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Spatiotemporal variations of nitrous oxide (N_2O) emissions from two reservoirs in SW China

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ABSTRACT

Greenhouse gas emissions from hydroelectric dams have recently given rise to controversies about whether hydropower still provides clean energy. China has a large number of dams used for energy supply and irrigation, but few studies have been carried out on aquatic nitrous oxide (N_2O) variation and its emissions in Chinese river-reservoir systems. In this study, N_2O spatiotemporal variations were investigated monthly in two reservoirs along the Wujiang River, Southwest China, and the emission fluxes of N_2O were estimated. N_2O production in the reservoirs tended to be dominated by nitrification, according to the correlation between N_2O and other parameters. N_2O saturation in the surface water of the Wujiangdu reservoir ranged from 214% to 662%, with an average fluctuation of 388%, while in the Hongjiadu reservoir, it ranged from 201% to 484%, with an average fluctuation of 312%. The dissolved N_2O in both reservoirs was over-saturated with respect to atmospheric equilibrium levels, suggesting that the reservoirs were net sources of N_2O emissions to the atmosphere. The averaged N_2O emission flux in the Wujiangdu reservoir was 0.64 μmol m^{-2} h^{-1}, while it was 0.45 μmol m^{-2} h^{-1} in the Hongjiadu reservoir, indicating that these two reservoirs had moderate N_2O emission fluxes as compared to other lakes in the world. Downstream water of the dams had quite high levels of N_2O saturation, and the estimated annual N_2O emissions from hydropower generation were 3.60×10^5 and 2.15×10^5 mol N_2O for the Wujiangdu and the Hongjiadu reservoir, respectively. These fluxes were similar to the total N_2O emissions from the reservoir surfaces, suggesting that water released from reservoirs would be another important way for N_2O to diffuse into the atmosphere. It can be concluded that dam construction significantly changes the water environment, especially in terms of nutrient status and physicochemical conditions, which have obvious influences on the N_2O spatiotemporal variations and emissions.

1. Introduction

Because nitrous oxide (N_2O) contributes to global warming and stratospheric ozone depletion, the increasing concentrations of N_2O in the atmosphere have received considerable attention (Houghton et al., 2001; Ravishankara et al., 2009; Wuebbles, 2009). The current atmospheric N_2O concentration is about 319 ppbv, and this concentration has kept increasing steadily over the past century by approximately $0.25 \pm 0.05\%$ yr^{-1} (IPCC, 2007). N_2O is the third most important natural long-lived greenhouse gas, after CO_2 and CH_4, and the global warming potential (GWP) of N_2O is 296 times that of CO_2 (IPCC, 2007). Contributors to atmospheric N_2O include vehicles and industrial facilities (Becker et al., 1999), but most of the N_2O is released by natural environments such as soils (Bremner, 1997; Andersson et al., 2003), oceans (Hashimoto et al., 1999; Bange, 2006), estuaries (Dong et al., 2004), wetlands and marshes (Mander et al., 2003; Chen et al., 2010), rivers (García-Ruiz et al., 1999; McMahon and Dennehy, 1999; Stow et al., 2005; Garnier et al., 2009), reservoirs (Hendzel et al., 2005; Liu et al., 2011) and lakes (Wang et al., 2009; Chen et al., 2011). Soils are among the predominant sources of N_2O emissions (Houghton et al., 2001). Considerable efforts have been made to quantify N_2O emissions in terrestrial ecosystems; however, N_2O emission from aquatic systems has received less attention, despite the fact that aquatic systems are a globally significant source of N_2O that contributes 25–30% of the total emissions (Battle et al., 1996; IPCC, 2007).

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Currently, some N_2O fluxes have been documented from N-enriched rivers, estuaries and coastal water, as well as from freshwater lakes and reservoirs (McMahon and Dennehy, 1999; Cole and Caraco, 2001; Huttunen et al., 2003a,b; Beaulieu et al., 2009; Wang et al., 2009; Liu et al., 2011). These reports suggest that much of the N_2O emitted from aquatic ecosystems is derived anthropogenically. The increase in N loading by human activities can result in eutrophication and affect the exchange of N_2O between water and the atmosphere (Huttunen et al., 2003a). About one third of global terrestrial and aquatic N_2O emissions are considered to be anthropogenic (Seitzinger et al., 2000); however, there remains considerable uncertainty about the magnitude of anthropogenic N_2O emitted from aquatic ecosystems. China and Southeast Asia accounted for approximately 50% of the N_2O emissions from rivers, estuaries and continental shelves on the basis of dissolved inorganic N export by rivers around the world (Seitzinger and Kroeze, 1998). Relatively few direct studies have been conducted to evaluate N_2O emissions in freshwater environments such as the rivers, reservoirs and lakes of China. The eutrophic rivers, lakes and reservoirs may represent an important source of N_2O in China, which may indicate the presence of serious errors in the current estimation of regional N_2O emissions.

In fact, the importance of hydroelectric river-reservoir/lake systems in emitting or absorbing N_2O has been poorly investigated. In recent years, hydrological alterations associated with dam and reservoir development have seriously disturbed the terrestrial water cycle. Up until 1996, there were approximately 42,000 large dams in rivers worldwide (Rosenberg et al., 2000), and the number of the dams increased more rapidly during the last decade than it has previously. What is more, in order to better exploit the water resources, a series of hydropower dams were built in a single river, forming many reservoirs distributed from upstream to downstream. This became a typical landscape in China, which has the largest number of hydropower dams in the world. It is reported that there are presently over 40,000 reservoirs in operation in the Changjiang drainage basin in the subtropical region, but there are few reports regarding their N_2O emissions.

The potential for reservoirs to contribute substantial amounts of N_2O to the atmosphere is high, and higher average N_2O saturations have been observed in surface waters of eutrophic lakes than oligo- and meso-trophic lakes (Huttunen et al., 2003a; Mengis et al., 1997; Wang et al., 2009). As an intermediate form between natural lakes and rivers, reservoirs can be considered conceptualised continua of aquatic environments with regard to the environmental factors that control water quality and biological productivity. As a rule, reservoirs become eutrophic more quickly than natural lakes because they receive higher sediment and nutrient loads than lakes. At present, the effects of anthropogenic nutrients inputs on N_2O emissions in reservoirs are not understood thoroughly. Production of N_2O in aquatic environments is a by-product of two microbial processes: nitrification and denitrification, which are governed principally by temperature, pH, DO, inorganic N and the shift of the oxic–anoxic interface (Mengis et al., 1997; Hendzel et al., 2005; Stow et al., 2005; Garnier et al., 2006). Different factors will cause the spatiotemporal variations of N_2O in reservoirs, limiting the accurate assessment of N_2O emissions. This lack of understanding of circumstances may enhance or limit N_2O fluxes. The spatiotemporal variations of N_2O must be considered in defining relationships between N_2O emissions and major environmental influences. Then, N_2O emissions and their spatiotemporal variation in reservoirs, as well as the impact that hydroelectric reservoirs have on N_2O, became major concerns.

Consequently, this study focused on two reservoirs on Wujiang River in Southwest China, which belong to the Changjiang drainage basin and have the climate of subtropical zones. The main objective of this study are the following: (1) to examine the dissolved N_2O saturation in the reservoirs, then ascertain the N_2O spatiotemporal variations over a whole year; (2) to evaluate the emission fluxes of N_2O; and (3) to investigate the potential impacts of reservoirs on dissolved N_2O.

2. Materials and methods

2.1. Study site

The Wujiang River, which is one of the largest tributaries in the upstream portion of the Changjiang River Basin, mainly flows through a karst area in Guizhou Province, Southwest China (Fig. 1). The Wujiang River Basin is subject to a subtropical monsoon humid climate, and the perennial mean temperature in the basin is 14.8 °C. The multi-year average annual rainfall is about 1100 mm. There are widely developed formations along the Wujiang River catchment underlain by limestone, dolomitic limestone, and shale.

The Hongjiadu (HJD) and Wujiangdu (WJD) reservoirs are situated in the northwest and north of Guiyang, respectively; the former is in the upstream reaches of the Wujiang River, while the latter is in the midstream section of the river. The two reservoirs are closely connected and were constructed on the mainstream of Wujiang River in 2004 and 1979, respectively. Presently, the two reservoirs have different trophic statuses, providing excellent comparative conditions for research on dissolved N_2O.

