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Gas-chromatographic Measurements of Dinitrogen Oxide in Air

Hisafumi Muramatsu, Michio Hirota,* and Yukio Makino
Meteorological Research Institute, 1-1 Nagamine, Yatabe-machi, Tsukuba-gun, Ibaraki 305

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To obtain an average tropospheric mixing ratio of dinitrogen oxide over Japan, 90 air samples were collected by aircraft at altitudes up to 7 km from Autumn, 1978, to Spring, 1979, and were analysed by the GC-ECD method. The mean volume-mixing ratio of N_2O was 0.31_0 ppm, and the standard deviation was 0.01_4 ppm. These results show that the tropospheric N_2O is well mixed and that its mixing ratio is higher than 0.30 ppm.

The natural dinitrogen oxide is produced by the nitrification of the ammonium ion as well as the denitrification of nitrates through microbiological activity in soil and water.[1—6)]

Though some sinks of N_2O have been proposed,[6—8)] the atmospheric N_2O is rather unreactive in the troposphere and is transferred to nitrogen monoxide mainly by Reaction (1) in the stratosphere:[9)]

$$\begin{aligned} N_2O + O(^1D) &\longrightarrow N_2 + O_2 \\ &\longrightarrow 2NO. \end{aligned} \qquad (1)$$

The NO is strongly related to the stratospheric ozone (O_3) by Reaction (2); *i.e.*, an increase in NO leads to a depletion of the stratospheric O_3:[10—13)]

$$\begin{array}{lll} & NO + O_3 \longrightarrow NO_2 + O_2 & \\ & NO_2 + O \longrightarrow NO + O_2 & (2) \\ \hline \text{net} & O_3 + O \longrightarrow 2O_2. & \end{array}$$

To know the behavior of the N_2O in the atmosphere, from the ground surface[8,14—26)] through the troposphere[14,17,20,26—32)] to the stratosphere,[14,17,27,30—37)] and also in the sea and over the sea surface[17,29,38—43)] is important in understanding the global nitrogen cycle[1,2,44)] and the stratospheric O_3 chemistry.[10—13)]

In a previous study,[45)] several measurements of the atmospheric N_2O were performed at the Meteorological Research Institute, Koenji, Tokyo, by the gas chromatographic (GC) method, using a thermal conductivity detector (TCD); the error of the measurement was estimated to be about ±7%. It has been shown, however, that an electron-capture detector (ECD) has an increased sensitivity for N_2O at elevated temperatures[46)] and needs an air sample of only a few millilitres, while the N_2O must be preconcentrated from about 30 l of air when a TCD is used.[14,15,19,38,39,47)]

To obtain an average tropospheric mixing ratio of N_2O over Japan, air samples obtained by aircraft from Autumn, 1978, to Spring, 1979, have been analysed by the GC-ECD method.

Experimental

Sampling of Air. Three aircraft, an Aerocommander 685, a Piper Seneca, and a Cessna 404, were used for the air sampling. On the aircraft, the air was sampled through a silicone rubber tube or a *tylon* tube (1 m×8 mm i.d.) in stainless steel cylinders (Whitey, 0.3, 0.5, and 1.0 l) by means of two air pumps connected in series up to the pressure of 3.5—4.0 kg/cm². Before use, the cylinders were evacuated by means of an oil rotary pump and heated to 200 °C for several hours. DK shut-off valves (Whitey) were used for these cylinders. The N_2O concentration was constant for more than 40 d (<±2.0%) in the cylinder.

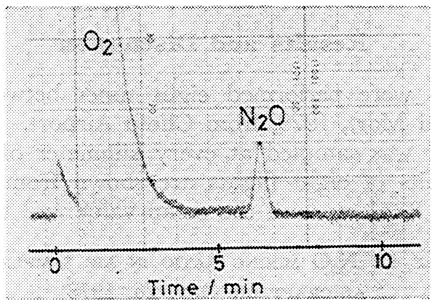

Fig. 1. The typical chromatogram of N_2O.
Standing current: 2.0 nA, pulse frequency: 2.5 kHz, detector temperature: 300 °C, sample air: 2 ml. N_2O was 0.34 ppm.

