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## GROUND BASED NO<sub>2</sub> and O<sub>3</sub> MEASUREMENTS BY VISIBLE SPECTROMETER AT SYOWA BASE (69°S), ANTARCTICA

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### ABSTRACT

The column amounts of NO<sub>2</sub> and ozone have been measured using visible spectroscopy at Syowa Base (69°S) since March 1990. Ozone was also measured at the same location with a Dobson spectrometer as well as ozonesondes being flown regularly. The characteristic features of the seasonal and diurnal variations of NO<sub>2</sub> are presented. The column ozone values from the visible spectrometers are compared with the Dobson data. The very low values of NO<sub>2</sub> in mid winter and early spring are consistent with the conditions predicted to be needed for heterogeneous ozone destruction in early spring. In late spring and summer of 1991, NO<sub>2</sub> amounts were considerably smaller than in 1990, presumably due to the effect of Mt. Pinatubo eruption.

### 1. INTRODUCTION

Reactive nitrogen plays important roles in the chemistry of the cold polar stratosphere. HNO<sub>3</sub> forms aerosols composed of nitric acid trihydrate at temperatures higher than required for water ice particle formation. These aerosols can provide sites for heterogeneous reactions. On the other hand, NO<sub>2</sub> sequesters ClO by converting it into ClONO<sub>2</sub>. The removal of NO<sub>2</sub> through denitrification is essential for the significant chemical loss of ozone by active chlorine.

The column amounts of NO<sub>2</sub> and ozone can be measured by observing scattered sunlight coming from zenith direction. For this purpose, scanning spectrometers have been operated since March 1990 at Syowa Base, Antarctica.

### 2. SLANT COLUMN DATA FOR 1990

Two Jobin Yvon monochrometers using focal lengths of 200 mm (H20) and 320 mm (HR320) have been modified for automatic operation for twilight observations. The spectrometer systems and the analysis technique are the same as described in Johnston and McKenzie [1989]. The measurements by H20 started on March 26 (day number 85) and those by HR320 started on May 7 (day number 127) in 1990. The slant column amounts of NO<sub>2</sub> and ozone for solar zenith angles (SZAs) obtained by H20 are shown in Figure 1(a) and (b) and by HR320 are shown in Figure 2(a) and (b). At Syowa base between May 26 (day 146) and July 18 (day 199) in winter, the SZA does not become smaller than 90 degrees. On the other hand between November 26 (day 330) and January 16 (day 16) in summer, the SZA does not become larger than 90°. Due to the change of the air mass factors depending on the SZAs, the slant column amounts obtained at SZAs different from 90° need to be corrected to be compared with those at SZA = 90°. The average SZA dependence of the column amount of NO<sub>2</sub> and ozone just prior to day 146 and just after day 199 has been used to estimate the slant column amounts at SZA = 90° from the data at SZAs of 91, 92, and 93°. Similarly, between the day 330 and 16, slant column amounts for SZA = 90° have been estimated from the data at SZA = 89, 88, and 87°.

Vertical column amounts of ozone have been derived from the slant column amounts assuming an air mass factor of 18 and compared with the Dobson values in Figure 1 (b). Dobson measurements were made by the Japan Meteorological Agency. Generally the visible and Dobson measurements agree to within about 10 %.

