

Variations of NO Concentration Released from Fertilized Japanese Upland Soil Under Different Soil Moisture Conditions

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Abstract

Oxides of nitrogen play important roles in atmospheric chemistry. Soil has been recognized as a major natural source of NO, and its emission depends on soil parameters such as soil nitrogen availability, soil moisture and temperature. It is necessary to understand effects of these controlling parameters on soil NO emission. In order to understand soil moisture effects on NO emission, variations of NO concentration and existence of its equilibrium concentration were observed from ammonium fertilized Japanese upland soil prepared for different soil moisture conditions. The closed chamber technique was employed for this study. The significant increases in NO with soil moisture were found. Maximum was occurred at sample ID4 (55% of water-filled pore space (WFPS)), but it decreased as soil moisture increased. No significant NO concentration was emitted from soil sample without fertilizer, but there was significant NO in fertilized soil samples. The magnitudes of NO from soil increased with time and reached at steady state within ten minutes approximately. These results suggest that nitrogen input from fertilizer takes charge in the first step of sharp increase in NO emission, and then soil moisture becomes important factor to control NO emission from the soils. NO concentrations from soil were compared to those one-day after the experiment. Results from the comparison analysis suggest that the soil NO flux might have been stimulated by soil disturbances like mixing, and this is much more effective in dry soils rather than in wet soils. It was found that much less NO came out from soils after a day; suggesting that most of NO was released from the soils within a day after fertilizer application during our experiment. The length of NO releasing time span may depend on the amounts of fertilizer applied, soil moisture condition, and other soil physical parameters.

Key words : soil NO emission, fertilized soil nitrogen, soil moisture, closed chamber technique, NO flux, NO control factors

1. INTRODUCTION

Recent experiments and model calculations indicate that oxides of nitrogen (NO_x) play important roles in atmospheric chemistry. They participate not only in the acidification of precipitation but also in the formation

of ozone (O₃) in the troposphere. In the lower atmosphere, O₃ is formed as a by-product of the photo-oxidation of hydrocarbons, while oxides of nitrogen act as a catalyst. It is essential to understand the characterization of the levels of oxides of nitrogen in tropospheric photochemistry. Nitrogen oxide (NO_x=NO+

NO_2) is a major known species of total odd nitrogen (NO_x) and has both anthropogenic and natural sources. The natural emissions of NO have been underestimated and often misunderstood in the regional or global budget. It has been recognized that NO emission from soil is a major natural source and depends on soil parameters, i.e. mainly soil nitrogen availability, soil moisture and temperature (Kim *et al.*, 1997; Aulakh, 1992). Soil NO emission occurs as a result of microbial activities, through the processes of nitrification and denitrification. Their emissions from agricultural lands have been known to be enhanced by application of nitrogen based fertilizers. Especially, in rural regions with intensive agricultural activities, soil NO flux may be comparable to the local anthropogenic input (Yienger and Levy, 1995). Therefore, it is necessary to understand effects of these controlling factors, such as soil nitrogen availability and soil moisture, on soil NO emission. The object of this laboratory study is to elucidate effect of soil moisture on soil NO flux from an agricultural soil prepared for different soil moisture conditions. The closed chamber technique was employed to measure NO concentrations from soil. The behaviors of NO concentrations emitted from soil were interpreted and discussed.

2. MATERIALS AND METHODS

2.1 Instrument control

A modified commercial chemiluminescent NO analyzer (TECO 42C) was employed to measure NO concentration emanating from soil samples in a closed conical flask. Sample flow of the NO analyzer has been adjusted to 0.185 lpm for sample injection method. Fig. 1 shows the schematic diagram of the NO concentration measurement system used for the study. Sample line of the instrument has been modified; zero grade air always flows through sample line as a carrier gas and gives the background signal. Sample gas is injected with a syringe through the sample port where a septum is plugged on the line. The sample air is carried by zero air and transported into a reaction chamber in which reaction of NO in the sample with O_3 takes place. Peak height and area for each sample injection are recorded by chart recorder and integrator (Shimadzu Chromatopac C-R6A). The peak area is converted to the NO concentration corresponding to its magnitude.

