

N₂O MEASUREMENT IN THE POLAR ATMOSPHERE: PRELIMINARY RESULTS AND PLANS

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Abstract: Preliminary results of the measurement of atmospheric N₂O density distribution suggest that the local effect of the N₂O source is not negligible. The effect of relative humidity on the mixing ratio of N₂O is found in present analysis, and this means that it is necessary to simultaneously measure the N₂O mixing ratio and H₂O density. Monitoring of the N₂O ratio at Syowa Station will help us to understand the global N₂O distribution and the local effect of the N₂O emission strength on its global budget.

1. Introduction

Atmospheric nitrous oxide (N₂O) plays an important role in stratospheric chemistry. The reaction of N₂O with excited oxygen O(¹D) which is produced through photodissociation of the stratospheric ozone,



is the most important source of stratospheric nitrogen oxides, NO_x which catalytically destroy the atmospheric ozone.

According to recent studies (McELROY *et al.*, 1976; CRUTZEN, 1976; LIU *et al.*, 1977; JOHNSTON, 1977), the continued use of nitrogen fertilizer possibly increases the atmospheric abundance of N₂O, thereby causing an increase of NO_x and eventually a depletion of the stratospheric ozone.

It is therefore important to research the following points to understand in detail the NO_x-ozone problem and its relation to man's activities:

- (1) stratospheric photochemistry including catalytic O₃ destruction processes by NO_x,
- (2) the radiative effect of NO_x on stratospheric energy balance,
- (3) the residence time of N₂O in the atmosphere,
- (4) the nature of N₂O sources and sinks.

JUNGE (1974) developed an empirical relationship between the standard deviation of a set of tropospheric minor constituent measurements and these atmospheric residence times, and inferred a 5-year residence time of N₂O. According to HAHN and JUNGE (1977), the N₂O residence times thus calculated range from 1 or 2 years up to greater than 28 years. Many investigators (*e.g.*, CICERONE *et al.*, 1978;

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ROY, 1979; GOLDAN *et al.*, 1978) pointed out that the residence time estimated by JUNGE's approach (1974) was possibly invalid, partly because (1) the local effect of N_2O sources and sinks was not considered and partly because (2) large standard deviations of measurements and hence the short residence time of N_2O were certainly due to artifacts of the previous experimental technique. PIEROTTI and RASMUSSEN (1977) carefully reviewed the many measurements that had been made over the previous 30 years, and concluded that very recent N_2O measurements by electron-capture gas-chromatography were more precise than those available before 1975, and that the atmospheric residence time of N_2O might be considerably longer than 25 years if JUNGE's idea (1974) is applied. Also, the fact that atmospheric N_2O has such a long residence time makes it a tracer in order to understand the global-scale transport processes on minor constituents in the atmosphere. However, large uncertainties are still present in our knowledge of the residence time, source, and sink of N_2O .

Dominant sources of atmospheric N_2O are attributed to microbiological denitrification and nitrification, and known sinks are photolysis by solar ultraviolet radiation in the stratosphere as well as biological processes, including denitrification and nitrogen fixation, on the surface of the earth (DELWICHE, 1981). The microbiological activity is certainly affected by various environmental conditions in addition to the use of nitrogen fertilizer and consequently we consider that the source strength of N_2O is not uniform. This is not a small problem because none of the research subjects mentioned above can be solved without the knowledge of the distribution of N_2O sources and their temporal variations.

We have performed monitoring of the atmospheric N_2O density distribution over Nagoya and its outskirts since the summer of 1979 to try to identify sources of N_2O and estimate the strength of these sources. In addition to this, the humidity of air was also measured using a Lyman- α /OH fluorescence hygrometer to test the humidity effect on the N_2O mixing ratio in the lower atmosphere.

Here we should like to describe our preliminary results and to present the monitoring plan of N_2O at Syowa Station, Antarctica to clarify the spatial and temporal changes of the strength of N_2O sources.

2. Experimental Techniques and Instrumentation

2.1. Sample collection

Aircraft (Cessna 402) measurements of N_2O density and related atmospheric parameters were carried out over Nagoya and its outskirts on June 24, 1981 and January 13, 1982. The flight courses chosen here are shown in Fig. 1. On the map, the ground surface condition is illustrated using four different types: industrial area, city area, farm area and woodlands.

