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SHORT NOTE

AIRCRAFT MEASUREMENTS OF NOx IN THE LOWER TROPOSPHERE ABOVE THE COAST OF JAPAN

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Abstract

Concentrations of NO_x in altitude regions of 0.5-3.0 km above the coastal area of Japan were measured. The measured mixing ratios range from 1 to 30 ppb depending on the altitude, location and time of the observations. From the measured mixing ratio, it can be said that relatively large amounts of NO_x emitted at ground level are often transported at least as far as 3 km vertically and 200 km horizontally.

1. Introduction

NO_x (=NO + NO_2) plays an important role in the cycle of the chemistry of the troposphere. NO_x is considered to be produced by various processes in the troposphere such as lightning(e.g. Dawson,1980), decomposition of PAN(Crutzen,1979) and photolysis of nitrite in seawater(Zafiriou and McFarland,1981). However the strengths of these sources are quite uncertain. In the global budget of NO_x , anthropogenic emission of NO_x is now considered to be also an important source(e.g. Levine et al.,1981). Therefore it is crucial to determine the background levels of the concentrations of nitrogen oxides to estimate the importance of these sources. Recent

observations of NO_x by McFarland et al.(1979), Kelly et al.(1980) and Kley et al.(1981) have shown that the mixing ratio of NO_x is well below 1 ppb in unpolluted air masses. As a first step in the study of background NO_x, we conducted aircraft surveys of the vertical and horizontal distribution of NO_x in the lower troposphere over the coastal area of the middle part of the Japanese main island of Honshu in 1977 and 1978 in order to investigate the transport of NO_x from anthropogenic source regions.

2. Instrumentation

The instrument used for the measurements of NO_x is a commercial chemiluminescent detecter(Monitor Labs Inc., Model 8440E). NO is measured by the detection of light intensity which occurs as a result of the following reaction, when a sufficient amount of O_3 is present:

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad , \quad NO_2^* \rightarrow NO_2 + h\nu$$

NO_2 is reduced to NO through a molybdenum converter operated at 315°C and then detected by the above chemiluminescent method in the form of NO.The instrument is calibrated in the laboratory with NO/N_2 gas dynamically diluted from a few hundreds ppm NO/N_2 standard. The detection and accuracy limit of the instrument is 1 ppb. The outside air has been introduced through an aluminum pipe with a 3 cm diameter and a 2.5 m length into a 16-liter sampling chamber to which the detecter is connected. The sensitivity of the instrument is dependent on the pressure and temperature of sampled air. This effect is estimated from laboratory calibration to induce an error of about 30 % for the absolute values of the observed mixing ratio of NO_x at maximum altitude for the present experiment.

3. Observation

3-1. Vertical distribution

The locations and times of the aircraft measurements of NO_x vertical distribution are shown in Figure 1. Six NO_x profiles obtained in 1977 and 1978 are shown in Figure 2. All of the profiles have been obtained from measurements above the Pacific coast area except for the profile obtained at point 3 in Figure 1, which is located above the

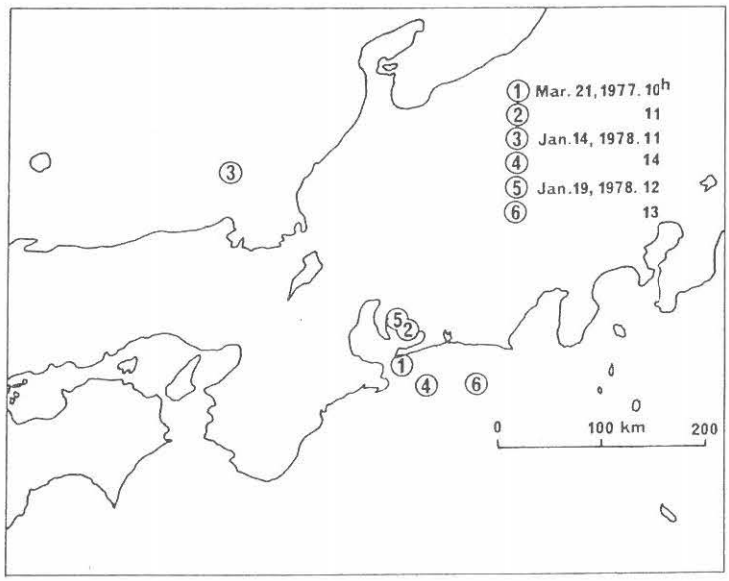

Figure 1;Locations of the aircraft measurements of the vertical distribution of NO_x.

