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Agricultural land use and pond management influence spatial-temporal variation of CH₄ and N₂O emission fluxes in ponds in a subtropical agricultural headstream watershed

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Small water bodies are hotspots of biogeochemical cycles with large spatial and temporal heterogeneity of their greenhouse gas emission fluxes. To reveal the spatial and temporal variabilities of methane (CH_4) and nitrogen dioxide (N_2O) emission fluxes in small water bodies in subtropical agricultural headwater watersheds, monthly measurements of CH₄ and N₂O fluxes were performed in 53 ponds from May 2018 to July 2020. Results showed that the fluxes of CH₄ and N₂O exhibited distinct spatial and temporal variations, and generally showed a trend of high emission rate in summer and low emission rate in winter. Agricultural land use and pond management had important impacts on CH₄ and N₂O emission fluxes in ponds. The CH₄ and N₂O emission fluxes were significantly higher in the ponds with the landscape of farmland, tea plantation and residential area than those of forest, which might be relevant to the eutrophication of pond water bodies. The mean N₂O emission flux in intensive fishing ponds was much higher than that in grass-fed fishing ponds and no fishing ponds. Moreover, the sustained-flux global warming potential (SGWP) in the eutrophic pond water bodies of farmland, tea plantation and residential area are significantly higher than that in oligotrophic water bodies of forest ponds. Our CH₄ and N₂O emission results suggest that the reduction potential of 4.98 kg C ha⁻¹ y⁻¹ for CH₄ and 0.42 kg N ha⁻¹ y⁻¹ for N₂O will occur in future if ecological management measures are implemented to improve the pond water quality from eutrophication to oligotrophic conditions.

KEYWORDS

 CH_4 and $\mathsf{N}_2\mathsf{O}$ emission, eutrophication, headwater watershed, land use, pond management, small water bodies

1 Introduction

Methane (CH₄) and nitrous oxide (N₂O) are key radiatively active greenhouse gases (GHGs) in the atmosphere contributing to global warming, which contribute 16% and 6%, respectively, to global radiative forcing (World Meteorological Organization, 2016). According to Intergovernmental Panel on Climate Change (IPCC) (2013), the global warming potential (GWP) of CH₄ is approximately 34 times greater than that of carbon dioxide (CO₂), while the GWP of N₂O is 298 times harmer than CO₂ over a time span of 100 years. With the ever-increasing CH₄ and N₂O concentrations in the atmosphere, the global warming and its potential ecological imbalance has aroused researchers' wide concern all over the world (Bastviken et al., 2008; Jacinthe et al., 2012; Paudel et al., 2015).

Aquatic ecosystems are regarded as very important sources/ sinks of atmospheric GHGs, such as CH_4 and N_2O . Although small freshwater lakes and reservoirs cover about 3.7% of the Earth's non-glaciated surface, they are yet sites of intense biogeochemical activity and represent large sources of CH_4 and N_2O emissions (Verpoorter et al., 2014; Prairie et al., 2018). Therefore, GHG emissions from aquatic systems are increasingly concerned. Numerous studies on the emission fluxes of GHGs from aquatic ecosystems has focused on rivers (Yang et al., 2015), natural lakes (Bastviken et al., 2008), and large reservoirs (Soumis et al., 2004). The above-mentioned researches pointed out that the emission fluxes of GHGs were influenced by nutrient contents, climatic conditions, water depths, water pH, water thermal regimes, biological activity, etc. (Williams and Crutzen, 2010; Natchimuthu et al., 2014).

Ponds and small reservoirs, as two major artificial wetlands, emitted plenty of atmospheric CH₄ and N₂O, largely due to the periodic dry/wet alteration episodes and intensive organic material and nitrogen fertilizer inputs (Zou et al., 2005; Hu et al., 2012; Liu et al., 2016). Interestingly, relative to the size of small water bodies, ponds and small reservoirs seem to contribute disproportionately to GHG emissions (Ollivier et al., 2018; Gorsky et al., 2019). The very small ponds (<0.001 km²), which represent 8.6% of lakes and ponds by area globally, were estimated to account for more than 15% of CO2 emission and 40% of CH4 emissions (Holgerson and Raymond, 2016). Compared with large reservoirs such as lakes and oceans, it may be seriously underestimated about the importance of ponds and small reservoirs with shallow water depth, small area and diverse and complex physical and geographical characteristics in the global biogeochemical cycle. In particular, such ponds and small reservoirs are often prone to hypoxia, which may be an important but long neglected CH₄ emission source. However, there is still lack of field direct measurements of CH₄ and N₂O emissions from ponds and small reservoirs to gain an insight into regional or global estimates of CH₄ and N₂O source strengths (Laurion et al., 2010; Abnizova et al., 2012; Kauffman et al., 2018).

