ATTEMPTS TO MEASURE N_2O USING A BRAZILIAN MADE CHROMATOGRAPH

Takenori Yamaguchi[1]; Milton Alexandre Teixeira Vargas[2];
Ariovaldo Luchiari Junior[2];Nobuo Kosuge[3]

ABSTRACT - The environmental impact of the intensive cultivation of Cerrados has not been well evoluated due to the lack of research that quantify the emission of air pollutants through the agricultural systems used. In the global scale, one of the main atmospheric pollutants is the gas N_2O due its contribution to the greenhouse effect and its role in the decrease of the ozone layer. Emission of N_2O in some agricultural systems in Cerrados were measured using a brazilian made gas chromatograph eqquiped with an electron capture detector. Atmospheric N_2O values varied from 281 to 297 ppb, smaller than other values described in the literature to other regions. Soil emission of N_2O (μg/100 cm²/day) in areas planted with some crops were 21.6 ± 3 (cassava), 20.5 ± 17 (bare lance) 17.5 ± 12 (soybean). In soils covered with grassland, only trace emission of N_2O were detected.

Introduction

Carbon dioxide (CO_2), methane (CH_4), dinitrogen monoxide (N_2O) and halo-carbons (fluon gases) are emitted through human and natural activities such as industries, agriculture, volcanoes and microorganisms. These gases are absorbed by the infrared ray radiated from the earth and they cause a rise of temperature in the atmosphere-earth's surface system. Those gases are called the greenhouse effect gases.

Recently, the greenhouse effect gases have increased in the atmosphere. According to the atmosphere-ocean joint model, the rise of temperature in the atmosphere is estimated to be 2°C in 2040 and 4°C in 2100 at the temperature zone of the northern hemisphere. The gases also have been known to destroy the ozone layer in the stratosphere (16).

---

[1] Soil Science Specialist, Consultant from EMBRAPA/JICA.

[2] Eng.-Agr., Ph.D., EMBRAPA/Centro de Pesquisa Agropecuária dos Cerrados (CPAC), Caixa Postal 08223, CEP 73301-970 Planaltina,DF.

[3] Soil Sciences Specialist, Consultant from EMBRAPA/JICA.

Even a small amount of N_2O or CH_4 accelerates the greenhouse effect in the atmosphere. Dinitrogen monoxide (N_2O) and CH_4 at the present concentration in the atmosphere has played about one fourth of role for the temperature rise by the all greenhouse effect gases. Dinitrogen monoxide is mainly emitted by activities of organisms and has existed from the old time in the atmosphere. The gases have increased by human activities, for example, by the combustion of fossile fuel, incineration of biomass and application of fertilizers, etc. Above all, it is pointed out that arable land is one of the emission sources of N_2O, and the application of nitrogen fertilizer in large quantities would cause the increased emission of N_2O from soil.

The present report deals with characteristics of N_2O, emission source, concentration in the atmosphere, quantity of emission, and control of N_2O.

1. Characteristics of N_2O

Dinitrogen monoxide is stable at normal temperature, and it does not react with oxygen (O_2), ozone (O_3) and hydrogen (H_2), but it strongly reacts to other substances as an oxidizing agent at high temperature. It is not decomposed by visible radiation.

Dinitrogen monoxide is equally distributed in the toposphere and its life span is estimated as 170 years. After diffusion, in the stratosphere the gas is decomposed to N_2 and O by ultra-violet ray, and nitrogen monoxide (NO) is produced by the reaction between N_2O and the excited oxygen atom O (^1D). The newly produced NO and O_3 change to NO_2 and O_2, and NO_2 reacts with O to produce NO and O_2.

The ozone layer in the stratosphere has been destroyed by these repeated chemical reactions. The chemical reactions are shown as follows:

$$N_2O \rightarrow N_2 + O$$
$$N_2O + O\ (^1D) \rightarrow N_2 + O_2$$
$$N_2O + O\ (^1D) \rightarrow 2NO$$
$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$

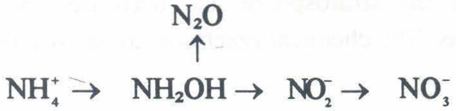
2. Emission sources of N_2O

Soil is considered to be the principal emission source of dinitrogen monoxide. The are non-biological and biological procedures to produce O. The former occurrs when nitrite ion (NO_2^-) or hydroxylamine (NH_2OH) are accumulated in acidic soil, and the reaction is called chemical denitrification. Amounts of N_2O produced by this reaction is usually very small, and chemical denitrification is characterized to occur without soil microbes.

