Sub-daily Variations in Nitrous Oxide Fluxes from the Littoral Zone of a Temperate Eutrophic Lake

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Abstract

Lakes are sources of nitrous oxide (N₂O). However, labor-intensive gas analysis has confined evaluations of temporal variability in lakes to the seasonal time scale. We used a state-of-the-art laser-based N₂O analyzer combined with a floating chamber to examine sub-daily variations in N₂O emissions from a shallow eutrophic lake in Japan. We conducted intense daytime field campaigns during different seasons to reveal differences in sub-daily variations in N₂O emissions from the water surface in conjunction with the dynamics of dissolved N₂O concentrations in the lake water. The study revealed that N₂O fluxes varied within a day: emissions increased in response to increased wind speeds. Variations in surface dissolved N₂O concentrations caused by water mixing were also important during the summer, when accumulation of N₂O initially occurred in the lake bottom layer during stably stratified conditions. During winter, the lake water was well mixed and dissolved N₂O concentrations were uniform throughout the water column; thus, wind speed was the only factor controlling the diurnal variations in N₂O emissions. These findings demonstrate the need to consider diurnal variability when estimating cumulative N₂O emissions accurately over long periods.

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Key Points:

- \(\text{N}_2\text{O}\) emissions from a shallow eutrophic lake increased in response to increased wind speeds within a day.
- \(\text{N}_2\text{O}\) emissions were affected by sub-daily variations in surface dissolved \(\text{N}_2\text{O}\) concentrations caused by diffusion of \(\text{N}_2\text{O}\) from the lake bottom.
- Diurnal \(\text{N}_2\text{O}\) emission characteristics should be considered when estimating cumulative emissions over long periods.
Abstract
Lakes are sources of nitrous oxide (N$_2$O). However, labor-intensive gas analysis has confined evaluations of temporal variability in lakes to the seasonal time scale. We used a state-of-the-art laser-based N$_2$O analyzer combined with a floating chamber to examine sub-daily variations in N$_2$O emissions from a shallow eutrophic lake in Japan. We conducted intense daytime field campaigns during different seasons to reveal differences in sub-daily variations in N$_2$O emissions from the water surface in conjunction with the dynamics of dissolved N$_2$O concentrations in the lake water. The study revealed that N$_2$O fluxes varied within a day: emissions increased in response to increased wind speeds. Variations in surface dissolved N$_2$O concentrations caused by water mixing were also important during the summer, when accumulation of N$_2$O initially occurred in the lake bottom layer during stably stratified conditions. During winter, the lake water was well mixed and dissolved N$_2$O concentrations were uniform throughout the water column; thus, wind speed was the only factor controlling the diurnal variations in N$_2$O emissions. These findings demonstrate the need to consider diurnal variability when estimating cumulative N$_2$O emissions accurately over long periods.

Plain Language Summary
Lakes are sources of nitrous oxide (N$_2$O), a significant greenhouse gas that destroys stratospheric ozone. However, temporal variability in N$_2$O emissions has mainly been evaluated seasonally due to labor-intensive gas analysis. Observations of diurnal variability are critical to understanding N$_2$O dynamics in lakes and to evaluating cumulative gas emissions over a given period. We used the floating-chamber technique combined with a fast-response laser-based N$_2$O analyzer with field capability to examine sub-daily variations in N$_2$O emissions from a shallow eutrophic lake in Japan. We found that N$_2$O emissions increased primarily in response to increases in wind speed. Variations in surface dissolved N$_2$O concentrations caused by water mixing were also important during the summer, when N$_2$O accumulated in the lake bottom layer during stably stratified conditions. The lake water was well-mixed in winter, and dissolved N$_2$O concentrations were uniform throughout the water column; thus, wind speed was the sole factor controlling diurnal variations in N$_2$O emissions. These findings demonstrate the need to consider diurnal variability when estimating cumulative N$_2$O emissions accurately over long periods.

1 Introduction
Nitrous oxide (N$_2$O) is an important greenhouse gas (Arias et al., 2021) that destroys
stratospheric ozone (Ravishankara et al., 2009). N₂O is produced by microbial transformation that occurs in the soil and aquatic environments during nitrification and denitrification (Firestone and Davidson, 1989; Wrage et al., 2001; Megonigal et al., 2005) and is emitted into the atmosphere. It has been estimated that between 2007 and 2016 about 17 Tg N yr⁻¹ of N₂O were emitted into the atmosphere globally, 57% of which comprised natural emissions (Tian et al., 2020, Canadell et al., 2021). Approximately 76% of this N₂O would have been consumed by photolysis and reactions in the stratosphere, leaving about 4 Tg N yr⁻¹ to accumulate in the atmosphere during the same period (Tian et al., 2020). Despite the high global-warming potential of 273 on a mass basis over a 100-year time horizon for N₂O (Forster et al., 2021), observations of N₂O emissions are limited compared to those for carbon dioxide and methane, and a high degree of uncertainty in the N₂O budget remains. Further understanding of the temporal and spatial variations in N₂O emissions from various ecosystems is fundamental to reducing the uncertainty in the N₂O budget, and in turn, to predicting atmospheric warming and stratospheric ozone concentrations.

