Nitrous oxide emissions from a waterbody in the Nenjiang basin, China

Qiao-Qi Sun, Charlotte Whitham, Kun Shi, Guo-Hai Yu and Xiao-Wei Sun

ABSTRACT

Using static, closed chambers and gas chromatography techniques, nitrous oxide (N_2O) emissions have been monitored for 1 year (2009–2010) on an inland running waterbody downstream of the Nenjiang basin, China. During the freezing period, holes were dug in the ice in order to obtain nitrous oxide samples. Here, we have focused on water-air gas exchange and factors which might influence N_2O emissions and flux. Initial results indicate: (1) N_2O flux rates reach peak emission in January and the annual emissions of N_2O were low, being estimated at $0.35 \pm 0.20\ \mu g m^{-2} h^{-1}$; significant seasonal differences only appeared between January and July; (2) N_2O flux rates have strong regularity and ice has been the main barrier to nitrous oxide release during winter; (3) 24-hour monitoring revealed that N_2O flux remained steady during 9:00–17:00; (4) N_2O emissions have significant relationships with ammonium nitrogen and total phosphorus concentrations in water ($r = 0.4467$, $p = 0.020$ and $r = 0.4793$, $p = 0.011$, respectively). The N_2O flux released from the waterbody is determined by the chemical concentrations in the water. Following these results, we suggest that moderate use of N and P fertilizer at intensive agricultural areas will be beneficial in decreasing greenhouse gas emissions from this waterbody.

Key words | ammonium nitrogen, Nenjiang basin, nitrous oxide, riverine wetland, total phosphorus

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INTRODUCTION

Riverine wetlands include running water ecosystems, floodplains and many kinds of associated fauna and flora that play a significant role in hydrological dynamics (Junk *et al.* 1989; Bayley 1995). Running water ecosystems occupy only a portion of the world's freshwater, but are important for the benefits they provide for human beings, through human settlement, irrigation, water supplies, electricity generation and waste disposal, to name some examples. However, some natural functions have been hindered as a result of man-made infrastructures. For instance, the building of dams and reservoirs has been known to destroy flooding rhythms and frequencies within such ecosystems (Malmqvist & Rundle 2002).

Carbon dioxide, methane and nitrous oxide are considered to be three kinds of greenhouse gas that currently cause global warming, and nitrous oxide has a more serious greenhouse effect of almost 300 times that compared with carbon dioxide (IPCC 2007). It also acts as a catalyst in the stratosphere for the destruction of ozone (Cicerone 1987). Denitrification is often considered as the main removal process of N and is an important factor contributing to the release of greenhouse gases (Hefting *et al.* 2003). Freshwater ecosystems including groundwater, lakes and rivers, account for nearly 20% of total global denitrification (Seitzinger *et al.* 2006). There is much evidence to indicate that nitrous oxide released at a speed of 2.8–4.3 Tg N yr^{-1} into the atmosphere, has increased in recent decades (Nevison *et al.* 1995), and Mosier (1998) detected a N_2O release rate of 0.3% per year to the atmosphere from soil processes in particular (Mosier 1998). As a result of human activities, one third of global nitrous oxide emissions are released from aquatic ecosystems (Seitzinger *et al.* 2000). More than 80% comes from the Northern Hemisphere mid-latitude regions and 35% (1.9 Tg N yr^{-1}) of global nitrous oxide emissions

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come from rivers, estuaries and continental shelves (Seitzinger *et al.* 2000).

Some researchers have also investigated the key factors causing nitrous oxide release from aquatic ecosystems. Previous studies showed that dissolved inorganic nitrogen, oxygen concentration dynamics in water, water temperature, pH, ammonium concentrations and other factors, significantly affect nitrous oxide release (Seitzinger & Kroeze 1998; McMahon & Dennehy 1999; Dong *et al.* 2004; Garnier *et al.* 2006).