Denitrification is the reaction which nitrate or nitrite nitrogen are reduced to gases nitrogen (N_2) or nitrogen oxide (NO) by heterotrophic bacteria under anaerobic conditions and at the same time organic or inorganic substances are oxidized to release energy. That reaction is as follows:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O\uparrow \rightarrow N_2\uparrow$$

In the course of denitrification , N_2O is emitted into the atmosphere. As mentioned above, nitrification is the phenomena that ammonium salts are oxidized to nitrite ion (NO_2^-) and nitrate ion (NO_3^-) by nitrifying bacteria in the soil. Nitrifying bacteria, which oxidize ammonium salts and assimilate carbon by the energy produced during nitrification, are chemo-autotrophs represented by two types of nitrifying bacteria. One of them is nitrogen-dioxide-bacteria which produces nitrite-nitrogen ($NO_2^- - N$), and the other is nitrate-bacteria which oxidize nitrite-nitrogen to nitrate-nitrogen ($NO_3^- - N$). When ammonium ion (NH_4^+) exists in soil under aerobic contition, N_2O is produced in the course of nitrification of NH_4^+, and Nitrosomonas genus of bacteria are mainly related to that procedure. The reaction of nitrification is as follows:



$$NH_4^+ \rightarrow \overset{\overset{N_2O}{\uparrow}}{NH_2OH} \rightarrow NO_2^- \rightarrow NO_3^-$$

When NO_2^- or NH_2OH is added to soil, N_2O is emitted even under aerobic condition. It seems N_2O is produced noy only enzymic reation but also by chemical ones. Among N_2O producing procedures, it is considered that nitrification has the major effect on the N_2O concentration in the atmosphere. A large amount of N_2O is emitted from arable lands, because nitrogen fertilizers such as urea and ammonium salts have been used. Besides, N_2O is also emitted from rivers, lakes and sea by activity of denitrifying bacteria.

Combustion of fossil fuels, wastes, sludge, and biomass are regarded as the another sources of N_2O. Factories have proved to be one of the sources of N_2O for long years, and N_2O has been produced from petroleum, natural gas, coal, NH_4^+ and HNO_3 used through their industrial production. Exhaust gas of automobiles also contain high concentration of N_2O in ppm scale.

3. Concentration of N_2O in the atmosphere

Concentration of N_2O in the atmosphere has increased at the rate of about 0.3% (0.14 - 1.04 ppb) annually by measurement in the North Atlantic Ocean and the Antarctic Continent performed from 1975 to 1985. According to research on ice core, N_2O concentration had been stable in the range of 285 ± 1 ppb from about 3,000 years ago to 19th Century, but after the Industrial Revolution, increase of N_2O concentration has been observed.

Recently, World Meteorological Organization (WMO) reported that N_2O concentration in the atmosphere has increased from 0.2 to 0.3% for the past 10 years. Combustion of fossil fuel, incineration of biomass and application of fertilizer, etc. are pointed out for the cause.

4. Amount of emitted N_2O

Emission of N_2O is affected by various environmental factors. Important factors are soil pH, organic matter contents, soil moisture, oxygen partial pressure, temperature and amount of precipitation. It is very difficult to estimate the amount of N_2O in global scale, because the procedure of production and extinction of N_2O have complicated relation to biochemical reaction in Nature.

Seiller et al. (1987) reported that the major sources of N_2O by human activities are fertilizer and incineration of biomass, and the emitted N_2O per year is 1.5 TgN (trilion g), and it corresponds to 10% of the total emission.

Lately, IPPC reported that combustion of fossil fuels, incineration of biomass and fertilizer applied to soil are considered N_2O sources by human activity, and the quantity of N_2O emission has increased in recent years.