The detailed characteristics of the two reservoirs are described in Table 1.

2.2. Sampling

Samples were collected monthly from July 2007 to June 2008 at two reservoirs along the Wujiang River, Hongjiadu reservoir (HJD; 26°53′N, 105°51′E) and Wujiangdu reservoir (WJD; 27°19′N, 106°46′E). The sampling stations are shown in Fig. 1. Sampling sites in the reservoirs were located in the central part of the river, generally 0.4–0.5 km before the dams. Samples downstream of the dams were collected 0.5 m under the water surface, while sampling along the water column was conducted at depths of 0.5 m, 5 m, 15 m, 30 m and 60 m in the reservoir using a Niskin bottle.

2.3. Environmental variables

Water temperature (T), dissolved oxygen (DO) and chlorophyll levels were measured *in situ* using an automated multi-parameter monitoring instrument (United States Gimcheon Instruments Inc. YSI 6600 v2). Water samples were filtered through 0.22 μm membrane filters (Millipore) and stored in −4 °C in the dark until analysed. The concentrations of NO_3^- were measured using an automatic flow analyser (SKALAR Sans Plus Systems). In addition, the TP was determined spectrophotometrically (Unico UV-2000) using the molybdenum blue method after alkaline potassium persulfate digestion. The TN was also analysed spectrophotometrically (Unico UV-2000) after alkaline potassium persulfate digestion.

2.4. N_2O measurement and fluxes calculation

For N_2O concentration measurements, water samples were collected in serum bottles and then amended with 10 mol L^{-1} sodium hydroxide (NaOH) as a preservative, after which the bottles were sealed with rubber stoppers. The headspace equilibrium technique was then used to determine the concentrations of dissolved gases (Mengis et al., 1997; Wang et al., 2009). Specifically, approximately 20 ml of ultra-pure N_2 was injected into the sample bottle to displace the water. The bottles were then vigorously

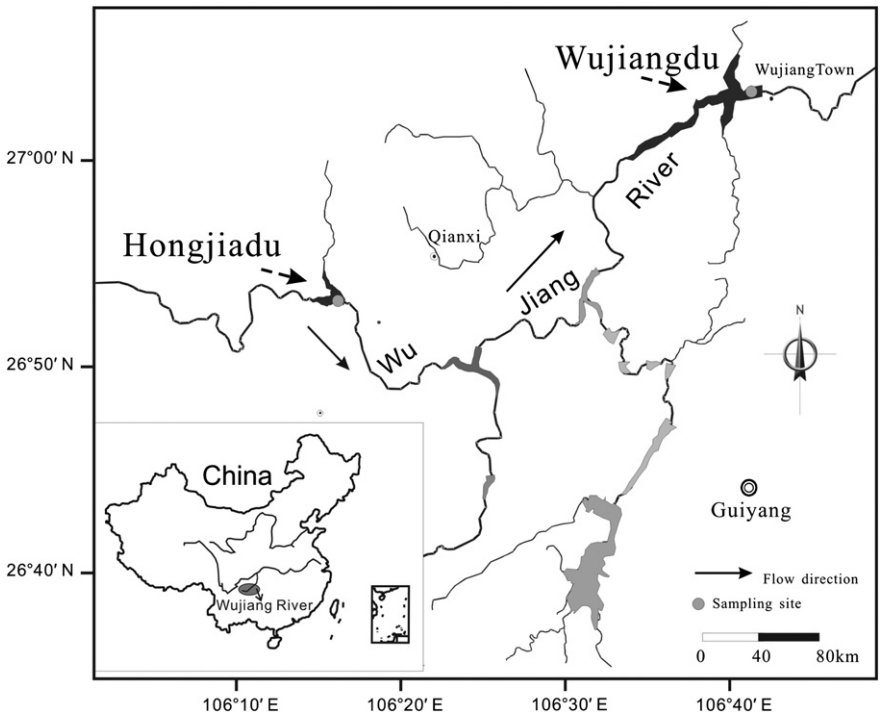

Fig. 1. Map showing the location of the HJD and WJD reservoirs in Wujiang River, also revealing the geographic relationship between two reservoirs.

shaken for 30 min in a water bath at 25 °C to allow samples to equilibrate. The N_2O concentrations in the headspace were subsequently analysed using an ECD-GC (HP6890) equipped with a packed Porapak Q (80/100 mesh) column (4.5 m × 3 mm). The column and ECD detector were conditioned at 50 °C and 320 °C, respectively. A mixture of Ar/CH_4 (95/5 v/v) was applied as the carrier gas at a flow rate of 20 ml min^{-1}. The formula described by Butler and Elkins (1991) was used to calculate the headspace gas concentrations, which were determined with a mean error of ±4%. The gas concentrations were expressed based on the degree of saturation relative to air (Mengis et al., 1997):

$$\text{Degree of } N_2O_{\text{saturation}} = C_{N_2O}/C_{N_2O\text{atm}} \times 100 \quad (1)$$

$$C_{N_2O\text{atm}} = K \times C_A \quad (2)$$

where C_{N_2O} is the measured concentration, $C_{N_2O\text{atm}}$ is the saturated concentration of N_2O in water at the given water temperature and C_A is the atmospheric N_2O concentration of the sampling sites. The saturated concentration of N_2O in water was calculated using Henry's Law, where K is the Bunsen coefficient.

The AOU (apparent oxygen utilization) and ΔN_2O were calculated as follows:

$$AOU = DO_{sat} - DO_{meas} \quad (3)$$

$$\Delta N_2O = C_{N_2O} - C_{N_2O\text{atm}} \quad (4)$$

where DO_{sat} is the saturation dissolved oxygen (DO) concentration in water and DO_{meas} is the measured concentration of DO.

The exchange flux of N_2O at the gas–water boundary layer of the surface water was calculated using the following:

$$F = K\Delta C = \frac{D}{Z}(C_s - C_{eq}) \quad (5)$$

$$D = 5.06 \times 10^{-9}\frac{T}{\eta V_b^{0.6}} \quad (6)$$

where F is the gas exchange flux, ΔC is the difference between the N_2O concentration in the air and water, K is the gas transfer velocity, D is the gas diffusion coefficient, which was calculated using Equation (6), obtained from Lerman (1979), η is the viscosity of the water, V_b is the molar volume of the gas, which was suggested to have a value of 36.4 cm^3 mol^{-1} (Satterfield, 1970) and Z is the thickness of the boundary layer, which is an empirical constant related to wind speed (Emerson, 1975). Taking into account the variations in wind speed during each sampling month, Z was estimated to have a value between 180 and 570 μm.

2.5. Statistical analysis

Statistical analysis was conducted using SPSS Statistics 17.0.0, Grapher 7.0 and Microsoft Excel based on Windows XP. In all

Table 1
The characteristics of the studied reservoirs in Wujiang River.

Reservoirs	Drainage area (km^2)	Height of dam (m)	Normal level/dead storage level (m)	Total volume (10^8 m^3)	Water surface area (km^2)	Time of construction	Storage capacity
Hongjiadu	9900	182	1140/1076	49.25	80.5	2004	Over year regulation
Wujiangdu	27790	165	760/720	21.40	47.8	1979	Seasonally regulation

analyses where $p < 0.05$, the factor and the relationship tested were considered statistically significant.

3. Results

3.1. Trophic conditions and environmental variables

Results for total nitrogen (TN), total phosphorous (TP), chlorophyll and dissolved oxygen concentrations are listed in Table 2. During the entire sampling year, TN ranged from 3.44 to 5.42 mg L^{-1} in HJD and 2.66 to 4.34 mg L^{-1} in WJD. Even though WJD had less TN than HJD, both reservoirs maintained high concentrations, which were even higher than that of the hyper-eutrophic Taihu lake (Zhai and Zhang, 2006). TP in WJD was significantly higher than that in HJD (Table 2), with an average value of 0.12 mg L^{-1}, and was also close to that of Taihu lake (Zhai and Zhang, 2006). The contrasts in concentrations of TN and TP indicated that the two reservoirs had dramatically different trophic conditions. The two reservoirs were located in different areas; HJD was far from heavy industrial activities and significant population centres, and WJD was located in the vicinity of light commercial activity, such as raising fish in net cages and the discharge of sewage.

