

## Denitrification, organic matter and redox potential transformations in Cambisols

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Received June 7, 2003; accepted September 15, 2003

**A b s t r a c t.** Two greenhouse gases: N<sub>2</sub>O and CO<sub>2</sub> as well as C<sub>org</sub> and redox potential transformation were investigated. Fourteen Cambisols (0–10 cm) developed from sand, silt, loess, loam and clay characteristic for Poland were incubated under flood conditions in closed flasks at 20°C temperature for 7 days. According to denitrification activity the soils were divided into two groups – of lower (I) and higher (II) activity. Production of nitrous oxide lasting 3–5 days was followed by its absorption in the case of three soils out of fourteen. The total N<sub>2</sub>O amount reached from 3–91% of the initial nitrate – N content and was positively correlated with the C<sub>org</sub> content. Diurnal N<sub>2</sub>O production was positively correlated with C<sub>org</sub> and diurnal CO<sub>2</sub> emission. The N<sub>2</sub>O absorption rate for the three soils was 0.16 mg N<sub>2</sub>O-N kg<sup>-1</sup> day<sup>-1</sup>, 20.6 mg N<sub>2</sub>O-N kg<sup>-1</sup> day<sup>-1</sup> and 3.3 mg N<sub>2</sub>O-N kg<sup>-1</sup> day<sup>-1</sup> in sandy, loamy and in the clay soil, respectively. The diurnal fluxes of carbon dioxide ranged from 1.24 to 9.96 mg of CO<sub>2</sub>-C kg<sup>-1</sup> d<sup>-1</sup> and from 26.8 to 144 mg of CO<sub>2</sub>-C kg<sup>-1</sup> for I and II group, respectively. Diurnal carbon dioxide production showed a high positive correlation with C<sub>org</sub>. The soils investigated were characterised by a very wide range of redox potential measured for the maximal cumulative N<sub>2</sub>O emission from +417 to +233 mV. The beginning of N<sub>2</sub>O emission from the light textured soils was observed above 400 mV while from the heavier textured soil below 400 mV. N<sub>2</sub>O emission was correlated with soil redox potential.

**K e y w o r d s:** N<sub>2</sub>O emission, N<sub>2</sub>O absorption, redox potential, soil respiration, CO<sub>2</sub>:N<sub>2</sub>O ratio

### INTRODUCTION

Soils are important sources of several greenhouse gases such as water vapour, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O (Maljanen *et al.*, 2003; Xu-Ri *et al.*, 2003). In general, denitrification and chemolithotrophic nitrification are accepted as the dominant sources of N<sub>2</sub>O in most terrestrial ecosystems (Firestone and Davidson, 1989; Martikainen *et al.*, 1993). In the field, both processes are often limited by substrate-availability (nitrate,

ammonium), especially in N-limited forests (Gundersen and Rasmussen, 1990). The three main factors controlling soil denitrification rates are generally considered to be the concentration of oxygen, nitrate concentration and the availability of easily metabolizable organic matter (Tiedje, 1988; Horn *et al.*, 1994). These factors interact in a complicated manner with microorganisms on a microscale level in the soil, creating the large spatial and temporal variability in denitrification that has been observed in several studies (Parkin *et al.*, 1987; Svensson *et al.*, 1991).

Redox potential (Eh) is the aeration parameter characterising the intensity of soil redox transformations. The work of Smith *et al.* (1983) and Włodarczyk (2000) indicates that N<sub>2</sub>O emission and absorption can occur in soil if the Eh falls below 300 mV.

In the present investigation two greenhouse gases, nitrous oxide and carbon dioxide emission and N<sub>2</sub>O absorption as well as redox potential and the turnover of organic matter, were investigated under flooded soils amended with nitrate in order to better recognise the expected interrelations between these factors.

### MATERIALS AND METHODS

Fourteen arable Polish top soils (0–10 cm) used in the study were Cambisols developed from different parent material: sand (Nos 39, 342, 434, 543, and 772), silt (Nos 113, 224 and 984), loess (No. 672), loam (Nos 110, 328, 351 and 922) and clay (No. 947). Samples of these soils for the laboratory experiment were taken from the Bank of Soils situated in the Institute of Agrophysics in Lublin containing 1000 soil profiles. The 100 g portions of air-dry, sieved (1 mm sieve) soils were saturated with water and put on

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ceramic tension plates at 100 hPa (pF 2.0) for conditioning at 20°C in the dark. After 48 h of pre-incubation, moist soil samples (equal to 5 g of air-dry weight) were placed in 38 cm<sup>3</sup> glass vessels and enriched with KNO<sub>3</sub> (2 ml of solution containing 1 g NO<sub>3</sub><sup>-</sup>-N kg<sup>-1</sup>) and distilled water (4 ml). The nitrate introduced equalled 200 mg NO<sub>3</sub><sup>-</sup>-N kg<sup>-1</sup> and the soil/water ratio was about 1:1 (w/w). The vessels with suspensions were tightly sealed with rubber stoppers and incubated in N<sub>2</sub> atmosphere with 2% (v/v) C<sub>2</sub>H<sub>2</sub>. The average concentration of O<sub>2</sub> in the headspace at the start of the incubation was 1.2%. Paraffin film was affixed to the stoppers to ensure a hermetic seal.