The instrument was calibrated periodically with certified master gas of 0.410 ppm and 0.097 ppm of NO in N_2 gas (Japanese Oxygen Gas Co.). Sensitivities of

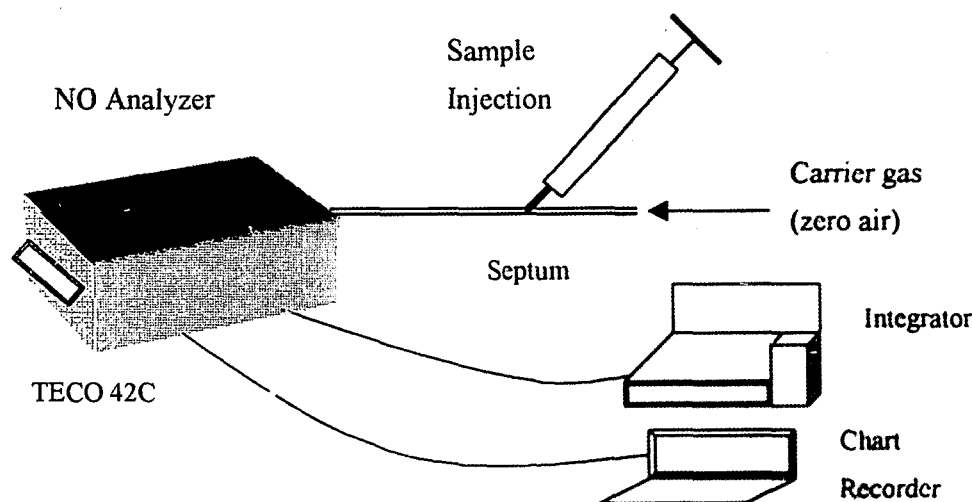


Fig. 1. Schematic diagram of modified NO gas analyzer.

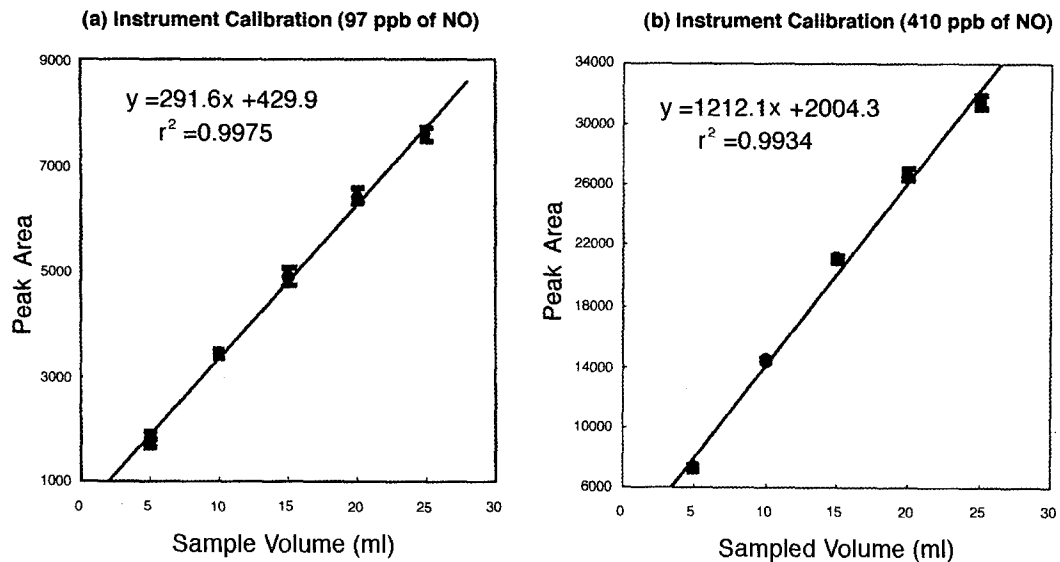


Fig. 2. Relationship between peak area and sample volume for using (a) 0.097 ppm and (b) 0.410 ppm of NO master gas. Each black circle and bars represent an average and one standard deviation resultion from five times injections for sample volume, respectively.

