Arrhenius Equation Construction And Nitrate Source Identification Of Denitrification At The Lake Taihu Sediment–Water Interface With 15N Isotope

Qiuxia Ma
Hohai University https://orcid.org/0000-0002-8362-9319
Min Pang
Southern University of Science and Technology
Yong Pang (ypang@hhu.edu.cn)
Hohai University
Lu Zhang
Nanjing Institute of Geography and Limnology Chinese Academy of Sciences
Zhilin Huang
Hohai University

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Arrhenius equation construction and nitrate source identification of denitrification at the Lake Taihu sediment−water interface with ^{15}N isotope

Qiuxia Ma[1], Min Pang[2], Yong Pang[1,*], Lu Zhang[3], Zhilin Huang[1]

[1] College of Environment, Hohai University, Nanjing, 210098, China

[2] School of Environmental Science and Technology, Southern University of Science and Technology, Shenzhen, 518055, China

[3] State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing, 210008, China

Corresponding author: Yong Pang Email: ypang@hhu.edu.cn

Abstract: Total nitrogen in Taihu Lake, China has gradually decreased since 2015 while the total phosphorus concentration has exhibited an increasing trend, indicating an asynchronous change. The dominant nitrogen removal process in freshwater ecosystems is denitrification which primarily occurs at the sediment–water interface. In this study, ^{15}N isotope incubation experiments were attempted to analyze the effect of water temperature on denitrification, to construct the regional denitrification Arrhenius equations considering water temperature, and to identify the nitrate source of denitrification in Lake Taihu sediments. The results indicated that the potential N_2 production rates and denitrification rates generally decreased in the west to east direction, which was significantly positively correlated with the nitrate concentration of overlying water by Pearson correlation coefficient analysis ($P<0.05$). In addition, when the water temperature was lower than 30°C, the rates of the potential N_2 production and denitrification were higher with an increase in water temperature, but when the water temperature was overhigh, denitrification was inhibited. The ratio of the total denitrification rate of nitrate from the water column in the sediment to the total denitrification rate during the incubation experiment was above 0.5 at each sampling site. This indicated that the denitrification in the Lake Taihu sediment primarily occurred at the expense of nitrate from the water column. Research on denitrification has important implications for improving the water quality of Lake Taihu, and the findings of the study act as a reference for the water environment treatment of other shallow eutrophic lakes in China and globally.

Keywords: denitrification; Arrhenius equation construction; nitrate source identification; ^{15}N isotope; water temperature

1 Introduction

Nitrogen enters a lake as inorganic and organic nitrogen through atmospheric deposition, surface runoff, and biological nitrogen fixation, and is absorbed and assimilated by algae, aquatic plants, and benthos (Cottingham et al., 2015; He et al., 2020). These nutrients can be released into the water column through leakage or mortality by organisms (Zhang et al., 2009; Jiang et al., 2019). Human activities have accelerated the input of reactive nitrogen to the biosphere (Frostegard et al., 2021). The increasing input of nitrogen into water is one of the principal anthropogenic stressors leading to lake water eutrophication (Chen et al., 2012; Li et al., 2020).

Denitrification, anaerobic ammonium oxidation, and dissimilatory nitrate reduction to ammonium are crucial pathways of dissimilatory nitrate reduction in aquatic ecosystems (Kuypers et al., 2003; Jiang et al., 2019; Jiang et al., 2020; Ahmad et al., 2021). In addition, some researchers have proposed that denitrification is the primary nitrogen removal process in freshwater ecosystems, which occurs at the sediment−water interface (Saunders and Kalff, 2001; Veraart et al., 2011) and is greatly affected by water temperature (Liao et al., 2018; Wang et al., 2018). Additionally, water temperature can directly or indirectly affect denitrification by affecting the dissolved oxygen concentration, nitrogen release, and microbial activity (Gebremariam et al., 2021; Minuti et al., 2021; Wang et al., 2021). Therefore, studies on the effect of denitrification at the sediment−water interface are vital for understanding lake water eutrophication.

