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RESEARCH REVIEW

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Diurnal variability in soil nitrous oxide emissions is a widespread phenomenon

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Abstract

Manual measurements of nitrous oxide (N_2O) emissions with static chambers are commonly practised. However, they generally do not consider the diurnal variability of N_2O flux, and little is known about the patterns and drivers of such variability. We systematically reviewed and analysed 286 diurnal data sets of N_2O fluxes from published literature to (i) assess the prevalence and timing (day or night peaking) of diurnal N_2O flux patterns in agricultural and forest soils, (ii) examine the relationship between N_2O flux and soil temperature with different diurnal patterns, (iii) identify whether non-diurnal factors (i.e. land management and soil properties) influence the occurrence of diurnal patterns and (iv) evaluate the accuracy of estimating cumulative N_2O emissions with single-daily flux measurements. Our synthesis demonstrates that diurnal N_2O flux variability is a widespread phenomenon in agricultural and forest soils. Of the 286 data sets analysed, ~80% exhibited diurnal N_2O patterns, with ~60% peaking during the day and ~20% at night. Contrary to many published observations, our analysis only found strong positive correlations ($R > 0.7$) between N_2O flux and soil temperature in one-third of the data sets. Soil drainage property, soil water-filled pore space (WFPS) level and land use were also found to potentially influence the occurrence of certain diurnal patterns. Our work demonstrated that single-daily flux measurements at mid-morning yielded daily emission estimates with the smallest average bias compared to measurements made at other times of day, however, it could still lead to significant over- or underestimation due to inconsistent diurnal N_2O patterns. This inconsistency also reflects the inaccuracy of using soil temperature to predict the time of daily average N_2O flux. Future research should investigate the relationship between N_2O flux and other diurnal parameters, such as photosynthetically active radiation (PAR) and root exudation, along with the consideration of the effects of soil moisture, drainage and land use on the diurnal patterns of N_2O flux. The information could be incorporated in N_2O emission prediction models to improve accuracy.

KEYWORDS
climate mitigation, diurnal variability, emission factors, greenhouse gas, soil N_2O emissions, temporal variability

1 | INTRODUCTION

Nitrous oxide (N_2O) is a greenhouse gas (GHG) with a global warming potential 298 times that of carbon dioxide (CO_2) and a lifetime of over 110 years (Myhre et al., 2013). The atmospheric concentration of N_2O has increased from 273 ppb in 1800 to 330 ppb in 2017 (European Environment Agency, 2019) with agriculture being one of the biggest anthropogenic sources contributing 60%–70% of anthropogenic N_2O emissions globally (Cowan et al., 2019). According to the Fifth Assessment by the Intergovernmental Panel on Climate Change (IPCC) (Ciais et al., 2013), global annual estimates for N_2O emissions from soils under natural vegetation and from agriculture are 6.6 (3.3–9.0) Tg N yr^{-1} and 4.1 (1.7–4.8) Tg N yr^{-1}, respectively, equivalent to the uncertainty of ±43.2% and ±37.8%. There is significant potential to mitigate these agricultural N_2O emissions through improved land management (Winiwarter et al., 2018), however, the assessment of mitigation strategies requires accurate quantification of emissions which is currently lacking.

The temporal variability of soil N_2O flux contributes significantly to the uncertainty of emission estimates (Jungkunst et al., 2018; Lammirato et al., 2018). The three-tier system introduced by the IPCC classifies methodological approaches based on the quantity of information involved, where Tier 3 approaches consist of methods with the highest analytical complexity including direct flux measurements and complex models (Bickel et al., 2006; de Klein et al., 2006). However, these approaches generally ignore short-term temporal (i.e. diurnal) variability of N_2O flux (Giltrap et al., 2010; Grace et al., 2020), partly due to the computational challenges imposed by higher temporal resolutions, as well as the lack of diurnal N_2O flux data to validate the model predictions. Current guidance for measuring N_2O flux recommends that single-daily measurements are taken in mid-morning (ca. 10:00 hr) because it corresponds closely to the time of daily average soil temperature and thus should represent the daily average flux if the temperature is the main driver (Charteris et al., 2020; IAEA, 1992; de Klein & Harvey, 2015; Parkin & Venterea, 2010). However, it has been shown that diurnal variability of N_2O emissions is not solely controlled by soil temperature (Keane et al., 2018, 2019; Shurpali et al., 2016), thus mid-morning fluxes may not capture daily mean fluxes adequately. With exceptions such as ECOSYS (Metivier et al., 2009), process-based simulation models of soil N_2O emissions (e.g. ECOSSE, DNDC and DAYCENT) (Cai et al., 2003; Del Grosso et al., 2001; Smith et al., 2010) are generally not configured to simulate diurnal variability of N_2O flux, as they take and produce daily averages of data inputs and outputs (Gilhespy et al., 2014). In addition, the validation of model outputs is generally limited to single-daily or weekly N_2O flux measurements (Babu et al., 2006; Bell et al., 2012; Cai et al., 2003; Necpálová et al., 2015).

Although manual N_2O flux measurements at sub-daily frequencies are not commonly practised due to high costs of labour and time, they have provided evidence of diurnal variations in N_2O flux which have been shown to vary from fivefold to tenfold in magnitude (Christensen, 1983; Dobbie & Smith, 2003; Maljanen et al., 2002; Scheer et al., 2012; Shurpali et al., 2016; Williams et al., 1999). In addition, there have been significant technological advances in automated chamber systems in recent years, enabling real-time, in situ N_2O flux measurements at sub-daily frequencies (Brummer et al., 2017; Keane et al., 2019). This has led to an increase in the availability of published sub-daily N_2O data across a range of agricultural and forest soils, which can be examined to assess the prevalence and timing of peak N_2O fluxes.

Regardless of manual or automated measurements, many studies reporting sub-daily data have observed a daytime peak in N_2O fluxes, often attributed to the diurnal patterns in soil temperature (Blackmer et al., 1982; Hosono et al., 2006; Liang et al., 2018; Scheer et al., 2014; van der Weerden et al., 2013; Williams et al., 1999). However, a number of studies have reported night-time peaks of N_2O flux, which were out of phase with the timing of maximum soil temperature (Scheer et al., 2012; Shurpali et al., 2016; Smith et al., 1998; Zona et al., 2013). The temperature sensitivity (Q_{10}) of soil N_2O production measured in lab studies ranges from two to three (Christensen, 1983; Denmead et al., 1979; van der Weerden et al., 2013), which is at odds with the observed amplitudes in diurnal N_2O fluxes (e.g. over an order of magnitude for N_2O fluxes) and the associated soil temperature ranges (<10°C) in various studies (Christensen, 1983; Dobbie & Smith, 2003; Maljanen et al., 2002; Scheer et al., 2012; Shurpali et al., 2016; Williams et al., 1999). However, there has been very limited research on the drivers and mechanisms underpinning diurnal variation in N_2O fluxes, in part because the prevalence of diurnal N_2O flux variability, as a widespread phenomenon in global soils, has not been clearly demonstrated.

Quantifying the prevalence and understanding the drivers of diurnal N_2O flux variability would enable improvements in N_2O flux measurement strategies and N_2O emission estimation models, which are pivotal to the calculation of national N_2O budgets and the development and monitoring of N_2O mitigation strategies. To our knowledge, no study has specifically addressed this challenge. We therefore conducted a systematic review and data synthesis of peer-reviewed publications to address the following research questions (RQ):

1. How common is diurnal variability in N_2O flux in cropland, grassland and forest soils, and do N_2O fluxes always follow the same pattern with a daytime peak?
2. Are soil N_2O fluxes strongly correlated with soil temperature regardless of the time of peaking?
3. Are diurnal N_2O flux patterns strongly associated with particular non-diurnal factors (e.g. soil abiotic properties and land use)?
4. Given that N_2O fluxes vary diurnally, how representative are single-daily measurements at mid-morning or any other time for estimating cumulative N_2O emissions?

