

# Diurnal fluxes of CO<sub>2</sub> and N<sub>2</sub>O from cattle-impacted soil and implications for emission estimates

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## ABSTRACT

Short-term diurnal changes in emissions of CO<sub>2</sub> and N<sub>2</sub>O were determined in a cattle overwintering area during three specific periods of the year. Production of both N<sub>2</sub>O and CO<sub>2</sub>, as determined with gas chambers buried in soil and spatially distributed changed rapidly, and the general course of fluxes of the two gases was different. CO<sub>2</sub> emissions were basically controlled by temperature, and most gas chambers showed the same trends in CO<sub>2</sub> flux, indicating low spatial heterogeneity. In contrast, N<sub>2</sub>O emissions were much more spatially heterogeneous and each chamber had its own time course of emission; therefore, the relationship between flux and temperature was more complicated for N<sub>2</sub>O than CO<sub>2</sub>. For estimating gas emissions over long periods, we strongly recommend the use of frequent emission measurements during periods of high gas fluxes.

**Keywords:** greenhouse gas; emission estimates; nitrous oxide; carbon dioxide; pasture

High spatial heterogeneity and temporal variability is a common feature of soil microbial processes. The variability of N<sub>2</sub>O emissions from soils in space and time is usually considered as extreme (e.g., Velthof and Oenema 1995, Röver et al. 1999), and often most of the gas is produced during short periods in a limited area, in so-called 'hot spots' (Parkin 1987). Hot spots can be created for example by intensively decomposing organic particles, or they can develop at the interface of nitrogen-rich organic particulates and the surrounding soil, where nitrification and denitrification (the two major processes producing N gases) occur in close proximity (Petersen et al. 1996, Jarvis 1997).

Production of N<sub>2</sub>O often follows nitrogen input into the soil. In pastures, a substantial portion of nitrogen input is in the form of animal urine and excrement. Distribution of microsites producing N<sub>2</sub>O is quite heterogeneous. On the other hand, emissions of CO<sub>2</sub>, which is also produced during decomposition of excrements, are normally less heterogeneous. In our previous investigations, a

cattle overwintering area in South Bohemia was identified as an important source of N<sub>2</sub>O because of substantial excrement deposition, impacts on soil physical properties, and limited N use by plants in winter (Šimek et al. 2006, Hynšt et al. 2007a).

The present work supplemented previous results of long-term measurements with more detailed investigations. We hypothesized that conditions favorable for N<sub>2</sub>O production in soil and N<sub>2</sub>O emission from soil occur in a relatively short-time period during the first stages of decomposition of accumulated excrements, and that emissions of N<sub>2</sub>O are proportional to temperature. The objective of the present work was to determine short-term patterns of N<sub>2</sub>O and CO<sub>2</sub> emissions from soil in the cattle overwintering area. Because numerous overwintering areas in the Czech Republic represent potentially significant sources of trace gases, it is important to gain knowledge about gas flux patterns from this type of agricultural system. Knowledge of gas flux patterns would improve estimates of amounts of N and C released from the soil to the atmosphere.

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## MATERIALS AND METHODS

**Experimental site, gas flux determination, and laboratory analyses.** The experiments were carried out at the moderately cattle-impacted locality in a cattle overwintering area at the Borová Farm, Southern Bohemia (Šimek et al. 2006, Hynšt et al. 2007a). The soil on the site is a sandy loam haplic phaeozem (arenic; WRB system) containing 60–80% sand, 14–32% silt, and 6–14% clay (USDA classification system). Soil pH ( $H_2O$ ) was 7.25, soil organic carbon and total nitrogen content were 4.04 and 0.89%, respectively. The site receives on average 650 mm precipitation, and the mean annual temperature is 7°C.

Gas fluxes were determined using non-vented manually closed chambers (Hynšt et al. 2007a), buried 5 cm in soil and spatially distributed. The amounts of  $N_2O$  and  $CO_2$  were quantified using an HP 5890 gas chromatograph and an HP P200H Portable Gas Microchromatograph (both Hewlett Packard, USA).

Soil (–10 cm) and air (+10 cm) temperatures were recorded using a data logger equipped with Ni-sensors (Comet L0121, France). Soil samples from 0–15 cm layer were sieved (5 mm) on the day of sampling and stored at 4°C until the next day, when soil mineral N content ( $NH_4^+-N$  and  $NO_3^--N$ ) was measured colorimetrically in 1M KCl extracts (Zbiral et al. 1997).

