Introduction

Nitrous oxide (N\textsubscript{2}O), a trace gas that contributes to stratospheric ozone destruction and atmospheric warming, has a radiative forcing of +0.17 W/m\textsuperscript{2} nowadays [1], and its atmospheric concentration has increased from 270 ppbv in the pre-industrial era to 328 ppbv in 2016 [2]. Among the greenhouse gases covered by the Kyoto Protocol, N\textsubscript{2}O is the third largest contributor to global warming after carbon dioxide (CO\textsubscript{2}) and methane (CH\textsubscript{4}), which is responsible for 7\% of anthropogenic global warming and has a global warming potential about 298 times that of CO\textsubscript{2} and a long residence time (~114 years) in the atmosphere [3]. Wetlands and watercourses are important N\textsubscript{2}O sources, e.g., it has been estimated that 106, 93-111, and 974 Gg N\textsubscript{2}O/yr were emitted from reservoirs, rivers, and coastal zones, respectively [4-6]. Reservoirs, as a kind of inland water, are different from streams, rivers and lakes, because the river impoundment significantly changes the water environment, especially in terms of nutrient status and physicochemical conditions, which has an impact on the spatiotemporal variability of N\textsubscript{2}O emission [7]. The spatiotemporal variability of N\textsubscript{2}O
emission was reported from several hydroelectricity reservoirs in China, but the patterns were distinct in the different reservoirs, e.g., N2O fluxes in Wujiaodu, Hongjiadu, and Dongfeng reservoirs reached their maximum in November, September, and April, respectively [7, 8], while the peak value of N2O emission from Three Gorges Reservoir occurred in June and July [9, 10], which indicated that N2O emissions from different reservoirs differed widely both among systems and through time [11].

The effects of thermal stratification, N and O2 availability on N2O production were complicated by nitrification and denitrification in the water column [11]. A high N load into reservoirs, including ammonia (NH4+), nitrite (NO2-), and nitrate (NO3-) could increase the substrates for nitrification and denitrification, thus there were the positive correlations between N2O concentrations and nitrogen content (i.e., NH4+, NO2-, TN) in reservoirs and rivers in China [7, 8, 12]. Besides nutrient status, water temperature and dissolved oxygen (DO) also influenced N2O formation. Similar to natural lakes, thermal stratification often existed in those large and deep reservoirs, and the seasonal alternation between thermal stratification and destratification could promote the exchange of energy, dissolved gas, and other substances between epilimnion and hypolimnion in the water column [13]. Furthermore, DO would stratify due to the response to thermal structure in reservoirs by the regulation of chromophoric dissolved organic matter [14], and DO concentration was crucial for N2O production and has a negative relationship with N2O emission from reservoirs and rivers [7, 12]. Thus, the seasonal variability of N2O emissions were probably determined by the nutrient status and thermal structure of a reservoir.

Xin’anjiang Reservoir is the largest reservoir in eastern China, with a water area of 478 km2 and a mean water depth of 34 m, and is a mesotrophic lake (DO) also influenced N2O formation. Similar to natural (29°28’39”N, 119°03’03”E) was located in the main inflow inlet of Xin’anjiang Reservoir, and had a watercourse width of 0.3 km. 3 sampling points were chosen from the margin to pelagic zones in the NW transect. The NE transect (29°38’44”N, 119°03’03”E), SW transect (29°44’03”N, 118°43’04”E) was located in the main inflow river, which occupies 60-70% of total surface runoff of the reservoir [16]. In addition, the reservoir’s main body consists of northeast (NE) lake, southwest (SW) lake, southeast (SE) lake, and central lake.

Xin’anjiang Dam, located in Tongguan Gorge, was the first immense hydropower station which was designed, equipped, and constructed all by Chinese after the foundation of the People’s Republic of China in 1949. Xin’anjiang Dam began to be built in 1957 and water storage started in 1959. The height and length of the dam was 105 m and 462 m, respectively. At maximal operating level the reservoir volume is 17.8 billion m3, and the annual mean discharge of Xin’anjiang River is 357 m3 s-1. The average turnover time of the impounded water is estimated to be ~2 years [17].

Xin’anjiang Reservoir is located in the north edge of a subtropical zone with humid monsoonal climatic condition, with the annual mean temperature of 17.7°C, annual accumulated precipitation of 2015.1 mm, and evaporation of 712.9 mm in 2015. Water level fluctuated between 98.5 m to 104.5 m in Xin’anjiang Reservoir. Four seasons are easily divided throughout the year in the reservoir, i.e., spring (March to May), summer (June to August), autumn (September to November), and winter (December to February). Xin’anjiang Reservoir is warm monomictic, with a long period of thermal stratification [13].

