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Effects of soil temperature on nitric oxide emission from a typical Chinese rice–wheat rotation during the non-waterlogged period

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Abstract

Measurements of nitric oxide (NO) emission from a typical Chinese rice–wheat rotation are continuously made during the non-waterlogged period by using an automatic system based on static chamber techniques. A positive correlation exists between NO emission and soil moisture content when surface soil temperature is > 20 °C. The diurnal variability in NO emission is characterized with day-peak, night-peak and irregular patterns, which are in close association with wheat growth. The diurnal NO emission under the day-peak pattern is correlated with the simultaneously observed surface soil temperature, whereas that under the night-peak and irregular pattern is dependent on surface soil temperature at 7 ± 2 and 3 ± 2 h before NO observation, respectively. The effect of soil temperature on NO emission is well described by $F = \alpha \cdot e^{\beta \cdot T}$, where F is NO flux, T soil temperature, and α and β empirical coefficients. The parameter Q_{10}; that is, the change in NO emission per 10 °C soil temperature, is correlated with the rates of fertilizer-N application. An approach orientated from the Arrhenius equation, $F = e^k e^{-E_a/(R \cdot T_K)} + e^k e^{-E_a/(R \cdot \Delta T_K)} \sin[(t\text{-}6\text{-}\tau)/12\pi]$, is developed in order to predict diurnal NO emission, where T_K is the daily average soil temperature, ΔT_K the deviation of soil temperature from the daily average, E_a the apparent activation energy, R the gas constant, t a given time within the one-day cycle, τ delayed time for appearance of the diurnal NO emission peak, and k an empirical coefficient. Based on the results, the authors recommend that intermittent measurement of NO emission from a similar ecosystem would be best taken around 17:00. The molar ratio of NO/N_2O over the non-waterlogged period is > 1 when soil moisture content was less than the field capacity, suggesting that NO emission was mainly derived from nitrification under this condition.

Keywords: apparent activation energy, cultivated lands, nitric oxide emission, soil moisture, soil temperature, temporal variability

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Introduction

Nitric oxide (NO), as one of the important indirect greenhouse gases, plays a critical role in regulating the oxidation capacity of the troposphere, influencing the lifetime of the long-lived greenhouse gases – for example, methane – and contributing to the greenhouse effect by being directly involved in the production and depletion of tropospheric ozone (Ehhalt *et al.*, 2001). Emission from soils is currently the second largest source of atmospheric NO, following the combustion of fossil fuels (Delmas *et al.*, 1997; Ehhalt *et al.*, 2001). With the advances in techniques for reducing the NO emission from combustion processes, however, this source is expected to reduce by 90% in the near future (e.g. Bradley & Jones, 2002). If so, the future biological source from soils is likely to override other sources. The global NO emission from soils ranges from 4 to 21 TgN year^{-1} (e.g. Davidson & Kingerlee, 1997; Lee *et al.*, 1997; Ehhalt *et al.*, 2001), of which *ca.* 40% is from cultivated lands (e.g. Davidson & Kingerlee, 1997). Field

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measurements have indicated that the NO emission is closely associated with farming practices including fertilization, irrigation and soil plowing (e.g. Jambert *et al.*, 1997; Sanhueza, 1997), soil temperature and moisture content (e.g. Yamulki *et al.*, 1995).

For the purpose of estimating regional inventories, NO emission from terrestrial ecosystems has been roughly linked with land use type as well as air temperature (T_{air}) at the regional or national scale by using an exponential equation $F = \alpha \cdot e^{\beta \cdot T}$ (Williams *et al.*, 1992a), where F is NO flux, T soil temperature, which is a function of T_{air}, and α and β empirical coefficients. The change in NO emission per 10 °C soil temperature (Q_{10}), which could be calculated from $Q_{10} = e^{10\beta}$, is a key parameter to describe temperature dependence of NO emission (Williams *et al.*, 1992b). The temperature dependence of NO emission from wheat fields was also expressed by the Arrhenius equation $F = A \cdot e^{-E_a/(R \cdot T_K)}$(e.g. Yamulki *et al.*, 1995), where T_K is soil temperature in kelvins, E_a apparent activation energy, R the gas constant and A the pre-exponential factor. Both equations were generally applied in empirical, semi-empirical and process-oriented biogeochemical models (e.g. Williams *et al.*, 1992a; Ding & Wang, 1996; Li *et al.*, 2000). The parameter Q_{10} or E_a was usually considered as a constant – for example, $Q_{10} = 2.0$ (e.g. Williams *et al.*, 1992a; Li *et al.*, 2000) and $E_a = 75\,\mathrm{kJ\,mol^{-1}}$ for methane (CH_4) production in rice paddy fields (Ding & Wang, 1996) in modeling studies. However, any parameter of the equations may be conditionally constant because of the complex regulating factors and the intrinsic temporal/spatial variability in NO emission from cultivated lands. Accordingly, accurately quantifying the parameters of either equation and linking them with regulating factors of NO emission, with which few studies to date have dealt, are fundamental for developing process-oriented models as tools for calculating inventories, prediction and scenario analysis of regional NO emissions.

Zheng *et al.* (2003) reported the seasonal variability in NO emission during the non-waterlogged period of a rice–wheat rotation, based on a continuous *in situ* measurement made in 1996–97 in southeastern China. Based on data of the same measurement, this paper seeks to identify the diurnal variability, to investigate the temperature dependence of both seasonal and diurnal variability and to discuss the parameters of both equations mentioned above and try to link them with regulating factors of NO emission.