Gas-chromatographic Analysis. GC measurements were performed using a Shimadzu Gas Chromatograph GC-6AM equipped with an ECD (10 mci ^{63}Ni, 300 °C). Nitrogen gas (99.9995%) passed through the tube filled with molecular sieve 5A (1/16 in. pellets) was used as the carrier gas at a flow rate of 40 ml/min. The sample air was transferred to a 2-ml gas sampler (Shimadzu, MGS-4) and then introduced into a glass column (3 m×3 mm i.d.) filled with 30—60 mesh molecular sieve 5A.† The peak of N_2O appeared 5 min after that of oxygen gas at the column temperature of 245 °C.

The reference gas of 1 ppm N_2O was prepared by diluting 15 μl of pure N_2O (>98%, Showa Denko) in 15 l of air, which was measured by means of a gas meter and passed through a tube (30 cm×3 cm i.d.) containing silica gel and three U-shaped tubes (8 mm i.d.) containing drierite, ascarite, and molecular sieve 5A (1/16 in. pellets, 0 °C) respectively. A 15 μl portion of N_2O was measured by means of a gas-tight syringe (SGE, 100A-RN-GSG). The molecular sieve tube was heated to 350 °C for 3 h before use. The air purified by this method was also used as a zero gas. The error in repeated measurements of single reference gas was less than ±0.9%. The concentrations of five reference gases made in 20-l *tedlar* bags over a period of a week were in good agreement with each other; *i.e.*, the standard deviation was 1.7%.

A typical chromatogram of N_2O is shown in Fig. 1. The peak heights of N_2O were proportional to the quantities of N_2O from 0.39 ng to 3.9 ng, which corresponded to 0.1 ppm and 1 ppm of N_2O in 2 ml of air respectively. The error in repeated peak-height measurements for 0.3 ppm of N_2O was about ±2%. The total error in the measurements of N_2O was estimated as about ±4%.

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† Porapak Q and QS and Porasil B and C were also suitable for the analysis of N_2O.[29)]

In the present study, measurements were performed as follows; the reference gas was first measured, and then the sample air was measured two times, and finally the reference gas was measured again. The volume-mixing ratio of N_2O in the sample air was calculated from the ratio of the two mean values of the sample air and the reference gas. The average difference between two measurements of 90 air samples was ±2%. The detection limit in this method was about 0.01 ppm of N_2O in 2 ml of air.

The temperature of the ECD was controlled in a range of ±2 °C. No effect of this temperature variation could be detected on the chromatogram.

Results and Discussion

Flights were performed eight times between Oct., 1978, and Mar., 1979, from Chofu Airport. In many cases, air was sampled at every kilometer of altitude. The results of eight flights are shown from Table 1 to Table 8, along with the mean value and the stand-

TABLE 1. N_2O MIXING RATIO IN AIR SAMPLED BY AIRCRAFT ON OCT. 26, 1978

Altitude km	Location a)	Volume-mixing ratio of N_2O/ppm
1	Yokohama	0.31_2
2	Yokosuka	0.32_3
3	Takeyama	0.29_6
4	Enoshima	0.34_5
6	Enoshima	0.32_2
7	Oiso	0.29_9
7	Miyakejima	0.30_8
4	Niijima	0.33_3 c)
3		0.35_1 c)
2	Jogashima	0.33_1 c)
1		0.33_5 c)
1		0.32_6 c)
0	Chofu b)	0.33_5 c)
	Mean	0.31_5
	SD	0.01_6

a) When the location is not shown, the air was sampled between the former and the latter locations. It is the same in Tables 2—8. b) Air was sampled just before landing. c) Air was sampled in a 5-l *tedlar* bag. These values were not included in the calculation of the mean value and the SD.

TABLE 2. N_2O MIXING RATIO IN AIR SAMPLED BY AIRCRAFT ON DEC. 7, 1978

Altitude km	Location	Volume-mixing ratio of N_2O/ppm
0.5		0.35_8
0.5	Zushi	0.31_8
0.5	Niijima	0.32_6
0.5	Mikurajima	0.30_3
1·5	Mikurajima	0.31_5
1.7	Niijima	0.32_0
1.5	Jogashima	0.32_5
	Mean	0.32_4
	SD	0.01_2

TABLE 3. N_2O MIXING RATIO IN AIR SAMPLED BY AIRCRAFT ON DEC. 12, 1978.