The air distribution system in the aircraft is shown in Fig. 2. Air was taken from the inlet nozzle which was installed so as to avoid the contamination of exhaust gas from the engine, and distributed to individual pieces of equipment, air sampler, integrating nephelometer, and hygrometer through the air buffer chamber. Air sampling for N_2O measurements was carried out with Pyrex glass bottles

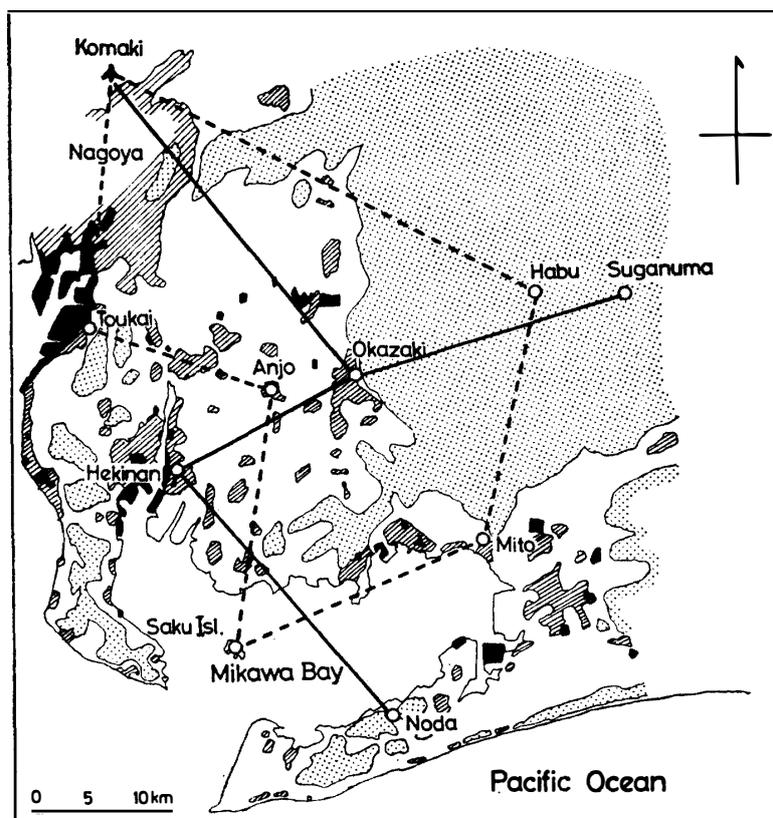


Fig. 1. A map of the sampling area. The solid line shows the flight course on June 24, 1981 and the broken line that on January 13, 1982, respectively. The black portion of the map is an industrial area, the shaded area is city area, the dotted area is woodlands, and the white area is farm or sea.

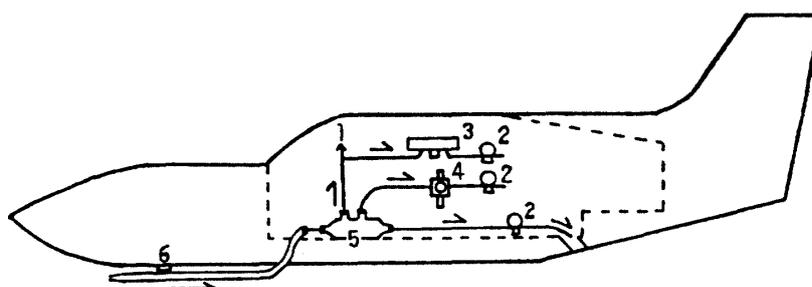


Fig. 2. Schematic diagram of the instrumental arrangement in the Cessna 402. 1. Air sample opening for N₂O sampling, 2. Pump, 3. Integrating nephelometer, 4. Lyman- α /OH fluorescence hygrometer, 5. Air sample chamber, 6. Thermometer, \rightarrow Air flow.

(Corning 7740), of which the volume was about 500 ml. Both ends of the bottle were fitted with silicon tips used for gas-chromatographic injection packing. The sampling bottles were prepared by repeated evacuation with a rotary vacuum pump and flashing with He, and finally evacuated before being loaded aboard. Just before the sampling, the bottles were scoured once using air in the neighborhood of the sampling air, in order to minimize the contamination, then the sample air was pressurized into the bottles in the range from 1.8×10^5 Pa (0.2 km height) to $1.4 \times$

10^5 Pa (4.0 km height) with a stainless steel bellows pump (Charles Austen Pump Co., Ltd., CAPEX 1). Air in the sampling bottle was brought back to the laboratory of the Water Research Institute and the mixing ratio of N_2O was measured by a gas-chromatograph with non-radioactive electron-capture detector (Yanaco, Model G-180EN).