Ponds and small reservoirs have many positive ecosystem functions such as biodiversity maintenance, carbon sequestration, pollutant absorption and cultural services including education and aesthetics, but it remains unclear whether the ponds and small reservoirs might also provide some negative functions, i.e., the negative contribution of excessive CH₄ and N₂O emissions to global climate change (Moore and Hunt, 2012). To test for hypothesized disservices of ponds and small reservoirs in subtropical region of southern China, we selected the subtropical agricultural headwater watershed of Jinjing as the study area, and set long-term observation points of ponds to explore the CH₄ and N₂O emissions. The principal objectives of this study were to 1) determine CH₄ and N₂O emissions from ponds in the headwater watershed of Jinjing; 2) reveal the spatial and temporal patterns of CH₄ and N₂O emissions in the studied ponds; 3) evaluate the reduction potential of CH₄ and N₂O emissions in the ponds.

2 Materials and methods

2.1 Study area and sampling sites

This study area is located in the agricultural headwater watershed of Jinjing (27°55′-28°40′N, 112°56′-113°30′E) (Figure 1A), in the northeastern Changsha County of Hunan province, southern subtropical China. The watershed covers an area of 105 km², and is the upper headwater of the Dongting Lake basin. It has a subtropical monsoonal climate, with mean annual temperature and precipitation of 17.2°C and 1,422 mm, respectively. The topography of the area is undulating hilly mountain terrain, with an altitude ranging between 56 and 440 m above the sea level. The major soil type is red soil (Haplic Acrisol) as defined in the Genetic Soil Classification of China (GSCC) (Shi et al., 2004) referenced to the FAO/UNESCO taxonomy (FAO, 1988). Five main types of land use in the study area include forest, agricultural land, tea plantation, residential land and water bodies (Zhou et al., 2020).

Fifty-three ponds were sampled in this study (Figure 1B), and the management of these studied ponds are dominated by grassfed fishing ponds (n = 35), intensive fishing ponds (n = 7) and no fishing ponds (n = 11). The landscape types around the selected ponds consist of agricultural land, forest land, mixed land, residential land and tea plantation.

2.2 Measurement of CH₄ and N₂O emission fluxes

The water sampling of the selected ponds was performed once a month from May, 2018 to July, 2020 at a fixed time



(around the 20th every month). Water samples from the ponds were collected at 0-10 cm in the surface of the water using a 50-ml syringe. After reaching the sampling point, a syringe was used to slowly suck 50 ml of water sample at 0-10 cm in the surface of the water, to avoid disturbing the water body, and try to ensure that there are no bubbles in the syringe (no oxygen/low oxygen environment). After 20 ml of water sample was discharged, the pressure regulating valve of the high-purity nitrogen cylinder should be adjusted. When the flow is moderate and stable, fill 20 ml of nitrogen into the syringe, shake it for about 100 times, and keep it at room temperature for at least 24 h to balance the water and gas in the syringe. After the water and gas are balanced, the headspace gas of the syringe is injected through 0.45-µm filter head of the syringe into a pre-vacuumized airtight test tube (12 ml), and the gas is collected into the vacuum bottle as much as possible. The CH4 and N2O fluxes were detected using a gas chromatograph (Agilent 7890A), and two replications were conducted in each site.

The CH_4 and N_2O emission fluxes at the water-air interfaces of ponds were calculated using the following equations (Liss and Slater, 1974):

$$F = K_w \times \left(c_{obs} - c_{eq}\right) \tag{1}$$

where K_w is the gas transfer velocity (cm·h⁻¹); c_{obs} is the gas concentration measured in the water (mmol·L⁻¹), c_{eq} is the concentration of the gas in the surface water in equilibrium with the concentration in the atmosphere (mmol·L⁻¹). c_{obs} was calculated as follows (Johnson et al., 1990):

$$c_{obs} = C_h \times \left(\beta \times R \times \frac{T}{22.4} + \frac{V_h}{V_w}\right)$$
(2)

where C_h is the gas concentration in the vial headspace (µmol L⁻¹); β is Bunsen solubility coefficients (L L⁻¹) (Wiesenburg and Guinasso, 1979); *R* is the gas constant; *T* is the temperature (K); V_h represents the vial headspace volume (ml); and V_w is the volume of water sample (ml).

 c_{eq} was calculated in the following equation based on Henry's law (Sander, 2015).

$$c_{eq} / c_g = K_H^{\theta} \times e^{\left(\left(-\frac{\Delta_{gol} H}{R} \right) \times \left(\frac{1}{T} - \frac{1}{T^{\theta}} \right) \right)} \times R \times T$$
(3)

where c_g is the gas concentration above the ponds; K_H^{θ} represent Henry's law constant at T^{θ} (298.15 K); $\Delta_{sol}H$ is the enthalpy of dissolution; *R* is the gas constant; and *T* is the temperature (*K*).