According to the variations of atmospheric temperature, data from reservoirs could also be divided into two groups: one for warm seasons (i.e., from March to September) and one for cold seasons (i.e., October to February). In cold seasons, the water temperature had less variation along the water columns. However, in warm seasons, an obvious decline was observed when river water passed through the dams. In the case of HJD, for example, the temperature difference between the surface and bottom water reached 18.3 °C in July 2007. This difference was mainly attributed to the development of a thermal gradient in the water column from May to September. Significant spatiotemporal thermal stratification was observed during the warm seasons in both the HJD and WJD reservoirs, whereas thermal stratification was absent in cold seasons, when the water mixing process brought the profiles into thermal equilibrium.

Chlorophyll could only be detected in the upper layer (depth < 15 m) of each reservoir. The average concentrations in warm seasons were 20.45 μg L^{-1} and 2.66 μg L^{-1} in the WJD and HJD reservoirs, respectively, with average values of 1.01 μg L^{-1} and 0.53 μg L^{-1} for the rest of the year (Fig. 2), suggesting that a significant difference in chlorophyll concentrations was observed between the two reservoirs.

DO is a vital parameter influencing the emissions and concentration variations of N_2O. During the thermal stratification periods in warm seasons, DO in the bottom waters dropped to very low levels, but the surface waters had supersaturated DO concentrations. Vertically, DO, varied from 148.44 μmol L^{-1} to 407.81 μmol L^{-1}, with an average value of 209.38 μmol L^{-1} in warm seasons in the WJD reservoir. A discontinuous water layer was observed in warm seasons in HJD from July 2007 to September 2007. At a 15 m depth, the DO concentration was only 12.19 μmol L^{-1}, which indicated that an anoxic water column existed near the thermocline. The averaged DO concentration in surface waters in HJD was 260.31 μmol L^{-1}, which was much lower than that in WJD. Generally, surface water had higher DO concentrations in warm seasons than that in cold seasons, suggesting strong photosynthesis. In cold seasons, the DO had little variation longitudinally because the water columns became well mixed.

3.2. Spatiotemporal variation of N_2O saturation

3.2.1. Variations of saturated N_2O in surface waters

N_2O saturation in the surface water of Wujiangdu reservoir ranged from 214% to 662%, with an average value of 388%, and in Hongjiadu reservoir, saturation ranged from 201% to 484%, with an average value of 312%. Significant differences in N_2O saturation were observed between the HJD and WJD reservoirs (Table 3), and N_2O saturation levels in surface waters in WJD were much higher than those in HJD. In addition, the N_2O saturation levels in the present study were much lower than those in the northern portion of Taihu lake (Wang et al., 2009), which had a saturation value of 689 ± 472%, that were higher than those of reservoirs in NW Ontario, Canada, in which the N_2O concentrations were only about 7.3 nmol L^{-1} (0.44 μg L^{-1}) (Hendzel et al., 2005). However, all surface waters in the two reservoirs were supersaturated with respect to equilibrium atmospheric N_2O concentration (319 ppbv; IPCC, 2007), which indicated that the two reservoirs represented net sources of N_2O to the atmosphere.

Significant seasonal N_2O variations were observed, with higher N_2O saturation in cold seasons than warm seasons, i.e., higher N_2O saturations were found in WJD from October 2007 to January 2008 than during other months, ranging from 497% to 662% (Fig. 2). Accordingly, in HJD, N_2O saturation was high from September 2007 to December 2008, ranging from 350% to 484%. The seasonal changes in N_2O saturation coincided with increasing values of TN and TP during these months (Table 2), suggesting an effect of trophic status on N_2O. The same correlations between N_2O saturation and trophic status were also found in other research studies, i.e., Taihu lake (Wang et al., 2009). Additionally, the observed increases of N_2O in cold seasons were also corresponded to changes in parameters such as temperature (*T*), dissolved oxygen (DO) and chlorophyll concentrations (Fig. 2).

Table 2
The seasonal water parameters in the reservoirs of HJD and WJD, SW China.

	TN/mg L^{-1}		TP/mg L^{-1}		Chlorophyll/μg L^{-1}		DO/mg L^{-1}	
	WJD	HJD	WJD	HJD	WJD	HJD	WJD	HJD
Jul. 07	3.26 ± 0.25	5.16 ± 1.17	0.20 ± 0.12	–	17.08 ± 25.73	2.12 ± 1.15	7.51 ± 3.34	5.16 ± 2.82
Aug. 07	2.99 ± 0.11	4.05 ± 0.53	0.04 ± 0.02	–	8.34 ± 10.01	1.12 ± 1.34	8.67 ± 1.45	4.85 ± 3.12
Sep. 07	2.87 ± 0.35	3.87 ± 0.80	0.13 ± 0.08	0.01	8.18 ± 9.02	2.20 ± 1.92	8.23 ± 2.22	4.08 ± 2.77
Oct. 07	2.79 ± 0.13	4.32 ± 0.30	0.11 ± 0.02	0.01	0.70 ± 0.60	1.30 ± 1.12	5.65 ± 0.60	4.00 ± 0.77
Nov. 07	4.34 ± 0.26	5.42 ± 0.22	0.07 ± 0.01	0.03 ± 0.03	0.74 ± 0.59	0.30 ± 0.12	7.05 ± 0.31	5.45 ± 0.02
Dec. 07	3.29 ± 0.08	3.85 ± 0.04	0.22 ± 0.03	0.06 ± 0.01	–	–	7.17 ± 0.10	6.43 ± 0.07
Jan. 08	3.52 ± 0.09	3.59 ± 0.24	0.12 ± 0.01	0.05 ± 0.01	0.16 ± 0.19	–	8.03 ± 0.02	6.69 ± 0.34
Feb. 08	3.38 ± 0.04	3.73 ± 0.13	0.13 ± 0.02	0.08 ± 0.01	1.42 ± 1.18	0.30 ± 0.16	9.13 ± 0.26	7.74 ± 0.07
Mar. 08	3.67 ± 0.20	3.44 ± 0.35	0.06 ± 0.02	0.01	8.42 ± 9.58	0.16 ± 0.19	10.91 ± 1.50	8.23 ± 0.87
Apr. 08	3.57 ± 0.19	3.39 ± 0.15	0.11 ± 0.04	0.03 ± 0.01	5.88 ± 6.78	0.12 ± 0.14	9.41 ± 1.00	8.26 ± 1.17
May. 08	3.69 ± 0.48	3.79 ± 0.29	0.17 ± 0.10	0.03 ± 0.02	4.30 ± 5.12	1.38 ± 1.1	9.18 ± 1.32	7.59 ± 1.20
Jun. 08	2.66 ± 0.11	4.04 ± 0.69	–	–	6.16 ± 8.86	–	–	4.79 ± 3.26

Data are average concentration ± mean deviation.
"–" means undetected or under limitation.

