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Gas-chromatographic Measurements of Dinitrogen Oxide in Surface Air

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Synopsis. The mixing ratio of N_2O in surface air was measured at Tsukuba between July and September, 1980. The mean was 0.32_5 ppm, and the standard deviation was 0.00_8 ppm. No difference in the N_2O content was found between the air blowing from the northeast or south and calm air.

Recently many measurements of atmospheric dinitrogen oxide have been performed by gas-chromatographic (GC) methods using an electron-capture detector (ECD),[1] and the mixing ratio of the tropospheric N_2O has been found to be almost constant in the range from 0.31 to 0.34 ppm, within about a 10% systematic error among many laboratories.[2–7] In this study, the results of measurements of N_2O in the surface air at the Meteorological Research Institute, Tsukuba, will be reported, since the major source of the atmospheric N_2O is the activity of microorganisms in soils and waters, and since the diurnal variation has, for example, previously been reported in surface air.[8,9]

Experimental

Air 1 m above a ground surface covered with weeds was sampled by means of an air pump into a 2-ml gas sampling tube and was then transferred into a stainless steel column (6 ft× 1/8″ o. d.) filled with Porapak Q or QS (50—80 mesh, 35 °C). GC measurements were performed using a Perkin-Elmer Gas Chromatograph Sigma 1-Sigma 10 system equipped with an ECD (350 °C). A 95% Ar–5% CH_4 mixture was used as the carrier gas at a flow rate of 25 ml min^{-1}. The reference air, which was compressed into a 50-l stainless steel container up to 7 kg cm^{-2} and which could be used for 40—50 d, was first analyzed; then, after one hour, the outdoor air was sampled and analyzed. Such a pair of measurements was repeated every 6 h. The mixing ratio of N_2O in the reference air was determined by a previously reported method.[7] The error in the repeating measurements of the reference air was about 1%, and the detection limit was about 0.00_4 ppm. The total error in the measurements was estimated to be about ±5%.

Results and Discussion

Figure 1 shows the measurement results at Tsukuba from July to September, 1980, together with the temperature and wind data, which were obtained from the Aerological Observatory. The mean value for 60 measurements was 0.32_5 ppm, and the standard deviation (*SD*) was 0.00_8 ppm. Similar results have been obtained in many measurements of surface air in the U.S.A.,[2–5] Japan,[10,11] New Zealand,[2] Australia,[6] and England;[12] *i.e.*, the mixing ratio of N_2O in surface air is almost constant, more than 0.30 ppm.

In Fig. 2, the results are plotted for each wind direction. Figures 1 and 2 show that no difference in the mixing ratio of N_2O was found between the air blowing from the northeast or south and calm air, though a high mixing ratio of N_2O was expected to be observed under calm meteorological conditions at Tsukuba, a suburban agricultural area. The mixing ratios also showed no correlation with the temperature, even under calm conditions. Accordingly, no diurnal variation was observed. Similar results were obtained in Yokohama[13] and Kobe.[11] This must be due to the height of the air sampling;[9] 1 m above the ground surface, N_2O would be well mixed.

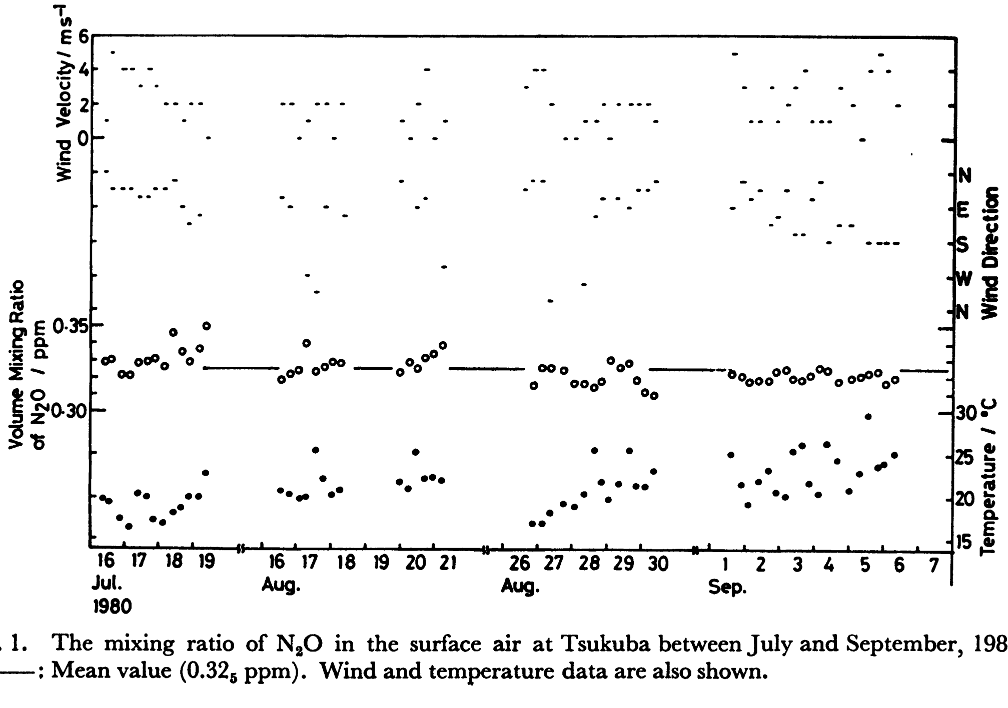

Fig. 1. The mixing ratio of N_2O in the surface air at Tsukuba between July and September, 1980. ——: Mean value (0.32_5 ppm). Wind and temperature data are also shown.

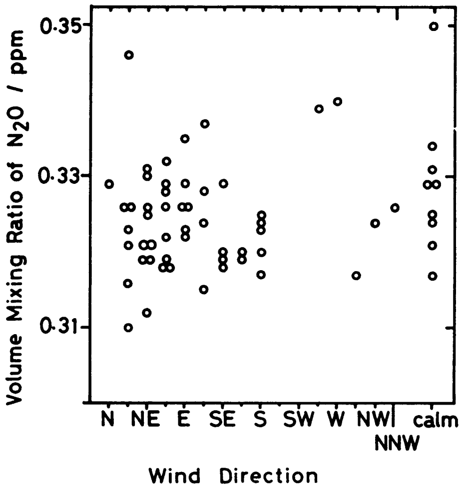

Fig. 2. The dependence of the mixing ratio of N_2O on the wind direction at Tsukuba.

The mean mixing ratio of N_2O observed at Tsukuba was almost equal to that of urban air at Kobe in the same year (mean value=0.319 ppm; *SD*=0.011 ppm).[11] Nearly the same mixing ratios were also observed from several measurements at Koenji, Tokyo, in the previous year (1979). The mean value was 0.32_7 ppm, and the *SD* was 0.00_9 ppm for 16 measurements between March and June.[†] This also shows that no difference in the mixing ratio of N_2O between urban and suburban air was found.

Much lower mean mixing ratios have been reported: 0.26 ppm in the summer of 1976[14] and 0.25 ppm in the summer of 1977[13] at Yokohama. The analytical method was improved from a GC-TCD one to a GC-MS one without preconcentration, and the *SD* of the measurement values decreased from 0.04 ppm to 0.015 ppm. One reason for the discrepancy between the GC-ECD method in the present study and the GC-MS one[13] would be that the calibration gas was composed of pure N_2 instead of purified air in the latter study. It is known at least that the sensitivity of ECD is raised by the presence of O_2.[15]

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[†] Measurements were performed using a column filled with molecular sieve 5A.[7]