Environmental Pollution 297 (2022) 118769

Contents lists available at ScienceDirect

Environmental Pollution

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

Oxic urban rivers as a potential source of atmospheric methane☆

Feng Zhao [a,b], Yongqiang Zhou [a], Hai Xu [a,*], Guangwei Zhu [a], Xu Zhan [b], Wei Zou [a], Mengyuan Zhu [a], Lijuan Kang [a], Xingchen Zhao [a]

[a] State Key Laboratory of Lake and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing, 210008, PR China
[b] School of Environmental and Civil Engineering, Jiangnan University, Wuxi, 214122, PR China

ARTICLE INFO

Keywords:
Methane (CH_4)
Urban river
Algal blooms
Human activities
Xin'an river

ABSTRACT

Urban rivers play a vital role in global methane (CH_4) emissions. Previous studies have mainly focused on CH_4 concentrations in urban rivers with a large amount of organic sediment. However, to date, the CH_4 concentration in gravel-bed urban rivers with very little organic sediment has not been well documented. Here, we collected water samples from an oxic urban river (Xin'an River, China; annual mean dissolved oxygen concentration was 9.91 ± 1.99 mg L^{-1}) with a stony riverbed containing very little organic sediment. Dissolved CH_4 concentrations were measured using a membrane inlet mass spectrometer to investigate whether such rivers potentially act as an important source of atmospheric CH_4 and the corresponding potential drivers. The results showed that CH_4 was supersaturated at all sampling sites in the five sampling months. The mean CH_4 saturation ratio (ratio of river dissolved CH_4 concentration to the corresponding CH_4 concentration that is in equilibrium with the atmosphere) across all sampling sites in the five sampling months was 204 ± 257, suggesting that the Xin'an River had a large CH_4 emission potential. The CH_4 concentration was significantly higher in the downstream river than in the upstream river ($p < 0.05$), which suggested that human activities along the river greatly impacted the CH_4 level. Statistical analyses and incubation experiments indicated that algae can produce CH_4 under oxic conditions, which may contribute to the significantly higher CH_4 concentration in August 2020 ($p < 0.001$) when a severe algal bloom occurred. Furthermore, other factors, such as heavy rainfall events, dissolved organic carbon concentration, and water temperature, may also be vital factors affecting CH_4 concentration. Our study enhances the understanding of dissolved CH_4 dynamics in oxic urban rivers with very little organic sediment and further proposes feasible measures to control the CH_4 concentration in urban rivers.

1. Introduction

Methane (CH_4) is an important greenhouse gas that contributes greatly to global warming (Montzka et al., 2011; Wang et al., 2020b). Despite its low concentration in the atmosphere compared with that of carbon dioxide (CO_2), its warming effect is more than 28 times that of CO_2 (IPCC, 2013). Inland freshwater bodies (such as rivers, lakes, and reservoirs) are hotspots of global CH_4 emissions (Bastviken et al., 2011; Deemer et al., 2016; Stanley et al., 2016). It was reported that global CH_4 emissions from inland freshwater bodies reached 103.3 Tg CH_4 yr^{-1}, and CH_4 emissions from rivers reached 1.5 Tg CH_4 yr^{-1} based on measurements from regional-scale rivers (Bastviken et al., 2011). Among all rivers, urban rivers are considered relatively important sources of CH_4 emissions (Ortega et al., 2019; Li et al., 2020; Wang et al., 2020a). According to a recent study conducted by Zhang et al. (2021b), the average CH_4 diffusive flux from urban rivers in the Chaohu Lake Basin of China was 7 mmol CH_4 m^{-2} d^{-1}, which was 7 times higher than that from nonurban rivers in that region. Similarly, high CH_4 ebullition was also observed from urban rivers (Wang et al., 2021). The greatest difference between river water and lake (or reservoir and ocean) water is that river water has a shorter water residence time. At the same time, urban rivers received a high level of pollutants (e.g., nutrients, organic matter, and CH_4) due to intense human activities (Alshboul et al., 2016; Yin et al., 2021) and may become hotspots for CH_4 emission. Therefore, investigating the CH_4 dynamics in urban rivers can help us further understand its contribution to the CH_4 level in downstream waters and the global CH_4 budget.

Traditionally, CH_4 was considered to be primarily produced through

☆ This paper has been recommended for acceptance by Pavlos Kassomenos.

* Corresponding author. Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, 73 East Beijing Road, Nanjing, 210008, PR China.
E-mail address: hxu@niglas.ac.cn (H. Xu).

https://doi.org/10.1016/j.envpol.2021.118769
Received 21 June 2021; Received in revised form 20 December 2021; Accepted 27 December 2021
Available online 29 December 2021

anaerobic fermentation of acetate driven by methanogens under strictly anoxic conditions (Zamanpour et al., 2020). However, CH_4 oversaturation has been observed in some oxic water columns (Karl et al., 2008; Damm et al., 2010; Tang et al., 2016), which seems to contradict the traditional concept. Traditional explanations for this paradox include transport from nearby anoxic sediment or shorelines (Hofmann et al., 2010) and production within microanoxic areas such as detritus (de Angelis and Lee, 1994). However, an increasing number of studies have found that CH_4 can also be produced under oxic conditions. Different from the prevailing paradigm that methanogens are strict anaerobes, some methanogens have been reported to be remarkably tolerant to oxygen (Angel et al., 2011), and some microorganisms may produce CH_4 through a different pathway that does not require oxygen-sensitive enzymes, which may be potential explanations for CH_4 oversaturation in fully aerobic waters (Tang et al., 2016). Furthermore, numerous studies have revealed that the CH_4 concentration was positively correlated with the Chl*a* concentration in oxic waters, which indicated that algae may play a role in the CH_4 paradox. CH_4 production driven by cyanobacteria has been attributed to the demethylation of methyl phosphonates (White et al., 2010). Recently, several studies demonstrated that algae can produce CH_4 by converting bicarbonate to CH_4 through photosynthesis under oxic conditions (Bižić et al., 2020; Günthel et al., 2020). In addition, some genera of cyanobacteria, such as *Anabaena*, have the ability to fix nitrogen, along with the production of CH_4. For example, Conrad and Seiler (1980) observed high CH_4 concentrations during a nitrogen-fixing algal bloom in 2010. Zheng et al. (2018) reported that CH_4 could be produced by nitrogenase during nitrogen fixation. One possible mechanism for this is that nitrogen fixation induced by cyanobacteria can provide hydrogen for methanogens to produce CH_4 (Berg et al., 2014; Tang et al., 2014). Current studies have mainly focused on oxic CH_4 production in deep lakes and reservoirs and have pointed out that oxic CH_4 production made a large contribution to total CH_4 emissions from these waters (Donis et al., 2017; Günthel et al., 2019). However, to date, CH_4 oversaturation in gravel-bed urban rivers with very little organic sediment and its relationship with algae remain unclear.

Due to human activities or landforms, the riverbeds of some rivers are stony and often covered with inorganic materials (e.g., gravels, coarse pebbles, and large stones) rather than organic sediment (Fig. 1d). It seems that the CH_4 concentrations in the water column in such rivers may be low since organic sediment is considered a hotspot for CH_4 production and is an important source of water column CH_4 (Conrad et al., 2009; Mach et al., 2015; Emilson et al., 2018). However, urban rivers are often polluted due to intense human activities. The pollution may cause algal blooms, which may have a potential impact on CH_4 concentration. Additionally, wastewater from municipal wastewater treatment plants (WWTPs) may also contain a large amount of dissolved CH_4 (Wang et al., 2011; Alshboul et al., 2016), which may be an additional source of CH_4 due to discharging the treated wastewater into the rivers (Alshboul et al., 2016). Thus, we speculate that the CH_4 concentration in these rivers may be underestimated. However, to the best of our knowledge, no study has focused on CH_4 concentration and its potential drivers in oxic urban rivers with very little organic sediment.

We hypothesized that oxic urban rivers with very little organic sediment could be a potential source of atmospheric CH_4 and that human activities and algal blooms could potentially affect CH_4 concentration in these rivers. Therefore, we chose an oxic urban river with a low amount of organic sediment as our study area. Five-month field observations and incubation experiments were conducted. The purposes of this study were (1) to measure the CH_4 concentrations to investigate whether oxic urban rivers with a low amount of organic sediment can act as a potential source of atmospheric CH_4; (2) to explore potential factors affecting CH_4 concentrations in these rivers; and (3) to provide suggestions for managing CH_4 concentrations in these rivers.

