Study of SO₂ and NO₂ behaviour during the ozone-hole event at Antarctica by Brewer Spectrophotometer

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सार – एंटार्कटिक में स्थित भारतीय स्टेशन 'मैत्री' (70.7 डिग्री द.,11.7 डिग्री पू.) में सितम्बर 1999 से दिसम्बर 2006 तक ब्रीवर स्पेक्ट्रोफोटोमीटर से सल्फर डाइऑक्साइड के उर्ध्वाधर कॉलम घनत्व का माप लिया गया। साथ ही साथ नाइट्रोजन डाइऑक्साइड, ओज़ोन और यू.वी.-बी. के अधिकतम मान के भी माप लिए गए। इस शोध पत्र में हमें वसन्त ऋतु में सल्फर डाइऑक्साइड में वृद्धि का पता चला है। इसी अवधि में नाइट्रोजन डाइऑक्साइड के कॉलम में भी वृद्धि पाई गई परन्तु यह सल्फर डाइऑक्साइड के समान नहीं है। SO₂ और NO₂ में ये परिवर्तनशीलता समतापमंडल में ओज़ोन कॉलम की कमी के कारण धरातल पर यू.वी.-बी. फ्लक्स में वृद्धि के समान नही थी। SO₂ कॉलम में परिवर्तनशीलता को ओज़ोन–छिद्र घटना के दौरान यू.वी.-बी. विकिरण में भेदन गहराई की अधोमुखी प्रवृत्ति द्वारा बताया गया है।

ABSTRACT. Vertical column density of sulphur dioxide has been measured at Maitri (70.7°S, 11.7°E), the Indian station in the Antarctica from September, 1999 to December, 2006 by a Brewer Spectrophotometer. Simultaneously, nitrogen dioxide, ozone and the maximum value of UV-B have also been measured, we found an increase in SO₂ during spring. An increase in NO₂ column was also found during this period but not identical with that of SO₂. These variations in SO₂ and NO₂ are not in phase with the increase in UV-B flux at the ground due to the decrease of ozone column in the stratosphere. The variation of SO₂ column is explained by the downward shift of penetration depth of UV-B radiation during the ozone-hole event.

Key words – Brewer spectrophotometer, Ozone hole, Ultraviolet Radiation, Aerosol layer.

1. Introduction

Nitrogen dioxide is a member of NO_x family which catalytically destroys ozone in the stratosphere. For this reason and since it is easy to measure, measurements of this species have been made by various groups at various places of the earth by using ground-based, balloon-borne and space craft techniques. One important feature of this species as emerged from theses studies in low and mid-latitude, is that it builds up during forenoon hours, remains almost constant during afternoon hours and then decays during nighttime. This makes its sunrise value lower than the sunset value. This feature is explainable by simple chemistry. However, if there is no night, as in case of Antarctica from middle of November to middle of January, diurnal variation of NO_2 is not expected during this period. India Meteorological Department installed a Brewer spectrophotometer at Maitri (70.7° S, 11.7° E) in July 1999 and since then has been measuring the column densities of NO_2. Simultaneously sulphur dioxide, ozone and the maximum value of UV-B are also being measured.

Sulphur dioxide is a pollutant. It enters the atmosphere as a result of natural phenomena and anthropogenic activity: the most important sources being the combustion of fossil fuels, the oxidation of organic materials in soil and of dimethyl sulfate (DMS) over oceans and volcanic eruptions. It is an important source of formation of sulfate aerosol layer in the lower stratosphere and hence has great impact on both atmospheric chemistry and the radiation field of the earth's atmosphere. SO_2 is produced from the photo-dissociation of COS [Crutzen, 1976] by absorption of UV radiation in the spectral region 186-260 nm. The absorption of UV radiation in the special range 135-218 nm would also lead to dissociation of SO_2. A dramatic decrease in column ozone (called ozone hole) at Antarctica occurs during the month of spring [Farman *et al.*, 1985]. During these months the UV radiation absorbed by O_3 layer in the stratosphere will penetrate below stratosphere and change the behaviour of special species in that region. The majority of SO_2 is found below stratosphere. It is, therefore, likely that a change in the distribution of SO_2 will occur during these months. A large amount of increase in SO_2 and correspondingly a decrease in ozone in the atmosphere after volcanic eruption have been reported. [Sahai *et al.*, 1997]. But the effect on SO_2 when reverse occurs, *i.e.*, when a decrease in ozone takes place during ozone-hole event in the Antarctic, is poorly known.