Inland waters are a source of N₂O (Huttunen et al., 2003b; Wang et al., 2006; McCrackin and Elser, 2011; Kortelainen et al., 2020; Zhou et al., 2021; Zheng et al., 2022). Average emission rates of 0.02–0.14 nmol m⁻² s⁻¹ from several Finnish lakes (Kortelainen et al., 2020) and of 0.00–0.65 nmol m⁻² s⁻¹ from several lakes in the Yangtze River basin in China (Zhou et al., 2021) have been reported. Inland and coastal waters have been estimated to emit 0.8 Tg N yr⁻¹ during 2007–2016, including natural emissions and indirect emissions from supplemental anthropogenic nitrogen (Tian et al., 2020). Furthermore, eutrophication occurring globally (Smith, 2003; Schindler and Vallentyne, 2008) is expected to enhance N₂O emissions (e.g., Salk and Ostrom, 2019; Zhou et al., 2021).

Temporal and intra- and inter-lake variations in N₂O emissions have been reported. These observations were based on the chamber or transfer velocity method combined with gas chromatography. N₂O emissions are higher during summer in some lakes (Huttunen et al., 2003b; Wang et al., 2006, 2007; Xiao et al., 2019; Miao et al., 2020), while maximum emissions have also been reported during the winter (Liu et al., 2011; Musenze et al., 2014; Miettinen et al., 2015; Descloux et al., 2017; Zhou et al., 2021; Lian et al., 2022). A study based on data obtained from several Finnish lakes showed that N₂O emissions tended to be higher during the winter (Kortelainen et al., 2020). N₂O emissions are generally higher in the littoral zone or eutrophic zone of lakes (Huttunen et al., 2003b; Wang et al., 2006, 2007, Zhu et al., 2015; Xiao et al., 2019). Inter-lake differences in N₂O emissions have been reported for Finnish lakes (Huttunen et al., 2003a; Kortelainen et al., 2020) and Chinese lakes (Zhou et
al., 2021), and N$_2$O emissions are higher in lakes with higher trophic levels. The roles of nitrification and denitrification in determining dissolved N$_2$O concentrations and N$_2$O emissions have also been reported (e.g., Yoh et al., 1983; Mengis et al., 1997; Senga et al., 2002; Beaulieu et al., 2014; Salk et al., 2016; Lian et al., 2022; Tang et al., 2022a, b).

Gas emissions from bodies of water vary diurnally in response to wind-speed variation and water mixing, and the associated variation in surface-water dissolved gas concentrations (Wanninkhof et al., 2009; Taoka et al., 2020). Observations of such diurnal variations are critical to understanding N$_2$O dynamics in lakes and to evaluating the cumulative gas emissions over a given period. However, due to technical limitations, sub-daily variation in N$_2$O emissions from lakes has rarely been examined. To the best of our knowledge, Ni et al. (2022) is the only study that has reported the diurnal variation in N$_2$O emissions from a lake based on the transfer velocity approach. Most previous studies have relied on gas chromatography to quantify N$_2$O concentrations. The sampling and subsequent analysis are labor-intensive, and the frequency of measurements has been limited. Highly accurate laser-based N$_2$O analyzers with a rapid response have recently become available, and their capability for use in the field potentially expands the ability to observe N$_2$O emissions at high temporal resolution such as at 1 h intervals.

In this study, we used a laser-based N$_2$O analyzer combined with a chamber to examine N$_2$O emissions from a eutrophic lake in Japan. We conducted intense field campaigns during the day and during different seasons to reveal the sub-daily variations in N$_2$O emissions. Along with the flux observations, we also observed variation in dissolved N$_2$O concentrations to infer the processes involved.

2 Materials and Methods

2.1 Study site

The observations were conducted at Lake Suwa (lake center: 36° 2’ 50”N, 138° 5’ 14”E, 759 m asl, Fig. 1), a shallow mid-latitude lake in Nagano Prefecture, Japan. According to a survey in 2013, the lake is 13.3 km$^2$ in area, with mean and maximum depths of 4.3 and 6.4 m, respectively. The area of the watershed is 531.2 km$^2$, and includes cities with a combined population of more than 180,000 inhabitants. The trophic level is eutrophic, with a total nitrogen concentration at the lake center in 2022 of 0.677 mgN L$^{-1}$ and a total phosphorus concentration of 51.4 μgP L$^{-1}$. Phytoplankton blooms occur during the spring and autumn. Water caltrop (Trapa japonica Flerov, a floating-leaved plant) and Esthwaite waterweed (Hydrilla verticillata (L.f.) Royle, a submerged plant) typically grow up to 200 m
from the shore during summer (Fig. 1c, d). Further details on the lake’s characteristics can be found in Park et al. (1993, 1998), Iwata et al. (2018, 2020), and Urai et al. (2021, 2022).

Figure 1. (a) The location and topography of Lake Suwa, (b) the bathymetry, and (c, d) the dominant aquatic vegetation, which comprised water caltrop and Esthwaite waterweed. In panel (b) the observation pier is indicated by a black star and the lake-center observation point is indicated by a white star.

The climatological mean air temperature in this area is 11.4°C, with a minimum monthly mean temperature of −1.1°C in January and a maximum monthly mean temperature of 24.1°C in August, according to the Japan Meteorological Agency. The average annual precipitation is 1,301.5 mm. Precipitation is greater during the warm months, and about 70% of the annual precipitation falls between May and October.

The observations were conducted at a pier (36° 2’ 48”N, 138° 6’ 30”E) located on the southeast shore of the lake. The measurement points were about 45 m away from the shore and the water depth at the pier was about 1.8 m during the summer and 2.0 m during the winter.