2 | METHODS

We systematically identified peer-reviewed publications that reported sub-daily N_2O flux measurements from agricultural (cropland

and grassland) and forest soils and extracted N_2O flux and soil temperature data, dividing the data into individual data sets of 24-hr cycles. We first examined the prevalence of specific diurnal patterns of N_2O flux by normalizing the N_2O fluxes of each data set (Huang et al., 2014; Keane et al., 2018) and categorizing the data sets into three pre-defined diurnal patterns: daytime peaking, night-time peaking and non-diurnal (RQ1). Since the basis of the current recommended sampling time for single-daily flux measurement relies on N_2O flux following the diurnal cycles of soil temperature, we also investigated the degree of correlation between N_2O flux and soil temperature by fitting a linear regression model to each data set and calculating the correlation coefficient (RQ2). Then, we assigned the non-diurnal factors such as soil pH, bulk density, soil texture, N fertilization, land-use type, soil moisture and season of flux measurements provided in the literature to the corresponding data sets and examined whether diurnal patterns are associated with particular soil properties and/or management characteristics. (RQ3). Lastly, we compared the daily N_2O emission estimates calculated from single-daily measurements with those calculated from at least five sub-daily measurements (RQ4).

2.1 | Literature search and inclusion criteria

A literature search was conducted on two major scientific literature databases—'Web of Science Core Collection' and 'ScienceDirect'—with the search terms list below. The 28 August 2019 was selected as the cut-off date, no literature searches were conducted after which.

- Title: ('greenhouse gas' OR 'N2O' OR 'nitrous oxide') AND ('flux' OR 'fluxes' OR 'emission' OR 'emissions')
- Abstract: 'diurnal' OR 'diel' OR 'high frequency' OR 'automated' OR 'automatic' OR 'high temporal' OR 'highly temporal'
- Anywhere: 'soil' OR 'soils'

A total of 314 journal articles (Web of Science: 215, ScienceDirect: 99) published between 1983 and 2019 were identified in the initial database search. Duplicate articles (n = 83) were subsequently removed, and a set of inclusion criteria to select studies eligible for data extraction. The inclusion criteria are listed as follows:

- N_2O flux measurements were performed on cropland, grassland or forest soils;
- Five or more N_2O flux measurements were taken in every 24-hr cycle;
- The first and last measurement points of each 24-hr cycle were within 00:00–03:59 and 20:00–23:59, respectively.

This resulted in a compilation of 46 journal articles eligible for data extraction (detailed in Supporting Information S1) and yielded 286 diurnal data sets of N_2O flux. Of the 286 data sets, 160 contained soil temperature (5–10 cm) data, 157 contained soil pH data, 115 contained bulk density data, 175 contained soil texture data, 135 contained soil moisture data and 261 contained data of season of flux measurements. Information on N fertilization and land use was provided in all articles.

2.2 | Data extraction and transformation

For each selected publication, N_2O flux and soil temperature (if provided) data were extracted from figures and converted into a numerical format using a data recovery tool—'Engauge Digitizer' (Mitchell et al., 2020). Continuous time-series graphs were first divided into individual data sets per 24-hr cycle (i.e. 00:00–23:59) with N_2O flux data standardized to μg N_2O-N m^{-2} hr^{-1}. Hour and minute were also converted to decimal units (0.00–23.99 hr), where data were presented as 24-hr graphs of average or standardized N_2O flux (i.e. deviations from daily mean N_2O flux) over their measurement periods (e.g. 10 days), data from each graph were extracted as one data set.

To investigate the diurnal patterns of N_2O flux, we followed the approach of Huang et al. (2014) and Keane et al. (2018), who eliminated the magnitude differences between days by normalizing N_2O flux for every 24 hr (each data set). Normalized N_2O flux data (N_2O_{norm}) were bound between 0.0 and 1.0 using the following equation (Equation 1):

$$N_2O_{norm,t} = \frac{N_2O_t - N_2O_{min}}{N_2O_{max} - N_2O_{min}}, \quad (1)$$

where $N_2O_{norm,t}$ is the normalized N_2O flux at one point in time (t), N_2O_t is the N_2O flux at t, N_2O_{min} is the minimum N_2O flux in a data set, and N_2O_{max} is the maximum N_2O flux in a data set.

2.3 | Data analyses

2.3.1 | Categorization of diurnal patterns of N_2O flux

To determine the prevalence of different diurnal patterns of N_2O flux (RQ1), data sets were categorized as 'daytime peaking', 'night-time peaking' or 'non-diurnal' based on the following characteristics:

- Daytime peaking: N_2O flux increases in the daytime and decreases at night-time, resembling a typical diurnal oscillation of soil temperature;
- Night-time peaking: N_2O flux decreases in daytime and increases at night-time, acting in contrast to a typical diurnal oscillation of soil temperature;
- Non-diurnal: N_2O flux fluctuates inconsistently or shows a continuous upwards or downwards trend throughout the diurnal cycle.

We developed and used three sets of objective conditions, listed below, to categorize data sets into diurnal patterns. Data sets that met all the conditions in a category were classified as such. To avoid incorrect categorization of non-diurnal data sets from a single occurrence of high or low flux during daytime or night-time, the conditions for daytime and night-time peaking required the occurrence of the two highest fluxes and the two lowest fluxes, respectively, to take place within the specified time ranges. Since daytime involves morning and afternoon, we specified the daytime range to be 04:30–19:30 hr to capture both morning and afternoon peaking of N_2O flux and subsequently defined two subcategories ('morning peaking' and 'afternoon peaking') within the daytime peaking category. The third condition ensured that over 50% of the total daily emission occur in the daytime in daytime peaking data sets and vice versa in night-time peaking data sets. Since the hours between the first and last flux measurements in data sets were often <24 hr, we adjusted the 50% threshold for each data set using Equation (2). We then calculated the percentage of emission within three 12-hr periods (04:00–16:00 hr, 06:00–18:00 hr and 08:00–20:00 hr). The percentages of emission were calculated by dividing the emission within those 12-hr periods with the total emission of the data set. The emission of each 12-hr period was computed using a trapezoidal integration function (in R package 'pracma').

For the daytime peaking category, two subcategories were defined to identify morning peaking and afternoon peaking of N_2O flux. The categorization conditions for each diurnal pattern are listed below:

- Daytime peaking:
  1.. Both the highest and second highest N_2O_{norm} occur between 04:30–19:30 hr;
  2.. The lowest N_2O_{norm} occurs between 00:00 and 09:00 or 18:00 and 00:00 hr;
  3.. The percentage of emission calculated within 04:00–16:00 hr or 08:00–20:00 hr is greater than the adjusted threshold (Equation 2);
  ▪. If the percentage of emission calculated within 04:00–16:00 hr exceeds the threshold and the afternoon emission percentage, the data set is considered as 'morning peaking';
  ▪. If the percentage of emission calculated within 08:00–20:00 hr exceeds the threshold and the morning emission percentage, the data set is considered as 'afternoon peaking'.
- Night-time peaking:
  1.. Both the lowest and the second lowest N_2O_{norm} occur between 04:30–19:30 hr;
  2.. The highest N_2O_{norm} is between 00:00 and 09:00 hr or 18:00 and 00:00 hr;
  3.. The percentage of emission calculated between 06:00 and 18:00 hr is smaller than the calculated threshold.
- Non-diurnal:
  1.. Data set is neither daytime peaking nor night-time peaking.

$$\text{Adjusted threshold} = \frac{24}{\text{Hours between the first and last measurement in data set}} \times 50\%. \quad (2)$$

To determine whether the types of diurnal N_2O pattern are dependent on the magnitude of N_2O flux, data sets were categorized as high magnitude fluxes, where the maximum N_2O flux value was ≥100 μg N_2O-N m^{-2} hr^{-1}, or low magnitude fluxes, where the maximum N_2O flux value was <100 μg N_2O-N m^{-2} hr^{-1} (Lognoul et al., 2019); and the proportions of each diurnal pattern within these categories were calculated.