2.   Instrumentation and data

An automated Brewer spectrophotometer (Mark IV, No. 153) was installed at Maitri, by the India Meteorological Department in July 1999. Regular measurements of the total column O_3, NO_2, SO_2 and the maximum value of UV-B flux were started here from September 1999. The details of this instrument and the methods by which these parameters are measured are described by Vanicek *et al*. (2003) (see also Kerr *et al*., 1980; 1985; Chakrabarty and Peshin, 2007). Three similar Brewer instruments are also operating at India Meteorological Department in New Delhi, Pune and Kodaikanal where Dobson instruments are taking routine O_3 observations daily. Simultaneous running of Standard Dobson Instrument No. 112 and Brewer instruments at New Delhi has shown that ozone values obtained by these two instruments do not differ by more than 2%. The data obtained at Maitri for the years 1999 to 2005 have been used in the present work.

3.   Results

Fig. 1 shows a plot of vertical column density of SO_2, O_3, NO_2 and the maximum value of UV-B flux for the period 14 September, 1999 to 30 December, 2003 measured by Brewer spectrophotometer. Since we are focusing on ozone-hole event, we show the occurrence of this event first [Fig. 1(a)]. Total ozone column was measured in both d (direct Sun) and z (zenith sky) modes. Fig. 1(a) shows a plot of total ozone values obtained in d mode. The ozone-hole event is clearly seen in these figures in all the years. Starting from the middle of September 1999, as the year pass, ozone column decreases till about the middle of November, when becomes the minimum. After this time it increases rapidly and reaches the maximum in January. From January onwards ozone slowly decreases up to about April. After April, data are not reliable due to cloudy and bad weather condition. The same trend is seen during the above mentioned months in 2000, 2001, 2002 and 2003. The minimum values during 1999, 2000, 2001, 2002 and 2003 were found to be 136, 115, 113, 173 and 119 D.U. respectively. The *z*-mode ozone values were found to be within ± 5% of the *d*-mode values. But the nature of variation of ozone in both the modes was seen to be the same. It is to be noted that in Fig. 1(a) we do not have regular data for about three months May, June and July during winter. The occasional Brewer observations taken by us near full moon days with moon as source during 1999 and 2000 winter months show that winter ozone values are higher than the April values. Roscoe *et al*. (1997) measured total ozone during these months and reported that during June-July, *i.e*., during winter, ozone values were the maximum in Antarctica. Roscoe *et al*. (1997) further shows that ozone

starts decreasing from the end of winter, *i.e*., July and becomes the minimum in spring. Our results agree with the results of Roscoe *et al*. (1997).

Fig. 1(b) shows a plot of SO_2 column for the same period mentioned above. It can be seen from this figure that SO_2 value increases rapidly from the middle of September up to the end of October remains almost constant up to the middle of January and then decreases in April. The same pattern is seen during 2000, 2001, 2002 and 2003. On the average during the ozone-hole period, the SO_2 column increases from a value less than 0.5 to ~2.5 D.U.

Fig. 1(c) shows a plot NO_2 column for the same period mentioned above. It can be seen from this figure that starting from the middle of September in 1999, NO_2 column increases till about the middle of January and then decreases. The same pattern is seen in 2000, 2001, 2002 and 2003. On the average, during the ozone hole period, the NO_2 column increases from a value less than 0.1 to ~1 D.U. The variation of SO_2 is neither exactly identical to that of NO_2 nor of O_3. Also there is no correlation between NO_2 and O_3 variations. The correlation between NO_2 and O_3 variations during ozone hole event was studied with a small amount of data obtained by visible absorption spectroscopy technique earlier by Shibasaki *et al*. (1986) and Keys and Johnston (1986).