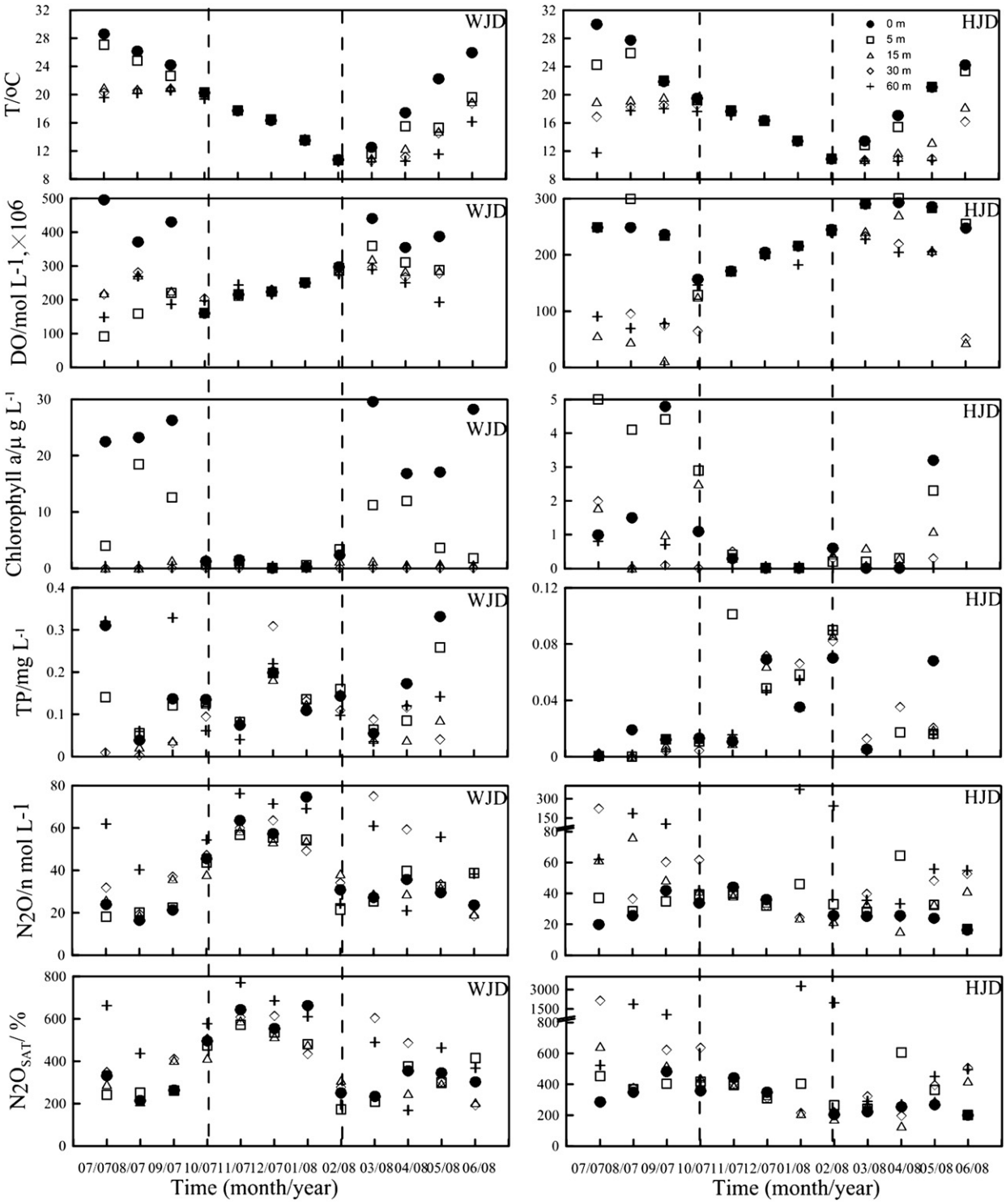

Fig. 2. Monthly variations of water temperature, DO, Chlorophyll, TP, and N_2O saturation in HJD and WJD reservoirs. The zone divided by dashed line means the distribution of warm seasons and cold seasons. From Oct. 07 to Feb. 08 was the period without thermal stratification (cold seasons), the rest months were thermal stratified months (warm seasons).

3.2.2. Spatiotemporal variations and longitudinal patterns of N_2O saturation

Seasonal thermal stratification of reservoirs has been well studied (Huttunen et al., 2003b; Hendzel et al., 2005). Water temperature affected the longitudinal patterns of N_2O saturation by directly influencing various biogeochemical processes in the reservoir (Mengis et al., 1997), the variations of which are presented in Fig. 2. Totally, along with thermal stratification in warm seasons, there were significant seasonal and longitudinal variations of N_2O saturation in the water columns of the two reservoirs. In cold

Table 3
Distributions of Monthly N_2O concentrations and saturations in WJD and HJD along the Wujiang River, SW China.

	N_2O^V/nmol^{-1}		N_2O surface/ nmol^{-1}		N_2O_{sat} surface/%	
	WJD	HJD	WJD	HJD	WJD	HJD
Jul. 07	32.41 ± 11.88	80.51 ± 56.51	23.89	19.92	332	288
Aug. 07	23.06 ± 6.88	70.59 ± 48.33	16.49	25.76	214	351
Sep. 07	29.30 ± 7.38	58.04 ± 19.35	21.50	42.16	264	484
Oct. 07	45.80 ± 4.06	43.69 ± 7.17	45.71	33.79	497	361
Nov. 07	63.10 ± 5.57	41.33 ± 2.21	63.62	44.10	643	445
Dec. 07	60.25 ± 5.83	34.01 ± 1.58	57.45	36.18	556	350
Jan. 08	60.23 ± 9.33	116.78 ± 127.93	74.69	–	662	–
Feb. 08	29.85 ± 5.54	70.82 ± 70.50	30.89	25.61	251	208
Mar. 08	43.48 ± 19.68	32.36 ± 4.51	27.19	25.28	234	223
Apr. 08	36.95 ± 10.07	32.75 ± 13.03	35.64	25.81	356	255
May. 08	36.64 ± 7.69	38.76 ± 10.62	29.69	23.99	345	269
Jun. 08	27.76 ± 8.73	36.39 ± 15.86	23.58	16.43	304	201

"N_2O^V" means volume weighted N_2O average concentration ± mean deviation.
"N_2O_{sat} surface" means saturation in surface layer.
"–" means samples are undetected.

seasons without thermal stratification, longitudinal N_2O saturation in WJD remained relatively uniform but still remained very highly saturated at the bottom of HJD (Fig. 2).

The differences in N_2O saturation levels of the whole vertical depths (0.5, 5, 15, 30 and 60 m) are showed in Fig. 3. Data were analysed and tested using *T*-test statistical analyses by SPSS Statistics 17.0.0. In warm seasons (mainly in thermal stratification periods), N_2O saturation in bottom water (depth = 60 m) was significantly higher than that in upper waters (depth = 0.5, 5 and 15 m) in WJD (all P values < 0.05). N_2O saturation in deep waters (depth = 30 and 60 m) was also obviously higher than waters in depth of 0.5 m ($P = 0.12$ and 0.22) and depth of 5 m ($P = 0.08$ and 0.15) in warm seasons in HJD reservoir. In cold seasons (mainly in non-thermal stratification periods), N_2O saturation levels in bottom waters (depth = 60 m) were significantly higher than that in upper waters (depth = 0.5, 5, 15 and 30 m) in HJD (all P values < 0.05). No obvious differences were found in WJD in cold seasons. Overall, bottom waters had higher saturation levels of N_2O than upper water columns, indicating that N_2O production in the bottom waters was much greater than in the upper layers.

In warm seasons, the average levels of N_2O saturation in WJD and HJD were 421% and 781% in the bottom waters. In cold seasons, average N_2O saturation levels reached 556% in WJD and 1130% in HJD at the bottom. However, N_2O saturation downstream of the dams decreased significantly relative to bottom waters, with average values of 616% in WJD and 400% in HJD during warm seasons and average values of 382% in WJD and 353% in HJD during cold seasons. The difference of N_2O saturation levels between bottom waters and downstream of the dams suggesting the N_2O releases behind the dams should be seriously treated.

In order to evaluate N_2O production in HJD directly, we examined several instances of extremely high concentrations in different months. Extremely high N_2O concentrations of 221.78 nmol L^{-1}, 185.63 nmol L^{-1} and 104.19 nmol L^{-1} were observed in the bottom water of HJD between July and September, 2007. High N_2O concentrations of 372.63 and 247.06 nmol L^{-1} were also observed in January and February, 2008, respectively. These trends were similar to those observed in lakes in Switzerland (Mengis et al., 1997).

3.3. N_2O emission fluxes in hydroelectric reservoirs

Based on the climatological wind speed data provided by the meteorological observatory and the N_2O saturation in the surface water of the two reservoirs, conservative estimates of fluxes of N_2O in HJD and WJD are shown in Fig. 4.

Exchange fluxes of N_2O were estimated in the HJD and WJD reservoirs. Total calculated N_2O fluxes were three times as high in cold seasons as compared to warm seasons in WJD (average value of 1.10 μmol m^{-2} h^{-1} versus 0.36 μmol m^{-2} h^{-1}). In most months in HJD, fluxes of N_2O varied less, with an average of 0.48 μmol m^{-2} h^{-1} in cold seasons and 0.43 μmol m^{-2} h^{-1} in warm seasons. For the entire year, average N_2O fluxes in WJD were 0.64 μmol m^{-2} h^{-1}, while in HJD, the average flux was 0.45 μmol m^{-2} h^{-1}.

