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Nitrous oxide and methane emissions from different soil suspensions: effect of soil redox status

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Abstract Four soil samples from fields of different land use [US (paddy field), China (paddy field) and Belgium (maize and wheat fields)] were incubated as soil suspension (soil:water ratio 1:4) to study the N_2O and CH_4 emission under different soil redox potential conditions. The results show that the N_2O emission was regulated within a narrow redox potential range of +120 to +250 mV, due to the balance of N_2O production and its further reduction to N_2. Methane emission occurred below a soil specific redox potential point, and the emission rates were inversely related to soil redox potentials. Both linear and exponential relationships between CH_4 emission and the soil redox potential were significant. By extrapolating the linear relationship of CH_4 emission against soil redox potential, the critical redox potentials for CH_4 production were estimated at about –170 (US paddy soil), –150 (Chinese paddy soil), –215 (Belgian maize soil), and –195 mV (Belgian wheat soil), respectively. In addition, the results indicate that a soil with a lower critical redox potential for CH_4 production had a higher CH_4 production potential. In this study, N_2O and CH_4 emissions were found to occur at a distinctly different soil redox potential condition. The range of soil redox potential values where both N_2O and CH_4 emissions were low was different for different soils, but it was situated between +120 and –170 mV. This is a wide redox potential range enabling field management practices to minimize both N_2O and CH_4 emissions from wetland ecosystems.

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Introduction

Nitrous oxide (N_2O) and methane (CH_4) are two important greenhouse gases emitted mainly from biotic sources (Duxbury et al. 1993). Most N_2O is formed from denitrification in oxygen deficient environments, although it can also be produced from nitrification in aerobic conditions (Williams et al. 1992; Rice and Rogers 1993). Methane is produced under low redox potential conditions by obligate anaerobes through either carbon dioxide (CO_2) reduction or transmethylation processes (Vogels et al. 1988). Methanogenesis and N_2O production are affected by many physical and biochemical factors, such as soil pH, redox potential, organic matter content, temperature, and soil moisture content. The content of soil oxidants (O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-} and CO_2) used as electron acceptors for organic matter degradation contributes significantly to these processes. The reduction of various oxidants in homogeneous soil suspensions occurs sequentially at corresponding soil redox potential values (Ponnamporuma 1972). Flooded paddy fields are considered as one of the most important sources of atmospheric CH_4 and N_2O, because of the coexistence of both aerobic and anaerobic environments (Reddy et al. 1989). Methane production rate is usually high in flooded soils with high organic carbon content. Such soils are net N_2O emitters as well if not constantly flooded, because of nitrate for denitrification being formed during temporary oxidizing conditions, enabling nitrification to take place (Byrnes et al. 1993). A reduced flooding duration increases the N_2O production, whereas continuously flooding maintains anaerobic conditions and hence enhances CH_4 production (Neue 1993). It is obvious that the factors affecting CH_4 and N_2O emission are complicated and internally related. A better understanding of this relationship is needed in order to be able to possibly mitigate the emission of these important

greenhouse gases through changes in agricultural practices.

The objectives of this laboratory study with four different soils were: (1) to investigate the soil redox potential range at which N_2O and CH_4 are produced, (2) to estimate the critical soil redox potential for initiation of CH_4 production, and (3) to study the relationship between CH_4 production and soil redox potential. The results should help to identify the redox potential range at which both gas emissions are at a minimum, and thereby to provide a basis for developing management strategies that will minimize the emissions of these greenhouse gases.

Materials and methods

Soils and incubation procedure

The four soils used in this study were from the United States, China and Belgium. One paddy soil was taken from the Rice Experiment Station, Crowley, Louisiana, USA. The second paddy soil was from the Shenyang Experimental Station of Ecology, Chinese Academy of Sciences, Liaoning, China. The other two soils were sampled from the wheat and maize field at the Experimental Farm of Ghent University, Belgium. All four soils were air-dried, sieved (1 mm), and thoroughly mixed before use. Some basic soil characteristics are listed in Table 1. We determined soil texture by the hydrometer method, soil organic matter by the dry combustion method (Nelson and Sommers 1982), total N by the Kjeldahl method (Bremner and Mulvaney 1982), and pH by a pH electrode with soil:water ratio of 1:4.

