Total column density variations of ozone (O_3) in presence of different types of clouds

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The zenith sky scattered light spectra were carried out using zenith sky UV-visible spectrometer in clear and cloudy sky conditions during May–November 2000 over the tropical station Pune (18°32′N, 73°51′E). These scattered spectra are obtained in the spectral range 462–498 nm between 75° and 92° solar zenith angles (SZAs). The slant column densities (SCDs) as well as total column densities (TCDs) of NO_2, O_3, H_2O and O_4 are derived with different SZAs in clear and cloudy sky conditions. The large enhancements and reductions in TCDs of the above gases are observed in thick cumulonimbus (Cb) clouds and thin high cirrus (Ci) clouds, respectively, compared to clear sky conditions. The enhancements in TCDs of O_3 appear to be due to photon diffusion, multiple Mie-scattering and multiple reflections between layered clouds or isolated patches of optically thick clouds. The reductions in TCDs due to optically thin clouds are noticed during the above period. The variations in TCDs of O_3 measured under cloudy sky are discussed with total cloud cover (octas) of different types of clouds such as low clouds (C_L), medium clouds (C_M) and high clouds (C_H) during May–November 2000. The variations in TCDs of O_3 measured in cloudy sky conditions are found to be well matched with cloud sensitive parameter colour index (CI) and found to be in good correlation. The TCD_{cloudy} are derived using airmass factors (AMFs) computed without considering cloud cover and CI in radiative transfer (RT) model, whereas TCD_{model} are derived using AMFs computed with considering cloud cover, cloud height and CI in RT model. The TCD_{model} is the column density of illuminated cloudy effect. A good agreement is observed between TCD_{model}, TCD_{Dob} and TCD_{GOME}.

1. Introduction

Tropospheric clouds can considerably affect the zenith sky measurements of trace gases such as NO_2, O_3, H_2O and O_4 (Erle *et al* 1995; Wagner *et al* 1998; Bassford *et al* 2001). Clouds also influence the satellite measurements of stratospheric as well as tropospheric trace gases. Radiative transfer, cloud chemical processes and the transport arising from the dynamics of clouds play an important role in the measurement of trace gases (Rajeevan 1996; Lal *et al* 2007). However, it is treated that the slant path of light in the atmosphere gets enhanced due to multiple Mie-scattering or by photon diffusion inside the clouds (Van Roozendael *et al* 1994; Erle *et al* 1995; Wagner *et al* 1998; Pfeilsticker 1999). Photon diffusion may increase the strength of the absorption lines detected at the ground. Clouds may enhance the scattered light intensity relative to clear skies due to additional Mie-scattering in the zenith sky. The reduction in the measured intensity may be caused by light extinction inside clouds. The enhancements in optical path lengths and hence the concentrations of the trace gases can be observed in high thick clouds while decreases can be expected in thin high clouds (Pfeilsticker *et al* 1998; Wagner *et al* 1998). Oxygen collision complex $(O_2)_2$ or in brief, O_4 is a collision complex of two oxygen molecules with its absorption being proportional to the

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square of the partial pressure of molecular oxygen. The spectroscopic data show that the O_4 absorption lines are not saturated in clear sky conditions (Erle *et al* 1995; Pfeilsticker *et al* 1997; Meena *et al* 2004), therefore potentially useful for cloud detection. At the longer wavelength, zenith scattered light intensity increases as compared to short wavelength particularly in cloudy sky measurement (Erle *et al* 1995). Therefore, colour index (CI), which is the ratio of two different intensities (longer to short wavelength) of observed intensity spectrum may be increased in cloudy sky conditions compared to clear sky (Wagner *et al* 1998).

Van Roozendael *et al* (1994) have noticed that during twilight period, the pollution episodes near the ground can significantly increase the measured total absorption and thus introduce large errors in the observation of stratospheric NO_2. However, the observations have been made during morning hours (twilight period) to get larger pathlength for more absorption. Because the gases such as NO_2, O_3, H_2O and O_4 are minor in the atmosphere, which could be detected in twilight (morning and evening) period only by zenith sky UV-visible spectrometer. The zenith sky scattered sunlight observed at twilight traverses a much longer stratospheric path than scattered sunlight observed at noon. Hence, the apparent slant column density of the above gases have a maximum concentration in twilight spectra than noon spectra. Vertical column amounts of the gases can be derived by dividing observed slant column densities with an appropriate enhancement factor called as airmass factor (AMF). AMF can be calculated by air scattering radiative transfer (RT) model in which many horizontal rays traversing the atmosphere at long paths and then being scattered in the zenith (Solomon *et al* 1987; Fiedler *et al* 1993; Meena *et al* 2003).