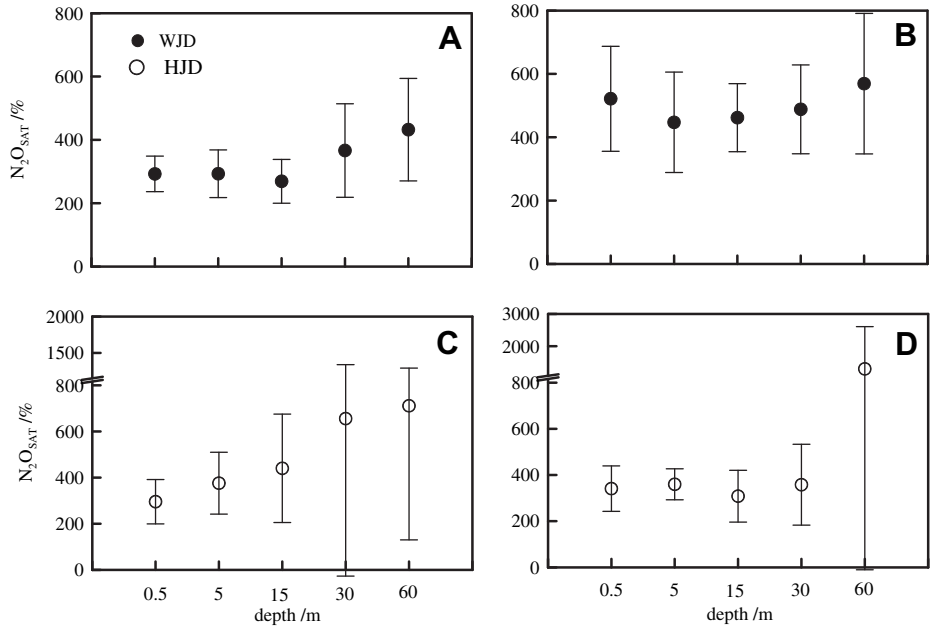

Fig. 3. The N_2O saturation differences of the whole vertical depths (0.5 m, 5 m, 15 m, 30 m and 60 m) in WJD (A, B) and HJD reservoirs (C, D) in warm seasons (A, C) and cold seasons (B, D).

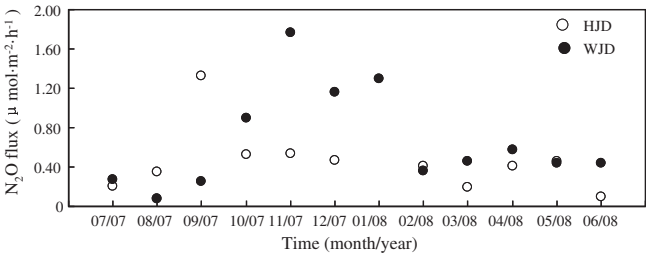

Fig. 4. Monthly variations of N_2O diffusion fluxes in water–gas interface in HJD and WJD reservoirs.

4. Discussion

4.1. The influence of environmental variables on N_2O saturation

Effects of environmental variables and nutrients on N_2O concentrations and saturation levels were assessed by correlation analysis. Because of the absence of thermal stratification in cold seasons, no significant correlations were found in the two reservoirs. The correlation in warm seasons is shown in Table 4 and Table 5.

On the whole, N_2O saturation levels were positively correlated with NH_4, NO_3, TN and N_2O concentrations in HJD, suggesting that increased N loading promoted the production of N_2O, as expected. Saturated N_2O concentrations also had a negative correlation with DO levels, indicating that N_2O was produced primarily in anoxic environments, rather than in the oxic portions of the water column. These correlations were in good agreement with the longitudinal and spatiotemporal variations of N_2O saturation noted previously. The relationship between N_2O saturation and other environment variables was not significant in WJD in warm seasons, suggesting the complexity of N_2O production in reservoirs.

As previously noted (Table 2), significant contrasts in trophic conditions were observed between the two reservoirs, and these are considered to be factors influencing the spatiotemporal distribution of N_2O. In surface waters, higher N_2O saturation was observed in cold seasons than in warm seasons, suggesting that environmental variables played an important role. First, in winter, the degradation of organic matter provided sufficient N for N_2O accumulation in surface water. Second, the oxic environment in surface waters provided nitrifiers with good conditions for producing N_2O. Third, the water mixing process in cold seasons brought N_2O concentrations into equilibrium along the reservoirs' vertical profiles, with the upwelling of bottom water leading to high levels of N_2O saturation. Fourth, reservoirs were generally in storage periods in winter, when power generation processes were less active than during non-storage periods, and this could prolong the water retention time in reservoirs, leading to increased accumulation of N_2O.

4.2. N_2O saturation and nutrient conditions

Eutrophic lakes/reservoirs generally have higher levels of N_2O saturation than other lakes worldwide (Mengis et al., 1997; Huttunen et al., 2003a,b; Wang et al., 2009). While aquatic N_2O is an intermediate of nitrification and denitrification, inputs of nutrients can increase the potential for both of these reactions (Lilkanen and Martikainen, 2003); moreover, sufficient DO and suitable temperatures create ideal conditions for the production of N_2O, which is likely accompanied by the removal of nutrients such as nitrate and phosphate (Seitzinger et al., 2000; Garnier et al., 2006). As a result, variable N inputs and degrees of eutrophication act as the primary controls on the distribution of N_2O saturation levels (Huttunen et al., 2003a,b; Wang et al., 2009).

Accordingly, it was expected that the N_2O saturation level would increase significantly with increasing anthropogenic N inputs, but this expectation did not match our observations. Extremely high levels of saturation of N_2O were observed in the bottom waters of HJD, rather than in WJD, a pattern which is likely to be strongly associated with the nutrient status of the reservoirs. Due to the younger age of the HJD reservoir, there is almost no obvious anthropogenic N loading, and the sole source of N input is likely to be the two influent rivers of the reservoir, which had minimal effects on N_2O. Even though HJD is a relatively new reservoir far from cities and industrial factories, N_2O saturation levels, TN and dissolved inorganic nitrogen (DIN) concentrations were higher than in WJD (Table 2), indicating that the major N input was likely from flooded soil and vegetation. Flooding of large areas of farmland and vegetation by dam construction can lead to the degradation of organics, providing plenty of nitrogen from the sediment–water interface to the reservoir. In conclusion, nitrogen sources in reservoirs may be quite different, especially for reservoirs of different ages, and this may be responsible for the high degree of N_2O saturation observed in the waters at the bottom of HJD.

Reservoirs are important sinks for regional anthropogenic N, including nitrogenous pollutants from fertilisers, industrial contamination, and human sewage (Bunting et al., 2007; Gulati and van Donk, 2002). Hence, reservoirs are likely to have high levels of N_2O saturation. WJD had been accumulating suspended particulates and nutrients from its upstream tributaries for a longer period than HJD because it was impounded much earlier than HJD. Sufficient inputs of suspended organic matter could contribute to increasing the levels of primary productivity and the concentrations of phytoplankton and zooplankton in the reservoir. Indeed, significant algal blooms were observed during the summer in the WJD reservoir, as observed from the increasing chlorophyll

Table 4
Correlation between N_2O saturation and environmental variables in HJD in warm seasons.

	T	DO	Chlorophyll	NH_4	NO_3	TN	TP	N_2Oc	N_2O_{sat}
T	1	0.057	0.619**	0.216	−0.023	0.032	−0.106	−0.083	0.039
DO		1	0.256	−0.128	−0.791**	−0.662**	0.420*	−0.570**	−0.563**
CHL			1	−0.093	−0.099	−0.024	0.111	−0.073	0.005
NH_4				1	0.245	0.168	−0.194	0.347*	0.388*
NO_3					1	0.746**	−0.374	0.711**	0.724**
TN						1	−0.383	0.766**	0.769**
TP							1	−0.309	−0.327
N_2Oc								1	0.991**
N_2O_{sat}									1

**Correlation is significant at the 0.01 level (2-tailed).
*Correlation is significant at the 0.05 level (2-tailed).

Table 5
Correlation between N_2O saturation and environmental variables in WJD in warm seasons.