However, greenhouse gas emission research is seldom carried out in riverine wetlands, especially in high-intensity agricultural mid-latitude areas of China. Some results have demonstrated a relationship between riverine wetlands and methane or carbon dioxide (Nahlik & Mitsch 2010), although valuable studies are still lacking. Worse still, the effects of human activities on riverine wetlands (riparian ecosystems, floodplains and running waterbodies) in China are quite substantial, as a result of agriculture for example, further highlighting the need for this type of research. An investigation by Liu *et al.* concluded that total N inputs caused by human activities increased by 11.12 Tg N from 1980 to 2000 in the Yangtze River basin (Liu *et al.* 2008). Furthermore, riverine N export tripled and atmospheric pollutants increased by 2.5 times within the Greater Hangzhou Area of southeastern China from 1980–2004 (Gu *et al.* 2011). Amounts of inorganic N compounds like fertilizer, herbicides, pesticides, dairy effluents or industrial waste disposal for example, are also being heavily used in these areas (Galloway *et al.* 2008).

Taking global warming efficiency and its substantial effect on ozone layer into account, it is important for us to calculate greenhouse gas emissions from inland rivers, particularly when such studies are not so numerous. This research aims to address the following questions: (1) What are the seasonal and diel variations in N_2O flux rates in a inland running waterbody ecosystem? (2) What are the relationships between N_2O emissions and the physical and chemical parameters of water from the Nenjiang basin? Based on these questions, data were collected for 1 year (2009–2010) and after analysis, we have outlined the temporal dynamics of N_2O emissions and discussed which main factors drive greenhouse gas release. According to our results, suggestions are also provided for future river basin protection and management strategies.

MATERIALS AND METHODS

Site description and experimental design

The research area was located downstream of Nenjiang basin, northeast China. The river acts as a boundary between Jilin and Heilongjiang provinces and also provides one edge of the MoMoge Nature Reserve. It is located on the Songnen-plain, which has mainly been a grain-producing area. The basin here represents an inland running water ecosystem and is situated at mid-latitude temperate zones, which differs from other tropical research sites such as those in the Amazon basin. The site here has obvious seasonality, with the lowest (January) and highest (July) temperatures measured at −16.7 and 23.7 °C (from 1971–2000 average data), respectively; average annual temperatures reach only 5.9 °C (from 1971–2000 average data). The total annual precipitation is 402.4 mm, and varies monthly (range = 1.2–133.4 mm) (from 1971–2000 average data). All the meteorological data come from a local meteorological station located at Zhenlai, in the southern part of Jilin province. We also calculated the average water height over 50 years until present, using data collected from a local hydrological station (Figure 1).

The experiment sites were chosen close to the MoMoge Nature Reserve so that strong human disturbance could be avoided. We selected two sites (45°53′58″N, 123°59′55″E and 45°57′59″N, 123°57′35″E) along the river, where Site 2 was relatively higher upstream compared with Site 1. In order to keep the equipment floating on the river, the static chambers used for gas sampling were set up further than 3m away from the riparian habitat. Three static chambers were used at each site so that readings could be tripled. Static chambers were positioned 15m apart, to prevent any mutual interference when operated or when N_2O emissions were monitored.

Nitrous oxide flux measurements and analysis

A floating static chamber was used for gas sampling on the river. Its construction mainly consisted of a tyre-base with a cylindrical metal chamber inside (of radius 50 cm and height 65 cm). The chamber inside contained two exhaust