**Diurnal variation and spatial heterogeneity of gas fluxes.** Field measurements were conducted in three seasons: in early May (when high  $N_2O$  emissions were expected; Hynšt et al. 2007a), in mid-July, and in early November. The flux measurements always started at 9 a.m. For each measurement, the chambers were closed and gas samples were taken at time 0 and 60 min. After the second sampling, the chambers were opened for 2 h and then the next measurement was performed. These experiments lasted 24 h. Gas samples were transported to the laboratory and immediately analyzed by gas chromatography. Another experiment was performed on the same site in May. Flux measurements as described above started at 3 p.m. and continued for the next 45 h. The third experiment was conducted in April, used 32 measuring points, and lasted 2 weeks.

**Gas fluxes following the input of nutrients.** This experiment was conducted to estimate  $N_2O$  emissions from artificially created ‘hot-spots’ formed using glucose and  $KNO_3$  amendments (Hynšt et al. 2007b). The experiment was performed in May and lasted 36 h. Flux measurement started at 9 a.m. when the chambers were closed, and gas samples were taken after 0 and 60 min. Then

2 000 ml of a nutrient solution corresponding to 500 kg N/ha and 500 kg C/ha was applied immediately to each chamber. The chambers were then closed at 3-h intervals and gas samples were taken.

**Statistics.** Pearson’s correlation coefficients were calculated to test for possible relationships between the environmental variables and  $N_2O$  and  $CO_2$  fluxes. Data processing and analyses were conducted using Statistica 7.

## RESULTS

**Diurnal variation and spatial heterogeneity of gas fluxes.** Three individual experiments examining the time course of gas emissions showed substantial differences in  $N_2O$  and  $CO_2$  fluxes (Figure 1).  $CO_2$  fluxes (Figure 1B) had a pronounced diurnal time course, especially in experiments carried out in May and July, when emissions were maximum around noon or early afternoon and were minimum from 3–6 a.m. Despite rather similar time courses among the seasons, there were substantial differences in average minimum and maximum fluxes within each season. Mean  $CO_2$  fluxes ranged from 33 to 100 mg  $CO_2-C/m^2/h$  in May, from 143 to 406 mg  $CO_2-C/m^2/h$  in July, and from 14 to 36 mg  $CO_2-C/m^2/h$  in November. Diurnal variation in the  $CO_2$  fluxes was related to temperature in May and July (Figure 1B).

Like the  $CO_2$  fluxes,  $N_2O$  fluxes (Figure 1A) varied during the day but the time course for  $N_2O$  production was different from that for  $CO_2$  production. In general, the time courses for  $N_2O$  production in May, July, and November differed. The maximum emission was 50.6 times higher than the minimum emission in May, 4.2 times higher in July, and 3.6 times higher in November. In contrast to the  $CO_2$  fluxes, the diurnal variation of  $N_2O$  fluxes was not related to the diurnal variation in temperature (Figure 1A). Data analysis suggested that the  $N_2O$  fluxes were positively skewed and that it might be better to use medians instead of means. In contrast to  $CO_2$  data,  $N_2O$  medians were often much lower than the corresponding arithmetic means (Figure 1). This finding was confirmed in the second experiment performed in May (Figure 2). It was obvious that the arithmetic means were strongly influenced by data from two chambers, A and D (Figure 2A). The spatial heterogeneity of  $N_2O$  fluxes was even more evident when comparing the cumulative  $N_2O-N$  fluxes during the 45-h experimental period. Six chambers exhibited fluxes of 22, 28, 31, 42, 229, and 376 mg  $N_2O-N/m^2$ , with an arithmetic mean of 121 and a median of 37 mg  $N_2O-N/m^2$ . Statistical