2.2 Observations and data processing

The N₂O analyzer was a MIRA Ultra N₂O/CO gas analyzer (Aeris Technologies, Inc., Hayward, CA, USA), which employs laser absorption spectroscopy in the middle infrared region. The pressure in the measurement cell is stabilized at 140 hPa. The analyzer outputs the N₂O concentration at a rate of 1 Hz. It has a built-in pump, with a flow rate of 0.2 L min⁻¹. The water vapor concentration in the measurement cell is analyzed simultaneously, and the
dilution effect on the N₂O concentration is accounted for by the analyzer. To evaluate instrumental stability before the field experiments, the N₂O mixing ratio was measured in a compressed air cylinder (340.3 ppb) continuously for 15 h in the laboratory. Allan variance analysis of the data provided a 1-s Allan deviation of 0.34 ppb. The lowest deviation was 0.04 ppb at 105 s of integration time.

The sample inlet and outlet of the analyzer were connected to a floating chamber by two pieces of tubing, and the rate of concentration change during chamber deployment was recorded to calculate N₂O flux from the water surface (Fig. S1a). The chamber was a transparent acrylic cylinder with the top welded closed. The inner diameter of the chamber was 24 cm and the height was 15 cm. A float was attached to the chamber so that the foot of the chamber was submerged 1 cm and the chamber headspace was closed when it floated on the lake surface. Two ports were attached to the top of the chamber to connect the tubes. Polytetrafluoroethylene (PTFE) tubes with an outer diameter of 1/4 inch connected the analyzer to the chamber. In front of the inlet of the analyzer, a PTFE membrane filter (PF-020, Advantec, Tokyo, Japan) was inserted to prevent polling the measurement cell. Strings were attached to the top of the chamber to lift and lower it. The chamber observations were made at three fixed plots on the pier within a 10-m distance during the first or second half of an hour. During the half-hour periods, the chamber was floated on the lake surface for 4 min in each plot.

The rate of concentration change was determined using the least squares method. Some N₂O concentration data that displayed a steady increase or decrease over time were extracted based on the time record of chamber deployment. The N₂O flux, \( F \) (nmol m\(^{-2}\) s\(^{-1}\)), was calculated as follows.

\[
F = \frac{dC}{dt} \frac{V}{A} \quad \text{Eq. 1}
\]

where \( dC/dt \) is the rate of N₂O concentration change over time (nmol m\(^{-3}\) s\(^{-1}\)), \( V \) is the volume of the chamber headspace (m\(^3\)), and \( A \) is the cross-sectional area of the chamber (m\(^2\)). The air temperature and pressure observed at the pier were used to convert the N₂O mixing ratio (ppm) into density (nmol m\(^{-3}\)). The uncertainty of each flux was calculated from the 95% confidence \( dC/dt \) interval. The flux detection limit was determined from the range of flux not significantly different from zero using the uncertainty calculated for all fluxes following Lammirato et al. (2018), and the limit was ± 0.005 nmol m\(^{-2}\) s\(^{-1}\).

The headspace technique was used to measure the dissolved N₂O concentration in the lake water using the laser-based N₂O analyzer (Fig. S1b). The procedure was similar to that described by Iwata et al. (2020) for dissolved methane concentrations. The N₂O concentration
in the headspace gas was equilibrated with the sampled lake water in the vial and was analyzed by injecting it into the air flowing through the N\textsubscript{2}O analyzer. Compressed air in a cylinder was used as the carrier gas. A T-joint was inserted in the flow line to exhaust excess air, with the flow rate adjusted to about 0.2 L min\textsuperscript{-1}. The lake water was sampled at three depths (10 and 100 cm below the water surface, and 20 cm above the sediment surface) during the same half-hour period as the flux observations and was poured into 30-mL glass vials. The vials were overflowed with approximately 100 mL sample water, and sealed with a septum and aluminum cap. After adjusting the vial temperature to 25°C, 3 mL nitrogen was injected into the vial to create headspace; the vial was then shaken vigorously for 2 min and placed on its side for more than 10 min to achieve equilibrium. A small amount (0.5–0.7 mL) of equilibrated gas was sampled from the headspace and injected into the air flowing through the analyzer. The time series of N\textsubscript{2}O concentrations revealed a peak when the equilibrated gas sample reached the measurement cell, and the peak area was integrated.

N\textsubscript{2}O concentrations were quantified using a calibration line obtained from a gas standard. The N\textsubscript{2}O concentration of carrier air (344.8 ppb) was also considered to calculate the sample gas concentration. The Bunsen coefficient (Weiss and Price, 1980) was used to calculate the dissolved N\textsubscript{2}O concentration from the headspace concentration. The calculation was similar to that of Magen et al. (2014). To evaluate the total uncertainties in the concentration determination, we calculated the uncertainties for each procedure. We summed them in quadrature assuming that the uncertainties in each procedure were independent (Taylor, 1997). The details are described in the Supplemental Information (Text S1). The median value of uncertainty calculated for all samples was 0.0004 μmol L\textsuperscript{-1} or 2.7% of the absolute concentration.

Intense measurement campaigns were conducted eight times during the daytime between July 2022 and May 2023. Only the flux measurement was conducted at hourly intervals on July 7, July 14, and August 25, 2022. On August 28, October 12, and November 16, 2022, and February 27 and May 27, 2023, both the flux and dissolved concentration measurements were taken at hourly intervals.

