B51 Study on anthropogenic sources and sinks of greenhouse gases

(2) Study on sources and sinks of atmospheric CH_4 and N_2O

<4> Development of mitigation options of nitrogen oxides emission from agro-ecosystems in Asia

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Abstract

Nitrous oxide (N_2O) and nitric oxide (NO) emissions from soil are affected by many factors. Nitrogen source supply to the soil, especially N fertilizer input, soil moisture and soil type appear to be the most important factors to control the N_2O and NO emission rate. In this study, incubation experiments were conducted to determine the effect of the urea form and the soil moisture on N_2O and NO emissions in Japanese Andosols. The results showed that there were no significant differences in the total amount of N_2O and NO emissions over 77 days between non-coated urea treatment and coated urea treatment except for NO emission at 40% wfps (water filled pore space) where it was reduced by 23% when coated urea was applied. But as compared to easily decomposable urea, coated urea did reduce N_2O and NO emissions in the earlier period shortly after fertilization. The results also indicated that soil moisture had a much more significant effect on N_2O and NO emissions than the form of urea, especially for N_2O. From 40% to 100% wfps, there were a positive relationship between N_2O emission and soil water content and a negative relationship for NO. The flux ratio of NO/N_2O was governed by soil moisture with a greatest value at the lowest wfps treatments for each fertilizer treatment. The soil moisture condition could be the most important controlling factor for N_2O and NO emissions when a rich N supply existed in soil.

Keywords: Nitrous oxide flux, nitric oxide flux, soil moisture (wfps), coated urea

Introduction

Nitrous oxide (N_2O) and nitric oxide (NO) are the important constituents of the global nitrogen cycle. Increase in the atmospheric concentration of N_2O contributes not only to global warming but also directly to destruction of stratospheric ozone layer.

Atmospheric NO contributes to acid rain and photochemical smog in the lower atmosphere. (IPCC, 1990; Cicerone, 1989; National Research Council, 1977). Twenty-two percent of the total N_2O emission comes from agricultural lands, especially fertilized soils (Bouwman, 1994). Agricultural soils that receive N fertilizers are also the large source of NO emission, especially in areas where the moisture content remains below field capacity when N fertilizer is still present in the soil (Davidson, 1996). These gaseous N emissions are also a large amount of economic loss in addition to their environmental impact.

The consumption of N fertilizer in the world is increasing at a rate of 6-7% per annum during the 1990s and expected to keep this rate in 21st century to increase the food production to meet the growing demand of world population (Minami, 1997). Urea is the most popular N fertilizer in the world, accounting to about 50% of total amount of N fertilizer application. In order to both reduce N_2O and NO emission and improve the efficiency of N utilization, alternating urea fertilization practice, mainly including the use of slow-released urea, such as coated urea, and of nitrification inhibitors, is being taken into consideration by researchers. Nitrification and denitrification are the most important biological processes in the production of N_2O and NO in soil (Firestone and Davidson, 1989). Following the application of urea to soil, NH_4^+ released from the hydrolysis of urea is oxidized to NO_2^- and NO_3^- by chemoautotrophic nitrifying bacteria, and during this nitrification several possible biochemical pathways exist for N_2O and NO production (Firestone and Davidson, 1989). Denitrifying bacteria can use the nitrogen oxides from nitrification process for terminal electron acceptors in respiration while available O_2 is limited, and hence, production and consumption of N_2O and NO occur. Thus, applying coated urea instead of easily decomposable urea to control the mineral N supply is expected to be the useful way for the reduction of N_2O and NO production. However, the observations from various regions were contradictory (Tsuruta, 1995; Frank, 1996; Chen, 1997). Whether or not coated urea could be used as an effective technique for reduction of N_2O and NO emissions from fertilized soils is still uncertain. We have felt that the differences in soil physical-chemical properties, texture and environmental conditions, especially water regime, might be the important causes for this uncertainty.