Water vapor content was monitored by a Lyman- α /OH fluorescence hygrometer, in order to test the relationship between humidity and the mixing ratio of N_2O . The details of this hygrometer have already been described in a previous paper (IWASAKA *et al.*, 1981) and we do not intend to repeat all of it. This hygrometer has two advantages for aircraft measurement: (1) rapid response (10^{-3} s) and (2) high sensitivity in comparison with a conventional type hygrometer.

In the later observation on January 13, 1982, the atmospheric temperature and light scattering coefficient of air were measured by Ni-resistance thermometer, and by integrating nephelometer (Meteorological Research Inc., Model 1550B), respectively.

2.2. Analysis

Gas-chromatographic analyses were performed as follows: The air sample in the sampling bottle was introduced into a pre-evacuated volumetric gas sampler (4 mm i.d., 100 ml stainless steel column), and N_2O was adsorbed on a column with molecular sieve 13X (3 mm i.d., 50 cm length) under room temperature; then the adsorbed N_2O was introduced into the gas-chromatograph by heating the column up to 250°C within 150 s. Gas-chromatography was carried out with Polapack QS (3 m length) as an adsorbent and He as a carrier gas at 60°C of column temperature. The peak area was calculated with an electronic integrator (Yanaco, System-1000) and the N_2O concentration was calibrated with a standard N_2O sample, which was prepared from a commercial N_2O cylinder (Nagoya Kosan, 99.9% up) by static dilution with He. The pressure in the air sample contained in the gas sampler was measured by a manometer, and the N_2O concentration was represented by the ppbv of whole air in the standard condition.

The precision of the N_2O concentration measurement, as determined by repeated analysis of two kinds of air samples (one of them is laboratory air contained at the same time in 6 sampling bottles; the other is air from a commercial cylinder contained in Tedlar bags), and represented as the relative standard deviation, is 1.7% (number of measurements; $n_m=18$) and 1.1% ($n_m=20$), respectively. These values correspond to the precision in the analysis of summer and winter samples, respectively.

For the comparison, the ambient air in the laboratory was determined during analysis of the sample air. Average N_2O concentrations of 330.7 ± 5.7 (number of samples; $n=8$) and 323.6 ± 8.6 ($n=21$) were obtained in July 26–31, 1981, and in February 9–March 2, 1982, respectively.

3. Result

Figure 3a shows the vertical profile of N_2O concentration on June 24, 1981.

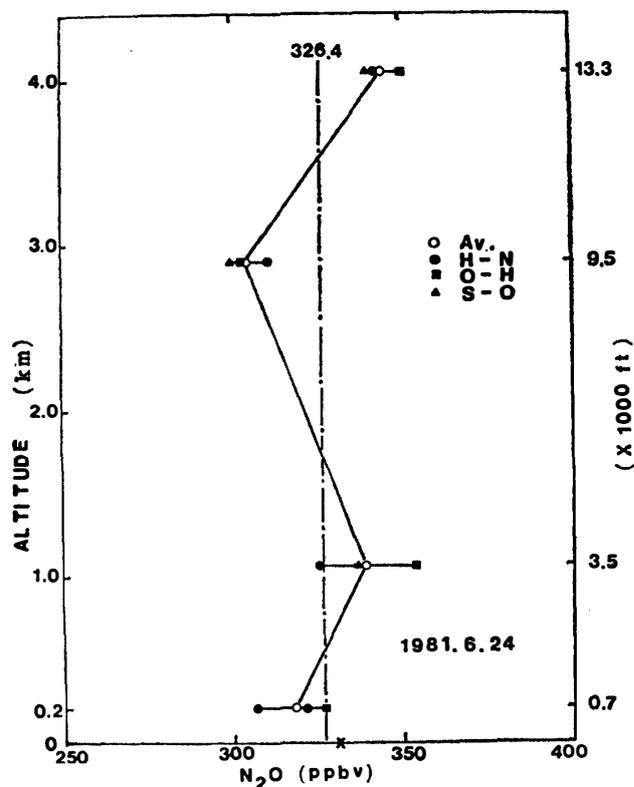


Fig. 3a. Vertical profile of N₂O mixing ratio (ppbv of whole air) on June 24, 1981. ○: Average value at the indicated altitude, ●: sampling between Hekinan and Noda, ■: sampling between Okazaki and Hekinan, ▲: sampling between Suganuma and Okazaki, ×: average N₂O mixing ratio of the ambient air in the laboratory of the Water Research Institute during July 26–31, 1981.