The most commonly used acetylene inhibition technique is currently considered unsuitable for quantifying the denitrification rates, mainly because of the catalytic decomposition of NO in the presence of acetylene and O_2 (Wu et al., 2019). Nitrogen isotopes have been widely used for understanding

inorganic nitrogen sources, migration, and transformation in various environments ((Bu et al., 2017; Jin et al., 2017; Meng et al., 2021). Natural abundance nitrogen ($\delta^{15}N$) and oxygen isotopes of nitrate ($\delta^{18}O$) are important tools for evaluating the sources and transformations of natural and contaminant nitrate (NO_3^-) in the environment (Granger and Wankel, 2016). Lewicka−Szczebak et al. (2014) quantified denitrification in arable soils based on stable isotope analyses of emitted N_2O ($\delta^{15}N$ and $\delta^{18}O$). Kim et al. (2018) analyzed $\delta^{15}N$ and $\delta^{18}O$ using a Finnigan MAT delta plus XL isotope ratio mass spectrometer at the Isotope Science Laboratory to assess denitrification in a hyporheic zone.

However, these papers did not propose the relationship between water temperature and denitrification rate, and these methods failed to distinguish the source of substrate nitrate in denitrification.

In this study, Lake Taihu in China, a shallow eutrophic lake, was chosen to investigate the effect of water temperature on denitrification at the sediment−water interface with ^{15}N isotope, and the regional denitrification rate equations considering water temperature were established based on the experimental results. The nitrate source of denitridication was identified by direct measurement of the potential N_2 production and denitrification rates. Direct measurement of N_2 production has the advantage of quantifying the denitrification rate of using NO_3^- from overlying water and the denitrification rate of using NO_3^- from nitrification within the sediment (Steingruber et al., 2001; Tang et al., 2014).

2 Materials and methods

2.1 Study area description and sample collection

Lake Taihu, located in the eastern plain of China (Jiang et al., 2020), is a large eutrophic shallow

(area 2338 km^2, mean depth 1.9 m) freshwater lake (Zhang et al., 2009). The water temperature ranges from 0°C to 35°C, which is affected by atmospheric temperature (Liu et al., 2015). Lake Taihu has multiple functions, such as flood control, shipping, aquaculture, supporting tourism and recreation, among which the most important function is of water supply (Qin et al., 2015).

Samples were collected from five sites referred to as routine monitoring points of the Lake–Watershed Science Sub Center, National Earth System Science Data Center, National Science & Technology Infrastructure of China (http://gre.geodata.cn) (Fig.1A).

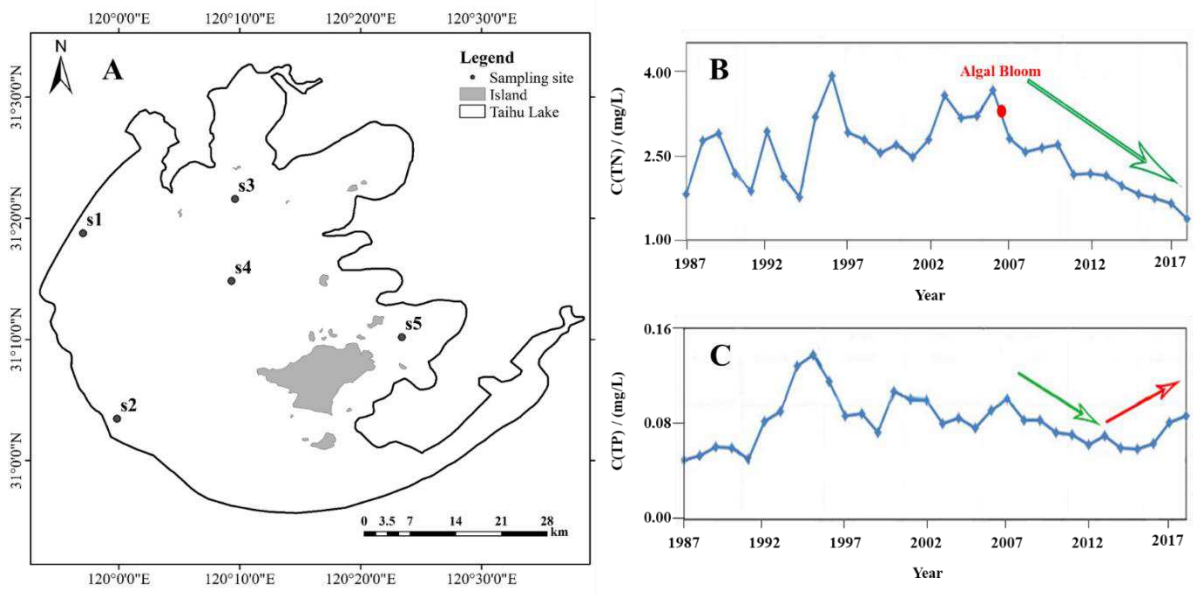

Fig. 1. Study area and locations of Lake Taihu, China (A), and mean annual concentration of total nitrogen (TN) (B) and total phosphorus (TP) (C) from 1987 to 2018.