5. Control of N_2O emission

In order to meet a demand of food in the world, it is unavoidable to expand arable land and increase fertilizer application. Areas of paddy field over the world had increased from 86 x 10^6 ha to 145 x 10^6 ha for 50 years (1935 through 1985), and the percentage of the world's production of nitrogen fertilizer had also increased by 60% for 10 years (1974 through 1983). That increasing tendency had continued since them.

As mentioned above, most part of N_2O emitted from arable land soil is considered to be produced in the course of nitrification. If we can control the procedure of nitrification in soil, N_2O emission could be decreased or be kept at the present state. The following countermeasures are proposed; improvement of application time of nitrogen fertilizer, split application of the fertilizer, use of slow-release or coated fertilizer, combined use of organic and nitrogen fertilizers, and use of urease inhibitor etc. Early practical use of some techniques to reduce N_2O emission is requested.

It is pointed out that N_2O flux in low land, upland, grassland and irrigation water have to be investigated, because a large quantity of N_2O is produced in agro-ecosystems. The balance of N_2O production-extinction in the global scale is not yet proved. It is necessary to get further information to resolve the problem.

Material and Methods

1. Methods of collection of air and soil gases

1) Collection of air samples

Five liter of air was collected by an air pump in a Tedlar gas sampling bag. Ten ml of the collected air was sucked from the bag into a vacuum sample tube and used for gas chromatography. Vaccum tubes for drawing blood were used for the collection of the air.

2) Collection of soil gases

A Wagner's pot (about 14 liters in volume) was placed on the surface of the soil upside down, and the drainage outlet of the pot was closed with a stopper. The air which accumulated in the pot was taken out by an injection needle through the stopper to a vaccum sample tube (10 ml).

2. Preparation of standard N_2O

The standard N_2O gas was prepared by the following procedure. A vaccum was created in a gas sampling bottle (500 ml in volume) by using a vaccum pump, and 0.5 l of N_2 (Ultra-pure nitrogen gas, 99.995%) was injected with a 100 ml syringe. An aliquot of 5 μl pure N2O (> 98%, Showa Co., Ltd.) was added with a gas-tight syringe to the sampling bottle containing N_2 and the gases were mixed together well.

3. N_2O measurement by gas chromatography with electron capture

The gas chromatograph used was "CROMATÓGRAFO DE GÁS MODELO 370, INSTRUMENTOS CIENTÍFICOS C. G. LTDA." made in Brazil.

In order to increase the sensibility to N_2O of the gas chromatograph and also to eliminate the fluctuations in the measurement values, all the parts of the gas chromatograph were checked. After repeated tests under different conditions, N_2O could be detected on a ppm scale by the gas chromatograph under the following conditions.

Carrier gas: N_2, Ultra-pure nitrogen gas, 99.995%.
Pre-column: Filled with Drierite ($CaSO_4$) and Ascarite (NaOH), placed at room temperature (not heated).
Separation Column: Column 3 m in length and 2 mm in diameter filled with Porapak Q and heated at 60°C.
Detector: Electron capture detector, ECD ^3H, heated at 210°C.
Flow rate of carrier gas: 45 ml/min.
Electric conditions of amplifier: 64 x 10 kV, 10^{-8} A for N_2O in N_2
32 x 10 kV, 10^{-8} A for N_2O in air.

Samples of air and soil gases to be analysed were injected with a gas-tight syringe to the gas chromatograph. Through the pre-column the samples with the carrier gas were dehumidified and carbon dioxide was absorbed. The pre-column should not be heated. The gas samples flowing to the separation column filled with Porapak Q and N_2O were parti-tioned by the filler. The partitioned N_2O was detected by ECD ^3H (tritium) under the above mentioned conditions.

Results

1. Emission of N_2O in the field of CPAC

The concentration of dinitrogen monoxide emitted from the soil and atmosphere in different fields of CPAC was determined. Disposable plastic cups (500 ml in volume) were used for collecting the soil gases, and they were placed upside down on the soil surface for 24 hours. Soil gas in the cups and atmosphere of the fields were collected in vaccum sample tubes. To obtain accurate values, the samples were sent to the National Institute of Agro-Environmental Sciences (NIAES), Tsukuba, Japan, and the concentration of N_2O was measured by gas chromatography. The results are shown in Table 1. The soil emission of N_2O varied from 17,5 to 21,5(μg/100 cm²/day), within the different crops. Values at atmospheric N_2O varied from 282 to 297 ppb, smaller then other values cited in the literature.