The soils were incubated in microcosms at room temperature (25°C) using a modification of the technique of Patrick et al. (1973). Four hundred grams of each soil was weighed into a 2.3-l Erlenmeyer flask, to which 1.6 l of deionized water was added. The soils were pre-incubated with no stirring and exposure to oxygen for 1 month in order to remove original nitrate, and to allow methanogens to grow. All four microcosms were then stirred with a magnetic stirrer and purged with air (160 ml min^{-1}) for 2 days to oxidize the soil, so that the soils could experience the whole range of aerobic to anaerobic conditions during the incubation. The incubation was started when 4 g dextrose (4.0 mg C g^{-1} soil) was added as an energy source for the microorganisms, and potassium nitrate (KNO_3) was added to provide 50 µg N g^{-1} soil to each soil suspension. The redox potential of each soil suspensions was monitored daily by two Pt electrodes and a calomel reference electrode that were connected to a millivolt meter (Cole-Parmer, Illinois). Each flask was capped with a rubber stopper, in which a septum was installed for gas sampling. A gas inlet and outlet was installed so that the accumulated gases in the headspace could be purged if needed. The microcosms were sealed, and the soil suspensions were continuously stirred by a magnetic stirrer during the incubation without O_2 supply.

Table 1 Main characteristics of the soils used

Sample soil	Texture	Organic matter (g kg^{-1})	Total N (g kg^{-1})	pH
US paddy soil	Silt loam	15.7	0.80	5.7
Chinese paddy soil	Clay loam	16.2	0.76	6.7
Belgian maize soil	Loamy sand	35.3	1.60	6.0
Belgian wheat soil	Silt loam	21.2	1.10	7.7

N_2O and CH_4 measurement

During the incubation period the microcosms were purged with pure N_2 1 day prior to each sampling. Twenty four hours after N_2 purging the accumulated headspace gas was withdrawn using a syringe, and duplicate samples were transferred into an evacuated vial (10 ml Vacutainer, Becton Dickinson, New Jersey). The experiment was repeated twice in order to verify the results and to collect enough data, especially for N_2O emission because the soil redox potential dropped quickly at the beginning of the incubation (from +400 to 0 mV in 4 days). Nitrous oxide and CH_4 were analyzed with a Tremetrics 9001 gas chromatograph using an electron capture detector (ECD) for N_2O and a flame ionization detector (FID) for CH_4 . The emission rates of N_2O and CH_4 were calculated as the amount of gas accumulation divided by the accumulation time and the amount of soil used. Redox potential values and N_2O and CH_4 emission rates were reported as a mean of two replicate measurements. The significance of the relationship between redox potentials and CH_4 emissions was determined statistically by the Student *t*-test.

Results and discussion

A well-oxidized soil has a redox potential range up to +400 to +700 mV. Flooded soils may reach redox potential values of lower than –300 mV due to the absence of O_2 and the activity of facultative and obligate anaerobic bacteria (Patrick and Mahapatra 1968). Here, the rate of change in the soil redox potential was soil specific. It depended on the original content of soil oxidants and reductants, as well as on the difference in population and types of soil microbial communities. The soil redox potential values measured in this study were generally in the range of +400 to –300 mV. For the two paddy soil suspensions, about 1 month was required to undergo such a redox potential change, while about 2 months were required for the two upland soil suspensions. The two upland soils required a longer time to be reduced because, due to the original aerobic environment in fields, it is likely they had more oxidized components (such as iron oxides) than flooded paddy soils. Some oxidized compounds in paddy soils that have undergone cycles of flooding and draining tend to be converted to their mobile counterparts (i.e. Fe^{3+} to Fe^{2+} and SO_4^{2-} to H_2S) that move out of the field (either to the atmosphere or to the underground water body) following flooding (Ponnamperuma 1972). The difference in microbial community between upland and paddy soils may also account for the different time required to complete the above redox potential range. Inubushi et al. (1997) observed a delay of CH_4 initiation in an upland soil compared with a paddy soil, possibly due to the slow development of reducing conditions in the upland soil. At the end of the experiment, the pH values of the four soil suspensions reached a narrow range with 6.7 for the US paddy soil, 7.2 for the Chinese paddy soil, 6.5 for the Belgian maize soil, and 6.9 for the Belgian wheat soil, respectively.