Materials and methods

Nitric oxide emission during the non-waterlogged period of a rice–wheat rotation was continuously measured in 1996–97 in a suburb of Suzhou, China (31°16′N, 120°38′E), using an automatic system based on static chamber techniques and chemiluminescent NO analysis (Zheng *et al.*, 2003). Zheng *et al.* (2000) describe the location, climate, soil properties and farming practices of the experimental site. The non-waterlogged period spanned from the wheat-growing season to the following fallow period. A local prevailing winter wheat cultivar, *Triticum aestivum* L. cv. Yangmai 5, was planted in four plots of 12 × 8 m on November 1, 1996 and harvested on May 27, 1997. After the wheat harvest, the field remained bare until the rice transplanting on June 18. No irrigation was performed during the wheat-growing period, but the plots were wetted through irrigation for 1 week before flooding and plowing on June 17. Three treatments of fertilization were applied, including no fertilizer (plot A), organic manure plus synthetic fertilizers (plot B) and synthetic fertilizers only (plots C and D), which were the same as Zheng *et al.* (2003). The organic manure was wheat straw aerobically fermented for about 5 months. Two synthetic fertilizers, compound fertilizer ($N : P_2O_5 : K_2O = 12 : 6 : 7\%$, respectively) and urea, were applied. In each fertilized plot, fertilizer-N was applied at 191 $\mathrm{kgN\,ha^{-1}}$ for the wheat-growing season, with organic manure and compound fertilizer applied prior to wheat sowing and split application of urea adopted (Zheng *et al.*, 2003). Three subplots were set in plot B and two subplots were set in each of the other plots. A translucent chamber (length × width × height = 70 × 70 × 90 cm), with its top remaining open during the no-measurement periods, was permanently fixed over each subplot. Nitric oxide fluxes from all the subplots were continuously observed at 4-hourly intervals. The increasing rate of NO concentration during each 1-hourly enclosure of a chamber was determined through automatically taking four air samples at a flow rate of 250 $\mathrm{ml\,min^{-1}}$ and analyzing them on-line with a 42C NO–NO_2–NO_x Analyzer (Thermo Environmental Instruments Inc., USA) which was calibrated at 250 $\mathrm{ml\,min^{-1}}$ of standard gas flow rate (Zheng *et al.*, 2003). Nitric oxide fluxes were calculated from the observed increasing rate of NO concentration, air temperature and air pressure. Zheng *et al.* (2003) discussed in detail the automatic measurement equipment, the procedures for sampling and analysis, and calculation of NO fluxes.

Soil temperature and moisture content were also simultaneously observed. The soil temperature at 2-cm depth as suggested by Yamulki *et al.* (1995) inside and outside the chamber was simultaneously recorded at every 10 min during the whole observation period by using thermocouples (Butterbach-Bahl *et al.*, 1997). The soil temperature at 5-cm depth outside the chamber was also continuously measured, but only during the first 2 months after wheat sowing because of thermocouple failures. The moisture content (percentage by dry soil weight) of the upper cultivated layer (0–10 cm in depth) was generally measured once a week during non-rainy periods, using the standard method of drying soil samples in an oven at 105 °C for 12 h. The moisture content was measured for 3 days after any rainfall or irrigation event. In addition, the diurnal uptake rates of NH_4^+ by wheat roots of the heading stage were measured by culturing actively growing wheat plants with an ammonium solution, of which the initial concentration was 15 mgN l^{-1} and detecting the ammonium concentration decrease after each 3-hourly culture. Three replicates were measured. Photosynthetic active radiation (PAR) data were directly obtained from the local meteorological station located about 200 m away from the experimental site.

The effects of soil temperature on NO emission are discussed using primarily only the data obtained from the 2-cm soil layer inside the chamber, unless otherwise indicated. Similarly, a single probability value (P) given in the present paper represents the result of a statistical t-test analysis at a confidence level of 95%, unless otherwise stated.

Results and discussion

Effect of soil temperature on seasonal NO emission

Seasonal variation in NO emission as affected by soil temperature During the period from November to January (NJ) when the wheat was in the seedling stage, the NO emission decreased gradually when the surface soil temperature declined. During this period, there was no significant relationship between the daily averages of soil temperature and the daily means of NO fluxes from the unfertilized plots (Table 1). For the fertilized plots, however, an exponential dependence was observed. The corresponding R^2 value given in Table 1 suggests that the

Table 1 Parameters of $F = \alpha . e^{\beta . T}$ determined with daily average nitric oxide (NO) emission (F) and daily mean soil temperature [=](T) for various cases

Parameters						
α (ngN m^{-2} s^{-1})	β (°C^{-1})	Q_{10}[@]	R^2	P (n)	Remarks	Sources
ND[^]	ND				NJ[!], unfertilized	#
1.4 ± 0.1[&]	0.075 ± 0.010	2.1 ± 0.2	0.46 ± 0.22	< 0.001 (2)	MJ[%], unfertilized	#
2.2 ± 0.3*	0.058 ± 0.017	1.8 ± 0.3	0.26 ± 0.08	< 0.05 (2)	Combined NJ and MJ, unfertilized, temperature ranging from 1°C to 28 °C	#
2.9 ± 1.1*	0.117 ± 0.019	3.3 ± 0.6	0.39 ± 0.02	< 0.001 (5)	NJ, fertilized, in association with a fertilizer application rate of 66 kgN ha^{-1}	#
18.3 ± 13.0	0.056 ± 0.026	1.8 ± 0.5	0.26 ± 0.10	< 0.05 (5)	MJ, fertilized	#
9.5 ± 6.9*	0.087 ± 0.032	2.5 ± 0.8	0.39 ± 0.10	< 0.001 (5)	Combined NJ and MJ, fertilized, temperature ranging from 1 to 28 °C, in association with a fertilizer application rate of 191 kgN ha^{-1}	#
3*	0.073 ± 0.011	2.1 ± 0.2	NR[+]	NR	Wheat fields received fertilizer at a rate of 40 ± 9 kgN ha^{-1}	$
9*	NR	NR	NR	NR	Corn fields received fertilizer at a rate of 121 ± 13 kgN ha^{-1}	$
4*	NR	NR	NR	NR	Cotton fields received fertilizer at a rate of 58 ± 5 kgN ha^{-1}	$

[=] Temperature of 2-cm soil in depth within the chamber.

[@] Temperature coefficient; that is, the change in NO emission per 10 °C soil temperature.

R, Correlation coefficient.

P, Significant level indicated with the probability of exponential simulation for individual subplots.

n, Number of observed subplots.

[^] Not detected.

[!] The period from November to January.

[#] This study.