Soils were incubated at 20°C for seven days. After 1, 2, 3, 5, and 7 days the concentration of N<sub>2</sub>O and CO<sub>2</sub> in the headspace was determined chromatographically using a Shimadzu GC-14 (Japan) fitted with a thermal conductivity detector at 60°C. Gas samples were separated on a 2 m column packed with a Porapak Q and a Molecular sieve and maintained at 40°C. Helium was the carrier gas flowing at a rate of 40 ml min<sup>-1</sup>. The concentrations of N<sub>2</sub>O and CO<sub>2</sub> were corrected for gas dissolved in the water by using the published values of the Bunsen absorption coefficient. Incubation vessels were prepared in three replicates. Additionally, a set of 12 samples obtained by the same procedure

was prepared for each soil. These vessels were opened successively in three replications after 1, 2, 3, and 7 days of incubation to measure pH and redox potential (Eh), (Gliński and Stepniewski, 1995).

The diurnal N<sub>2</sub>O and CO<sub>2</sub> production rates were calculated for the ranges of a linear increase of the headspace N<sub>2</sub>O content only (as the production divided by the time).

The linear ( $y=a+bx$ ), multiplicative ( $y=ax^b$ ), exponential ( $y=e^{a+bx}$ ) and logarithmic ( $y=aln x+b$ ) models were used in the regression analysis and in each case the model with the highest R<sup>2</sup> was selected as the best fit for the experimental data.

## RESULTS AND DISCUSSION

### N<sub>2</sub>O emission and absorption

The soils investigated showed a high variation in soil texture, organic carbon content, pH and endogenous nitrate content (Table 1).

N<sub>2</sub>O production for the soils amended with 200 mg NO<sub>3</sub><sup>-</sup>-N kg<sup>-1</sup> and in an anaerobic manner, incubated for 7 days, followed a specific and a different pattern. According to denitrification activity, the soils investigated were divided into two groups. Soils, which showed lower activity

**Table 1.** Basic properties of the investigated Cambisols

Parent material	Soil group	Soil number	Soil fractions (%)			pH	C <sub>org</sub> (%)	Native	Native+added
			1-0.1	0.1-0.02	<0.02			NO <sub>3</sub> <sup>-</sup> -N	NO <sub>3</sub> <sup>-</sup> -N
			(mm)			(mg kg <sup>-1</sup> )			
Sand	I	342	70	11	19	7.07	0.44	29.90	229.9
	I	434	71	18	11	4.45	0.74	18.50	218.5
	I	772	76	11	13	4.50	0.49	13.70	213.7
	I	39	89	6	5	4.64	0.67	4.53	204.5
	II	543	57	23	20	5.99	0.88	9.70	209.8
Silt	I	224	81	8	11	6.32	0.32	6.47	206.5
	I	113	66	26	8	4.50	0.92	58.40	258.4
	II	984	16	48	36	4.87	1.24	7.87	207.9
Loam	I	351	71	8	21	7.53	0.57	17.90	217.9
	I	110	42	25	33	4.38	0.67	10.20	210.2
	II	328	48	22	30	6.03	0.77	9.46	209.5
	II	922	16	57	27	4.45	1.89	5.37	205.4
Clay	II	947	4	64	32	5.29	2.31	32.90	232.9
Loess	II	672	1	60	39	4.85	0.94	67.40	267.4

(I) where  $N_2O$  production was below  $7 \text{ mg of } N_2O\text{-N kg}^{-1} \text{ d}^{-1}$  of soil, and higher activity (II), where  $N_2O$  production was up to  $47.2 \text{ mg of } N_2O\text{-N kg}^{-1} \text{ d}^{-1}$  (Table 2). Eight soils belong to the first group; four of them are developed from sand (Nos 39, 342, 434 and 772), two soils are developed from loam (Nos 110 and 351) and two are developed from silt (Nos 113 and 224). Six soils belong to the second group; one is developed from silt (No. 984), two are developed from loam (Nos 328 and 922), one is developed from sand (No. 543), one is developed from loess (No. 672) and one is developed from clay (No. 947).

to group I and ranging from 208 to  $270 \text{ mg of } NO_3^- \text{-N kg}^{-1}$  (Table 1). It seems probable that the next five soils (Nos 543, 984, 672, 328, and 922) had a low affinity to nitrate (Fig. 1b).