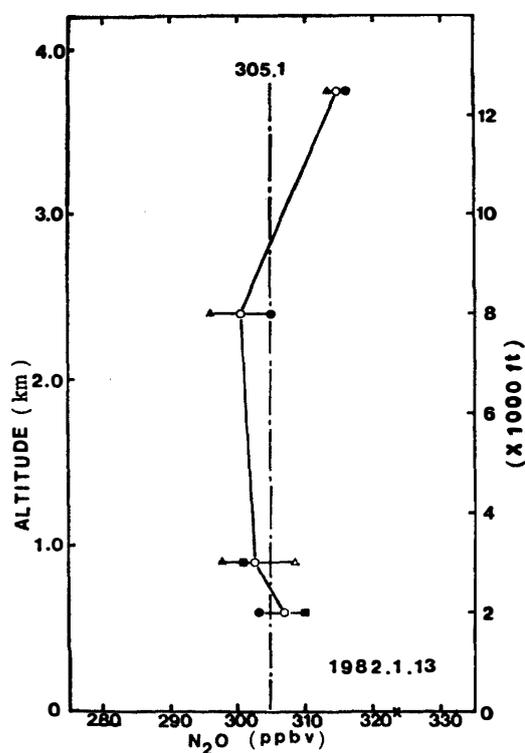


Fig. 3b. Same as Fig. 3a for January 13, 1982. ○: Same as Fig. 3a, ●: sampling between Saku Isl. and Mito, ■: sampling between Anjo and Saku Isl., ▲: sampling between Mito and Habu, △: sampling between Habu and Komaki, ×: same as Fig. 3a for February 9–March 2, 1982.

The average N₂O concentration throughout the flight course was 326.4 ± 18.7 ppbv ($n=12$). Standard deviations among different areas in the same altitude were smaller than those among different altitudes in the same area. Standard deviations among different areas at higher altitudes (2.9 km, 4.1 km) were smaller than those at lower altitudes (0.2 km, 1.1 km). The difference of the average N₂O concentration in different altitudes was significant as being beyond the analytical error. At the lower altitudes (0.2 km, 1.1 km), the N₂O concentration seems to be affected by the ground condition, *i.e.* a higher value on the flat land area than on the marine area.

Figure 3b shows the vertical profile of N₂O concentration on January 13, 1982. The average N₂O concentration throughout the flight course was 305.1 ± 7.7 ppbv ($n=17$), which is significantly lower compared with both data obtained from the summer flight, and the ambient air in the laboratory (323.6 ± 8.6 ppbv).

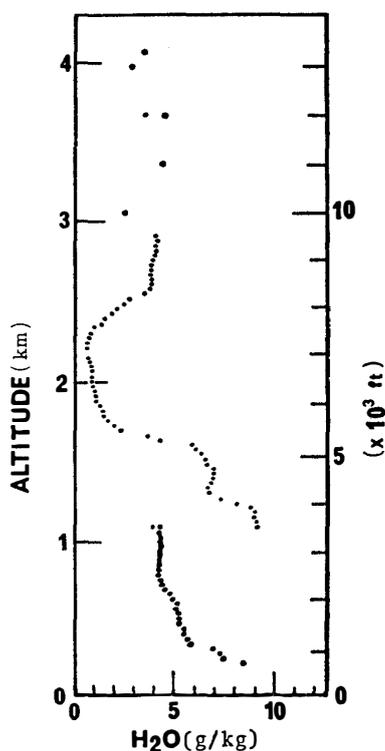


Fig. 4a. Water vapor content (g/kg) measured on June 24, 1981.
 ●: Measurement at Noda, ○: measurement at Suganuma.

