lead to the decrease of CO_2 partial pressure in water body.

3. CH_4 diffusion flux is positively correlated with CH_4 partial pressure and water temperature, and negatively correlated with DO and conductivity. This is because the calculation of diffusion flux in this study is based on Fick's law, that is, the phase at the high concentration side diffuses to the low concentration side, i.e. the greater the CH_4 partial pressure in water, the greater the CH_4 diffusion flux at the water–air formation. The same high water temperature helps CH_4 gas at the bottom of the river rise to the surface water body and then diffuse into the atmosphere. In the process of methane generated at the bottom of the river rising to the water surface, the part of CH_4 gas will be oxidized, so the more DO consumed by oxidation, the less CH_4 gas diffused into the atmosphere. It is possible that some dissolved carbon in water is converted into CH_4 and released in the water–air formation, which leads to the decrease of water conductivity, so there is a negative correlation between water conductivity and CH_4 diffusion flux.
4. CO_2 diffusion flux is positively correlated with CO_2 partial pressure and water temperature, and negatively correlated with conductivity, DO and pH. Similarly, the size of CO_2 partial pressure in water determines the intensity of CO_2 gas diffusion. The greater the CO_2 partial pressure, the greater the diffusion flux. Higher water temperature is also beneficial to CO_2 gas escaping from the water surface. The greater the DO in water, the more beneficial it is to the photosynthesis of plankton in water. This process can reduce the generation of microbial respiration in water and thus reduce the CO_2 content in water, so the less CO_2 generated in water is released into the atmosphere. Because of the ion balance of CO_2 gas in water, the change of pH value will affect the ion balance. The smaller the pH value, the greater the hydrogen ion concentration, so the greater the CO_2 gas released from water.

4. DISCUSSION

4.1. Difference of greenhouse gas flux between the fluctuating backwater area and the perennial backwater area

The diffusion fluxes of CO_2 and CH_4 in the water–air formation of reservoirs are usually affected by many factors such as reservoir age, type, hydrological condition and plant community (Jian *et al.*, 2018; Jinlong *et al.*, 2018). Especially, due to the influence of reservoir operation conditions, different backwater areas of reservoirs lead to hydrological differences in water areas, which may lead to temporal and spatial differences in carbon conversion rate and phytoplankton biomass. The research shows that the average retention time of continental runoff under natural conditions is 16–26 days. However, after a dam is constructed, the water retention time, water depth, hydrodynamic conditions, water mass mixing mode and so on have changed significantly compared with natural rivers. The average retention time of artificial interception can be increased to 60 days (Lei, 2012; Humborg *et al.*, 2000). In this study, Zhutuo and Mudong are located in the fluctuating backwater area of the Three Gorges

Reservoir, and their greenhouse gas fluxes have more significant fluctuations than Wanzhou in Zhongxian County and Fuling in the transition section. Yao and other scholars have studied the characteristics of CO_2 release flux in the water–air formation between Zhuyi River and Caotang River, the first tributary of Fengjie in the Three Gorges Reservoir Area. The results show that the trend of CO_2 flux in the Zhuyi River backwater area is close to the reservoir level, while that in the Caotang River backwater area is close to the river level as a result of the different hydrological conditions in their backwaters (Yao *et al.*, 2017). Zhe and other scholars have similar results in Pengxi River, a tributary in the middle of the Three Gorges Reservoir area, and Longxi River at the tail of the reservoir area (Zhe *et al.*, 2013). In addition, the hydrological conditions in the backwater area are affected by the regulation of water level in the reservoir area, and also show seasonal hydrological and ecological characteristics, which will also lead to seasonal differences in CH_4 diffusion flux.