2.2 Chemical analysis

For the lake water quality observation, electrical conductivity, pH, dissolved oxygen, and water temperature were measured using a multiparameter water quality analyzer (YSI Professional Plus, 6600V2, USA) at the sampling sites. Other factors related to denitrification are the environmental factors including nitrite (NO_2^-), nitrate (NO_3^-), and ammonia nitrogen (NH_4^+). NO_2^- was detected by

spectrophotometric method, and NO_3^- was measured by ultraviolet spectrophotometry, and NH_4^+ was measured by Nessler's reagent spectrophotometry (Jiang et al., 2019).

The sediment water content was calculated by drying the samples at 105°C for 24 h to a constant weight. The dried samples were burnt at 550°C for 6 h in a muffle furnace to measure the loss on ignition.

2.3 Incubation experiment

The intact sediment cores were placed vertically in the laboratory, and the lake water was filled with a syringe along the pipe wall, by to ensure that the samples were least disturbed. The samples were divided into three groups and incubated in a constant temperature incubator at the 25°C, 30°C, and 35°C for 24 h (Liu et al., 2015). To avoid the influence of algal photosynthesis in the sediment and the water on denitrification, the column samples were wrapped with aluminum foil during cultivation. The sediment cores were incubated in the denitrification incubation system, that included five buckets filled with filtered lake water, a peristaltic pump with constant water flow, sealed pistons, inlet pipes, and outlet pipes. The inlet pipe had to be controlled to be lower than the outlet pipe and maintained approximately 1 cm away from the sediment. The filtered lake water was pumped into the sediment cores by a peristaltic pump at a flow rate of 0.78 mL/min, ensuring the overlying water was fully mixed.

After the pre−culture experiment, $^{15}NO_3^-$ was added to each bucket to achieve a final concentration of 100 μmol/L, and then steadily incubated at three temperatures for another 24 h (Veraart et al., 2011). The inlet water of each sampling site was carefully collected into the Labco bottles without bubbles using syringes, and the outlet water directly overflowed into the Labco bottles. Following this, 0.2 mL 50% $ZnCl_2$ was added to each Labco bottle. Eventually, the content of soluble gas ($^{28}N_2$, $^{28}N_2$, and $^{30}N_2$) in the water sample was determined using a membrane interface mass spectrometer (MIMS). In addition, 25

mL of inlet and outlet water samples were collected and filtered through 0.45 μm cellulose acetate membranes to determine the concentration of NO_3^-.

2.4 Calculation method of potential N_2 production and denitrification rates

Denitrification in the sediment can occur at the expense of NO_3^- from the water column or from NO_3^- produced within the sediment by nitrification (Steingruber et al., 2001). The main pathway can be identified using the $^{15}NO_3^-$ isotope pairing technique (Fig. 2). The dissolved gases used to calculate the denitrification rates were $^{29}N_2$ and $^{30}N_2$, and their corresponding potential production rates r_{29} and r_{30} were calculated as follows (Tang et al., 2014; Jiang et al., 2020):

$$r_i = \frac{(C_i - C_{i0}) \cdot v}{A} \times 60, \quad (1)$$

where r_i (μmol·m^{-2}·h^{-1}) is the release rate of $^iN_2$ (i=29, 30), C_i, C_{i0} (μmol·L^{-1}) are the concentrations of $^iN_2$ in the inlet and outlet water, respectively, v (mL·min^{-1}) is the flow rate of the peristaltic pump, A (m^2) is the surface of the incubated sediment, and the time conversion factor is 60.