2.3.2 | N_2O flux and soil temperature

All statistical analyses of extracted data were performed in R version 3.6.1 (© The R Foundation). The correlation between N_2O flux and soil temperature in each diurnal pattern (RQ2) was examined by calculating the Pearson's correlation coefficients (*R*) between N_2O flux and soil temperature (5–10 cm soil depth) in the available data ($n = 160$). Additional soil temperature data points were generated by linearly interpolating the extracted soil temperature data. An *R* value between N_2O flux and interpolated soil temperature was computed using the correlation function (in R package 'ggpubr'). The data sets were then grouped according to their diurnal pattern.

2.3.3 | Non-diurnal factors and diurnal N_2O flux patterns

To examine whether diurnal N_2O flux patterns are strongly associated with particular non-diurnal factors (RQ3), soil pH, bulk density, soil texture, N fertilization, land-use type, soil water-filled pore space (WFPS) and season of flux measurements data were used where available (Table S1). Since only one of the extracted studies provided diurnal soil moisture data corresponding to its diurnal N_2O flux data (Du et al., 2006), a point-by-point diurnal relationship between soil moisture and N_2O flux (one similar to the N_2O–temperature relationship described in Section 2.3.2) could not be established and investigated in our analysis. Given the data structures of soil moisture provided by most of the studies (e.g. numerical indication of soil moisture ranges or soil moisture variations over the entire measurement period), we could only assign data sets into different soil WFPS level categories (i.e. ≤34.9%, 35%–54.9%, 55%–74.9% and ≥75%) according to the provided soil volumetric moisture content or WFPS data. Volumetric moisture content data were converted to WFPS levels using the bulk density value of the soil. Subsequently, the association between WFPS level category and diurnal N_2O flux pattern was examined.

Data sets originating from the same study site were assigned the same factor values or characteristics unless specified otherwise. To investigate the association between diurnal patterns and non-diurnal factors, we assumed that all data sets and their diurnal patterns were independent of one another and plotted the distribution of numerical factors (i.e. pH and bulk density) in each diurnal pattern category, or the relative frequency of diurnal patterns in categorical factors (i.e. soil texture, N fertilization, land use, soil WFPS level and season).

For numeric factors, data sets of soil pH (n = 157) and bulk density (n = 115) were grouped according to their diurnal pattern category. Boxplots showing the distribution of soil pH and bulk density in soils exhibiting the three diurnal patterns were produced, and the interquartile range and median of each category were extracted. The significant differences in soil pH and bulk density among the daytime peaking, night-time peaking and non-diurnal categories were tested using the Kruskal–Wallis test.

For categorical factors (i.e. soil texture, N fertilization, land use, WFPS level and season), data sets were first grouped according to their parameter category (Table 1), then the proportions of each diurnal pattern in each parameter category were quantified and visualized in stacked bar charts. Only one data set was collected during winter months, it was therefore not included in the analysis of seasonal effect on diurnal N_2O flux patterns. To reduce the number of soil texture groups and better visualize the effect of soil texture, data sets were reclassified into three soil classes according to their drainage property from the results of Groenendyk et al. (2015). These were defined as follows:

- Well drained: sand, loamy sand and silt;
- Imperfectly drained: sandy clay loam, silty clay, silty clay loam, silty loam and sandy loam;
- Poorly drained: clay, sandy clay, clay loam and peaty gley.

2.3.4 | Calculation of biases of cumulative N_2O emissions with single-daily measurement at different sampling times

Using a single time-point sampling at different times of day to estimate cumulative daily emissions can significantly over- or underestimate cumulative emissions. To assess this bias, we compared the cumulative N_2O emissions estimated by single-daily measurement (C-N_2O_{single}) against those estimated by sub-daily measurements (C-$N_2O_{sub\text{-}daily}$) (RQ4). Positive and negative biases indicate over- and underestimations of N_2O emissions, respectively. As single-daily flux measurements take place in the morning or afternoon in standard practises, five sampling times (08:00, 10:00, 12:00, 14:00 and 16:00 hr) were selected for the bias calculation. In each data set, N_2O flux values at the five sampling times were linearly interpolated from the sub-daily N_2O fluxes provided by the database. C-N_2O_{single} values at the sampling times were calculated by multiplying the interpolated N_2O flux by 24, which then returned a daily C-N_2O for each sampling time in each data set. The C-$N_2O_{sub\text{-}daily}$ value was calculated with the provided N_2O fluxes using a trapezoidal integration function (in R package 'pracma'). Since the sampling hours (i.e. number of hours between the first and the last measurement in a day) in most data sets were less than 24, the daily C-$N_2O_{sub\text{-}daily}$ of each data set was corrected by dividing the calculated C-$N_2O_{sub\text{-}daily}$ by the hours between the first and the last measurement and then multiplying it by 24. For each data set, the bias between C-N_2O_{single} (at a sampling time) and C-$N_2O_{sub\text{-}daily}$ was calculated using Equation (3):

$$\text{bias}_{st} = \frac{\text{C - N}_2\text{O}_{\text{single,st}} - \text{C - N}_2\text{O}_{\text{sub - daily}}}{\text{C - N}_2\text{O}_{\text{sub - daily}}} \times 100\%, \quad (3)$$

In Equation (3), bias_{st} represents the bias of the single-daily measurement at a certain sampling time, C-$N_2O_{single,st}$ represents the cumulative daily N_2O emission calculated using interpolated N_2O flux at a certain sampling time and C-$N_2O_{sub\text{-}daily}$ represents the cumulative daily N_2O emission calculated with the provided N_2O flux measurements using trapezoidal integration.

The mean value, upper and lower confidence interval (CI; 95%) of each bias_{st} from all the data sets were generated using a non-parametric bootstrap function (in R package 'Hmisc') based on 1000 replications.

3 | RESULTS

3.1 | Categorization of diurnal patterns of N_2O flux

Out of the 286 data sets, 173 (60.5%), 55 (19.2%) and 58 (20.3%) were categorized as daytime peaking, night-time peaking and non-diurnal, respectively. Within the daytime peaking data sets (n = 173), 34 (19.8%) were classified as morning peaking and 138 (80.2%) as afternoon peaking. Daytime, afternoon peaking emissions were therefore the most commonly occurring diurnal pattern identified across all studies. In the high magnitude flux data sets (n = 131), 52.7% were categorized as daytime peaking, 18.3% as night-time peaking and 29% as non-diurnal, whereas in the low magnitude flux data sets (n = 155), 67.1% were categorized as daytime peaking, 20%

TABLE 1 Number of data sets with categorical parameters

Soil drainage class			N fertilization		Land use		
Well drained	Imperfectly drained	Poorly drained	Fertilized	Unfertilized	Cropland	Grassland	Forest
8	137	30	258	28	210	43	33
WFPS level				**Season**			
≤34.9%	35%–54.9%	55%–74.9%	≥75%	Spring	Summer	Autumn	
27	45	57	6	98	138	24	

as night-time peaking and 12.9% as non-diurnal. The magnitude of N_2O flux has little effect on the diurnal pattern of N_2O flux. Line plots of the N_2O_{norm} and categorization description of all data sets are supplied in Supporting Information S2.

