

N₂O emissions from forest and grassland soils in northern China *

Liu Ye, Mu Yujing, Yang Wenxiang

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Abstract—Nitrous oxide(N₂O) is a major trace gas in the atmosphere. It plays an important role in global warming and ozone depleting. In this paper, we set up a install to determine the N₂O emission flux from forest and grassland soil. We observed an interesting phenomenon: in our sampling sites, the soil always acts as a source of N₂O, but sometimes it acts as a sink when the temperature is lower than 15℃.

Keywords: nitrous oxide; emission flux forest; grassland soil.

1 Introduction

At present time, some global environmental problems, such as depletion of stratospheric ozone, global warming, may impact on our living conditions on the earth. Those attract many scientists' interesting. Study on the trend of trace gases in the atmosphere is useful for understanding these important global problems. Nitrous oxide(N₂O), as a major trace gas in the atmosphere, not only plays as an important greenhouse gas, but also a major source of NO which can cause ozone depletion in the stratosphere. The concentration of nitrous oxide in the atmosphere is about 310 ppbv, and the increasing rate is 0.25%—0.31% per year(Prinn, 1990). Among all of greenhouse gases, nitrous oxide is the third large one following carbon dioxide(CO₂) and methane(CH₄). Although its concentration is a thousand times smaller than CO₂, the radiate forcing of nitrous oxide is about 200 times higher than that of CO₂ from the greenhouse effect(Shine, 1990). The absorption is from 7.7 μm to 17μm(Ramanatham, 1985). Since the last century, the concentrations of several important greenhouse gases have increased, such as CO₂, CH₄, chlorofluorocarbons(CFCs), N₂O and tropospheric ozone(Dickinson, 1986). It is estimated that nitrous oxide contributes about 5% of the total greenhouse effect in the world(Houghton, 1990).

Current knowledge indicates that the NO in the stratosphere does not come from direct emissions, but from N₂O emitted at the surface. By movements of air, nitrous oxide can be transported into the stratosphere, in which the molecule can be destroyed by either direct photolysis, as in Equation (1), or transformed with O(¹D) atoms in Equation(2):



* This study was supported by the National Natural Science Foundation of China



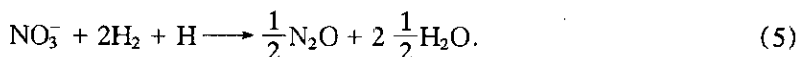
Equation (2) is the major source of stratospheric nitrogen oxide, which can regulate stratospheric ozone by catalytic reactions in Equation (3) and Equation (4) (Rowland, 1991):



Nitrous oxide emits far more NO into the stratosphere than any other sources (Jackman, 1980). Model calculations also show that the global total column ozone will decrease nearly 10%—16%, if the concentration of nitrous oxide in the atmosphere is doubled (from 300 ppbv to 600 ppbv; Whitten, 1983). It is obviously that the potential harmful effect of the global environment caused by nitrous oxide is going to be one of important problems of the environmental sciences.

The growth in atmospheric nitrous oxide is caused by a large number of poorly known minor sources, including agricultural soils, soils under natural vegetation, aquatic sources, biomass burning, fossil fuel combustion, industrial sources, and traffic and so on. Recently, potential N_2O sources (Khalil, 1992) have been identified, such as atmospheric chemistry sewage treatment, land disturbance, animal manure, waste incineration, and even global warming effect on N_2O emission from biogenic sources.

Although some researches show that the oceans may be a large source of their gas, soils in north hemisphere are still considered as major source of nitrous oxide. In soils, nitrification and denitrification, are responsible for most of NO and N_2O produced. Nitrous oxide is a product of both nitrification and denitrification (Skiba, 1992). Emissions from soils are estimated about 90% of all N_2O emissions:



Ice core records of N_2O show an increase of about 8% over the industrial period (IPCC, 1990). The Greenland record suggests a pre-industrial level of about 260 ppbv, 10 to 25 ppbv lower than previous records (IPCC, 1990). The Antarctic core shows that N_2O was lower during glacial periods, which consistent with the hypothesis that soils are a major natural source of nitrous oxide (Donoso, 1993).

To study the sources and sinks of N_2O and its atmospheric chemical characters is an important research subject. There are quite a lot of research reports about the measurements of N_2O emissions on agriculturally used soils, effects of fertilizer application, and biomass burning, but the measurements on grassland and forest soil, the major natural source of N_2O emissions besides agricultural soil, are still limited. The major sink of N_2O is the photodissociation in the stratosphere; a secondary loss of about 10% occurs through reaction with $\text{O}(^1\text{D})$. Important evidence of N_2O consumption by soils was reported by Donoso (Donoso, 1993), but there are insufficient data to determine whether soil provides a significant global N_2O sink. Rydne also observed a high rate of N_2O loss on grassland. Sink activity as high as $11.6 \text{ ng Nm}^{-2} \cdot \text{s}^{-1}$ has been measured (Rydne, 1981). Because of the limited works on natural N_2O sources of forest and grassland, there is lack of reports on whether forest and grassland soil can be a sink of this gas. This work studies the N_2O emission flux from forest and grassland soils in China, so that we can

make a complete assessment of the emissions of N₂O in China in the future.