The denitrification rates of $^{15}NO_3^-$ (D_{15}) and unlabeled $^{14}NO_3^-$ (D_{14}) can be calculated by the production rate of $^{29}N_2$ (r_{29}) and $^{30}N_2$ (r_{30}), it can normally be expressed as (Steingruber et al., 2001):

$$D_{15} = r_{29} + 2 \cdot r_{30}, \quad (2)$$

$$D_{14} = D_{15} \times \frac{r_{29}}{2 \cdot r_{30}}, \quad (3)$$

The total denitrification rate during the incubation experiment (D_{tot}) and the total denitrification rate of nitrate from the water column (D_{wtot}) were determined by the following equations:

$$D_{tot} = D_{14} + D_{15}, \text{ and} \quad (4)$$

$$D_{wtot} = D_{15} / \varepsilon \,, \tag{5}$$

where ε is the $^{15}NO_3^-$ abundance during the incubation and is calculated by the following equation:

$$\varepsilon = \frac{\left[NO_3^-\right]_a - \left[NO_3^-\right]_b}{\left[NO_3^-\right]_a} \,, \tag{6}$$

where $\left[NO_3^-\right]_a$ and $\left[NO_3^-\right]_b$ are the concentrations referred to after and before the addition of $^{15}NO_3^-$ tracer addition, respectively.

The nitrate source can be identified by the ratio of D_{wtot} to D_{tot} (γ):

$$\gamma = \frac{D_{wtot}}{D_{tot}} \,, \tag{7}$$

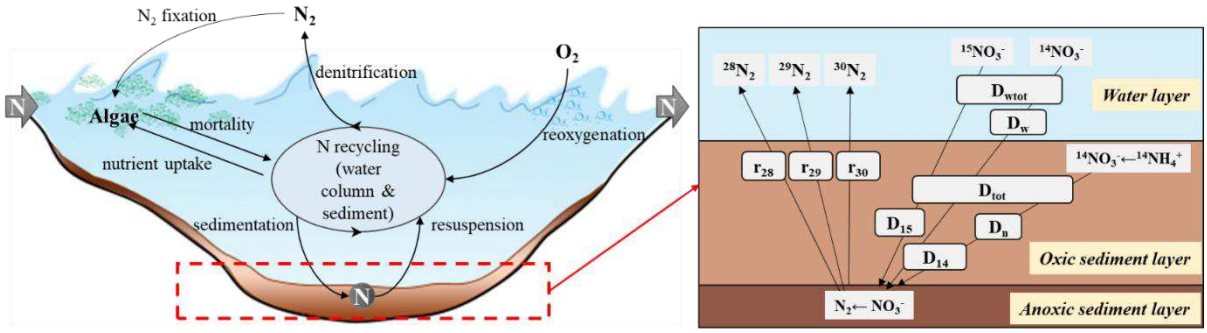

Fig. 2. Schematic representation of the nitrogen cycle (A) and the transformation rates during a $^{15}NO_3^-$ tracer experiment (B) in shallow lakes (Steingruber et al., 2001; Qin et al., 2020). r_{28}, r_{29}, and r_{30} are the release rates of $^{28}N_2$, $^{29}N_2$, and $^{30}N_2$, respectively. D_{wtot} is the total uncoupled denitrification rate using nitrate from the water column. D_w refers to the denitrification rate of nitrate from the water column without tracer addition. D_n is the coupled denitrification rate using nitrate from the sediment. D_{15} and D_{14} are the denitrification rates of $^{15}NO_3^-$ and $^{14}NO_3^-$, respectively. D_{tot} is the total denitrification during the incubation experiment.

3 Results and discussion

3.1 Basic physicochemical parameters of the lake water and sediment

The basic physicochemical parameters of the lake water and sediment at the sampling sites are shown in Table 1. As for the lake water observation, the pH and water temperature of the five sampling sites were approximately 8 and 25°C, respectively. The dissolved oxygen of s1, and s2 was higher than that of s3, s4, and s5, but the electrical conductivity was evidently lower than that of s3, s4, and s5. In terms of sediment, the average sediment water content of s1, and s2 was nearly 64.35%, and that of the s3, s4, and s5 was approximately 50.24%. The difference in the sediment water content was not significant. However, the loss on ignition of s3, s4, and s5 was approximately eight times that of s1, and s2 because of the presence of more aquatic plants in the east of Lake Taihu (Ticha et al., 2019).