2. Materials and methods

2.1. Study area

This study was conducted in the Xin'an River in Huangshan city, Anhui Province, China (Fig. 1a). The Xin'an River is located in the northern subtropics. The annual average temperature in this area is approximately 15 °C. The average temperatures range from 1 to 4 °C and 27–29 °C in January and July, respectively. The water originates from

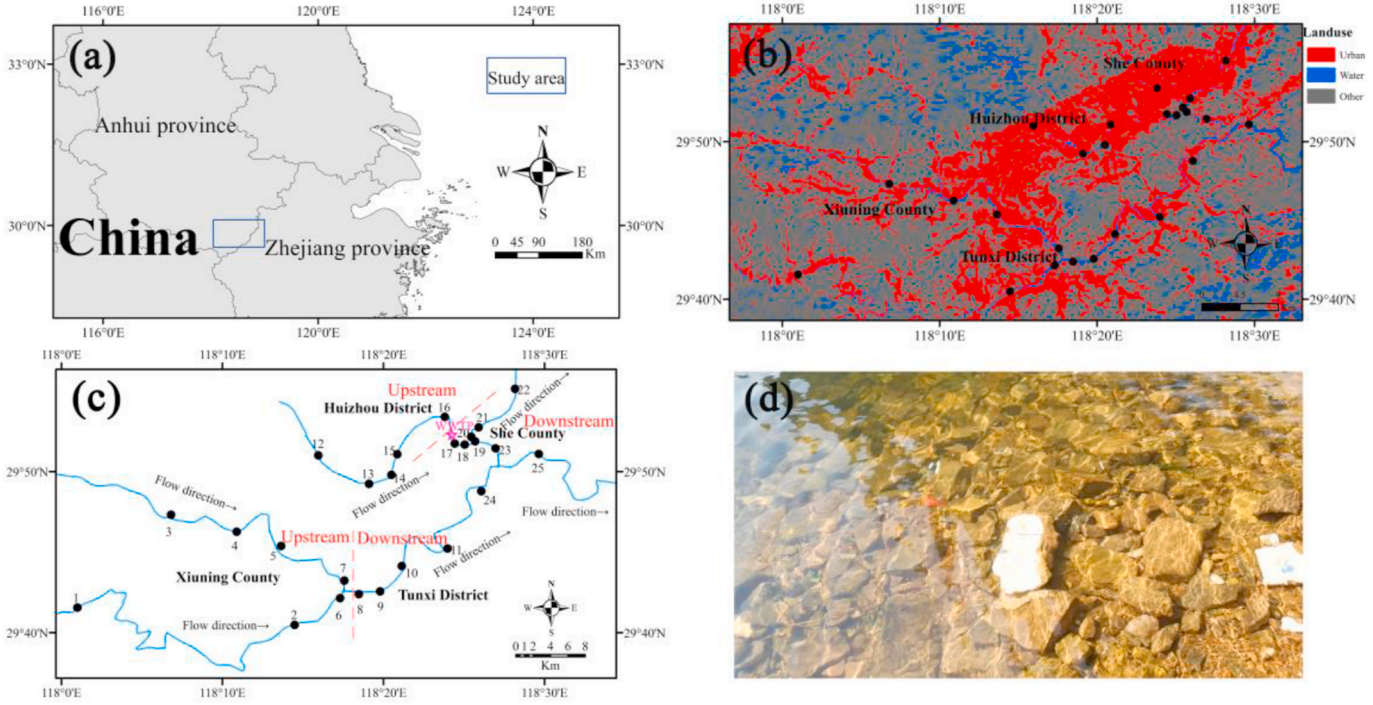

Fig. 1. (a) The study area, (b) land use in the sampling area, (c) specific sampling sites, and (d) sediment of the river.

Liugujian at the junction of Anhui Province and Jiangxi Province. The mainstream of Xin'an River in Anhui Province is 242.3 km long and covers an area of 6500 km^2, accounting for 11.9% of the area of the Qiantang River Basin. Xin'an River contains two large tributaries (Tributary 1 and Tributary 2, Fig. 1c). Tributary 1 contains two smaller tributaries (Hengjiang and Jianjiang), which converge in Tunxi District. Xiuning County (sites 1–7) is located upstream of Tributary 1, while Tunxi District (sites 8–11, 24) is located downstream of Tributary 1. Tributary 2 includes two urban areas, Huizhou District and She County. Huizhou District (sites 12–16) is the upstream area, and She County (sites 17–23, 25) is the downstream area. Sites 17–20 are the nearest four sites downstream of the WWTP (within 3 km, Fig. 1c). The riverbed of the Xin'an River is mainly covered with inorganic sediment (e.g., gravels, coarse pebbles, and large stones) rather than organic sediment (Fig. 1d).

We selected 25 sites from the upstream Xin'an River to the confluence of Xin'an Reservoir. These sampling sites were located in four areas, including Xiuning County, Tunxi District, Huizhou District, and She County, which are four urban areas of Huangshan city (Fig. 1b). Water samples were collected in July 2020 (rainy month), August 2020 (summer), October 2020 (autumn), January 2021 (winter), and April 2021 (spring). The spatial distribution of the sampling sites is shown in Fig. 1c.

2.2. Sample collection

A 5-L water sampler (Uwitec, Austria) was used to collect 5 L of surface water from bridges, and a peristaltic pump (Jihpump, China) connected with a gas-tight rubber tube (internal diameter: 3 mm, Yingtong, China) was used to transfer the bubble-free water to a 12 mL vial (Labco Exetainer, UK). One end of the rubber tube was placed 10 cm below the surface water in the water sampler because the direct collection of surface water might cause bubbles and affect the subsequent measurement. The other end was placed in the vial. The vial was screwed tightly with no headspace after being filled with water. Two quantitative syringes (Cofoe, China) were used to add 0.1 mL of saturated $ZnCl_2$ solution for microbial inactivation. Three duplicate samples were prepared. These samples were collected to measure the N_2:Ar ratio and CH_4 concentration using a membrane inlet mass spectrometer (MIMS, Bay Instrument, USA). A 2 L water sample was transferred to a clean plastic bottle and then placed into a cooling box for subsequent measurement of physical and chemical properties. Lugol iodine solution was added to a 1 L water sample to identify the algal community structure.

2.3. Measurement of key water quality parameters

Water temperature (WT), dissolved oxygen (DO), and fluorescent dissolved organic matter (fDOM) were measured by a multisensor sonde (YSI 6600 V2, USA). A 100 mL unfiltered water sample was used to determine the concentrations of total nitrogen (TN) and total phosphorus (TP). A 500 mL water sample was filtered through 0.70-μm membrane filters (Whatman GF/F, UK) for subsequent determination of the concentrations of chlorophyll *a* (Chl*a*) and dissolved organic carbon (DOC). The measurements of nutrients and Chl*a* concentrations were done according to standard methods (APHA, 2012). The DOC concentrations were measured using a Shimadzu TOC-L analyzer. The samples for identifying the algal community structure and algal concentration were treated with a Lugol iodine solution (1%, V/V) and allowed to settle for 48 h. The cell density was then directly measured in a 0.1 mL counting chamber (Hengke, China), and an Olympus BX53 microscope was used at a magnification of 400 × . The method for identifying algae was derived from Hu and Wei (2007).

2.4. Method for quantifying the nitrogen fixation capacity and CH_4 concentration

The method for quantifying the nitrogen fixation capacity in this study was the N_2:Ar method, a relatively new method that has been widely used in aquatic environments (Schmale et al., 2019; Loeks--Johnson and Cotner, 2020; Zhao et al., 2022). The analytical instrument was MIMS, which has been used to measure concentrations of dissolved N_2, Ar, and O_2 in natural water samples for decades (Kana et al., 1994). More details about this method can be obtained from previous studies (Schmale et al., 2019; Loeks-Johnson and Cotner, 2020). MIMS was also used to measure the dissolved CH_4 concentration instead of the traditional method (headspace combined with gas chromatography) since the MIMS method has a great advantage in CH_4 determination compared with the traditional method. More details regarding the MIMS method for measuring CH_4 concentration and its advantages can be found in the reference (Zhao et al., 2021).

2.5. Calculations of CH_4, O_2, and N_2: Ar saturation ratio

Water flow velocity, the slope of the river, wind speed, and WT are important factors that control CH_4 diffusion from rivers (Borges et al., 2018; Wang et al., 2020a). CH_4 diffusion can be obtained from direct measurement using floating chambers or calculated based on models using the factors mentioned above (Clough et al., 2007; Zhang et al., 2021b). Because we did not measure the water flow velocity and the slope of the river, we only calculated the CH_4 saturation ratio. Although the CH_4 saturation ratio cannot directly reveal the CH_4 emissions from rivers to the atmosphere, it can represent the CH_4 emission potential.

The CH_4 saturation ratio was calculated using the following equation:where C_m represents the measured CH_4 concentration (μmol L^{-1}) using MIMS and C_{eq} (μmol L^{-1}) is the equilibrium CH_4 concentration under the corresponding temperature, which was calculated through WT, atmospheric pressure, and volume ratio of CH_4 to the air of the ambient air (Xiao et al., 2017). A CH_4 saturation ratio >1 indicates that CH_4 is supersaturated in the water, while a CH_4 saturation ratio <1 represents CH_4 undersaturation.

The calculations of DO and N_2:Ar saturation ratios were the same as that of CH_4.

2.6. Incubation experiment

An incubation experiment was conducted to test the effect of algae, sediment, and organic soils from the riparian zone on CH_4 concentrations in oxic water in the Xin'an River in September 2021. Five treatments were performed. Treatment 1 (T1): 1 L of river water was collected and filtered using a 64-μm filter screen (Hengke, China) to remove the algae. Then, the filtered water was transferred to a gas-tight and transparent incubation core. Treatment 2 (T2): 1 L of river water (Chl*a* concentration 112.1 μg L^{-1}) was collected into a gas-tight and transparent incubation core. The core was sealed without headspace using a gas-tight tip. Treatment 3 (T3): Based on T2, algae collected from the river were added to the core and ensured that the final Chl*a* concentration was ~200 μg L^{-1}. Treatment 4 (T4): Based on T2, organic solids were collected from the nearby riparian zone and were added to the core (volume ratio (organic solids: water column = 1: 5)). Treatment 5 (T5): Based on T2, sediments (mainly composed of gravels and pebbles) were collected from the river and were added to the core (volume ratio (sediments: water column = 1: 5)). Three replicates were conducted for each of the five treatments. The incubation cores were placed into the river to ensure that the growth of algae was not limited by light. Furthermore, algae can produce O_2 through photosynthesis under light thereby facilitating oxic conditions in the water. The incubation experiment lasted for 7 days. Water (20 mL) was collected each day to measure the concentrations of dissolved CH_4 and DO using MIMS. The 20-mL water was replaced by 20-mL distilled water using two 30-mL gas-tight

syringes (Cofoe, China). On the last day, the overlying water was pumped using a peristaltic pump, and the water was prepared to measure the concentrations of TN, TP, Chl*a*, and DOC. More details regarding the incubation experiment can be found in the supporting information.