Fig. 1(d) shows a plot of UV-B flux values for the same period as mentioned above. One can see from this figure that when ozone column decreases from the middle of September, UV-B flux increases. And when ozone column reaches its minimum towards the middle of November, UV-B flux is the maximum. After that time, as the ozone column starts increasing, UV-B starts decreasing, till up to December/January when it is maximum and then starts decreasing. The same trend is seen in 2000, 2001, 2002 and 2003 also. On the average, during the ozone hole period, the UV-B increases from a value less than 40 to ~200mWm². A comparison of Fig. 1(a) with Fig. 1(d) shows that an anti correlation between ozone column and UV-B flux exists. A comparison of Figs. 1(b&c) with Fig. 1(d) shows that the variation of SO_2 and NO_2 is different from that of UV-B flux.

4.   Discussion

The UV-B radiation emitted from the Sun is almost completely absorbed by the ozone layer in the stratosphere and only a very small fraction reaches the Earth's surface. Consequently, as O_3 amount decreases during springtime, UV-B flux reaching the surface of the Earth increases.

The density of SO_2 is nearly 10% in the stratosphere and 90% in the troposphere. Its lifetime in the upper
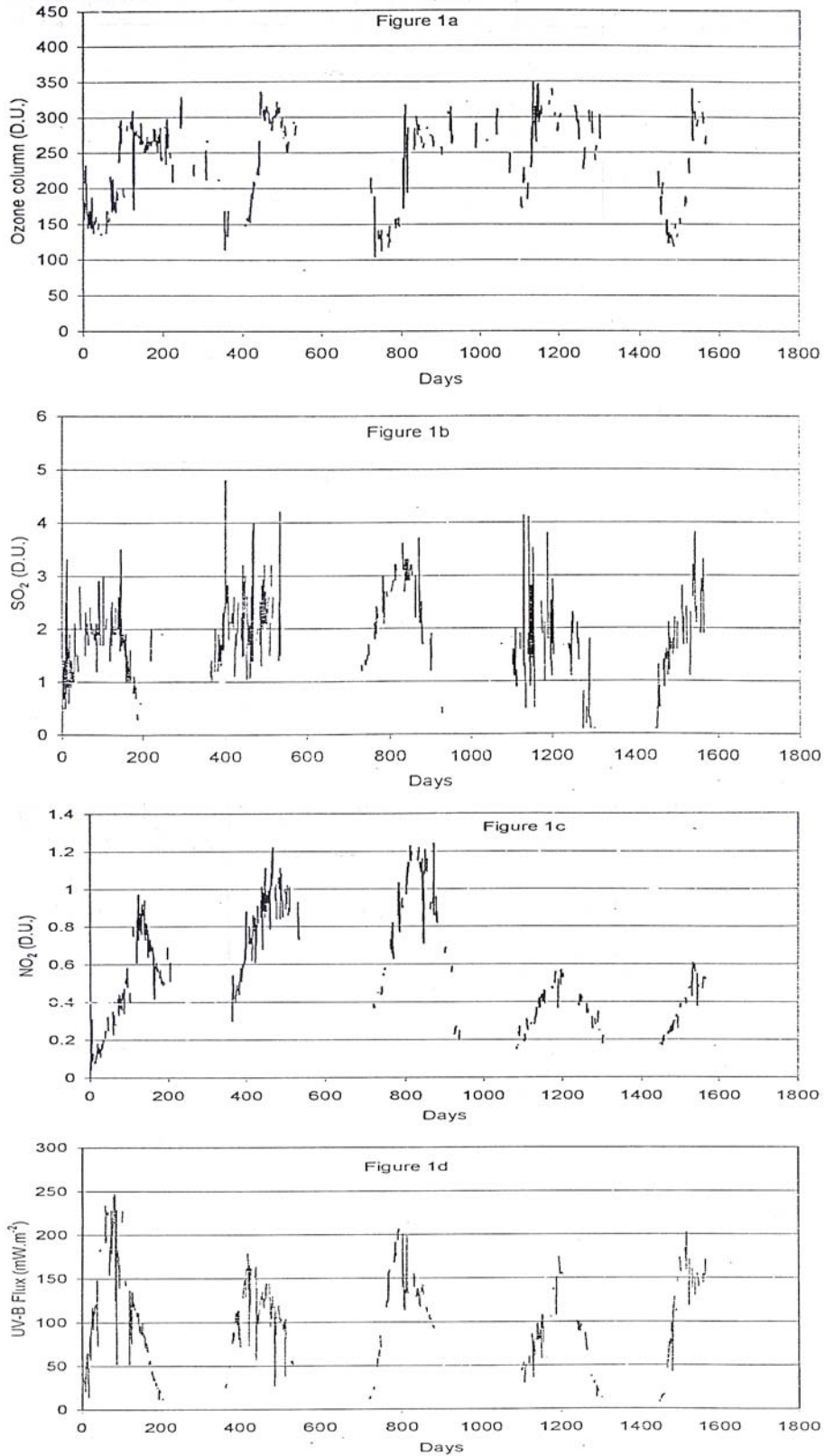
Figs. 1(a-d).   Daily values obtained by Brewer spectrophotometer from 14 September, 1999 to 30 December, 2003. (a) Vertical column density of O$_3$; (b) Vertical column density of NO$_2$, and (c) Maximum UV-B flux values. Day 1 corresponds to 14 September, 1999
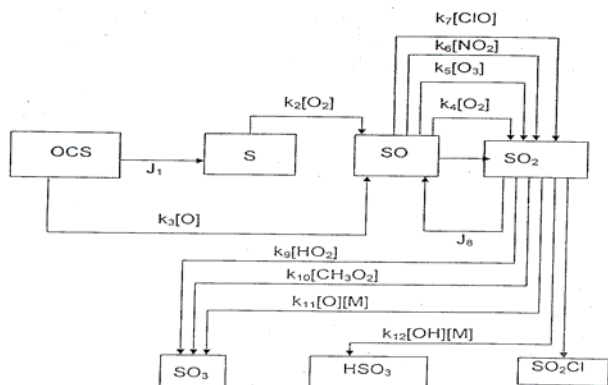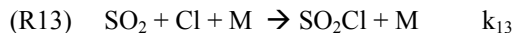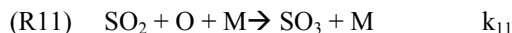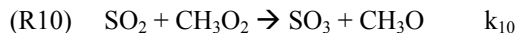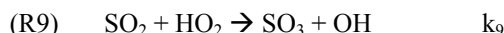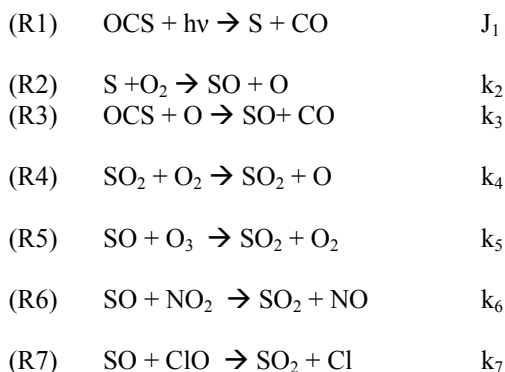
Fig. 2. A simplified chemical scheme for the study of SO_2 variation