2 Site description

Nitrous oxide emission flux is measured at two types natural soils without any forms of fertilizer applications. One of the sampling sites is selected at Beijing Forest Eco-System Research Station, Chinese Academy of Sciences, which is located at Mentougou Xiaolongmen (39°58' N, 115°26' E), elevation 1150 m. Soils of this region are primarily clay, and the vegetation is pine forest, believed to be undisturbed in historical times. Average soil temperatures at 5 cm depth at the undisturbed forest sites were: -1°C, 2°C, 12°C, 15°C, 17°C, 21°C, 17°C, 4°C for January, March, April, June, July, August, September, December respectively. Rains were slight for this region during spring and heavy during summer.

The other sampling site is selected at a typical grassland in northern China which was located at Bashang Guyuan County, Hebei Province. Therefore, we can measure the emission of N₂O by grassland soils.

3 Experimental method

The emission flux of N₂O was determined by a closed chamber method. The flux chamber was made by thin iron sheet. The top of the chamber is moveable and the bottom of the chamber is open. The frame of chamber was inserted into soil to prevent air leaking into and out of the chamber. The volume of the chamber is (47 × 52 × 42) cm³. The inner wall of the chamber was covered with a Velton film in order to reduce the absorption of N₂O on the wall.

The flux chambers were put on the ground of the pine forest at the eastern side of the mountain. One of the chambers covered the soil, and the other covered the leaf mould land. Two hundred ml of air sampler in the chamber was collected by a grass syringe just after closing the cover of the chamber. During a given time interval the other samplers were collected. The air samplers were kept in some aluminum combined polyester gas sampler bags.

The concentrations of nitrous oxide of the samplers were determined by gas chromatography with electron capture detection (ECD). The models of GC are PYE-Unican 304 and HEWLETT PACKADD series II. PYE-Unican 304 gas chromatography was equipped with a ⁶³Ni ECD, a CRIB chromatopac and a packed glass column of 80—100 mesh Porapak Q. The sensitivity of this analytical method is 9.4×10^{-13} g/s. The linear range was in the range from 0—1000 ppbv. The temperature of detector was 300°C. Injection temperature was 120°C and column temperature was kept at 55°C. The flow rate of ultra pure N₂ was 25.5 ml/min. External standard and retention time were used as a qualitative analysis index for N₂O, and the retention time under these condition is 3'3". The secondary standard of N₂O was supported from Institute of Standard Material, Beijing. The concentration of the secondary standard was 328 ppbv. HEWLETT PACKADD Series II gas chromatography was equipped also with ECD and a packed stainless steel column. A computer controlled the sampling gas through a sampling tube (6 ml) and a ten-valve. The water in

the air sample was absorbed before it entered the detector. The flow rate of ultra pure N_2 was 25 ml/min. The concentration of the secondary standard was 315 ppbv. Column temperature was 90°C. Injection temperature was room temperature. Detector temperature was 330°C.

An external standard method was used for quantitative analysis of N_2O :

$$C_{(2)} = \frac{C_{(1)} V_{(1)} S_{(2)}}{V_{(2)} S_{(1)}}$$

Where, $C_{(1)}$ is the concentration of the secondary standard N_2O sample (ppbv); $V_{(1)}$ is the injection volume of the secondary standard N_2O sample (ml); $S_{(1)}$ is the height or area of peak of standard sample; $C_{(2)}$ is the concentration of the sample; $V_{(2)}$ is the injection volume of the sample; $S_{(2)}$ is the height or area of peak of sample.

4 Results

4.1 N_2O measurements with closed-chamber

Closed-chamber are usually shallow to allow an increase in N_2O concentration to measurable levels in the shortest possible time, and it was true for our design (420 mm high). The N_2O emission flux was calculated as Equation (6):

$$F(\mu g/m^2 \times h) = D \times H \times \frac{\Delta C}{\Delta t},$$

$$H = \frac{V}{A}.$$

Where, D is the density of the gas; H , V and A are height, volume and area of the chamber; C is the changing concentration of the gas. The results of measurement for N_2O emission flux from forest soil and grassland are shown in Fig.1. Both the forest and grassland soil are natural soils, without any fertilizer application. It is obviously that N_2O emission flux varied with seasons. During the summer, from June to September, the value of the flux is always positive. It indicates that N_2O emitted from forest and grassland soil to the atmosphere, and it seems that soils were the source of N_2O then. The maximum value of N_2O emission flux was $18 \mu g/(m^2 \cdot h)$, and the minimum value was $0.4 \mu g/(m^2 \cdot h)$.