This paper describes the slant column density (SCD, integrated concentration along the slant absorption path) and total column density (TCD, the vertically integrated concentration) variations of NO_2, O_3, H_2O and O_4 in clear and cloudy sky conditions between 75° and 92° solar zenith angles (SZAs). The TCD variations of these gases are derived in cloudy sky condition using model calculated AMF with and without considering cloud cover as well as colour index during May–November 2000. Model computed TCDs of O_3 are compared with Dobson spectrophotometer and satellite-based global ozone measurement experiment (GOME) measurement during the above period. The variations in TCDs of O_3 measured under cloudy sky are also discussed with total cloud cover (octas) of different types of clouds such as low clouds (C_L), medium clouds (C_M) and high clouds (C_H). Cloud sensitive parameter colour index (CI) are computed and correlated with TCDs of O_3 measured under cloudy sky conditions.

2. Methodology

The zenith scattered intensity observations were carried out under clear sky (path of the sun rays and zenith sky was cloudy free) and cloudy sky (clouds observed in the light path and at zenith) conditions during May–November 2000. Intensity observations on fully overcast days are not considered here. The total cloud cover data from Indian Daily Weather Report (IDWR) reported by Indian Meteorological Department (IMD) were collected during the time span of these observations. To make the comparisons of total column ozone derived by UV-visible spectrometer, ground-based Dobson spectrophotometer and satellite based GOME data are used. The spectrometer data are analyzed using differential optical absorption spectroscopy (DOAS) technique. Trace gas concentration n is derived from Lambert–Beer's law:

$$I = I_o \exp(-\sigma n l), \qquad (1)$$

where I is the measured spectrum intensity (i.e., zenith sky scattered light intensity) at the ground, I_o is the reference spectrum intensity outside the atmosphere, however, it is difficult to measure the spectra outside the atmosphere. Therefore, noon time spectrum is taken as a reference spectrum, l is the optical path length (cm), σ is the absorption cross section (cm^2 molecule^{-1}) of the absorbing molecule and n is the absorber concentration (molecules cm^{-3}). In case of O_4, an absorbance of O_2–O_2 by Greenblatt *et al* (1990) is calculated as absorbance A is given by:

$$A = \sigma[O_2]^2\, l, \qquad (2)$$

where l is the optical path length (cm), $[O_2]$ is the concentration of oxygen (molecules cm^{-3}), σ is the absorption cross section with the unit of cm^5 molecule^{-2}. The absorption cross sections of O_3 (Burrows *et al* 1999) and NO_2 (Burrows *et al* 1998) were taken as a reference absorption signature. Absorption cross section of O_4 was taken from Greenblatt *et al* (1990), and for H_2O was taken from the HITRAN 92 library (Rothman 1992). The absorber concentration is derived from extracted differential optical density (DOD):

$$\mathrm{DOD} = \left[-\ln\left(\frac{I}{I_o}\right)\right]' = \sigma' n l, \qquad (3)$$

where σ' is the differential absorption cross section, 'nl' is the differential slant column density (SCD_{diff}) of the absorbers (molecules cm^{-2}), which is derived by

$$SCD_{diff} = \frac{DOD}{\sigma'}. \quad (4)$$

In the case of O_4, SCD_{diff} is in the unit of molecules^2 cm^{-5}. The SCD is obtained by adding the amount of an absorber in reference spectrum (SCD_{ref}):

$$SCD = SCD_{diff} + SCD_{ref}. \quad (5)$$

The TCDs of the absorbing gases are then derived by:

$$TCD(\theta) = \frac{SCD(\theta)}{AMF(\theta)}, \quad (6)$$

where AMF is the airmass factor, which describes the ratio of SCD to TCD. Here, AMF is calculated by air scattering radiative transfer model (Meena *et al* 2003). The TCD(θ) are to be derived in clear and cloudy sky condition with SZA(θ). Thus, the influence of different types of clouds can be studied by comparing the TCD_{cloudy} and TCD_{clear}. Besides these cloud sensitive parameters such as oxygen dimmer O_4 (at 477 nm) and colour index (CI) are also included in the measurement. Colour index (CI) is defined as the ratio of the two different wavelength intensities (here 490 and 466 nm) where the absorptions by the gases are negligible (Sarkissian *et al* 1991),

$$CI = \frac{I(\lambda_2)}{I(\lambda_1)}. \quad (7)$$

In the cloudy sky conditions, the intensities of measured spectra at the longer wavelengths are enhanced compared to clear sky conditions. Corrected AMFs are to be calculated after inclusion of cloud cover and CI in the model, which result in corrected TCD, i.e., TCD_{model}.