The gas transfer velocity was normalized to a Schmidt number of 600 ($S_c = 600$, for CO₂ at 20°C) using the following equation:

$$k = k_{600} \times (S_c/600) \tag{4}$$

where S_c is Schmidt number of gas at *in situ* temperature. For the exponent, n = 2/3 at low wind speed (U₁₀ < 3.7 ms⁻¹) and n = 1/2 at high wind speed (U₁₀ > 3.7 ms⁻¹) was used (Liss and Merlivat, 1986). Wind-based model fitted for the small lakes described by Cole *et al.* (2010) was used to determine k_{600} (m d⁻¹):

$$k_{600} = 0.497 + 0.064 \times U_{10}^{1.8} \tag{5}$$

where U_{10} is wind speed at a 10-m height (m s⁻¹).

2.3 Water quality sampling and measurement

The seven water quality indicators (pH, temperature, TN, TP, DO, NO₃⁻-N and NH₄⁺-N) of the selected ponds were measured by simultaneous sampling with CH₄ and N₂O emission fluxes from May 2018 to July 2020. The collection of field water samples was carried out according to the water quality-guidance on sampling techniques, issued by Ministry of Ecology and Environment of the People's Republic of China (HJ494-2009, https://www.mee.gov.cn/ywgz/fgbz/bz/). About 1000 ml of surface water samples were collected with 1 L plastic bottles. The water samples were instantaneous, and the sampling locations were fixed each time. The collected samples were stored in the refrigerator at -20°C, and the concentrations of nitrogen and phosphorus components were measured within 48 h. Additionally, the water quality indicators of dissolved oxygen (DO), pH and water temperature of the water bodies were measured in situ by a Hash portable water quality meter (HI8320, United States). The concentration of TN in water was determined by the method of alkaline potassium persulfate digestion Ultraviolet Spectrophotometry (GB 11894-89), while the concentration of TP in water was measured by the potassium persulfate oxidation and molybdenum-antimony antispectrophotometric method (GB 11893-89). All contents of N and P components were determined with continuous flow analysis instrumentation (AA3, Germany). The water quality indicators in ponds were expressed as their monthly average values in subsequent parts.

2.4 Statistical analysis

One-way analysis of variance was performed to examine the differences in annual $\rm CH_4$ and $\rm N_2O$ emissions between different

treatments. The differences between the treatments were further examined by Hochberg's GT2 test. Multiple linear analysis (MLR) was carried out in R. All statistical analysis were performed using SPSS version 19.0 (SPSS Inc., United States) at the 0.05 significance level. All statistical plots were generated using Origin 2018 (OriginLab Corp. United States). The spatial distributions of all targets of interest were mapped were mapped in ArcGIS 10.2 software (ESRI Inc., United States).

3 Results

3.1 Characteristics of the environmental parameters in ponds

The pond environmental parameters and water quality under three management types were summarized in Table 1. The ages of ponds varied from 12 to 92 years, and also differed in depths and surface areas, with the mean depth and areas of 1.31 m and 6,070 m², respectively. The water chemistry indicators (pH, DO, and T) and the contents of nitrogen and phosphorus components (TN, TP, NH4⁺-N, and NO3⁻-N) differed among the ponds under three management types. The water in the ponds under three management types was all slightly alkaline, with a mean pH around 8.0. The annual mean water temperatures during the sampling period showed slight variations in different types of ponds, with the highest mean temperature appeared in the "intensive fishing" ponds and the lowest in the "no fishing" ponds, respectively. Generally, DO concentrations varied from 5.48 to 14.04 mg L^{-1} with the overall state of DO saturation. The mean concentrations of both TN and TP reached the highest in the "intensive fishing" ponds, while the lowest in the "no fishing" ponds. Similar trends were found for the concentrations of NH4⁺_N in the ponds under three management types, with the highest in the "intensive fishing" ponds and lowest in the "no fishing" ponds. On the contrary, the mean concentrations of NO₃⁻_N reached the highest in the "no fishing" ponds, while the lowest in the "intensive fishing" ponds.

