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N_2O emission and sorption in relation to soil dehydrogenase activity and redox potential

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A b s t r a c t. Two soils: a peaty-muck soil (Eutric Histosol) and a brown soil (Eutric Cambisol) developed from sand) were incubated anaerobically with addition of KNO_3 (100 mg NO_3^--N kg^{-1} and 2% C_2H_2) for the determination of N_2O emission or with addition of 1% N_2O for the determination of N_2O sorption. The rates of nitrous oxide, nitrate, dehydrogenase activity, redox potential and CO_2 production at 20°C were measured over 14 days. The peaty-muck soil showed about 4 times higher denitrification activity (as measured by N_2O emission and NO_3^- depletion) and on average 27 times higher dehydrogenase activity than the brown sandy soil. In turn, the brown sandy soil was characterized by better capacity for nitrous oxide sorption and more intensive respiration activity. Production of CO_2 and redox potential were not influenced by the form of N which was added. Dehydrogenase activity in the organic soil was significantly higher with N_2O-treatment than with nitrate-treatment ($P<0.001$).

K e y w o r d s: N_2O emission and sorption, dehydrogenase activity, redox potential, peaty-muck and brown sandy soils

INTRODUCTION

Nitrous oxide (N_2O) is an important greenhouse gas but the kinetics of its exchange between the atmosphere and soils is still poorly investigated. The concentration of this gas in the atmosphere has increased considerably over the past few decades, and continues to increase. Most N_2O is formed by denitrification in oxygen deficient environments, although it can also be produced by nitrification in aerobic conditions [13]. Increasing N-inputs into agricultural soils are suspected to be responsible for increased N_2O emission into the atmosphere. Soil can remove atmospheric N_2O under conditions favourable for N_2O reduction [7,14]. This is probably only a minor sink on the global scale, but elimination of N_2O in the stratosphere is so slow that even a small soil sink can contribute significantly to reduction of the atmospheric residence time of N_2O [6].

The soil oxidation-reduction status (Eh) has been shown to be an important factor affecting soil biological activity and transformations of natural compounds and xenobiotics in soils [1,2] as well as both N_2O production and sorption [14]. Therefore, Eh could be important in assessing the potential hazard for O_3 layer destruction.

Soil biological activity is a significant component of soil quality and is the catalytic agent responsible for many transformations occurring in soil, most notably the reactions involved in nutrient cycling. Dehydrogenases, playing an essential role in the initial stages of soil organic matter oxidation, reflect total oxidative activity of the soil microflora [3,4,15].

The aim of the present paper was to determine the N_2O emission and sorption against a background of soil dehydrogenase activity, redox potential and CO_2 production in an organic and in a mineral soil under anaerobic conditions.

MATERIALS AND METHODS

Soil samples were collected from the Ap horizons of two soils differed in their biological activity and properties such as genesis, C-organic content and pH. The soils were an organic peaty-muck soil (Eutric Histosol) and a mineral brown soil developed from sand (Eutric Cambisol). The basic characteristic of the soils are shown in Table 1.

Five-gram soil samples were incubated in 60 cm^3 glass vessels in an N_2 atmosphere at 20°C. Two treatments were used: (1) with addition of 5 ml of KNO_3 (100 mg NO_3^--N per kg dry soil) and 2% (v/v) of C_2H_2 for the determination

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T a b l e 1. Selected properties of the soils used in the study

Soil material	Soil size fractions (%)			NO_3^--N (mg kg^{-1})	C_{org} (%)	pH in H_2O
	1–0.1 mm	0.1–0.02 mm	<0.02 mm			
Peaty-muck soil	n.d.*	n.d.	n.d.	8.97	35.1	7.27
Brown sandy soil	89	6	5	1.95	0.67	4.80

*n.d. – not determined.

of N_2O emission and (2) with addition of 5 ml distilled water and 1% of N_2O for the determination of N_2O sorption. Analyses were performed at the start (2 h) and after 1, 2, 3, 7, 8, 9, 10 and 14 days of incubation in three replications.

The concentrations of N_2O and CO_2 in the headspace were 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 with the carrier gas He flowing at a rate of 40 ml min^{-1}, and which was maintained at 40°C. The concentrations of N_2O and CO_2 were corrected for gas dissolved in the water by using published values of the Bunsen absorption coefficient.

The content of NO_3^--N in the soil was assayed after extraction with 0.05 M $CaCl_2$ (Tecator autoanalyser FIA-STAR 5010). Soil redox potential was measured by Pt-electrodes with a saturated calomel electrode as a reference. Soil dehydrogenase activity was determined with TTC according to Casida *et al.* [5].