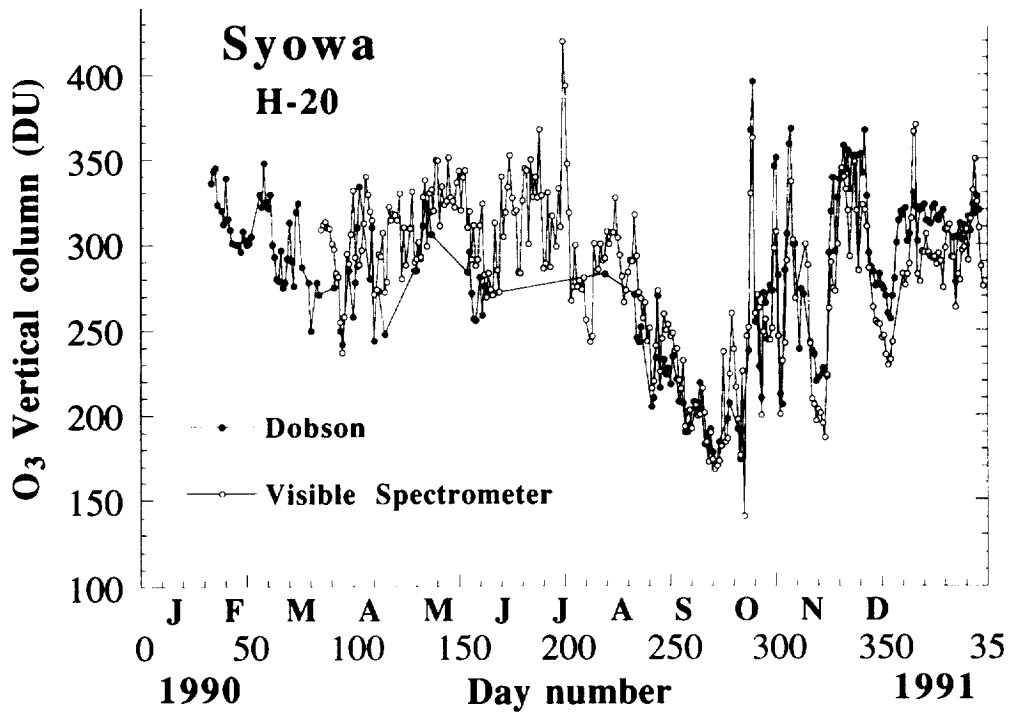


Fig. 2 (a): Total ozone observed with an H20 visible spectrometer at Syowa station in 1990 (open circles). Air mass factor of 18 was used to convert the observed slant column into the vertical column. Measurements by a Dobson spectrometer at the same site are shown as closed circles.

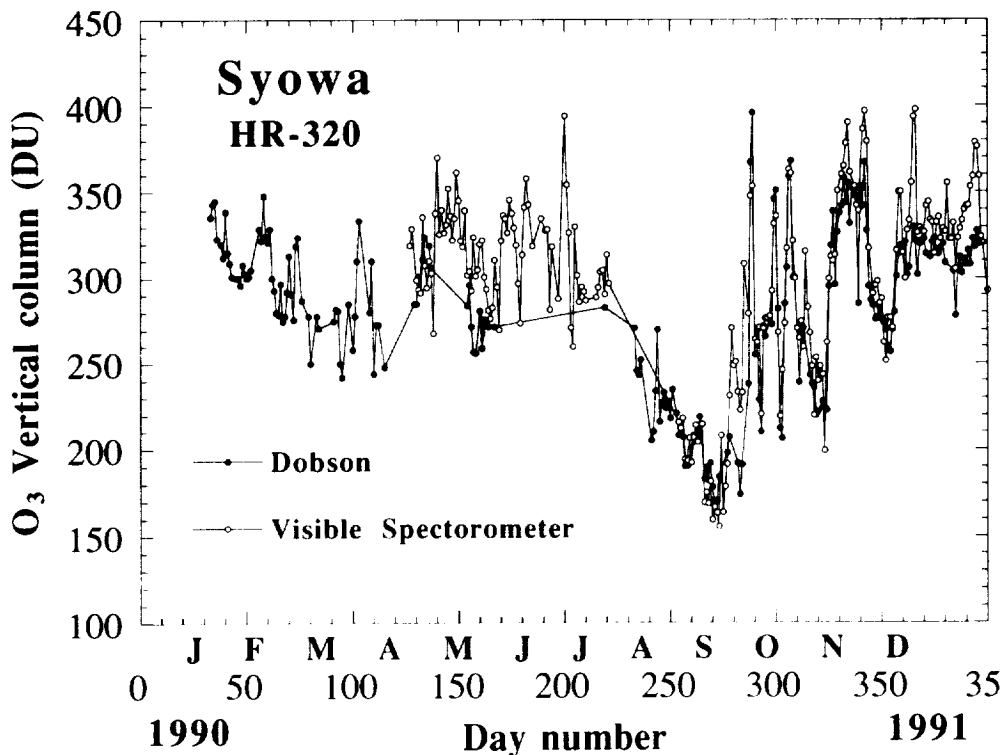


Fig. 2 (b): Same as Fig. 1 (a) but for the results from an HR320 spectrometer.