2.7. Data analyses

IBM SPSS 19.0 was used to analyse the spatial and temporal differences in variables (e.g., CH_4 concentration and key water quality parameters). If the data met the normality, independence, and homogeneity of variance criteria, one-way ANOVA (analysis of variance) was used. If the data met the normality and independence criteria but not the homogeneity of variance criteria, Welch corrected analysis of variance was used. If the preconditions of the parametric test were not met, the nonparametric Kruskal–Wallis test was used. The selection of the multiple comparison method adopts the LSD (least significant difference) test according to whether the data meet the homogeneity of variance. If the *p value* is less than 0.05, it indicates that there is a significant spatial (or temporal) difference in variables. The box plot was used to statistically show the differences in dissolved CH_4 concentrations between the upstream river and downstream river, as well as the differences among five different sampling months. All correlations were completed using Pearson correlation analysis with $p < 0.05$ indicating a significant correlation between two variables. Logarithmic treatment was performed if necessary. The analytical software was IBM SPSS 19.0. Figures were completed using Origin 9.5 and ArcGIS 10.4.1.

3. Results

3.1. Characteristics of key physical and chemical variables

The average WT was 27.1 ± 1.49 °C, 32.8 ± 1.04 °C, 19.4 ± 0.81 °C, 8.67 ± 1.60 °C and 19.9 ± 1.36 °C in July 2020, August 2020, October 2020, January 2021, and April 2021, respectively (Table 1). The DO concentration was high at most sampling sites in the five sampling months, ranging from 6.38 to 16.0 mg L^{-1} (Table S1), with a mean concentration of 9.91 ± 1.99 mg L^{-1}. A high TN concentration (1.63 ± 0.48 mg L^{-1}) was observed in July 2020, but it decreased significantly in August 2020 ($p < 0.001$), with an average value of 1.07 ± 0.52 mg L^{-1} (Table 1). The mean TN concentration increased noticeably in October 2020 and January 2021, particularly in January 2021. The monthly variations in TP concentrations were very different compared with those of TN. The lowest TP concentration was observed in October 2020, with a mean value of 46.7 ± 28.1 μg L^{-1}, while the highest value appeared in July 2020 (Table 1). The N:P ratio was low in summer, with a mean value of 14.5 ± 3.17, but it was high in other seasons, especially in winter, with a mean value reaching 35.1 ± 15.2. The Chl*a* concentrations were high in August 2020, ranging from 1.26 to 95.5 μg L^{-1}, but were low in the other four months (Table S1). The organic carbon concentrations were very low in Xin'an River, and the average concentrations of DOC in July 2020, August 2020, October 2020, January 2021, and April 2021 were 1.53 ± 0.52 mg L^{-1}, 2.05 ± 0.51 mg L^{-1}, 1.39 ± 0.53 mg L^{-1}, 1.34 ± 0.57 mg L^{-1}, and 1.37 ± 0.35 mg L^{-1}, respectively (Table 1). On a spatial scale, TN and TP concentrations across the sampling sites also showed large variation. Generally, the annual mean concentrations of TN, TP, and Chl*a* were significantly higher in the downstream river than those in the upstream river ($p < 0.001$ for TN and TP and $p = 0.029$ for Chl*a*).

Table 1
Key variables of the water samples in the five months.

	July 2020	August 2020	October 2020	January 2021	April 2021
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
WT (°C)	27.1 ± 1.49	32.8 ± 1.04	19.4 ± 0.81	8.67 ± 1.60	19.9 ± 1.36
DO (mg L^{-1})	8.11 ± 0.10	9.48 ± 2.20	10.1 ± 1.11	11.5 ± 2.03	10.4 ± 1.58
TN (mg L^{-1})	1.63 ± 0.48	1.07 ± 0.52	1.39 ± 0.62	2.10 ± 0.98	1.54 ± 0.42
TP (μg L^{-1})	92.8 ± 50.0	78.7 ± 4.64	46.7 ± 28.1	79.0 ± 69.6	67.4 ± 30.5
N:P ratio	19.3 ± 3.86	14.5 ± 3.17	33.6 ± 11.6	35.1 ± 15.2	25.0 ± 6.79
DOC (mg L^{-1})	1.53 ± 0.52	2.05 ± 0.51	1.39 ± 0.53	1.34 ± 0.57	1.37 ± 0.35
Chl*a* (μg L^{-1})	3.69 ± 4.36	22.5 ± 24.8	3.13 ± 3.31	2.36 ± 1.35	8.55 ± 5.25
CH_4 (μmol L^{-1})	0.47 ± 0.31	1.19 ± 1.02	0.42 ± 0.46	0.33 ± 0.27	0.51 ± 0.51

3.2. Gas saturation ratio

The CH_4 supersaturation ratio appeared highest in August 2020, reaching 479 ± 415, followed by July 2020 with 174 ± 115. High mean values were also observed in October 2020 and April 2021, with values of 136 ± 150 and 167 ± 166, respectively. The lowest values appeared in January 2021, with a mean value of 81.1 ± 66.7 (Fig. 2a). DO supersaturation was observed in July 2020, August 2020, October 2020, and April 2021, which was 1.02 ± 0.13, 1.32 ± 0.32, 1.10 ± 0.12, and 1.14 ± 0.18, respectively, while it was unsaturated in January 2021, which was 0.98 ± 0.16 (Fig. 2b). In August 2020, we observed that N_2 was unsaturated with a mean N_2:Ar saturation ratio of 0.97 ± 0.008 and was significantly lower than that in July 2020, October 2020, January 2021, and April 2021 ($p < 0.001$), with a mean N_2:Ar saturation ratio of 1.01 ± 0.002, 0.999 ± 0.007, 1.01 ± 0.005, and 1.00 ± 0.007, respectively (Fig. 2c).

3.3. Spatial and temporal variations in CH_4 concentrations

On a temporal scale, the CH_4 concentration was significantly higher in August 2020 than in the other four months ($p < 0.05$, Table S2 and Fig. 3a), with a mean value of 1.19 ± 1.02 μmol L^{-1}. However, there was no significant temporal difference in CH_4 concentration among the other four months ($p > 0.05$, Table S2 and Fig. 3a). The CH_4 concentration in October 2020 was slightly lower than that in July 2020, with an average of 0.42 ± 0.46 μmol L^{-1}. In January 2021, the mean dissolved CH_4 concentration was 0.33 ± 0.27 μmol L^{-1}, which was the lowest among the five sampling months (Fig. 3a). Similarly, the distribution of dissolved CH_4 concentration also showed a large difference on a spatial scale. Generally, the dissolved CH_4 concentration was low in the upstream river, but it was significantly higher in the downstream river, especially in She County ($p < 0.05$, Table S2 and Fig. 3b). As shown in Fig. 3b, the mean CH_4 concentration of the five sampling months was 0.26 ± 0.28 μmol L^{-1} in upstream Xiuning County, but it was significantly higher in downstream Tunxi District ($p < 0.05$, 0.66 ± 0.83 μmol L^{-1}). Similarly, a low CH_4 concentration was found in upstream Huizhou District (0.49 ± 0.41 μmol L^{-1}), but it was significantly higher in downstream She County ($p < 0.05$, 0.88 ± 0.73 μmol L^{-1}). A significant difference in dissolved CH_4 concentration was observed between Tributary 1 and Tributary 2 ($p < 0.001$, Table S2 and Fig. 3c), with mean dissolved CH_4 concentrations of 0.43 ± 0.61 μmol L^{-1} and 0.72 ± 0.65 μmol L^{-1} for Tributary 1 and Tributary 2, respectively. Furthermore, the CH_4 concentrations were much higher at sites near a large WWTP (1.25 ± 0.83 μmol L^{-1}) than at the other sites (0.45 ± 0.52 μmol L^{-1}) in the five sampling months ($p < 0.001$, Table S2 and Fig. 3d).

3.4. Pearson correlation analyses

Fig. 4 shows the results of the Pearson correlation analysis. DOC and FDOM were positively correlated with the CH_4 saturation ratio ($p <$

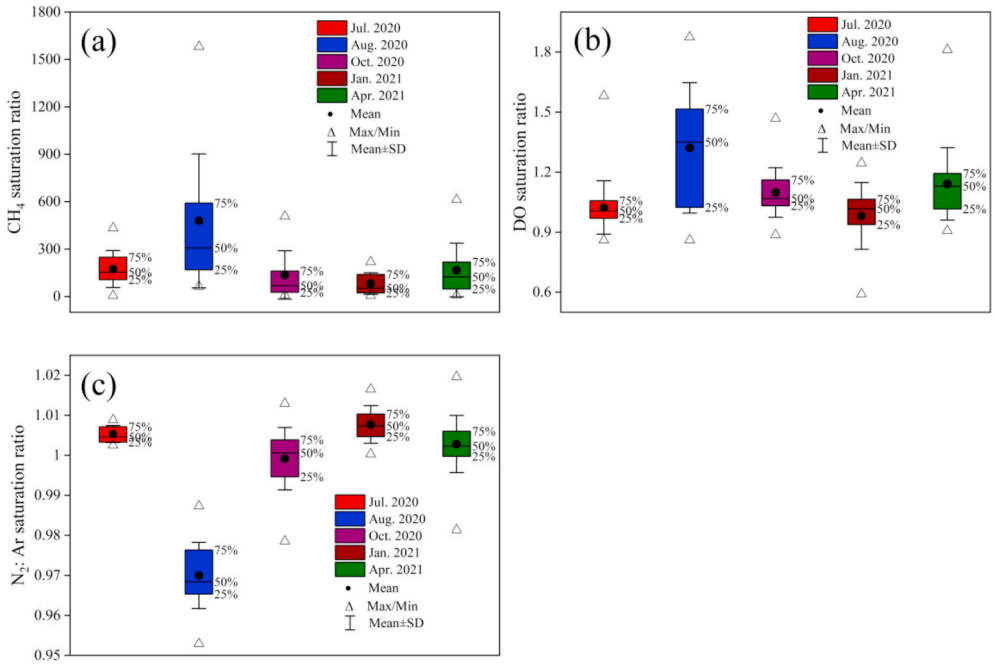

Fig. 2. A, b, and c show the box plots of the CH_4 saturation ratio, DO saturation ratio, and N_2:Ar saturation ratio in the five sampling months, respectively.