The objectives of this laboratory study are two-fold: (1) to determine the influence of varying the form of urea on N_2O and NO emission in Japanese andosols and Chinese brown soil under different soil moisture regimes; (2) to examine the relationship between wfps of soil and N_2O and NO emission.

Materials and methods

Soils

The soils used in this study were an andosol in an upland field of National Institute of Agro-Environmental Sciences in Tsukuba, Japan and a meadow brown soil from Shenyang Experimental Station of Ecology, Chinese Academy of Sciences in Shenyang, China. Bulk samples from the surface 15cm of the two soils were passed through a 2mm seive, air-dried, and stored at room temperature until the start of incubation experiment. The main soil properties are shown in table 1.

Table 1. Soil properties

Soil type	Total C($g \cdot kg^{-1}$)	Total N($g \cdot kg^{-1}$)	pH	Bulk density
Andosol	46	3.8	5.6	0.7
Brown soil	16.2	0.8	6.7	1.05

Fertilizers

The easily decomposable urea (U) and POCF Type 30 coated urea (CU) used in the commercial base from CHISSO-ASAHI Fertilizer Co., Ltd., Japan were tested in this experiment. The Type 30 coated urea means that 80% of the applied nitrogen will be released at 20°C (68°F) over 30 days. Each nitrogen fertilizer treatment, also including an unfertilized control (CK), was studied at 3 soil moisture conditions corresponding to soil wfps values of 40%, 70% and 100%.

Incubation experiment

One hundred grams of the air-dried soils were weighed into 350ml conical flasks. Then, the appropriate fertilizer corresponding to the treatments was added to get a final N concentration of 200ppm (dry soil base) and mixed with soil. Preliminary experiment indicated that the sieved soils had a bulk density of 0.7g cm^{-3}. Assuming a soil particle density of 2.65g cm^{-3}, distilled water was added to bring the soil moisture conditions to the appropriate wfps values shown above. The flasks were then covered with aluminium foils with needle holes to maintain an aerobic atmosphere in the flask and incubated at 25°C. During the incubation, the soil moisture contents were maintained unchanged by weighing method. Thirty-three replicates for each treatment were adopted. Four of it was used for N_2O and NO measurement. The rest was used for NO_3^--N and NH_4^+-N measurement.

One day after the application of fertilizer the air of the headspace were sampled and measured for N_2O and NO. And then, after every 3 or 4 days these two gases were analyzed. For NO measurement developed by Kim (1997) and McTaggart (1997), the flasks were allowed to aerate for around 30 minutes prior to being capped with butyl rubber stopper. The first 5ml sample was collected by a plastic syringe immediately after capping and analyzed immediately. The two more samples were collected and injected at every 3 minutes' interval. After the third sampling, the flask was re-opened and waited for a while to allow the air to establish equilibrium inside the flask and then re-capped and incubated. After 5 hours closure 1ml headspace gas was sampled by airtight syringe and injected for N_2O measurement. NO_3^--N and NH_4^+-N analysis in soil samples were carried out on 1, 8, 15, 22, 29, 36, 43, 50, 57, 64, 71 and 78 days of incubation, respectively. Every sampling day, three replicates were selected randomly and extracted with 250ml 10% KCl solution for 30 minutes and then filtered and stored in the deep freezer until the analysis.

Sample analysis

Nitrous oxide concentrations were analyzed by a Shimadzu 8A gas chromatograph equipped with an electron capture detector at 340°C, a main separating column packed with Porapak Q and a carrier gas of 5% methane in Argon. Standard gas of 300ppb and 9.8ppm (provided by Japanese Oxygen Gas Co.) were used for calibration of N_2O analysis. NO analyses were carried out on a Chemiluminescence NOx analyzer manufactured by Thermo Environmental Instruments Inc. USA (model 42C). Standard gas of 0.097ppm and 0.41ppm (provided by Japanese Oxygen Gas Co.) were used for calibration during analysis. The N_2O and NO emission rates were calculated as the average increase in concentration over the closure period and expressed as μg N_2O-N•kg $soil^{-1}$•day^{-1} and μg NO-N•kg $soil^{-1}$•day^{-1}, respectively. NH_4^+ and NO_3^- will be measured by continuous flow colorimetric analysis using TRAACS 2000 Random Access Sampler.