River-type hydrological characteristics can be found in low water-level operation in summer, and lake-type water hydrological characteristics can be found in high water-level operation in winter. Therefore, DO, Chl-*a*, pH and nutrients also show seasonal changes, which leads to seasonal differences in phytoplankton growth due to the instability of water ecological environment (Jinlong *et al.*, 2018). On the other hand, the variable backwater area may have more concentrated road-source carbon input in a short time than the perennial backwater area, because the carbon deposition time of soil on both sides of the variable backwater area is obviously longer than that of the perennial backwater area, which may be the potential basic condition for the peak change of greenhouse gases in different backwaters.

4.2. Comparative analysis of CO_2 and CH_4 diffusion fluxes in this study and other backwater data

According to Table 3, the average value of CO_2 diffusion flux in the water–air formation in this study is at a medium level in the data of CO_2 diffusion flux in the water–air formation of some reservoirs and rivers collected by the author in recent years. Among them, the data of the tributaries of the Three Gorges Reservoir present a complicated situation of CO_2 flux, and the different hydrological conditions of the tributaries lead to great differences in CO_2 flux. Le and other scholars show significant differences in water area types in the study of Xin'anjiang Reservoir. The inflow area (fluctuating backwater area) has a higher flux, which decreases in the middle section and increases sharply in front of the dam (Le *et al.*, 2017). This difference may be due to the fact that the input of exogenous carbon source in the fluctuating backwater area is larger than that in the middle section, and the rapid flow rate is conducive to CO_2 diffusion, while the flow rate in the middle section decreases and the carbon storage is much smaller than that in front of the dam. This phenomenon is similar to this study to a certain extent.

The generation of CH_4 in water mainly comes from on-site generation, sediment release and methane-rich water input. Considering the low content of POC in total suspended particulate matter in the Three Gorges Reservoir, the contribution of on-site generation to CH_4 in water may be low (Qian *et al.*, 2018). According to Table 4, the CH_4 diffusion flux of this study is relatively small among the collected CH_4 diffusion fluxes of typical reservoirs. The reason may be that the Three Gorges Reservoir is a large reservoir of deep-water channel type, and its submerged area is relatively small, which slows down the release of greenhouse gases from rivers. In addition, there is a significant relationship between methane flux and temperature. The methane flux released from Manso (Dos Santos *et al.*, 2006) and Petit Saut (Qian *et al.*, 2018) reservoirs in the tropics is higher than that in temperate and cold zones. However, there is a small difference between cold and temperate zones, which may be due to the decreasing effect on methane release from reservoirs with the decrease of temperature.

4.3. Discussion on the mechanism of the reservoir carbon cycle

In addition to environmental factors, which have a certain influence on the production of greenhouse gases in aquatic ecosystems, the existence of algae has an important relationship with the production of greenhouse

Table 3. | Part of the data of exchange flux of CO_2 between the formation of water and air in the world.

Description	Position	CO_2 diffusion flux at water–air formation/mmol $(m^2\ d_2^{-1})$	Remarks
Karst Deep Water Reservoir-Wanfeng Lake	China	15.30	
Lower Jinsha River	Yunnan, China	53.78	
Xin'anjiang Reservoir	East China region of China	65.67 (Le *et al.*, 2017) 19.99 (Le *et al.*, 2017) 837.27 (Le *et al.*, 2017)	Storage office Midpiece Dam front
Hongfeng Lake	China	20.2 (Yingchun *et al.*, 2007)	
Wan'an Reservoir	China	12.74 (Hangyuan *et al.*, 2011)	
Xiangxi River	China	5.88 (Yan *et al.*, 2011)	Hubei province West, Three Gorges Reservoir
Zhuyihe backwater area	China	−73.26 to −30.38	Fengjie, Three Gorges Reservoir
Backwater area of Caotang River tributary	China	81.43 ~ 136.72	Fengjie, Three Gorges Reservoir
Pengxi river	China	73.2 (Zhe *et al.*, 2013)	Yunyang, Three Gorges Reservoir
Hudson River	USA	16.08 ~ 36.00 (Yuchuan, 2011)	
Amazonian rivers	South America	134.64 ~ 244.32 (Grunwald *et al.*, 2009)	
Wanfenghu Reservoir backwater area	China	27.4~44.2 (Zhang *et al.*, 2008)	
Middle section of Three Gorges Reservoir	China	41.29 ± 4.46	This study

Table 4. | Part of the data of exchange flux of CH_4 between the formation of water and air in the world.