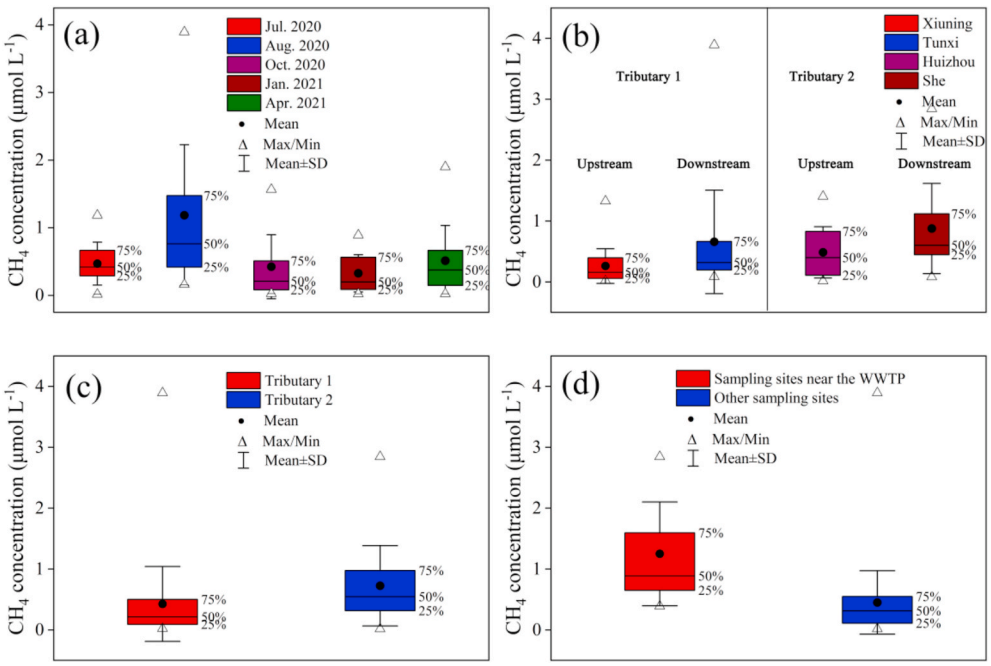

Fig. 3. (a) Temporal changes in dissolved CH_4 concentrations; (b) spatial differences in dissolved CH_4 concentrations between the upstream river and downstream river in the two tributaries (For Tributary 1, Xiuning County is the upstream river and Tunxi District is the downstream river; For Tributary 2, Huizhou District is the upstream river and She County is the downstream river); (c) spatial differences in dissolved CH_4 concentrations between Tributary 1 and Tributary 2; and (d) spatial differences in dissolved CH_4 concentrations between four nearest sites (site 17–20) at the downstream of the WWTP and other sites.

0.001). A positive correlation was found between WT and CH_4 saturation ratio ($p < 0.001$). A significant positive correlation appeared between the CH_4 saturation ratio and TP concentration ($p < 0.001$). No significant correlation was observed between CH_4 saturation ratio with TN concentration ($p > 0.05$). Interestingly, the CH_4 saturation ratio was positively correlated with the N:P ratios ($p < 0.001$). A significant positive correlation was also observed between the CH_4 saturation ratio and Chl*a* concentration ($p < 0.001$). We observed that the concentration of DO was positively correlated with the CH_4 saturation ratio ($p < 0.001$). The CH_4 saturation ratio also exhibited a significant correlation with the N_2 saturation ratio ($p < 0.001$); however, this correlation was negative, which was different from that of the DO saturation ratio.

3.5. *Algal communities in Xin'an River*

On a temporal scale, Bacillariophyta was the dominant phylum in July 2020, October 2020, January 2021, and April 2021, accounting for 47.29%, 47.77%, 85.32%, and 79.39%, respectively (Fig. 5a). In contrast, the proportion of Bacillariophyta was low in August 2020, accounting for only 10.03%. The contribution of Cyanophyta was high in July 2020, August 2020, and October 2020, which accounted for 38.92%, 40.44%, and 29.07%, respectively. A high Chlorophyta concentration was observed in August 2020, but it was very low in the other four months. The concentrations of the other three phyla, Pyrrophyta, Cryptophyta, and Euglenophyta, were very low in all sampling months

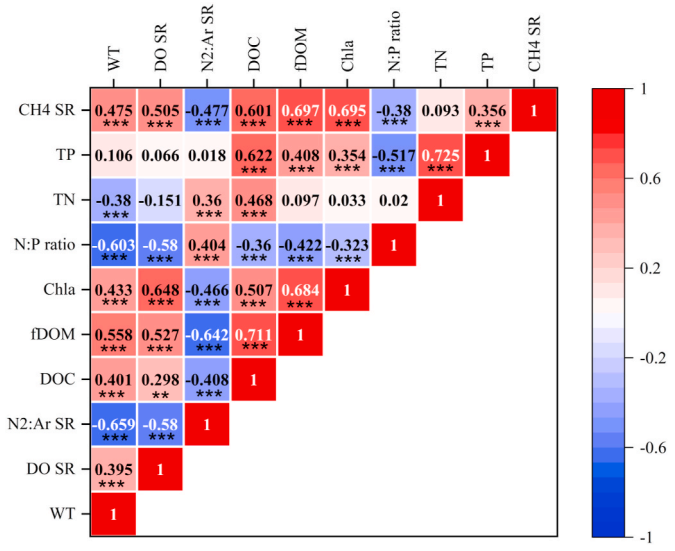

Fig. 4. Pearson correlation analysis of the environmental variables. SR indicates saturation ratio. ** and *** indicate $p < 0.01$ and $p < 0.001$, respectively.

(Fig. 5a). A high concentration of *Anabaena* was found in August 2020, but the *Anabaena* concentration was low in July 2020 and January 2021. No *Anabaena* was observed in October 2020 or April 2021 (Fig. 5b).

On a spatial scale, Bacillariophyta was the dominant phylum in the Xin'an River in July 2020, but the contribution of Cyanophyta to the total algal community was high in some areas (e.g., Tunxi District, Fig. S1). In contrast, the Xin'an River was dominated by Cyanophyta and Chlorophyta, and the proportion of Cyanophyta to the total community in the downstream river was much higher than that in the upstream river in August 2020. High proportions of Cyanophyta to the total community were also found in She County, but Chlorophyta was replaced by Bacillariophyta. The Cyanophyta concentration, as well as the proportion of Cyanophyta to the total community, was very low at all sampling sites in January 2021 and April 2021, and Bacillariophyta had a great advantage in community competition. High *Anabaena* concentrations were observed in the downstream river (Tunxi District and She County). However, very low *Anabaena* concentrations appeared in the other three months, and most sampling sites had no *Anabaena* (Fig. S2).

3.6. Incubation experiment

Fig. 6a shows the CH_4 concentrations in the five treatments during incubation experiments. The dissolved CH_4 concentration in the incubation core was almost 0 before incubation. No evident CH_4 accumulation was observed in T1, while obvious CH_4 production was found in the other five treatments. After a 7-day incubation, the final CH_4 concentrations were 0.006 ± 0.006 μmol L^{-1}, 0.08 ± 0.01 μmol L^{-1}, 0.12 ± 0.01 μmol L^{-1}, 0.26 ± 0.02 μmol L^{-1}, and 0.08 ± 0.03 μmol L^{-1} in T1, T2, T3, T4, and T5, respectively. Fig. 6b shows the DO concentrations during incubation experiments. The DO concentration decreased from 8.93 ± 0.09 mg L^{-1} to 7.50 ± 0.44 mg L^{-1} in T1. In contrast, DO concentrations increased sharply in the other four treatments, with final concentrations of 15.3 ± 1.00 mg L^{-1}, 16.4 ± 0.82 mg L^{-1}, 16.1 ± 0.80 mg L^{-1}, and 15.4 ± 0.56 mg L^{-1} for T2, T3, T4, and T5, respectively. The concentrations of TN and TP were highest in T4. Hight Chl*a* concentration was observed in T3.