the instrument for different sample volume injections were also examined with these NO master gases. Sample volume for the sensitivity analysis started with 5 ml, and increased 5 ml for the next up to 25 ml of sample volume. Therefore, five sample volumes of 5 ml, 10 ml, 15 ml, 20 ml, and 25 ml were tested for the analysis. Five times injections for each sample volume were made, and their peak areas were averaged for each sample volume. Averaged peak area for each sample injection was plotted against injected sample volume in Fig. 2. Strong linear relationships between peak area and sample injected volume ($R^2 > 0.99$) were resulted from the sensitivity analysis with different levels of NO master gases. The strong linearity between peak area and its sample volume enabled us to calculate unknown NO concentration corresponding to a given volume of sample air. To estimate NO concentration in a flask, an empirical formula was derived from the sensitivity experiment using 10 ml injection; and the formula to calculate NO concentration of the sample air taken was given by:

$$[NO]_{\text{sample}} = PA_{\text{sample}} \times [NO]_{\text{master}} / \overline{PA_{\text{master}}}, \quad (1)$$

where PA_{sample} is a peak area resulting from unknown 10 ml sample air injection, $[NO]_{\text{master}}$ is the master gas concentration (410 ppb in this research) which was used for getting an average peak area for 10 ml volume injection, $\overline{PA_{\text{master}}}$. The average peak area of 10 ml volume of the master NO gas injection, $\overline{PA_{\text{master}}}$, was found to be $41,510 \pm 235$ resulting from the sensitivity analysis. Accuracy of the empirical formula was tested for 10 ml sample injection with 0.097 ppm of NO master gas. An average peak area of 10 ml of the master NO gas has been used for the formula. The error only occurred within 2% of the NO concentration.

2. 2 Laboratory experiment

A Japanese upland soil was collected from a field site at the National Institute of Agro-Environmental Sciences, Tsukuba in Japan. A bulk sample from the surface of this soil was sieved (2-mm mesh) and air-dried for a day in a greenhouse before storage at 5°C until needed.

Table 1. Soil sample moisture levels in % WFPS (water filled pore space).

Soil samples ID	Soil water contents (%)	WFPS (%)	Remarks (* denotes adding water to fresh soil.)
1	52.7	50	Fresh soil without fertilizer treatment
2	52.7	50	Fresh soil with fertilizer treatment
3	54.2	52	Slightly wet* soil with fertilizer treatment
4	57.5	55	Moderately wet* soil with fertilizer treatment
5	60.1	57	Wet* soil with fertilizer treatment

One hundred grams of sieved soil was weighed out and put into a 350 ml conical flask. Five conical flasks were prepared with the same manner. Two of these flasks were used to examine background and fertilizer effects on NO emissions; one had only 100 g of fresh soil in it, and the other had the soil with fertilizer treatment. Ammonium fertilizer ((NH₄)₂PO₄) of 2.14 g (0.3 g N) was applied evenly on the soil surface. The same amount of the fertilizer was applied to the soils in other three sample flasks, and different amount of moisture was added to the soils in each flask. The sample flasks were shaken by hand for mixing them. Previous soil analysis indicates that a bulk density of the sieved soil was 0.7 g·cm⁻³ (Environmental Agency, 1996). Assuming a soil bulk density of 0.7 g·cm⁻³ and a soil particle density of 2.65 g·cm⁻³, soil moistures in WFPS (water filled pore space) were calculated. The soil moisture results were presented in Table 1 with their sample identity (ID) number.

It had taken about a half-hour to prepare the five different soil moisture samples that were used for measuring soil NO emission in the laboratory. Fluxes of soil NO in the flasks can be estimated from equation (2) that was derived from closed chamber technique (Watanabe *et al.*, 1997);

$$F = \rho \cdot V / A \cdot \Delta c / \Delta t \cdot 273 / (T + 273), \quad (2)$$

where F is flux (mg·m⁻²·min⁻¹), ρ is a gas density (mg·m⁻³), and V is volume of the flask (m³). If it is considered as a cylinder type chamber, A is a bottom area of the flask (m²), $\Delta c / \Delta t$ is the average changing rate of NO concentration with time (ppb·min⁻¹), and T is an average temperature in the flask (°C).

In order to estimate soil NO flux, emanating soil NO

concentrations were measured at each 10 ml sample injection. The sample flask was capped with a butyl rubber plug, and the first 10 ml sample was collected from the flask by a syringe one minute after capping and injected into sample line of the instrument immediately. The second and third sample were also collected next every minute and analyzed immediately by injection into the sample line of the NO analyzer. After collecting the third sample from sample ID1, the flask was opened until the last flask sample (Sample ID5) was completed. Soil flux in the flask may be stabilized with the air during the uncapping period, and then the flask was closed just before the next measurement cycle. NO concentrations emanating from different moisture conditions with ammonium fertilized soils were measured and compared in terms of soil NO emission.