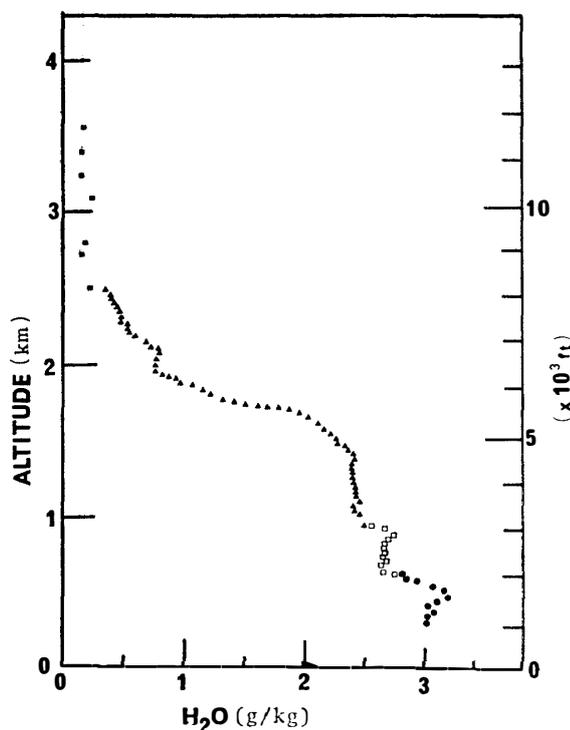


Fig. 4b. Same as Fig 4a for January 13, 1982.
 ■ □: Measurements at Anjo, ▲: measurements at Habu, ●: measurements at Mito.

Although the standard deviation was less than that of the summer flight, the same tendency was obtained, *i.e.*, a smaller standard deviation at the highest altitude and a lower value in the marine area at the lowest altitude.

As is described above, we simultaneously measured the water vapor content using a Lyman- α /OH fluorescence hygrometer (IWASAKA *et al.*, 1981; MURABAYASHI *et al.*, 1982). In Figs. 4a and 4b, we show vertical profiles of the water vapor content measured on June 24, 1981 and on January 13, 1982, respectively. Each point in these figures shows the average value measured per 10 s. The profile in Fig. 4a has the following features:

- (1) constant mixing region around 1.0 km and above 2.5 km.
- (2) a high mixing ratio at about 1 km height,

and the characteristics in Fig. 4b are

- (1) constant mixing region around 1.0 km and above 2.5 km.
- (2) decrease of the mixing ratio vs altitude in the altitude regions 0–0.9 km and 1.0–2.5 km.

During the aircraft measurement we recognized a cloud layer at about 1 and 5 km heights for the observation on June 24, 1981, and about 1 km height for the observation on January 13, 1982. The above-mentioned features should be related to such a weather condition.

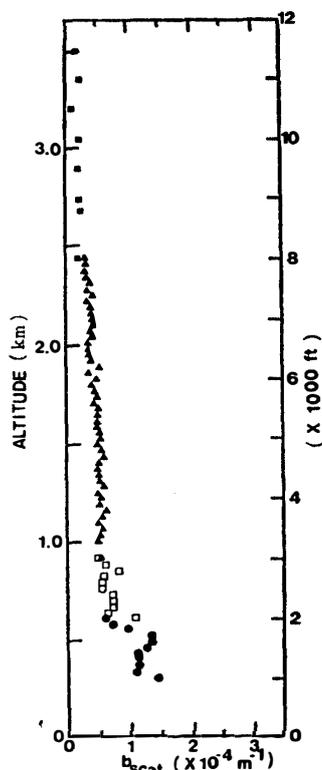


Fig. 5. Vertical profile of light scattering coefficient on January 13, 1982. This combines four vertical profiles over different points, the same as Fig. 4b.

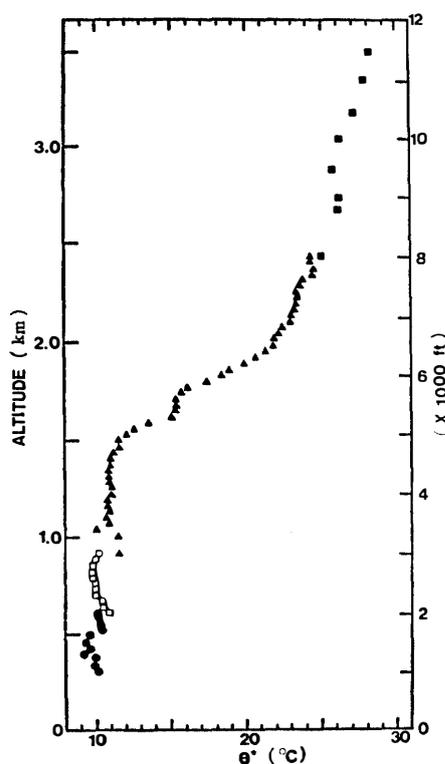


Fig. 6. Vertical profile of the potential temperature on January 13, 1982. This profile also combines four different ones similar to Fig. 5.