Results

The whole experiment was divided into two parts, Japanese andosols and Chinese brown soil. Here we presented some results from Japanese andosols, with an experiment studying Chinese brown soil still ongoing.

Nitrous oxide emission as affected by fertilizer form and soil moisture

The variations in N_2O emission rate with time following N fertilizer application were examined under different soil moisture conditions (Fig.s 1a, b, and c). In all the fertilizer treatments, including the CK, at 100% wfps there was a very large N_2O peak on the first day after incubation, and the amount of the initial peak from CK was almost equal to that from U and CU. This means these emissions might have mainly come from the mineral nitrogen, especially NO_3^-, originally existing in the soil at start of the experiment. This also implied significant N_2O production could occur immediately after wetting dry soil to 100% wfps.

Emissions from CK at all moisture contents remained very low ($<1.04\pm0.23\mu g$ N_2O-N•kg $soil^{-1}$•day^{-1}) with the exception of the initial peak at 100% wfps and almost undetectable after 1-2 weeks (Fig. 1a). U treatments at 70% wfps and 100% wfps had a fast emission 4 days after fertilization. Then, this fast emission at 70% wfps lasted around one week with a maximum rate of $24.50\pm9.99\mu g$ N_2O-N•kg $soil^{-1}$•day^{-1} before declining rapidly, and it approached the unfertilized control level after day 14. The emission at 100% wfps increased continuously reaching a maximum of $118.10\pm6.26\mu g$ N_2O-N•kg $soil^{-1}$•day^{-1} on day 7, not counting the initial peak, and then decreased but still maintained a relatively large and stable rate until the end of incubation. The N_2O emission from U treatment at 40% wfps remained low throughout ($<1.57\pm0.33\mu g$ N_2O-N•kg $soil^{-1}$•day^{-1}). As compared to U, all CU treatments had a similar dynamics of emission rate under the same soil moisture condition (Fig 1c) but the occurrence of emission peak was postponed and the significant emission lasted for a longer time before declining to near background levels. The maximum emission rates at 70% and 100% wfps occurring on 11days of incubation were $25.39\pm9.28\mu g$ N_2O-N•kg $soil^{-1}$•day^{-1} and $111.05\pm78.13\mu g$ N_2O-N•kg $soil^{-1}$•day^{-1}, respectively. The emission at 40% wfps also kept a lower level during the whole incubation with a maximum rate of $1.32\pm0.39\mu g$ N_2O-N•kg $soil^{-1}$•day^{-1}.

Nitric oxides emission as affected by fertilizer form and soil moisture

The changes in NO emission rate with time following N fertilizer application under different soil moisture conditions were shown in figures 2a, b, and c. In all treatments at 100% wfps there was almost no NO emission during the whole incubation. In all treatments at 40% wfps there was a similar initial rapid increase in NO emission on day 1. This suggested some emission might have derived from the mineral nitrogen originally existing in the soil. Emissions from CK at 40% wfps and 70% wfps occurred shortly after wetting the dry soil with a maximum of 36.90 ± 3.82 and $13.51\pm2.59\mu g$ NO-N•kg $soil^{-1}$•day^{-1} respectively, and the emission rate then gradually decreased to near background level during the following 10 days. Significant emissions from U at 70% wfps occurred within the first two weeks with the maximum rate reaching $140.76\pm18.40\mu g$ NO-N•kg $soil^{-1}$•day^{-1} on day 11. In U treatment at 40% wfps, emission occurred steadily within a range of 29.92 ± 3.66~64.80 ± 18.84 μg NO-N•kg $soil^{-1}$•day^{-1} within the first 60 days, and then declined rapidly. Similarly to N_2O emission, the pattern of NO emission from CU treatments was also similar to