3.2 Spatial-temporal variation of CH_4 and N_2O emission fluxes

The CH₄ and N₂O emission fluxes from ponds in the study area varied from 49 to 659 μ g m⁻² h⁻¹ (Figure 2A) and -2.5-29.7 μ g m⁻² h⁻¹ (Figure 2B), respectively, showing significant spatial variability. It is assumed that the spatial distribution patterns of the CH₄ and N₂O emissions were correlated with the spatial patterns of land use types in the study area (Figure 1B). Agricultural land use in the study area are mainly concentrated in the southwest region, while the northeast region has relatively few inhabitants and the land use is dominated by forests.

	Age	Area (m ²)	Depth(m)	DO	рН	T (°C)	TN	ТР	NH4 ⁺ -N	NO ₃ ⁻ -N
<i>Grass-fed fishing ponds (n = 35)</i>										
Minimum	12	426	0.34	6.87	7.29	18.5	1.08	0.08	0.14	0.04
Maximum	92	15828	2.50	14.04	9.01	21.0	10.01	0.77	0.76	8.57
Mean	67	3,268	1.11	9.33	8.09	19.9	2.62	0.28	0.33	0.60
St.d	4	517	0.09	0.27	0.06	0.1	0.27	0.02	0.03	0.24
Intensive fishing ponds $(n = 7)$										
Minimum	12	1,038	1.02	5.48	7.13	19.6	2.38	0.24	0.31	0.12
Maximum	92	8,305	2.20	11.81	8.88	20.9	7.23	0.72	1.51	1.12
Mean	56	3,835	1.49	9.07	7.94	20.2	4.22	0.39	0.97	0.50
St.d	14	947	0.16	0.97	0.22	0.2	0.60	0.06	0.16	0.15
No fishing ponds $(n = 11)$										
Minimum	22	326	0.62	6.07	7.67	18.3	0.54	0.04	0.13	0.06
Maximum	92	98723	4.20	10.78	9.03	20.5	3.99	0.29	0.74	2.50
Mean	60	16409	1.87	8.61	8.10	19.4	1.85	0.15	0.29	0.83
St.d	6	8,575	0.42	0.39	0.13	0.2	0.37	0.02	0.06	0.27
All ponds $(n = 53)$										
Minimum	12	326	0.34	5.48	7.13	18.3	0.54	0.04	0.13	0.04
Maximum	92	98723	4.20	14.04	9.03	21.0	10.01	0.77	1.51	8.57
Mean	64	6,070	1.31	9.15	8.07	19.8	2.67	0.27	0.41	0.64
St.d	3	1898	0.11	0.23	0.05	0.1	0.23	0.02	0.04	0.17

TABLE 1 Descriptive statistics of pond parameters in different management types of ponds.

Note: Units for DO, TN, TP, NH4_N, NO - N were mg L-1.

Pond management and land use affected the average annual emissions of CH_4 and N_2O . High values of average annual emissions of CH_4 and N_2O occurred in fish-farming ponds with 20.79 kg C ha⁻¹ y⁻¹ and 1.14 kg N ha⁻¹ y⁻¹, respectively, higher than those in non-fish-farming ponds. (Figures 3A,B). Meanwhile, the annual emissions of CH_4 and N_2O from ponds surrounded by land use types (tea plantation, mixed, residential, and agricultural land) are much higher than those from the ponds surrounded by forest (Figures 3C,D).

The CH_4 and N_2O emission fluxes in the study area fluctuate significantly during the 26 consecutive months of observation, showing a seasonal variation (Figure 4). In general, the observed CH_4 and N_2O emission fluxes were high in spring, summer and winter, and low in autumn (Figure 4). This may be related to the changes of rainfall and pond water volumes in the study area. Rainfall in the study area is mainly concentrated in spring and summer. Surface runoff formed by rainfall brings a large amount of terrestrial organic material into the ponds, which naturally stimulates pond CH_4 and N_2O emissions in spring and summer. In winter, the pond water volume reaches a minimum with decreasing of the pond water level due to persistent drought, which may largely reduce the total amount of dissolved greenhouse gases in the water column and increase the emissions of CH_4 and N_2O .

3.3 Estimation of reduction potential of CH_4 and N_2O emission fluxes

As shown in Table 2, cumulative CH_4 and N_2O emission over the annual cycle both reached the highest in the ponds with tea plantation ($32.22 \pm 5.23 \text{ kg C ha}^{-1} \text{ y}^{-1}$, $1.65 \pm 0.30 \text{ kg N ha}^{-1} \text{ y}^{-1}$), and they were significantly higher than those in the ponds with forest land, which represented the natural ponds (Table 2). The yearly CH_4 and N_2O emitted in ponds with agricultural lands was 34% and 143% greater than those in forest ponds, respectively.