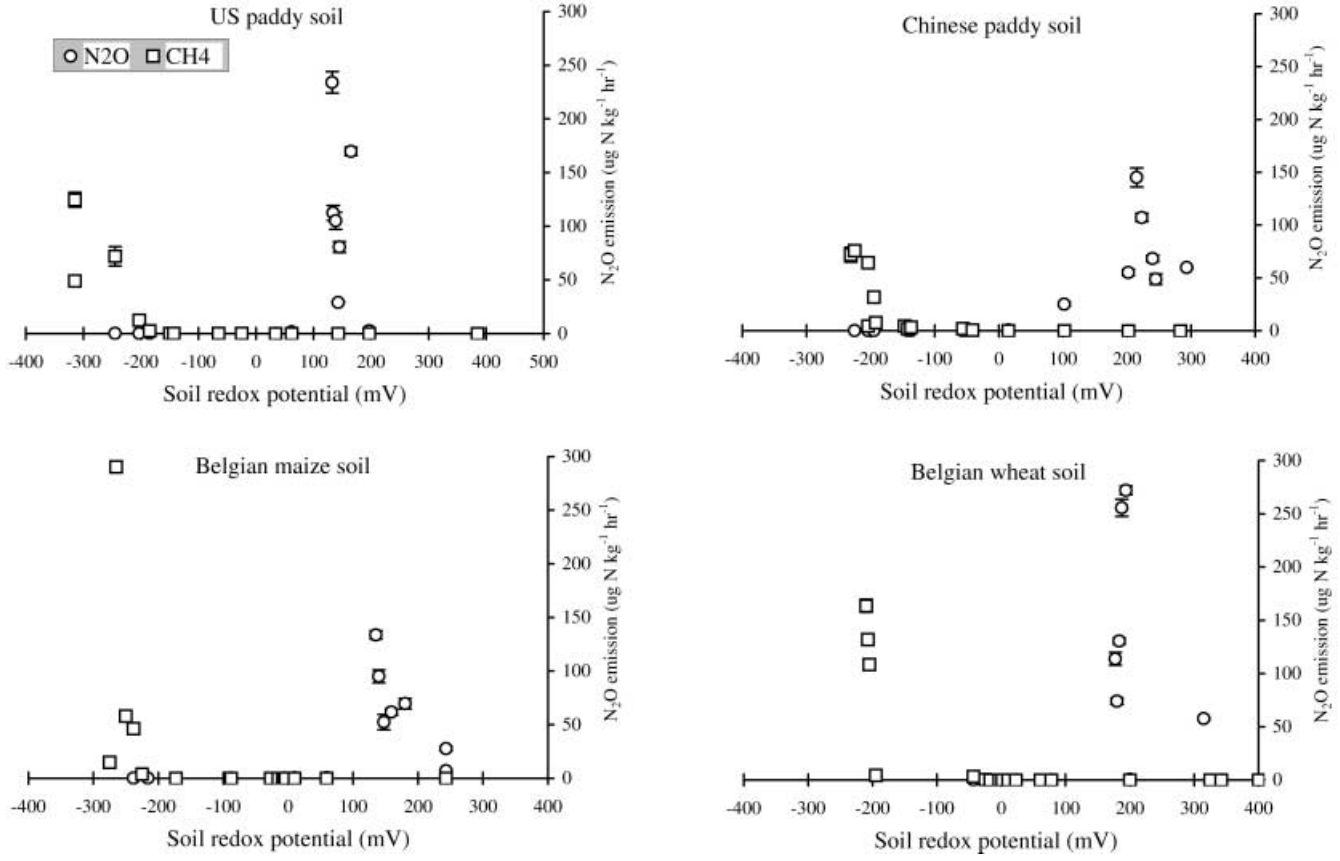

Fig. 1 Nitrous oxide (N_2O) and methane (CH_4) emissions at different soil redox potentials. *Points* represent the means ± standard deviation of two replicate gas samplings