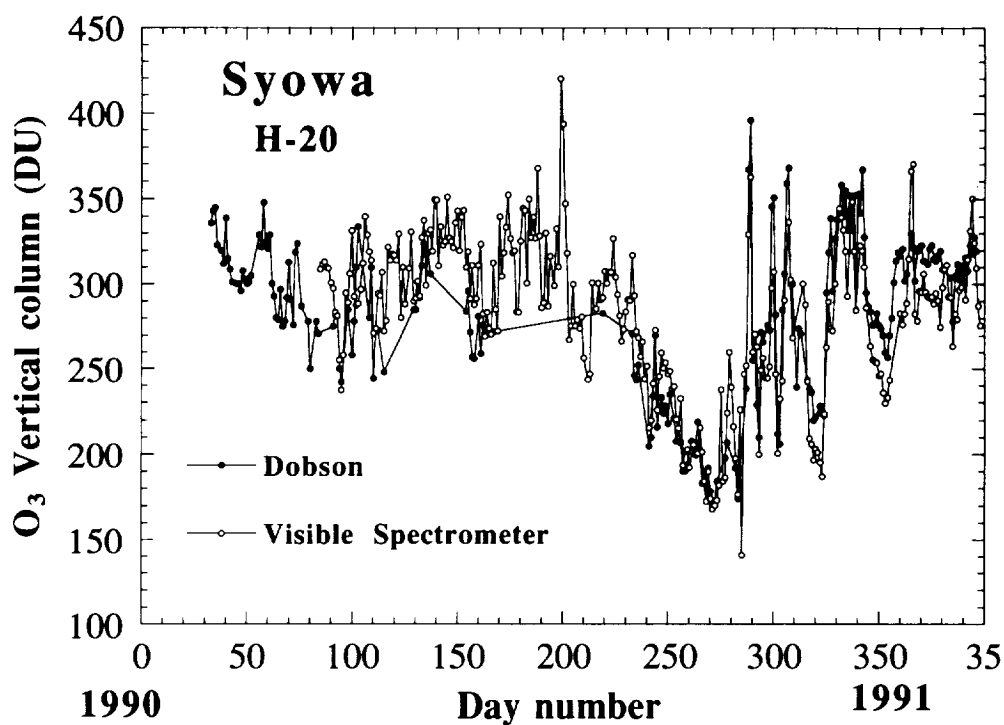


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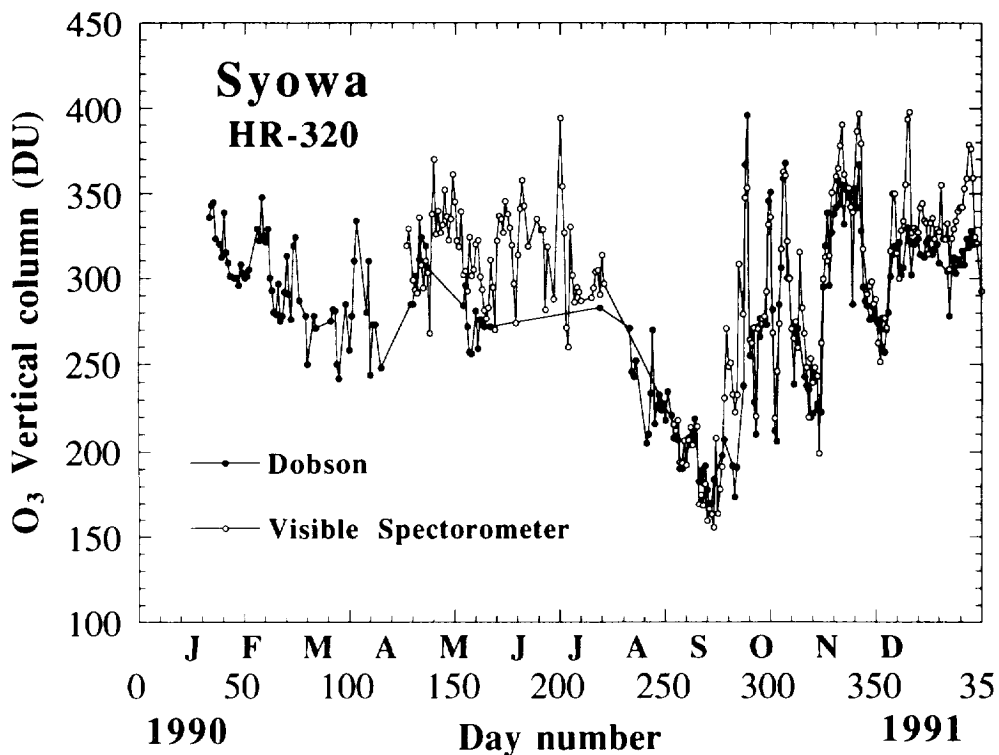


Fig. 2 (b): Same as Fig. 1 (a) but for the results from an HR320 spectrometer.