The sampling campaign was conducted in the 5 transects of the upstream river, the reservoir’s main body and the downstream river (Fig. 1). The NW transect (29°44’03”N, 118°43’04”E) was located in the main inflow inlet of Xin’anjiang Reservoir, and had a watercourse width of 0.3 km. 3 sampling points were chosen from the margin to pelagic zones in the NW transect. The NE transect (29°38’44”N, 119°03’03”E), SW transect (29°28’18”N, 118°44’39”E), and SE transect (29°28’39”N, 118°45’20”E) were located in open water areas of NE lake, SW lake, and SE lake, respectively. 5 sampling points were chosen from the margin to pelagic zones in the NE, SW, and SE transects, respectively. In addition, 4 sampling points were selected in the downstream river below the dam, with a distance of 0.35 km, 1 km, 4 km, and 7 km away from Xin’anjiang Dam, respectively.

**Experimental Procedures**

**Study Area**

Xin’anjiang Reservoir (29°28’-29°58’N, 118°42’-118°59’E) is also called Thousand-island Lake, because 1,078 islands are distributed in the reservoir. Xin’anjiang Reservoir has a basin area of 10,480 km2 when the normal water storage water level is 108 m. The storage water in Xin’anjiang Reservoir derives from 33 different tributaries, but Xin’anjiang River, i.e., the watercourse of northwest (NW) lake, is the most dominant upstream inflow river, which occupies 60-70% of total surface runoff of the reservoir [16]. In addition, the reservoir’s main body consists of northeast (NE) lake, southwest (SW) lake, southeast (SE) lake, and central lake.

The gas samples were collected by the static chambers, and 3 chambers were deployed simultaneously. The floating static chamber (65 cm in...
length × 45 cm in width × 40 cm in height) consisted of a plastic box without a cover that was wrapped in light-reflecting and heatproof materials to prevent temperature variation inside the chambers; in addition, plastic foam collars were fixed onto opposite sides of the chamber. The headspace height inside the chamber was about 35 cm. A silicone tube (0.6 cm and 0.4 cm outer and inner diameters, respectively) was inserted into the upper central side of the chamber to collect gas samples, and the gas samples were dried with plexiglass tubes filled with calcium chloride anhydrous (analytical reagent), which could remove the moisture in the gas samples and prevent the biological reactions. Another silicone tube was inserted into the upper corner side of the chamber to keep the air pressure balanced between the inside and the outside of the chamber. The gases in the headspace of the chamber were collected into air-sampling bags (0.5L; Hedetech, Dalian, China) four times every 7 min over a 21-min period using a hand-driven pump (NMP830KNDC; KNF Group, Freiburg, German).

Measurement Techniques and Flux Calculation

The N\textsubscript{2}O concentrations in the air-sampling bags were analyzed using a gas chromatograph (Agilent 7890A; Agilent Technologies, Santa Clara, USA) with a electron capture detector (ECD) and separated with a Teflon column (3 m × 3 mm) packed with Porpak-Q column (80-100 mesh). The oven, injector, and detector temperatures were at 70°C, 25°C, and 330°C, respectively. The flow rate of the carrier gas (pure N\textsubscript{2}) was 25 ml/min. Standard mixed gas (N\textsubscript{2}O: 0.308 ppm; provided by China National Research Center for Certified Reference Materials, Beijing) was used to quantify the N\textsubscript{2}O concentration in one of every 10 samples, which kept the coefficient of variation of the N\textsubscript{2}O concentration in the replicated samples below 1.5%.

The increasing rate of the gas concentration (\(\frac{dc}{dt}\)) within the static chamber was calculated as the slope of the linear regression of the gas concentration versus time. It was suggested that the nonlinear relationship between gas flux and time would be better to determine the steeper initial slope in the chambers [18]. Thus, the para-curve model was made preferential to the linear one. Otherwise, the linear model was accepted. Acceptance of the results was based upon two criteria: (1) the difference of N\textsubscript{2}O concentration between the initial gas sample and ambient air must be within 10% and (2) the correlation coefficient (R\textsuperscript{2}) had to be >0.90.

\[
F = \rho \times \frac{dc}{dt} \times \frac{273.15}{273.15 + T} \times H
\]

(1)

…where F is the diffusive N\textsubscript{2}O flux (\(\mu g \text{ m}^{-2}\text{ s}^{-1}\)); \(\rho\) is density of gas under standard conditions (1.962 kg m\textsuperscript{-3} for N\textsubscript{2}O); \(H\) is height of the top of the inverted chamber to the water surface (0.35 m here); 273.15 is absolute temperature at 0°C; and \(T\) is air temperate (°C).