2.3 Ancillary measurements

Meteorological and limnological observations at the pier were used to evaluate the variations in N\textsubscript{2}O flux and dissolved N\textsubscript{2}O concentrations. Meteorological data, including air temperature (HMP155, Vaisala, Vantaa, Finland), air pressure (PTB110, Vaisala), wind speed and direction (CSAT3, Campbell Scientific, Inc., Logan, UT, USA), and solar radiation (CNR4, Kipp & Zonen, Delft, The Netherlands) were obtained, and half-hourly averages
were used for analysis. Precipitation was observed at a nearby station operated by the Japan Meteorological Agency. The limnological observations included water temperature (107, Campbell Scientific) at five depths, sediment temperature (107, Campbell Scientific) at 5 cm depth, and dissolved oxygen (DO) concentrations (OPTOD, Aqualabo, Champigny-sur-Marne, France) at three depths, as well as water depth (CS451, Campbell Scientific). Wave height was calculated as a standard deviation of water depth observed at 1 Hz using a water-depth sensor. Half-hourly averages were used for the other limnological variables. Readers are referred to Iwata et al. (2020) for more details.

DO and water temperature (HOBO U26–001, Onset Computer Corp., Bourne, MA, USA) were also determined at the center of the lake (Fig. 1; depth 6.4 m, 1.89 km from the onshore measurement site) at depths of 0.5, 3.0, and 5.0 m below the surface during non-winter months. An additional sensor was installed at a depth of 4.0 m from late July to early October 2022. The data were recorded at 10-min intervals.

Dissolved inorganic nitrogen (DIN) concentrations were analyzed in water samples taken approximately biweekly at the lake center. The water samples were obtained at depths of 0, 3, and 5 m. Ammonium-nitrogen (NH$_4^+$-N) and nitrate-nitrogen (NO$_3^-$-N) were analyzed by ion chromatography (ICS-1500, Thermo Fisher Scientific, Waltham, MA, USA). We have only DIN data obtained from the lake center covering the entire study period. In addition to the lake center observations, water samples were taken at the observation pier from February 27 to May 27, 2023, to check differences in DIN concentrations between the lake center and the shore.

3 Results

3.1 Meteorological and limnological conditions

The air temperature during the study period was comparable to the climatological mean (1991–2020) except during September, March, and April, when the monthly mean air temperature was higher than the climatological mean by more than 1.0°C (Table S1). Air temperatures during the winter were generally higher than the climatological means, and thin surface ice formed discontinuously only for a few days. The monthly precipitation in 2022
was more than 50 mm greater than the climatological mean during the period July–September, and was less than the mean in October (Table S1).

The lake was stably stratified from July to September, with the difference in water temperatures between the lake surface and lake bottom being 1–3°C (Fig. 2). Subsequently, the lake water was well mixed, and it began to stratify the following March. From late June to late September, the DO concentrations in the lake bottom layer were less than 1 mg L\(^{-1}\). At the same time, the surface DO concentrations were lower than during the rest of the period, partly due to the development of dense floating-leaved vegetation that reduced light penetration into the lake water. On September 20 (day of year 263), the entire water column was mixed by a typhoon event (Typhoon Nanmadol). Subsequently, DO concentrations returned to the levels of early June, and the anoxic bottom condition was eliminated.

Before we started the \(N_2O\) flux observations, the typical \(NH_4^+\)-N concentration at the lake center was low (about 0.01 mgN L\(^{-1}\), Fig. 3). The lake water at the lake center had stably stratified by late June (Fig. S2), and \(NH_4^+\)-N concentrations in the bottom layer were higher during mid-summer, with substantial variability of 0.12–0.43 mgN L\(^{-1}\), while surface \(NH_4^+\)-N was depleted. The bottom \(NH_4^+\)-N concentrations decreased in early September. Subsequently, \(NH_4^+\)-N concentrations increased in all layers, and in October was about 0.09 mgN L\(^{-1}\). \(NH_4^+\)-N generally remained depleted in all layers through the rest of the study period. \(NO_3^-\)-N concentrations in all layers increased to 0.23 mgN L\(^{-1}\) from late April to mid-June. Concentrations decreased in early July and variation was more complex in July and August. The surface concentration increased to 0.12 mgN L\(^{-1}\) towards late July and was depleted by August. \(NO_3^-\)-N concentrations in all layers increased during early September, and there was a peak \(NO_3^-\)-N concentration of 0.48 mgN L\(^{-1}\) on September 13. Subsequently, the mean \(NO_3^-\)-N concentration in all layers was higher (0.24 mgN L\(^{-1}\)) during the winter and decreased toward late April. A sudden increase was observed in May 2023.

In 2023, the \(NH_4^+\)-N concentrations observed at the pier were similar to those at the lake center. The mean \(NO_3^-\)-N concentration was higher at the pier (0.44 mgN L\(^{-1}\)) than at the lake center in March, and in April and May the variability was similar to that at the lake center.

\(3.2\) Seasonal and spatial variation in \(N_2O\) flux

Intense measurement campaigns were conducted during the stably stratified period (July 7 and 14 and August 25 and 28, 2022; Fig. 2), revealing depleted DO in the bottom layer during the summer; the less-stratified period (October 12 and November 16, 2022 and May 27, 2023), revealing high DO concentrations throughout the water column during
autumn and spring; and a completely mixed period (February 27, 2023) during the winter.