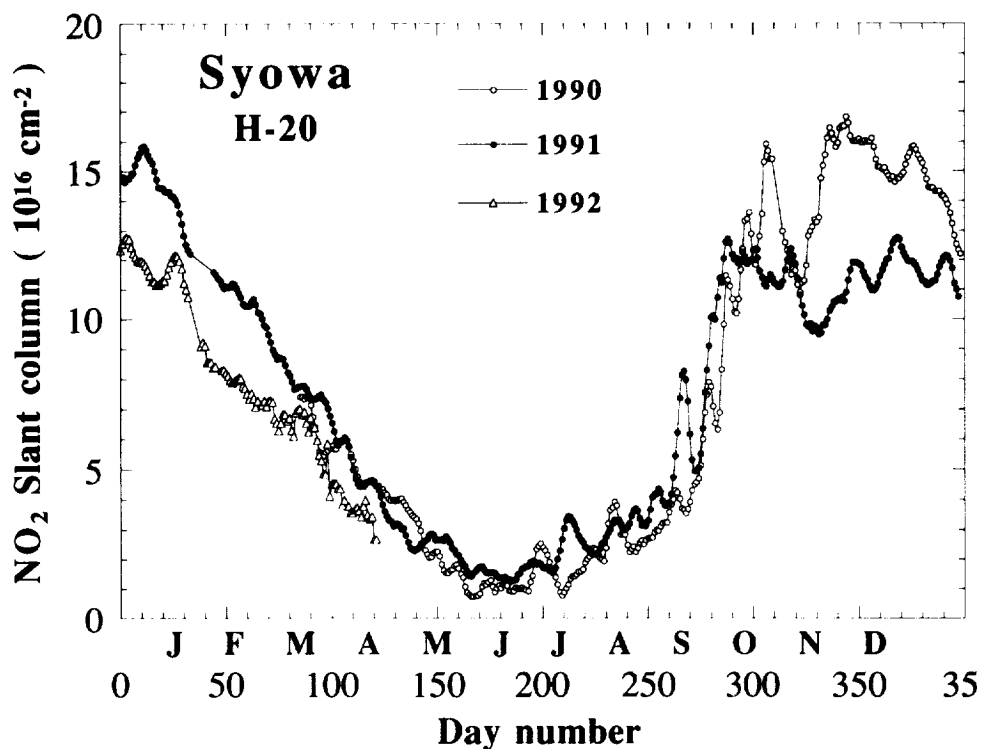


Fig. 3: 5-day running mean of the NO<sub>2</sub> column amount obtained in the evening from 1990 to April 29, 1992.

### 3. SEASONAL VARIATION of NO<sub>2</sub>

NO<sub>2</sub> column amounts continued to decrease in autumn and reached less than  $1 \times 10^{16} \text{ cm}^{-2}$  in mid-winter. It started to increase around day 210, but the rate of change in early spring is significantly smaller than in autumn. This feature has also been observed at other sites in Antarctica [Keys and Johnston, 1988]. NO<sub>2</sub> started a rapid increase around day 270, when ozone also started to increase due to the mixing of polar air with mid-latitude air. Most of the large changes in NO<sub>2</sub> between day 270 and 335 are associated with the changes in ozone. The large decrease in ozone around day 320 is due to transport of ozone poor air from higher latitudes to the latitude of Syowa. On the other hand, the decrease in ozone around day 350 is not associated with any corresponding change in NO<sub>2</sub>. After mid-summer, NO<sub>2</sub> started to decrease due to the shortening of daylight hours.

The seasonal variations of NO<sub>2</sub> observed in the afternoons in 1990, 1991, and 1992 are compared in Figure 3. The PM NO<sub>2</sub> amounts shown are the 5 day-running mean values. The seasonal variation in NO<sub>2</sub> in 1990 and 1991 is quite similar

between day 80 and 300. However, the NO<sub>2</sub> amounts became considerably smaller from day 320 in 1991 through 1992. This is presumably due to the effect of the increased amount of stratospheric aerosols associated with the Pinatubo eruption which occurred in June 1991. At 45°S, significant decreases in the NO<sub>2</sub> slant column were observed from August 1991. Part of the apparent decrease in the NO<sub>2</sub> can be due to the change in the effective scattering geometry caused by the increase of aerosol concentrations [Johnston *et al.*, 1992]. However a net decrease in NO<sub>x</sub> through heterogeneous reactions is suggested as likely to be contributing to the observed decrease in NO<sub>2</sub>. A similar effect is suggested to be occurring over Syowa.