Altitude km	Location	Volume-mixing ratio of N_2O/ppm
0.5	Fujisawa	0.31_1
1	Fujisawa	0.30_7
2	Fujisawa	0.32_6
3	Fujisawa	0.33_8
4	Fujisawa	0.32_4
5	Fujisawa	0.32_0
6	Fujisawa	0.33_6
7	Fujisawa	0.32_2
7	Oshima	0.30_9
0	Chofu	0.33_1
	Mean	0.32_2
	SD	0.01_0

TABLE 4. N_2O MIXING RATIO IN AIR SAMPLED BY AIRCRAFT ON JAN. 19, 1979

Altitude km	Location	Volume-mixing ratio of N_2O/ppm
1	Iruma	0.29_0
3	Higashimatsuyama	0.28_8
5	Fujioka	0.30_1
7	Harunasan	0.28_9
7	Kashiwazaki	0.29_8
6	Kashiwazaki	0.29_0
5	Kashiwazaki	0.31_0
4	Kashiwazaki	0.30_7
3	Nagaoka	0.29_8
2	Nagaoka	0.30_3
3	Harunasan	0.30_6
2	Gyoda	0.28_7
	Mean	0.29_7
	SD	0.00_8

TABLE 5. N_2O MIXING RATIO IN AIR SAMPLED BY AIRCRAFT ON FEB. 2, 1979

Altitude km	Location	Volume-mixing ratio of N_2O/ppm
3	Enoshima	0.29_8
3	Oshima	0.30_1
3	Niijima	0.30_4
3	Mikurajima	0.30_4
3		0.31_7
3	Hachijojima	0.32_2
1		0.31_9
1	Mikurajima	0.32_7
1	Miyakejima	0.31_3
1	Oshima	0.30_4
1		0.30_5
1	Kamakura	0.31_7
	Mean	0.31_1
	SD	0.00_9

Table 6. N_2O mixing ratio in air sampled by aircraft on Feb. 9, 1979

Altitude km	Location	Volume-mixing ratio of N_2O/ppm
2.5	Enoshima	0.28_9
2.5	Oshima	0.29_9
2.5	Shimoda	0.29_0
2.5	Omaezaki	0.28_0
2.5		0.29_5
2.5	Toba	0.29_8
0.75	Toba	0.30_1
0.75		0.30_3
0.75	Omaezaki	0.30_7
0.75	Irozaki	0.29_7
0.75	Oshima	0.31_7
0.75	Enoshima	0.30_3
	Mean	0.29_8
	SD	0.00_9

Table 7. N_2O mixing ratio in air sampled by aircraft on Feb. 16, 1979

Altitude km	Location	Volume-mixing ratio of N_2O/ppm
1	Eda	0.30_6
2	Yokohama	0.31_1
3	Enoshima	0.29_9
4		0.31_1
5		0.29_9
6	Oshima	0.31_0
7		0.30_2
6		0.30_9
4	Mikurajima	0.29_6
3	Miyakejima	0.30_5
2	Miyakejima	0.29_3
2		0.31_1
1	Mikurajima	0.31_0
1	Miyakejima	0.29_9
1	Niijima	0.31_4
1	Oshima	0.30_9
1	Enoshima	0.31_1
1	Eda	0.31_2
	Mean	0.30_6
	SD	0.00_6

ard deviation (SD) for each flight. The air samples taken on Dec. 7 and Dec. 12, 1978, and Jan. 19, Feb. 2, Feb. 9, and Mar. 27, 1979, were each measured for single reference gas respectively. The mean values of each altitude are shown in Fig. 2, along with the SDs(——). The number of samples at each altitude is also shown in Fig. 2. The value at 1.5 km was that of a constant-level flight on Dec. 7, 1978. The values at 2.5 km and 0.75 km were also those of constant-level flights on Feb. 9, 1979.