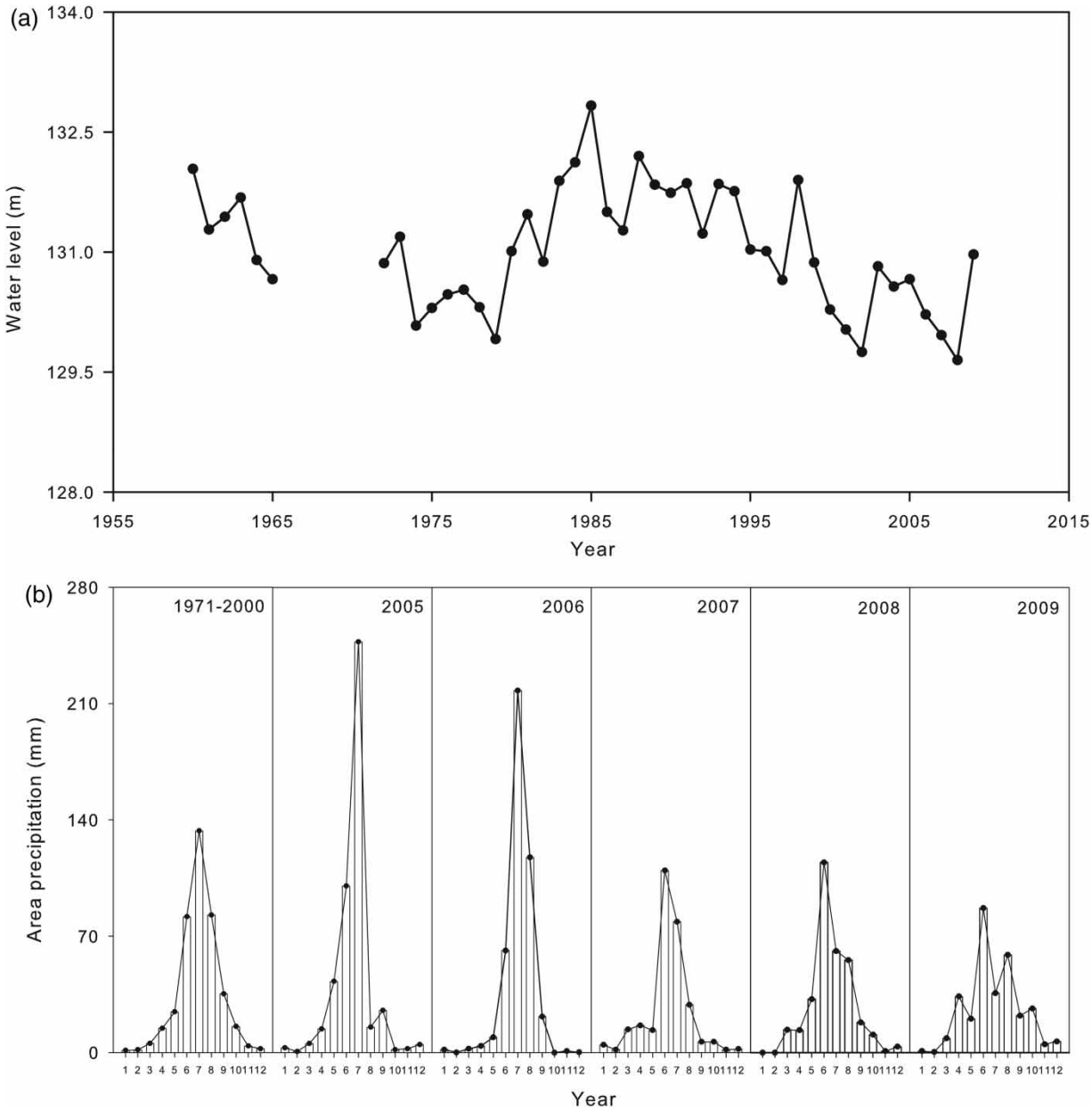

Figure 1 | Dynamics of (a) water levels and (b) area precipitation according to year variables.