It is interesting to see that the measured flux of N_2O always give negative value in the period of March to May, and September to the end of March in our observations during 1993 to 1996. This indicates that the soils were acting as a sink for atmospheric N_2O during these periods.

4.2 N_2O emissions diurnal variation

As shown in Fig.2, the concentration of N_2O was increasing in an hour just after closed the chamber. It appears that N_2O emitted from soil to the atmosphere. Then the value became decreasing. It reached the lowest level in 3 hours, and then began to increase again. In the period of 10:00 – 15:00 then, the changing of the temperature may be a main reason for this variation. The concentration of N_2O was keeping decreasing till next morning. It is obviously that measurement of the N_2O emission flux must be done within an hour after closed the chamber.

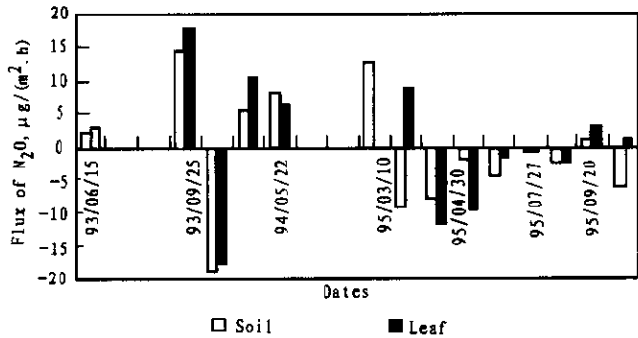


Fig.1 N₂O emissions from forest soil

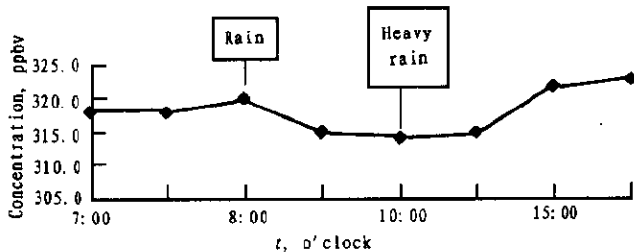


Fig.2 N₂O emission diurnal variation

5 Discussion

Although we found that soils of the forest and grassland sometimes acted as source of N₂O, and sometimes as sink of this gas, we still do not know the sink path anymore. In fact, we did not apply any fertilizer in the sampling site.

5.1 Effect of the component of the soil

Soils in Xiaolongmen Forest Eco-System Research Station are primarily black clay. They are natural soils without any forms of fertilizer application. The total nitrogen containing in the forest soil is shown in Table 1.

It seems that the nitrogen in the soil is always keeping in low level, about 0.22%—0.3%, and the value of the nitrogen is always keeping in the same level. The exchangeable elements and extractable elements in the soil are given in Table 2.

5.2 Effect of the moisture

The relationship between N₂O emissions and the moisture is shown in Fig.3. It was interesting to indicate that there is no obviously correlation between N₂O emissions and soil moisture content. N₂O emissions did not increase when it was rainy. The humidity and precipitation at the sampling site are both shown in Fig. 3. It was obviously indicated that the N₂O

Table 1 The total nitrogen containing in forest soil

Date	Background	pH	Organic carbon, %	Total nitrogen, %
90.07	3—12 cm soil	6.26	3.92	0.2
95.09	Leaf mould soil			0.36
	Leaf mould soil			0.40
95.09	Soil			0.20
	Soil			0.23
95.12	Leaf mould soil			0.15
	Leaf mould soil			0.20
95.12	Soil			0.20
	Soil			0.25
96.01	Leaf mould soil			0.50
	Leaf mould soil			0.48
96.01	Soil			0.26
	Soil			0.24

Table 2 The amount of exchangeable elements and extractable elements in the forest soil

The amount of exchangeable elements, ppm						
P	Al	Mn	K	Na	Ca	Mg
0.007	0.0004	0.0047	0.023	0.0017	0.44	0.041
The amount of extractable elements, ppm						
Cu		Zn		Fe		
0.00010		0.00028		0.015		

emission flux did not appear as a function of humidity and precipitation. In the situation of negative N_2O flux, the moisture and precipitation were varied, sometimes high, sometimes low. This is much different from Skiba's description (Skiba, 1992). His observations on agriculture soils showed that nitrous oxide emissions increased with increasing rainfall and soil moisture content. The exactly low nitrogen containing is considered to be the main reason which caused the difference of our results and that of Skiba's. The lack of rain ensured that the top soil layer was well aerated, thus preventing the development of anaerobic microsites where denitrification or production of N_2O by nitrification could have occurred in high nitrogen containing region, but in low nitrogen region, the increasing rainfall and soil moisture content did not increase the population of the anaerobic and emissions of N_2O . Therefore the moisture of the soil can not be considered as the main cause of negative N_2O flux from forest soil. It seems that the effect of soil humidity on N_2O emissions at this sampling site can be ignored.

