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Measurement of NO_2 and analysis of relationship between stratospheric NO_2 and O_3 over Zhongshan Station, Antarctica

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Abstract We have already continually taken the measurement of total column amount of O_3, NO_2 as well as stratospheric O_3, NO_2 over Zhongshan Station, Antarctica. This paper analyzes the seasonal variation of NO_2 and its relationship to O_3 during the Antarctic Ozone Hole in 1993～1995 and points out that the decrease of atmospheric NO_2 is one of the important reason to the strengthening of Antarctic Ozone Hole.

Key words Antarctica, Zhongshan Station, Ozone Hole, nitrogen dioxide.

1 Introduction

Since the discovery of Antarctic Ozone Hole in 1985 by Farman, through the recognition of the self-catalytic reaction to the destruction of ozone caused by nitrogen and chloride compound, especially the nitrogen dioxide during the Antarctic Ozone Hole period, it has been proved that NO_2 is very important in the equilibrium of ozone layer, especially in the forming and developing of Antarctic Ozone Hole. The stratospheric NO_2 is not only taking part in the self-catalytic reaction to the destruction of stratospheric ozone (the ozone amount is in the direct ratio to the [NO_2]/[NO] ratio), but it also can react with ClO to form $ClONO_2$, and thus weaken the chloride's destruction to ozone. It has been demonstrated through laboratory experiment, theoretical analysis and field observation that the decrease of stratospheric NO_2 amount is caused by the increase of atmospheric aerosol which is rich of sulphide because of the eruption of Pinatubo volcano. And the decrease of stratospheric NO_2 has sped the destruction of ozone and thus deepened the Antarctic Ozone Hole in the passed few years (Koike *et al*. 1993; Solomon *et al*. 1994).

From February, 1993, we have continually taken the measurements of total column amount of O_3, SO_2, UV-B radiation as well as the ozone profile through the Umkehr method in Zhongshan Station (69.22°S, 76.23°E). And we also have taken the measurements of total column amount of NO_2 as well as the stratospheric and tropospheric NO_2 amount by using the visible wavelength range. This paper chiefly analyzes the seasonal variation of NO_2 and the relationship between NO_2 and O_3 during the Antarctic Ozone Hole period.

2 Measurement method

When taking the measurement of total column amount of NO_2 by the Brewer Ozone Spectrophotometer, we use the wavelength of 431.42 nm, 437.34 nm, 442.82 nm, 448.10 nm, 453.22 nm as the measurement wavelength. We also use the direct sunlight, direct moonlight, zenith skylight as the light source to take the measurements. At the same time, we can continually take the measurements of stratospheric and tropospheric NO_2 amount by using the zenith scattering skylight as the light source during the sunrise and sunset period when the solar zenith angle is 75°～90°. This is just because that during the sunrise and sunset period the absorption of NO_2 to zenith skylight is chiefly due to the total column amount of NO_2 and its vertical distribution. Along with the changing of solar angle, the NO_2 amount at different height is determined by the ratio of solar light intensity at different wavelength. Through the multi-scattering model for zenith skylight at different height, the distribution of stratospheric and tropospheric NO_2 can be calculated. The method of calculation of the vertical distribution of NO_2 is a little similar but still has great difference to the Umkehr method of getting the ozone vertical distribution. The detailed retrieval method can be referenced to Mckenzie *et al*. (1991). The measurement methods of ozone and UV-B can be seen in Zhou *et al*. (1995). For the world standard Brewer instrument, the measurement error of total column amount of ozone is less than 1%, and the measurement error of total column amount of NO_2 is 1%～2%. Each time before taking any kinds of measurements, the instrument automatically do the calibration of wavelength and intensity using the mercury lamp and tungsten lamp respectively.