3. Results and discussion

An automatic UV-visible spectrometer was utilized to collect the zenith sky intensity observations during the morning hours in the spectral region 462–498 nm in which the gases such as NO_2, O_3, H_2O and O_4 have their absorption structures. Observations were made in clear and cloudy sky conditions at the tropical station Pune (18°32′N, 73°51′E) during May–November 2000.

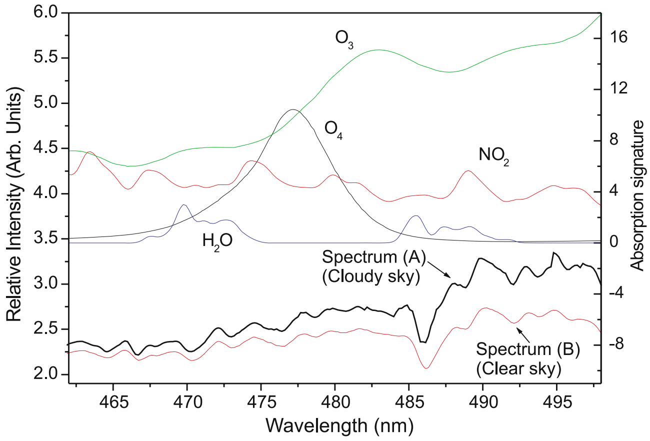

Figure 1. Zenith sky scattered light spectra measured at cloudy sky (A) at a SZA of 84°, when thick tropospheric clouds prevail and clear sky (B) of the same SZA of clear sky day.

Figure 1 displays the relative intensities of two zenith scattered light spectra (A and B) along with the absorption signatures of NO_2, O_3, H_2O and O_4. Spectrum (A) recorded at the SZA (84°) when atmosphere was cloudy and spectrum (B) is recorded at the same SZA of clear sky day. At short wavelength (blue), both spectra show similar intensities. While, at longer wavelengths ($>$ 486 nm) spectrum (A) of cloudy day exhibits increasingly more intensity than spectrum (B) of clear day. Both the spectra show the characteristic atmospheric absorption bands including solar Fraunhofer lines. Larger absorptions of the gases were observed in cloudy spectrum (A) compared to clear sky spectrum (B). Rayleigh scattering cross section exhibits a λ^{-4} dependence, the microphysical properties of clouds lead to essentially wavelength independent mean free paths in the UV-visible region of the spectrum (Van de Hulst 1980). Thus, for cloudy skies the intensities at the longer wavelengths are enhanced compared to a Rayleigh scattering atmosphere.

Figure 2 shows the SCD_{diff} variations with SZAs of NO_2, O_3, H_2O and O_4 in clear and cloudy sky conditions. Three days, namely, 16 June 2000 (clear sky), 15 June 2000 thick cumulonimbus (Cb) clouds (optically dense clouds) and 9 June 2000 high cirrus (Ci) clouds (thin high clouds in the sky) are considered for the study. The observations are made under clear and cloudy sky conditions at SZAs ranging from 75° to 92° during morning hours. The smooth increases of SCD_{diff} with SZA on 16 June 2000 are caused by the increasing atmospheric light paths approaching higher SZAs. The large variations in the SCDs for all the gases detected between 82° and 86° SZAs on 9 and