4. Discussion

4.1. Potential factors affecting CH_4 concentrations in the Xin'an River

4.1.1. Exogenous input

Organic sediment CH_4 production has been considered a crucial source of dissolved CH_4 in water columns according to previous studies (Conrad et al., 2009; Mach et al., 2015; Emilson et al., 2018). In this study, a stony riverbed covered with inorganic sediment (e.g., gravels, coarse pebbles, and large stones) was found along the entire Xin'an River (Fig. 1d). A previous study indicated that a microanoxic environment may form in deep sediment or within small inorganic particles and that this anoxic environment may be beneficial for anoxic CH_4 production (Hlaváčová et al., 2005). However, although we observed an increase in CH_4 concentration when adding sediments collected from the riverbed during the incubation experiment, this increase was very low (T5, Fig. 6a), indicating that the dissolved CH_4 was possibly from other pathways, such as oxic CH_4 production or directly from human discharged wastewater. The CH_4 concentrations were remarkably higher in the downstream river than in the upstream river ($p < 0.05$, Fig. 3b, Table S2), suggesting that human activities along the river had a strong influence on the CH_4 level. Alshboul et al. (2016) reported that the CH_4 in wastewater from WWTPs may potentially increase the CH_4 level in river water, which is similar to our results. In our study, we observed that the CH_4 concentrations at the four sampling sites near a large WWTP were significantly higher than those at other sampling sites (Fig. 3d), suggesting that high CH_4 concentrations there may have been related to wastewater from the WWTP.

Previous studies have shown that riparian zones of the river may be hotspots for CH_4 emissions (Sun et al., 2013), and changes in hydrological conditions may affect CH_4 emissions in the water level fluctuation zone (Shi et al., 2021). Here, we collected organic soils from the riparian zone and conducted an incubation experiment under flooding conditions. The results showed that the presence of organic soils could significantly increase the CH_4 concentration in the water (T4, Fig. 6a). This may have been because the overlying water separated the soil from the atmosphere, and the DOC in the porewater may have been converted to CH_4 by methanogens under anoxic conditions, which could result in an increase in dissolved CH_4 concentration in the water column. This

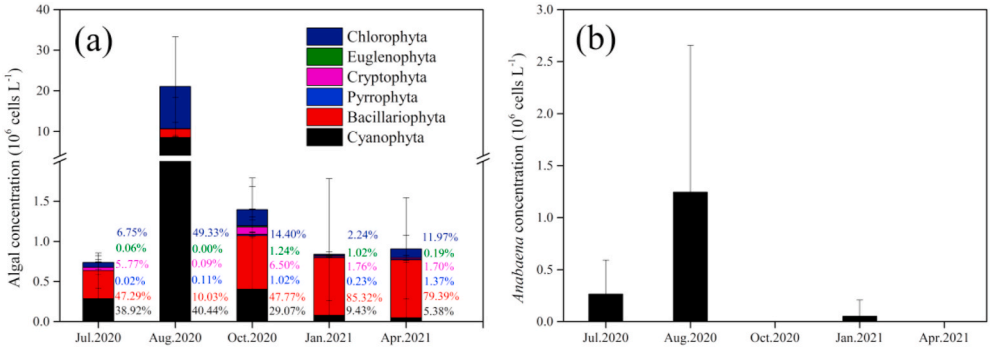

Fig. 5. (a) Algal communities over five months in the Xin'an River and (b) the concentration of *Anabaena*.

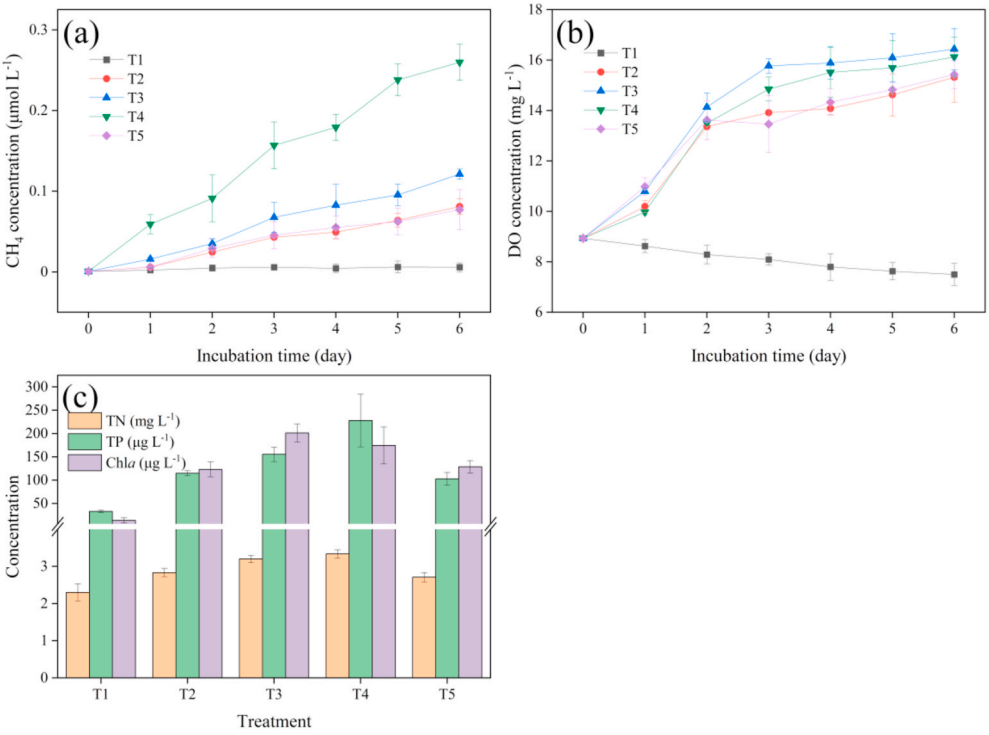

Fig. 6. Concentrations of dissolved CH_4 (a) and O_2 (b) in the incubation experiment. (c) Concentrations of TN, TP, and Chl*a* in the water on the last day. Error bars represent standard deviations. T1: river water with no algae; T2: river water; T3: river water + algae; T4: river water + organic solids collected from the riparian zone; T5: river water + sediment.

experiment showed that when surface water flows through the riparian zone, it may produce CH_4 that is discharged into the river, thus affecting the CH_4 concentration in the river water. The water level fluctuation and the increase in surface runoff caused by rainfall may expand this contribution to the CH_4 level in the river. In addition, although there is very little organic sediment in the mainstream of the Xin'an River, there may be a large amount of organic sediment in some relatively small and quiet tributaries or bays. According to our incubation experiment, the CH_4 production capacity of organic soils was stronger than that of high-concentration algae (Fig. 6a). In this case, small and quiet bays or tributaries may be hotspots for CH_4 production, and the produced CH_4 may diffuse laterally into the mainstream. Additionally, the CH_4 in the groundwater was reported to be very high (Taylor et al., 2021), which could be a potential source of river CH_4.

4.1.2. *Algae and nutrient concentration*

We analysed the correlation between the CH_4 saturation ratio and environmental factors based on Pearson correlation analysis. The results showed that DOC and fDOM were positively correlated with CH_4 saturation ratio (Fig. 4). This is because organic carbon is the substrate for anoxic methanogenesis. This seems contrary to our conclusion that CH_4 can be produced in oxic water. In fact, having algal particles and microcolonies may create anoxia, which could provide a suitable environment for anoxic methanogenesis. It has been shown that cyanobacteria often host methanogenic archaea (Batista et al., 2019; Cook et al., 2019). Therefore, we observed high CH_4 concentrations and saturation ratios, along with high cyanobacterial density in August 2020 when algal blooms occurred due to high temperature (Figs. 2 and 5). Interestingly, we found a significant positive correlation between the CH_4 saturation ratio and DO saturation ratio ($p < 0.001$, Fig. 4), which was different from the results in other studies (Xiao et al., 2021; Zhang et al., 2021b). We attributed this paradox to photosynthesis induced by algae since we observed a significant positive correlation between Chl*a* concentration and DO saturation ratio ($p < 0.001$, Fig. 4). Although algae-induced photosynthesis is not beneficial for anoxic methanogenesis because it can produce O_2 that would poison methanogenic archaea, its ability to produce DOC can support anoxic methanogenesis. Consequently, methanogenic archaea may adhere to algae and utilize the DOC derived from discharged human wastewater and/or photosynthesis to produce CH_4. Furthermore, an increasing number of studies have found that algae could convert bicarbonate to CH_4 under oxic conditions during photosynthesis (Günthel et al., 2020). A recent study also demonstrated that nitrogen-fixing cyanobacteria could produce CH_4 during nitrogen fixation (Zheng et al., 2018). In our study, we observed that the concentration of *Anabaena* (nitrogen-fixing cyanobacteria) was significantly higher in August 2020 than in the other four months ($p < 0.01$, Fig. 5b), and N_2 was unsaturated in this period (Fig. 2c), suggesting that nitrogen fixation could be another pathway to produce CH_4. A possible mechanism pointed out by Tang et al. (2014) is that nitrogen fixation can produce hydrogen for CH_4 production. Previous studies have demonstrated that oxic CH_4 production can contribute greatly to the atmospheric CH_4 budget in deep lakes and reservoirs (Donis et al., 2017; Günthel et al., 2019). In our study, although we did not quantify the specific contribution of oxic CH_4 production to CH_4 concentration, we observed that the Chl*a* concentration was positively correlated with the CH_4 saturation ratio (Fig. 4), suggesting that algae may also have an impact on CH_4 levels in rivers. Furthermore, the incubation experiment also indicated that algae can produce CH_4 under oxic conditions (T3, Fig. 5a). No evident CH_4 accumulation was observed when adding sediment collected from the riverbed (T5, Fig. 5a), indicating that the CH_4 in the water column in the Xin'an River was not produced mainly from sediment. However, the relative contribution of oxic CH_4 production induced by algae to the CH_4 concentration in the water column was much lower compared with the treatment that was added with organic solids (from the riparian zone) in the incubation experiment (T4, Fig. 5a), suggesting that the riparian zone may be a hotspot for CH_4 production under flooding, which is similar to the results in a recent study (Shi et al., 2021). These results indicated that oxic CH_4 production caused by algae may potentially increase the CH_4 concentration in gravel-bed rivers with very little

organic sediment, but its specific contribution is unknown and needs further study.