	T	DO	Chlorophyll	NH_4	NO_3	TN	TP	N_2Oc	N_2O_{sat}
T	1	−0.048	0.480**	0.188	0.144	−0.550**	0.256	−0.520**	−0.200
DO		1	0.675**	0.066	−0.387*	0.071	0.071	−0.178	−0.228
CHL			1	0.095	−0.318	−0.022	0.349	−0.299	−0.163
NH_4				1	0.110	0.016	−0.073	−0.240	−0.249
NO_3					1	0.019	0.076	−0.027	0.026
TN						1	−0.009	0.406*	0.237
TP							1	0.140	0.296
N_2Oc								1	0.929**
N_2O_{sat}									1

**Correlation is significant at the 0.01 level (2-tailed).
*Correlation is significant at the 0.05 level (2-tailed).

concentrations, and these blooms can affect dissolved nitrogen concentrations via respiration and metabolism (Table 2). Cage culture also contributed significant amounts of nitrogen to the reservoir. Specifically, construction of the dam changed the original rivers into reservoirs, providing the local population with the opportunity to raise fish in net cages. Due to the economic benefits of this activity, a town was built near the dam. The sewage from the town became another important N input to the reservoirs. Complicated sources of N input into WJD not only led to eutrophication but also significantly altered the water environment. To conclude, anthropogenic N inputs have a positive but limited effect on N_2O saturation levels in the aquatic environment.

WJD primarily receives N from fertiliser and the cultivation of fish in net cages. Based on hydrological data provided by the Bureau of Hydrology and Water Resources in Guizhou Province, approximately 4.74×10^6 kg N was estimated to have been discharged into the WJD reservoir in 2007, of which approximately 2.25×10^6 kg N flowed out of the reservoir and 2.49×10^6 kg N remained in the reservoir. Most of the trapped nitrogen was likely emitted into the atmosphere as N_2 and N_2O. Among the total inputs of N to the system, approximately 0.51×10^6 kg N were contributed by the cultivation of fish in net cages (the N content of fish feed was 4.5% and that of the fish was 3%). The large amount of N loading significantly promoted the high levels of N_2O saturation in the reservoirs.

4.3. N_2O production mechanisms in two reservoirs of Wujiang River

As previously noted, high N_2O saturation levels in surface waters were observed in cold seasons (Table 3). First, denitrification of NO_3^- and ammonitrification are not likely sources of N_2O under oxic conditions. High levels of N_2O and DO saturation in surface waters will reduce the contribution of assimilative NO_3^- reduction for N_2O production (Garnier et al., 2006). Second, the release of N_2O from the sediment–water interface and subsequent horizontal transport into the water column will enhance N_2O saturation in surface waters. This process was also suggested by Butler et al. (1988) to explain observed N_2O supersaturation in the surface water of a coastal lagoon. Third, it was suggested that N_2O may be produced either directly by algae or by denitrifying bacteria living on the algae that frequently bloom in eutrophic waters during warm seasons (Weathers, 1984; Law et al., 1993). Actually, the relationships between N_2O, DO and NO_3^- concentrations could provide valuable information about N_2O production in aquatic environments (Mengis et al., 1997; Garnier et al., 2006).

The relationship between N_2O and NO_3^- concentrations in warm and cold seasons (thermal stratification and non-thermal stratification months) was compared in the two reservoirs (Fig. 5). Significant positive relationships between N_2O and NO_3^- concentrations were observed in HJD reservoir, with obviously different slopes. A steeper slope of 0.33 ($n = 18$) in warm seasons as comparing to cold seasons (a slope of 0.11; $n = 17$) indicated a more rapid N_2O production rate in warm seasons, i.e., the same increase in NO_3^- will lead to a greater increase in N_2O concentrations. A similar correlation between N_2O and NO_3^- was not obvious in WJD, indicating the high complexity of the influence of N loading on N_2O saturation and emissions. It appeared that in WJD, N_2O saturation and production were not dominated by any single process. As a result, the mechanism(s) of N_2O production could not be easily understood, leading to significant uncertainty in evaluating N_2O emissions. However, an excellent positive correlation (coefficient = 0.91; $n = 9$) between N_2O and NO_3^- concentrations in autumn (from October 2007 to December 2007) was observed in WJD, with a slope of 0.24, indicating that nitrification was the main process producing N_2O in autumn.

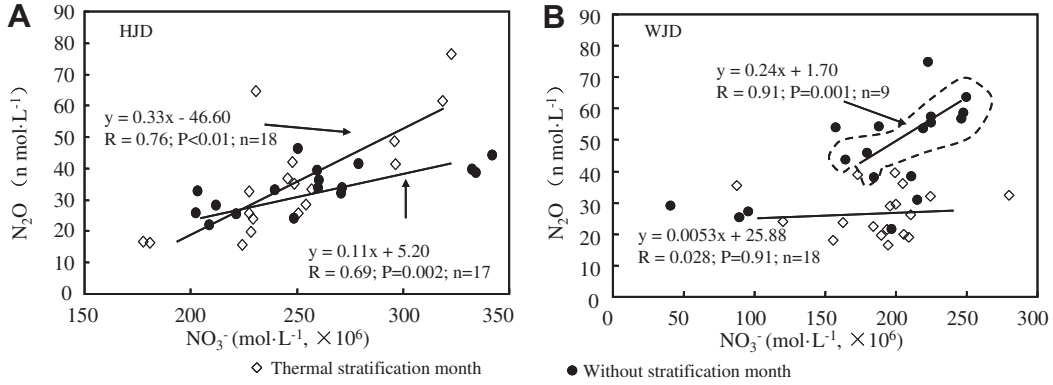

Fig. 5. N_2O versus NO_3^- in reservoir HJD and WJD in different thermal stratification period. The equation of correlations between N_2O versus NO_3^-, the sample numbers (n) and the value of coefficient of correlation (R) accompanied with level P values were showed. The marked area in (B) stands for samples collected from WJD reservoir in autumn.

Fig. 6 shows ΔN_2O plotted against AOU (apparent oxygen utilization). In the HJD, ΔN_2O had excellent linear correlation with AOU (coefficient = 0.62; $n = 53$), with a calculated regression coefficient of 0.11 nmol $L^{-1}\Delta N_2O/\mu mol\ L^{-1}$ AOU. The regression coefficient was found to be the same in summer (July 2007 to September 2007) in HJD (coefficient = 0.82; $n = 13$), whereas a positive linear correlation (coefficient = 0.41; $n = 54$) was observed for WJD throughout the entire year, with a calculated regression coefficient of 0.09 nmol $L^{-1}\Delta N_2O/\mu mol\ L^{-1}$ AOU. The regression coefficients for reservoirs in this study agree well with reported coefficients for lakes and oceans (Mengis et al., 1996; Suntharalingam and Sarmiento, 2000; Nevison et al., 2003). A linear correlation between ΔN_2O and AOU in oxic deep waters was established for almost all marine and lake environments, with reported regression coefficients ranging from 0.076 to 0.31 nmol $L^{-1}\Delta N_2O/\mu mol\ L^{-1}$ AOU (Suntharalingam and Sarmiento, 2000). In consideration with the good relationship between N_2O and NO_3^-, nitrification was likely the dominant biogeochemical process of N_2O production in HJD, but the processes in WJD were more complicated. Specifically, ΔN_2O/AOU ratios could be influenced by several processes. The oxidation of organic matter in the water column, the mixing of different water masses and biogeochemical processes such as denitrification and assimilative NO_3^- reduction may affect ΔN_2O/AOU ratios (Nevison et al., 2003). Overall, the complexity of ΔN_2O/AOU ratios also revealed the uncertainty of N_2O production in WJD.

4.4. N_2O fluxes compared with other areas

Like many river-reservoir systems receiving high anthropogenic nutrient inputs, the conditions in reservoirs on the Wujiang River are ideal for N_2O production in the water column and are likely to contribute significantly to N_2O emissions to the atmosphere (Garnier et al., 2006). The N_2O fluxes of rivers, lakes and reservoirs around the world are listed in Table 6. Due to the heavy anthropogenic influence, extraordinarily high levels of N_2O were reported in some rivers such as South Platte and Neuse rivers (McMahon and Dennehy, 1999; Stow et al., 2005). However, some reservoirs represented obvious sinks for N_2O (Hendzel et al., 2005). Compared with other rivers and lakes, the calculated N_2O fluxes in the HJD and WJD reservoirs were higher than those of most clean rivers but slightly less than those of contaminated rivers and eutrophied lakes. For example, WJD had a greater N_2O flux than that of a hyper-eutrophic lake and an N-enriched river, i.e., Taihu lake and Neuse river, especially in the cold seasons. Additionally, the two reservoirs had much higher fluxes than a natural river, i.e., Colne River. Overall, even though the two reservoirs had high N_2O fluxes, they were still moderate sources of N_2O emissions compared with soils and estuarine systems (Seitzinger et al., 2000; Garnier et al., 2009).