RESULTS AND DISCUSSION

Figure 1 shows the time course of nitrous oxide content in the headspace of soils amended with nitrate or N_2O. Incubation of the soils with nitrate enrichment resulted in emission of N_2O and simultaneous depletion of NO_3^-. The peaty-muck soil showed greater denitrification capacity with nearly 4-times higher N_2O production at the end of the incubation (up to 26.7 mg N_2O-N kg^{-1}) than the brown sandy soil (only 7.18 mg N_2O-N kg^{-1}). The brown sandy soil, however, exhibited greater N_2O sorption and one half of the introduced nitrous oxide was depleted during 6 days (Fig. 1a). The concentration of added N_2O in the start of incubation was 65.3 and 69.9 mg N_2O-N kg^{-1} in peaty-muck and brown sandy soils, respectively. The amount of nitrous oxide decreased after 14 days by 51% (down to 31.9 mg N_2O-N kg^{-1}) in peaty-muck and by 81% (down to 13.7 mg N_2O-N kg^{-1}) in brown sandy soil. The uptake of N_2O by soils was also observed by Letey *et al.* [9], Ryden [11] and Silvola *et al.* [12]. Włodarczyk [14] found that N_2O sorption in some Eutric Cambisols ranged from 10 to 100%, depending on soil and incubation time.

Denitrification corresponded to the consumption of introduced NO_3^-. About 45% of added nitrate (49.4 mg NO_3^--N kg^{-1}) was depleted in the peaty-muck and 11% (11.1 mg NO_3^--N kg^{-1}) in the brown sandy soil (Fig. 1b). The level of endogenous nitrate was rather low (8.97 mg NO_3^--N kg^{-1} in the organic soil and only 1.95 mg NO_3^--N kg^{-1} in the mineral soil). In the brown sandy soil all the native NO_3^- was exhausted after 7 days of anaerobic incubation. In the peaty-muck soil NO_3^- content decreased sharply at the beginning of the experiment and remained on a low level until the end of the incubation. Depletion of 49.4 mg of NO_3-nitrogen resulted in production of 26.7 mg N_2O-nitrogen in the peaty soil, and depletion of 11.1 mg of NO_3-N resulted in emission of 7.18 mg N_2O-N in the brown sandy soil. It means that about 54% and 65% of depleted nitrate-N were denitrified to the nitrous oxide-form by organic and mineral soil, respectively. The rest of the nitrate was presumably either transformed into the other denitri- fication products (NO_2, NO, N_2), reduced to NH_4^+ or assi- milated by soil microorganisms [7,8,10].

The anaerobic incubation resulted in relatively high CO_2 production, especially in the brown sandy soil (Fig. 1c). Respiration activity was not affected by the form of the introduced N. The intensive CO_2 production during first days of the incubation is typical for soils rewetted after air-drying [14]. The cumulative CO_2 in the headspace at the end of the incubation was 275 and 180 mg CO_2-C kg^{-1} in the brown sandy and the peaty-muck soil, respectively.

The brown sandy soil showed low dehydrogenase activity (maximally 0.015 nmol TPF g^{-1} min^{-1}), which was on average 27 times lower than in the peaty-muck soil (up to 0.32 nmol TPF g^{-1} min^{-1}), (Fig. 1d). The increase of the dehydrogenase activity on the first day of the incubation corresponded to the intensive respiration and resulted presumably from the start of the metabolic activity of the microorganisms due to water supply. Then, the activity decreased. The high level of this activity in the peaty-muck soil, however, was not accompanied by more intensive respiration (see Fig. 1c). The CO_2 concentration in the headspace increased until the end of the incubation but did not correlate with significant changes of the dehydrogenase