fans, a thermometer and a tube. The chamber was covered with aluminum foil, which can easily reflect heat from sunlight to prevent the inside temperature increasing too quickly or becoming too high (Sovik & Klove 2007). A syringe was used to collect gas samples at intervals of 0, 10, 20 and 30 minutes, and thereafter, gas samples were instantly transferred to vacuum bags (Zhang *et al.* 2005). Samples in the seasonal survey (a total of five sampling periods covering autumn, winter and summer) were taken during the period 9:00–11:00 am. For 24-hour monitoring, samples were taken every 3 hours in 1 day in June (total eight times per day). The same procedure was carried out during the freezing period, but because the downstream section of the Nenjiang basin was frozen, holes were dug in the ice in order to place the floating chambers. All gas samples were analyzed within 1 week after collection. N_2O

concentration flux was detected by Agilent7890A gas chromatography and was calculated using the following formula:

$$F = \frac{M}{V_0}\frac{P}{P_0}\frac{T_0}{T}H\frac{dc}{dt}$$

where F is gas flux ($\mu g\ m^{-2}\ h^{-1}$); M is the molar mass; P_0 and T_0 are standard conditions of pressure and temperature (1,013.25 hpa, 273.15 K) for gases; V_0 is the standard state of molar volume ($22.4\ L\ mol^{-1}$); H is the height of the chamber, P and T are actual pressure and temperature during sampling; and dc/dt is the slope of the regression curve as gas concentration variables respond to time.

Water parameter monitoring and analysis

Before each gas sample was taken, and from both sites, water samples were taken downstream of the Nenjiang basin. At each research site we gathered water samples and immediately in the field, recorded the pH and redox potential. Other indicators, such as TP, NO_3-N, NH_4-N concentrations were measured the same day, after leaving the field. All indicators were detected by Lovibond ET99722 and ET7902A, with related reagents.

Statistical analysis

One-way analysis of variance (ANOVA) with Duncan test was used to evaluate differences in N_2O flux rates in the Nenjiang basin. Spearman rank correlation analysis was used to identify relationships between greenhouse gas emissions and other variables of the river. All statistical analyses were carried out in the PASW Statistics 18.0 (2009) and all charts were made using SigmaPlot 11.0 software. Significance was examined at $\alpha = 0.05$.

RESULTS AND DISCUSSION

Temporal and diel variation of nitrous oxide flux

During the different sampling periods, N_2O emissions were monitored at the two sites (Figure 2). The highest N_2O emissions were reached in winter (January 2010) and lowest in summer (July 2010). Considering measures for the whole year, significant differences were only found between January and July, where N_2O flux had a mean of 1.247 ± 0.542 and $-0.770 \pm 2.561\ \mu g\ N\ m^{-2}\ h^{-1}$, respectively, indicating that the river functioned as a N_2O sink during the summer

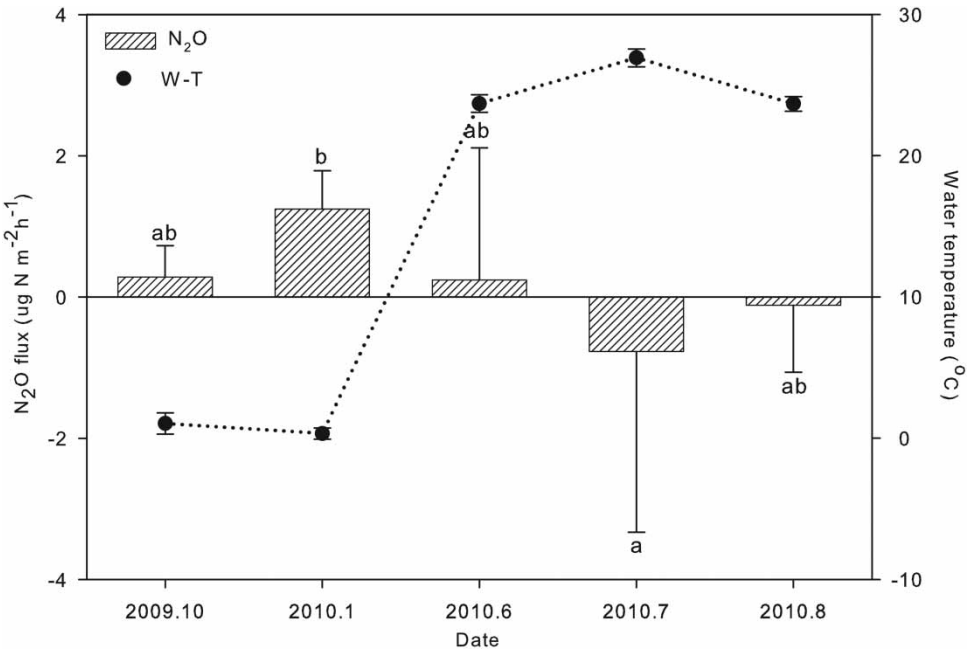

Figure 2 | N_2O flux and water temperature dynamics of Nenjing basin (W–T = water temperature, °C).