3.2 | Relationship between N_2O flux and soil temperature

In data sets with soil temperature data (n = 160), 80.6% had positive correlations (0.002 ≤ R ≤ 1.0) between N_2O flux and soil temperature at 5–10 cm depth (interpolated at N_2O flux measurement times) and 19.4% had negative correlations (−0.8 ≤ R ≤ −0.02). Only 33.1% of the 160 data sets showed strong positive correlations (i.e. R > 0.7). The interquartile ranges of R values for daytime peaking, night-time peaking and non-diurnal categories were 0.41 to 0.82, −0.19 to 0.15 and −0.03 to 0.67, respectively, whereas the median R values for the daytime peaking, night-time peaking and non-diurnal categories were 0.65, −0.06 and 0.32, respectively (Figure 1). This shows that daytime peaking data sets on average had stronger correlations than non-diurnal data sets. However, the wide range of R values in the daytime peaking category also implies that soil temperature is not consistently driving daytime N_2O flux peaks. Additionally, night-time peaking data sets only had a slightly negative R value on average which indicates little correlation exists between N_2O flux and soil temperature in night-time peaking data sets.

3.3 | Non-diurnal factors and diurnal patterns of N_2O

Soil pH in available data sets (n = 157) ranged from 3.0 to 8.6 (Figure 2a). The interquartile ranges of pH for daytime peaking, night-time peaking and non-diurnal categories were 5.9–7.4, 5.9–8.6 and 5.9–8.0, respectively. The median pH for the daytime peaking, night-time peaking and non-diurnal categories were 5.9, 7.2 and 5.9, respectively. No significant difference (p = 0.42) in soil pH was found among the diurnal pattern categories. However, the majority of daytime peaking and non-diurnal data sets, 59.6% and 64.3%, respectively, featured slightly acidic soils (i.e. pH at 5.0–7.0), with their median pH being 5.9, whereas a large portion (58.8%) of the night-time peaking data sets featured slightly alkaline soil (i.e. pH > 7.0) with a median of 7.2. The outliers in all three diurnal pattern categories (at pH = 3.0) were from the same study conducted on forest soil (Figure 2a).

Only 115 of the 286 data sets included bulk density data. The interquartile ranges of bulk density for daytime peaking, night-time peaking and non-diurnal categories were 0.92–1.21 g cm^{-3}, 1.05–1.35 g cm^{-3} and 0.92–1.24 g cm^{-3}, respectively (Figure 2b). All three categories had the same bulk density median of 1.16 g cm^{-3}. No significant difference (p = 0.68) in soil bulk density was detected among the diurnal pattern categories either. Among the three soil drainage classes, both well-drained and imperfectly drained soils were dominated by daytime peaking data sets, accounting for 62.5% and 60.6% of the corresponding soil drainage class category, respectively (Figure 3a). This was in agreement with the findings of soil WFPS categories since data sets with WFPS ≤ 34.9% (n = 27) and 35%–54.9% (n = 45) both predominantly showed daytime peaking patterns, accounting for over 70% in both WFPS level categories. Inversely, the majority of poorly drained soils were categorized as night-time peaking data sets (66.7%). Yet only data sets with a WFPS level of 55–74.9% showed an increasing proportion of night-time peaking pattern (36.8%), whereas those with WFPS level ≥75% (n = 6) were dominated by daytime peaking patterns (83.3%). However, the data sets with a WFPS level of ≥75% did not provide information on their soil texture and hence did not necessarily belong to poorly drained soils.

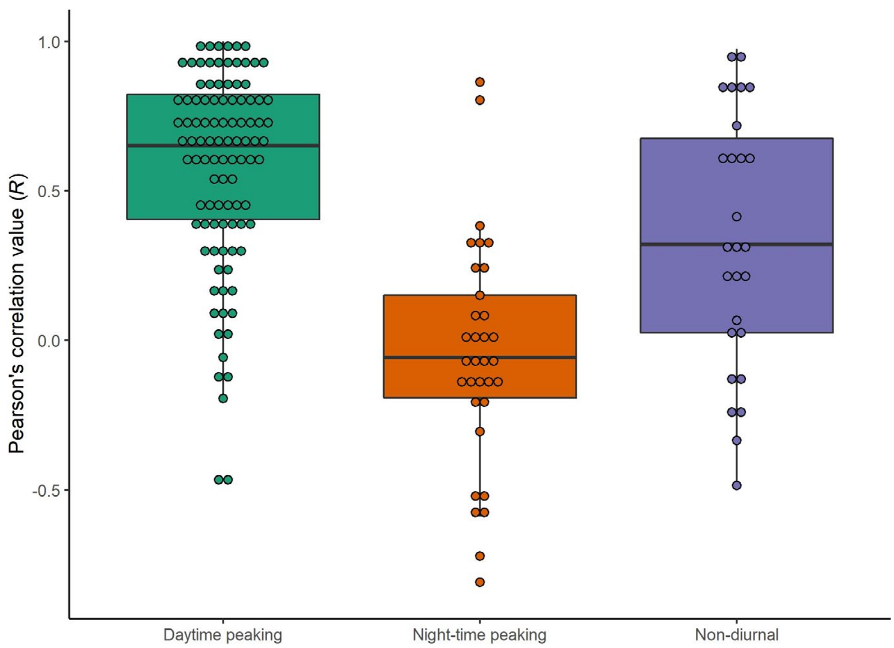

FIGURE 1 Differences in the relationship between soil temperature and N_2O fluxes in the three diurnal pattern categories. Boxes and whiskers represent the median (bold line in box), upper and lower quartile (top and bottom box line), maximum and minimum (top and bottom whisker) of Pearson's correlation coefficient (R) between N_2O flux and soil temperature (5–10 cm depth, interpolated at the times of N_2O flux measurement). Circles represent the R values of individual data sets

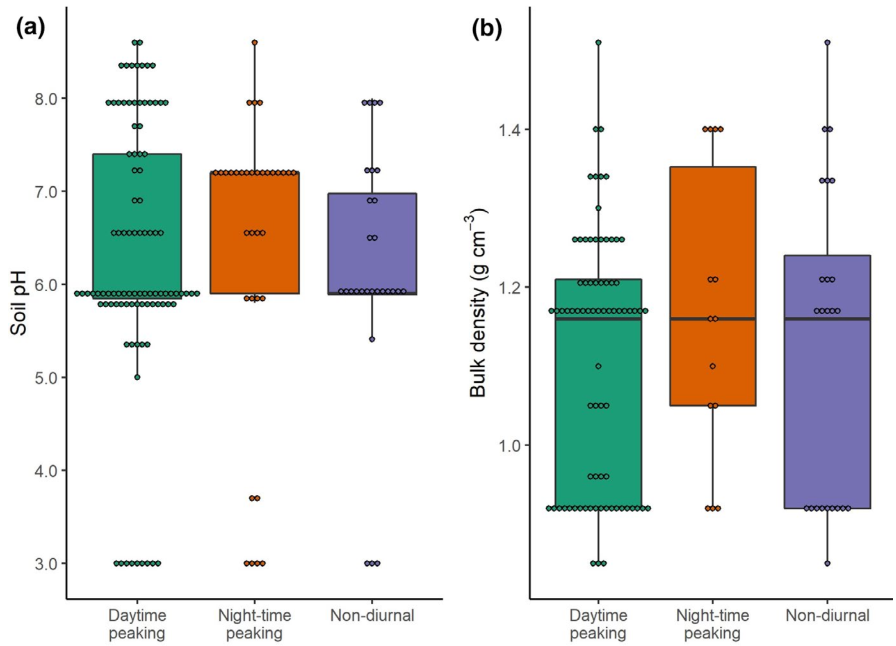

FIGURE 2 Distributions of (a) soil pH ($n = 157$) and (b) bulk density ($n = 115$) in the three diurnal pattern categories. Boxes and whiskers in (a) and (b) represent the median (bold line in box), upper and lower quartile (top and bottom box line), maximum and minimum (top and bottom whisker) of soil pH and bulk density, respectively. Circles in (a) and (b) represent the soil pH and bulk density values of soils from each data set