Table 1

Mean values of basic physicochemical parameters of lake water and sediment (the basic physicochemical parameters of lake water were measured at the sampling sites and those of sediment were determined in laboratory; all samples, n=3).

Site	Lake water				Sediment	
	pH	Water temperature (°C)	Dissolved oxygen ($mg \cdot L^{-1}$)	Electrical conductivity ($ms \cdot cm^{-1}$)	Water content (%)	Loss on ignition (%)
s1	7.55	24.5	8.59	0.30	61.72	1.76
s2	7.79	24.9	9.07	0.37	66.97	1.67
s3	8.91	25.6	7.39	0.59	49.30	14.88
s4	8.46	25.1	6.39	0.59	58.32	10.17
s5	8.58	25.0	7.09	0.52	43.09	16.32

3.2 Denitrification rates and construction of Arrhenius equation

The potential N_2 production and denitrification rates of the five sites at 25°C were determined by ^{15}N isotope incubation experiments with MIMS. The results indicated that the denitrification rate had a decreasing trend in the west to the east direction in Lake Taihu. The potential $^{29}N_2$ rates were higher than the $^{30}N_2$ rates at five sites (Fig. 3 A). The r_{29} of site s1 ranked first, r_{29} of s2 and s3 equally ranked second, and r_{29} of s5 was only half that of s1. The r_{30} of s3 was 23.01 μmol·m^{-2}·h^{-1}, second only to s2, and r_{30} of s4 was the smallest (7.54 μmol·m^{-2}·h^{-1}). The order of D_{tot} was the same as that of r_{29}, and the D_{tot} of s1 was 177.39 μmol·m^{-2}·h^{-1} (Fig. 3 B). Except for s4 and s5, the D_{wtot} of the other sites was more than 100μmol·m^{-2}·h^{-1}.

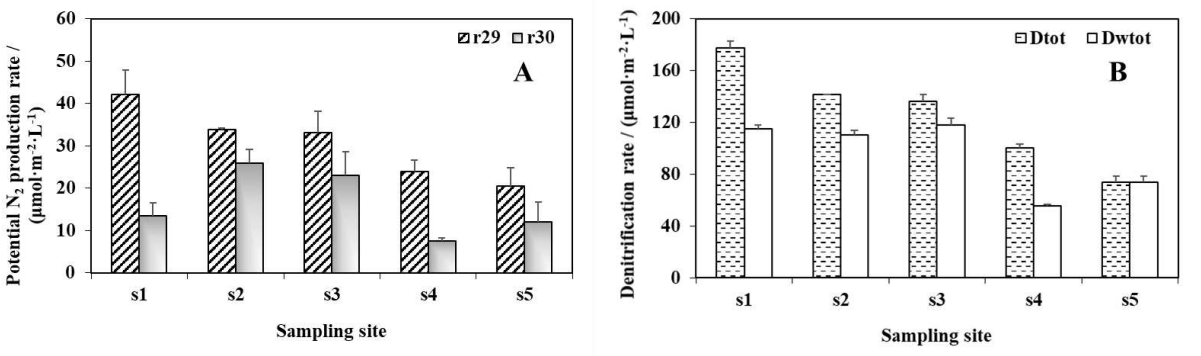

Fig. 3. Potential N_2 production (A) and denitrification rates (B) at five sampling sites (water temperature=25°C; all samples, *n*=3). r_{29} and r_{30} are the potential production of $^{29}N_2$ and $^{30}N_2$, respectively. D_{tot} is the total denitrification during the incubation experiment. D_{wtot} is the total denitrification rate of nitrate from the water column in the sediment.

For the purpose of exploring the reason why the total denitrification rate decreases from west to East, the concentrations of NO_2^-, NO_3^-, NH_4^+ and TN in the water at each sampling point of Taihu Lake were detected and analyzed. The concentration of NO_3^- in Lake Taihu was significantly higher than the concentration of NO_2^- and NH_4^+ (Fig. 4), and showed the same distinct regional differences as D_{tot},

decreasing from west to east.

For further study, the correlation between the total denitrification rate and the concentration of nitrogen compounds in Taihu Lake was analyzed by SPSS statistical software. The statistical results indicated that there was a more significant positive correlation between NO_3^- and D_{tot} (Table 2). And the reason for the spatial distribution of NO_3^- in Taihu Lake is that the western region of Taihu Lake Basin is the main source of pollutants in Taihu Lake, and the eastern region is the drainage area with good water quality (Zhang, 2021).