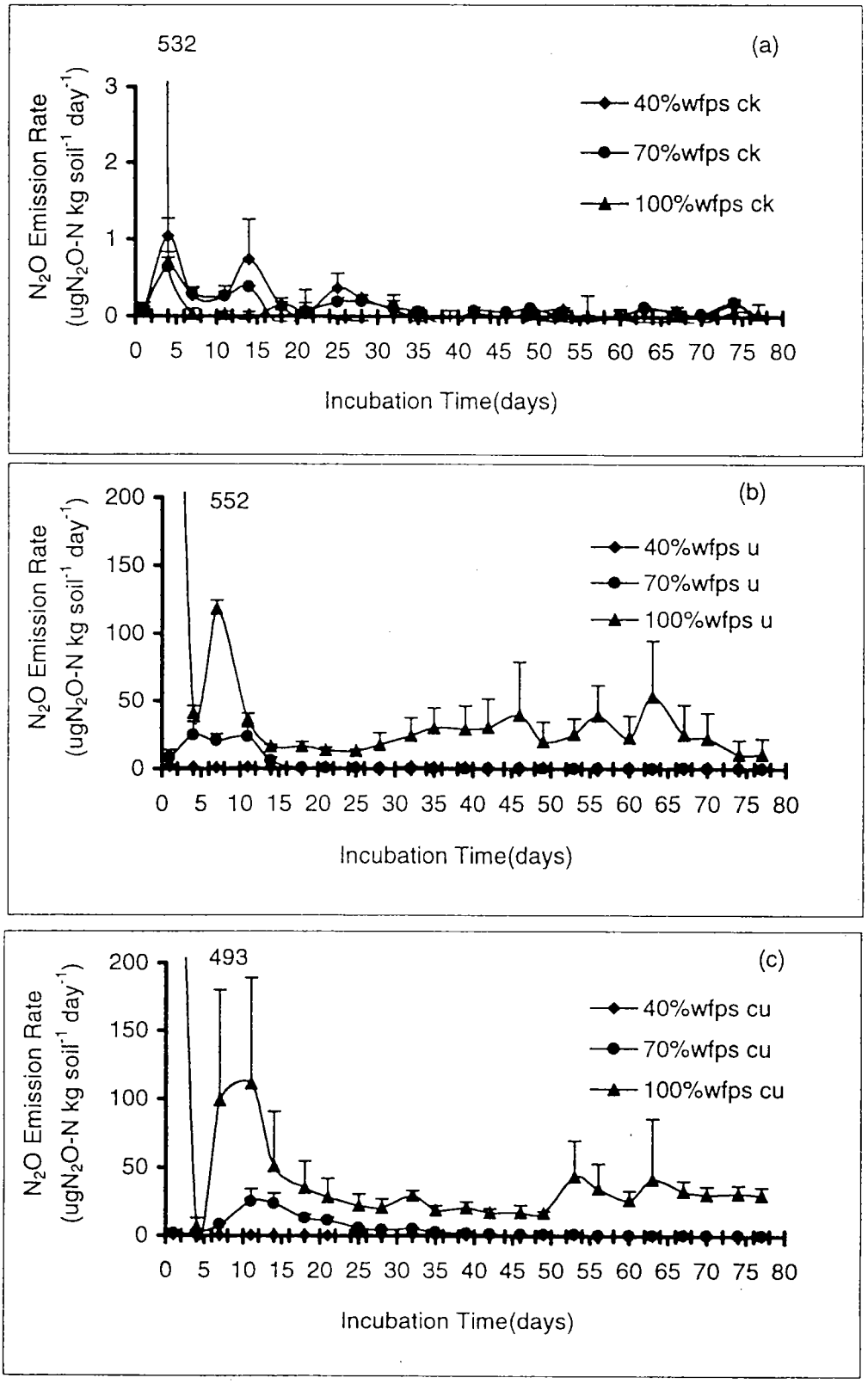


Fig. 1 Variations in N_2O emissions with time following N fertilizer application to Andosol under different soil moisture conditions