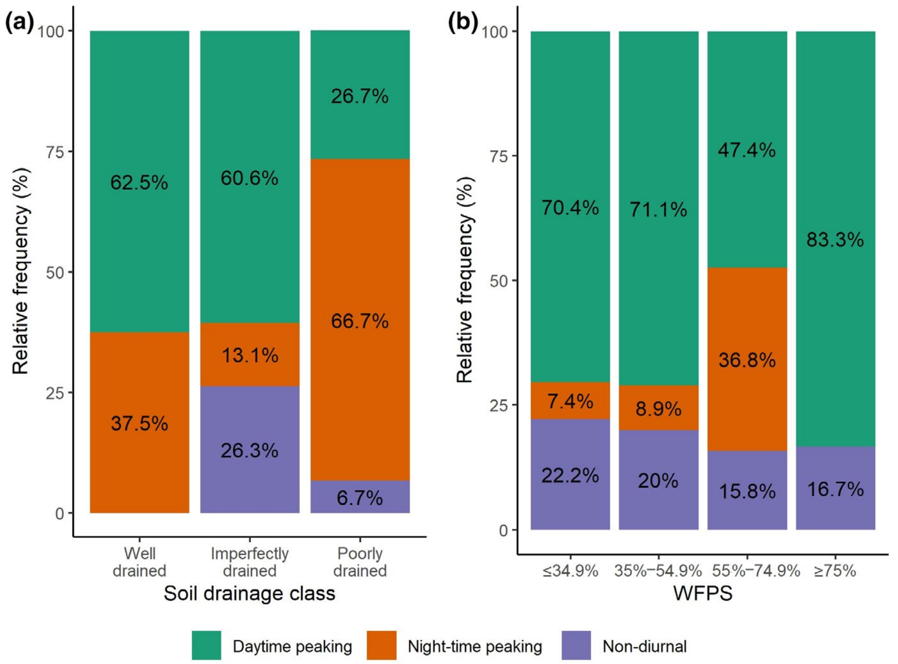

FIGURE 3 The relative frequency of diurnal N_2O flux patterns in (a) well drained ($n = 8$), imperfectly drained ($n = 137$) and poorly drained ($n = 30$) soils and in (b) soils at WFPS level ≤34.9% ($n = 27$), 35–55% ($n = 45$), 55%–74.9% ($n = 57$) and ≥75% ($n = 6$)

Data sets of fertilized soils ($n = 258$) showed a trend in diurnal pattern proportions similar to all data sets (Section 3.1), with daytime peaking, night-time peaking and non-diurnal data sets accounting for 58.9%, 20.5% and 20.5%, respectively (Figure 4a).

However, data sets of unfertilized soils ($n = 28$), exhibited a slightly different trend, with a larger daytime peaking proportion (75.0%) and a smaller night-time peaking proportion (7.1%). It should be noted that N fertilization could have an autocorrelation with land use as unfertilized soils consisted entirely of grassland ($n = 14$) and forest soils ($n = 15$). Cropland and forest soils also exhibited proportions similar to the general ratio of 3:1:1 in diurnal patterns (Figure 4b). Cropland soils ($n = 210$) exhibited a slightly lower daytime peaking proportion (55.2%) than forest soils ($n = 33$, 66.7%). Grassland soils ($n = 43$), on the other hand, featured predominantly daytime peaking data sets (81.4%) with a much lower night-time peaking percentage (7.0%) compared to the other two land-use types. Data sets collected in spring ($n = 98$) and autumn ($n = 24$) had similar proportions of daytime (~50%), night-time peaking (~20%) and non-diurnal (~30%) data sets, whereas those collected during summer months ($n = 138$) had a slightly larger proportion of daytime peaking data sets (62.3%) and a smaller proportion of non-diurnal data sets (16.7%) (Figure 4c).

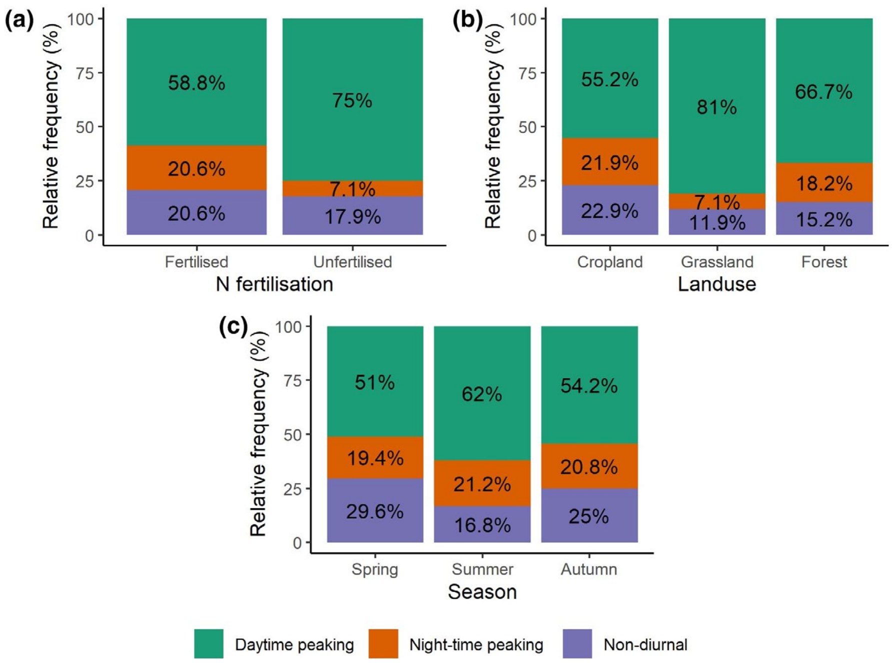

FIGURE 4 The relative frequency of diurnal N_2O flux patterns in (a) N fertilized (*n* = 258) and unfertilized (*n* = 28) soils, in (b) cropland (*n* = 210), grassland (*n* = 43), forest soils (*n* = 33) and in (c) spring (*n* = 98), summer (*n* = 138) and autumn (*n* = 24)

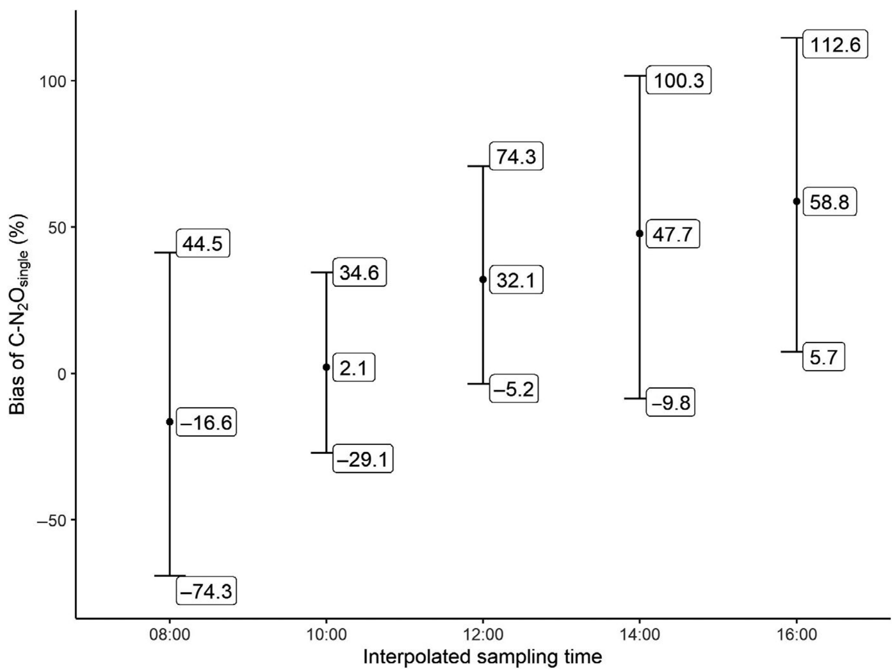

FIGURE 5 The effects of sampling time (interpolated) on the bias of C-N_2O_{single} (%) calculated against C-$N_2O_{sub\text{-}daily}$ from all data sets (*n* = 286); three annotated values are displayed above each sampling time. From top to bottom, they represent the upper CI, mean and lower CI (i.e. the bootstrap results based on 1000 replications) of percentage bias of C-N_2O_{single}

3.4 | Calculation of estimation biases by single-daily measurements

The bootstrap results (Figure 5) showed that sampling time significantly affected the magnitude of over- or underestimation (bias %) of cumulative N_2O emissions calculated at single time points (single-daily measurements). Cumulative N_2O emissions estimated from a single time point (C-N_2O_{single}) were most similar to those estimated from sub-daily measurements (C-$N_2O_{sub\text{-}daily}$) for the 10:00 hr sampling time, illustrated by the small mean bias value (+2.1%) and relatively small CI (64.9%). In comparison, earlier and later sampling times generated greater over- or underestimation with larger uncertainties ranging between 79.5% and 118.8%. A sampling at 08:00 hr resulted in a negative mean bias of −16.6%, whereas sampling at 12:00, 14:00 and 16:00 hr resulted in positive mean biases of 32.1%, 47.7% and 58.8%, respectively.