N_2O emission

Denitrification was considered to be the major source of N_2O production in this study as anaerobic conditions prevailed. The critical redox potential for denitrification found in a previous study using US paddy soil was approximately +350 mV (Patrick and Jugsujinda 1992). Nitrous oxide emissions from the four soils over a range of redox potential conditions are shown in Fig. 1. For all soils there was a narrow range of redox potential where N_2O accumulated significantly. The results show a significant N_2O accumulation in the soil redox potential range between +120 and +250 mV, while the maximum emission rate was between 140 and 280 µg N kg^{-1} h^{-1}. Little N_2O emission occurred at redox potential values higher than +250 mV or lower than +120 mV. The results also indicate the influence of different soil on the N_2O emission. The maximum N_2O emission varied twofold for the four soils, with the maize field soil showing 134 µg N kg^{-1} h^{-1} at a redox potential of +135 mV, the wheat field soil 272 µg N kg^{-1} h^{-1} at +194 mV, the US paddy soil 234 µg N kg^{-1} h^{-1} at +133 mV, and the Chinese paddy soil 145 µg N kg^{-1} h^{-1} at +215 mV. It is important to understand that N_2O emission is the balance of N_2O formation and further reduction, and both greatly depend on the origin of the soil, nitrate availability, pH and redox potential status. There was no clear relationship between the maximum N_2O accumulation and soil redox status. It should also be pointed out that we might miss the actual maximum N_2O accumulation in our measurements because of the rapid change in soil redox potential at the beginning of the incubation.

CH_4 emission

Methane emission from the four soils under different redox potential conditions is also shown in Fig. 1. Methane production occurred after extended anaerobic incubation in all four soils. The emission of CH_4 from soils is the net result of CH_4 production and oxidation. The CH_4 oxidation activity has been found mainly under aerobic conditions. However, there is evidence that CH_4 can be oxidized under anaerobic conditions, but the oxidation rate is comparatively low (Panganiban et al. 1979; Reeburgh 1980; Miura et al. 1992). Thus, the CH_4 emissions from the microcosms could be regarded as soil CH_4 production potentials. Methane production in the two upland soils, 19.4 mg C kg^{-1} h^{-1} at –265 mV in the maize soil and 10.9 mg C kg^{-1} h^{-1} at –210 mV in the wheat soil, was higher than in the two paddy soils, 4.15 mg C kg^{-1} h^{-1} (at –315 mV) in the US soil and 2.53 mg C kg^{-1} h^{-1} (at –225 mV) in the Chinese soil. A significant linear relationship was found between the

Table 2 Relationship between redox potential and CH_4 production and estimation of the critical redox potential for CH_4 production [E_h Soil redox potential (mV), C_1 CH_4 production (mg C kg^{-1} h^{-1}), C_2 Ln C_1, n number of samples]

Soil type	Exponential regression		Linear regression		
	Equation	R^2	Equation	R^2	Critical E_h
US paddy soil	E_h=–23.4×C_2-246.2	0.85 (n=5)**	E_h=–33.8×C_1-171.8	0.97***	–170
Chinese paddy soil	E_h=–23.2×C_2-201.5	0.90 (n=7)***	E_h=–30.4×C_1-149.3	0.90***	–150
Belgian maize soil	E_h=–11.4×C_2-231.9	0.68 (n=5)***	E_h=–3.0×C_1-214.3	0.68*	–215
Belgian wheat soil	E_h=–3.7×C_2-199.4	0.95 (n=4)**	E_h=–6.4×C_1-194.6	0.95**	–195

* 90% confidence level; ** 95% confidence level; *** 99% confidence level

natural logarithm of CH_4 emissions and the soil redox potentials in all four soil suspensions (Table 2). This corresponds to the result obtained previously on the same US paddy soil (Wang et al. 1993) and indicates that CH_4 production in the soils was of biological origin, and that the production activity increased exponentially when the soil redox potential dropped below a critical point.