### 4. DIURNAL VARIATION OF NO<sub>2</sub>

The ratio of the NO<sub>2</sub> amount at sunrise to that at sunset (AM/PM ratio) is a good indicator of the degree of the diurnal variation. It has been calculated from a 5-day running mean on the NO<sub>2</sub> slant column amount and is shown in Figure 4. The AM/PM ratio increases from about 0.7 in autumn to 0.9 in

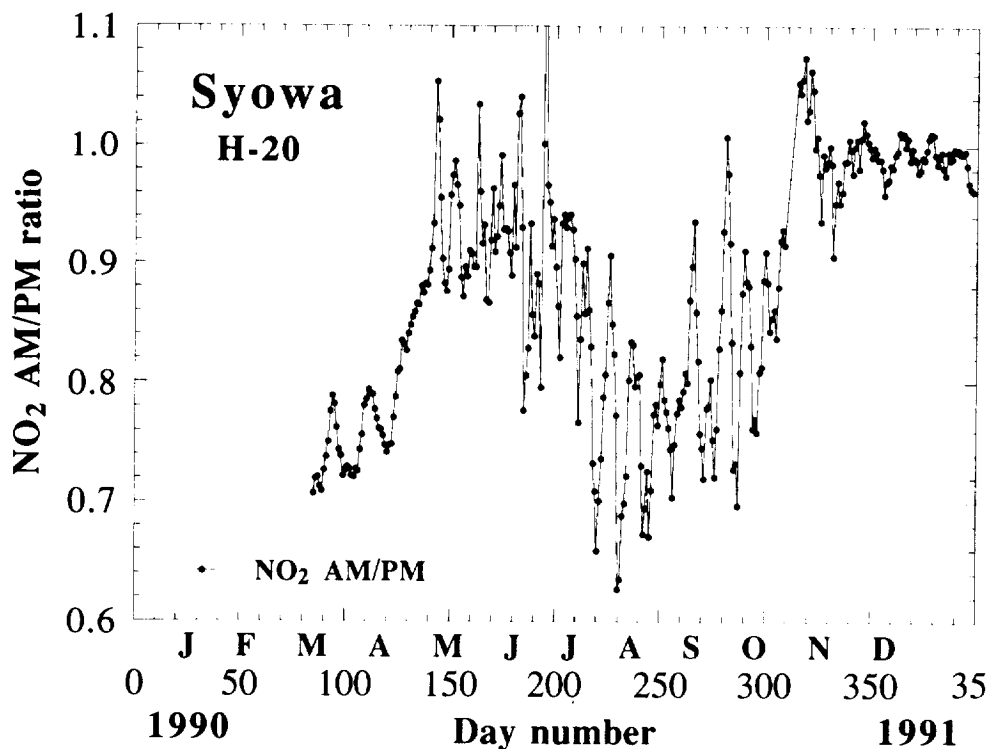


Fig. 4: Ratio of the  $\text{NO}_2$  amount obtained in the morning to that in the afternoon for 1990. The ratio was calculated from the 5-day running mean.

winter. At the end of winter around day 250, it again decreases to be between 0.7 and 0.8, although with much larger variability than in autumn. The large AM/PM ratio in mid winter is mostly due to the very small time difference between the morning and evening observations and partly due to the lack of photodissociation of  $\text{N}_2\text{O}_5$  at SZAs larger than  $90^\circ$  even at noon.

As can be seen from the AM/PM ratio, the diurnal variation stopped around day 315 and started again around day 30. Between day 315 and day 30, the minimum SZA is less than  $93^\circ$ . This feature is in agreement with the results of Keys and Johnston [1986] where they suggest  $\text{NO}_3$  is effectively photodissociated for SZA smaller than  $93^\circ$  and this in turn prohibits nighttime conversion of  $\text{NO}_2$  into  $\text{N}_2\text{O}_5$ . The amount of  $\text{NO}_2$  also started to decrease from day 30 due to the initiation of the conversion of  $\text{NO}_2$  into  $\text{N}_2\text{O}_5$ .

#### Acknowledgments.

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