troposphere is a few days. The increase of total SO_2 column from the start of spring could be either due to the increase of its production rate or decrease of loss rate in the region below the tropopause. The photo dissociation of OCS is the main source of SO_2. Thus in the beginning of spring when O_3 column is low, a large quantity of UV-B rays penetrate below the tropopause, dissociate OCS and increase the production rate of SO_2. As a result SO_2 column density starts increasing, the UV rays penetration depth will move up and slow down the production rate of SO_2 after the penetration depth has reached the stratosphere, any change in SO_2 density in the stratosphere will not effect the total column density of SO_2. This UV rays penetration depth moving down in the troposphere and then moving up in the stratosphere will, however, not affect the column density of NO_2 as 90% of this species lies in the stratosphere.

A simple calculation that follows will show how in the depleted ozone condition in the Antarctica, SO_2 density can increase significantly. A simplified chemical scheme used for that purpose is shown in Fig. 2 [Brasseur and Solomon, 1998, Turco *et al*., 1982]. It contains the following chemical reactions:
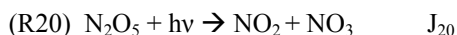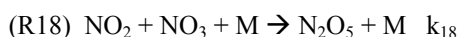
(R1) $OCS + hv \rightarrow S + CO$ J_1

(R2) $S + O_2 \rightarrow SO + O$ k_2
(R3) $OCS + O \rightarrow SO + CO$ k_3

(R4) $SO_2 + O_2 \rightarrow SO_2 + O$ k_4

(R5) $SO + O_3 \rightarrow SO_2 + O_2$ k_5

(R6) $SO + NO_2 \rightarrow SO_2 + NO$ k_6

(R7) $SO + ClO \rightarrow SO_2 + Cl$ k_7

(R8) $SO_2 + hv \rightarrow SO + O$ J_8

(R9) $SO_2 + HO_2 \rightarrow SO_3 + OH$ k_9

(R10) $SO_2 + CH_3O_2 \rightarrow SO_3 + CH_3O$ k_{10}

(R11) $SO_2 + O + M \rightarrow SO_3 + M$ k_{11}

(R12) $SO_2 + OH + M \rightarrow HOSO_2 + M$ k_{12}

(R13) $SO_2 + Cl + M \rightarrow SO_2Cl + M$ k_{13}

Using the above reaction scheme, the continuity equation for S, SO and SO_2 can be written. After doing a little algebra, for steady state, the expression for concentration of SO_2 at a particular height can be written as follows:

$$(SO_2) = \frac{J_1(OCS) + k_3(O)(OCS)}{\begin{array}{c} k_9(HO_2) + k_{10}(CH_3O_2) + k_{11}(O)(M) \\ + k_{12}(OH)(M) + k_{13}(Cl)(M) \end{array}} \quad (1)$$

We concentrate at 15 km and take temperature = 200 K (measured by us at 15 km by balloon-sonde on 15 September 1999). The value of [O] at 15 km, according to Shimazaki [1985], varies from 10^5 to 10^{-15} cm^{-3} from day to night. If we take $[O] = 10^5$ cm^{-3} and $k_3 = 10^{-16}$ cm^3s^{-1} (Whitten *et al*., 1980), then the value of k_3 [O] becomes $10^{-11}s^{-1}$. Whitten *et al*., (1980) have also given the value of J_1 at 15 km and 20 km as 1.9×10^{-11} and $1.4 \times 10^{-9}s^{-1}$ under normal condition. Thus, the value of J_1 and k_3 [O], under normal condition is comparable. However, during absence of ozone during ozone-hole phenomenon, the value of J_1 below stratosphere will increase significantly. Our measured UV-B flux on the ground shows that UV-B value has increased by a factor of ~5. If we incorporate this increase in the value of J_1 in Eqn. (1) the value of SO_2 increases by a factor of ~4. The increase of NO_2 column density from the start of the spring can be explained by the decrease of length of night since summer is approaching. In winter when there is no Sun, NO_2 is converted into N_2O_5, HNO_3 and probably HNO_3 $(H_2O)_3$ droplets. With the appearance of sunlight, and the increase of temperature, these species start getting photo-dissociated releasing NO_2. This NO_2 builds up during daytime and decays during nighttime. We take a simple chemistry of NO_2 used by us earlier (Chakrabarty *et al*., 2001). It contains the following chemical reactions:

(R14) $NO + O_3 \rightarrow NO_2 + O_2$ k_{14}

(R15) $NO_2 + hv \rightarrow NO + O$ J_{15}

(R16) $NO_2 + O \rightarrow NO + O_2$ k_{16}

(R17) $NO_2 + O_3 \rightarrow NO_3 + O_2$ k_{17}

(R18) $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ k_{18}

(R19) $NO_3 + hv \rightarrow NO_2 + O$ J_{19}

(R20) $N_2O_5 + hv \rightarrow NO_2 + NO_3$ J_{20}

(R21) $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ k_{21}

Using the above reactions, the continuity equation of NO_2 with time at a particular height can be written as:

$$d[NO_2]/dt = k_{14}[NO][O_3] + J_{19}[NO_3]$$
$$+ k_{21}[N_2O_5][M] + J_{20}[N_2O_5]$$
$$- J_{15}[NO_2] - k_{16}[NO_2][O]$$
$$- k_{17}[O_3][NO_2] - k_{18}[NO_3][NO_2]$$

The rate limiting steps governing the decay of NO_2 during night time are reactions R17 and R18 [Solomon and Garcia, 1983, Roscoe *et al*., 1986] and if NO_3 is considered to be in a steady state during night, then NO_2 nighttime variation will be governed by:

$$d[NO_2]/dt = -2k_{17}[O_3][NO_2]$$

This gives

$$[NO_2]sr = [NO_2]ss. Exp. (-2k_{17}[O_3]t) \qquad (2)$$

where sr stands for sunrise, ss stands for sunset values of NO_2 and t is the length of night. Since t is decreasing, the value of $[NO_2]$ sr will continue to grow. Also, NO_2 layer is at an altitude higher than that of ozone layer. Therefore, the depletion of ozone and the penetration of UV in the lower stratosphere will not affect on NO_2 column.