The sustained-flux global warming potential (SGWP) for gas fluxes was calculated on a 100-year timescale, to assess the climatic impact of the ponds (Neubauer and Megonigal, 2015). The SGWP showed significant difference among ponds under different agricultural land uses (Table 2), with the highest values found in tea plantation ponds (2232.9 \pm 262.1 kg CO₂-eq ha⁻¹ y⁻¹) and the lowest in forest ponds (812.0 \pm 121.4 kg CO₂-eq ha⁻¹ y⁻¹).

3.4 Effect of environmental factors on CH_4 and N_2O emission fluxes in ponds

The relationships between GHG fluxes (CH₄ and N_2O) and environmental parameters were further analyzed using multiple



linear regression method and listed in Table 3. In the grass-fed fishing ponds, CH₄ fluxes had no significant correlations with any environmental parameters (p < 0.01 or < 0.05). On the other hand, N₂O fluxes showed significant, positive correlations with DO, TN and NO₃⁻⁻N (p < 0.01) (Table 3). In the intensive fishing ponds, CH₄ fluxes were significantly and positively correlated with TP (p < 0.01), while N₂O fluxes were positively correlated with water depth (p < 0.01) (Table 3). As for no fishing ponds, we found that fluxes of both CH₄ and N₂O were positively correlated with TN and NO₃⁻⁻N (p < 0.01) (Table 3).

The relative importance of environmental factors to CH_4 and N_2O emissions was further identified by the MLR method (Figure 5). The Depths and NH_4^+ -N contents in ponds were identified as the most important factors for explaining 20% of the variance in the CH_4 emissions (Figure 5A), while the NO_3^- -N explained the highest (35.4%) variance of N_2O emissions (Figure 5B). The rdacca.hp R package was also adopted to calculate the contributions of different environmental factors to the variance of CH_4 and N_2O emissions. Results showed that the contribution of pond management was relatively the highest (Supplementary Figure S1).

4 Discussion

4.1 CH₄ and N₂O emission fluxes in ponds

The average water-to-air emissions of CH₄ and N₂O during the observed periods from the study ponds were within the ranges reported by previous studies (Table 4; Hu, 2015; Chen et al., 2016; Ma et al., 2018; Wu et al., 2018; Fang et al., 2022). The CH₄ fluxes from grass-fed fishing ponds were 20.79 \pm 1.95 kg C ha⁻¹ y⁻¹, which were substantially lower than recent reports in those fishing ponds in China, urban ponds in Netherland and stormwater ponds in United States (Hu, 2015; Gorsky et al., 2019; van Bergen et al., 2019; Fang et al., 2022), and also quite lower than the crab ponds (Hu, 2015; Ma et al., 2018), but much higher than that reported for shrimp ponds (Chen et al., 2016). Similar trends were found for the CH₄ fluxes in the intensive fishing ponds and no fishing ponds. In contrast, the N₂O fluxes in the grass-fed fishing ponds and no fishing ponds were 0.62 \pm 0.10 kg N ha⁻¹ y⁻¹ and 0.65 \pm 0.22 kg N ha⁻¹ y⁻¹, respectively, which were generally much lower than those recorded in reservoirs and rivers located within the same or different



climatic zones (Chen et al., 2016; Fang et al., 2022). Furthermore, the N₂O fluxes in the intensive fishing ponds were 1.14 ± 0.24 kg N ha⁻¹ y⁻¹, and were much less than crab ponds and mixed mariculture ponds (Ma et al., 2018; Wu et al., 2018). The possible explanations are that the various conditions in sediment substrate availability, water parameters (e.g., DO and mineral N) and water transport efficiency may jointly cause the differences of GHG emission fluxes among different types of ponds (Davidson et al., 2018; Wang et al., 2019; Audet et al., 2020).

4.2 Factors influencing CH_4 and N_2O emissions

Previous studies have found that large temporal variations in CH_4 and N_2O fluxes existed in various aquatic ecosystems, such as reservoirs (Musenze et al., 2014), lakes (Xiao et al., 2022) and rivers (Zhao et al., 2013). However, comparable information is rare for small

water bodies, particularly ponds (Chen et al., 2016; Zhang et al., 2022). Our results showed considerable temporal variations in the CH₄ and N₂O emissions from various ponds in the study area (Figures 4A,B). The emission fluxes of CH₄ and N₂O exhibited an evident seasonal variation among different ponds. Specifically, CH4 and N₂O fluxes were higher during summer (June-August) when water temperature tended to be higher than in other period (Yang et al., 2021), and decreased in the later parts of the experimental period after peaking in August. Temperature has an effect on the abiotic and biotic parameters such as plankton primary production, respiration, microbial activity, and nutrient availability, which in turn govern the production and consumption of GHGs (Kosten et al., 2012; Rosentreter et al., 2017; Xiao et al., 2022). The results of the multiple linear regression in this study indicated that water temperature explained 15.6% of the CH₄ fluxes (Figure 5A), implying that temperature is an important factor of CH4 emissions. The increase of CH4 emissions may also be caused by the ascending temperature, which stimulates the methanogenesis (Treat