Significant CH_4 production occurs under strictly anaerobic conditions. The critical soil redox potential for CH_4 production from the same US paddy soil has been reported to be –150 to –160 mV (Wang et al. 1993). The critical redox potential reported depended on both the soil and the method used to estimate the critical point at which CH_4 production commenced. In our study, the critical redox potential for CH_4 production was considered as a certain soil redox potential point below which the CH_4 emission rate reached a positive value. The critical redox potential is technically impossible to determine by direct examination of the logarithm plots of the emission values against the redox potential values. Therefore, we estimated this critical point by linear regression of the CH_4 emissions against the soil redox potential and extrapolating the linear curve to the point where the CH_4 emission was zero. The linear relationship between CH_4 production and soil redox potential was also found to be significant in these four soils, suggesting that the estimation of the critical redox potential for CH_4 production by this method is acceptable. The results show that the critical soil redox potential for CH_4 production to occur was in the range of –150 to –210 mV (Table 2).

The slope in the linear regression between the soil redox potential values and the CH_4 productions represents the increase of the CH_4 production rate with decreasing soil redox potential. The lower the critical soil redox potential for CH_4 production, the greater the change of CH_4 production with soil redox potential. A significant exponential relationship between the critical redox potentials for CH_4 production and the maximum CH_4 production rates recorded was also found in the four soils (Fig. 2). It suggested that a soil with a lower critical redox potential for CH_4 production had a higher potential for CH_4 production. The exponential relationship between soil redox potential and CH_4 production likely exists not only in a single soil, but also among different soils. We concluded that it is essential to keep a relatively higher soil redox potential in any kind of soil whenever CH_4 production control is required.

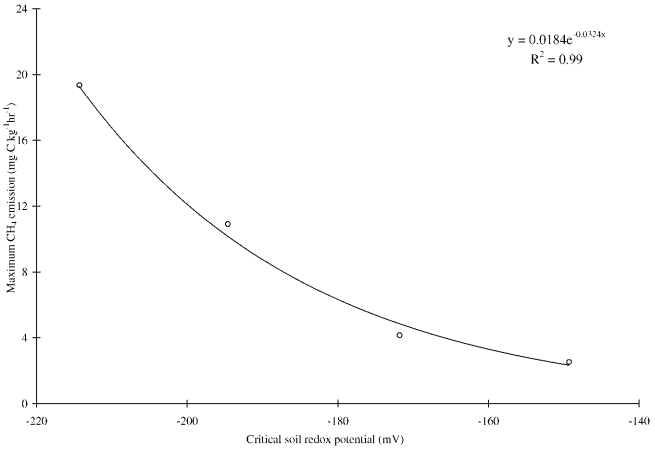

Fig. 2 Relationship between the critical redox potentials for methane (CH_4) production and the maximum CH_4 emission in different soils (significant at 99% level)

The estimation of the critical redox potentials for CH_4 production in this study was based on vigorous CH_4 productions at different redox status. Due to the inhibition of methanogenesis (both methanogen population and activities) by other oxidants, significant CH_4 production can only occur when such inhibition is taken away, as indicated by a critical low point of redox potential (Cicerone and Oremland 1988). Limited CH_4 production was observed during the initial phase of anoxia in rice soil slurries despite a high redox potential and the presence of oxidants (Roy et al. 1997). The presence of methanogens and the evolution of H_2 at the beginning of soil submergence make early initiation of methanogenesis thermodynamically possible, but it is only theoretically important and it does not provide information on the quantity of CH_4 produced. When CH_4 concentrations are plotted on a linear scale, CH_4 production mostly occurred after the complete reduction of SO_4^{2-} by sulfate-reducing bacteria (Yao and Conrad 1999).