3. RESULTS AND DISCUSSION

3.1 Equilibrium concentration of NO (Compensation point)

The existence of equilibrium concentration of NO (NO compensation point) has been observed frequently in field measurements (Kim *et al.*, 1994; Slemr and Seiler, 1991), and it was explicitly demonstrated in laboratory (Johansson and Galbally, 1984). The compensation points are defined as NO mixing ratios in ambient air at which the net NO emission rates are zero. Consequently, NO compensation points represent values averaged over the measuring period, and they will reflect the average physiochemical soil conditions. Physically, in the closed system, increase in concentration has been observed during the first few minutes.

Depending on the emission rate, an equilibrium steady state is reached generally after ten to thirty minutes when gas pressures of NO between the air and soil surface are balanced.

We measured the equilibrium NO concentrations for five sample flasks to elucidate the role of soil moisture on NO emission rate. The five sample flasks were capped with plug and left in room temperature of 23°C for 3 hours until NO concentration became steady. Then, steady NO concentrations in the flasks with different levels of soil moistures were measured. It was considered that the 3 hours after capping the flasks was long enough to reach at steady state of NO concentration in the flasks. Collecting samples from each sample flask by a syringe were injected into sample line immediately. The NO concentrations were calculated with an empirical formula (1). In the next day, NO equilibrium concentrations were examined again from the sample flask that was used in the first day experiment. In Fig. 3, NO equilibrium concentrations measured in both first and second day were plotted against their soil moisture levels.

The significant increases in NO equilibrium concentration with soil moisture were shown in first day, Fig. 3(a). On the first day, the concentrations increased with increase in soil moisture up to sample ID4, and then

slightly decreased at sample ID5 in relatively high wetting condition of soils. This result seemed to support some other previous field measurements (Davidson, 1991; Parton *et al.*, 1988; Anderson and Levine, 1987; Davidson *et al.*, 1986). Significant NO fluxes have been observed in dry soils and increased upon wetting, but it has been notified that soil moisture above a certain field capacity has reduced NO fluxes (Anderson and Levine, 1987). It was suggested that production of NO via nitrification or a combination of nitrification and abiological reactions dominates in dry soils (Davidson, 1991). Optimal moisture contents for nitrification range between about 30% and 70% WFPS (Parton *et al.*, 1988; Davidson *et al.*, 1986), with N₂O production occurring towards the wetter end of that range. From our result in Fig. 3(a), equilibrium soil NO concentration increased with soil moisture and had a maximum at sample ID4 (55% of WFPS); but it decreased toward the wetter soil, sample ID5 (57% of WFPS). In our experiment we did not examine soil NO flux yet, but equilibrium NO concentration. However, it has been understood that equilibrium NO soil concentration strongly depends on strength of soil NO emission; therefore, they may have analogy with respect to soil moisture.

In Fig. 3(b) for the second day experiment, a sharp

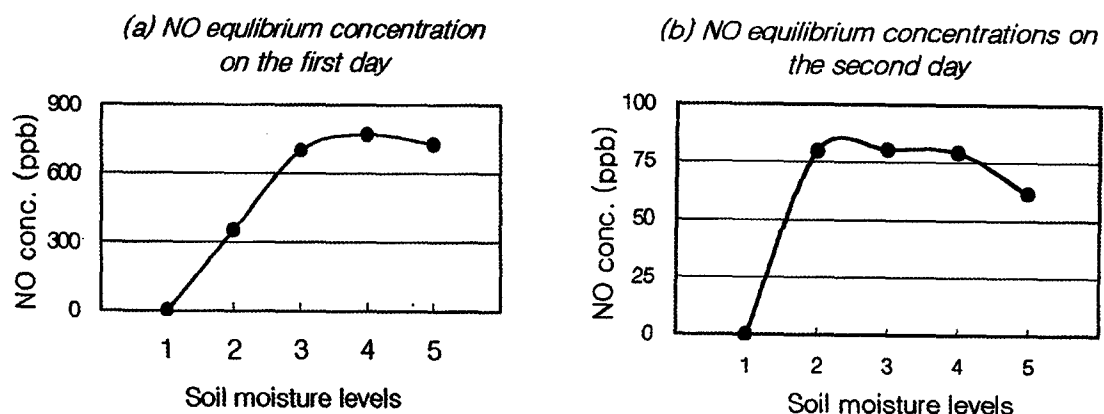


Fig. 3. NO equilibrium concentrations in the flasks for different levels of soil moisture. (a) NO equilibrium concentrations were measured 3 hours later after capping the flasks on the first sampling day, and (b) NO were measured 22 hours later after capping the flasks on the second sampling day.