Numerous studies have revealed that CH_4 production and emissions are associated with the eutrophication of waters. A significant correlation between CH_4 concentration or emission rate and nutrient concentrations was found in these studies (Zhang et al., 2021a; Xiao et al., 2021). Similar results were also observed in our study (Fig. 4). However, we found that the correlation between the CH_4 saturation ratio and TP concentration was more significant than that between the CH_4 saturation ratio and TN. We attributed this to the high N: P ratios. As shown in Table 1, the N:P ratios were very high in July 2020, October 2020, January 2021, and April 2021 and were even higher than the Redfield value (N:P ratio = 16). Besides, significant correlations between Chl*a* concentration with TP concentration and N:P ratio were observed but no significant correlation was found between Chl*a* concentration and TN concentration, which suggested that the growth of algae was generally limited by phosphorus rather than nitrogen during these four months. As a result, the nutrient could indirectly affect methanogenesis by controlling primary productivity, such as inducing the growth of algae. Furthermore, the low N:P ratio could shift the algal community from nonnitrogen-fixing algae to nitrogen-fixing cyanobacteria (Smith, 1983), which may also have an impact on the CH_4 concentration.

4.1.3. Rainfall events

The mean dissolved CH_4 concentration during the rainy month (July 2020) was significantly lower than that in August 2020 ($p < 0.001$, Fig. 3a) but relatively higher than those in the other three sampling months, which seems to contradict our conjecture that rainfall may lead to water level fluctuations, resulting in the lateral diffusion of CH_4 from the riparian zone to the river. Here, we discuss some potential reasons for this phenomenon. First, the very high precipitation during July 2020 (Fig. 7) may have diluted the CH_4 concentration in the river. Second, the disturbance caused by heavy rainfall may have aggravated CH_4 emissions (diffusion and ebullition) from the water to the atmosphere, resulting in a decline in the dissolved CH_4 concentration in the river. Third, the nutrient concentrations during the rainy period were generally higher than those during the post-rainy period (Table 1), but we observed that the Chl*a* concentrations were much lower than those in August 2020 ($p < 0.001$, Table 1). Heavy rainfall shifts the river to the flood period, resulting in a higher water velocity, while rapid flushing due to high water velocity is not conducive to the growth of cyanobacteria (Reynolds et al., 2006; Zou et al., 2020). As evidenced by the incubation experiment (Fig. 6), the presence of algae can significantly promote methanogenesis, which may be an important explanation for the lower CH_4 concentration in July 2020 compared with that in August 2020. Fourth, the increase of water discharge caused by heavy rainfall events may have reduced the river CH_4 level because the high water discharge can increase the CH_4 emission and reduce the CH_4 concentration according to a previous study (McGinnis et al., 2016). Fifth, we observed that the concentrations of DOC and FDOM during the rainy period were lower than those in August 2020 (Table 1), which may have been an important reason for the low concentration of CH_4. Last but not least, the low temperature caused by heavy rainfall (Fig. 7) could be another reason why the CH_4 concentrations were lower in July 2020 than in August 2020 since temperature is a vital factor that could affect CH_4 production (Yvon-Durocher et al., 2014).

4.1.4. WT

In this study, we found that the concentration of CH_4 in August 2020 with high WT was significantly higher than that in January 2021 with low WT ($p < 0.001$, Table 1). The dissolved CH_4 concentration in August 2020 was 3.61 times higher than that in January 2021. A significant relationship was also observed between the WT and CH_4 saturation ratio (Fig. 4). These findings indicated that WT was also an important factor affecting CH_4 concentration. An increase in temperature enhances the CH_4 production capacity by promoting the activity of methanogens and related enzymes (Yvon-Durocher et al., 2014). Furthermore, algal blooms are more likely to occur with increasing temperature (Paerl et al., 2012), which also enhances net CH_4 production and consequently increases the dissolved CH_4 concentration.

4.2. Comparison with other studies

We measured the CH_4 concentrations based on MIMS. The mean CH_4 concentration over five months was 0.58 ± 0.65 μmol L^{-1}, which was lower than the global mean value (1.35 ± 5.16 μmol L^{-1}) (Stanley et al., 2016). Although the concentration of CH_4 was low compared with the global average, the high CH_4 saturation ratios indicate that gravel-bed urban rivers with very little organic sediment still have strong CH_4 emission potential. The mean CH_4 concentration of this study was much lower than that of the other two urban rivers recently investigated by Zhang et al. (2021b) and Wang et al. (2021) in the Chaohu Lake Basin, China, and Beijing, China, respectively (mean CH_4 concentrations were 5.5 and 2.5 μmol L^{-1}, respectively). A possible reason for this is that the riverbed is stony, and there are very few organic sediments in the mainstream Xin'an River. Our incubation experiment showed that the addition of organic solids potentially increased the CH_4 concentration in the water column, which is consistent with several studies that reported that organic sediment was a hotspot of CH_4 production (Conrad et al., 2009; Mach et al., 2015; Emilson et al., 2018), and CH_4 diffusion from organic sediment was an important source of water column CH_4 (Martens et al., 1980). In addition, the eutrophication degree of the Xin'an River was lower than that of the urban rivers mentioned above. According to our results and previous studies, eutrophication can significantly affect CH_4 concentrations in the water column, which may also be a vital reason for the low CH_4 concentration in our study areas.

4.3. Implications for management

Reducing eutrophication is an effective method that can control CH_4

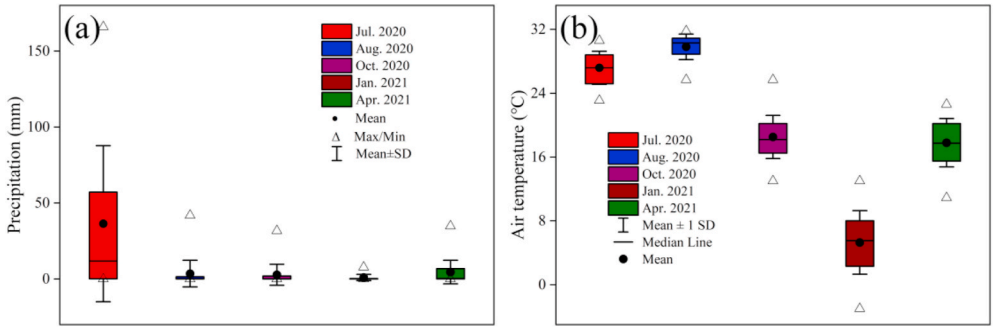

Fig. 7. Precipitation (a) and air temperature (b) in the five sampling months. The bottom line, middle line, and the top line of the box plot indicate the values at 25%, 50%, and 75%, respectively.

production and emission, as reported by numerous studies (Davidson et al., 2018; Beaulieu et al., 2019). However, not only nutrients (mainly nitrogen and phosphorus) but also the N:P ratios should be taken into consideration in the management of CH_4 production because we noticed that the CH_4 saturation ratio was negatively correlated with the N:P ratios (Fig. 4). This negative correlation may have been due to biological nitrogen fixation since the low N:P ratio was beneficial for nitrogen-fixing cyanobacterial growth, which could enhance CH_4 production and increase the CH_4 concentration. As a result, we recommend that nitrogen control should be applied cautiously in nitrogen-limited waters in the management of eutrophication, as well as in CH_4 mitigation.

The positive relationship between the CH_4 saturation ratio and WT (Fig. 4) indicates that the potential for CH_4 production and emission can be enhanced with increasing temperature. The temperature of urban regions is normally 2–4 °C higher than that in nonurban areas due to the heat island effect (Liu et al., 2015). In addition, heatwaves under climate change may also enhance methanogenesis and algal blooms, leading to intense CH_4 production and emission. Overall, the global warming caused by greenhouse gas (CH_4, N_2O, CO_2, etc.) emissions can provide a positive feedback on CH_4 production. Thus, urban wastewater should be treated efficiently to remove nutrients and organic matter. Furthermore, we observed that the CH_4 concentrations were much higher in the sampling sites near the large WWTP (Fig. 3d), indicating that municipal WWTPs should improve sewage treatment efficiency to reduce the CH_4 level in wastewater.

Organic sediment is one of the important sources of nutrients in the water column (Percuoco et al., 2015) and may become an important driving factor for algal growth (Wu et al., 2017). Sediment dredging is considered to be an effective measure to reduce nutrient release from organic sediment (Moore et al., 2017). In the Xin'an River with very little organic sediment, we observed that the concentrations of dissolved CH_4 and nutrients in the water were generally lower than those in some urban rivers with a large amount of organic sediment. Our incubation experiments show that the presence of organic soils can potentially enhance CH_4 production, along with the increase in CH_4 concentration in the water column (Fig. 6a). Moreover, the presence of organic soils can significantly increase the concentration of nutrients in the water and consequently induce the growth of algae (Fig. 6c). Therefore, dredging organic sediment in 'normal' urban rivers (urban rivers with a large amount of organic sediments) that are seriously affected by human activities may be feasible in controlling nutrient release from organic sediment, alleviating algal blooms, and reducing CH_4 concentrations and emissions.