5.3 Effect of the temperature

As shown in Fig.4, it is interesting to see that the flux values of N_2O emissions are usually negative when temperatures are 5—15°C. When temperatures are below 0°C, the soils stop emission of N_2O , so that the values of N_2O emission flux appear around zero. It means that soils

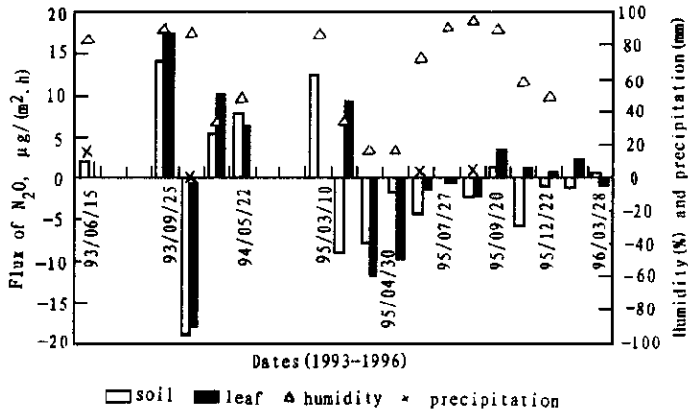


Fig.3 The relationship between N₂O emissions and humidity of forest soil

act as a sink of N₂O. So it seems that at low nitrogen soils the effect of temperature is the major factors that can affect N₂O emissions.

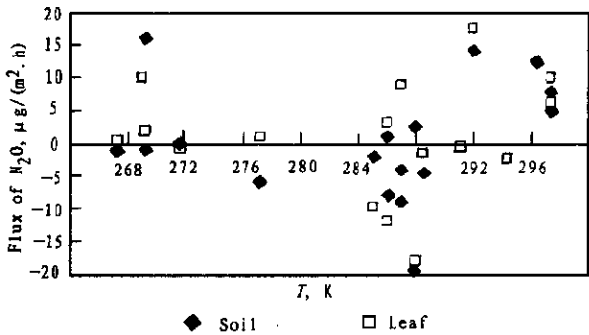


Fig.4 The relationship between temperature and emissions of N₂O

6 Conclusion

A chamber method was founded for measurement the N₂O emission flux from forest and grassland soils.

It is very interesting to observe that the values of the N₂O emission flux sometimes appear as negative. This means that soils act as a sink of N₂O at those times. This phenomenon is valuable for the N₂O emissions assessment of China in the future.

Our results indicate that soil temperature is the most important factor which can affect N₂O emissions at low nitrogen containing soils. The values of N₂O emission flux are always positive, but it appears negative when the temperatures are 5—15℃. This seems that soils sometimes act as a source of N₂O, and sometimes act as a sink.

Acknowledgements——Thanks to Mr. Mao Shisen who recommended the sampling site in

Xiaolongmen Forest Station and his great helping for our work. Thanks also to Mr. Dong Yunshe who provided the GC for us.

References

- Dickinson RE, RJ Cicerone. *Nature*, 1986; 319:109
- Donoso L, R Santana, E Sanhuega. *Geophy Res Lett*, 1993; 20:1379
- Rydne JC. *Nature*, 1981; 292:235
- Houghton JJ. *Climate change: The IPCC Scientific Assessment*. London: Cambridge University Press. 1990
- Jackman CH, JE Frederick, RS Stolarski. *J Geophys Res*, 1980; 85:7495
- Khalil MAK, RA Rasmussen. *J Geophys Res*, 1992; 97(14):651
- Prinn RD, D Cunnold, R Rasmussen, P Simmonds, F Alyea, A Grawford, P Fraser and R Rosen. *J Geophys Res*, 1990; 95:18:369
- Ramanathan V, RJ Cicerone, HB Singh and JT Kiehl. *J Geophys Res*, 1985; 90:5547
- Rowland, F Sherwood. *Annu Rev Phys Chem*, 1991; 42:731
- Shine KP, RG Derwent, DJ Wuebbles and JJ Morcrette. *Radiative forcing to climate*, in *Climate Change. The IPCC Assessment*, New York:Cambridge University Press. 1990:45
- Skiba U, KJ Hargreaves, D Fowler, KA Smith. *Environ*, 1992;26A(14):2477
- Whitten RC. *Atoms Environ*, 1983; 17:1995

(Received November 8, 1996)