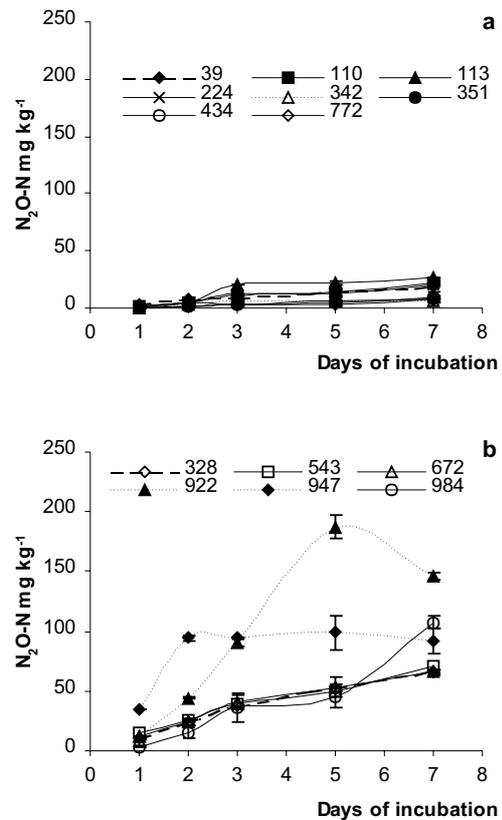
Soil No. 947 showed different denitrification activity. The  $N_2O$  production in the nitrate treatment followed first-order kinetics (Table 1) above  $233 \text{ mg}$  of initial  $NO_3^- \text{-N kg}^{-1}$  concentration (Fig. 1b). It seems that this soil had a higher affinity to nitrate than the rest of the soils investigated. In laboratory studies of potential denitrification, the  $NO_3^-$  concentration associated with this transition is thought to be relatively high, with values ranging from 40

**Table 2.** Basic characteristics of the functional groups observed in the tested Cambisols under anaerobic incubation

Functional classification of soils	Diurnal $N_2O$ emission ( $\text{mg } N_2O\text{-N kg}^{-1} \text{ d}^{-1}$ )	Eh (mV) at maximal denitrification	Diurnal $CO_2$ emission ( $\text{mg } CO_2\text{-C kg}^{-1} \text{ d}^{-1}$ )	$C_{\text{org}}$ (%)
Lower activity (I)	1.10–6.84	233–420	1.24–9.96	0.32–0.74
Higher activity (II)	9.40–47.2	237–391	3.83–32.6	0.77–2.31

The emission of nitrous oxide from the first group (I) of soils was very low and showed a small increase independently of any initial nitrate concentration (native + nitrate addition) during the seven days of incubation (Fig. 1a). The total cumulative emission of  $N_2O$  ranged from  $6.34$  to  $26.6 \text{ } N_2O\text{-N mg kg}^{-1}$  and the diurnal fluxes of nitrous oxide from this group ranged from  $1.10$  to  $6.84 \text{ mg of } N_2O\text{-N kg}^{-1} \text{ d}^{-1}$  (Table 2). The conclusion was drawn that in the first group of soils, denitrification was independent of the  $NO_3^-$  concentration with zero order reaction ranging between about  $205$  to  $230 \text{ mg of initial } NO_3^- \text{-N kg}^{-1}$  concentration (Table 1). It has been widely reported that with the increasing concentration of soil  $NO_3^-$ , denitrification changes from being dependent on  $NO_3^-$ , with the first order of Michaelis-Menten kinetics, to being independent of  $NO_3^-$ , that is, following zero order kinetics (Scholefield *et al.*, 1997). The low response of the soils investigated on the relatively high nitrate addition suggested that most of them had a low affinity (defined as the reciprocal of the Michaelis constant -  $K_M$ ) to nitrate which is the reaction of the medium for a given substrate.

The similar course of the cumulative curve of  $N_2O$  emission showed the second group (II) of soils as having a higher activity, except for one (No. 947); however, this group was characterised by a higher nitrous oxide production. The total cumulative emission of  $N_2O$  ranged from  $65.8$  to  $187.4 \text{ } N_2O\text{-N mg kg}^{-1}$  and the highest diurnal fluxes of nitrous oxide from this group was above  $47 \text{ mg of } N_2O\text{-N kg}^{-1} \text{ d}^{-1}$  (Table 2). In the case of the second group of soils the denitrification changes were independent of  $NO_3^-$  concentration with zero order kinetics in a concentration similar



**Fig. 1.** The course of cumulative nitrous oxide content (mean values + standard deviations) in the headspace during the incubation of the two soil groups: 8 soils with lower activity (a) and 6 soils with higher activity (b). A discontinuous line denotes soil where  $N_2O$  absorption was observed.