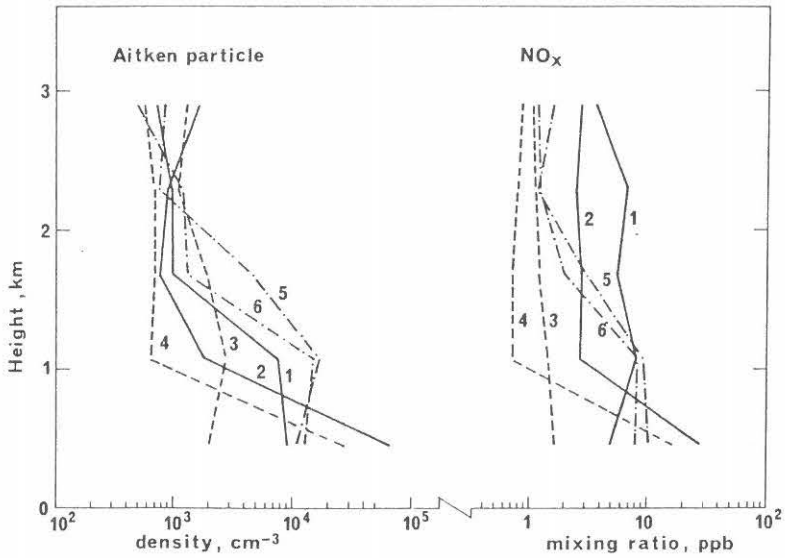

Figure 2; Measured vertical profiles of NO_x and Aitken particle concentrations. The number indicates the location shown in Figure 1.

Sea of Japan 50 km distant from the coast. At the lowest observation altitude of 0.5 km, the concentration ranges 5-30 ppb on the Pacific side while it is below 2 ppb on the side of the Sea of Japan. The concentration at the lowest altitude is significantly influenced by ground emission . Generally the Pacific coast is industrially active with a larger population and heavier traffic than the region facing the Sea of Japan. In addition to this, generally north-westerly wind prevailed during the observation period; this seems to have kept point 3 relatively free from possible direct pollution from land. On the other hand , the NO_x mixing ratio at higher altitudes does not necessarily reflect this situation. The NO_x mixing ratios at points 3 to 6 are lower than the detection limit above 2 km, while the mixing ratios at points 1 and 2 remain higher than 2 ppb even at 3 km. From this result it seems probable that transport processes, mainly in the vertical direction, determine the NO_x concentration above 1.5 km.

Densities of Aitken particles with radii larger than 0.012μm, which were simultaneously measured with a Pollak type counter(Takagi et al.,1981) are also shown in Figure 2 for reference. In Figure 3, all of the concentrations obtained for Aitken particles are plotted against the corresponding mixing ratios of NO_x. The correlation coefficient of the both quantities is 0.82.

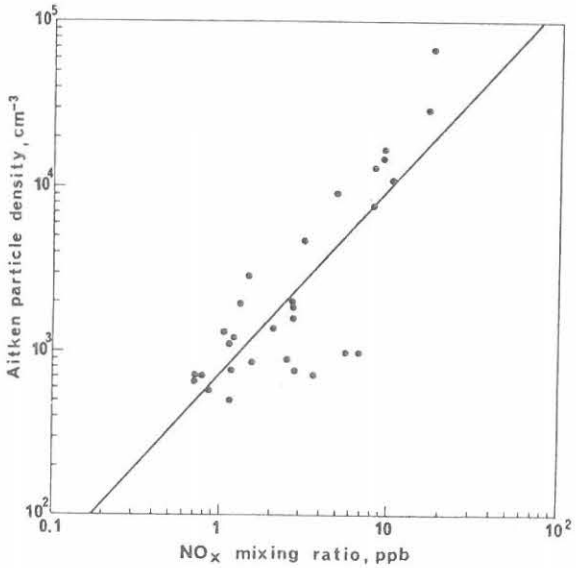

Figure 3; Aitken particle density versus NO_x mixing ratio obtained by the measurement of the vertical distributions. The straight line is the least square fit of the data.