[&] Mean ± 1σ, where σ is the standard deviation.

[%] The period from March to mid June.

*Data used for analyzing the relationship between fertilizer-N application rate and the parameter α or β or Q_{10}.

[+] Not reported.

[$] Williams *et al.* (1992a).

variation in soil temperature explained approximately 39% of the variation in NO emission from the fertilized wheat plots.

During the period from March to mid-June before rice transplanting (MJ), NO emission gradually increased as soil temperature rose, and an exponential dependence of the daily average NO fluxes on the daily means of soil temperature was observed for both the fertilized and unfertilized plots. The corresponding R^2 values (Table 1) suggest that the variation in the soil temperature could explain approximately 46% of the variation in NO emission from the unfertilized plots, but only approximately 26% from the fertilizer plots. No significant difference in Q_{10} was observed between the fertilized and unfertilized plots. The value of coefficient α for the fertilized plots, however, was higher than that for the unfertilized plots by a factor of 4–24. The differences in α as well as Q_{10} between the NJ and MJ periods for the fertilized plots were manifest. The α-value increased from *ca.* 3 ngNO–N m^{-2} s^{-1} during the NJ period to *ca.* 18 ngNO–N m^{-2} s^{-1} during the MJ period ($P = 0.006$), whereas the Q_{10} decreased from *ca.* 3.3 to *ca.* 1.8 ($P = 0.05$) and the corresponding R^2 declined from 0.39 to 0.26.

Considering the NJ and MJ periods in combination, a significant exponential relationship was observed between the daily average NO fluxes and the daily means of soil temperature (Table 1). The parameters α, Q_{10} and R^2 were 9.5, 2.5 and 0.39, respectively, for the fertilized plots, and 2.2, 1.8 and 0.26 for the unfertilized plots. The lower Q_{10} calculated from the unfertilized plots could be because of mineralization of soil organic matter and the subsequent nitrogen (N) conversion to NO. These processes might have been limited by lack of moisture in the upper soil layer, and hence were likely to proceed faster at a greater depth. Thus the measurement of soil temperature at 2-cm depth was likely to exaggerate the variations actually occurring at the depth of NO production through nitrification, and giving a relatively smaller Q_{10} value. For the fertilized plots, the Q_{10} was greater than 2.0 during the NJ period with a relatively higher soil moisture (40 ± 2%) but smaller than 2.0 during the MJ period with a relatively lower soil moisture (33 ± 6%). This further supports the above explanation.

As indicated above, the soil temperature was able to explain only 26–46% of the seasonal variation in NO emission. This suggests that other factors – for example, soil moisture – also simultaneously regulated the seasonal NO emission.

Soil temperature effect as influenced by rainfall and soil moisture A pulse of NO emission usually occurred following each irrigation or heavy rainfall event. During the entire non-waterlogged period, *ca.* 67% of the total NO emissions was observed when rainfall occurred prior to NO observations. A linear relationship existed between the daily NO emission and the corresponding precipitation when it was > 0 mm ($R^2 = 0.32$ and 0.41 for the fertilized and unfertilized treatments, respectively, and $P < 0.001$), suggesting that the rainfall influences the NO emission through modifying soil moisture.

Over the entire study period, a positive correlation was observed between the daily means of NO emission and the soil moisture for both the fertilized and unfertilized treatments under the condition that the daily means of soil temperature were $> 20\,^{\circ}$C (Fig. 1a, b). The R^2 values given in the figures suggest that variations in soil moisture explained *ca.* 58% of the day-to-day variation in NO emission occurring under this soil temperature condition. This positive correlation contrasts with the negative correlation reported by other researchers (e.g. Yamulki *et al.*, 1995), with reasons for the difference still remaining unclear. Under this soil temperature condition, however, no significant correlation between the daily means of soil temperature and the daily means of NO emission was observed. All daily means of soil temperature $> 20\,^{\circ}$C occurred during the period from May through mid June when the soil moisture widely ranged from 25 to 45%, with a mean of 35%. Under the soil conditions of daily mean temperature $< 20\,^{\circ}$C and moisture relatively higher (41 ± 4%), however, the NO emission was better correlated with the soil temperature (Fig. 1c, d) than with the soil moisture.

Laboratory studies have shown that the molar ratio of NO/N_2O is > 1 in nitrified cultures, whereas it is < 1 for denitrifiers (Anderson & Levine, 1986). Direct extrapolation of this laboratory result to the field situation may be difficult, as nitrification and denitrification are likely to simultaneously occur (Skiba *et al.*, 1992). Nevertheless, a relatively higher molar ratio of NO/N_2O indicates a more important contribution of nitrification to the NO emission, whereas a relatively lower ratio reflects a more important contribution of denitrification. The relative conditions of the various processes, however, may depend on the soil O_2 availability that is regulated by soil moisture (Williams *et al.*, 1992b). When the soil moisture is low, the molar ratio of NO/N_2O is greater than unity, otherwise is lower than unity (Yamulki *et al.*, 1995). Over the entire non-waterlogged period in this study, the molar ratio of NO/$N_2O > 1$ appeared at a frequency of *ca.* 86%, suggesting that the NO emission was primarily derived from nitrification in the soil. The molar ratio was negatively correlated ($R^2 = 0.94$, $P < 0.001$) with the soil moisture ranging from 25 to 50%, which could be described by the exponential equation $R_{\mathrm{mol}} = 7908e^{-0.206m}$ (Fig. 2). According to this equation, R_{mol} will approach a value of 1 when $m = 43.7\%$; that is, the field capacity or soil water holding capacity. This suggests that the NO released from the soil with a moisture content higher