and a source during winter (Figure 2). Over the whole year, N_2O emissions appear to have a tendency to fluctuate smoothly, giving Figure 2 its smooth sigmoidal shape. However, we cannot be certain about this relationship because unfortunately it was not possible to collect data during the spring months. We also added water temperature dynamics data to the chart of N_2O emissions to view any potential relation between them. The annual, average N_2O flux was 0.35 ± 0.20 μg N m^{-2} h^{-1} ($n = 27$) compared with results taken close to riparian zones in Tennessee, USA, which were 0.28 μg N m^{-2} h^{-1} (Walker *et al.* 2002).

The diel variation measurements of N_2O flux were executed in June 2010 (Figure 3). N_2O was emitted at a stable rate from the two sites implying that there were no significant fluctuations during the 08:00–17:00 period, in comparison to the results obtained from the fresh marshes in northeast China (Yu *et al.* 2010), that showed strong diel fluctuations. The N_2O diel flux for the whole day was fairly stable for Site 2. Site 1, however, showed more erratic fluctuations, particularly in the evening (20:00) and early in the morning (05:00).

Wetland ecosystems can be carbon sinks or sources, and this mainly depends on wetland age, development framework, and more so on environmental factors such as location and climate diversity (Kayranli *et al.* 2010). The N_2O flux is mainly driven by denitrification and concentrations diffused in the waterbody tend to move through the river bottom sediment–water interface and are released to the atmosphere through the gas–water interface (Wang *et al.* 2009). The N_2O concentrations fluctuate strongly and significantly when accompanied with dynamic environmental factors as shown by our investigation. We monitored N_2O flux along a temporal scale and results showed that the average annual emission was 0.35 ± 0.20 μg N m^{-2} h^{-1}, a weak source to the atmosphere. The flux rate measured in January was the highest efflux and may have been caused by N_2O being released after the ice layer was removed. We dug holes for collecting gas samples during the freezing period to maintain the same experimental procedures, and possibly that lead to the emissions being released immediately. The results demonstrated that low temperature and presence of a frozen layer would not restrict N_2O production in the water. Instead, the ice layer simply stopped the greenhouse gas being released into the atmosphere. We can be sure of this function of the ice layer when we compare greenhouse gas release between October and January: water temperature tested similar in both months, but there was no frozen layer present in