Figure 2. Seasonal variation in (a) solar radiation and precipitation, (b) air temperature and water temperature in the lake bottom layer, (c) temperature differences between the lake surface and bottom, and (d) dissolved oxygen concentrations. Arrows indicate the days of the intense measurement campaign.
Figure 3. Seasonal variations in (a) ammonium-nitrogen (NH$_4^+$-N) and (b) nitrate-nitrogen (NO$_3^-$-N) were observed at three depths (from the water surface) at the lake center (black symbol) and on the lake shore (orange symbol). Arrows indicate the days of the intense measurement campaign.

Table 1. Mean meteorological and limnological variables during the intense measurement campaigns.

<table>
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<td>Sediment temperature (°C)</td>
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<td>23.5</td>
<td>22.8</td>
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<tr>
<td>Wave height (cm)</td>
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<td>0.1</td>
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<td>1.1</td>
<td>0.9</td>
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<tr>
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<td>0.0</td>
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<td>8.0</td>
<td>9.0</td>
<td>11.9</td>
<td>8.3</td>
</tr>
<tr>
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<td>N/A</td>
<td>N/A</td>
<td>10.2</td>
<td>171.5</td>
<td>19.2</td>
<td>14.9</td>
<td>23.9</td>
</tr>
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</table>

Figure 4. Boxplot of the observed N$_2$O fluxes at three plots each day. The solid and open boxes indicate the fluxes at the plots with and without floating-leaved plants, respectively, present at the lake surface. The different letters near the boxes indicate plots with significant differences during a day. Significance was evaluated by the Games-Howell post hoc test. The plus symbols indicate outliers.
N$_2$O fluxes were small during summer (0.01–0.02 nmol m$^{-2}$ s$^{-1}$) and increased towards autumn (0.14 nmol m$^{-2}$ s$^{-1}$), when sediment and water temperatures decreased but DO concentrations in the bottom layer were high (Table 1, Figs. 2, 4). On a relatively calm day (February 27), N$_2$O fluxes were lower in winter than in autumn. Large N$_2$O fluxes were observed again in spring. The seasonal variation in N$_2$O fluxes observed in the plots without floating-leaved vegetation tended to be positively correlated with DO concentrations in the bottom layer ($r = 0.44, p = 0.32$). When the extremely large dissolved N$_2$O concentration at the surface observed on October 12 was omitted, N$_2$O fluxes tended to be positively correlated with dissolved N$_2$O concentrations ($r = 0.60, p = 0.40$). No correlation was found with sediment temperatures ($r = -0.20, p = 0.67$), wind speeds ($r = 0.11, p = 0.81$), or wave heights ($r = 0.14, p = 0.77$).

During summer, when aquatic plants were present, N$_2$O fluxes varied spatially between the plots on days with strong winds, although the plots were within 10 m of each other. On August 28, 2022, when the mean wind speed was 5.6 m s$^{-1}$ and the wave height was 0.86 cm (Table 1), N$_2$O flux was higher (0.06 nmol m$^{-2}$ s$^{-1}$, Fig. 4) in plot 2, where floating-leaved plants were locally absent because of a disturbance created by ship movement. On the same day, N$_2$O fluxes were lower in plots 1 and 3 (0.01 and 0.02 nmol m$^{-2}$ s$^{-1}$, respectively) than in plot 2. N$_2$O fluxes were spatially homogeneous after the aquatic plants had decayed or when wind speeds were low. On July 7, 2022, when floating-leaved plants had not yet fully developed to cover the water surface, wind speeds were moderate but N$_2$O fluxes were homogeneous.

3.3 Sub-daily variations in N$_2$O fluxes

The sub-daily variations in N$_2$O fluxes observed during the intense measurement campaigns are summarized in Fig. 5. The fluxes observed in plots with and without floating-leaved plants were averaged separately. Beginning in late summer, N$_2$O fluxes varied during the day. The variation was generally related to wind speed; the absolute magnitude of the N$_2$O flux was higher under stronger wind conditions (Table S2). On July 7 and August 25, increased wind speeds resulted in enhanced negative N$_2$O fluxes in the plots with floating-leaved vegetation, implying that the surface dissolved N$_2$O was undersaturated.
Figure 5. Sub-daily variations in (a–h) N$_2$O fluxes and (i–p) wind speeds were observed during the intense measurement campaigns. N$_2$O fluxes are shown separately for plots with (solid) and without (open) floating-leaved plants. Error bars indicate the standard deviation between plots.