3 Analysis of measurement results

Fig. 1 shows the three years' (1993, 1994, 1995) daily means variation of total column amount of O_3 and NO_2, through the figure we can see that generally speaking the daily mean value in 1993 and 1995 of total column amount of NO_2 is lower than that in 1994 during the springtime Antarctic Ozone Hole period, but for the comparison of NO_2 in 1993 and 1995, it is a little lower in 1995 than in 1993. This changing trend of total column amount of NO_2 is similar to that of total column amount of O_3. Summarily, the total column amount of ozone in the 1995 Ozone Hole period is apparently lower than that of 1993 and 1994, and the total column amount of ozone in 1993 is a little lower than that in 1994. Through the above analysis, we firstly can see the strengthen trend of Antarctic Ozone Hole in general in the three years and also you can find the bi-oscillate trend of ozone amount along with the bi-oscillate trend of global atmosphere. And, furthermore, for the three year's Antarctic Ozone Hole, not only the lowest value of total column amount of O_3 in 1995 is much lower than that in 1993 and 1994, but also the lasting time of 1995 Antarctic Ozone Hole is much longer than that of 1993 and 1994. For the seasonal variation of total column amount of NO_2 in a year, from summer to autumn, the total column amount of NO_2 changes from its maximum value to its lowest value. And at the winter polar night time, be-

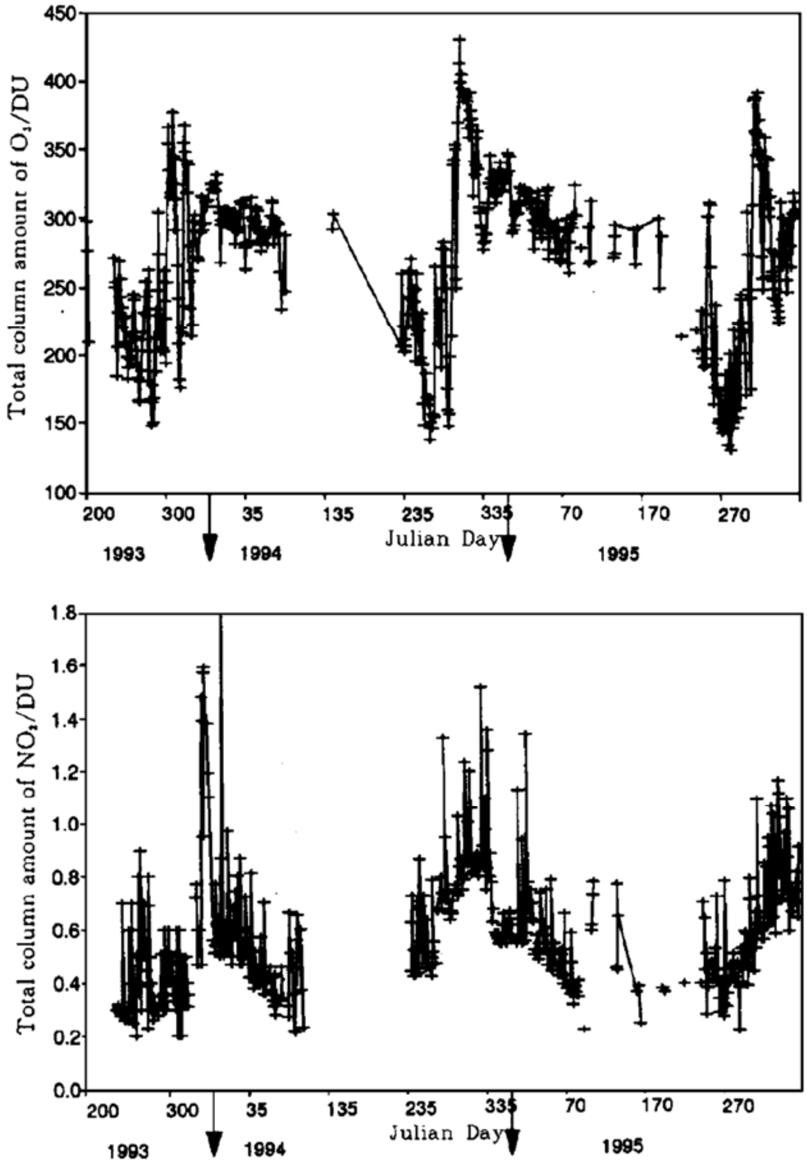

Fig. 1. The daily variation of total column amount of O_3, NO_2 in 1993～1995.