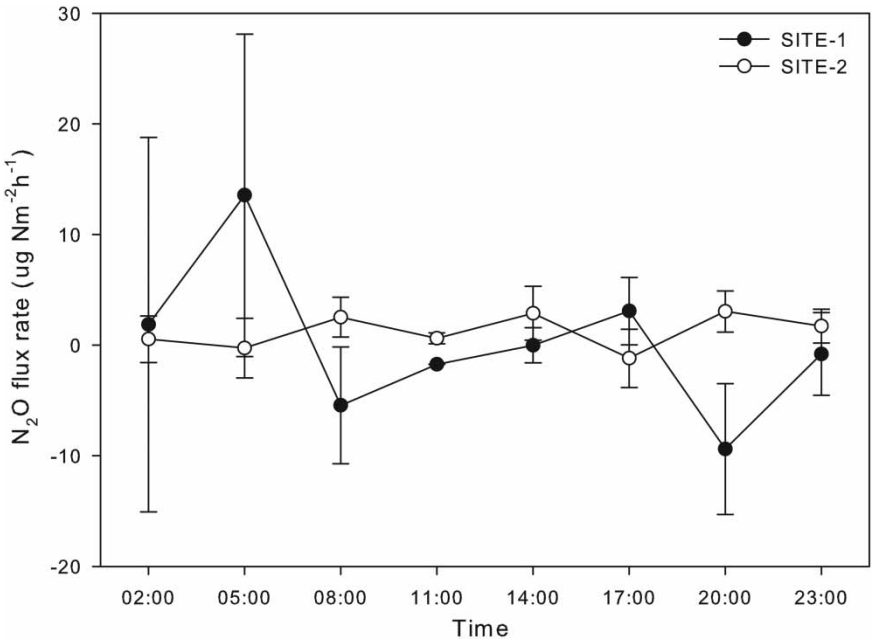

Figure 3 | Summer (June) diel variation of N_2O flux from two sites in Nenjiang basin.

October. Previous research monitored N_2O flux in marshlands during vegetation growing and non-growing seasons and found that the thaw of the frozen layer led to a significantly rapid increase in N_2O flux (Sun *et al.* 2009). Similarly, Silvennoinen *et al.* (2008) found a difference between N_2O release from frozen and unfrozen parts of the eutrophic Temmesjoki River. Samples were not obtained during freeze-thaw period (March–April), however, we can predict that the N_2O flux would have reached the apex of the whole year during this time, although this hypothesis needs to be tested in future investigations.

The measurements for diel variation of nitrous oxide during the 08:00–17:00 period did not show a strong fluctuation in N_2O emission. Combining this temporal data with water temperature measurements, we confirmed in this research and subsequent analyses that N_2O flux had little correlation with water temperature dynamics. This conclusion resembles that of researchers Mander *et al.* (2005) that in constructed wetlands and riparian buffer zones, N_2O flux had no significant correlation with air temperature and water temperature. Frozen environment and water temperature change therefore did not strongly influence enzyme activity and function in the water and denitrification processes for N_2O flux generation.

Variation of nitrous flux and affecting factors

The research also detected physical and chemical indicators including pH, water temperature and nitrate nitrogen (NO_3-N), ammonium nitrogen (NH_4-N) and total phosphorus (TP) concentrations in the Nenjiang basin (Table 1). Relationships between N_2O flux and some indicators have been found during the analysis (Figure 4): The N_2O flux has significant positive correlations with NH_4-N concentrations ($r = 0.4467$, $p = 0.020$, $n = 27$) and TP concentrations ($r = 0.4793$, $p = 0.011$, $n = 27$). Meanwhile, no significant correlations with water temperature were observed ($p = 0.075$, $n = 27$), as illustrated above.

Many factors might affect N_2O flux release in estuarine wetlands (Dong *et al.* 2004). Dissolved oxygen and nitrogen concentrations in the catchment show seasonal dynamics that could mainly determine microorganism biochemical processes, and induce differences in N_2O emission patterns, according to the results produced by Farias & Cornejo (2007). Denitrification microorganisms have a strong impact on N_2O generation under anaerobic environments, that would turn nitrogen compounds into N_2 and N_2O flux (Teixeira *et al.* 2010). We found in the Nenjiang basin the N_2O flux did not only relate to ammonium, but also to total phosphorus concentrations – there were significant positive correlations between them. Wang *et al.* (2009) showed N_2O fluxes were negatively correlated with water salinity but significantly positively correlated with nitrate, in one river of the Yangtze Delta (Wang *et al.* 2009). We also pointed out the significant correlation between TP and two kinds of inorganic nitrogen, but trends differ. One trend showed a positive correlation between TP and NH_4-N concentrations, the other showed a negative correlation