To examine the sub-daily variations in N$_2$O fluxes in combination with the dissolved N$_2$O concentrations, the data obtained during the intense measurement campaigns on August 28 and November 16 were further analyzed (Fig. 6). On August 28, the wind speed was 3.4 m s$^{-1}$ at 6:00 and increased gradually during the morning to 7.3 m s$^{-1}$. The strong wind persisted during the afternoon. The surface lake water was mixed down to 1.0 m due to the strong wind but the mixing did not reach the lake bottom, probably because the presence of aquatic vegetation and thermal stratification hindered the transfer of momentum to deep water. The DO concentration was about 1.9 mg L$^{-1}$ from the surface to a depth of 1.0 m. The DO concentration was zero in the bottom layer during the morning, but the actual DO concentration is unknown due to the negative bias. The zone of depleted DO extended to a depth of 1.0 m in the afternoon. The dissolved N$_2$O concentration in the surface layer was about 0.01 μmol L$^{-1}$, and N$_2$O accumulated in the bottom layer at concentrations ranging from 0.02 to 0.08 μmol L$^{-1}$ in the morning. The bottom N$_2$O concentrations decreased after 11:00 and became nearly identical to the surface concentrations. The surface N$_2$O concentrations did not vary substantially, but increased slightly at around 15:00, probably due to diffusion from the bottom layer. N$_2$O fluxes gradually increased from 0.04 nmol m$^{-2}$ s$^{-1}$ at 6:00 to 0.15 nmol m$^{-2}$ s$^{-1}$ at 15:00 and then decreased in parallel with the decrease in N$_2$O concentrations.
Figure 6. Sub-daily variations in (a) wind speeds, (b) water temperatures, (c) dissolved oxygen concentrations, (d) dissolved N$_2$O concentrations, and (e) N$_2$O fluxes and dissolved N$_2$O concentrations in the surface layer observed on August 28, 2022. (f–j) The same for November 16, 2022. Error bars for fluxes indicate the standard deviation between plots, and the error bars for concentrations indicate the uncertainty.

On August 28, the N$_2$O fluxes correlated positively with wind speeds ($r = 0.53$, $p = 0.07$). Nevertheless, only 29% of the variation was explained by wind speed (Fig. 7). The residuals from the linear model with wind speed were positively correlated with the dissolved N$_2$O concentrations ($r = 0.82$, $p = 0.001$). These results indicate that during this period the sub-daily variations in N$_2$O fluxes were affected by wind speeds and dissolved N$_2$O concentrations.

During the early morning of November 16, the wind speed was about 5.2 m s$^{-1}$, decreasing to 0.8 m s$^{-1}$ by 9:00 and then gradually increasing to 4.6 m s$^{-1}$ by 13:00 (Fig. 6). The waves were too high to continue the floating chamber observations, so flux data are available only until 13:00. Stratification was weak and the entire water column was oxygenated. The dissolved N$_2$O concentrations were almost uniform over the depth. The N$_2$O fluxes closely followed the variations in wind speed, which explained 77% of the variations in the N$_2$O fluxes ($r = 0.88$, $p = 0.02$). The residuals from the linear model with wind speed were not correlated with the dissolved N$_2$O concentrations ($p = 0.26$). The results obtained for
other less stratified and completely mixed conditions were qualitatively similar to those obtained on November 16 (Figs. S3–S5 and Tables S2–S3).

Figure 7. Relationships between (a) N₂O fluxes and wind speeds and between (b) the residuals from the linear model and the dissolved N₂O concentrations for August 28. (c, d) The same relationships for November 16.

4 Discussion

4.1 Physical controls on N₂O fluxes

The diffusion of a sparingly soluble gas across the air-water interface is limited by the molecular diffusion layer at the skin-water layer, and the gas flux is modeled by the gas transfer velocity and the concentration difference between the bulk water and the skin layer (Wanninkhof et al., 2009). The gas transfer velocity is expressed as a function of wind speed (Wanninkhof, 1992; Cole and Caraco, 1998; McGillis et al., 2001) and water-side buoyancy due to surface cooling (Rutgersson et al., 2011, Heiskanen et al., 2014; Tedford et al., 2014).

Our observations show that the sub-daily variations in N₂O fluxes depended on wind speed (Figs. 5 and 7, and Table S2), implying that lake surface mixing by momentum transfer from the atmosphere enhances N₂O emissions into the atmosphere, provided that the water is oversaturated with N₂O. In this study, we observed N₂O fluxes only during the day, when the water surface mixing layer gains energy; thus, buoyancy probably had little effect on the gas transfer efficiency (Rutgersson and Smedman, 2010; Heiskanen et al., 2014).
The gas transfer velocity, $k$, was calculated from the observed $\text{N}_2\text{O}$ flux and dissolved concentration as follows.

$$k = \frac{F}{(C_w - C_{eq})} \text{ Eq. 2}$$

where $C_w$ and $C_{eq}$ are the dissolved $\text{N}_2\text{O}$ concentrations in the bulk surface water and skin $\text{N}_2\text{O}$ concentration equilibrated with the atmosphere, respectively. The solubility coefficient (Weiss and Price, 1980) was used to calculate the skin $\text{N}_2\text{O}$ concentration from the atmospheric $\text{N}_2\text{O}$ concentration. By considering the temperature dependence of the $\text{N}_2\text{O}$ Schmidt number for freshwater (Wanninkhof, 1992), the transfer velocity converted into Schmidt number 600 is shown in Fig. 8, together with the proposed empirical functions (Wanninkhof, 1992; McGillis et al., 2001, 2004; Crusius and Wanninkhof, 2003). The wind speed at a height of 10 m was estimated using the relationship between the wind speed observed at the pier ($U_{\text{pier}}$) and that observed at 10 m ($U_{10}$) by the Japan Meteorological Agency ($U_{10} = 1.22U_{\text{pier}} + 0.24, R^2 = 0.92$). The transfer velocity increased as the wind speed increased, indicating more efficient transfer of dissolved gas under stronger wind. The transfer velocity generally followed the wind-speed dependence of empirical models, implying that the observed $\text{N}_2\text{O}$ fluxes and dissolved $\text{N}_2\text{O}$ concentrations were reasonably accurate. However, some of the variability in the calculated transfer velocities may be due to inconsistencies in the time the data represent: the flux data are averages of three measurements during 30 min, whereas the dissolved concentration data represent only a few minutes of sampling during the same half-hour. The root mean square errors for the four empirical functions were 6.3, 6.1, 5.9, and 7.9 cm h\(^{-1}\) for the Wanninkhof (1992), McGillis et al. (2001), Crusius and Wanninkhof (2003), and McGillis et al. (2004) models, respectively, when the one outlier (divergence of calculated $k$ due to very small $C_w - C_{eq}$) was omitted. These findings imply that the Crusius and Wanninkhof (2003) model is the most suitable for predicting $\text{N}_2\text{O}$ emissions based on the dissolved $\text{N}_2\text{O}$ concentrations in Lake Suwa.