cause of the interchanges among NO, NO_2, NO_3, N_2O_5 and O_3, the total column amount of NO_2 is far more less than that in summer time but a little higher than spring time Antarctic Ozone Hole and early winter time (The measurement values of total column amount of NO_2 and O_3 in winter are from the moonlight measurements). The total column amount of NO_2 reaches its lowest value in a year at spring time Antarctic Ozone Hole period. But through Table 1 and Fig. 2 we can see that there is a good direct ratio relationship between the daily means of total column amount of NO_2 and O_3 (the relative coefficient is 0.868 through the analysis of least square method), this might be because that the stratospheric NO_2 takes part in the heterogeneous reaction occurring on the surface of polar stratospheric cloud. This also shows the significant role of NO_2 amount to the development of Antarctic Ozone Hole. In fact, the decrease of NO_2 amount can not only decrease the trend of the reduction of O_3 caused by the self-catalytic reaction of NO-NO_2 but also can decrease the rates of self-catalytic reaction from ClO to $ClONO_2$ and Cl to $ClNO_2$ and thus decrease the reduction of O_3. From Fig. 2 we also can see that from the happening time of Antarctic Ozone Hole in early August to the most serious time of early October the NO_2 amount has a trend of decreasing. And the decrease of NO_2 amount reduces the forming rate of O_3. That the consuming of ozone is larger than the forming of ozone is one of the important reason for the development of Antarctic Ozone Hole from its forming to its strengthen. From spring time to early summer time, the NO_2 amount has a trend of increasing and along with the close of Ozone Hole, the NO_2 amount has a large increase. But in the early December of 1995, along with the decrease of total column amount of ozone after Ozone Hole period (in 1995, the total column amount of O_3 reaches over 320 DU after the close of Ozone Hole in early November, but in early December its value decrease to 220～270 DU again, and thus the value of UV-B goes over its value in Ozone Hole period), the stratospheric NO_2 decrease again from 0.4 DU to 0.1 DU and general speaking the NO_2 amount reaches its highest value around mid-summer time. We can get the same results from the analysis of NO_2 and O_3 data in 1993 and 1994 Ozone Hole period, except there exists no decrease in early December. Our measurement results are quiet similar to the measurement results in Mcmurdo Station made by Keys and Johnston (1988) and in Syowa Station made by Kondo *et al*. (1992).

Table 1. The monthly means of total column amount of O_3, NO_2 from August to December in 1993～1995

Year	Month	O_3/DU	NO_2/DU	Year	Month	O_3/DU	NO_2/DU
1993	Aug.	238.7	0.35	1994	Nov.	360.0	0.89
1993	Sept.	207.4	0.44	1994	Dec.	318.0	0.81
1993	Oct.	226.0	0.41	1995	Aug.	213.0	0.39
1993	Nov.	285.8	0.27	1995	Sept.	205.8	0.42
1993	Dec.	306.5	0.88	1995	Oct.	177.9	0.41
1994	Aug.	224.8	0.55	1995	Nov.	314.9	0.64
1994	Sept.	199.6	0.54	1995	Dec.	255.7	0.79
1994	Oct.	248.7	0.70				

Table 2. The comparison of total column amount of O_3, NO_2 and stratospheric and tropospheric NO_2 amount in 1995(Unit: DU)

Month	O_3	NO_2	Strato. NO_2	Trop. NO_2	Month	O_3	NO_2	Strato. NO_2	Trop. NO_2
Jan.	315.2	0.62	0.388	0.356	Sept.	205.8	0.42	0.158	0.261
Feb.	299.0	0.54	0.298	0.251	Oct.	177.9	0.41	0.206	0.218
March	276.3	0.37	0.181	0.185	Nov.	314.9	0.64	0.385	0.253
April	283.5	0.56	0.205	0.356	Dec.	255.7	0.79	0.256	0.538
Aug.	213.0	0.39	0.216	0.185					