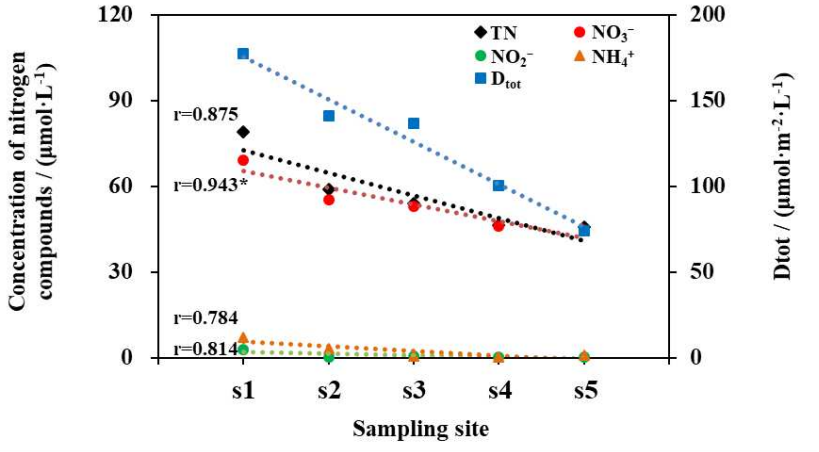

Fig. 4. Concentration of nitrogen compounds and D_{tot} at the five sampling sites (water temperature=25°C; all samples, *n*=3). r is Pearson correlation coefficient between D_{tot} and nitrogen compound (*. P<0.05, significant correlation). D_{tot} is the total denitrification rate during the incubation experiment.

In addition, experiments on the effect of water temperature on denitrification were carried out at s1, s2, s3 and s4 points. The results showed that water temperature had a significant effect on denitrification. Specifically, the D_{tot} and D_{wtot} increased with an increase in water temperature when the water temperature ranged from 25°C to 30°C (Fig. 5). The findings of this study were consistent with those of Ma et al. (2008) and Appelboom et al. (2010) on the relationship between water temperature and

denitrification. This was mainly due to denitrification reaction could completely take place when the water temperature was between 10°C and 30°C (Liao et al., 2018), and the increase of water temperature would reduce the solubility of oxygen in the water under the appropriate water temperature (Veraart et al., 2011; Zhao et al., 2011) (Table 1). In addition, high temperatures also tended to promote respiration instead of photosynthesis (Minuti et al., 2021), which further reduces dissolved oxygen. As an anaerobic reaction, denitrification was enhanced when the concentration of dissolved oxygen in water decreased.

High water temperature not only affects the dissolved oxygen in the water column, but also favors release of nutrients by stimulating microbial mineralization of sediment organic matter, which could increase pore−water nutrient concentrations, or could erode the oxidized microzone at the sediment−water interface by increasing oxygen demand (Holdren and Armstrong, 1980; Jiang et al., 2008; Gebremariam et al., 2021; Wang et al., 2021). Thus, the concentration of the substrate increases and denitrification is promoted, until the nitrate concentration is saturated (Silvennoinen et al., 2008).