Figure 5 shows the vertical distributions of light scattering coefficient, b_{scat} , in a later observation on January 13, 1982. The light scattering coefficient is considered to be proportional to the mass concentration of aerosols M under the condition of relative humidity less than 7% (CHARLSON *et al.*, 1969):

$$M (\mu\text{g}/\text{m}^3) = 3.8 \times 10^5 b_{\text{scat}} (\text{m}^{-1}).$$

Figure 5 suggests that the aerosol concentration is low above 0.6 km, and the influence of aerosols from a local source on the ground surface is apparent below 1 km.

In Fig. 6, we present the distribution of potential temperature estimated from the measured atmospheric temperature on January 13, 1982. Here the potential temperature θ^* is defined by

$$\theta^* = T(z) + \Gamma_d z,$$

where $T(z)$ is the air temperature measured at a height of z and Γ_d is the dry adiabatic lapse rate. A few unstable regions appeared below 0.6 km but there was a very stable region from 1.5 to 2.0 km. This is consistent with the fact that the profiles of b_{scat} and water vapor content have a clear discontinuity near 0.6 km.

4. Discussion

The atmospheric N_2O mixing ratio has been extensively studied since 1966 (GOODY, 1969; SCHÜTZ *et al.*, 1970) and more systematically with electron-capture gas-chromatography since 1975 (SINGH *et al.*, 1977; PIEROTTI and RASMUSSEN, 1977).

The reported values range from 250 to 400 ppbv, according to different investigators, but temporal and spatial variations are reported to be much smaller in each investigation except for the cases of GOODY (1969) and SCHÜTZ *et al.* (1970).

We obtained average N_2O mixing ratios of 326 ± 19 ($n=12$) and 305 ± 8 ppbv ($n=17$), between 0.2 km and 4.1 km heights in summer, and between 0.6 km and 3.8 km heights in winter flight, respectively. Also, we obtained average N_2O mixing ratios of 331 ± 6 ($n=8$) and 324 ± 9 ppbv ($n=21$) on the ambient air in our laboratory in July 1981 and February 1982, respectively.

The larger standard deviation of the N_2O mixing ratio in the summer flight is not only due to lower precision in the analysis but also due to different distributions of N_2O at different altitudes, because the standard deviations at the same altitude (5.5–14.4 ppbv) were significantly lower than those in the same area (14.3–23.8 ppbv). So we consider that higher N_2O mixing ratios at 1.1 km and 4.1 km and lower ones at 0.2 km and 2.9 km reflect the distributions of different air masses, from data of meteorological conditions at the sampling time (*i.e.* passing over the cold front).

On the other hand, the precision of the analysis was revised to a higher level by the time of the winter flight; then we obtained a smaller standard deviation of the total average of the N_2O mixing ratio. The difference between the highest (314.7 ± 1.8 ppbv) and the lowest values (300.4 ± 6.4 ppbv) of N_2O is significantly above the analytical error. The average value of N_2O was significantly lower compared with that of the summer flight, in spite of a slight difference of N_2O mixing ratio in the ambient air of our laboratory. These data suggest the occurrence of spatial and temporal differences of the N_2O mixing ratio in the troposphere, re-

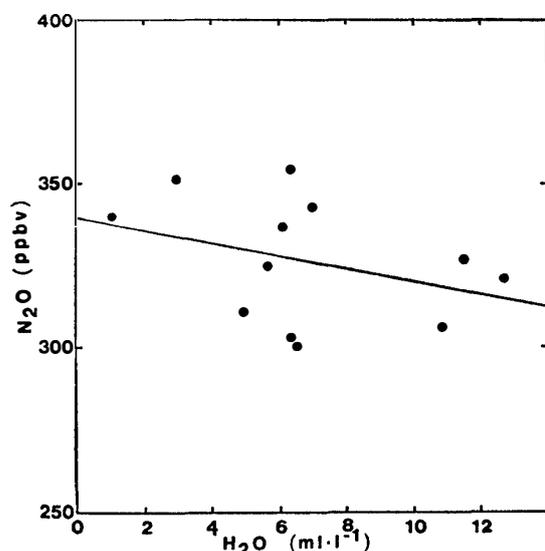


Fig. 7. Regression between N_2O mixing ratio (ppbv of whole air) in whole air and humidity (ml/l) in the sampling air on June 24, 1981.

flecting the source strength of N₂O on the ground level.