Table 2 shows the comparison of monthly means of total column amount of O_3 and NO_2 with the stratospheric and tropospheric NO_2. Fig. 3 shows the comparison of stratospheric NO_2 amount from morning(AM) and evening(PM) zenith skylight measurements to the total column amount of NO_2. From Table 2 and Fig. 3, we can see that the stratospheric NO_2 amount from PM measurement is larger than that from AM measurement. The tropospheric column NO_2 amount during and after Antarctic Ozone Hole changes along with the changing of the total column amount of NO_2 and is chiefly determined by the joint effect of the tropospheric photochemical process and

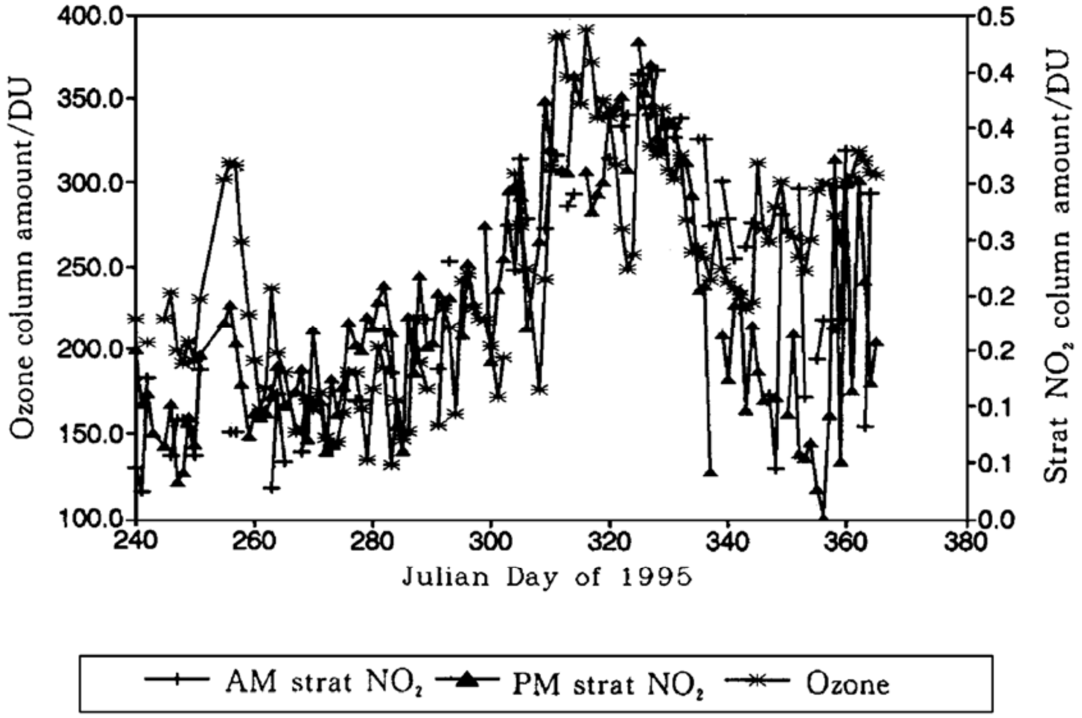

Fig. 2. Stratospheric NO_2 amount versus total column amount O_3 during Antarctic Ozone Hole in 1995.

the weather condition and pollution near the ground. But for the stratospheric NO_2 amount in and out of Antarctic Ozone Hole period, it changes greatly. The stratospheric NO_2 amount has a better direct ratio relationship to the total column amount of O_3 than the tropospheric ozone.