(Knowles, 1981) to  $100 \text{ mg of N kg}^{-1}$  soil (Aulakh *et al.*, 1992) being quoted as typical. Scholefield *et al.*, (1997) found that denitrification in Stagno-Dystric Gleysol responds to increasing  $\text{NO}_3^-$  supply within the range  $0\text{--}150 \text{ kg of N ha}^{-1}$  (equivalent approximately to  $0\text{--}150 \text{ mg kg}^{-1}$ ). In our investigations, the threshold of  $\text{NO}_3^-$  concentration is higher than  $200 \text{ mg kg}^{-1}$  ( $600 \text{ kg of N ha}^{-1}$ ).

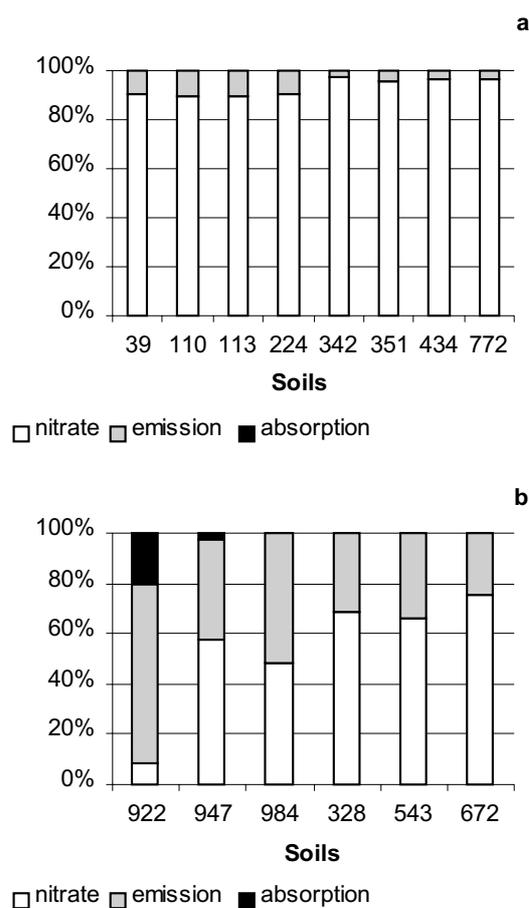
The total cumulative  $\text{N}_2\text{O}$  emission expressed as a percentage of the initial nitrate content was distinctly varied in the soil under investigation. As far as the percentage of the initial nitrate – N converted to nitrous oxide is concerned, the data presented in Fig. 2 indicates that it varied from 2.8 to about 91%. The differences between the particular soil groups was clear and ranged from 2.8 to 10.4% and from 24.6 to 91.2% for the first and second group, respectively.

After a day of the maximum content of  $\text{N}_2\text{O}$ , its step-wise disappearance from the headspace was observed. The absorption rates of  $\text{N}_2\text{O}$  were distinctly different in the groups of soil. As can be seen from Fig. 2, only three soils showed the ability to absorb  $\text{N}_2\text{O}$ , one from group I (No. 342) and two from group II (Nos 922 and 947). The nitrous

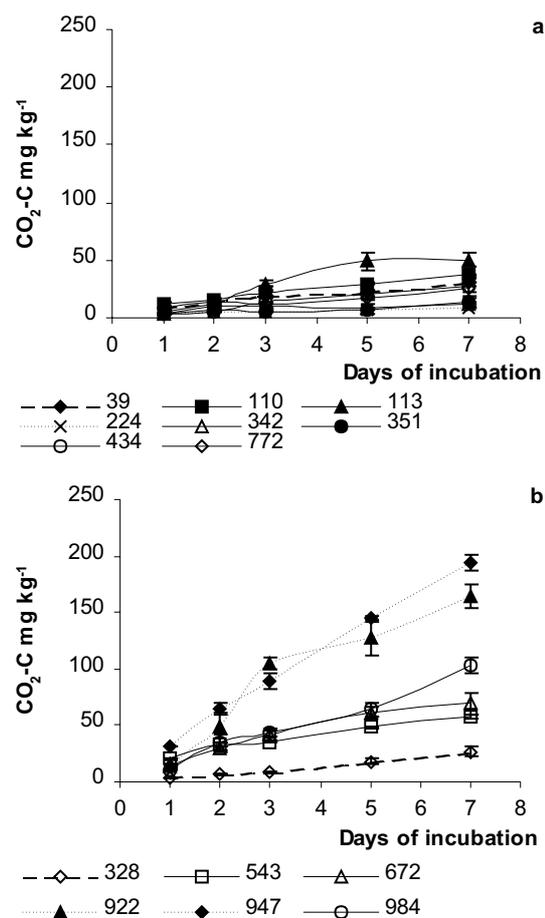
oxide generated underwent absorption during the incubation time in a different manner. The sandy soil (No. 342) absorbed about 10% of the  $\text{N}_2\text{O}$  emitted. The loamy soil (No. 922) showed the highest  $\text{N}_2\text{O}$  absorption (about 22%) while the lowest, (about 7%) was observed in the case of the clay soil (No. 947). The soils under investigation showed a distinct differentiation in the diurnal nitrous oxide absorption ( $0.16$  for sandy soil,  $3.3$  for clay, and  $20.6 \text{ mg N}_2\text{O-N kg}^{-1} \text{ d}^{-1}$  for the loamy soil).