The mean value of the total of 90 samples was 0.31_0 ppm, and the SD was 0.01_4 ppm (4.4%). The mean value of 48 samples, for which the difference between two measurements was less than ±2%, was 0.31_2 ppm, and the SD was 0.01_3 ppm (4.2%). These results show that the tropospheric N_2O is well mixed from the ground surface to the altitude of 7 km, and that its mixing ratio is higher than 0.30 ppm.[1,17,21,26,32] The latter has also been shown in the measurements of the surface air in Japan,[23,25] though the results in Refs. 19 and 24 were very low (0.25 ppm).[††] The mixing ratio of N_2O in the air over the sea surface is rather low (<0.29 ppm)[38,39,41–43] except for the values of the Caribbean Sea[40] and the NE Pacific Ocean.[17] This has been considered due to systematic errors among the analytical procedures.[42]

In a previous study, the mixing ratios of N_2O in the air over the ground surface were very scattered from 0.25 ppm to 0.45 ppm.[45] This wide distribution, which was also observed by Katou *et al.*,[19] has not

Table 8. N_2O mixing ratio in air sampled by aircraft on Mar. 23, 1979

Altitude km	Location	Volume-mixing ratio of N_2O/ppm
1	Kokubunji	0.31_8
2	Kawagoe	0.32_7
3	Omiya	0.31_4
4		0.31_8
5	Koga	0.31_9
6		0.31_9
7.5	Iwaki	0.32_1
7		0.33_0
6		0.33_0
5	Yamatsuri	0.30_8
4		0.31_3
3	Tochigi	0.31_5
	Mean	0.31_9
	SD	0.00_7

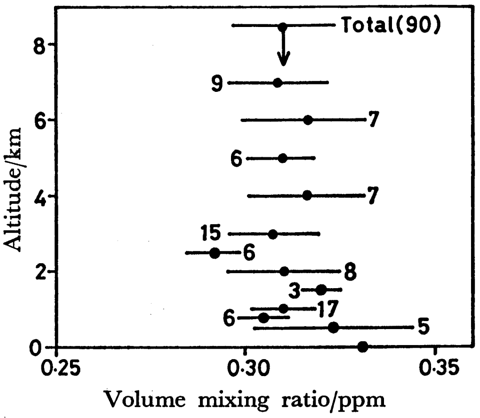

Fig. 2. The mean vertical distribution of N_2O.
●: Mean value at the same altitude, —: Its SD. The number of samples at the same altitude is also shown. a) The value of 1.7 km on Dec. 7, 1978 is included in the mean value of 1.5 km. b) The value of 7.5 km on Mar. 23, 1979 is included in the mean value of 7.0 km. c) The value of the ground surface is that at Chofu Airport.

[††] The cause of this discrepancy is now under investigation.

TABLE 9. N_2O MIXING RATIO IN AIR SAMPLED BY AIRCRAFT AND MEASURED BY THE GC-TCD METHOD

Date (1978)	Altitude km	Location	Volume-mixing ratio of N_2O/ppm
Feb. 2	7	Sagami Bay	0.32_2
	4	Sagami Bay	0.34_4
	2	Sagami Bay	0.29_3
Mar. 3	7	Hayama	0.32_0
	4	Miyakejima	0.34_0
	1	Oshima-Hatsushima	0.30_2
Oct. 26	3	Oshima	0.30_2
	1	Enoshima	0.32_4
		Mean	0.31_8
		SD	0.01_9

been observed in the measurements made by the GC-ECD method. The same results have been observed in the measurements made by a GC-MS method.24) Values such as 0.45 ppm are too high to be explained by the effect of the exhaust gas of automobiles.25) The error in the direct preconcentration of N_2O from the outdoor air must have been much larger than the estimated one (±3%).

The SD of the sample measurements was nearly equal to the error in the measuring technique. This would imply that the tropospheric mixing ratio of N_2O is more uniform than the results of the present study indicate and that the tropospheric lifetime of N_2O is quite long.26)

Before the ECD was equipped with, from 20 l to 30 l of air was sampled in *tedlar* or *aflon* bags. The N_2O in the sample air in these bags was preconcentrated on molecular sieve 5A (−72 °C) and then analysed by the same GC-TCD method as was adopted in the previous study.45) The concentration of N_2O in these bags was constant for at least a week.[†††] The results of 8 air samples, which are shown in Table 9, were considered to be in agreement with the results obtained by the GC-ECD method.

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[†††] This was ascertained by the GC-ECD method.