increase in NO concentration was observed only in between sample ID1 and ID2; and remained steady after. The levels of NO equilibrium concentrations on second day were an order of magnitude less than those on the first day. The fertilizer applied in sample ID2 might have brought the sharp increase in NO concentration owing to relatively high nitrogen availability in soil. However, no continuous increase from sample ID2 to sample ID3 was found. Not like first day result (Fig. 3(a)), absence of significant increase from sample ID2 to sample ID3 on the second day (Fig. 3(b)) could be attributed to a diminished moisture effect on soil NO emission. Soil moisture is likely to decrease due to longtime exposure of soil samples with open air during the experiment. The exposure to open air assures decrease in soil nitrogen availability, also. These two factors may have caused soil moisture effect to decrease. It may suggest that soil moisture affects not only soil NO emissions but also its equilibrium concentrations.

3. 2 Soil moisture effects

The changes of NO concentrations in the flasks with time were examined for the different levels of soil moisture. Sample from each flask was collected every minute by syringe and analyzed immediately. This sampling and analyzing procedure was made consecutively three times a sample flask. One set of experiment was done within about 15 minutes:

Fig. 4 shows the results from these three sets of experiments and increases in NO concentration with time. The increase rates of NO concentration with time are used in estimation of NO soil emissions for the sample flasks; it is proportional to soil NO emission. There was no significant NO emanating from soil in sample ID1, but significant NO was found in others. Time rate of NO increased with moisture after sample ID1. It appeared that nitrogen input from fertilizer took charge in the first sharp increase in NO emission, and then soil moisture became an important controlling factor. Maximum increase rate of NO gas and their concentrations occurred in sample ID3 (52% WFPS)

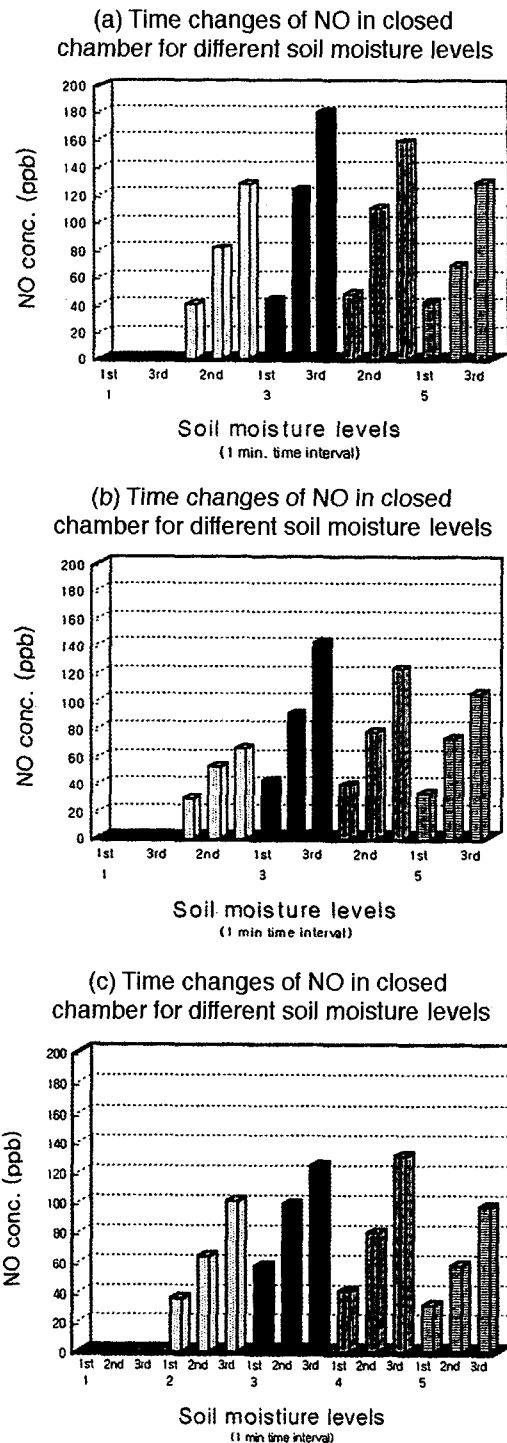


Fig. 4. Time change of NO concentrations for different soil moistures.