### Organic matter turnover

The lower cumulative emission of  $\text{CO}_2$  on seventh day of incubation was observed in the first group (I) of those soils studied, from  $8.7$  to  $50.4 \text{ mg of CO}_2\text{-C kg}^{-1}$  (Fig. 3a) compared with the second group. The diurnal fluxes of carbon dioxide (calculated only for the ranges of a linear increase of the headspace  $\text{N}_2\text{O}$  content) observed in this group ranged from  $1.24$  to  $9.96 \text{ mg of CO}_2\text{-C kg}^{-1} \text{ d}^{-1}$  (Table 2).



**Fig. 2.** Percentage of N-forms on the last day of incubation ( $\text{NO}_3^-$ -N,  $\text{N}_2\text{O}$ -N emitted and  $\text{N}_2\text{O}$ -N absorbed). 8 soils with lower activity (a) and 6 soil with higher activity (b).



**Fig. 3.** The course of cumulative carbon dioxide content (mean values + standard deviations) in the headspace during the incubation of the two soil groups: 8 soils with lower activity (a) and 6 soils with higher activity (b). A discontinuous line denotes soil where  $\text{N}_2\text{O}$  absorption was observed.

The low  $\text{CO}_2$  production was probably connected with the low organic matter content (0.32–0.74%).

The soils of the second group (II) (Fig. 3b), showed approximately a four times higher  $\text{CO}_2$  production which corresponded to the higher  $C_{\text{org}}$  content (0.77–2.31%). Carbon dioxide emission on the seventh day of incubation ranged from 26.8 to 144 mg of  $\text{CO}_2\text{-C kg}^{-1}$ . The diurnal flux of carbon dioxide from this group ranged from 3.83 to 32.6 mg of  $\text{CO}_2\text{-C kg}^{-1} \text{d}^{-1}$  (Table 2).

$\text{CO}_2$  production from most of the soils investigated during the first three days of anaerobic incubation followed linearly and independently of the denitrification activity of the soils studied (Fig. 3a,b). C mineralization in these soils apparently followed zero kinetics. After the third day of incubation,  $\text{CO}_2$  production slightly decreased in one soil with higher  $C_{\text{org}}$  content (No. 922). Any prolonged incubation (above three days) would have reduced the easily available organic C substrate. The adaptation of the microorganisms over two days to more heavily decomposable organic matter resulted in an increase of  $\text{CO}_2$  emission (Fig. 3b).

The results clearly indicate the influence of soil  $C_{\text{org}}$  on  $\text{CO}_2$  emission. Diurnal  $\text{CO}_2$  emission (Fig. 4) was positively correlated with the  $C_{\text{org}}$  content ( $R^2=0.91^{***}$ ).

The very small  $\text{CO}_2$  emission was accompanied by a very small  $\text{N}_2\text{O}$  emission in the case of the first group of soils while a proportionally higher  $\text{N}_2\text{O}$  and  $\text{CO}_2$  emission was observed in the second group of soils. Diurnal carbon dioxide production was closely related to diurnal  $\text{N}_2\text{O}$  emission (Fig. 5) and showed a high positive correlation ( $R^2=0.952^{***}$ ). Other authors (Dendooven and Anderson, 1995; Dendooven *et al.*, 1996; Swertes *et al.*, 1996) obtained similar results. They found that total denitrification rates were closely related to anaerobic  $\text{CO}_2$  production rates.

It should be emphasized that the diurnal nitrous oxide formed due to denitrification (Fig. 6) and the percentage of nitrate denitrified to nitrous oxide (Fig. 7) were positively related to the  $C_{\text{org}}$  content of the soil ( $R^2=0.95^{***}$  and  $R^2=0.60^{***}$ , respectively). The results proved the close connection of N and C transformation pathways in the metabolism of microorganisms inhabiting the soil system.