4 | DISCUSSION

Our data synthesis has demonstrated that diurnal variability in N_2O flux is a widespread phenomenon, with daytime peaking dominating (~60%) across the reviewed land-use types (cropland, grassland, and forest). However, daytime peaking was not found in all data sets with significant proportions of night-time peaking and non-diurnal pattern also identified, each accounting for ~20%. The relationship between N_2O flux and soil temperature was also revealed to be variable in the analysis, which contrasts with many literature's ascriptions of soil temperature to diurnal N_2O flux variations and hints that other diurnal or non-diurnal factors may also act as drivers or dampeners of diurnal variability. We showed that the relative occurrence of different diurnal patterns was strongly influenced by the drainage property of soil textural classes, with poorly drained soils featuring a majority of night-time peaking, and both well and imperfectly drained soils primarily exhibiting daytime peaking.

4.1 | Daytime diurnal N_2O flux variability and the role of soil temperature

The current recommended approach to address diurnal variability of N_2O flux is to measure N_2O flux at 10:00 hr or mid-morning, where daily mean soil temperature occurs, to capture the daily mean N_2O flux (Charteris et al., 2020; de Klein & Harvey, 2015) since past literature has provided evidence supporting that N_2O flux is controlled by soil temperature (Alves et al., 2012; Parkin, 2008; Smith & Dobbie, 2001). Using sub-daily data to estimate the uncertainty introduced by single-daily measurements revealed that the 10:00 hr recommended sampling time (Charteris et al., 2020; IAEA, 1992; de Klein & Harvey, 2015; Parkin & Venterea, 2010) would most likely capture the daily average N_2O flux compared to other sampling times since our study found diurnal N_2O fluxes peaking in the afternoon about half of the time (138 out of 286 data sets with a daytime-afternoon peaking pattern). However, due to the variability within the diurnal patterns of N_2O flux, sampling at 10:00 hr could still lead to significant over- or underestimation (Figure 5) when compared against sub-daily measurements, which more accurately capture diurnal variations of N_2O flux. This might be due to the absence of strong positive correlations ($R > 0.7$) between N_2O flux and soil temperature in 70% of the data sets. These findings suggest that soil temperature may not adequately represent diurnal variation in N_2O flux and imply that other diurnal variables could contribute to driving diurnal variation in N_2O flux.

A few studies have also observed diurnal peaks of N_2O flux preceding those of soil temperature (e.g. morning peaking of N_2O flux) (Akiyama & Tsuruta, 2003; Keane et al., 2018; Peng et al., 2019), and some reported a stronger relationship between N_2O flux and parameters driving photosynthesis such as solar radiation and photosynthetically active radiation (PAR) (Christensen, 1983; Keane et al., 2018; Shurpali et al., 2016). In those studies, plant inputs of labile organic C via root exudation driven by PAR were proposed as regulators of diurnal variations in N_2O flux (Keane et al., 2018, 2019; Shurpali et al., 2016). The potential influence of PAR mediated through plant metabolism is also supported by the study of Zona et al. (2013), where gross primary productivity explained 73% of diurnal N_2O variations in a growing season. However, Das et al. (2012) observed daytime peaks in N_2O flux with artificial PAR oscillations from bare soil in a temperature-controlled study, which they ascribed to soil surface warming resulting from the artificial PAR lighting. Their results, however, do not disprove the effect of root exudation of labile C on soil N_2O production, as both drivers could coincide in vegetated soil systems. Daytime activities such as irrigation, fertilization and grazing could also influence diurnal N_2O flux pattern. We found two extracted studies (data set $n = 14$) that performed daily irrigation in the morning with one irrigated with fertilizer solution (Flessa et al., 2002; Hosono et al., 2006), and two other studies (data set $n = 7$) that measured diurnal N_2O flux on actively grazed pastures (Wang et al., 2005; Williams et al., 1999). This could lead to daytime peaking of N_2O flux that might not be caused by soil temperature or other potential diurnal drivers since the increase in soil WFPS and/or N substrates (nitrate and ammonium) would promote denitrification and hence increase N_2O flux (Firestone & Davidson, 1989). Seasonal events such as freeze-thaw could also control the occurrence of daytime peaking of N_2O flux. Peng et al. (2019) observed morning peaking of N_2O flux in a temperate forest during a freeze-thaw period in spring, whereas afternoon peaking of N_2O flux was observed in summer. However, the relative importance of these potential drivers to the diurnal variability of N_2O flux could not be established in this study, as it requires more comprehensive data collection of the mentioned drivers of diurnal resolutions which are currently unavailable.

4.2 | Night-time N_2O flux diurnal variability and the role of soil temperature

Although night-time peaking of N_2O flux is uncommon (~20% of the data sets), its occurrence also contradicts the assumption of temperature as a main predictor. In a study that measured diurnal N_2O fluxes from a peaty gley soil, night-time peaking of N_2O flux was attributed to N_2O being produced at depth, creating a time lag of several hours between temperature-induced increases in N_2O production at depth and emissions at the surface (Smith et al., 1998). However, it is generally thought that N_2O production occurs mostly in the top few centimetres of the soils, even in peat soils (Goldberg et al., 2008; Shcherbak & Robertson, 2019; Toma et al., 2011). Furthermore, N_2O produced at depth is likely consumed during upward diffusion (Goldberg et al., 2008; Van Groenigen et al., 2005), especially under wet conditions with prolonged residence time, resulting in little emission of N_2O originated from deep subsurface soils (Clough et al., 2006). It is possible that night-time peaking of N_2O flux is a result of increased N_2O consumption during the daytime. Soil oxygen (O_2) availability controls N_2O production ($NO \rightarrow N_2O$) and

N_2O consumption ($N_2O \rightarrow N_2$), with the latter becoming more dominant when O_2 is severely limited (Castaldi, 2000; Knowles, 1982; McMillan et al., 2014; Morley et al., 2008; Schlüter et al., 2018). Increased O_2 consumption during daytime due to temperature-induced increases in soil respiration, coupled with the lack of O_2 supply in soils with restricted airflow, could result in lower N_2O flux during the day. As increased soil O_2 consumption during daytime has been reported in various studies (Hamerlynck et al., 2013; Lu et al., 2013; Tang et al., 2003) and has been shown to positively correlate with soil temperature (Chuang et al., 2004; Wang et al., 2016) and photosynthetic rate (Neales & Davies, 1966), it is plausible that more N_2O in soils is consumed during the day than at night. This theory could also explain the larger proportion of night-time peaking emissions identified in poorly drained soils (Figure 3a), as N_2O reduction could surpass N_2O production during daytime in soils with limited air permeability. This hypothesis is also supported by evidence that night-time peaking of N_2O flux as well as N_2O uptake during daytime have been observed in vegetated wetlands featuring high percentages of soil WFPS and limited O_2 availability (Windham-Myers et al., 2018; Yu et al., 2012). Additionally, studies have found that plants exhibit higher uptake of soil nitrate and ammonium during the day (Geßler et al., 2002; Macduff & Bakken, 2003; Okuyama et al., 2015), which could also potentially contribute to the occurrence of night-time peaking of N_2O flux due to the reduction in substrates for nitrification and denitrification during daytime.