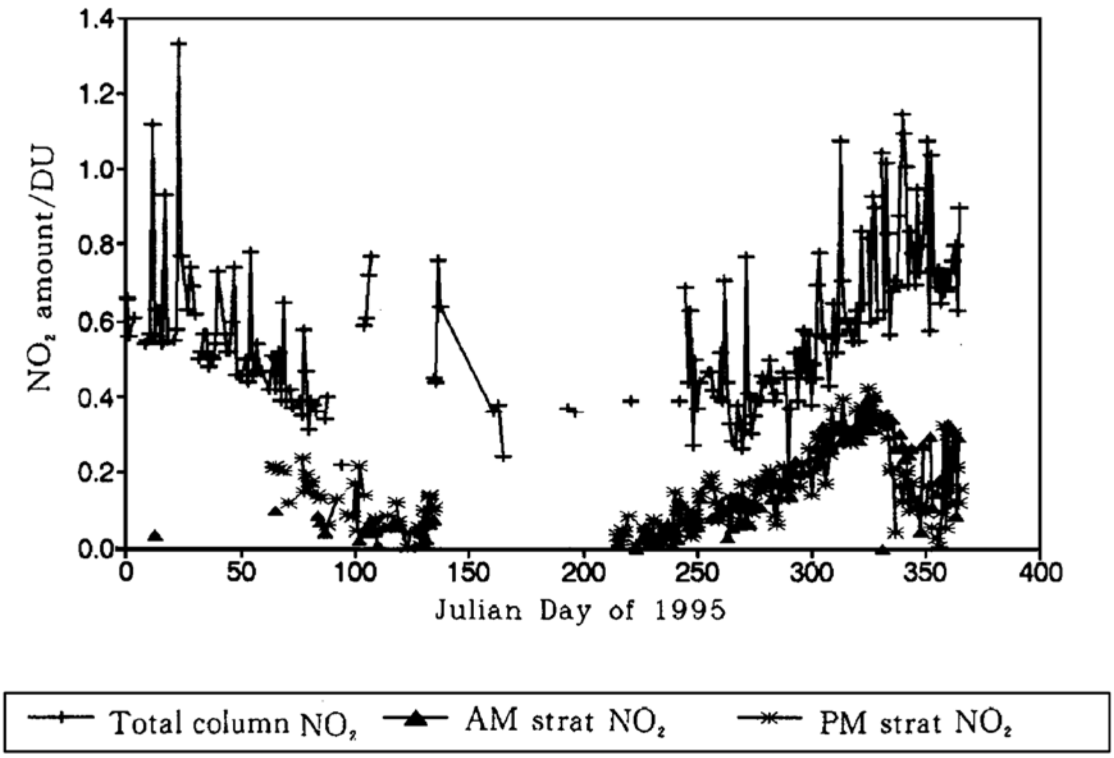

Fig. 3. The comparison of stratospheric and tropospheric NO_2 amount with total column amount of NO_2 during and after Antarctic Ozone Hole in 1995.

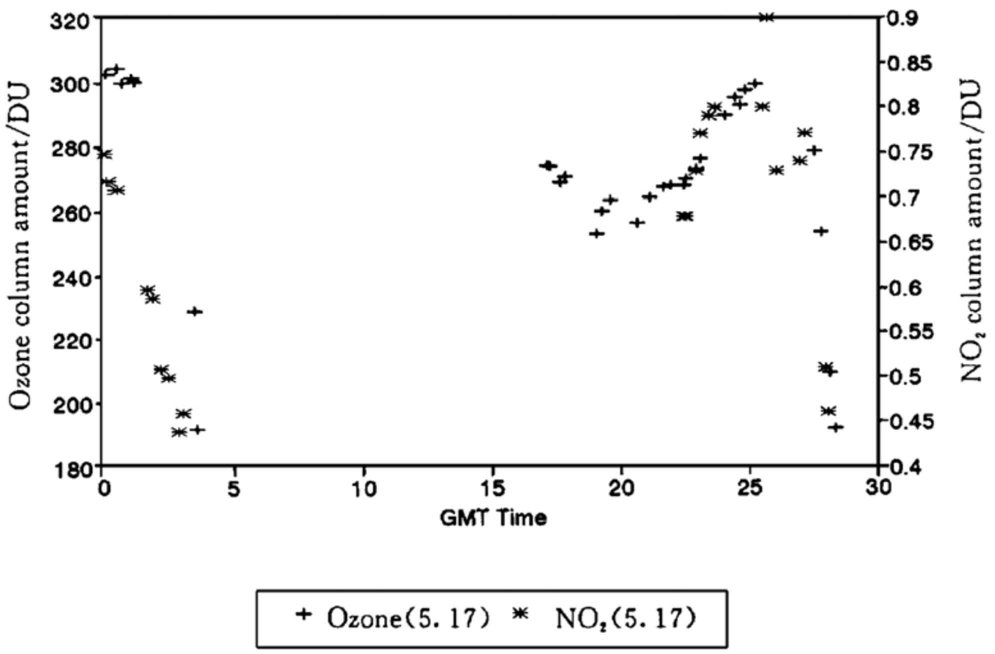

Fig. 4a. The total column amount of O_3, NO_2 measured by moon light on May 17, 1995.