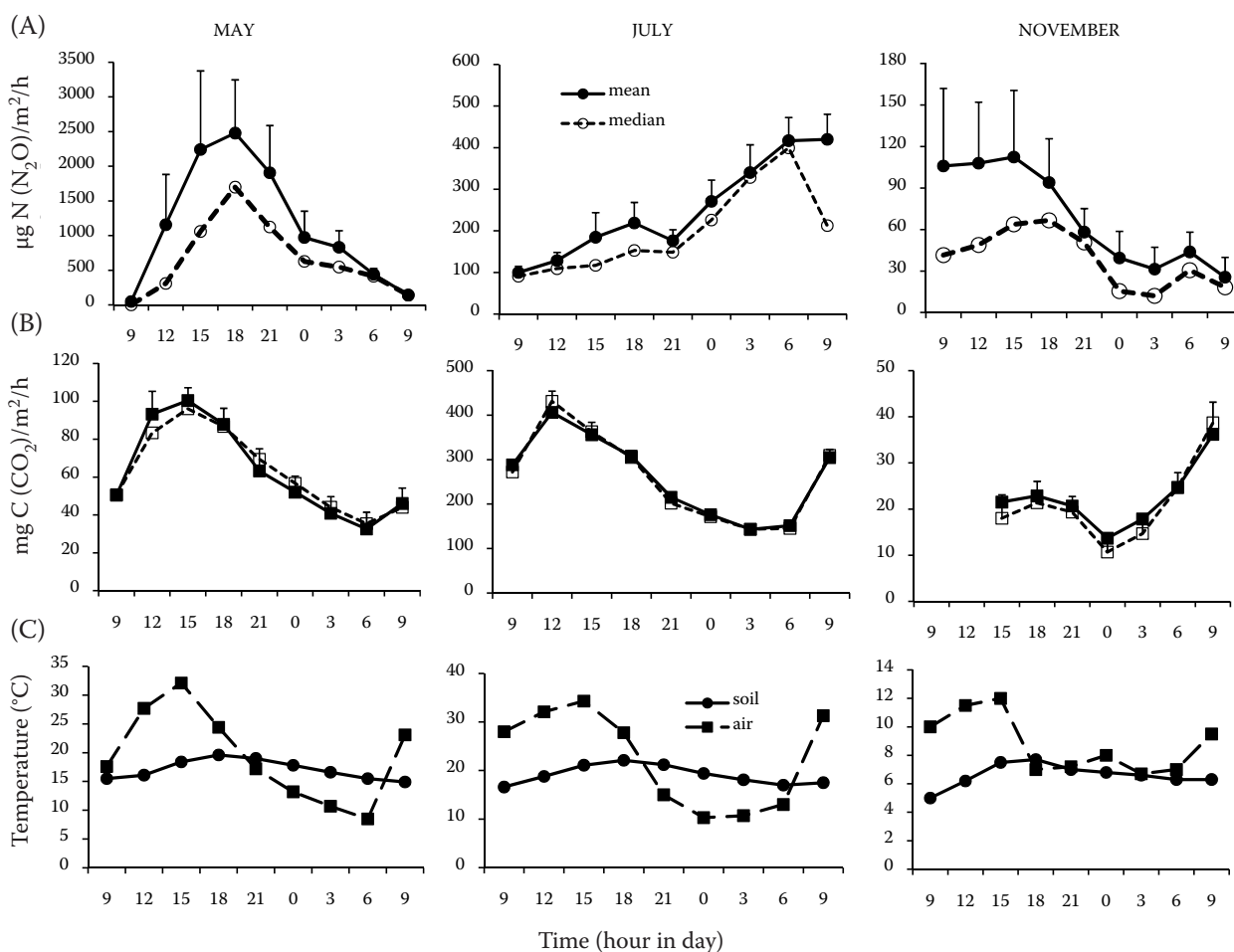


Figure 1. Arithmetic means ( $\pm$ SE) and medians of hourly  $\text{N}_2\text{O}$  emissions (A) and  $\text{CO}_2$  emissions (B), and time-course of air (10 cm above soil surface) and soil (10 cm below soil surface) temperatures ( $^{\circ}\text{C}$ ) in the cattle overwintering area, determined in May, July, and November. Emission data points represent averages and/or medians from 5 replicates (May) or 8 replicates

analysis indicated different relationships between  $\text{N}_2\text{O}$  and  $\text{CO}_2$  emissions and temperature in individual experiments (Table 1).