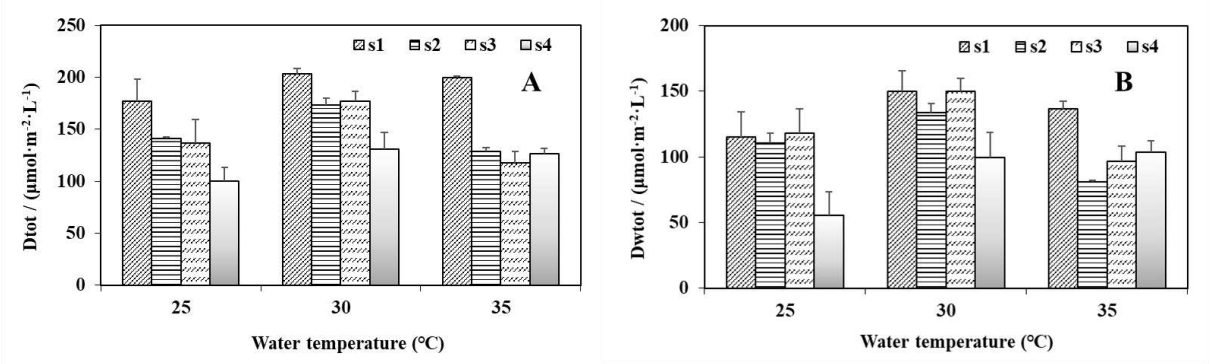

Fig. 5. D_{tot} (A) and D_{wtot} (B) rates of s1, s2, s3, and s4 at different water temperatures (all samples, n=3). D_{tot} is the total denitrificationduring the incubation experiment. D_{wtot} is the total denitrification rate of nitrate from the water column in the sediment.

On the other hand, temperature has a significant influence on the growth of microorganisms (Perez-Rodriguez et al., 2017). It was obvious from Fig. 5 that when the water temperature exceeded 30°C, the

189 appropriate temperature(Liao et al., 2018), D_{tot} decreased with the increase of water temperature. Through
190 experiments, Wang et al. (2018) found a response to temperature variation, the microorganisms
191 community presented a little difference after a temperature shock, and the N_2 concentration at 34°C was
192 lower than that at 25°C during denitrification. Furthermore, it had been reported that the predominant
193 denitrifying microorganisms belong particularly to the phylum Proteobacteria, when the water
194 temperature was more than 34°C, the activity of the phylum Proteobacteria in Lake Taihu may decrease,
195 resulting in a decrease in the denitrification rates (Xiao et al., 2015; Zhang et al., 2017).

196 Denitrification rate and water temperature conform to Arrhenius equation (Kaspar, 1982; Chi et al.,
197 2004):

$$D_{tot} = D_{tot\,20℃} \times \theta^{(T-20℃)}, \quad (8)$$

198 where $D_{tot\,20℃}$ (μmol·m^{-2}·h^{-1}) is the total denitrification rate during the incubation experiment at
199 20°C, θ is the Arrhenius temperature coefficient during denitrification.

200 Based on the experimental results of denitrification rate in Taihu Lake under the condition of
201 sufficient carbon source, the denitrification Arrhenius equation considering the concentration of water
202 temperature can be preliminarily obtained through statistical analysis (Table 2).

Table 2

Denitrification Arrhenius equation for at each sampling site in Taihu Lake.

Sampling site	Denitrification Arrhenius equation
s1	D_{tot}=166.01×1.0278$^{(T-20℃)}$
s2	D_{tot}=128.23×1.0418$^{(T-20℃)}$
s3	D_{tot}=120.94×1.0532$^{(T-20℃)}$
s4	D_{tot}=88.75×1.0546$^{(T-20℃)}$

3.3 Nitrate source identification of denitrification

As can be seen from Fig. 2 that the total denitrification rate (D_{tot}) was the sum of coupled denitrification rate rate using nitrate from the water column (D_n) and total uncoupled denitrification rate using nitrate from the sediment (D_{wtot}) (Svensson et al., 2001). Therefore, the ratio of D_{wtot} to D_{tot} (γ) can be expressed as:

$$\gamma = \frac{D_{wtot}}{D_{tot}} = \frac{D_{wtot}}{D_{wtot} + D_n}, \quad (9)$$

According to formula (9), if $\gamma > 0.5$, it meant that $D_{wtot} > D_n$, which indicates that the nitrate used for denitrification mainly came from water.

Based on D_{wtot} and D_{tot} of each sampling site, the γ was obtained. It was evident that the γ of the five sampling sites were above 0.5, as illustrated in Fig. 6, which showed that the denitrification at the Lake Taihu sediment–water interface primarily occurred at the expense of NO_3^- from the water column. Besides, when the water temperature rose from 25°C to 30°C, the γ increased slightly with the increase in water temperature, and the increase in s2 and s3 was relatively smaller. When the water

temperature approached 35°C, the response γ at each sampling site was inconsistent, but NO_3^- from the water column was still the main nitrate source of denitrification. In conclusion, the denitrification in the sediment−water interface mainly occurred at the expense of NO_3^- from the water column, and it was less affected by water temperature.