TABLE 1 - Emission of N_2O from CPAC fields.

Soils	Fields	Soil emission N_2O μg/100cm/day	Atmosphere ppb
Dark Red Latosol	cassava	21.6 ± 3.0	297.3 ± 14.0
	no cassava	20.5 ± 17.8	292.7 ± 12.7
	grass tr.	282.0 ± 24.0	
Red Yellow Latosol			
	soybean	17.5 ± 12.0	281.3 ± 14.6
	no soybean tr.	293.3 ± 23.0	
	grass tr.	282.0 ± 24.2	

2. Detection of N_2O in the atmosphere with CROMATÓGRAFO DE GÁS MODELO 370

Dinitrogen monoxide in the atmosphere was detected with a gas chromatograph, CROMATÓGRAFO DE GÁS MODELO 370, equipped at CPAC. One ml of atmosphere was used for gas chromatography. As shown on Figure 1, N_2O was detected on the chromatograms. The gas chromatographic conditions are also indicated in the legent of the figure.

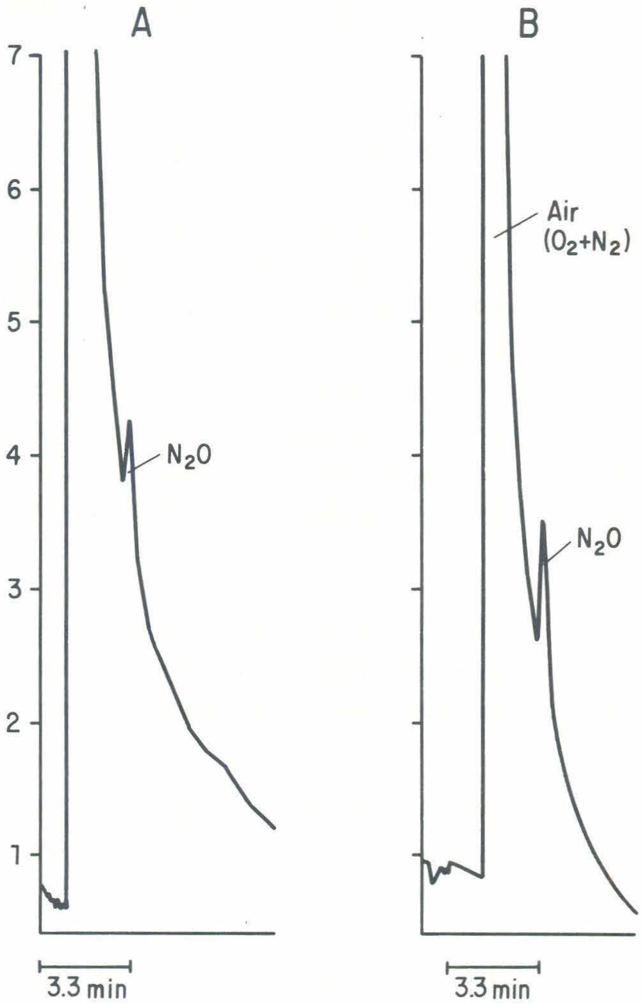


FIG. 1 - Typical chromatogram of N_2O in air.

Sample A: Air, B: Air + N_2O
Gas chromatographic conditions
Column 3 m x 2 mm i.d.
Packing Porapak Q
Temp. 55°C
Carrier gas Ultra-pure N_2 (99.995%)
Flow rate 45 ml/min
Detector ECD ^3H, Temp. 210°C
Amp. 10 x 32 kV, 10^{-8}

3. Detection of N_2O emitted from soil with different applications of fertilizer

Experimental plots with different applications of fertilizer were prepared in the field of CPAC. Non-cultivated or cultivated (20 cm in depth) fields were combined with the application of Chilean saltpeter or urea (80 kgN/ha). Each 185 g of samples was collected after 16 days of treatment. To the samples 40 ml of water was added and they were kept at 25°C in airtight glass bottles. After 11 days, N_2O in the soil gas of the bottles was detected by gas chromatography. Gas-chromatograms are shown in Figure 2.