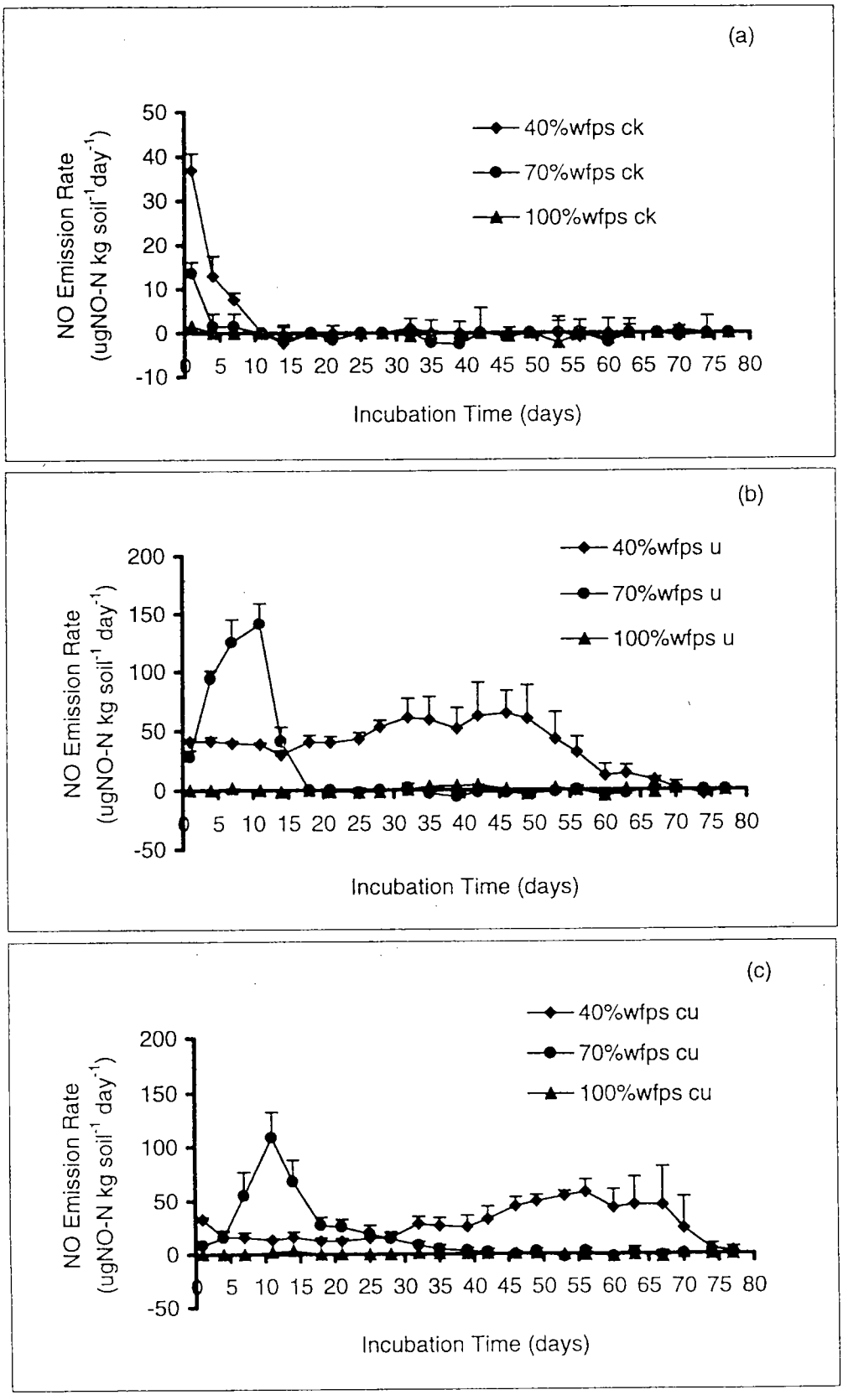


Fig. 2 Variations in NO emissions with time following N fertilizer application to Andosol under different soil moisture conditions