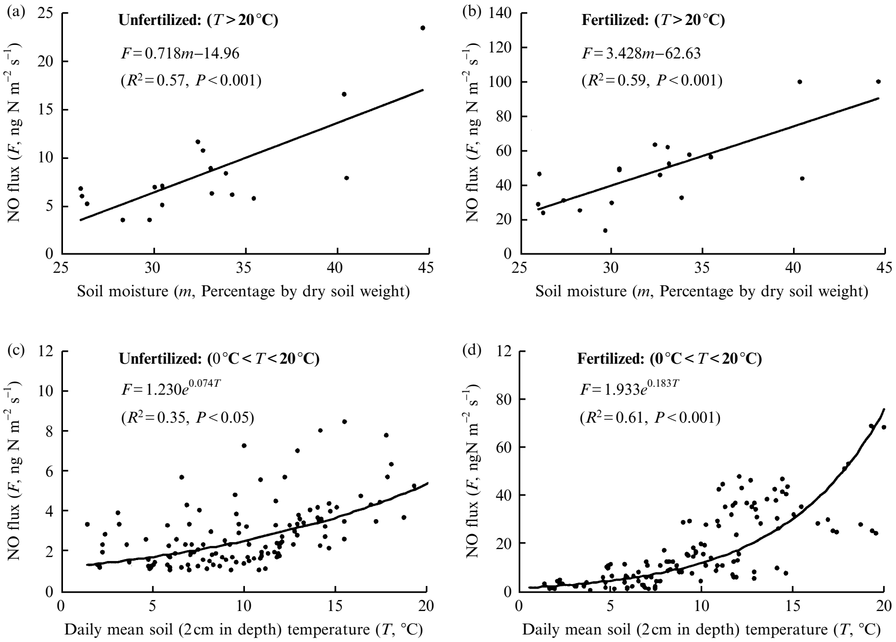

Fig. 1 Effects of soil moisture and temperature on nitric oxide (NO) emission from fertilized and unfertilized fields. The black dots are measured fluxes and the lines are fitted curves.

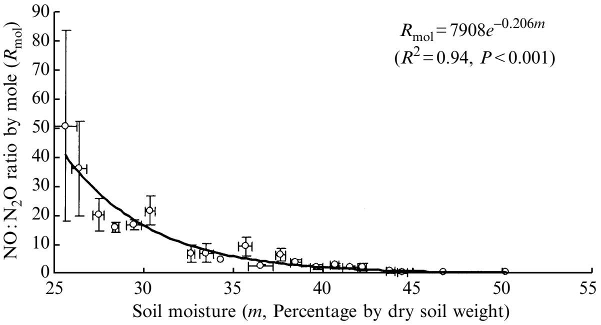

Fig. 2 Effect of soil moisture on the molar ratio of released nitric oxide (NO) and nitrous oxide (N_2O). The line is the fitted curve. The open circles are measured data, with vertical bars indicating the standard errors of the NO/N_2O ratios and horizontal bars indicating the standard deviation of soil moisture.

than the field capacity might be primarily derived from denitrification and otherwise might be primarily associated with nitrification.

Soil temperature effect as influenced by fertilizer-N application The α-values of 2.9 ngN $m^{-2}\,s^{-1}$ for the fertilized plots obtained during the NJ period, 9.5 ng N $m^{-2}\,s^{-1}$ for the same plots obtained during the combined NJ and MJ periods, and 2.2 ngN $m^{-2}\,s^{-1}$ for the unfertilized plots obtained during the combined NJ and MJ periods were associated with fertilizer application rates of 66, 191 and 0 kgN ha^{-1}, respectively (Table 1). Combining these α-values and fertilizer-N application rates for wheat crop with those from Williams *et al.* (1992a) for non-legume crops – including wheat, corn and cotton – which are marked with '*' in Table 1, the significant linear correlation between parameter α (ngN $m^{-2}\,s^{-1}$) and its corresponding fertilizer-N application rate (kgN ha^{-1}) can be described with the equation $\alpha = 0.045N_r + 1.53$ ($R^2 = 0.86$, $P = 0.008$), where N_r is the fertilizer-N application rate. Considering the correlation between the parameter α and *β* (see the section entitled Dependence of Diurnal NO Emission on Soil Temperature), the relationship between fertilizer-N application rate and β can be described with the equation $\beta = -0.0003N_r + 0.132$ ($R^2 = 0.80$, $P = 0.04$), and the influence of fertilizer-N application rate on Q_{10} can be described with the equation $Q_{10} = -0.0085N_r + 3.62$ ($R^2 = 0.77$, $P = 0.05$). In these equations for the Q_{10} and *β*, N_r is > 0 kgN ha^{-1}. It should be noticed that the α may be underestimated whereas *β* or Q_{10} may be overestimated when fertilizer-N is applied at a low rate, because of not considering the effects of N input from other sources – for example, atmospheric deposition. Nevertheless, these equations may allow for a convenient linkage between NO emission from croplands and soil temperature as well as fertilizer-N application rate, which may be a simple but useful approach for estimating regional NO emission.

Dependence of diurnal NO emission on soil temperature

Typical diurnal patterns of NO emission as regulated by wheat growth Three typical diurnal patterns of NO emission were observed over the non-waterlogged period. They were day-peak, night-peak and irregular patterns (Fig. 3). The diurnal peak of NO emission for the day-peak pattern appeared at around mid-day, whereas that for the night-peak pattern appeared from evening to around midnight, with the minimum emission occurring around mid-day. Under the irregular pattern, there was no certain time for peak emission occurrence.

The day-peak pattern occurred, in general, under clear weather. This pattern appeared at a frequency of 89% during the wheat seedling period (from November 1 to December 31), the wheat-maturing period (from May 9 to 27) and the fallow period following wheat harvest (from May 28 to June 17). The typical day-peak pattern was also observed over the entire non-waterlogged period when plants growing in the field were sparse, as happened at one of the subplots in plot D where the above-ground biomass of wheat was *ca*. 70% lower than the normal subplots (Zheng *et al*., 2003).

The night-peak pattern appeared at a frequency of 100% during the period from the early spring (around March 2) to the end of the wheat blooming stage (around April 14), when the wheat was actively growing.