The effect of soil redox status on CH_4 and N_2O emissions from the US paddy soil was previously studied under controlled redox range from +500 to –250 mV (Masscheleyn et al. 1993). However, carbon and nitrate were added at each redox level, and the redox range where both and CH_4 emissions were low was not clearly identified because nitrate was actually not present when

soil redox was maintained at a value lower than +100 mV. We used a different experimental approach in which the redox potential in the soil suspension was measured but not controlled. Nitrous oxide and CH_4 emissions from the soil suspensions were quantified by frequent sampling during the natural decrease of soil redox potential by microbial aerobic and anaerobic respiration. This is more similar to the actual rice field where soils are continuously flooded.

Redox potential range for minimum N_2O and CH_4 emission

Nitrous oxide and CH_4 emissions were found to occur at different soil redox potential conditions. There was a distinct soil redox potential range where neither N_2O nor CH_4 emissions were significant (Fig. 1). This soil redox potential range was slightly different among the four tested soils, because the critical redox potentials for either CH_4 production or N_2O accumulation were different. The range of minimum accumulation of both CH_4 and N_2O was generally situated between +120 and –170 mV. Nitrous oxide reduction was stronger than its production in such a redox potential range, while no significant CH_4 production occurred. These results are important for field practices with regard to greenhouse gases management. On the one hand, it indicates the risk of stimulating N_2O production in trying to diminish CH_4 production by increasing the soil redox potential (e.g. by soil drainage or withholding organic matter from the soil). It also demonstrates the difficulty of controlling N_2O emission by keeping the soil reduced enough only to favor N_2 production during the denitrification process, but not reduced enough to produce CH_4. On the other hand, such a wide redox potential range where neither of these two gases is accumulated should make it possible to minimize both N_2O and CH_4 emissions from wetland ecosystems by carefully regulating the water supply and organic matter amendments. It will be difficult to keep the soil profile in such a favorable redox range during the whole rice growing season. However, it is possible to significantly reduce the CH_4 emission by carefully managing irrigation and drainage practices without inducing significant N_2O emission, especially during periods of vigorous CH_4 flux. Organic matter, as an electron donor, is an important factor to regulate the N_2O/N_2 ratio in denitrification, because it will favor N_2O reduction to N_2 by releasing the electron competition between N_2O reduction and nitrate reduction. When electrons are abundant (i.e. when the soil is more reduced), denitrification tends to go to completion with N_2 as the end product (Murakami et al. 1987).

Implications of this study

Rice paddy fields are a favorable environment for both N_2O production and methanogenesis because of their changing redox potential status. An inverse relationship of N_2O and CH_4 emissions has been found in a long-term Chinese paddy field study (Chen et al. 1997). Water and nutrient management, effect of rice cultivars and other agronomic practices have been tested to mitigate CH_4 production and emission from paddy fields, and among them water management is the most effective (Yagi et al. 1990; Sass et al. 1992). Possibilities for reducing CH_4 emissions were evaluated in the National Inventories of the CH_4 and N_2O Workshop (Khalil 1993). One of the principles that must be followed in developing a practice to reduce CH_4 emissions from flooded rice soils is that the mitigation practice should not increase the emissions of other greenhouse gases, particularly N_2O. The results of our laboratory experiment provide further insight into the effect of soil redox potential on N_2O and CH_4 production and emission. It points to the importance of N_2O reduction, through which the N_2O emission is regulated in a narrow soil redox potential range. It also shows the risk for CH_4 production when the soil redox potential status drops to a lower level. In this study, we found a wide soil redox potential range where both N_2O and CH_4 emissions were low, which provides an opportunity to minimize the emissions of these two important greenhouse gases in the field.

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