According to Figure 2, a large quantity of N_2O was detected from the soil samples amended with Chilean saltpeter, and the N_2O values were higher in the samples from cultivated fields than in those from non-cultivated fields.

4. Improvement for the use of the gas chromatograph Stable and reproducible measurement values could be obtained, if the gas chromatograph equipment could be improved as follows:

1) Improvement of the heating control system: The separation column and detector do not keep a constant temperature, and the measurement values show wide fluctuations.
2) Improvement of connecting parts of column: There is no special part for the connection of the pipe and column and consequently gas leaks at the connection.
3) Fitting of flow-changeable cocks: In order to avoid the decrease of the sensibility of the detector, the fitting of a flow-changeable cock is important. The detector will not be polluted, if the gases flow out through the flow-change cock.
4) Records for maintenance: Deterioration of the equipment could be checked by appropriate records of measurements and repairs.

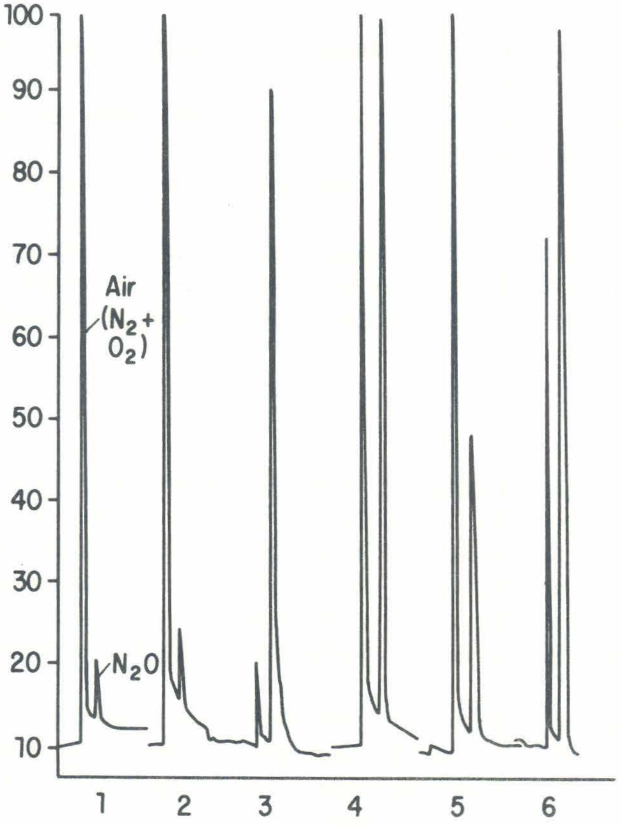


FIG. 2 - Emission of N_2O from soil with or without fertilizer application.

1: no-fertilizer, no-cultivation
2: no-fertilizer, 0-20 cm cultivation
3: chilean saltpeter application (80 kg N/ha), no-cultivation
4: chilean saltpeter application
(80 kg N/ha), cultivation
5: urea application (80 kg N/ha), no-cultivation
6: urea application (80 kg N/ha), 0-20 cm cultivation

4. Remarks on the utilization of the gas chromatograph

Users should have adequate knowledge of the principles of gas chromatography to check errors of measurement. Operation of a gas chromatograph without understanding the importance of stability and calibration can not produce accurate results. The following aspects are important in practice.

1) The separation column should be activated by heating sufficiently before the measurement.
2) A leak of gas at the column connection and change of gas flow rate should be checked carefully.
3) The temperature of the separation column and detector shoud be stable.
4) A sample should be injected to the gas chromatograph, after confirmation that the base line on the recorder is constant.
5) A sample must be injected quickly to the gas chromatograph to avoid gas leak.

Conclusion

The gas chromatograph, CROMATÓGRAFO DE GÁS MODELO 370, can be used for the detection of N_2O emitted from soil by denitrification. To obtain accurate measurements, the conditions of operation and previous remarks should be considered. If only the temperature control system and heat interception of the equipment were improved, measurements would be more efficient and the fluctuations in the measurements could be eliminated.

In order to improve the sensibility and reproducibility of the measurements with the Brazilian-made gas chromatograph, it is important that researchers discuss with the engineers of the manufacturer the problems which may arise during the gas-chromatographic analyses.