The time course of  $\text{N}_2\text{O}$  emissions in the 32 chambers in the April experiment is shown in Figure 3A. Although the chambers differed in the timing and level of maximal emission values, the emissions were not related to soil or air temperatures. Most chambers showed low values of cumulative  $\text{N}_2\text{O}$  production, ranging from 34 to 630 g  $\text{N-N}_2\text{O}/\text{ha}$  in the 2-week period, while only five chambers had values exceeding 1 000 g  $\text{N-N}_2\text{O}/\text{ha}$  (1 031–6584 g  $\text{N-N}_2\text{O}/\text{ha}$ ). Cumulative  $\text{N}_2\text{O}$  production was significantly correlated with initial soil  $\text{NO}_3^-$ -N concentration ( $r = 0.449$ ,  $P = 0.01$ ), while no relationship was found with final  $\text{NO}_3^-$ -N content and initial and final content of  $\text{NH}_4^+$ -N.  $\text{CO}_2$  emissions (data not shown) were also variable, but their time course was similar in all chambers; the emissions were weakly but significantly correlated with soil ( $r =$

0.279,  $P = 0.000007$ ) and air ( $r = 0.147$ ,  $P = 0.019$ ) temperatures. There was no overall correlation between  $\text{CO}_2$  and  $\text{N}_2\text{O}$  emissions.

**Gas fluxes following nutrient inputs.** The addition of nitrate nitrogen and glucose carbon in amounts corresponding to 500 kg N/ha and 500 kg C/ha rapidly and substantially increased  $\text{N}_2\text{O}$  fluxes from the soil. Values ranged from 15 to 586  $\mu\text{g N-N}_2\text{O}/\text{m}^2/\text{h}$  at 9 a.m. before addition but ranged from 9 200 to 52 000  $\mu\text{g N-N}_2\text{O}/\text{m}^2/\text{h}$  6 h after the treatment (Figure 4A). The emissions were significantly correlated with soil ( $r = 0.54$ ,  $P = 0.00002$ ) and air ( $r = 0.498$ ,  $P = 0.0001$ ) temperatures.  $\text{CO}_2$  emissions (Figure 4B) showed a similar time course as  $\text{N}_2\text{O}$  fluxes, except for the increase of fluxes after nutrient application. Consequently,  $\text{CO}_2$  emissions were significantly correlated with  $\text{N}_2\text{O}$  emissions ( $r = 0.73$ ,  $P = 0.00001$ ) and soil and air temperatures ( $r = 0.455$ ,  $P = 0.0006$  and  $r = 0.513$ ,  $P = 0.00008$ , respectively) (Figure 4 A,B,C).