Statistical Analysis

N\textsubscript{2}O fluxes were first tested by the Kolmogorov-Smirnov test to judge whether these data satisfied the normal distribution. If not, these N\textsubscript{2}O flux data would be transferred by elementary functions to satisfy the normal distribution. One-way analysis of variance (ANOVA) combined with the Tukey HSD test was used to analyze the differences in the average NO\textsubscript{x} flux among the different transects. The data were analyzed using the SPSS (statistical product and service solution) 18.0 statistical package.
**Results**

Seasonal Variability of N₂O Emission from Xin’anjiang Reservoir

**N₂O Emission from the Lacustrine Zone of Xin’anjiang Reservoir**

The average N₂O emission flux in the NE transect climbed sharply from January (22.40 ± 3.68 μg m⁻²·s⁻¹) to the maximum value in March (124.52 ± 58.84 μg m⁻²·s⁻¹), dropped to the minimum in June (12.12 ± 4.24 μg m⁻²·s⁻¹), and kept a low emission level until a minor increase in November (54.69 ± 24.91 μg m⁻²·s⁻¹, Fig. 2). The average N₂O emission flux in the SW transect firstly experienced a minor decrease from December 2014 (30.53 ± 7.43 μg m⁻²·s⁻¹) to February 2015 (16.58 ± 7.51 μg m⁻²·s⁻¹), witnessed a short pulse in March (86.78 ± 28.05 μg m⁻²·s⁻¹), but declined immediately in April (16.10 ± 17.12 μg m⁻²·s⁻¹), climbed slowly from June (4.33 ± 10.69 μg m⁻²·s⁻¹) to November (44.45 ± 10.95 μg m⁻²·s⁻¹), and finally dropped again in the remaining time (Fig. 2). The average N₂O emission flux in the SE transect started from December 2014 (26.47 ± 7.46 μg m⁻²·s⁻¹), fluctuated slightly until February 2015, increased suddenly to the maximum in March (79.56 ± 77.35 μg m⁻²·s⁻¹), then decreased slowly from April to July (5.39 ± 13.55 μg m⁻²·s⁻¹), climbed gently in the remaining time and finally returned to the original level (Fig. 2).

**N₂O Emission from the Riverine Zone of Xin’anjiang Reservoir**

The riverine zone of Xin’anjiang Reservoir could be divided into 2 parts, i.e., the upstream river and the downstream river. The average of N₂O flux in the upstream river kept a relative low emission level between 20 μg m⁻²·s⁻¹ to 50 μg m⁻²·s⁻¹, except for December in 2014 (109.67 ± 69.66 μg m⁻²·s⁻¹), March (172.00 ± 72.11 μg m⁻²·s⁻¹) and July (103.81 ± 49.59 μg m⁻²·s⁻¹) in 2015 (Fig. 3). The average N₂O emission flux in the downstream river decreased from December 2014 (571.59 ± 71.90 μg m⁻²·s⁻¹) to July 2015 (65.43 ± 69.69 μg m⁻²·s⁻¹) with fluctuation between February to May 2015, increased slightly from July to October (219.26 ± 309.06 μg m⁻²·s⁻¹), and fluctuated slightly in the last two months (Fig. 3).

Spatial Variability of N₂O Emission from Xin’anjiang Reservoir

The average N₂O emission flux in the downstream river (220.24 ± 153.68 μg m⁻²·s⁻¹) was significantly higher than that in the lacustrine zone and the upstream river (Fig. 4), which was over 4 times higher than the upstream river (49.85 ± 48.55 μg m⁻²·s⁻¹) and 5-8 times higher than the lacustrine zone (26.61-39.01 μg m⁻²·s⁻¹).

![Fig. 2. Dynamics of average N₂O emission from the main body of Xin’anjiang Reservoir.](image)

![Fig. 3. Dynamics of average N₂O emission from the riverine zone of Xin’anjiang Reservoir.](image)

![Fig. 4. Spatial variability of N₂O emission from the different regions of Xin’anjiang Reservoir.](image)
Discussion

Seasonal Variability of N₂O Emission

The average N₂O emission flux in the surfaces of Xin'anjiang Reservoir was 34.84 μg m⁻²·s⁻¹, which was lower than those in 3 Amazonian tropical reservoirs, comparable to those from subtropical and temporal reservoirs, but higher than those at the boreal reservoirs (Table 1). The geographic location of reservoirs is an important factor influencing N₂O emission flux because of the differences in temperature.

The maximal values of N₂O emission from the NW, NE, SW, and SE occurred in March simultaneously (Figs 2, 3), which presumably was related with the vertical mixing of the water column then [13]. An explanation was that the highest level of N₂O emission during the turnover periods derived from new N₂O production resulting from the nitrification of NH₄⁺ released from the hypolimnion. Lacking direct support by relevant N₂O data in this study, but elevated N₂O emission associated with nitrification during lake turnover periods have been reported in East Fork Lake Reservoir, Ohio, USA and Wujiangdu Reservoir, Guizhou, China [7, 11]. The dissolved N₂O saturation ratio increased significantly from prior to turnover periods to turnover periods, with supersaturation in the epilimnion, causing a strong concentration gradient between the atmosphere and water surface, and a high level of N₂O emission subsequently occurred in the air-water interface [7, 11].