FIGURE 4

Temporal variation of monthly CH_4 (A) and N_2O (B) fluxes and seasonal CH_4 (C) and N_2O (D) fluxes in the studied ponds For (A,B), lines within the boxes give the median, boxes represent the 25th and 75th percentile, indicating the lowest and highest values, excluding outliers, and circles represent outliers and extremes; For (C,D), lines within the boxes give the standard error, the mean and the median, representatively. The curves are normal distribution curves of all the sampling sites during different seasons).

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TABLE Z ANNUAL		emissions fi	luxes and <i>i</i>	Annual SGWP	in different	landscape	types of	bonas.

Land use of ponds	$CH_4(kg C ha^{-1} y^{-1})$	$N_2O(kg N ha^{-1} y^{-1})$	SGWP (kg CO_2 -eq ha^{-1} y ⁻¹)
Agricultural land $(n = 17)$	19.98 ± 2.72ab	0.68 ± 0.13b	1,224.7 ± 117.0b
Forest $(n = 15)$	14.94 ± 2.70b	$0.28 \pm 0.07 b$	812.0 ± 121.4b
Mixed land $(n = 3)$	13.92 ± 2.36ab	0.96 ± 0.35ab	1,082.8 ± 249.4b
Residential land $(n = 11)$	20.44 ± 2.68ab	$0.60 \pm 0.09b$	1,206.0 ± 112.7b
Tea Plantation $(n = 7)$	32.22 ± 5.23a	1.65 ± 0.30a	2232.9 ± 262.1a

Note: Different letters in a single column indicate significant difference among ponds with different land uses at the 0.05 probability level. SGWP was the sustained-flux global warming potential for use when gas fluxes persist over time and was calculated assuming a sustained gas flux rate of 1 kg m⁻² y⁻¹ over the 100 years period. SGWP = $34 \times CH_4 + 298 \times N_2O$ (IPCC, 2013).

et al., 2014). This result is also supported by Natchimuthu *et al.* (2014), which reported the temperature influenced the diffusive emission rate and transport efficiency of the CH_4 flux.

The mean CH_4 emission of all the ponds was 19.92 kg $C ha^{-1}y^{-1}$ in this study, acting as a weaker CH_4 source than inland waters. It is likely due to that the sediment condition of ponds may not be the optimum for

Pond types		Age	Area	Depth	DO	рН	Т	TN	ТР	$\rm NH_4^+ - N$	NO ₃ ⁻ -N
Grass-fed fishing ponds $(n = 35)$											
	CH4	-0.046	-0.058	-0.178	0.106	0.069	0.068	0.103	0.018	-0.040	0.054
	N2O	-0.116	0.056	0.011	0.347*	0.033	-0.082	0.485**	-0.252	-0.078	0.541**
Intensive fishing ponds $(n = 7)$											
	CH4	-0.339	-0.355	-0.296	0.229	0.475	0.392	0.148	0.876**	0.099	-0.411
	N2O	0.423	-0.353	0.912**	-0.672	-0.537	-0.159	-0.271	-0.294	-0.442	0.306
No fishing ponds $(n = 11)$											
	CH4	0.181	-0.460	-0.519	0.564	-0.085	0.579	0.678*	-0.267	-0.022	0.717*
	N2O	0.431	-0.391	-0.245	0.420	-0.120	0.518	0.759**	-0.311	0.415	0.824**

TABLE 3 Pearson's correlation coefficients between CH₄ and N₂O emission fluxes and environmental variables in different management types of ponds.

*and ** indicate correlation significant at the 0.05 and 0.01 level, respectively.



methanogenesis, since the optimum pH of CH_4 production was near neutral (Wang et al., 1993; Kirschke et al., 2013; Zhang et al., 2022). However, the pH ranged from 7.13 to 9.03 in this study. The relatively higher pH values were probably the main limiting factors for CH_4 production in the selected ponds.