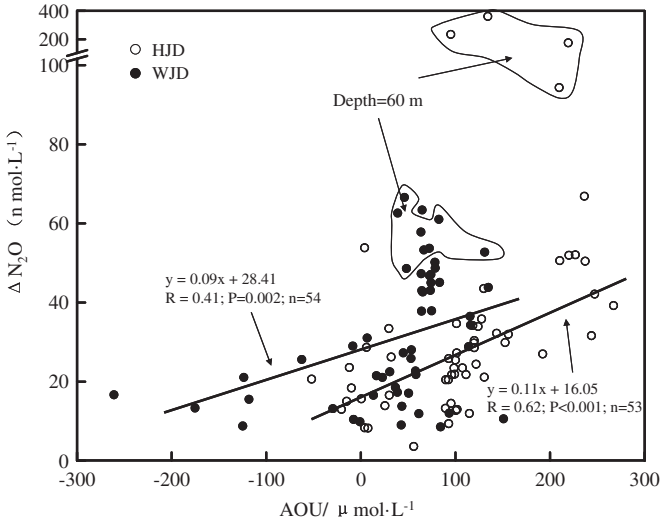

Fig. 6. ΔN_2O versus AOU in HJD and WJD reservoirs. The results of linear regression of two reservoirs showed in the figure were based on the linear correlation analysis with all the data in the column ($n = 53, 54$). Samples in depth of 60 m was marked out, generally, they have a higher saturation than others.

Table 6
Fluxes of N_2O in other related rivers, lakes and reservoirs.

Names	Location	N_2O fluxes ($\mu mol\ m^{-2}\ h^{-1}$)	References
River Hudson	America	0.23 ± 0.14	Cole and Caraco, 2001
River Colne	England	0.04–0.17	Dong et al., 2004
Lake Taihu	China	−6.38 to 47.75 (Littoral Zone) −4.02 to 3.73 (Pelagic Zone)	Wang et al., 2006
Lake Taihu	China	0.41–0.58	Wang et al., 2009
Lake Mochou	Antarctica	0.22 ± 0.48	Liu et al., 2011
Lake Tuanjie		0.18 ± 0.20	
Lake Daming		0.51 ± 0.49	
ELA in Ontario	Canada	<0.0033	Hendzel et al., 2005
Lake Kevaton	Finland	0.09–0.50	Huttunen et al., 2003b
River Swaleouse	England	14–100	García-Ruiz et al., 1999
River South Platte	America	0.27–97.02	McMahon and Dennehy, 1999
River Neuse	America	~−0.60–4.60	Stow et al., 2005
Hongjiadu (HJD)	China	0.45 (0.10–1.32)	This research
Wujiangdu (WJD)	China	0.64 (0.08–1.76)	This research

Base on the N_2O fluxes and the surface area of the two reservoirs (WJD is 47.8 km^2, HJD is 80.5 km^2), the annual emissions from the reservoirs were estimated to be 3.17×10^5 mol N_2O (i.e., 8.88×10^3 kg $N{-}N_2O$) and 2.81×10^5 mol N_2O (i.e., 7.87×10^3 kg $N{-}N_2O$) from HJD and WJD, respectively, which were much less than the N_2O fluxes from water bodies in the Seine Basin ($250{-}460 \times 10^3$ kg $N{-}N_2O\ yr^{-1}$, Garnier et al., 2009) and South Platte and Potomac Rivers (2.5×10^5 kg $N\ yr^{-1}$; McMahon and Dennehy, 1999). Although they are not significant sources of N_2O due to the small surface areas of these reservoirs, the huge numbers of similar reservoirs in China contribute to N_2O emissions from such water bodies representing a significant concern.

Another important source of N_2O emission was downstream waters. Supersaturated N_2O in bottom waters would be released into the atmosphere during power generation below the dam. In 2007, the water flow downstream of the dam in HJD was approximately 2.02×10^9 m^3, and the annual average concentration of N_2O was 106.19 nmol L^{-1}. Therefore, 2.15×10^5 mol N_2O was released during power generation, which was close to the amount of emissions from surface water in HJD. The water flow downstream of the dam in WJD was approximately 7.51×10^9 m^3, and the annual average N_2O concentration was 47.90 nmol L^{-1}. Therefore, 3.60×10^5 mol N_2O was released during power generation, which was higher than that from surface water. Our calculations show that N_2O emissions by downstream waters released from reservoirs were as significant as emissions from surface waters, indicating the significant effect of hydropower generation on N_2O emissions. Based on the annual electric energy production of 33.40×10^8 kW h for WJD and 15.94×10^8 kW h for HJD (http://192.168.4.1/gsgk/zjdz/3213.htm), for 1 kW h of electrical power, the reservoirs release 5.37 mg $N{-}N_2O$ from WJD and 9.35 mg $N{-}N_2O$ from HJD, respectively. These findings indicate that urgent attention is needed to address N_2O emission from discharge water below dams.

5. Conclusion

The study investigated the spatiotemporal variation and diffusion flux of N_2O as well as correlations with environmental parameters in two reservoirs of the Wujiang River, China. First, hydropower dam interception has resulted in seasonal and longitudinal variations of water parameters and environmental variables, i.e., the decline of *T* and DO concentrations in the bottom of the water column in warm seasons and the increase of N_2O saturation, nutrients levels and trophic conditions. Second, because of the development of thermal stratification in the warm season, N_2O saturation levels in the surface water were generally lower in warm seasons than in cold seasons. Significant spatiotemporal variations in N_2O concentrations were observed, with higher N_2O saturation and emission in the deep water column during cold seasons than that in surface waters during the warm season. In addition, fluxes of N_2O from the surface of the reservoirs represented a continuous source during the sampling year. Compared to other reservoirs and lakes in the world, the N_2O fluxes of the two reservoirs studied were moderate. However, deep waters of the two reservoirs remained quite highly saturated with N_2O in all seasons, indicating that hydropower generation will release significant amounts of N_2O into the atmosphere, a consequence that should not be ignored.

Nitrification may be a major factor affecting the distribution of N_2O in these water bodies. High levels of anthropogenic N inputs had a limited, positive effect on N_2O production and emission. Despite the fact that the reservoirs studied had lower total amounts of N_2O diffusion than larger lakes due to their small water surface areas, the potential for N_2O emissions in reservoirs should be clearly understood. Further research should not only focus on the N_2O fluxes from the water–gas interface but also on N_2O diffusion during hydropower generation.