4.4. Limitations of this study

In this study, we only measured the dissolved CH_4 concentrations and calculated the CH_4 saturation ratios. Neither diffusive nor ebullitive fluxes were directly measured. Consequently, we could not accurately quantify the CH_4 emission from oxic urban rivers such as the Xin'an River and compare it with the global mean value. Additionally, CH_4 ebullition was reported to be more important than diffusion in shallow rivers due to the presence of a large amount of organic sediment (Wang et al., 2021). However, the contribution of CH_4 ebullition to total CH_4 emissions in gravel-bed rivers with very little organic sediment, such as the Xin'an River, is still unclear and is an important issue for future research. CH_4 oxidation is a vital pathway that can reduce CH_4 in water bodies (Hao et al., 2020; Xia et al., 2021). However, we did not quantify the CH_4 oxidation capacity in this study. Future studies can focus on CH_4 oxidation in gravel-bed urban rivers such as the Xin'an River and can calculate its contribution to CH_4 reduction. Lastly, although our incubation experiments and field observations suggest that algae can produce CH_4 under oxic conditions and may further affect the CH_4 concentration in the water column, their specific contribution to the total CH_4 concentration in gravel-bed urban rivers with very little organic sediment is still not clear and is worth studying in the future.

5. Conclusions

The Xin'an River is a gravel-bed urban river with very little organic sediment and high DO concentrations. Using a membrane inlet mass spectrometer, we measured the dissolved CH_4 concentrations and calculated the CH_4 saturation ratios for five months, including four seasons and a rainy month. The results showed that CH_4 was supersaturated across all sampling sites in the five months, which suggested that gravel-bed urban rivers with very little organic sediment also have large CH_4 emission potential. The significant correlation between the CH_4 saturation ratio and Chl*a* concentration and evident CH_4 accumulation in the oxic water column during incubation when algae were added indicated that algae may be a potential factor that can affect the CH_4 concentration in oxic waters; however, their specific contribution to the total CH_4 concentration in the water column remains unknown. The water CH_4 concentrations were significantly higher in the downstream river than in the upstream river, indicating that human activities along the river had a large impact on CH_4 concentrations. Other factors, such as WT, heavy rainfall events, and organic matter, can also potentially affect the CH_4 concentration in such rivers. Furthermore, the algal blooms caused by human discharged nutrients can potentially increase the CH_4 levels in river water. Based on our results, necessary measures should be considered to reduce the CH_4 concentrations in urban rivers, such as reducing the concentrations of nutrients, organic matter, and CH_4 in wastewater from human activities.

Credit author statement

Feng Zhao: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Software; Visualization; Roles/Writing - original draft. Yongqiang Zhou, Wei Zou and Mengyuan Zhu: Writing - review & editing. Guangwei Zhu: Funding acquisition; Hai Xu: Funding acquisition; Investigation; Project administration; Resources; Supervision; Validation; Writing - review & editing. Xu Zhan, Lijuan Kang and Xingchen Zhao: Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was supported by the Strategic Priority Research Program of Chinese Academy of Sciences (XDA23040201) and the National Natural Science Foundation of China (41830757, 42077161).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.118769.

References

Alshboul, Z., Encinas-Fernandez, J., Hofmann, H., Lorke, A., 2016. Export of dissolved methane and carbon dioxide with effluents from municipal wastewater treatment plants. Environ. Sci. Technol. 50 (11), 5555–5563.

Angel, R., Matthies, D., Conrad, R., 2011. Activation of methanogenesis in arid biological soil crusts despite the presence of oxygen. PLoS One 6 (5), e20453.

APHA, 2012. Standard Methods for Examination of Water and Wastewater 22ed. American Public Health Association, Washington.

Bastviken, D., Tranvik, L.J., Downing, J.A., Crill, P.M., Enrich-Prast, A., 2011. Freshwater methane emissions offset the continental carbon sink. Science 331 (6013), 50.