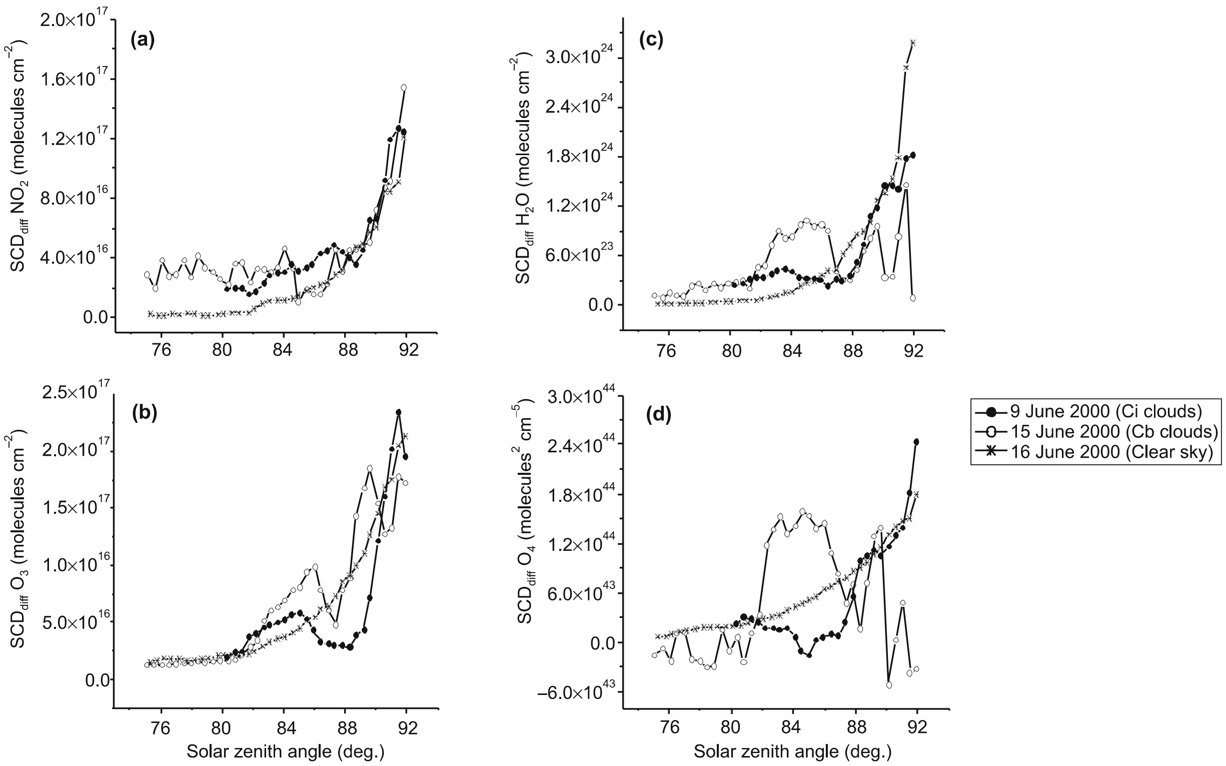

Figure 2. Differential slant column densities (SCD_{diff}) of **(a)** NO_2, **(b)** O_3, **(c)** H_2O, and **(d)** O_4 with solar zenith angles (SZAs) for clear and cloudy sky days.

15 June 2000 are considerable. Clouds change the paths of the observed photons in two ways; first, clouds shield the atmospheric absorption below the cloud and thus reduce the absorptions compared to the clear sky case. In addition, multiple scattering inside the clouds can enhance the absorption path and thus increase the atmospheric absorption.

The photon path length may enhance in optically thick clouds by photon diffusion. Photon diffusion increases the strength of the absorption detected at the ground. The reductions are noticed in SCDs of O_3, H_2O and O_4 (figure 2b, c, d) in thin high clouds observed on 9 June 2000. Optically thin tropospheric clouds decrease the photon path length. The path length decreases mainly due to the diffused light transmitted by the cloud to the ground, which is a mixture of the scattered and direct sunlight. In cloudy sky conditions, the light received at the ground from the zenith may have passed the troposphere on a vertical rather than a slant path, hence reduction occurs in SCDs. However, in case of NO_2, the optical path may be slant rather than vertical and hence SCDs reductions are not seen. The study also reveals that large enhancements/reductions are noticed in the SCDs of H_2O and O_4, they being the tropospheric gases.