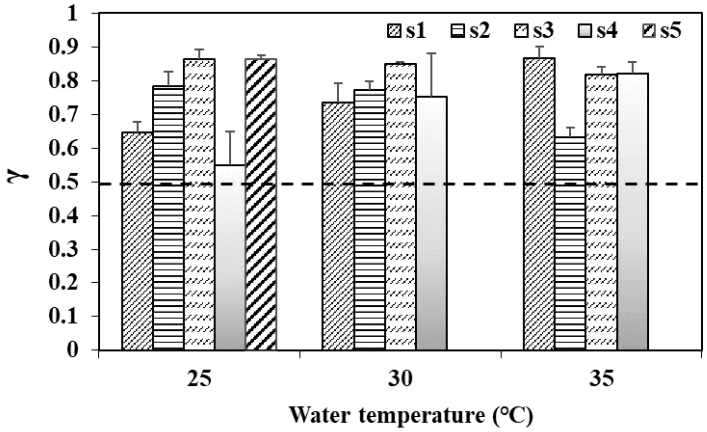

Fig. 6. Results of the ratios of D_{wtot} to D_{tot} (γ) in incubation experiments at the sites s1, s2, s3, s4, and s5. D_{tot} is the total denitrification during the incubation experiment. D_{wtot} is the total uncoupled denitrification rate using nitrate from the water column.

3.4 Practical implications of denitrification in shallow eutrophic lakes

Due to human activities, such as large-scale synthetic ammonia and large-scale application of chemical fertilizer, a large amount of exogenous nitrogen enters Taihu Lake, resulting in cyanobacteria bloom and threatening human drinking water and ecological security (Li et al., 2013). And denitrification is considered to be the main biological pathway of nitrogen removal, which is of great significance to reduce Lake nitrogen pollution and eutrophication control (Richardson et al., 2004).

Moreover, the algal−bacteria system in the water column can form an important niche that favors denitrification during cyanobacteria blooms (Chen et al., 2016; Chen et al., 2018). In general, the life of

algae is primarily divided into growth and decline periods, and then algae subsides to the bottom of the lake. During the growth period, the oxygen produced by photosynthesis of algae provides an aerobic environment for the nitrifying bacteria attached to the cell mass. This can promote the nitrification of nitrifying bacteria to produce NO_3^-, the substrate for denitrification (Liu et al., 2019). During the decline period, algae are gradually degraded into low molecular weight organic acids (directly available organic carbon) that can be used by denitrifying bacteria (Li et al., 2013).

In general, the concentration of TN in water can characterize the effect of nitrogen removal when the external pollution source is certain. From 2003 to 2006, Lake Taihu maintained a high TN concentration, resulting in cyanobacteria blooms in 2007, following which the Cyanobacteria died and were accumulated as sediments. According to the monitoring data, the TN concentration in Lake Taihu gradually decreased from 2008 to 2018 (Fig.1 B). And this further proves that algae contribute to the denitrification during the decay period.

Therefore, the study of denitrification in various regions of Taihu Lake can deepen the understanding of nitrogen cycle process in Taihu Lake and contribute to the effective development of water environment and eutrophication control in Taihu Lake.

4 Conclusions

In the present study, the effect of water temperature on denitrification was analyzed by ^{15}N isotope incubation experiments, and the nitrate source of denitrification in Lake Taihu sediment was identified. The results indicated that the denitrification rate showed a decreasing trend in the west to east direction in Lake Taihu. When the water temperature was lower than 30°C, the rates of the potential N_2 production and denitrification were higher with an increase in water temperature, but when the water temperature

was overhigh, denitrification was inhibited. And the NO_3^- from the water column was the main nitrate source of denitrification according to the ratio of D_{wtot} to D_{tot}. These findings, and denitrification Arrhenius equations considering water temperature, and further research on denitrification can play an important role in improving the water quality of Lake Taihu, and bear significance for the water environment treatment of other shallow eutrophic lakes in China and globally.

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.

Credit Author Statement

Qiuxia Ma: Investigation, Formal analysis, Writing—original draft preparation, Writing—review and editing, Visualization

Min Pang: Conceptualization, Methodology, Resources, Supervision

Yong Pang: Conceptualization, Resources, Data Curation

Lu Zhang: Methodology, Data Curation

Zhilin Huang: Investigation, Data Curation

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