4.3 | Biological pathway for diurnal N_2O flux amplification

Supported by several studies (Langarica-Fuentes et al., 2018; Oburger et al., 2014; Ueno & Ma, 2009; Wu et al., 2017), we propose a biological pathway wherein the diurnal rhythms of root exudation of photosynthates could amplify diurnal N_2O fluxes beyond what can be explained by temperature alone. We suggest that root exudation during and after the photoperiod promotes denitrification activity and hence increases N_2O production in soils. Denitrification and nitrifier denitrification are two main microbial processes driven by O_2 limitation (Bollmann & Conrad, 1998; Khalil et al., 2004; Zhu et al., 2013) which contribute to the majority of the N_2O production in soils (Kool et al., 2010; Opdyke et al., 2009; Wrage-Mönnig et al., 2018). Reduced soil O_2 concentration and increased soil respiration during daytime have been reported previously (Keane et al., 2019; Shurpali et al., 2016; Zimmermann et al., 2009). It is likely that during the daytime, photosynthetically assimilated C is translocated to the plant roots and exuded into the rhizosphere, where potential denitrification activity is greater (Hamonts et al., 2013). Exuded C is then rapidly respired by heterotrophs (Kelting et al., 1998; Sun et al., 2017), which subsequently depletes O_2 in the soil and drives denitrification and nitrifier denitrification. (Knowles, 1982; Wrage et al., 2001). Several of our included studies have also shown diurnal N_2O fluxes to closely follow ecosystem respiration rates (CO_2 fluxes measured by dark chambers) (Brumme & Beese, 1992; Flessa et al., 2002; Laville et al., 2017; Maljanen et al., 2002; Savage et al., 2014), highlighting the positive effects of ecosystem respiration on N_2O flux. Root exudation can also directly fuel N_2O production (Azam et al., 2002; Gillam et al., 2008; Henderson et al., 2010), as most denitrifiers and some nitrifiers are heterotrophic and would consume the labile C in the exudate to gain energy. However, the exact effect of photosynthesis on the diurnal rhythm of root exudation is only partially understood. Although isotopic labelling experiments have reported rapid rhizosphere respiration of assimilated C (within 2 hr) upon plant exposure to light (Dilkes et al., 2004; Gavrichkova & Kuzyakov, 2017), various time lags from less than an hour to more than a day between photosynthesis and soil respiration of assimilated C have been reported (Kuzyakov & Gavrichkova, 2010). Furthermore, soil temperature has been demonstrated to enhance root-derived C exudation rates (Yin et al., 2013; Zhang et al., 2016), which could explain the positive correlations between N_2O flux and soil temperature in some data sets. However, the temperature effects on root exudation have been shown to vary among species (O'Leary, 1966), and the time lag between soil temperature and root exudation is still unexplored thus far. Depending on the diurnal dynamics of soil O_2 concentration, N_2O flux might exhibit a daytime peaking or night-time peaking diurnal pattern. A field study in which night-time peaking diurnal N_2O patterns were observed from a poorly drained grassland soil also provided isotopic evidence suggesting a shift from nitrification in the early morning to denitrification in the afternoon (Yamulki et al., 2001). This shift in soil N-cycling processes concurs with the theory of increased root exudation of C during photoperiods promoting denitrification. Nonetheless, a thorough understanding of the diurnal behaviour of root exudation in different plant species in different soil conditions, such as soil C and N availability and pH, is crucial to the understanding of how plants influence the dynamics of N_2O production and consumption through root exudation with current knowledge on this topic still limited (Kuzyakov & Gavrichkova, 2010). Furthermore, little research has been able to decouple PAR and soil temperature to demonstrate the sole effect of PAR on N_2O flux in vegetated soil systems.

4.4 | Non-diurnal N_2O flux variability and the role of soil temperature

In the case of non-diurnal patterns, non-diurnal data sets overall showed a weak positive correlation ($0 < R < 0.7$) between N_2O flux and soil temperature (Figure 1); this could be explained by the immediate positive effect of N addition in some studies (Huang et al., 2014; Kostyanovsky et al., 2019; Scheer et al., 2008). In experiments, fertilization events often took place in the morning, which resulted in a continuous increase in N_2O flux in the following hours (Kostyanovsky et al., 2019; Simek et al., 2010; Smith et al., 1998). The upward trend of N_2O flux could coincide with soil temperature during the daytime but lasts through the evening and night, resulting in a slight positive correlation between N_2O flux and soil temperature. The rest of the non-diurnal data sets with no visible trend was likely due to the disruption of the diurnal N_2O flux patterns caused by rainfall (Ball et al., 1999; Charteris et al., 2020; van der Weerden et al., 2013). It was reported that soil N_2O production declines substantially when soil WFPS reaches over 80% as denitrification shifts to completion (i.e. $N_2O \rightarrow N_2$) due to soil anoxia (Congreves et al., 2019; Davidson, 1993; Neill et al., 2005). As rainfall events do not have a diurnal rhythm and could obstruct O_2 influx into the soil by increasing the percentage soil WFPS, they could subsequently change the dynamics between soil N_2O production and consumption and therefore interrupt pre-existent diurnal patterns of N_2O flux.