The major processes of N_2O production in ponds and reservoirs could be concluded as the following three processes: aerobic nitrification, anaerobic denitrification and dissimilatory nitrate reduction to ammonium (Schlesinger, 2009; Yuan et al., 2021). N_2O production generally occurs under conditions of high NO_3^- -N concentration and low oxygen (Zhou et al., 2017), which is supported by our results. Our study showed that there was a significant positive correlation between N_2O emissions with NO_3^- -N and TN in grass-fed fishing ponds and no fishing ponds

(p < 0.01 for both ponds) (Table 3). Moreover, the multiple linear regression for all the ponds also showed that the environmental variables of NO3--N and TN explained 35.4% and 29.5%, respectively, for N₂O emissions (Figure 5B). These results suggested that the concentrations of NO3⁻-N and TN played vital role in affecting N2O fluxes. The NO₃⁻-N in water is generally regarded as an important nitrogen source of N₂O, the concentration of NO₃⁻-N in water will affect the production of N₂O. Nitrification is an aerobic process that oxidizes NH4+-N to NO3--N and releases N2O as a by-product; whereas denitrification can either produce N2O or transform it into N₂ in a final reaction favored under highly reduced anoxic conditions. Thereby, to reduce NO₃⁻-N supply for denitrification will be conducive to reducing the N2O emission in ponds. Algal blooms usually occurred in most ponds and reservoirs during summer. The temporal N2O

TABLE 4 Comparison of CH₄ and N₂O emission fluxes from pond and reservoir studies.

Type of ponds	Location	Sample dates	CH ₄ emission (kg C ha ⁻¹ y ⁻¹)	N ₂ O emission (kg N ha ⁻¹ y ⁻¹)	References
Crab pond	Changshu, China (31°32′93″N, 120°41′88″E)	2016.03-2017.03	51.6 ± 4.0	3.32 ± 0.10	Ma et al. (2018)
Crab with aquatic vegetation	Changshu, China (31°32′93″N, 120°41′88″E)	2016.03-2017.03	54.3 ± 4.6	3.34 ± 0.13	Ma et al. (2018)
Crab without aquatic vegetation	Changshu, China (31°32′93″N, 120°41′88″E)	2016.03-2017.03	47.7 ± 1.1	3.28 ± 0.04	Ma et al. (2018)
Mixed-fish	Changshu, China (31°32′93″N, 120°41′88″E)	2016.03-2017.03	64.4 ± 3.2	2.99 ± 0.04	Ma et al. (2018)
Fish	Xinghua, China (32°52′N, 119°50′E)	2017.08-2019.08	83.62 ± 15.27	$1.17~\pm~0.10$	Fang et al. (2022)
Crab	Xinghua, China (32°52′N, 119°50′E)	2017.08-2019.08	68.26 ± 4.30	1.59 ± 0.06	Fang et al. (2022)
Shrimp monoculture	Qingdao, China (36°18′N, 120°00′E)	2014.03-2015.03	5.7	ND	Chen et al. (2016)
Shrimp and sea cucumber polyculture	Qingdao, China (36°18′N, 120°00′E)	2014.03-2015.03	0.68	ND	Chen et al. (2016)
Crab	Xinghua, China (32°52′N, 119°50′E)	2013.06-2015.06	32.4	2.69	Hu., (2015)
Fish	Xinghua, China (32°52′N, 119°50′E)	2013.06-2015.06	42.0	2.28	Hu., (2015)
Fish	Xinghua, China (32°52′N, 119°50′E)	2014.06-2015.06	42.31 ± 12.67	2.99 ± 0.75	Wu et al. (2018)
Reservoir	Goiás, Brazil (17°45′56′′S, 48°34′06′′W)	2004.11-2005.08	32.05	ND	Bergier et al. (2011)
Urban pond	Netherland (51°46′30′′S, 5°51′11.22′′E)	2013.06-2014.05	404.1	ND	van Bergen et al. (2019)
Stormwater pond	Virginia, United States (37°14′N, 76°43′W)	2018.06-2018.08	488.3	0.23	Gorsky et al. (2019)
Grass-fed fishing	Changsha, China (27°55′–28°40′N, 112°56′–113°30′E)	2018.05-2020.07	20.79 ± 1.95	0.62 ± 0.10	This study
Intensive fishing	Changsha, China (27°55′–28°40′N, 112°56′–113°30′E)	2018.05-2020.07	14.59 ± 2.50	1.14 ± 0.24	This study
No fishing	Changsha, China (27°55′–28°40′N, 112°56′–113°30′E)	2018.05-2020.07	20.57 ± 4.31	0.65 ± 0.22	This study

Note: ND is short for "no data".

emission variation showed the highest value observed in summer. It is likely to be related with algal blooms in ponds, which could provide large amounts of organic matter and promote the N_2O production. Moreover, algal photosynthesis can release NO_3^- -N and DO, which would increase the proportion of N_2O production in coupled denitrification and nitrification (Yang et al., 2015).