BREMNER *et al.* (1980) reported seasonal variability in the emission of N₂O from soil and showed extensive emission of N₂O in summer in contrast to negligible emission in winter. Our result of higher average N₂O mixing ratio in summer than in winter may reflect such a source strength of N₂O.

The humidity of the lower atmosphere is usually not only very high but is also very variable in comparison with the humidity in the middle or upper atmosphere, and therefore the air drawn into sample bottles has possibly significant dependence of the whole air mixing ratio of N₂O on the humidity. According to GOLDAN *et al.* (1978), the N₂O mixing ratio sampled near the ground changed by a few percent owing to the water vapor in the sampled bottles. Here, we also measured the absolute humidity of the sampling air (see Fig. 4). In Fig. 7, we test the dependence of the N₂O mixing ratio in whole air ($= [\text{N}_2\text{O}] / ([\text{H}_2\text{O}] + [\text{N}_2] + [\text{O}_2])$) on the humidity of air ($= [\text{H}_2\text{O}] / ([\text{N}_2] + [\text{O}_2])$) for the summer samples. Although the humidity range was narrow (0.3–4.0 ml/l) and the confidence level of the regression was low, the same tendency (lower N₂O mixing ratio in higher humidity) was also obtained for the winter samples. These data indicate the dependence of the whole air-mixing ratio of N₂O on the fraction of H₂O in the sampled air, and confirm the idea of GOLDAN *et al.* (1978).

The profile of potential temperature in Fig. 6 shows the possibility that vertical air motion existed below about 0.9 km and this effect can be found in profiles of H₂O and the b_{scat} distribution. This means that the dynamical air motion can affect the mixing ratio of N₂O through the H₂O effect, and that the problem of local source effect of N₂O is not so simple.

5. Conclusion

In this paper, we described preliminary results on the distribution measurements of atmospheric N₂O over Nagoya. Our data are not complete enough to completely understand the local N₂O source effect and the problem of the water vapor effect on the mixing ratio of N₂O, and further observation is necessary. However, we can conclude, at least, that the observation system of N₂O was practically established.

Our results of average N₂O mixing ratios (326.4 and 305.1 ppbv in the summer and winter flights, respectively) are lower than those reported by PIEROTTI and RASMUSSEN (1977) but higher than recent ones (GOLDAN *et al.*, 1981; WEISS *et al.*, 1981). The absolute accuracy of atmospheric N₂O measurements depends mainly on the standard N₂O preparation (*cf.* GOLDAN *et al.*, 1981).

In the near future, we are planning the following work as the next stage of this research series: (1) Intercalibration of N₂O mixing ratio using a standard sample, and (2) Measurement of N₂O mixing ratio at Syowa Station, Antarctica. Task (1) is necessary due to the great desirability of directly intercomparing data from many laboratories, some of which disagree by as much as 15% (see PIEROTTI and RASMUSSEN, 1977). Knowledge about the global distribution of N₂O is necessary to discuss the residence time of N₂O in the atmosphere, and the local source

effect of N_2O on its global budget. Recently, a large number of measurements have been reported; however, the information on the emission rate or the density distribution in the high latitude region is very limited, and this becomes a serious problem in determining the global distribution of N_2O and its time change. Therefore the work (2) should make an important contribution. Additionally, the measurements at Syowa Station are helpful in understanding the elementary processes of N_2O emission since the polar region has remarkably different conditions than other regions.

The boundary conditions of Antarctica apparently differ from those in middle and low latitude regions. Most of the Antarctic Continent is always covered by snow and/or ice, and this has various effects on the emission processes of N_2O . For example, ice covering the ground and sea surface acts as a barrier for N_2O to flow from the sea and the ground surface to the atmosphere. In addition to this, the microbiological activity is possibly different from the other regions owing to the low temperature environment. Therefore a comparison of the emission rate of N_2O in the polar region with that in the other regions may provide very useful information in understanding various factors which control the emission of N_2O and the global transport of it.

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