Figure 3 shows the variations in TCD of NO_2, O_3, H_2O and O_4 with SZA for clear and cloudy sky conditions. The TCDs of all these gases are derived in clear and cloudy sky conditions using AMFs computed by RT model in which cloud parameters are not considered. In clear sky condition, i.e., on 16 June 2000 all gases have negligible variation of an average of TCDs of NO_2 5×10^{15} molecules cm^{-2}, O_3 7.5×10^{18} molecules cm^{-2} ($\sim$ 280 DU), H_2O 2×10^{23} molecules cm^{-2} and O_4 2×10^{43} molecules^2 cm^{-5}, which are almost constant for all SZAs. In cloudy sky condition, i.e., on 15 June 2000 thick clouds were present (in the light path and at zenith) near 84° SZA. At the SZA of 84° NO_2 and O_3 absorption enhancements are observed up to a factor of 2 while in the case of tropospheric gases O_4 and H_2O enhancements are observed up to a factor of 4 in the presence of Cb clouds compared to clear sky. The study reveals that the enhancements in the densities of the above gases are due to enhancement in optical path length by photon diffusion, multiple Mie-scattering in optically thick clouds. Similarly, the reductions in the densities are due to reductions in optical path lengths by diffused light shortly transmitted by the cloud to the ground.

Figure 4 shows the TCD variations of O_3 in clear and cloudy sky conditions along with total cloud cover (octas) of different types of clouds such as low clouds (C_L), medium clouds (C_M) and high clouds (C_H) from May to November 2000. TCD_{cloudy} is

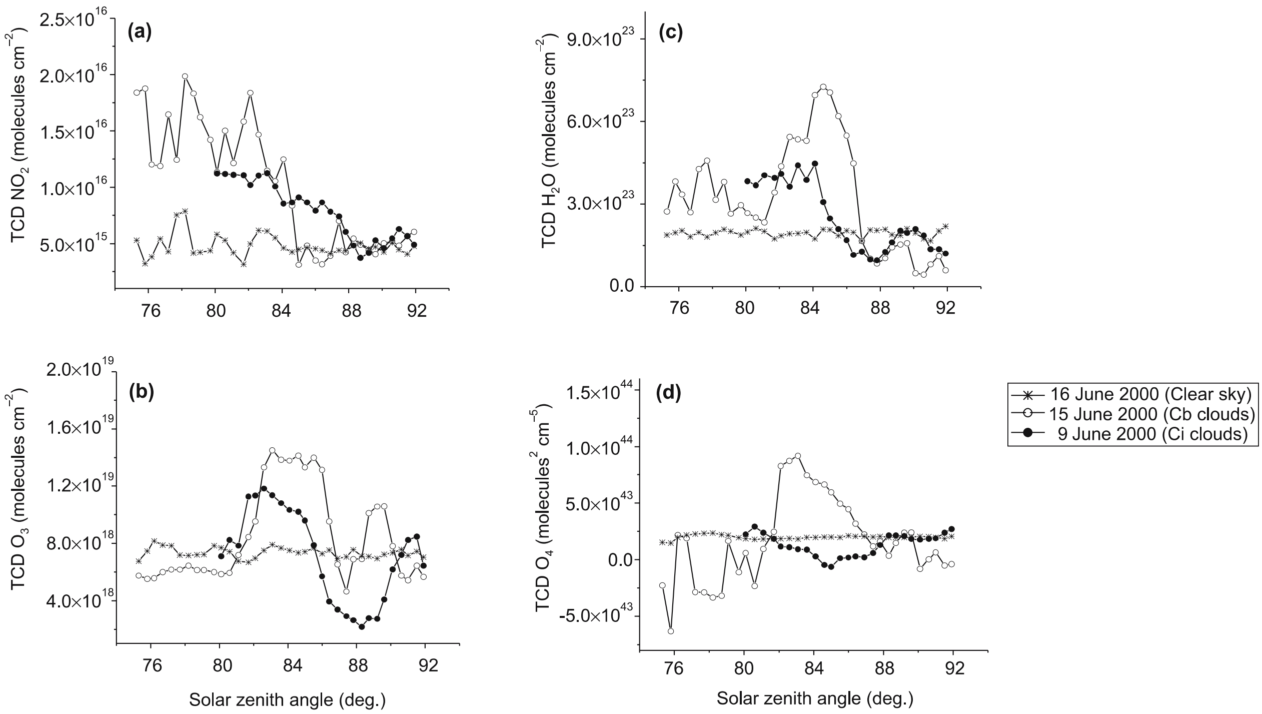

Figure 3. Total column densities (TCDs) of **(a)** NO_2, **(b)** O_3, **(c)** H_2O, and **(d)** of O_4 with solar zenith angles (SZAs) for clear and cloudy sky days.