Fig. 4a shows the daily variation of the total column amount of O_3, NO_2 measured by moon light on May 17,1995. From the figure and the other measurement results during the full moon periods from April to August,we can find that under stable weather condition, the NO_2 amounts increase greatly after sunset and decrease slowly during the night and decrease greatly again before sunrise. Fig. 4b shows daily variation of the total column amount of O_3, NO_2 measured by sun light on October 10 and 18, 1995. From the two figures and the other O_3, NO_2 measurement results in the same period, we can find that no matter in the polar night period or the Ozone Hole

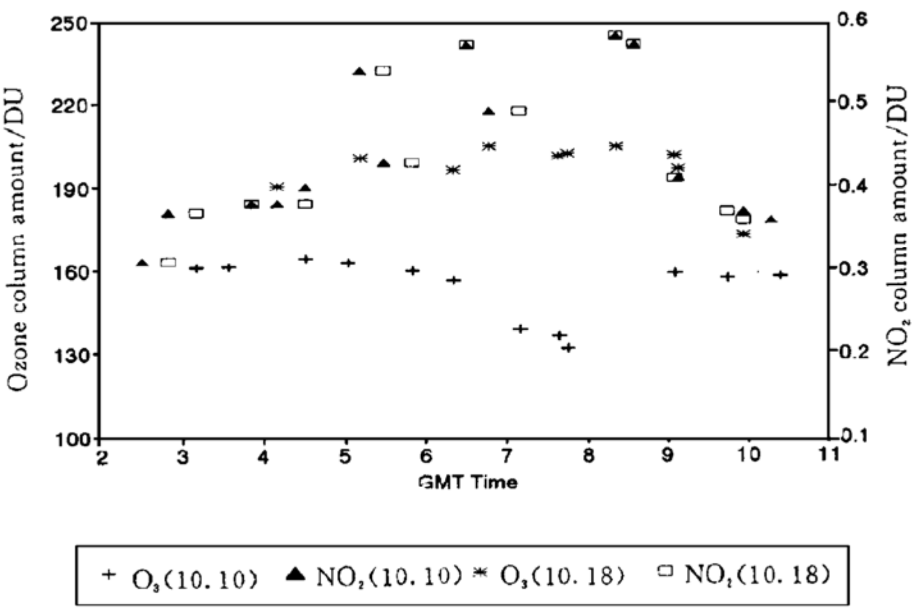

Fig. 4b. The total column amount of O_3, NO_2 measured by sun light on October 10 and 18, 1995.

period, there is a good sensitive relationship between the total column amount of NO_2 and O_3. This shows that although the intensity of sun light is about 10^5 times larger than that of moon light and there is a little difference of stratospheric temperature in the two periods, the heterogeneous reaction happened on the surface of polar stratospheric cloud in the two periods. The only difference is that the reacting ratio under sun light is much larger than that under moon light (The prerequisite is the existing of low stratospheric temperature). If we further analyzes the daily variation of total column amount of O_3 and NO_2 in the passed three years and the meteorological sounding data of Davis Station which is about 100 km away from Zhongshan Station, we can find that under stable weather condition (little wind in stratosphere and lower temperature than −76℃), there is a direct ratio relationship between the total column amount of NO_2 and O_3 (for example, on October 18, 1995). This might be mainly because of the heterogeneous reaction process. If there is a strong wind in stratosphere and the process of dynamic transportation plays an important role, there is a complicated relationship between the total column amount of NO_2 and O_3, and there is an inverse relationship between the two in general (for example, on October 10, 1995).