for each set of experiment, which was defined as slightly wet soil condition. These values were decreasing toward wetter soil conditions. These observational results suggest that soil NO emission rate strongly depended on soil moisture until it reached at a certain optimal moisture level such as about 52% WFPS in this study. As mentioned earlier, the optimal moisture

levels were observed frequently from previous field measurements and were reported in a range between 30% and 70% WFPS (e.g., Anderson and Livine, 1987; Davidson *et al.*, 1986).

The results from the three sets of experiments were shown in Fig. 4(a), (b) and (c) in order, respectively. NO change with time in the flask samples was dimini-

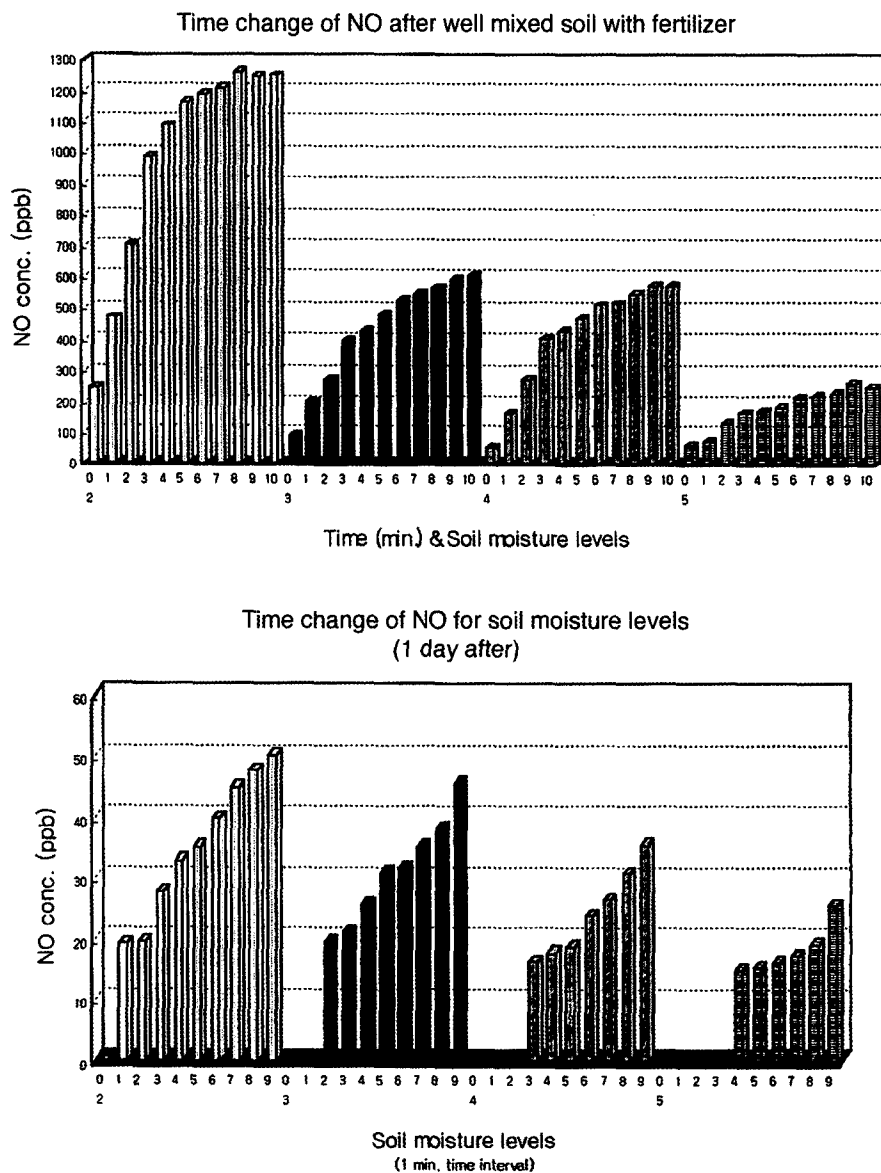


Fig. 5. Time change of NO concentration after well mixed soil with fertilizer.

shed with sequential number of set of experiment. Both NO concentration released from soils and increase rates were found to be maximum in the first set of experiment. We speculate that NO gas in the fertilized soil is released quickly by certain amounts over a relatively short period (less than 15 minutes) and discharged slowly after.