It can be said that the general trends of the profiles, as well as the absolute values of Aitken particles, the bulk of which are also considered to be of anthropogenic origin, are well correlated with those of NO_x. The parallelism between NO_x and aerosol profiles is interpretted to mean that both types of pollutants are emitted from the same region and transported in the same mode. To explain further the differences of each NO_x profile quantitatively, detailed information concerning the sources of NO_x on the ground and the conditions of transport would be required.

3-2. Horizontal distribution

To investigate also the horizontal transport of NO_x from land to sea we made a two dimensional survey over a rectangular sea area(200x250 km) adjacent to land at an altitude of 1 km on March 26, 1977. The NO_x contour map, which was obtained from the measurememts taken during the 4-hour flight from 9:30 to 13:30, is given in Figure 4. The NO_x concentration is 6 ppb near the coast and drops sharply to 1-2 ppb toward the sea, but it again increases to 3 ppb at the outer edge of the observation area. Aerosol particles simultaneously measured on the same flight show similar pattern to that of the NO_x concentrations(Morita et al.,1977). This pattern is rather odd and quite different from the usual concept that NO_x disperses uniformly from land source area toward the sea. Some possible causes of this

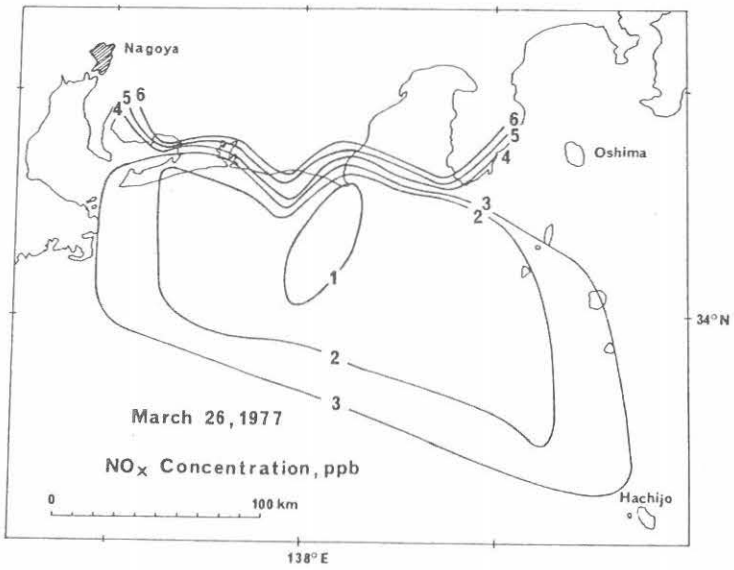

Figure 4; Contour of the NO_x concentration measured at the altitude of 1 km on March 26,1977.

abnormal pattern do come to mind, however. First we shall consider the possibility of wind change during the 4-hour observation period. The outer boundary of the contour was obtained from the measurement at an earlier time, and the low mixing ratio in the center of the observation area was recorded in the afternoon near the end of the observation. At the altitude of 1 km, the local wind system, such as an alternation of land breeze to sea breeze in the early morning, may have some influence on NO_x distribution. Another possibility is that the subsiding air mass of a scale smaller than 50 km may have cleaned just the middle part of the observation area. However, we have no observational support for these hypotheses. Anyway, it can be said that the pollutants are transported as far as 200-300 km from the Japanese Islands, retaining considerably higher concentrations depending on the weather situation.

4. Summary

We have seen that NO_x emitted from land areas can reach as high as 3 km vertically and can be transported horizontally at least 200-300 km downwind. It will therefore be interesting to make subsequent observations at areas more distant from land to study the fate of anthropogenically emitted NO_x in relation with natural sources and sinks. This will require, however, a more sophisticated NO_x detecter with a much higher sensitivity. We are making efforts to develop an instrument which is able to answer this requirement.

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