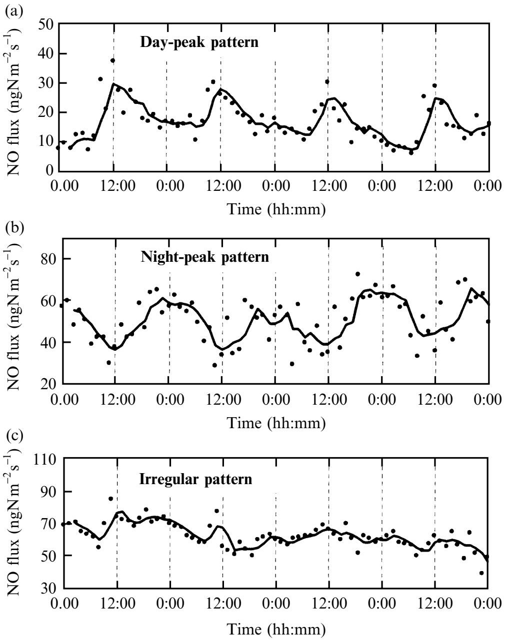

Fig. 3 Typical patterns of diurnal nitric oxide (NO) emission. The black dots are measured fluxes and the coarse lines are drawn with 3-point moving average values. (a) Observed on November 19–22, 1996. (b) Measured on April 8–11, 1997. (c) Observed on May 4–7, 1997.

During the period from the end of wheat blooming stage (around April 15) to the beginning of the maturing stage (around May 8), the irregular pattern of diurnal NO emission appeared, with one occasional peak occurring from late afternoon to midnight or sometimes two peaks appearing at around mid-day and midnight. The irregular pattern also occurred under rainy or overcast weather of other periods.

Because of the intrinsic diurnal variability in NO emission, intermittent measurement made at non-representative time is very likely to lead to over- or underestimation. In order to identify the representative time for intermittent measurement of NO emission based on the continuously measured diurnal data, we define a term of correction factor as the ratio of the daily average emission obtained from the diurnal multi-measurements to the flux measured at a given time within the day. Whenever a correction factor is not significantly different from 1.0, the corresponding time is defined as the representative time, at which an intermittently measured NO flux is considered representative for the daily total/average emission. Based on the diurnally measured NO fluxes, we quantified the correction factors and plotted their diurnal distribution for the individual patterns in Fig. 4, wherein the representative time is indicated with combined $_{\pi}$ and R_{t}.

Based on the results shown in Fig. 4, we recommend a common representative time of around 17:00 for intermittent measurements in an ecosystem similar to that of this study. In the case of the irregular pattern, a possible bias of +10% may be derived from the intermittent measurement made at this recommended time. If an intermittent measurement is taken at non-representative time, a bias of $\pm 40\%$ is possible to be produced (Fig. 4).

The periods characterized with the typical diurnal patterns could be identified with the normalized wheat development stage (*ds*), which is defined as a ratio of the days after wheat sowing to the total days of the wheat-growing season. For the day-peak pattern, $0 \leq ds \leq 0.50$ or $ds > 0.87$; for the night-peak pattern, $0.50 < ds \leq 0.77$; and for the irregular pattern, $0.77 < ds \leq 0.87$.

Possible mechanisms for effects of plant growth on diurnal pattern The day-peak diurnal pattern of NO emission was also observed in the cropland of the southeastern United States (Aneja *et al*., 1995). A single observation made in a wheat field near London showed a diurnal pattern consistent with that of soil temperature (2-cm depth) (Yamulki *et al*., 1995). The results given in the previous section suggest that whether the diurnal pattern of NO emission was consistent with that of the simultaneously measured soil temperature depended on plant growth status. The influence of plant growth on the diurnal pattern was likely because of (i) competition for

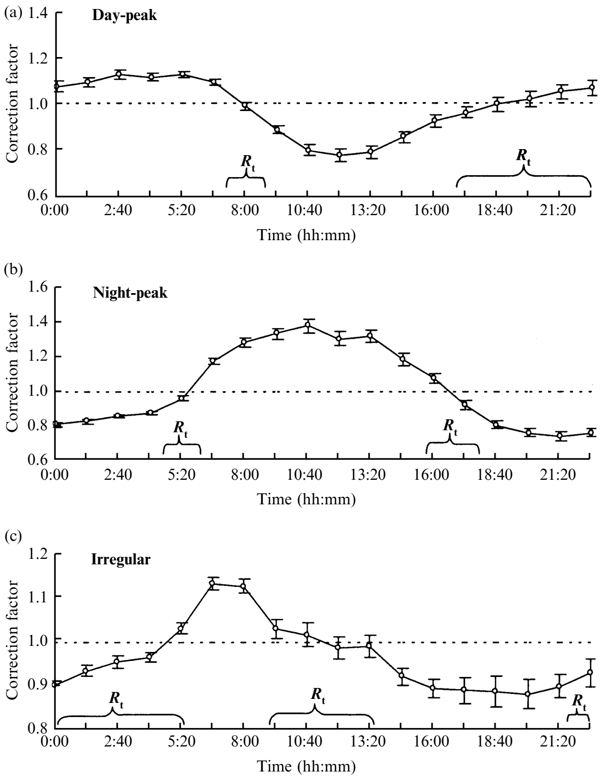

Fig. 4 Correction factor and representative time for intermittent measurement. The vertical bars are standard errors. The combination of $_{\pi}$ and R_t indicates the representative time for intermittent observation. (a), (b) and (c) are for the day-peak, night-peak and irregular pattern, respectively.