In the present study, water pH may impact temporal variations of N_2O fluxes from aquaculture ponds in the coastal zone. In previous studies by Clough *et al.* (2011) and Yang *et al.* (2015), pH governed the processes of nitrification and denitrification and thus affected the temporal variations of N_2O emission in aquatic environments. Lower pH may inhibit the reductase activity of nitrous oxide and thus contribute to higher N_2O production from the sediment (Stow et al., 2005). The N_2O flux in this study showed a negative correlation with pH in intensive fishing ponds and no fishing ponds (Table 3), indicating that pH was an environmental factor influencing the temporal variation of N_2O fluxes.

Pond management is one of the most important differences between aquaculture systems and other aquatic ecosystems (Glaz et al., 2016; Chanda et al., 2019; Wang et al., 2019). The TN and TP contents in intensive fishing ponds were 4.22 mg L^{-1} and 0.39 mg L⁻¹, respectively, which was much higher than those in grass-fed fishing ponds and no fishing ponds. Compared to the environmental quality standards for surface water (GB 3838-2002), these ponds showed obvious tendency to eutrophication. Similar patterns were found for the CH4 and N₂O emissions, with higher emissions found in intensive fishing ponds, and much lower in grass-fed fishing ponds and no fishing ponds. The ANOVA results also indicated that the CH₄ and N₂O fluxes in the ponds with tea plantation were significantly higher than those in ponds with the land use of agricultural land, forest and residential land. These results suggested that pond management and agricultural land use in the subtropical hilly region have aggravated the eutrophication of pond water bodies in the study area, and therefore, indirectly increased the emission of CH₄ and N₂O in the ponds. To strengthen farmland drainage and the treatment of pond sewage in the study area is not only conducive to reducing the eutrophication of ponds in the study area, but also helpful to make the ponds more environmentally friendly with respect to the mitigation of global warming (Beaulieu et al., 2019; Zhang et al., 2021).

4.3 Potential roles of ponds in reducing CH_4 and N_2O emissions

Compared with the oligotrophic water bodies of forest ponds, the mean annual CH₄ and N₂O emission fluxes of all ponds in Supplementary Table S1 were adopted to calculate the reduction potential. Our CH₄ and N₂O emission results suggest that the reduction potential of 4.98 kg C ha⁻¹y⁻¹ for CH_4 and 0.42 kg N ha⁻¹y⁻¹ for N₂O will occur in future if ecological management measures are implemented to improve the pond water quality from eutrophication to oligotrophic conditions. The SGWP in the eutrophic pond water bodies of farmland, tea plantation and residential area are significantly higher than that in oligotrophic water bodies of forest ponds. On the 100-year horizon, the SGWP values in the ponds were positive, showing a trend of accelerating global warming. Compared with forest ponds, the tea plantation ponds, residential land ponds, and agricultural land ponds have the reduction potential of 1,420.9 kg CO₂-eq $ha^{-1} y^{-1}$ (175%), 394.0 kg CO₂-eq $ha^{-1} y^{-1}$ (49%), and 412.8 kg CO2-eq ha⁻¹ y⁻¹ (51%), respectively, to mitigate global warming. The results of this study suggest that small water bodies such as ponds should be more considered when evaluating the potential of the aquatic system in reducing CH₄ and N₂O emissions and mitigating global warming.

5 Conclusion

The present study discussed the spatial and temporal variability of CH4 and N2O emissions from ponds in a subtropical agricultural headwater watershed. Pond management and agricultural land use exacerbated the eutrophication of pond water bodies in the study area, indirectly increasing CH₄ and N₂O emissions from ponds. The SGWP in eutrophic pond waters disturbed by humans was significantly higher than that in oligotrophic water bodies of forest ponds that were not disturbed by humans. If pond ecological management measures are implemented in the study area to improve pond water quality from eutrophication to hypotrophication, the reduction potential of CH₄ and N₂O will amount to $4.98 \text{ kg C ha}^{-1} \text{ y}^{-1}$ and $0.42 \text{ kg N ha}^{-1} \text{ y}^{-1}$, respectively. Therefore, small water bodies such as ponds should be more considered when evaluating the potential of the aquatic system in reducing CH₄ and N₂O emissions and mitigating global warming.

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Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

JZ contributed to conception, design and experiments of the study and revised the manuscript. MF performed the statistical analysis and wrote the original draft. WZ contributed to experiments of the study and data analysis. JW revised the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

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