that from U treatments at the same wfps value, and for 70% wfps the occurrence of a fast emission was postponed and the significant emission lasted for a much longer time. For CU at 40% wfps, the significant emission rate varied during 12.65±2.76 to 58.10±11.52 μg NO-N•kg soil^{-1}•day^{-1}, but much lower than in the U treatment within the first 30 days.

Integrated N_2O and NO emissions with time during 77 days incubation affected by fertilizer form and soil moisture

Figures 3, 4 showed the integration of N_2O and NO emissions as a function of time following the application of fertilizer to andosols in Tsukuba, Japan under different soil moisture conditions. In all the CK treatments, the integrated emissions of both N_2O and NO only increased very slowly within the first several days, indicating a minor emission of N_2O and NO from soil organic N source. It is obvious that the application of chemical N fertilizer is the main source of N_2O and NO emitted from agricultural soils.

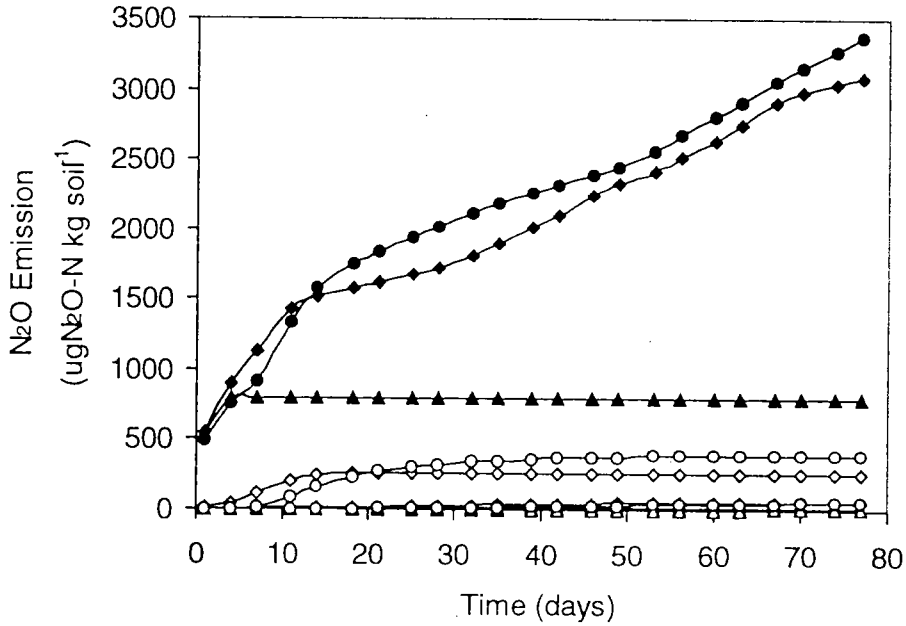
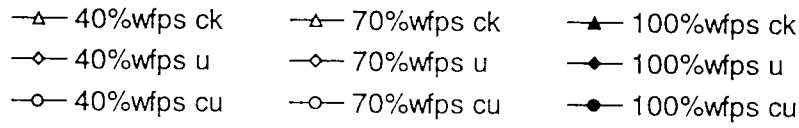