4.5 | Non-diurnal factors and diurnal variability of N_2O flux

The data synthesis reveals that the occurrence of specific diurnal patterns of N_2O flux may also be influenced by non-diurnal factors. Although no significant difference was found among the pH values of diurnal pattern categories (Figure 2a), the night-time peaking category exhibited a higher pH median value (pH = 7.2) than the daytime peaking and non-diurnal categories (pH = 5.9) (Figure 2a). This agrees with the findings of Hénault et al. (2019) and Čuhel et al. (2010), which demonstrated increased N_2O reduction activities (i.e. N_2O consumption) by denitrifers in alkaline conditions. Soils with higher pH could possess higher potentials for N_2O consumption and hence increased likelihoods of night-time peaking, due to increased soil O_2 depletion during daytime by increased soil respiration (Makita et al., 2018; Tang et al., 2003), which subsequently leads to favourable conditions for N_2O reduction (Firestone & Davidson, 1989; Morley et al., 2008). The boxplot results of bulk density (Figure 2b) indicated that bulk density has little association with the occurrence of diurnal patterns, as we found similar median values and wide spreads of interquartile ranges of bulk density among the diurnal pattern categories with no significant difference between one another. Conversely, our findings of the proportion of diurnal patterns in soil drainage classes (Figure 3a) and WFPS levels (Figure 3b) suggest that soil gas diffusivity, which is regulated by both factors, could potentially determine the occurrence of specific diurnal patterns. The proportion of daytime peaking in well and imperfectly drained soils was similar to that of the overall data sets (~60%); however, in poorly drained soils, the majority of the data sets were night-time peaking (67%). Similarly, proportions of daytime peaking data sets (~70%) were larger in soils with relatively low WFPS levels (i.e. ≤34.9% and 35%–54.9%) than in soils with a WFPS level of 55%–75% (47%). Night-time peaking data sets also accounted for a higher proportion in soils with a WFPS level of 55%–75% (37%) compared with lower WFPS levels. Conversely, a majority of daytime peaking data sets (83%) and no night-time peaking data set were observed in soils with a WFPS level of ≥75%. However, this observation is unlikely to be conclusive given the small number of data sets with soil WFPS ≥ 75% (n = 6), which originated from two studies where one raised its soil WFPS to 80% in the morning at the start of the flux measurements (Kostyanovsky et al., 2019), and the other conducted flux measurements during a freeze-thaw period (Peng et al., 2019). Both would have led to increased soil WFPS, and thus N_2O flux during daytime. Our findings of the increase in night-time peaking proportion in soils with reduced gas diffusivity support the theory suggested in Section 4.2, where we highlighted the possibility of N_2O consumption overtaking N_2O production during daytime under limiting O_2 conditions. In this review, poorly drained soils comprised soils with high clay or organic matter content (Section 2.2.3), which have been shown to have lower total porosity and gas diffusivity than well and imperfectly drained soils (Chamindu Deepagoda et al., 2011; Moldrup et al., 2000). Likewise, an increase in WFPS reduces the gas diffusivity of soils (Chamindu Deepagoda et al., 2011). Multiple studies have demonstrated the effect of gas diffusivity on N_2O flux, showing increasing N_2O flux when gas diffusivity reduces from 0.03 to 0.005 and decreasing N_2O flux when gas diffusivity goes below 0.005 (Balaine et al., 2016; Chamindu Deepagoda et al., 2019, 2020). Low gas diffusivity (<0.005) can cause O_2 limitation in soil and subsequently prompt nitrifiers and denitrifiers to shift from N_2O production to consumption (Balaine et al., 2016; Bollmann & Conrad, 1998; Sutka et al., 2006). Since soil O_2 is less readily replenished in poorly drained soils and in soils with high WFPS, localized soil anoxia, where N_2O reduction overrides N_2O production, is likely to develop in these soils during daytime when soil respiration rate increases (Keane & Ineson, 2017; Makita et al., 2018; Tang et al., 2005). However, we have not found any study that examined the effects of soil texture on the diurnal dynamics of soil O_2 concentration under the same conditions (e.g. bulk density, volumetric water content and vegetation), which leaves the relationship between soil texture and diurnal N_2O patterns still unclear. In addition, while the general regulatory effect of soil moisture and WFPS on N_2O flux is well studied (Schindlbacher et al., 2004), there is still little research focused on diurnal variations in soil moisture, along with its interactions with other diurnal variables such as soil temperature and soil respiration, leading to its effect on diurnal N_2O fluxes. For example, Denmead et al. (2010) observed diurnal oscillations of soil WFPS inverse to those of soil temperature, which could dampen the temperature effect on diurnal N_2O fluxes. Therefore, we suggest future research should collect diurnal data of soil moisture or WFPS, soil temperature, and N_2O flux from soils of different textures and drainage properties to investigate the interactive effects of soil physical factors on diurnal N_2O fluxes.

Nitrogen fertilization is another non-diurnal factor that was expected to have an effect on diurnal N_2O patterns since many studies reported daytime peaking diurnal patterns only after the application of N fertilizers (Laville et al., 2017; Lognoul et al., 2019; Shurpali et al., 2016; Skiba et al., 1996). Yet, our findings (Figure 4a) show daytime peaking diurnal patterns occur more often in unfertilized soils than in fertilized soils, indicating that high soil N levels do not cause daytime peaking diurnal patterns. This is reiterated with the higher percentages of daytime peaking in low magnitude flux data sets (67%) than in high magnitude flux data sets (53%) (Section 3.1). Land-use type has also been shown to govern the diurnal patterns of N_2O flux. Higher proportions of daytime peaking emissions were recorded in data sets with grassland (81%) and forest (67%) soils compared with cropland (55%) soils (Figure 4b). Very little literature has reported the direct relationship between land use and the diurnal pattern of N_2O flux. One study that was conducted on a field consisting of two established land-use systems (pasture and cropland) found greater gas diffusivity in the pasture than in the cropland (Kreba et al., 2017). This suggests that land use could indirectly influence the occurrence of diurnal N_2O patterns through changing the soil gas exchange dynamics. Future research should include similar experiments to test the effects of land use on the diurnal patterns of N_2O flux. Despite similar proportions of diurnal N_2O flux patterns being found among three seasons (Figure 4c), most of the diurnal N_2O flux data sets were collected during summer (n = 138) and spring (n = 98) months, with only a small number of data sets collected in autumn (n = 24) and winter (n = 1) months. This may have resulted in a potential bias in the overall diurnal patterns of N_2O flux, as those in winter were not analysed due to the lack of data.

4.6 | Potential bias of single-daily measurements

As discussed in Section 4.1, N_2O flux does not always follow the diurnal oscillation of soil temperature. Measuring N_2O flux at times of daily average soil temperature might not capture the daily average N_2O flux and could lead to over- or underestimation of daily fluxes. Our analysis (Figure 5) confirmed that 10:00 hr was the optimal sampling time as it resulted in the smallest magnitude of under- or overestimation. This agrees with the recommended time of sampling suggested by several publications. However, there was still a significant uncertainty (CI ranged between −29% and +35%) as the single time-point sampling failed to capture the inconsistent occurrence of diurnal variations in N_2O flux. Most studies that suggested a recommended time of sampling based their extrapolations on their sub-daily N_2O flux measurement campaign(s) on a single field site which usually exhibited a more-or-less consistent diurnal pattern of N_2O flux for the duration of the campaign(s), which is often the duration of a season (Chang et al., 2016; Reeves & Wang, 2015; Savage et al., 2014; van der Weerden et al., 2013). However, some studies have shown differences in the diurnal behaviour of N_2O flux at different sites (Alves et al., 2012; Smith et al., 1998) and times of year (Shurpali et al., 2016; Zona et al., 2013). Besides, studies have also provided different recommended times of sampling. For instance, Parkin (2008) who measured N_2O emissions from cropland found sampling at 12:00 hr would only be 8% higher than the daily mean N_2O flux; whereas Smith and Dobbie (2001) measured N_2O emissions from two grassland sites and suggested sampling to take place at 03:00, 11:00 and 19:00 hr, as it produced N_2O flux representative of the daily mean. This could be the result of varying diurnal patterns of N_2O flux in different ecosystems which further underlines the potential uncertainty of single-daily N_2O flux measurements. Hence, sub-daily flux measurements should be employed when possible to account for the diurnal variability of N_2O flux and accurately measure cumulative N_2O emissions.

5 | CONCLUSION

Our work has, for the first time, conclusively demonstrated that diurnal variability of N_2O flux is a widespread phenomenon across agricultural and forest soils. Daytime peaking of N_2O flux was the most common diurnal pattern observed, but it did not consistently occur across soil drainage classes, soil WFPS levels, N fertilization status, seasons and land-use types. This analysis has shown that single-daily measurements produce emission estimations with large uncertainties due to the inconsistency in diurnal N_2O flux patterns, with soil temperature only partially explaining diurnal variations in N_2O flux. There is a paucity of published data on diurnal variables (e.g. PAR, plant C inputs, soil moisture and N substrates) which may interact to influence diurnal N_2O fluxes, and this limits our understanding of the drivers of diurnal N_2O fluxes. The interactive effects of these variables as well as other non-diurnal factors (e.g. land use and soil drainage property) on diurnal N_2O flux variations need to be addressed in future research. At present, analyses of the drivers of diurnal N_2O flux variability are limited by the lack of diurnal data on soil inorganic N content, soil labile C content and soil moisture. Collection and incorporation of such data into analyses of diurnal N_2O flux in future research will help address this and better predict the diurnal variability of N_2O flux.

Without a comprehensive understanding of the drivers of diurnal N_2O fluxes, our current ability to accurately model and upscale diurnal N_2O fluxes are limited. We do not know the persistence and occurrence of diurnal N_2O flux patterns over entire crop life cycles or seasons. In addition, the significance of diurnal variability of N_2O flux is still not acknowledged or addressed in national and global GHG emission reporting, contributing to N_2O emission estimate uncertainties and hindering the development of mitigation strategies. Nevertheless, recent developments in real-time monitoring of GHG fluxes have increased the availability of sub-daily N_2O flux data. This will play a key role in improving the accuracy of current model predictions of N_2O emission through emergent research on the diurnal variability of N_2O flux.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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