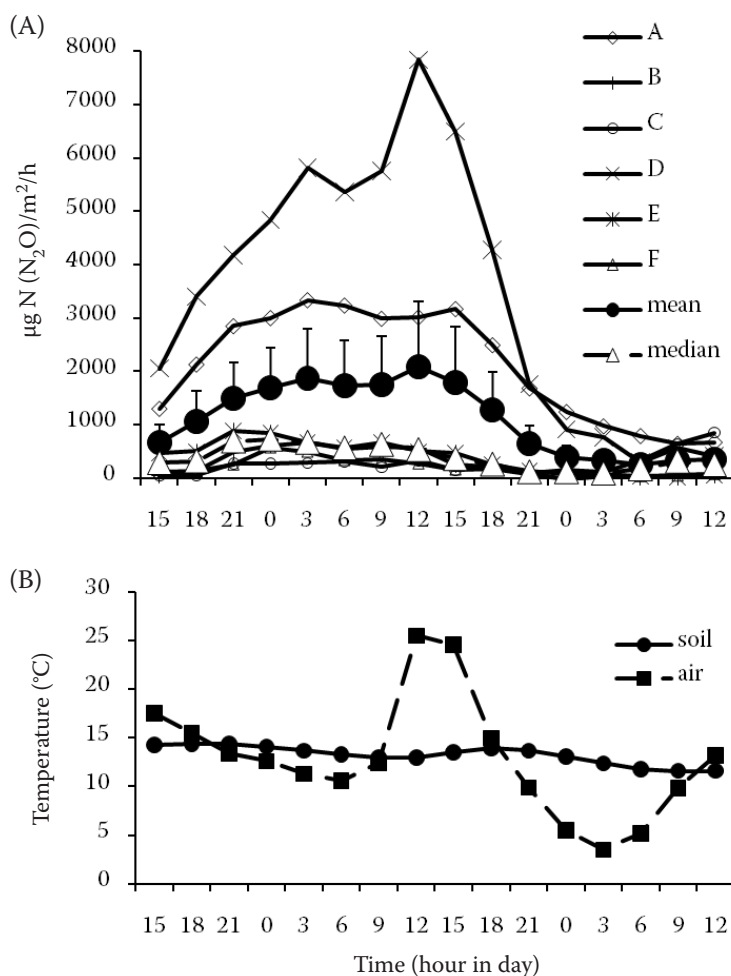


Figure 2. Emission data from 6 chambers (A–F) and arithmetic means (+SE) and medians of hourly  $\text{N}_2\text{O}$  emissions (A), and air (10 cm above soil surface) and soil (10 cm below soil surface) temperatures (B) during a 45-h measurement in May

## DISCUSSION

The results show that production of  $\text{N}_2\text{O}$  and  $\text{CO}_2$  can change quickly. The general course of fluxes of the two gases was different, and  $\text{CO}_2$  emissions were much more controlled by temperature, which is in agreement with numerous studies. In contrast to the results of Lloyd and Taylor (1994), who reported on exponential relationship between  $\text{CO}_2$  fluxes and soil temperature, this relationship was always linear in the range of temperature covered (5–30 $^{\circ}\text{C}$ ) in the current study. That the fluxes

often followed the changes in above-ground air temperature suggests that soil organisms in the top soil layers were largely responsible for  $\text{CO}_2$  production in soil and  $\text{CO}_2$  emission from soil; the same effect was found for example in organic boreal soils by Maljanen et al. (2002). In contrast to the temperature of deeper soil layers, the temperature of surface soil layers is closely related to air temperature. Strong daily fluctuation of  $\text{CO}_2$  emissions could have important implications for estimates of cumulative annual flux of  $\text{CO}_2$ ; our data show that any flux estimates must be used

Table 1. Pearson's correlation coefficients for relationships between  $\text{N}_2\text{O}$  emissions, and  $\text{CO}_2$  emissions and soil and air temperatures during diurnal measurements

Season	<i>n</i>	$\text{CO}_2$ emissions	Soil temperature	Air temperature
May	45	0.234	<b>0.502</b>	0.272
July	72	–0.287	–0.119	–0.375
November	–	<b>0.585</b>	0.004	<b>0.233</b>
		<i>n</i> = 56	<i>n</i> = 72	<i>n</i> = 72
May, 2 <sup>nd</sup> experiment	96	–0.220	0.154	<b>0.238</b>

Significant coefficients ( $P < 0.05$ ) are highlighted, *n* = number of correlated pairs