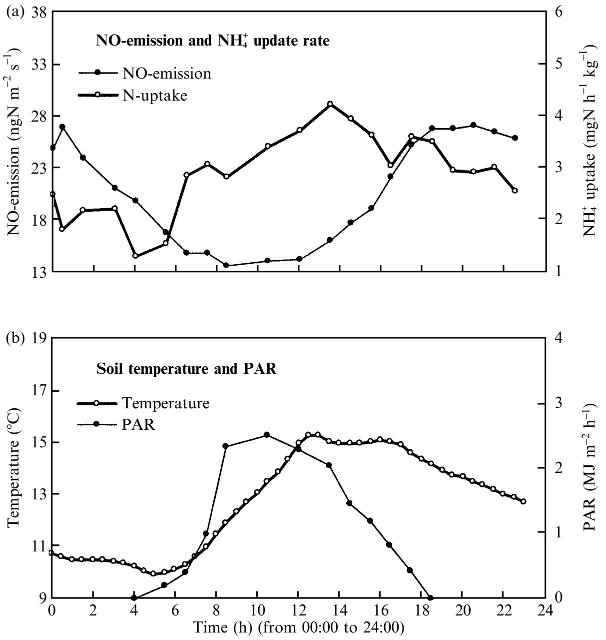

Fig. 5 Diurnal nitric oxide (NO) emission, NH$_4^+$ uptake, soil temperature (2-cm depth) and photosynthetic active radiation (PAR). (a) nitric oxide emission is represented with black dots and fine line, and NH$_4^+$–N uptake rates are represented with open circles and coarse line. (b) Soil temperature is represented using open circles and coarse line, and PAR is represented using black dots and fine line.

available N between plant roots and bacteria responsible for NO production, (ii) canopy uptake of NO released from the soil (e.g. Johansson, 1989; Jacob & Bakwin, 1991; Lovett & Lindberg, 1993) and (iii) shifting the soil layer responsible for NO production to a deeper depth because of plant uptake of extractable N.

Once ammonium or nitrate is taken up by the plants, it has few opportunities to be nitrified or denitrified, and consequently less NO is produced and released. The extractable N remaining in the soil, however, has more opportunities for nitrification or denitrification, whereby NO is produced as an immediate product (Williams *et al.*, 1992b). When soil temperature and moisture are suitable, the availability of ammonium and nitrate in the soil as substrates for nitrifers and denitrifers, respectively, may become the key factor for regulating the NO emission. Thus, intensive uptake of extractable N by plant roots may lead to a relatively lower NO flux, and vice versa. This competition mechanism may partially explain the night-peak pattern frequently observed during the active wheat-growing period, which is supported by Fig. 5, where the diurnal distributions of simultaneously measured NH$_4^+$ uptake rates, NO fluxes, soil temperature and PAR are shown. During the period when wheat grows vigorously, NH$_4^+$ and/or NO$_3^-$uptake may override other regulating factors of NO emission – for example, soil temperature – which might be supported by the fact that the night-peak pattern was observed on every non-rainy day. When plant growth is less vigorous, or in bare soils, soil temperature under clear weather may override other regulating factors – for example, NH$_4^+$ and/or NO$_3^-$ uptake – which might be supported by the fact that the day-peak pattern occurred only under clear weather and was very consistent with that of surface soil temperature.

A lower NO flux may be obtained from relatively lower concentrations of NO measured during the period of a chamber enclosure. In comparison with bare soils or fields with less vigorous plants, the NO concentrations over the canopy of actively growing wheat were likely lower because of canopy uptake (e.g. Jacob & Bakwin, 1991). In addition, the canopy uptake of NO was likely intensified by relatively higher air temperature and/or more active photosynthesis at around mid-day. When wheat plants were growing vigorously, therefore, a night-peak pattern occurred, with the diurnal minimum flux appearing at around mid-day, likely because of canopy uptake of NO as affected by air temperature and/or photosynthesis. Further study, however, is required to support this explanation.

During the period of vigorous wheat growth, N substrates are likely less available for NO production in the upper *ca.* 10 cm of soil layer, where $>90\%$ of the wheat roots are located (data not shown), because of intensive root uptake. Most of the NO released during this period is, therefore, likely derived from the deeper soil layer, where the diurnal peak of soil temperature is usually delayed for some hours (e.g. Zheng *et al.*, 1997). This might be supported by the fact that the diurnal peak of NO emission during this period was delayed for *ca.* 7 h, relative to the diurnal peak of soil temperature at 2-cm depth.

Dependence of diurnal NO emission on soil temperature During the 83-day periods characterized with the day-peak pattern, significant exponential correlation between the diurnal NO fluxes and the simultaneously measured soil temperature was observed in 65 clear days. The average values for the parameters α, β and Q_{10} are listed in Table 2 separately for the NJ period, and the late phase of the MJ period including the wheat-maturing stage and the fallow period. The β- or Q_{10}-values were not significantly different between the two periods. The values of α during the late MJ period, however, were significantly higher than those during the NJ period by a factor of *ca.* 4 ($P<0.001$). This suggests that under the same soil temperature the diurnal NO emissions occurring in the MJ period were more intensive than in the NJ period. When the dry soil was wetted through heavy rainfall or irrigation and then exposed to sunny weather, the diurnal NO emissions strongly depended on the simultaneously measured soil temperature, with an extremely higher Q_{10} upto 8–20 – for example, the cases of May 28 and June 9–10 (not included in Table 2). But 1 or 2 days later, the Q_{10}-value declined to the usual level. The wetting-induced change in Q_{10} might be because of complex reasons, such as stimulation of mineralization and microbe growth, and so on. The weather of those days in which no temperature dependence was observed was usually rainy or overcast.

During the 41-day period characterized by the night-peak pattern, the diurnal NO emissions were exponentially correlated with the soil temperature measured at 7 ± 2 h in advance (Table 2) in 22 days. In the 10 days with heavy rainfall events prior to the observations, the diurnal NO emissions significantly depended on the soil temperature measured at *ca.* 6 ± 2 h in advance, with an extremely higher Q_{10} up to 25–40700 (Table 2). The extremely high Q_{10} usually declined to the normal level after very few days. In the remaining days, which were under heavily rainy weather, no temperature dependence was observed even though the typical night-peak pattern occurred.

During the wheat-growing period characterized by the irregular pattern, the diurnal NO emissions under non-rainy weather were correlated with the soil temperature observed at 3 ± 2 h in advance (Table 2). In the rainy days, however, no temperature dependence was observed.

Based on the diurnal multi-measurements over the entire non-waterlogged period, the correlation between parameters α (ngN m^{-2} s^{-1}) and β (°C^{-1}) can be established with the equation $\beta=0.184\alpha^{-0.3855}$ ($R^2=0.55$, $P<0.001$).