The effects of aquatic plants, particularly emergent plants, on gas transfer efficiency have been reported in the literature. Emergent plants function as a water surface barrier to the wind, and the transfer efficiency of gas at the air-water interface is highly reduced under lower water-side turbulence (Poindexter and Variano, 2013; Ho et al., 2018). However, vegetation also increases the gas transfer velocity by enhancing water-side turbulence from wakes around the vegetation’ stems (Nepf et al., 1997; Tseng and Tinoco, 2020). In this study, the presence of dense floating-leaved plants reduced the gas transfer velocity locally (Fig. 8), probably because some of the leaves protruding into the air acted as a barrier to the
wind and the actual wind velocity just above the water surface was therefore low. Wave
heights were also reduced under high wind speeds when the floating-leaved plants were fully
developed in summer (Fig. S6). The floating nature of the leaves and stems may have
suppressed wake turbulence in the water, resulting in the low gas transfer velocity. The
density of floating-leaved plants was probably low during the early summer, and the effect of
these plants on reducing the water surface turbulence was weak, which resulted in the
homogeneous N2O fluxes in plots with and without these plants (Fig. 4a, b). This observation
is supported by Fig. S6, where the relationship between wind speeds and wave heights in
early summer (July) is similar to that observed in the fall and winter, when floating-leaved
plants were absent.

Figure 8. Determined transfer velocity converted into Schmidt number 600 against wind speed at 10 m.
The open and filled symbols indicate the data without and with floating-leaved plants, respectively. The
empirical functions plotted are the Wanninkhof (1992: W1992, dashed-dotted line), McGillis et al. (2001:
M2001, dashed line), Crusius and Wanninkhof (2003: CW2003, dotted line), and McGillis et al. (2004:
M2004, solid line) models.

Strong winds may enhance N2O fluxes by indirectly influencing the surface dissolved
N2O concentrations through water mixing into the lake bottom water (Taoka et al., 2020), but
this effect requires an accumulation of dissolved N2O in the bottom layer before mixing
occurs. Such an effect was observed on a windy day during the summer (Figs. 6 and 7). This
is particularly important in shallow lakes, where water-side turbulence generated from a
strong wind can cause mixing into the bottom water layer even under initially stably stratified
460 conditions (Lorke, 1998; MacIntyre and Melack, 2010). The accumulation of dissolved N$_2$O in the lake bottom layer is discussed in the next section.

462 **4.2 Biological controls on N$_2$O fluxes**

463 Surface dissolved N$_2$O concentrations are another important factor determining N$_2$O fluxes from lakes. Thus, in addition to water mixing that distributes dissolved N$_2$O within the lake, understanding the balance between N$_2$O production and consumption and related biological processes is fundamentally important to describing the variations in N$_2$O fluxes. In this study, we had only DIN data obtained at the lake center for the entire study period; thus, any discussion of the DIN data needs to be careful. However, hereafter we assume that similar seasonal variations in DIN concentrations may be possible in the littoral zone where we observed N$_2$O fluxes, as the water depth was not greatly more at the lake center (6.4 m) than in the littoral zone (1.8–2.0 m).

472 In summer, when mixing of the lake water was confined into the middle layer, dissolved N$_2$O accumulated in the lake bottom layer in the littoral zone of Lake Suwa (Fig. 6d), implying that the N$_2$O source was the lake sediment surface, as reported by Law et al. (1992) and Mengis et al. (1996). Dissolved N$_2$O accumulation has also been reported at the oxic-anoxic interface (Knowles et al., 1981; Yoh et al., 1983; Mengis et al., 1997). Under high temperatures, NH$_4^+$ can be produced in sediment by mineralization, and may accumulate in the bottom water layer during stably stratified conditions as observed at the lake center (Fig. 3). N$_2$O was produced by nitrification and denitrification from NH$_4^+$ at the oxic-anoxic water interface, as both nitrifying and denitrifying bacteria were present in the surface sediment collected from Lake Suwa (Text S2, Fig. S7), but N$_2$O reduction to N$_2$ can be suppressed by even small amounts of oxygen (Betlach and Tiedje, 1981; Knowles, 1982). This may have resulted in dissolved N$_2$O accumulating in the morning during the summer (Fig. 6), when lake-water mixing and N$_2$O diffusion to the surface water were limited.