For the decrease of O_3 from the middle of September upto the end of October, the theory relies on the combination of dynamical and chemical mechanisms and heterogeneous reactions occurring on polar stratospheric clouds (PSC) droplets. The central feature of the chemistry is the conversion of reservoir compounds into catalytically active chlorine molecules on the surface of PSC. When the Sun comes out in spring, Cl_2 generated from the reservoir is rapidly split into chlorine atoms. These chlorine atoms destroy ozone as follows:

(R22) $Cl_2 + hv \rightarrow Cl + Cl$ J_{22}

(R23) $Cl + O_3 \rightarrow ClO + O_2$ k_{23}
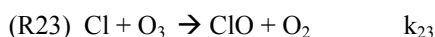
But the destruction of ozone by these reactions will not last long because chlorine monoxide does not release active chlorine by the following catalytic chain reaction as the concentration of oxygen atoms in the lower stratosphere is far too small (Wane, 2000):

(R24) $ClO + O \rightarrow Cl + O_2$ k_{24}
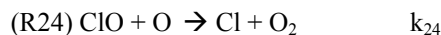
Hence, several other reactions have been put forward (Wane, 2000). It is to be noted that ozone depletion takes place around 16-20 km. The sulfate aerosol layer is also around 18-20 km during non-volcanic period (Crutzen, 1976). At this altitude SO_2 can undergo photo-dissociation by radiation in the 200-230 nm rage forming O and SO.
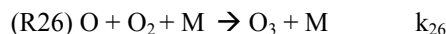
(R8) $SO_2 + hv \rightarrow SO + O$ J_8

This SO can react with O_2 to form SO_2 and O as follows:

(R4) $SO + O_2 \rightarrow SO_2 + O$ k_4

If we add R8 and R4 we essentially get

(R25) $O_2 + hv \rightarrow O + O$ k_{25}
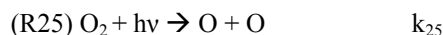
Thus without any loss of SO_2, we get a good amount of supply of O which can react with ClO by R24 to release Cl and destroy O_3 by R23. But this O can also produce ozone through the reaction:

(R26) $O + O_2 + M \rightarrow O_3 + M$ k_{26}

This process can continue till ozone density increases to normal level in about two months' time and absorbs 200-230 nm radiation.

5. Conclusion

India Meteorological Department has measured simultaneously NO_2, O_3 and UV-B flux at ground for more than 5 years at Maitri by Brewer spectrophotometer. Analysis of data shows that NO_2 has seasonal variation with peak in summer. Analysis also shows that during no-night condition in summer, NO_2 has diurnal variation with peak around noon time. We can explain the seasonal and diurnal variations of NO_2 column if we consider that there is an increase in NO density from winter to summer and an increase in NO density with decrease in solar zenith angle during the daytime. Both neutral chemistry model study that includes transport and measurements are needed to validate our results.

Column density of SO_2 has been measured from September, 1999 to December, 2003 at Maitri, the Indian station at Antarctica by Brewer spectrophotometer. Simultaneously nitrogen dioxide, ozone and maximum

value of UV-B have also been measured. An increase in SO_2 column has been found during ozone-hole event. This increase is due to the downward penetration of UV-B flux in the troposphere under ozone depleted condition of the stratosphere during ozone-hole event. This UV-B radiation dissociates COS in the upper troposphere and increases the production rate of SO_2. The column density of NO_2 also shows an increase after the onset of spring but not identical with that of SO_2 column. This increase in NO_2 column is due to the decrease of the length of night as the summer is approaching. The additional available from the dissociation of SO_2 could take part both in the depletion as well as the production of ozone during ozone-hole event.

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