Apparent activation energy determined with diurnal multi-measurements We calculated the apparent activation energy of NO emission from the Arrhenius equation (e.g. Yamulki *et al.*, 1995) for each day with significant temperature dependence. Over the entire non-waterlogged

Table 2 Parameters of $F=\alpha\cdot e^{\beta\cdot T}$ determined with diurnal nitric oxide (NO) emission (F) and diurnal soil (2-cm depth) temperature (T) simultaneously measured or observed at some hours in advance (τ)

	Parameters						
Diurnal pattern[1]	α (ngNM^{-2}s^{-1}	β (°C^{-1})	Q_{10}	R^2	P (n)	τ	Remarks
Day-peak	5.0 ± 2.7	0.074 ± 0.024	2.1 ± 0.5	0.59 ± 0.21	<0.05 (27)	0	The NJ period, under clear weather
	19.3 ± 12.3	0.066 ± 0.028	2.0 ± 0.6	0.57 ± 0.23	<0.05 (23)	0	The late MJ period, under clear weather
Night-peak	9.0 ± 6.8	0.127 ± 0.045	3.9 ± 1.8	0.65 ± 0.21	<0.001 (22)	7 ± 2	Under non-rainy weather
	1.3 ± 1.6	0.649 ± 0.248	7257 ± 14356	0.66 ± 0.17	<0.001 (10)	6 ± 2	Shortly after a heavy rainfall event
Irregular	18.7 ± 12.3	0.075 ± 0.051	2.5 ± 1.9	0.65 ± 0.16	<0.001 (19)	3 ± 2	Under non-rainy weather during the transition period (see the text) of wheat growth

[1] See the section entitled 'Typical Diurnal Patterns of NO Emission as Regulated by Wheat Growth'. P, Significant level indicated with the probability of exponential simulation for individual day. n, Number of days. τ, Hours in advance for soil temperature measurement.

period, the E_a values greatly varied from 11 to 833 kJ mol^{-1}. The E_a values less than 150 kJ mol^{-1} appeared at a frequency of 89%.

The E_a values greater than 150 kJ mol^{-1} usually appeared on the second or third day after wetting the dry soil through rainfall or irrigation, accompanied with a pulse NO emission. A similar pulse response of NO emission to irrigation was also observed in Swiss wheat fields (Gut *et al*., 1999). When soil moisture content was approximately 42%, which was very close to the field capacity, extremely high E_a generally appeared, with a very large standard deviation (Fig. 6a). The pulse response of NO emission to water addition or the extremely high E_a was likely because of acceleration of nitrification and denitrification, which were associated with accumulation of nitrate over the dry period (Scholes *et al*., 1997; Zheng *et al*., 1997) and consumption of nitrate following the wetting event as well as production of ammonium as a product of stimulated mineralization (Zheng *et al*., 2000). When the soil was continuously wetted, however, no pulse NO emission occurred, and the E_a or the NO flux declined to a lower level. No E_a could be determined for a day within which such a wetting event occurred because no temperature dependence was observed. This was because of the immediate pulse response of NO emission to water addition (e.g. Scholes *et al*., 1997), as the effect of water addition overrode the influence of temperature.

The E_a values less than 150 kJ mol^{-1} occurred when soil moisture content was less than the field capacity and were relatively stable with a mean of 56 kJ mol^{-1}and a standard deviation of 28 kJ mol^{-1} (92 observations) over the entire non-waterlogged period. This result was consistent with Johansson & Granat (1984) (65–83 kJ mol^{-1}) and Slemr & Seiler (1984) (44–103 kJ mol^{-1}), but lower than Yamulki *et al*. (1995) (108 kJ mol^{-1} from a single observation) and Williams *et al*. (1988) (97 ± 11 kJ mol^{-1}).

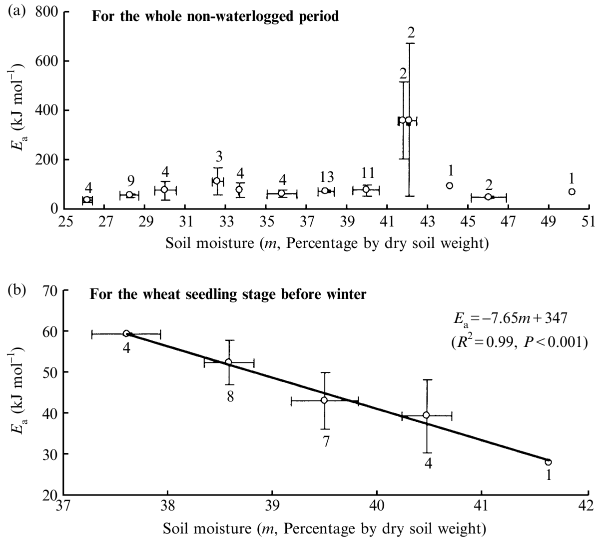

Fig. 6 Effect of soil moisture on apparent activation energy. The horizontal bars are standard deviation of soil moisture and the vertical ones are the standard errors of apparent activation energy, E_a. The number next to each datum point indicates the observations.

As the Arrhenius equation is just a different expression of temperature dependence, a correlation between E_a and Q_{10} or β should exist. This was corroborated by the equation $Q_{10} = e^{0.0155 \cdot E_a}$ or $\beta = E_a/640$ ($R^2 = 0.99$, $P < 0.001$), both of which were formulated with all the E_a-, Q_{10}- and β-values obtained from the diurnal multi-measurements over the entire non-waterlogged period. These empirical equations suggest that the increase of apparent activation energy will strengthen the temperature dependence of NO emission. In other words, the temperature dependence will be affected by any factor that influences apparent activation energy. Understanding the relationships between the parameters of $F = \alpha \cdot e^{\beta \cdot T}$ and those of the Arrhenius equation may be helpful for process-orientated modeling of NO emission from managed or unmanaged terrestrial ecosystems.