The peak of N₂O emission from the downstream river was different from the other locations, with the maximum in December 2014 to January 2015 (Fig. 3), which was probably induced by the interference of the water discharge and the variation of dissolved N₂O concentration before the dam. Water discharge rate decreased from December 2014 to February 2015, and reached the minimum at February (Fig. 5). The variability of dissolved N₂O concentrations before the dam was likely an important indicator for the seasonal N₂O emission from the downstream river. Unfortunately, the dissolved N₂O concentrations were not measured during our experiments.

Spatial Variability of N₂O Emission

A significantly high N₂O emission flux was observed in the downstream river (Fig. 4), which was about 3-7 times higher than the average N₂O fluxes in the 4 transects before the dam. Similarly, N₂O emissions from the downstream rivers of the 2 tropical reservoirs

<table>
<thead>
<tr>
<th>Country</th>
<th>Methods*</th>
<th>Sampling periods</th>
<th>N₂O fluxes (μg m⁻²·s⁻¹)</th>
<th>References</th>
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<tr>
<td>Petit Saut</td>
<td>French Guiana</td>
<td>FC</td>
<td>May and Dec., 2003</td>
<td>177.76 ± 111.76</td>
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<td>Three Gorges</td>
<td>China</td>
<td>FC</td>
<td>2009-2011</td>
<td>14 ± 21</td>
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<td>5 reservoirs in Guizhou Province</td>
<td>China</td>
<td>TBL</td>
<td>Jul., 2007 to Jun., 2008</td>
<td>19.22 (8.36-28.2)</td>
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<tr>
<td>Xin'anjiang</td>
<td>China</td>
<td>FC</td>
<td>Dec., 2014 to Jan., 2016</td>
<td>34.84 (27.91-50.11)</td>
</tr>
<tr>
<td>Eguzon</td>
<td>France</td>
<td>TBL</td>
<td>2011</td>
<td>32.45 ± 31.35</td>
</tr>
<tr>
<td>William Huasha</td>
<td>USA</td>
<td>TBL</td>
<td>May to Oct., 2012</td>
<td>78.75(-2200 -4400)</td>
</tr>
<tr>
<td>Eagle Creek</td>
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<td>TBL</td>
<td>2005-2008</td>
<td>83.75 ± 307.92</td>
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<tr>
<td>Yudushan</td>
<td>China</td>
<td>FC</td>
<td>May to Oct., 2009</td>
<td>16.51</td>
</tr>
<tr>
<td>29 boreal reservoirs</td>
<td>Canada</td>
<td>FC</td>
<td>1993 to 2003</td>
<td>3.37 (-5.57-10.34)</td>
</tr>
<tr>
<td>Lokka</td>
<td>Finland</td>
<td>FC</td>
<td>Jun. to Sep., 1994, 1995</td>
<td>-3.52 - 11.44</td>
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<td>Porttipahta</td>
<td>Finland</td>
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<td>Jun. to Sep., 1994, 1995</td>
<td>-0.88 - 10.56</td>
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<td>ELA in Ontario</td>
<td>Canada</td>
<td>BLM</td>
<td>2000-2001</td>
<td>-0.15 - -0.042</td>
</tr>
</tbody>
</table>

*Note: FC: Floating Chambers; BLM: Boundary Layer Method
reasons for N2O emission variability in the space and water column should be further studied to reveal the mechanism of nitrification and denitrification in the surface sediments [19, 28].

...in the downstream river; (2) in waters, which was oversaturation compared with the total N2O emission from reservoir previously. The monitoring campaign that covers the different locations in March and the downstream river. A long-term spatiotemporal variability, with a high emission level the N2O produced in the hypolimnion water column downstream river might have the following origins: (1) solubility of N2O (1: 1.5 vol./vol. dissolved in water at 20°C and standard atmospheric pressure) would keep plenty of dissolved N2O concentrations in the river waters, which was oversaturation compared with the nearby atmosphere in the downstream river; (2) in situ production in the river, by denitrification in the sediments and/or nitrification in the water column or surface sediments [19, 28].

...spacetime scales.

Conclusions

N2O emission from Xin’anjiang Reservoir has spatiotemporal variability, with a high emission level in March and the downstream river. A long-term monitoring campaign that covers the different locations of the reservoir should be carried out to estimate the total N2O emission from reservoir previously. The mechanism of nitrification and denitrification in the water column should be further studied to reveal the reasons for N2O emission variability in the space and temporal scales.

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Conflict of Interest

The authors declare no conflict of interest.

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