References Bibliografics

BOUWMAN, A.F. Soils and the greenhouse effect. New York: J. Wiley, 1990. p.25-32.

HAHN, J. Nitrous oxide in Oceans. New York: J. Wiley, 1981. cap. 10.

HIROTA, M. Gas-chromatographic measurements of nitrous oxide (N_2O) in air using a molecular sieve trap. **Bulletin of Chemical Society of Japan**, v. 51, p.3075-3076, 1978.

HIROTA, M.; MURAMATSU, H.; MAKINO, Y.; SASAKI, T.; TOYAMA, Y. The vertical distribution of atmospheric CF_2Cl_2, $CFCl_3$, and N_2O over Japan. **Journal of Meteorology Society of Japan**, v. 62, p.158-165, 1984.

HIROTA, M.; MURAMATSU, H.; SASAKI, T.; MAKINO, Y.; ASAHI, M. Atmospheric concentration and distribution of CF_2Cl_2, $CFCl_3$ and N_2O over Japan between 1979 to 1986. **Journal of Meteorology Society of Japan**, v. 66, p.703-708, 1988.

INOUE, K.; MINAMI, K. Measurement of nitrous oxide (N_2O) flux emitted from grassland soil. Nogyo Kisho (Agricultural Meteorology) v. 41, p.145-149, 1985. Em japonês.

KELLER, M. et al. J. Geophysical Research, v.91, p.11791, 1986.

MINAMI, K.; FUKUSHI, S. Methods for measuring N_2O flux from water surface and N_2O dissolved in water from agricultural land. **Soil Science and Plant Nutrition**, v. 30, p.495-502, 1984.

MINAMI, K. Emission of nitrous oxide (N_2O) from agro-ecosystem. **Japan Agricultural Research Quarterly**, v. 21, p.22-27, 1987.

MINAMI, K.; OHSAWA, A. Emission of nitrous oxide dissolved in drainage water from agricultural land. In: BOUWMAN, A.F. ed., J. Wiley (1990). no prelo.

MINAMI, K.; FUKUSHI, S. Effects of phosphate and calcium carbonate application on emission of N_2O from soil under aerobic conditions. **Soil Science and Plant Nutrition**, v. 29, p.517-524, 1983.

MINAMI, K. Fluctuation of N_2O flux and dissolved N_2O in agricultural water zone. **Kankyo Joho Kagaku**, v. 17, p.53-56, 1988. Em japonês.

MURAMATSU, H.; HIROTA, M.; MAKINO, Y. Gas-chromatographic measurements of dinitrogen oxide in air. Bulletin of Chemical Society of Japan, v. 55, p.117-120, 1982.

SEILER, P.J.; CONRAD, R. Contribution of tropical ecosystem to the global budgets of trace gases, especially CH_4, H_2, CO, and N_2O. In: DICKSON, R.E. ed., Geophysiology of Amazonia, vegetation and climate interaction. New York: J. Wiley, 1986. p.133-160.

TOGUCHI, M.; OHNO, S.; FUKUNISHI, H. Remote sounding of vertical profiles atmospheric ozone and nitrous oxide with tunable diode leser heterodyne spectrometer. **Journal of Meteorology Society of Japan**, v. 68, p.79-93, 1990.

WMO. Scientific assessment of stratospheric ozone. Global ozone research and monitoring project. **Report N_2O**, v. 1, p.250-252, 1989.

WMO/UNEP IPPC. Greenhouse gases and aerosols. Scientific assessment of climate change. **Section 1**, 3rd draft, 18-56, 1990.

YOH, M.; YAGI, A.; TERAI, H. Significance of low-oxygen zone for nitrogen cycling in a freshwater lake. Production of N_2O by simultaneous denitrification and nitrification. **Japanese Journal of Limnology**, v.51, p.163-171, 1990.

YOH, M. Experimental examination on nitrous oxide accumulation during nitrification in a freshwater lake. Japanese Journal of Limnology, v.51, p.237-248, 1990.

YOSHIDA, N. et al. Nature 342, 895, 1989.

YOSHIDA, N. et al. Nature 335, 528, 1988.