Batista, A.M.M., Woodhouse, J.N., Grossart, H.P., Giani, A., 2019. Methanogenic archaea associated to Microcystis sp. in field samples and in culture. Hydrobiologia 831, 163–172.
Beaulieu, J.J., Jake, J., DelSontro, T., Downing, J.A., 2019. Eutrophication will increase methane emissions from lakes and impoundments during the 21st century. Nat. Commun. 10, 1375.
Berg, A., Lindblad, P., Svensson, B.H., 2014. Cyanobacteria as a source of hydrogen for methane formation. World J. Microbiol. Biotechnol. 30 (2), 539–545.
Bižić, M., Klintzsch, T., Ionescu, D., Hindiyeh, M.Y., Günthel, M., Muro-Pastor, A.M., Eckert, W., Urich, T., Keppler, F., Grossart, H.-P., 2020. Aquatic and terrestrial cyanobacteria produce methane. Sci. Adv. 6 (3), eaax5343.
Borges, A.V., Darchambeau, F., Lambert, T., Bouillon, S., Morana, C., Brouyere, S., Hakoun, V., Jurado, A., Tseng, H.C., Descy, J.P., Roland, F.A., 2018. Effects of agricultural land use on fluvial carbon dioxide, methane and nitrous oxide concentrations in a large European river, the Meuse (Belgium). Sci. Total Environ. 610–611, 342–355.
Clough, T.J., Buckthought, L.E., Kelliher, F.M., Sherlock, R.R., 2007. Diurnal fluctuations of dissolved nitrous oxide (N_2O) concentrations and estimates of N_2O emissions from a spring-fed river: implications for IPCC methodology. Global Change Biol. 13 (5), 1016–1027.
Conrad, R., Seiler, W., 1980. Contribution of hydrogen production by biological nitrogen fixation to the global hydrogen budget. J. Geophys. Res. Oceans 85 (C10), 5493–5498.
Conrad, R., Claus, P., Gasper, P., 2009. Characterization of stable isotope fractionation during methane production in the sediment of a eutrophic lake, Lake Dagow, Germany. Limnol. Oceanogr. 54 (2), 457–471.
Cook, K.V., Li, C., Cai, H., Krumholz, L.R., Hambright, D., Paerl, H.W., Steffen, M.M., Wilson, A.E., Burford, M.A., Grossart, H.P., Hamilton, D.P., Jiang, H., Sukenik, A., Latour, D., Meyer, E.I., Padisák, J., Qin, B., Zamor, R.M., Zhu, G., 2019. The global Microcystis interactome. Limnol. Oceanogr. 65 (S1), S194–S207.
Damm, E., Helmke, E., Thoms, S., Schauer, U., Kiene, R.P., 2010. Methane production in aerobic oligotrophic surface water in the central Arctic Ocean. Biogeosciences 7 (3), 46–48.
Davidson, T.A., Audet, J., Jeppesen, E., Landkildehus, F., Lauridsen, T.L., Søndergaard, M., Syvaranta, J., 2018. Synergy between nutrients and warming enhances methane ebullition from experimental lakes. Nat. Clim. Change 8 (2), 156.
de Angelis, M.A., Lee, C., 1994. Methane production during zooplankton grazing on marine phytoplankton. Limnol. Oceanogr. 39 (6), 1298–1308.
Deemer, B.R., Harrison, J.A., Li, S., Beaulieu, J.J., DelSontro, T., Barros, N., Bezerra-Neto, J.F., Powers, S.M., dos Santos, M.A., Vonk, J.A., 2016. Greenhouse gas emissions from reservoir water surfaces: a new global synthesis. Bioscience 66 (11), 949–964.
Donis, D., Flury, S., Stöckli, A., Spangenberg, J.E., Vachon, D., McGinnis, D.F., 2017. Full-scale evaluation of methane production under oxic conditions in a mesotrophic lake. Nat. Commun. 8, 1661.
Emilson, E.J.S., Carson, M.A., Yakimovich, K.M., Osterholz, H., Dittmar, T., Gunn, J.M., Mykytczuk, N.C.S., Basiliko, N., Tanentzap, A.J., 2018. Climate-driven shifts in sediment chemistry enhance methane production in northern lakes. Nat. Commun. 9, 1801.
Günthel, M., Donis, D., Kirillin, G., Lonescu, D., Bizic, M., McGinnis, D.F., Grossart, H., Tang, K.W., 2019. Contribution of oxic methane production to surface methane emission in lakes and its global importance. Nat. Commun. 10, 5479.
Günthel, M., Klawonn, I., Woodhouse, J., Bižić, M., Ionescu, D., Ganzert, L., Kümmel, S., Nijenhuis, I., Zoccarato, L., Grossart, H., Tang, K.M., 2020. Photosynthesis-driven methane production in oxic lake water as an important contributor to methane emission. Limnol. Oceanogr. 65 (12), 2853–2865.
Hao, Q., Liu, F., Zhang, Y., Wang, O., Xiao, L., 2020. *Methylobacter* accounts for strong aerobic methane oxidation in the Yellow River Delta with characteristics of a methane sink during the dry season. Sci. Total Environ. 704, 135383.
Hlaváčová, E., Rulík, M., Čáp, L., 2005. Anaerobic microbial metabolism in hyporheic sediments of a gravel bar in a small lowland stream (Sitka stream, Czech Republic). River Res. Appl. 21 (9), 1003–1011.
Hofmann, H., Federwisch, L., Peeters, F., 2010. Wave-induced release of methane: littoral zones as a source of methane in lakes. Limnol. Oceanogr. 55 (5), 1990–2000.
Hu, H.J., Wei, Y.X., 2007. The Freshwater Algae of China: Systematics, Taxonomy and Ecology. Science Press, Beijing.
IPCC, 2013. Climate Change 2013: the Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. United Nations, Geneva.
Kana, T.M., Darkangelo, C., Hunt, M.D., Oldham, J.B., Bennett, G.E., Cornwell, J.C., 1994. Membrane inlet mass spectrometer for rapid high-precision determination of N_2, O_2, and Ar in environmental water samples. Anal. Chem. 66 (23), 4166–4170.
Karl, D.M., Beversdorf, L., BjörRkman, K.M., Church, M.J., Martinez, A., Delong, E.F., 2008. Aerobic production of methane in the sea. Nat. Geosci. 1, 473–478.
Li, X., Yao, H., Yu, Y., Cao, Y., Tang, C., 2020. Greenhouse gases in an urban river: trend, isotopic evidence for underlying processes, and the impact of in-river structures. J. Hydrol. 591, 125290.
Liu, K., Chen, S., Zhang, L., Yang, H., Zhang, R., Li, X., 2015. Analysis of the urban heat island effect in Shijiazhuang, China using satellite and airborne data. Rem. Sens. 7, 4804–4833.
Loeks-Johnson, B.M., Cotner, J.B., 2020. Upper Midwest lakes are supersaturated with N_2. Proc. Natl. Acad. Sci. U. S. A. 117 (29), 17063–17067.
Mach, V., Blaser, M.B., Claus, P., Chaudhary, P.P., Rulík, M., 2015. Methane production potentials, pathways, and communities of methanogens in vertical sediment profiles of river Sitka. Front. Microbiol. 6 (506).
Martens, C.S., Klump, J.V., 1980. Biogeochemical cycling in an organic-rich coastal marine basin—I. Methane sediment-water exchange processes. Geochem. Cosmochim. Acta 44 (3), 471–490.
McGinnis, D.F., Bilsley, N., Schmidt, M., Fietzek, P., Bodmer, P., Premke, K., Lorke, A., Flury, S., 2016. Deconstructing methane emissions from a small Northern European river: hydrodynamics and temperature as key drivers. Environ. Sci. Technol. 50 (21), 11680–11687.
Montzka, S.A., Dlugokencky, E.J., Butler, J.H., 2011. Non-CO_2 greenhouse gases and climate change. Nature 476, 43–50.
Moore, M., Locke, M.A., Jenkins, M., Steinriede, R.W., McChesney, D.S., 2017. Dredging effects on selected nutrient concentrations and ecoenzymatic activity in two drainage ditch sediments in the lower Mississippi River Valley. Int. Soil Water Conserv. Res. 5 (3), 190–195.
Ortega, S.H., González-Qiujano, C.R., Casper, P., Singer, G.A., Gessner, M.O., 2019. Methane emissions from contrasting urban freshwaters: rates, drivers, and a whole-city footprint. Global Change Biol. 25 (12), 4234–4243.
Paerl, H.W., Paul, V.J., 2012. Climate change: links to global expansion of harmful cyanobacteria. Water Res. 46 (5), 1349–1363.
Percuoco, V.P., Kalnejais, L.H., Officer, L.V., 2015. Nutrient release from the sediments of the great bay estuary, N.H. USA. Estuarine. Coast. Shelf Sci. 161, 76–87.
Reynolds, C.S., 2006. Ecology of Phytoplankton. Cambridge University Press, Cambridge.
Schmale, O., Karle, M., Glockzin, M., Schneider, B., 2019. Potential of nitrogen/argon analysis in surface waters in the examination of areal nitrogen deficits caused by nitrogen fixation. Environ. Sci. Technol. 53 (12), 6869–6876.
Shi, W., Du, M., Ye, C., Zhang, Q., 2021. Divergent effects of hydrological alteration and nutrient addition on greenhouse gas emissions in the water level fluctuation zone of the Three Gorges Reservoir, China. Water Res. 201, 117308.
Smith, V.H., 1983. Low nitrogen to phosphorus ratios favor dominance by blue green algae in lake phytoplankton. Science 221, 669–671.
Stanley, E.H., Casson, N.J., Christel, S.T., Crawford, J.T., Loken, L.C., Oliver, S.K., 2016. The ecology of methane in streams and rivers: patterns, controls, and global significance. Ecol. Monogr. 86 (2), 146–171.
Sun, Q.-Q., Shi, K., Damerell, P., Whitham, C., Yu, G.-H., Zou, C.-L., 2013. Carbon dioxide and methane fluxes: seasonal dynamics from inland riparian ecosystems, northeast China. Sci. Total Environ. 465, 48–55.
Tang, K.W., McGinnis, D.F., Frindte, K., Brüchert, V., Grossart, H.P., 2014. Paradox reconsidered: methane oversaturation in well-oxygenated lake waters. Limnol. Oceanogr. 59, 275–284.
Tang, K.W., McGinnis, D.F., Ionescu, D., Grossart, H., 2016. Methane production in oxic lake waters potentially increases aquatic methane flux to air. Environ. Sci. Technol. Lett. 3 (6), 227–233.
Taylor, K.A., Risk, D., Williams, J.P., Wach, G.D., Sherwood, O.A., 2021. Occurrence and origin of groundwater methane in the stellarton basin, Nova Scotia, Canada. Sci. Total Environ. 754, 141888.
Wang, J., Zhang, J., Xie, H., Qi, P., Ren, Y., Hu, Z., 2011. Methane emissions from a full-scale A/A/O wastewater treatment plant. Bioresour. Technol. 102 (9), 5479–5485.
Wang, R., Zhang, H., Zhang, W., Zheng, X., Butterbach-Bahl, K., Li, S., Han, S., 2020a. An urban polluted river as a significant hotspot for water–atmosphere exchange of CH_4 and N_2O. Environ. Pollut. 264, 114770.
Wang, Y., Levis, J.W., Barlaz, M.A., 2020b. An assessment of the dynamic global warming impact associated with long-term emissions from landfills. Environ. Sci. Technol. 54 (3), 1304–1313.
Wang, G., Xia, X., Liu, S., Zhang, L., Zhang, S., Wang, J., Xi, N., Zhang, Q., 2021. Intense methane ebullition from urban inland waters and its significant contribution to greenhouse gas emissions. Water Res. 189, 116654.
White, A.E., Karl, D.M., Björkman, K.M., Beversdorf, L.J., Letelier, R.M., 2010. Phosphonate metabolism by *Trichodesmium* IMS101 and the production of greenhouse gases. Limnol. Oceanogr. 55 (4), 1755–1767.
Wu, Z., Liu, Y., Liang, Z., Wu, S., Guo, H., 2017. Internal cycling, not external loading, decides the nutrient limitation in eutrophic lake: a dynamic model with temporal Bayesian hierarchical inference. Water Res. 116, 231–240.
Xia, F., Jiang, Q., Zhu Zou, B., Liu, H., Quan, Z., 2021. Ammonium promoting methane oxidation by stimulating the Type Ia methane-oxidizing bacteria in tidal flat sediments of the Yangtze River estuary. Sci. Total Environ. 793, 148470.
Xiao, Q., Zhang, M., Hu, Z., Gao, Y., Hu, C., Liu, C., Liu, S., Zhang, Z., Zhao, J., Xiao, W., Lee, X., 2017. Spatial variations of methane emission in a large shallow eutrophic lake in sub-tropical climate. J. Geophys. Res. Biogeosci. 122 (7), 1597–1614.
Xiao, Q., Hu, Z., Hu, C., Islam, A.R.M.T., Bian, H., Chen, S., Liu, C., Lee, X., 2021. A highly agricultural river network in Jurong Reservoir watershed as significant CO_2 and CH_4 sources. Sci. Total Environ. 769, 144558.
Yin, H., Islam, M.S., Ju, M., 2021. Urban river pollution in the densely populated city of Dhaka, Bangladesh: big picture and rehabilitation experience from other developing countries. J. Clean. Prod. 321, 129040.
Yvon-Durocher, G., Allen, A.P., Bastviken, D., Conrad, R., Gudasz, C., St-Pierre, A., Thanh-Duc, N., del Giorgio, P.A., 2014. Methane fluxes show consistent temperature dependence across microbial to ecosystem scales. Nature 507 (7493), 488–491.
Zamanpour, M.K., Kaliappan, R.S., Rockne, K.J., 2020. Gas ebullition from petroleum hydrocarbons in aquatic sediments: a review. J. Environ. Manag. 271, 110997.
Zhang, L., Liao, Q., Gao, R., Luo, R., Liu, C., Zhong, J., Wang, Z., 2021a. Spatial variations in diffusive methane fluxes and the role of eutrophication in a subtropical shallow lake. Sci. Total Environ. 759, 143495.
Zhang, W., Li, H., Xiao, Q., Li, X., 2021b. Urban rivers are hotspots of riverine greenhouse gas (N_2O, CH_4, CO_2) emissions in the mixed-landscape Chaohu Lake Basin. Water Res. 189, 116624.

Zhao, F., Xu, H., Kana, T., Zhu, G., Zhan, X., Zou, W., Zhu, M., Kang, L., Zhao, X., 2021. Improved membrane inlet mass spectrometer method for measuring dissolved methane concentration and methane production pate in a large shallow lake. Water 13 (19), 2699.

Zhao, F., Zhan, X., Xu, H., Zhu, G., Zou, W., Zhu, M., Kang, L., Guo, Y., Zhao, X., Wang, Z., Tang, W., 2022. New insights into eutrophication management: importance of temperature and water residence time. J. Environ. Sci. 111, 229–239.

Zheng, Y., Harris, D.F., Yu, Z., Fu, Y., Poudel, S., Ledbetter, R.N., Fixen, K.R., Yang, Z., Boyd, E.S., Lidstrom, M.E., Seefeldt, L.C., Harwood, C.S., 2018. A pathway for biological methane production using bacterial iron-only nitrogenase. Nat. Microbiol. 3, 281–286.

Zou, W., Zhu, G., Cai, Y., Xu, H., Zhu, M., Gong, Z., Zhang, Y., Qin, B., 2020. Quantifying the dependence of cyanobacterial growth to nutrient for the eutrophication management of temperate-subtropical shallow lakes. Water Res. 177, 115806.