The soils tested varied in molecular  $\text{CO}_2\text{:N}_2\text{O}$  ratio (Table 3). As a rule, the molecular ratio between  $\text{CO}_2$  and the  $\text{N}_2\text{O}$  production systematically decreased in the soils included in the first group (I). The widest ratios (2.7–14.5) were observed during the first day of incubation and probably mainly as a result of an excess of  $\text{CO}_2$  production coinciding with a lag in  $\text{N}_2\text{O}$  production at the beginning of incubation. Swertes *et al.* (1996) found that denitrification rates during the first phase of denitrification are determined by the pre-existing enzymatic capacity to denitrify rather than by the availability of nitrate or carbon. The wide  $\text{CO}_2\text{:N}_2\text{O}$  ratio (more than 2) at the beginning of our incubation might suggest that denitrification and fermentative  $\text{CO}_2$  production took place simultaneously. Generally, the rate of

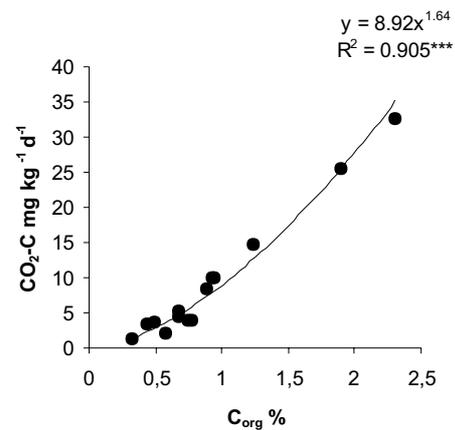


Fig. 4. Diurnal  $\text{CO}_2\text{-C}$  emission versus of  $C_{\text{org}}$  content under consideration.

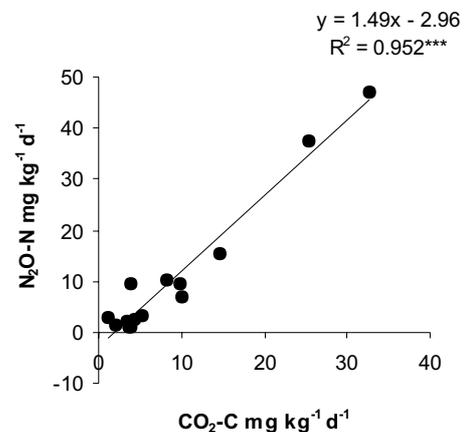


Fig. 5. Diurnal  $\text{N}_2\text{O-N}$  emission versus diurnal  $\text{CO}_2\text{-C}$  emission under consideration.

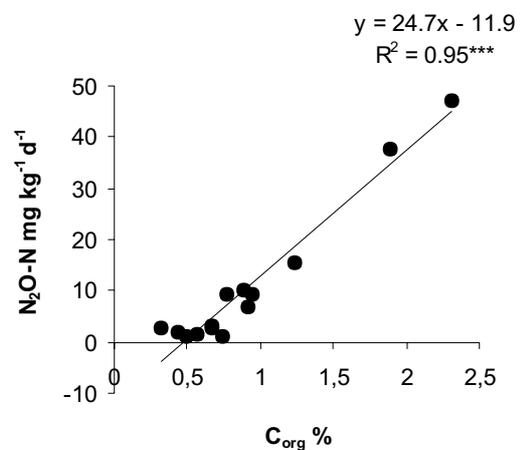
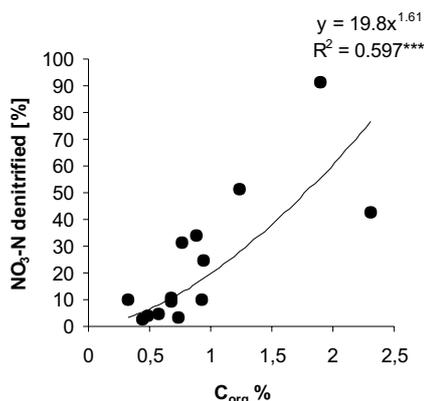


Fig. 6. Diurnal  $\text{N}_2\text{O-N}$  emission versus of  $C_{\text{org}}$  content under consideration.



**Fig. 7.** Total headspace N<sub>2</sub>O-N expressed as percent of the initial NO<sub>3</sub><sup>-</sup>-N content versus C<sub>org</sub> content.