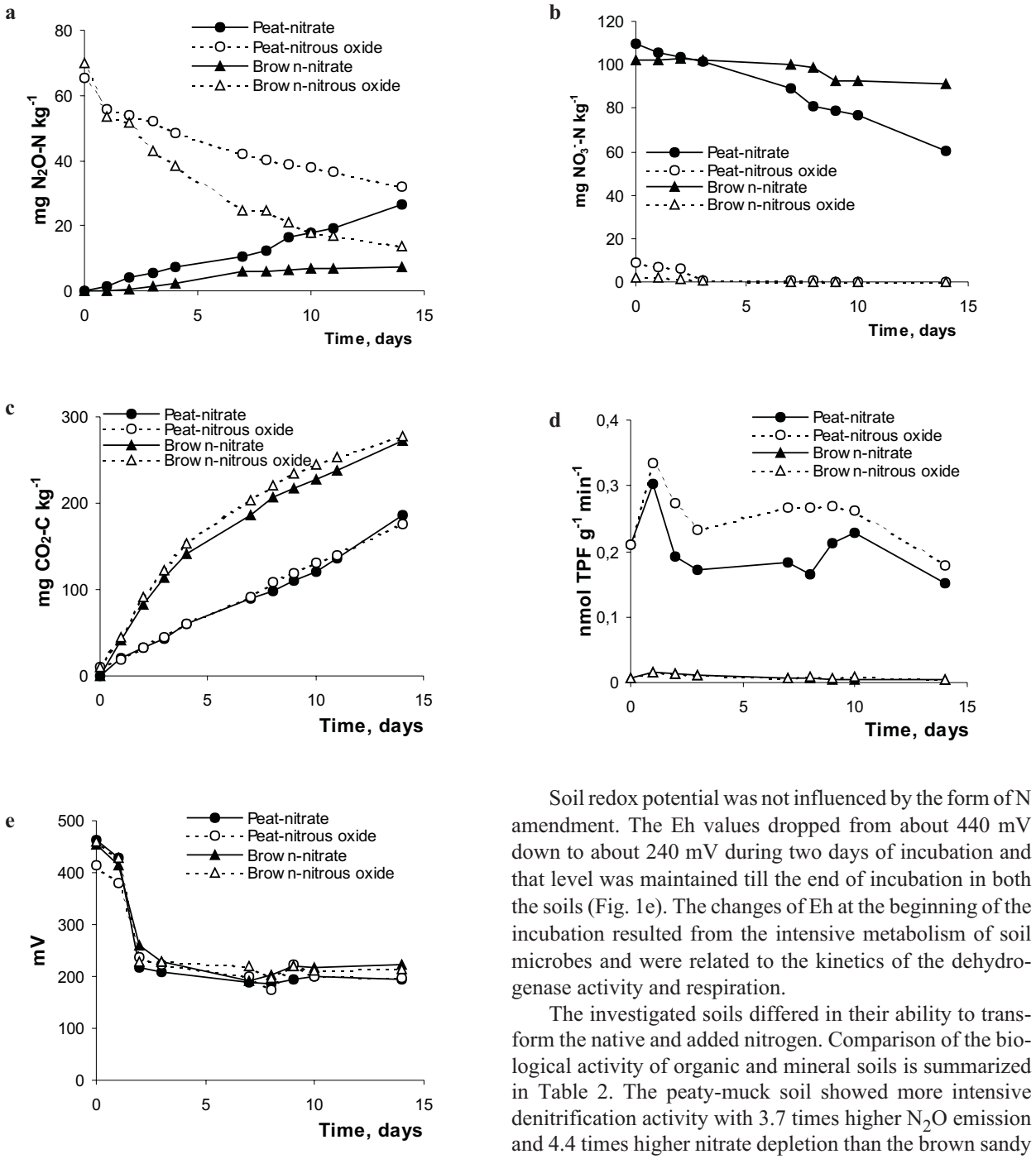

Fig. 1. Nitrous oxide kinetics (a), nitrate kinetics (b), carbon dioxide kinetics (c), dehydrogenase activity (d) and redox potential (e) in peaty-muck and brown sandy soils amended with nitrate (black) or nitrous oxide (white).

activity. However, a small increase of dehydrogenase activity could be observed for peat soil treated with nitrate – after its depletion (9th day of the incubation). Both soils showed lower dehydrogenase activity when incubated with nitrate (significant decrease for the peaty-muck soil, $P<0.001$).

Soil redox potential was not influenced by the form of N amendment. The Eh values dropped from about 440 mV down to about 240 mV during two days of incubation and that level was maintained till the end of incubation in both the soils (Fig. 1e). The changes of Eh at the beginning of the incubation resulted from the intensive metabolism of soil microbes and were related to the kinetics of the dehydrogenase activity and respiration.

The investigated soils differed in their ability to transform the native and added nitrogen. Comparison of the biological activity of organic and mineral soils is summarized in Table 2. The peaty-muck soil showed more intensive denitrification activity with 3.7 times higher N_2O emission and 4.4 times higher nitrate depletion than the brown sandy soil. Moreover, the dehydrogenase activity of the organic soil exceeded many times (on average 27 fold) that of the mineral soil. In contrast, the mineral soil was characterized by greater capacity for sorption of introduced nitrous oxide as well as a more intensive respiration activity than the organic soil. The redox potential was comparable for both soils and treatments. Production of CO_2 and redox potential were not influenced by the form of N added. The dehydrogenase activity in the organic soil was significantly higher in N_2O-treatment than in nitrate-treatment ($P<0.001$).

T a b l e 2. Comparison of the biological activities of soils tested

Process	Peaty-muck soil	Brown sandy soil
N_2O emission	4 times higher	lower
N_2O sorption	lower	2 times higher
Respiration	lower	1.5 times higher
NO_3^- reduction	4 times higher	lower
Dehydrogenase activity	27 times higher	lower
Redox potential	comparable	comparable

CONCLUSIONS

1. Peaty-muck soil showed higher denitrification capacity with nearly 4-times higher N_2O production at the end of the incubation (up to 26.7 mg N_2O-N kg^{-1}) than the brown sandy soil (only 7.18 mg N_2O-N kg^{-1}).

2. Better N_2O sorption, however, was exhibited by the brown sandy soil where one half of the introduced nitrous oxide was depleted during 6 days.

3. Denitrification corresponded to the consumption of introduced NO_3^-. About 45% of the added nitrate were depleted in the peaty-muck and 11% in the brown sandy soil, while 54% and 65% of depleted nitrate-N were denitrified to the nitrous oxide-form by organic and mineral soil, respectively.

4. Respiration activity was not influenced by the form of introduced N. The cumulative CO_2 content in the headspace at the end of the incubation was higher in the brown sandy than in the peaty-muck soil.

5. Soil redox potential was not influenced by form of N amendment.

6. The dehydrogenase activity in the organic soil was 27 times higher than in the sandy soil and was significantly higher with N_2O-treatment than with nitrate-treatment.

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