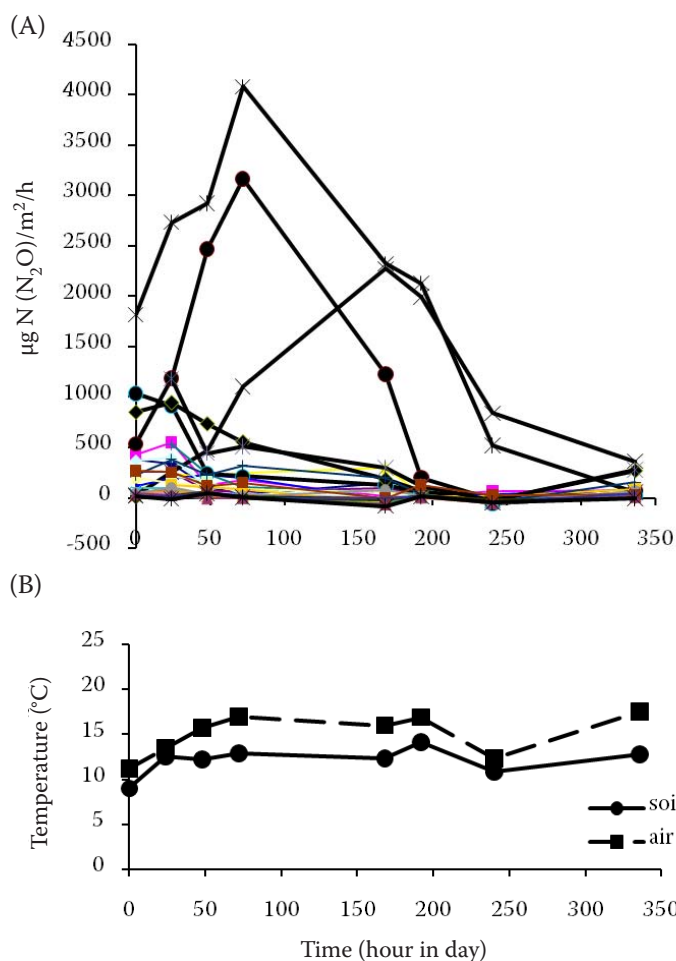


Figure 3. Hourly  $\text{N}_2\text{O}$  emissions in 32 individual chambers distributed regularly at the study site during a 2-week period in April. Air (10 cm above soil surface) and soil (10 cm below soil surface) temperatures determined at the beginning of each of 8 measurements are shown in part B

with care, especially if longer periods are to be covered.

In contrast to  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  emissions were much less predictable, and the possible relationship between temperature and emissions was often more complicated (Figure 1). Most chambers showed the same trend of  $\text{CO}_2$  flux, while in the case of  $\text{N}_2\text{O}$ , each chamber had a different time course of emissions. High temporal and spatial variability of  $\text{N}_2\text{O}$  emissions was often observed in earlier field studies (e.g., Velthof and Oenema 1995, Velthof et al. 1996, Röver et al. 1999) and is a typical feature of  $\text{N}_2\text{O}$  fluxes. Together with known general features of  $\text{N}_2\text{O}$  fluxes, our results

also suggest that obtaining reasonable estimates of  $\text{N}_2\text{O}$  flux requires that period(s) of high fluxes be identified and that detailed measurements be made during that period on the spatial distribution and temporal variability of emissions. With these data,  $\text{N}_2\text{O}$  fluxes can be then reliably estimated.

The daily fluctuation of  $\text{N}_2\text{O}$  emissions in soil amended with C and N in the present study is roughly in agreement with the results obtained under other conditions (e.g., Williams et al. 1999, Hyde et al. 2005). Diurnal cycles of  $\text{N}_2\text{O}$  emissions were also found in soil monoliths transferred to a greenhouse, with maxima occurring at night (Thomson et al. 1997), and were associated with diurnal cycles in

Table 2. Pearson's correlation coefficients for relationships between  $\text{CO}_2$  emissions and soil and air temperatures during diurnal measurements. Significant coefficients ( $P < 0.05$ ) are highlighted,  $n$  = number of correlated pairs

Season	$n$	Soil temperature	Air temperature
May	45	<b>0.499</b>	<b>0.772</b>
July	72	0.227	<b>0.856</b>
November	56	-0.174	0.139
May, 2 <sup>nd</sup> experiment	96	<b>0.407</b>	<b>0.720</b>