Description	Position	climate zone	CH_4 diffusion flux at water–air formation/mmol $(m^2\ d_4^{-1})$	Remarks
Porttipahtaf	Finland	Frigid zone	6 (Huttunen *et al.*, 2002)	
Cabonga	Canada	Frigid zone	13.9 (Tremblay *et al.*, 2005)	
Roosevelt	USA	Temperate zone	3.2 (Zhe *et al.*, 2013)	
Shasta	USA	Temperate zone	9.5 (Huttunen *et al.*, 2002)	
Manso	Brazil	Tropical	42 (Dos Santos *et al.*, 2006)	
Petit Saut	Guyana	Tropical	34.8 (Abril *et al.*, 2005)	
Pengxi river	China	Temperate zone	1.2 (Zhe *et al.*, 2013)	
Nihe Reservoir	China	Temperate zone	20.22 (Hongxian *et al.*, 2012)	
Miyun reservoir	China	Temperate zone	0.45 (Meng *et al.*, 2011)	
Middle section of Three Gorges Reservoir	China	Temperate zone	0.168 ± 0.028	This study

gases and the carbon cycle mechanism of reservoirs. Xigong mentioned in his research on the relationship between algae and the carbon cycle in the water–air formation in Xiangxi River reservoir bay that the existence of algae may reduce the carbon release in the reservoir. This is because its own carbon sequestration can absorb part of CO_2 in the water body in a short time, thus reducing the release of greenhouse gases. Xigong's research results show that Chl-*a* is negatively correlated with CH_4 partial pressure in the water body (Xigong, 2013). However, there is no obvious correlation between Chl-*a* observed in this study. It may take a long time for algae to decline and settle to the final decomposition. In the mineralization of microorganisms, CO_2, as the decomposition product of organic carbon, will still be released into the reservoir again, which essentially only delays the release rate of carbon into the atmosphere. Therefore, this correlation is not obvious in a long-term observation.

5. CONCLUSIONS

(1) The range of $p(CO_2)$ and $p(CH_4)$ of surface water in the study area is 1,246.99 ~ 4,495.20 and 21.63 ~ 588.28 μatm, respectively. $p(CO_2)$ in surface water gradually decreases from upstream to downstream, while $p(CH_4)$ has no obvious change. $p(CO_2)$ and $p(CH_4)$ are higher in summer and lower in winter. From the river area to the transition area of the Three Gorges Reservoir, the diffusion flux of CO_2 in the water–air formation decreases, which indicates that the reservoir can alleviate the release of CO_2 in river water, while the diffusion flux of CH_4 in the water–air formation is roughly equal.

(2) During the complete reservoir operation period from May 2016 to February 2017, the CO_2 diffusion flux in the water–air formation in the study area was positive, showing the characteristics of 'source', with an average value of $41.29 \pm 4.46\ \mathrm{mmol \cdot m^{-2} \cdot d^{-1}}$; CH_4 diffusion flux in the water–air formation is positive, showing the characteristics of 'source', with an average value of $0.168 \pm 0.028\ \mathrm{mmol \cdot m^{-2} \cdot d^{-1}}$. The variation trend of CO_2 and CH_4 diffusion fluxes is basically consistent with $p(CO_2)$ and $p(CH_4)$.

(3) CH_4 diffusion flux in the water–air formation is positively correlated with $p(CH_4)$ and water temperature, and negatively correlated with conductivity and DO. CO_2 diffusion flux in the water–air formation is positively correlated with $p(CO_2)$ and water temperature, and negatively correlated with conductivity, DO and pH. Other environmental factors have no obvious correlation, which needs further study.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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