In order to examine the releasing time span of NO gas from soil, levels of NO concentration on both first day and second day were compared in their magnitudes. After three sets of experiments were completed on first day, soil and fertilizer within the sample flasks were well mixed by shaking. Ten samples were collected and analyzed successively for each flask sample with the same method before. Comparing NO concentrations in well-mixed case of Fig. 5(a) with the results in Fig. 4, we found significant increase in NO concentrations (about ten times higher in sample ID2) from soils. Even in this case, however, there was no significant NO emission in the soil without fertilizer treatment (sample ID1). NO concentrations in sample ID2 were significantly high (ranging from 200 ppb at first sample to 1200 ppb at the last sample 10 minutes after the first sample) which has least soil moisture among the samples. In case of fresh soil sample with fertilizer treatment (sample ID 2, 50% WFPS), NO concentrations continuously increased up to ~1,200 ppb for next 10 minutes and remained constant. Trends of NO concentrations were similar in the wetter soils, but the levels of NO were reduced significantly. Those magnitudes in relatively wet soil conditions of sample ID3 and ID4 ranged from approximately 100 ppb at first sample to 600 ppb at the last sample. However, it was reduced to less than 250 ppb (ranged from 50 ppb to 250 ppb) under the wettest soil condition, sample ID5. These results suggest that the soil NO flux might have been stimulated by soil disturbances by mixing, and this was much more effective in dry soils than in wet soils. Next day, experiment was repeated with the same sample flasks. NO concentrations from the sample flasks were found to be significantly less (ranged from 0 to 50 ppb) than those on the first day experi-

ment. There were no signs of NO gas emission mostly within 2 minutes. Increasing rates of NO with time were lessened significantly on the second day experiment. It suggests that most of NO was released from soils at least within a day after fertilizer application during the experiment. Length of time span may depend on the amounts of fertilizer applied, soil moisture condition, and other soil physical parameters.

4. SUMMARY AND CONCLUSION

NO concentrations emitted from Japanese upland soils treated with ammonium fertilizer were measured by closed enclosure technique through controlled laboratory experiments. Five different conditions of soil samples were prepared in 350 ml conical flasks. One was fresh dried soil without any treatment, and others were added same amount of fertilizer and different amount of water. Both the magnitudes and time rates of change of NO concentrations released from these different characteristics of soil samples were examined and compared. The NO fluxes from these soils were computed from NO concentrations measured by closed chamber technique based on mass balance. There were differences in the magnitudes of NO concentrations between soils with and without ammonium fertilizer treatment. The significant increase in NO concentration was thought to be mainly due to fertilizer. However, results from the experiment also indicated importance of moisture effects on soil NO emission. Previous results from other field experiments had shown that NO concentrations from the soils increased with soil moisture contents under intermediate moisture level (30% ~ 55% WFPS), but NO decreased beyond these moisture levels. Trend of NO concentration with soil moisture during our experiments was consistent with the results from the previous field measurements. Emission rate of NO was maximum at sample ID3 (52% of WFPS), but it decreased toward the wetter soil. It may suggest that NO production via nitrification or a combination of nitrification and abiological reactions dominates in dry soils. Existence of the equilibrium con-

centrations was observed for each flask sample. In this study, NO equilibrium concentrations increased with increase in soil moisture up to 55% WFPS (sample ID4), and then slightly decrease under relatively high wetting condition of soils (sample ID5). An order of magnitude lower NO equilibrium concentrations on second day indicated that most of NO was released from soils within a day after fertilizer application. NO releasing time span may be dependent on the amounts of fertilizer applied, soil moisture condition, and other soil physical parameters (i.e., temperature and soil porosity).

We found that agricultural activities, such as nitrogen fertilizer treatment and irrigation, have a critical influence on emanating nitrogen from the soils. There are probably other physiochemical parameters to control soil nitrogen emission. In order to elucidate dependency of soil nitrogen emissions on these controlling parameters, more efforts should be made for gathering experimental data on the variety of soil conditions. Well-designed field and laboratory experiments for measurements of soil NO flux should be conducted from many different soil characteristics along with careful data analysis.

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