Fig.3 Integrated N_2O emissions over time during 77 days incubation



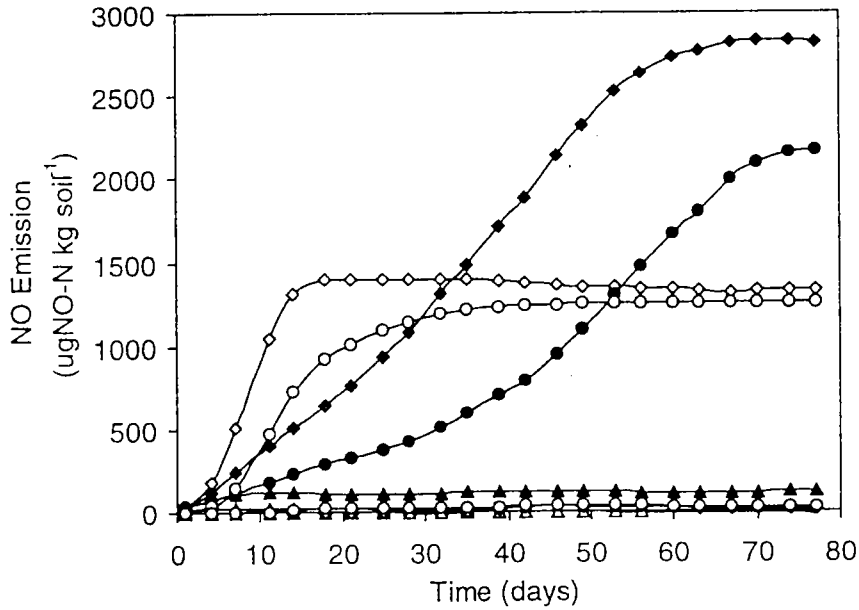


Fig. 4 Integrated NO emissions over time during 77 days incubation

—▲— 40%wfps ck —△— 70%wfps ck —△— 100%wfps ck
—◆— 40%wfps u —◇— 70%wfps u —◇— 100%wfps u
—●— 40%wfps cu —○— 70%wfps cu —○— 100%wfps cu

The accumulation of N_2O in the treatments of U and CU at 70% wfps increased with time until around 2 weeks and 5 weeks respectively, and more N_2O was accumulated in the U than in the CU during the first 3 weeks. The integrated N_2O emission from U and CU at 100% wfps were much higher than at 70%wfps throughout, with a larger accumulation in U than in CU within the first 2 weeks, while those from 40% wfps were quite smaller, and keeping lower in U than in CU. For NO, as mentioned previously, there was no emission at 100% wfps observed. At 40% and 70% wfps cumulative NO emissions maintained greater in U than in CU during the whole incubation, although increase in accumulations stopped earlier in U than in CU. More NO was emitted at 70% wfps than at 40% wfps in the earlier incubation. The cumulative N_2O and NO emissions during 77 days were shown in Figure 5.

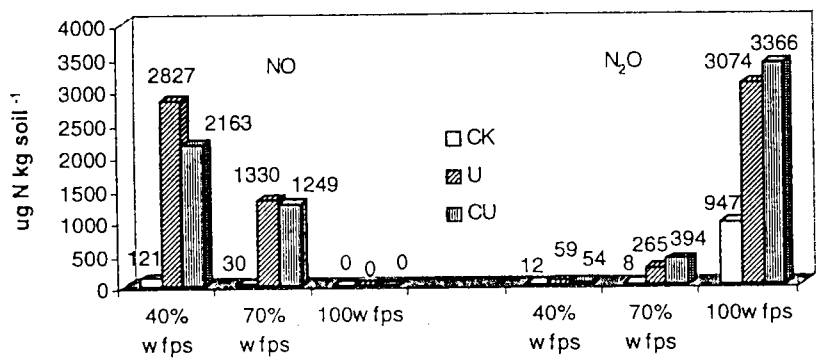


Fig. 5 Cumulative NO and N_2O emissions over 77 days following N fertilizer application under different soil moisture conditions

The total losses of N as N_2O and NO of U and CU under different soil moisture conditions during the whole incubation period were shown in Table 2.