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References

Andersson, M., Kjøller, A., Struwe, S., 2003. Soil emissions of nitrous oxide in fire-prone African savannas. Journal of Geophysical Research 108, 4630–4639.
Bange, H.W., 2006. Nitrous oxide and methane in European coastal waters. Estuarine Coastal and Shelf Science 70, 361–374.
Battle, M., Bender, M., Sowers, T., Tans, P.P., Butler, J.H., Elkins, J.W., Ellis, J.T., Conway, T., Zhang, N., Lang, P., Clarke, A.D., 1996. Atmospheric gas concentrations over the past century measured in air from firn at the South Pole. Nature 383, 231–235.
Beaulieu, J., Arango, C., Tank, J., 2009. The effects of season and agriculture on nitrous oxide production in headwater streams. Journal of Environmental Quality 38, 637–646.
Becker, K., Lörzer, J., Kurtenbach, R., Wiesen, P., Jensen, T., Wallington, T., 1999. Nitrous oxide (N_2O) emissions from vehicles. Environmental Science & Technology 33, 4134–4139.
Bremner, J.M., 1997. Sources of nitrous oxide in soils. Nutrient Cycling in Agroecosystems 49, 7–16.
Bunting, L., Leavitt, P., Gibson, C., McGee, E., Hall, V., 2007. Degradation of water quality in Lough Neagh, Northern Ireland, by diffuse nitrogen flux from a phosphorus-rich catchment. Limnology and Oceanography 52, 354–369.
Butler, J.H., Elkins, J.W., 1991. An automated technique for the measurement of dissolved N_2O in natural waters. Marine Chemistry 34, 47–61.
Butler, J.H., Pequegnat, J.E., Gordon, L.I., Jones, R.D., 1988. Cycling of methane, carbon monoxide, nitrous oxide, and hydroxylamine in a meromictic, coastal lagoon. Estuarine, Coastal and Shelf Science 27, 181–203.
Chen, H., Yuan, X., Gao, Y., Wu, N., Zhu, D., Wang, J., 2010. Nitrous oxide emissions from newly created littoral marshes in the drawdown area of the three Gorges reservoir, China. Water, Air, & Soil Pollution, 1–9.
Chen, H., Wang, M., Wu, N., Wang, Y., Zhu, D., Gao, Y., Peng, C., 2011. Nitrous oxide fluxes from the littoral zone of a lake on the Qinghai-Tibetan Plateau. Environmental Monitoring and Assessment. doi:10.1007/s10661-011-1896-y Online First™.
Cole, J., Caraco, N., 2001. Emissions of nitrous oxide(N_2O) from a tidal, freshwater river, the Hudson River, New York. Environmental Science & Technology 35, 991–996.
Dong, L.F., Nedwell, D.B., Colbeck, I., Finch, J., 2004. Nitrous oxide emission from some English and Welsh rivers and estuaries. Water, Air, & Soil Pollution: Focus 4, 127–134.
Emerson, S., 1975. Chemically enhanced CO_2 gas exchange in a eutrophic lake: a general model. Limnology and Oceanography 20, 743–753.
García-Ruiz, R., Pattinson, S.N., Whitton, B.A., 1999. Nitrous oxide production in the river Swale-Ouse, North-East England. Water Research 33, 1231–1237.
Garnier, J., Cébron, A., Tallec, G., Billen, G., Sebilo, M., Martinez, A., 2006. Nitrogen behaviour and nitrous oxide emission in the tidal Seine River Estuary (France) as influenced by human activities in the upstream watershed. Biogeochemistry 77, 305–326.
Garnier, J., Billen, G., Vilain, G., Martinez, A., Silvestre, M., Mounier, E., Toche, F., 2009. Nitrous oxide (N_2O) in the Seine river and basin: observations and budgets. Agriculture, Ecosystems & Environment 133, 223–233.
Gulati, R., van Donk, E., 2002. Lakes in the Netherlands, their origin, eutrophication and restoration: state-of-the-art review. Hydrobiologia 478, 73–106.
Hashimoto, S., Gojo, K., Hikota, S., Sendai, N., Otsuki, A., 1999. Nitrous oxide emissions from coastal waters in Tokyo Bay. Marine Environmental Research 47, 213–223.
Hendzel, L., Matthews, C., Venkiteswaran, J., St Louis, V., Burton, D., Joyce, E., Bodaly, R., 2005. Nitrous oxide fluxes in three experimental boreal forest reservoirs. Environmental Science & Technology 39, 4353–4360.
Houghton, J.T., Ding, Y., Griggs, D.J., Noguer, N., van der Linden, P.J., Xiaosu, D., Maskell, K., Johnson, C.A., 2001. Climate Change 2001: The Scientific Basis. Cambridge University Press, Cambridge, UK.
Huttunen, J., Alm, J., Liikanen, A., Juutinen, S., Larmola, T., Hammar, T., Silvola, J., Martikainen, P., 2003a. Fluxes of methane, carbon dioxide and nitrous oxide in boreal lakes and potential anthropogenic effects on the aquatic greenhouse gas emissions. Chemosphere 52, 609–621.
Huttunen, J.T., Juutinen, S., Alm, J., Larmola, T., Hammar, T., Silvola, J., Martikainen, P.J., 2003b. Nitrous oxide flux to the atmosphere from the littoral zone of a boreal lake. Journal of Geophysical Research-Atmospheres 108, 4421–4430.
Intergovernmental Panel on Climate Change (IPCC), 2007. The Science of Climate Change. Cambridge University Press, New York.
Law, C., Rees, A., Owens, N., 1993. Nitrous oxide production by estuarine epiphyton. Limnology and Oceanography 38, 435–441.
Lerman, A., 1979. Geochemical Processes. Water and Sediment Environments. John Wiley and Sons, Inc, United States of America.
Lilkanen, A., Martikainen, P.J., 2003. Effect of ammonium and oxygen on methane and nitrous oxide fluxes across sediment-water interface in a eutrophic lake. Chemosphere 52, 1287–1293.
Liu, Y., Zhu, R., Ma, D., Xu, H., Luo, Y., Huang, T., Sun, L., 2011. Temporal and spatial variations of nitrous oxide fluxes from the littoral zones of three alga-rich lakes in coastal Antarctica. Atmospheric Environment 45, 1464–1475.
Mander, Kuusemets, V., Lõhmus, K., Mauring, T., Teiter, S., Augustin, J., 2003. Nitrous oxide, dinitrogen and methane emission in a subsurface flow constructed wetland. Water Science and Technology, 135–142.
McMahon, P., Dennehy, K., 1999. N_2O emissions from a nitrogen-enriched river. Environmental Science & Technology 33, 21–25.
Mengis, M., Gachter, R., Wehrli, B., 1996. Nitrous oxide emissions to the atmosphere from an artificially oxygenated lake. Limnology and Oceanography 41, 548–553.
Mengis, M., Gachter, R., Wehrli, B., 1997. Sources and sinks of nitrous oxide (N_2O) in deep lakes. Biogeochemistry 38, 281–301.
Nevison, C., Butler, J., Elkins, J., 2003. Global distribution of N_2O and the N_2O-AOU yield in the subsurface ocean. Global Biogeochemical Cycles 17, 1119–1136.
Ravishankara, A., Daniel, J.S., Portmann, R.W., 2009. Nitrous oxide (N_2O): the dominant ozone-depleting substance emitted in the 21st century. Science 326, 123.
Rosenberg, D.M., McCully, P., Pringle, C.M., 2000. Global-scale environmental effects of hydrological alterations: introduction. BioScience 50, 746–751.
Satterfield, C.N., 1970. Mass Transfer in Heterogeneous Catalysis. MIT Press, Cambridge, UK.
Seitzinger, S.P., Kroeze, C., 1998. Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems. Global Biogeochemical Cycles 12, 93–113.
Seitzinger, S., Kroeze, C., Styles, R., 2000. Global distribution of N_2O emissions from aquatic systems: natural emissions and anthropogenic effects. Chemosphere - Global Change Science 2, 267–279.
Stow, C.A., Walker, J.T., Cardoch, L., Spence, P., Geron, C., 2005. N_2O emissions from streams in the Neuse River watershed, North Carolina. Environmental Science & Technology 39, 6999–7004.
Suntharalingam, P., Sarmiento, J., 2000. Factors governing the oceanic nitrous oxide distribution: simulations with an ocean general circulation model. Global Biogeochemical Cycles 14.
Wang, H.J., Wang, W.D., Yin, C.Q., Wang, Y.C., Lu, J.W., 2006. Littoral zones as the "hotspots" of nitrous oxide (N_2O) emission in a hyper-eutrophic lake in China. Atmospheric Environment 40, 5522–5527.
Wang, S.L., Liu, C.Q., Yeager, K.M., Wan, G.J., Li, J., Tao, F.X., Lue, Y.C., Liu, F., Fan, C.X., 2009. The spatial distribution and emission of nitrous oxide (N_2O) in a large

eutrophic lake in eastern China: anthropogenic effects. Science of the Total Environment 407, 3330–3337.
Weathers, P., 1984. N_2O evolution by green algae. Applied and Environmental Microbiology 48, 1251–1253.
Wuebbles, D.J., 2009. Nitrous oxide: no laughing matter. Science 326, 56–57.
Zhai, S., Zhang, H., 2006. Water quantity and waste load variation of rivers around Lake Taihu from 2000 to 2002. Journal of Lake Sciences 18, 225–230.