N<sub>2</sub>O and CO<sub>2</sub> emission was apparently higher in more heavily textured soils (developed from clay and loam). Notwithstanding, those soils where sand is dominant as the parent material showed a low capacity to denitrify. It seems that the wide molecular ratio was connected with the very low denitrification activity observed in the soils investigated and with the conversion of polymerised carbon compounds into readily available forms during drying, especially sand soils. Burford and Bremner (1975) found that the capacity to denitrify was directly related not just to the total, but also to the carbon which was water-soluble and able to be mineralized in reaction mixtures of sand, silt, and clay incubated at 20°C for 7 days. During subsequent incubation, the CO<sub>2</sub>:N<sub>2</sub>O ratios were lower on the seventh day of incubation

reaching values from 3.6 to 0.4, indicating that most of the soil investigated had adapted to the anaerobic conditions and that the denitrification process had pre-dominated. The simultaneous exhaustion of readily available C stopped CO<sub>2</sub> production (Fig. 3). Pidello *et al.* (1996) studied N<sub>2</sub>O and CO<sub>2</sub> emission under different redox potential conditions. The ratio between CO<sub>2</sub> and N<sub>2</sub>O production was continuously more than 2 suggesting that denitrification and fermentative CO<sub>2</sub> production had taken place simultaneously.

The molecular ratio between the CO<sub>2</sub> and the N<sub>2</sub>O production, which well reflected the capacity for denitrification, showed a completely different course in the second group (II) of the soils investigated (with the exception of soil No. 984). The ratios were less diversified at the beginning of incubation (i.e., 3.2–0.3) and after the second day of incubation decreased below 2 (Table 3) indicating that N<sub>2</sub>O was the dominant product of denitrification. According to stoichiometric calculations, the relationship between N<sub>2</sub>O production and CO<sub>2</sub> equals 2 when N<sub>2</sub>O is the only product of denitrification (Delwiche, 1981). Soils classified in group II were characterised by a low molecular ratio between the CO<sub>2</sub> and the N<sub>2</sub>O production and the probably higher level of pre-existing enzymes which participated in dissimilar nitrate reduction.

It is concluded from our study that most of the soils were not well adapted to anaerobic conditions and showed a low capacity to denitrify; this is probably connected partly with the soil texture. The rest of the soils studied had a high capacity for denitrification. The molecular ratio between CO<sub>2</sub> and N<sub>2</sub>O production amply reflected the differences in the soil's capacity to denitrify where nitrate is the only electron acceptor.

**Table 3.** The molecular ratio between the CO<sub>2</sub> and the N<sub>2</sub>O production (CO<sub>2</sub>:N<sub>2</sub>O) calculated for the investigated soils

Functional classification of soils	Soil No.	Day of incubation				
		1	2	3	5	7
Lower activity (I)	342	6.5	2.7	1.7	1.7	1.7
	434	8.8	4.5	3.7	3.4	3.6
	772	14.5	3.4	3.1	4.5	3.2
	39	2.7	1.6	2.0	1.7	1.7
	113	5.8	2.9	1.5	2.1	1.9
	224	2.7	1.2	0.4	0.6	0.4
	351	7.5	3.2	1.9	1.7	1.4
	110	12.1	3.8	2.0	2.0	1.7
	984	3.2	2.3	1.2	1.4	1.0
Higher activity (II)	947	0.9	0.7	0.9	1.5	1.5
	672	1.2	1.2	1.0	1.2	1.1
	328	0.3	0.3	0.2	0.3	0.4
	922	1.4	1.1	1.2	0.7	0.7
	543	1.3	1.3	0.9	1.0	0.8

### Nitrous oxide content versus soil redox potential

Several factors are known to influence the rate of denitrification directly or indirectly. One of the most important is redox potential (Eh). Under anaerobic conditions, the redox potential systematically dropped during incubation of the flooded soils (except for soil No. 672). The redox potential at the beginning of the incubation ranged from +301 to +434 mV and from +342 to +400 mV for the first and the second group of soils, respectively (Table 4). It should be emphasised that the Eh value above 400 mV corresponded with the lowest N<sub>2</sub>O emission after first day of incubation. It seems probable that it is the threshold value for the beginning of the denitrification process under the conditions investigated. These soils are characterised by their high resistance to reduction processes. Other laboratory studies have shown that the high redox potential of the soils investigated at low water tensions is indicative of their high redox buffering capacity ( $t_{300}$ ) Stepniowski *et al.* (2000). Gliński and Stepniowska (1986) defined index  $t_{300}$  as the time needed to lower the soil redox potential under flood conditions at a fixed temperature to a level of 300 mV.

After seven days of incubation, the Eh values apparently decreased in the soils investigated (by 3–121 mV) with the exception of one where the Eh value increased insignificantly from +377 to +391 mV (soil No. 673).

According to the data in Table 2 the highest cumulative N<sub>2</sub>O emission from the first group of soil corresponded to the Eh value from +233 to +417 mV. A slightly lower redox potential value was noticed in the case of soils with higher

denitrification activity and ranged from 237 to 391 mV. The amount of denitrified N<sub>2</sub>O was the highest in the range of Eh values from about +250 to +319 mV. Generally, the soils investigated were characterised by a very wide range of redox potential measured for maximal cumulative N<sub>2</sub>O emissions (+417 to +233 mV) (Table 2).