485 Despite the limited water mixing, the dissolved N$_2$O concentrations in the bottom layer decreased from late morning to afternoon. The main reason for this decrease was N$_2$O reduction by denitrification in the more developed anoxic conditions of the bottom water layer, as implied by the decrease in DO concentrations in the middle water layer. However, the observed rate of decrease (approximately 300 nmol L$^{-1}$ d$^{-1}$) was higher than the rate of N$_2$O reduction obtained in incubation experiments by Tang et al. (2022a) for the initial N$_2$O concentration. This implies that some of the N$_2$O accumulated in the bottom water layer was diffused to the upper water layer under enhanced lake water mixing due to the continuously higher wind speeds during the afternoon. This may have increased the dissolved N$_2$O
concentrations in the surface layer and in turn, enhanced emissions into the atmosphere. Subsequently, decreased N$_2$O transfer from the bottom water layer and diffusion to the atmosphere may have decreased the dissolved N$_2$O concentrations in the surface layer and reduced emissions to the atmosphere.

The seasonal variations in N$_2$O fluxes were related to the variations in dissolved N$_2$O concentrations in the surface water, which may have been caused by a shift between oxic and anoxic conditions and a balance between N$_2$O production and consumption processes. In this discussion, we assume that similar seasonal variations in NH$_4^+$ and NO$_3^-$ concentrations occurred in the littoral zone, with additional consideration regarding differences in water depth and distances to inlet rivers. NH$_4^+$ and NO$_3^-$ were depleted in the surface water during the summer (Fig. 3), probably through continuous uptake by phytoplankton and aquatic plants (Wetzel, 2001; Smith et al., 2014). In addition, nitrifying bacteria were not present in the surface water collected from Lake Suwa (Fig. S7b). The NH$_4^+$ may have been produced in the bottom anoxic layer and accumulated, as observed at the lake center (Fig. 3a). Occasional water mixing transfers oxygen to the bottom layer in the littoral zone, where NH$_4^+$ is converted into NO$_3^-$ and N$_2$O via nitrification and denitrification (Tang et al., 2022b), but most of the N$_2$O is further reduced to N$_2$ before diffusing to the surface (Zhou et al., 2021; Liang et al., 2022) when the bottom anoxic layer develops. The littoral zone is affected by lateral transfer of NO$_3^-$ from river inflows, but this does not seem to have contributed substantially to increased dissolved N$_2$O concentrations in the oxic surface water. The absence of a strong net N$_2$O source resulted in lower dissolved N$_2$O concentrations in the surface water during the summer, resulting in lower N$_2$O emissions (Fig. 4). In some cases, N$_2$O uptake occurred (Fig. 5a, c), implying that the surface water was undersaturated with N$_2$O during those times, as observed in farm waterbodies in Canada (Webb et al. 2019). The N$_2$O emissions could also have been suppressed by the lower transfer velocity (Fig. 8) resulting from the presence of dense floating-leaved plants during the summer.

The NH$_4^+$ in the bottom layer was rapidly oxidized during the late summer, as the lake water was oxygenated and NO$_3^-$ was produced (Fig. 3). The entire water column was oxic during the fall and winter, and most of the NH$_4^+$ produced by mineralization was continuously converted into NO$_3^-$ and N$_2$O via nitrification on the lake bottom. This may have resulted in the relatively high and persistent dissolved N$_2$O concentrations, leading to higher N$_2$O fluxes during the fall and winter (Table 1 and Fig. 4).

4.3 Study limitations

The observations in this study were conducted only during the day, so variations in
N₂O fluxes during the night remain unknown. Night-time observations may be necessary for a complete understanding of the diurnal characteristics of N₂O fluxes. Wind speeds at this lake are generally lower during the night; however, transfer efficiency can be enhanced due to water convection related to the lake surface cooling, as suggested by Rutgersson and Smedman (2010). In addition, surface dissolved N₂O concentrations can vary due to water convection, provided that N₂O accumulates in the bottom layer. A complete understanding of the diurnal variability would enable us to design sampling times to deduce more accurate cumulative N₂O flux over longer periods. In future studies, micrometeorological observations using the aerodynamic gradient technique combined with a laser-based N₂O analyzer may help to clarify the complete diurnal variability in N₂O fluxes.

Extremely high dissolved N₂O concentrations were observed on October 12 (Table 1), with higher concentrations and variability in the surface water than in deeper water (Fig. S3). The higher concentrations imply that an N₂O source was present on the lake surface, as some types of cyanobacteria and green algae produce N₂O (Weathers, 1984; Fabisik et al., 2023). However, the high variation in dissolved N₂O concentrations was not reflected in the N₂O emissions on that day (Table S3); thus, we do not know if the variation occurred on the surface water of the lake or the reason for this variation.

5 Conclusions

We evaluated the sub-daily variations in N₂O emissions from a eutrophic lake during different seasons. Diurnal variations primarily depended on wind speed, as strong wind enhances transfer efficiency at the air-water interface. Emissions during the summer were positively correlated with surface dissolved N₂O concentrations. N₂O accumulated in the bottom water was distributed by water mixing, which enhanced N₂O emissions. We also clarified that the presence of floating-leaved vegetation suppressed transfer efficiency at the air-water interface, influencing the spatial and seasonal variations in N₂O emissions. These findings demonstrate the need to consider diurnal variability, presumably including the nighttime, to estimate cumulative N₂O emissions accurately over long periods.

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Open Research

All data used in this study are publicly available in the Zenodo repository at the following link: https://doi.org/10.5281/zenodo.11070279.

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