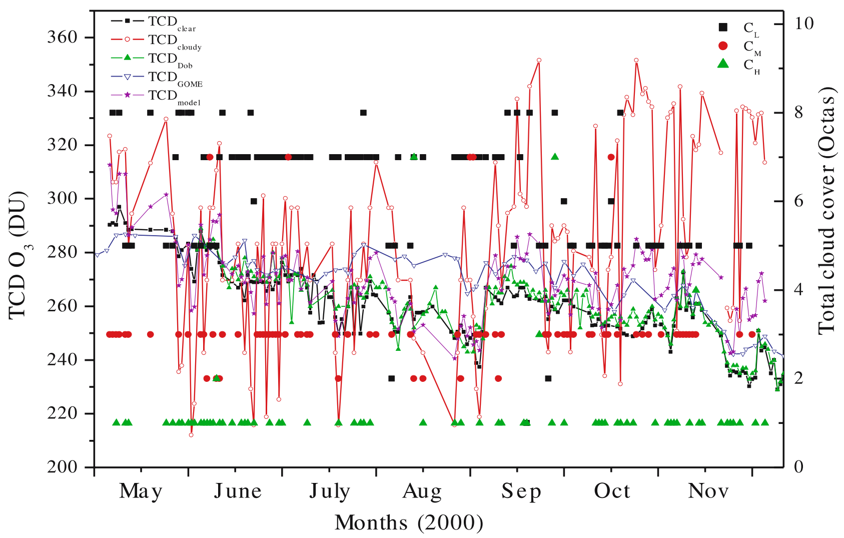

Figure 4. Total column density (TCD_{model} and TCD_{cloudy}) variations of O_3 in cloudy sky conditions during May to November 2000. TCD_{Dob}, TCD_{GOME} and total cloud cover (octas) are also plotted in the figure.

derived using AMFs computed without considering cloud cover and CI in RT model, whereas TCD_{model} is derived using AMFs computed with considering cloud cover, cloud height and CI in RT model. The TCD_{model} is the column density of illuminated cloudy effect. A good agreement has been observed between TCD_{model}, TCD_{clear}, TCD_{Dob} and TCD_{GOME}. During the monsoon season (June to September) C_L cloud base height is about 0.8 km and C_M cloud base height is about 3.5 km which prevail over the station while in the post-monsoon (October–November) isolated patches of these clouds and sometimes optically thick Cb clouds were in existence over the measuring site. Most of the days, the sky was covered with C_L 7 octa, C_M 3 octa and C_H 1 octa during the above period. Large enhancements and reductions are noticed in TCD_{cloudy} measured under cloudy

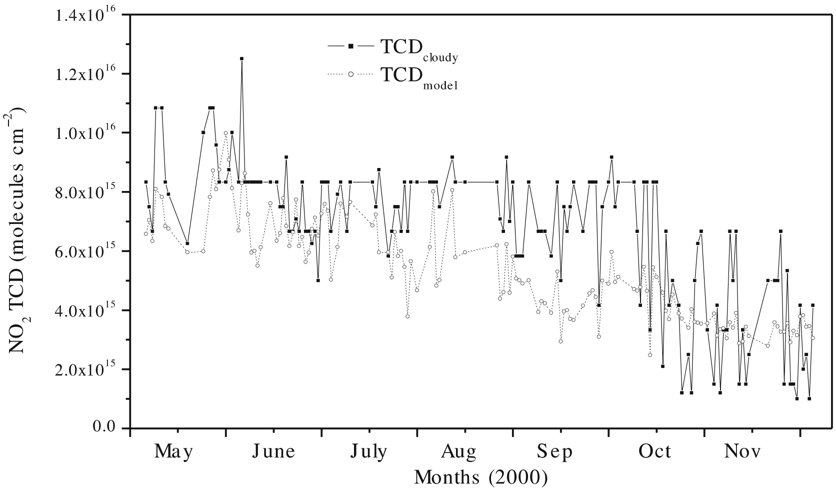

Figure 5. Variations of NO_2 TCD_{model} and TCD_{cloudy}. The TCD_{model} is cloud effect illuminated column density.