The value of redox potential corresponding to the absorption of N<sub>2</sub>O was below +340 mV (Table 3). Patrick (1960) showed that denitrification can occur when the redox potential of soil has decreased to below about +340 mV. Masscheleyn *et al.* (1993) reported N<sub>2</sub>O emission from rice paddy soils with various redox potentials, ranging from +500 to –250 mV. Two maximums for N<sub>2</sub>O evolution were found, at +400 mV where nitrification was the source and at 0 mV where N<sub>2</sub>O was produced by denitrification.

The amount of nitrous oxide formed due to denitrification showed a negative correlation with the Eh value in most of the soils investigated (Table 5). This close relationship between denitrification and redox potential was confirmed by the correlation between the molecular CO<sub>2</sub>:N<sub>2</sub>O ratio and Eh (Table 6). Pidello *et al.* (1996) studied N<sub>2</sub>O and CO<sub>2</sub> emission under conditions of different redox potentials. The ratio between the CO<sub>2</sub> and the N<sub>2</sub>O production was correlated with the Eh value.

Our results incline us to the conclusion that the threshold value of the redox potential for the emission of N<sub>2</sub>O is very wide for different soils and depends on many factors. The beginning of N<sub>2</sub>O emission from the light textured soils developed from sand was observed above +400 mV while this was below +400 mV for the heavily textured soils.

**Table 4.** The redox potential (mV) of the investigated soils

Functional classification of soils	Soil No.	Day of incubation			
		1	2	3	7
Lower activity (I)	342	379	364	339	315
	434	434	429	430	412
	772	413	410	229	311
	39	410	385	235	299
	113	420	400	385	417
	224	301	311	212	233
	351	326	295	234	266
	110	392	373	313	308
Higher activity (II)	543	356	377	232	237
	984	399	390	397	319
	947	342	331	280	221
	672	377	378	389	391
	328	356	350	352	334
	922	400	393	333	302

**Table 5.** Values for the correlation coefficient ( $R^2$ ) obtained between cumulative content of  $N_2O$ -N in the headspace of gas for the phase of emission and redox potential

Soil No.	Function	$R^2$	n
I group			
342	$y = -6.1335x + 382.17$	0.779***	9
434	$y = 436.41e^{-0.0071x}$	0.299*	15
772	Not significant		
39	$y = -64.12 \ln(x) + 457.72$	0.394**	15
113	Not significant		
224	$y = -31.872 \ln(x) + 316.51$	0.622***	15
351	$y = -22.707 \ln(x) + 297.17$	0.512**	15
110	$y = -29.26 \ln(x) + 394.33$	0.809***	15
II group			
543	$y = 912.64x^{-0.3324}$	0.639***	15
984	$y = 405.88e^{-0.0021x}$	0.810***	15
947	$y = 0.9675x + 381.07$	0.496**	12
672	Not significant		
328	$y = -0.3429x + 360.05$	0.411**	15
922	$y = -31.756 \ln(x) + 487.33$	0.651***	12

Significance level: \*\*\* $p < 0.001$ , \*\* $p < 0.01$ , \* $p < 0.05$ .

**Table 6.** Values for the correlation coefficient ( $R^2$ ) obtained between the molecular ratio of  $CO_2:N_2O$  for the diurnal  $N_2O$  emission and redox potential

Group of soil	Function	$R^2$	n
I group	$y = 8E - 06x^{2.1977}$	0.356***	108
II group	$y = 0.0045x - 0.484$	0.107**	78

#### CONCLUSIONS

1. The diurnal flux of nitrous oxide was no more than 6.84 mg of  $N_2O$ -N  $kg^{-1} d^{-1}$  in the first group of soils (I) with lower denitrification activity and was above 47 mg of  $N_2O$ -N  $kg^{-1} d^{-1}$  in the second group of soils (II) with higher activity.

2. The diurnal fluxes of carbon dioxide ranged from 9.96 to 32.6 mg of  $CO_2$ -C  $kg^{-1} d^{-1}$  in the first (I) and second (II) groups of soils, respectively.

3. The total cumulative  $N_2O$  emission expressed as a percentage of the initial nitrate content varied from 2.8 to about 91%.

4. Three soils showed an ability to absorb  $N_2O$  and absorbed from 7 to 22% of the nitrous oxide emitted.

5. Diurnal  $N_2O$  and  $CO_2$  production was positively correlated with  $C_{org}$ .

6. The beginning of  $N_2O$  emission from the light textured soils was observed above +400 mV while from the heavier textured soil this was below +400 mV.

7.  $N_2O$  emission was negatively correlated with the soil redox potential.

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