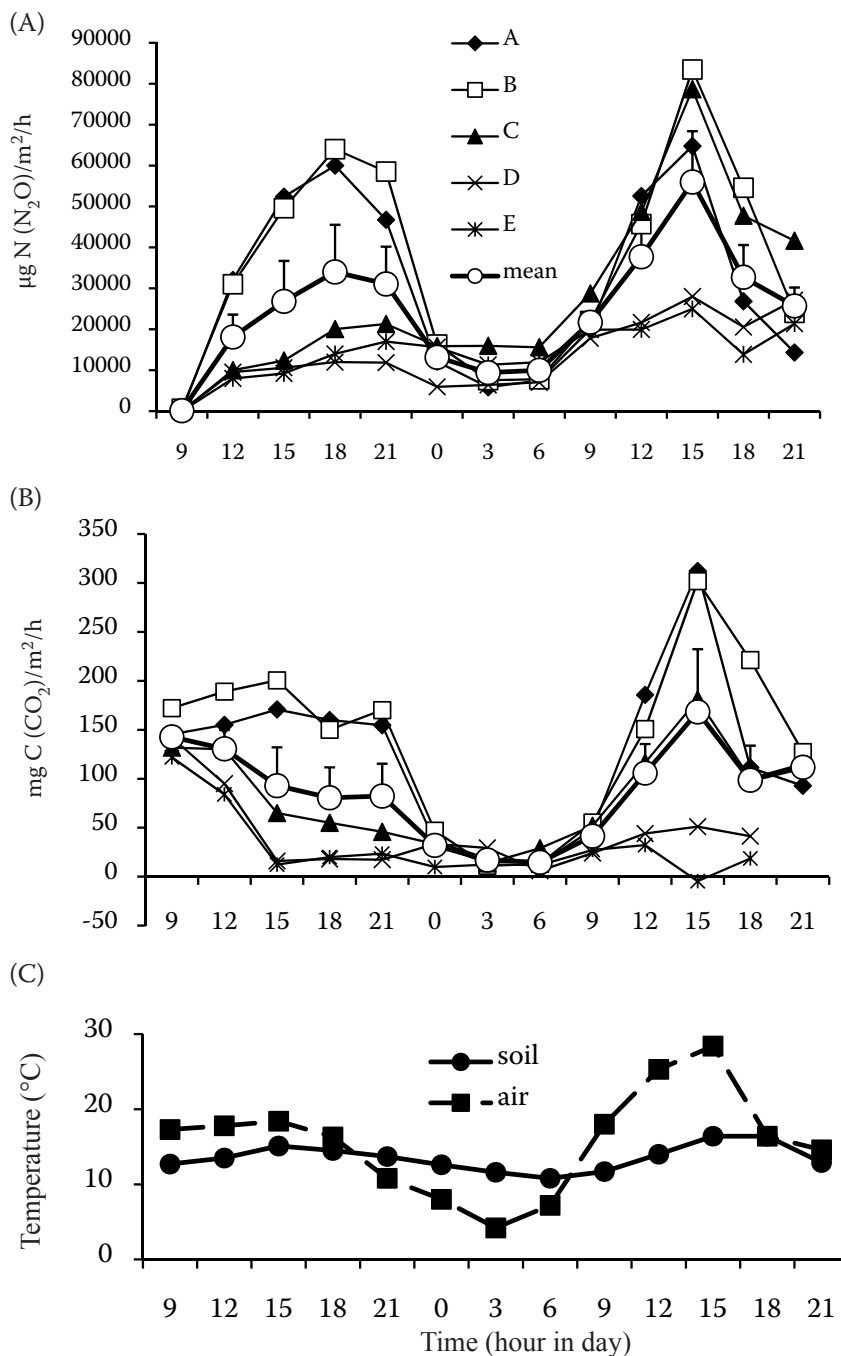


Figure 4. Emission data from 5 chambers (A–E) and arithmetic means (+SE) of hourly  $\text{N}_2\text{O}$  emissions (A) and  $\text{CO}_2$  emissions (B), following the addition of nutrients, and time course of air (10 cm above soil surface) and soil (10 cm below soil surface) temperatures ( $^{\circ}\text{C}$ )

soil temperature (Smith et al. 1998). Other studies, however, did not document diurnal changes in  $\text{N}_2\text{O}$  fluxes (e.g., Smith and Dobbie 2001). Our results suggest that emissions of  $\text{N}_2\text{O}$  are closely correlated with nitrogen inputs related to cattle and confirm that measurement of emissions after experimental additions of nutrients to soil can provide information about the ‘emission factor’, i.e., the proportion of added N that is emitted from the soil as  $\text{N}_2\text{O}$  (Hynš et al. 2007b). Although emission of gases can also be strongly affected by plants, the effect of vegetation was not a focus of the current study.

This study documents variations in the emissions of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  from the soil of a cattle overwintering area.  $\text{CO}_2$  was produced continually in the soil, and its emission was often correlated with temperature. The pattern of  $\text{N}_2\text{O}$  flux was much less predictable than that of  $\text{CO}_2$ . Production of  $\text{N}_2\text{O}$  was characterized by sharp, short-term peaks of fluxes at each microsite, i.e., emissions were heterogeneous in space and time. Obviously, the estimates of gas production and cumulative fluxes in general and those of  $\text{N}_2\text{O}$  in particular must be based on detailed knowledge of diurnal variations in fluxes in the given period. Our results suggest

that estimation of annual fluxes of  $\text{N}_2\text{O}$  should be based on detailed investigation of emissions during periods of increased fluxes. Emission estimates published in past decades, which were often based on only a few field flux measurements, must be used with caution.

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