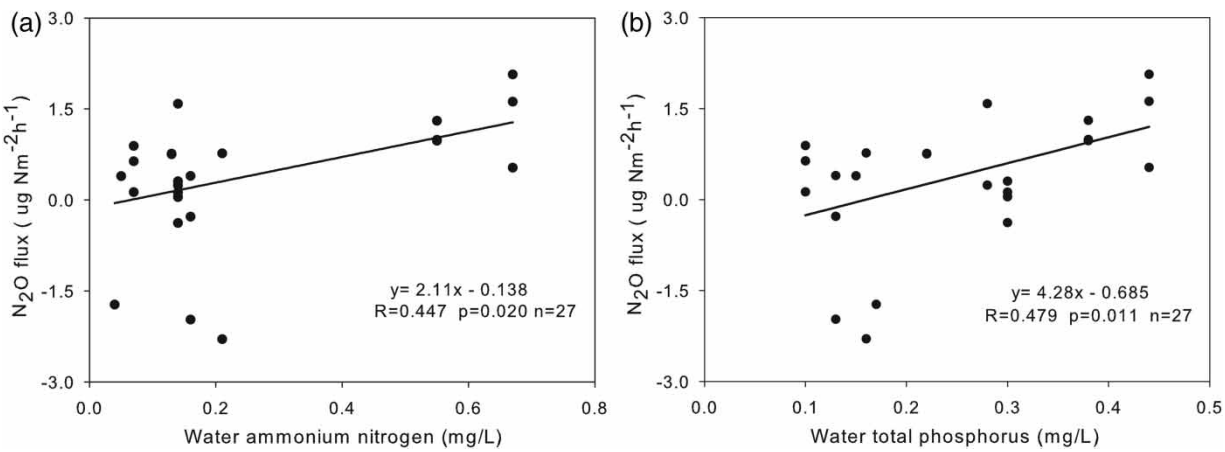

Figure 4 | The relationship between N_2O flux and concentrations of ammonium nitrogen (a) and total phosphorus (b) in Nenjiang basin.

between TP and NO_3-N concentrations. The TP concentrations appear to be regulating these chemical processes.

CONCLUSIONS

The interpreted relationship between N_2O fluxes and chemical parameters of water showed that ammonium nitrogen and total phosphorus concentrations have strong impacts on N_2O production in this waterbody. Also, as total phosphorus appears to be regulating concentrations of different kinds of inorganic nitrogen, it could be said to play a key role in the process of greenhouse gas production.

Meanwhile, low temperature does not significantly affect N_2O production in the hydrosphere and release to the atmosphere. On the contrary, the ice-layer interferes with the exchange of greenhouse gases between the water and the atmosphere. For future research, we suggest both simulated experiments under laboratory conditions and field monitoring to be carried out to explain the microbial process of N_2O production in low temperate and freeze-thaw environments. The period of freeze-thaw after the ice-layer disappeared will be a key phase during the whole year of the N_2O emission release. We need to pay attention to such important periods in order to evaluate greenhouse gas emissions accurately over a temporal scale. For example, a longer temporal scale or monitoring in different months could be used in later studies to improve the accuracy of these results.

In China, riverine floodplains or riparian habitats are normally situated downstream of rivers, and are mainly used as agricultural or pasture areas, and also are often home to large human populations. As well as being important for people's livelihoods, we have also mentioned their significance in terms of being a large source of global nitrous oxide emissions – 35% ($1.9\ Tg\ N\ yr^{-1}$) of global nitrous oxide emissions come from rivers, estuaries and continental shelves (Seitzinger *et al.* 2000) and hence the relevance of this study. In our research, additional inorganic N and P input to the river directly or indirectly has been found to affect N_2O production and dynamics, and such additions of these compounds are mainly caused by human activities. Consequently, efforts should be made to reduce emissions through decreasing the use of nitrogen and phosphorus compounds, by using suitable amounts and types of fertilizer and also by adapting to more responsible farming practices.

This study has shed some light on the patterns and potential drivers of nitrous oxide flux in an inland running waterbody, and has hopefully contributed to the limited literature in this specific field and location. However, many more theories and hypotheses should be tested for later work that together with practical advice can help formulate sound recommendations for river basin management.

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