An Arrhenius equation approach for predicting diurnal NO emission

Based on the experimental results of this study, an approach oriented from the Arrhenius equation:

$$F = e^k e^{-E_a/(R \cdot T_K)} + e^k e^{-E_a/(R \cdot \Delta T_K)} \sin[(t\text{-}6\text{-}\tau)/12\pi] \qquad (1)$$

was developed in order to simulate diurnal NO emission. In Eqn (1), F is the NO flux for a given time (ngN m^{-2} s^{-1}), E_a the apparent activation energy (J mol^{-1}), T_K the daily average soil temperature (K), ΔT_K the difference between soil temperatures of the given time and the daily average (K), t the given time (h), τ the time delay for the diurnal peak emission relative to the soil temperature maximum (h), k an empirical coefficient, and R the gas constant (8.314 J k^{-1} mol^{-1}). During the wheat seedling stage prior to winter period, when there was a negative linear correlation between Ea and soil moisture content (Fig. 6b), k was linearly correlated with soil moisture content. The correlation can be described with the equation $k = -3.589\,m + 162.7$ ($R^2 = 0.997$, $P < 0.001$), where m is soil moisture content (percentage by dry soil weight). During the MJ period, k empirically ranged from 24.7 to 34.6 (Systat, 1989), with a mean of 29.6 ± 4.2. The τ has been determined in the section entitled Dependence of Diurnal NO Emission on Soil Temperature as *ca*. 7 h for the period characterized with the night-peak pattern, *ca*. 3 h for the transition period with the irregular pattern and, 0 h for the period with the day-peak pattern. Based on the results given in the sections entitled 'Typical Diurnal Patterns of NO Emissions as Regulated by Wheat Growth' and 'Dependence of Diurnal NO Emission on Soil Temperature', the values of which should be adopted for τ can be determined by the value of the normalized development stage of wheat.

On the right side of Eqn (1), the first term gives the daily average of NO emission calculated from the daily average soil temperature. The second term gives the diurnal fluctuation associated with the extent of the soil temperature departure from the daily average.

We calculated the diurnal NO fluxes by using Eqn (1) for three periods, which are (i) the wheat seedling stage (Fig. 7a), (ii) the vigorous wheat-growing stages and the following transition period (Fig. 7b) and (iii) the wheat-maturing stage and the following fallow period (Fig. 7c). During the first period, the E_a was observed to be $45 \pm 22\,\mathrm{kJ\,mol^{-1}}$ when the soil moisture was >42 or $<37\%$ (three observations), and $E_a = -7.65\,m + 347$ for $37 \leq m \leq 42\%$, where m is soil moisture content (percentage by dry soil weight) (Fig. 6b). During the second and third periods, the E_a was determined as $73 \pm 32\,\mathrm{kJ\,mol^{-1}}$ (37 observations) and $52 \pm 28\,\mathrm{kJ\,mol^{-1}}$ (23 observations), respectively. The computed and measured NO fluxes for the fertilized plots shown in Fig. 7 suggest that diurnal NO emission can be well predicted from soil temperature and soil moisture ($R^2 = 0.87$, $P < 0.001$). However, the coefficient k is likely regulated by various parameters. A further study is, therefore, required to quantify the parameter k with accessible data sets of meteorology, soil properties and farming practices.

Conclusions

During the non-waterlogged period of a rice–wheat rotation, an exponential correlation between NO emission and soil temperature existed, in general, for both seasonal and diurnal time scales, with the parameters of the exponential function different among various cases. The NO emission was positively correlated with soil moisture content when surface soil temperature was $>20\,^{\circ}\mathrm{C}$. Three typical diurnal patterns of NO emission were identified. They were closely in association with plant growth and were characterized by day-peak, night-peak and irregular patterns. Diurnal NO emission was exponentially correlated with simultaneously measured surface soil temperature under the day-peak pattern, but exponentially dependent on the surface soil temperature at *ca.* 7 h and *ca.* 3 h before NO observation under the night-peak and irregular pattern, respectively. A linkage between fertilizer-N application rate and temperature dependence of NO emission was established, which may allow for estimating regional NO emission through fertilizer consumption and temperature. An approach oriented from the Arrhenius equation was developed in order to predict NO emission with accessible data sets – for example, soil temperature and soil moisture. Intermittent measurement of NO emission was recommended to be taken at around 17:00. The NO emission was mainly derived from nitrification when soil moisture content was less than the field capacity.

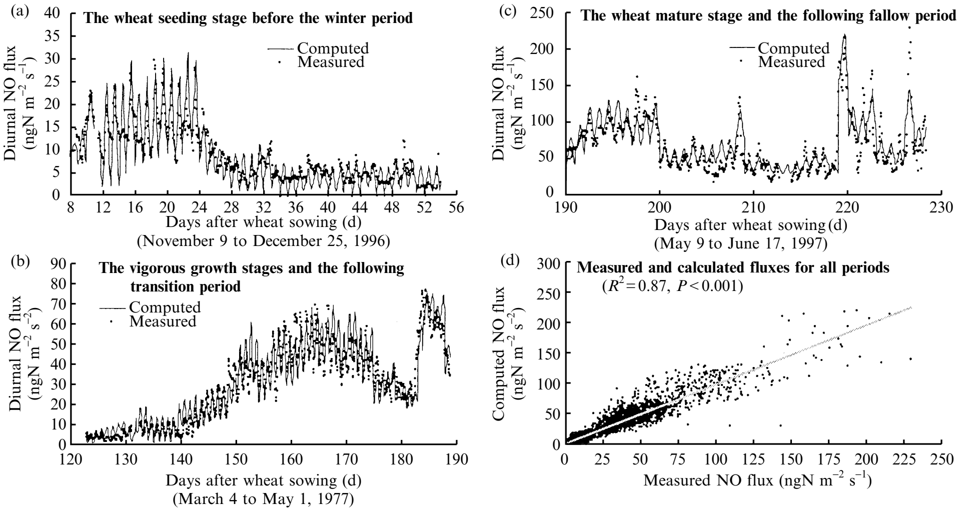

Fig. 7 Measured and computed diurnal nitric oxide (NO) emission. Panel (a) gives the wheat-seedling stage before winter, (b) the vigorously growing stage of wheat and the following transition period and (c) the wheat-maturing stage and the following fallow period. The measured and computed fluxes of all the non-waterlogged period are compared in (d).

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