Table 2 Total losses of N as N_2O and NO of fertilizer during a 77-day period of incubation

Treatments	U			CU		
	40%wfps	70%wfps	100wfps	40%wfps	70%wfps	100wfps
% of applied N (as N_2O)	0.02	0.13	1.20	0.02	0.19	1.21
% of applied N (as NO)	1.35	0.65	0	1.02	0.61	0

Effect of fertilizer form and soil moisture on NO/N_2O ratio

The ratio of NO/N_2O was mainly controlled by the soil moisture condition instead of the form of urea (Fig. 6). The NO/N_2O ratio for both U and CU treatments significantly increased with a decrease in soil moisture content, with an average of 48.39±17.27, 5.38±1.53, and 0.00 for U and 42.60±16.89, 3.46±2.13 and 0.00 for CU at 40%, 70% and 100% wfps, respectively.

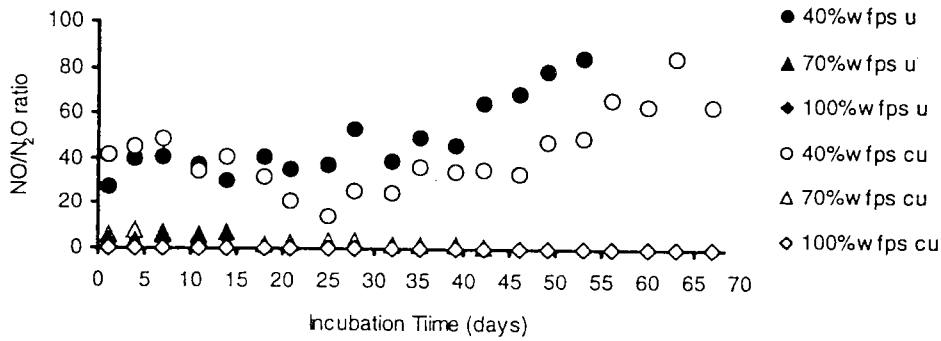


Fig. 6 The flux ratio of NO/N_2O effected by fertilizer form and soil moisture

Discussions

The results showed that there were no significant differences in the total amount of N_2O and NO emissions over 77 days between U and CU except for NO emission at 40 % wfps where it was reduced by 23% when coated urea was applied. But in comparison with easily decomposable urea, coated urea did reduce the emission of N_2O and NO in the earlier period shortly after fertilizer application because of the controlled release of NH_4^+ from coated urea. In the actual field, the uptake of N by crops might mitigate the N_2O and NO emissions in later period, but the similar results have also been observed in some field experiments (Tsuruta, 1995, 1998). Probably due to the rapid nature of the nitrification, much of the release-controlled NH_4^+-N could still have been nitrified before being taken up by crops in broadcasting application.

Our results also indicated that soil moisture had a much more significant effect on N_2O and NO emissions than the form of urea, especially for N_2O, implying that the patterns of N_2O and NO emission would be mainly controlled by soil moisture when a rich N supply maintained in soil. N_2O Emission rates from both U and CU treatments increased with the increase of soil moisture from 40% wfps to 100% wfps; while an inverse relationship between soil water content and NO emission was observed. The ratio of NO/N_2O was governed by soil moisture with a greatest value at the lowest wfps treatments for each fertilizer treatment. Many studies have shown that soil moisture is an important factor on the dynamics of N_2O emission. Lin and Doran

(1984) found that there was a positive linear relationship between wfps and aerobic microbial activity including nitrificatioon from 30% to 70%, but at higher moisture contents aerobic activity was reduced. The highest N_2O emission in this study occurred at 100% wfps, indicating that the main source of N_2O emission could be denitrification when soil moisture is high, although it does be nitrification at lower soil moisture. The highest NO emission was found at 40% wfps while no NO emission at 100% wfps, therefore, NO emission might have mostly been derived from nitrification although it is believed that NO could be produced also via denitrification (Firestone and Davidson, 1989).

The overall NO emission was significantly greater than N_2O in both the U and the CU from 40% to 70% wfps in a range of which the moisture contents vary in most upland soils. Tsuruta (1995) reported that the total amount of NO emission was 7-19 times greater than N_2O in a field experiment.

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