Fig. 5 shows the variation of the ratio of stratospheric NO_2 by the skylight of sunrise (AM) and sunset (PM) in 1995 over Zhongshan Station. From the figure we can see that the ratio of AM/PM increases from 0.7 in autumn time to 0.9 in winter time gradually (Themain reason for the decrease of difference between AM and PM NO_2 amount is because of the shorter shining time of sun just before polar night). The ratio between the two decreases from 0.8 in early August to 0.65 in early September and then gradually increases to 0.9 in the end of October during the spring time ozone hole period and finally it can reach around 1.0 in summer. The changing of the ratio is chiefly due to the changing of shining time of sun. But in early December, 1995 along with the decrease of total column amount of O_3 after Ozone Hole period, the ratio of AM/PM can reach to 1.5～2.0. Solomon (1992) pointed out that this ratio actually reflected the relationship between stratospheric aerosol and its profile with the stratospheric temperature, and thus this ratio plays an important role in the study of Antarctic stratospheric chemical reaction between NO_X and O_3.

4 Conclusion

(1)The seasonal variation of total column amount of NO_2 (especially the stratospheric NO_2 amount) is quiet similar to that of total column amount of O_3 over Zhongshan Station. There is a better direct ratio relationship between the NO_2 and O_3 amount during Antarctic Ozone Hole. (2) From the analysis of the NO_2 and O_3 amount variation in a day, there is a direct ratio relationship between NO_2 and O_3 amount under stable weather condition (little wind in stratosphere and lower temperature than −76℃), this might be mainly due to the heterogeneous reaction. There is a complicated relationship (generally an inverse proportion) between the NO_2 and O_3 amount if there is a strong wind in the stratosphere and this might be mainly because

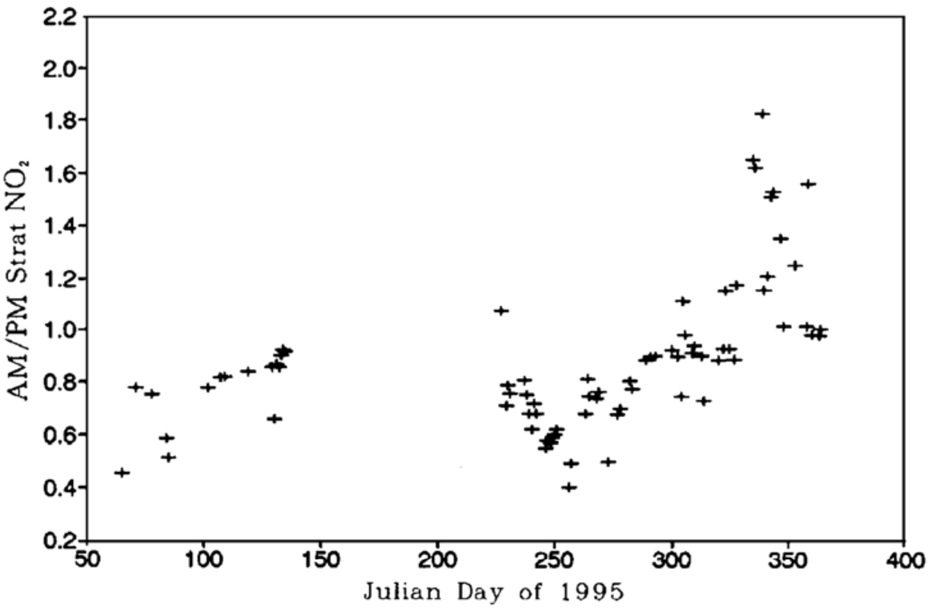

Fig. 5. The variation of the ratio of stratospheric NO_2 by the skylight of sun rise (AM) and sun set (PM) in the year 1995 over Zhongshan station.

of the process of dynamic transportation. (3) The yearly variation of the ratio of stratospheric NO_2 by the skylight of sunrise (AM) and sunset (PM) is very important to the study of Antarctic stratospheric chemical reaction between NO_X and O_3.

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