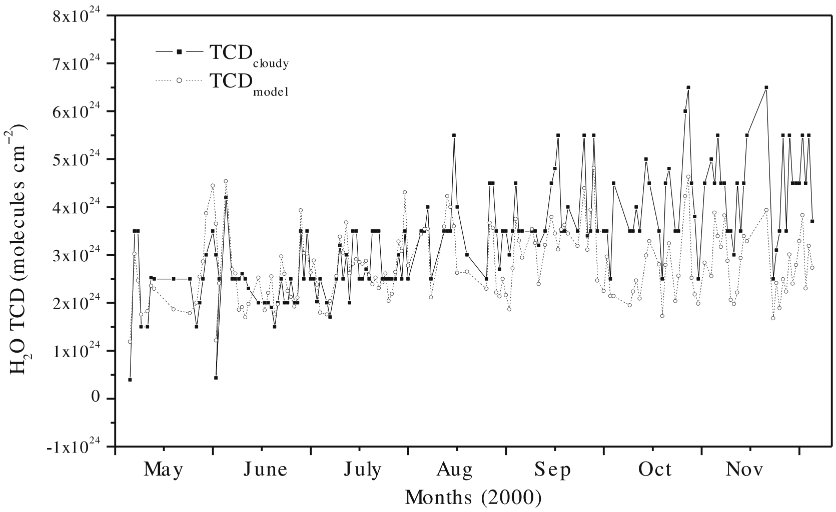

Figure 6. Variations of H_2O TCD_{model} and TCD_{cloudy}.

sky condition compared to TCD_{clear}, TCD_{Dob} and TCD_{GOME} taken under clear sky (figure 4). In pre-monsoon season TCD_{cloudy} of O_3 is observed to be 1.2 times higher than the TCD_{clear} and in post-monsoon TCD_{cloudy} is observed to be 1.3 times higher than TCD_{clear} as well as TCD_{Dob}. The enhancement can be attributed to multiple reflections between layers of clouds that prevail during monsoon and pre-monsoon season, and reduction can be attributed to the optically thin clouds. The large enhancement noticed during post-monsoon period (October–November), may be the combined effect of multiple reflections between patches of isolated clouds, multiple Mie-scattering due to aerosols and water vapour molecules, and diffusion in optically thick clouds. Figure 5 shows the NO_2 TCD measured under cloudy sky condition; TCD_{model} and TCD_{cloudy} are derived using AMFs computed by RT model with and without considering cloud cover as well as colour index in the model, respectively. The TCD_{cloudy} is found to be more fluctuated than TCD_{model}. Both the TCDs are higher in May and lower in November months. Figure 6 shows the H_2O TCD derived by the same method as NO_2. The H_2O densities are found to be higher in November month where C_L, C_M and C_H clouds are in 5, 3 and 1 octas, respectively. The O_4 TCD_{model} and TCD_{cloud} are shown in figure 7. Both the TCDs are higher in November and lower in May. The H_2O and O_4 are the tropospheric gases, which are enhanced in post-monsoon that is attributed to multiple Mie-scattering and multiple reflections between patches of clouds.

Wagner *et al* (1998) and Pfeilsticker *et al* (1998) have noticed that the photon diffusion in optical thick clouds and the multiple reflections between layers and patches of clouds can greatly enhance the light path. If there is NO_2 located at the cloud

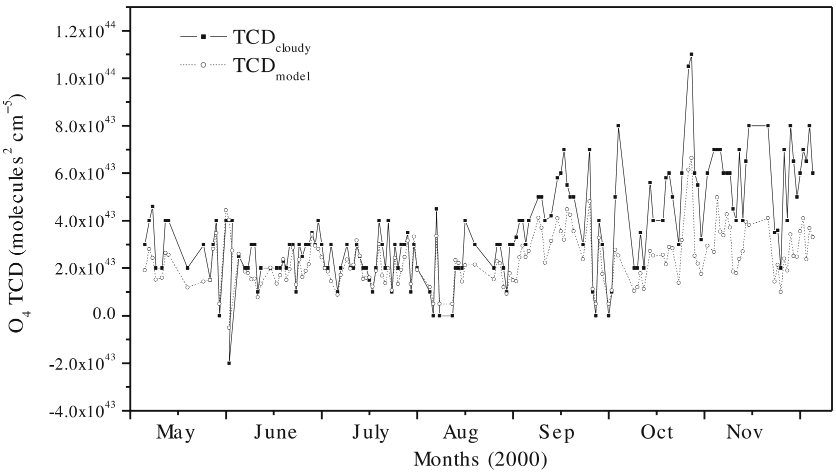

Figure 7. Variations of O_4 TCD_{model} and TCD_{cloudy}.

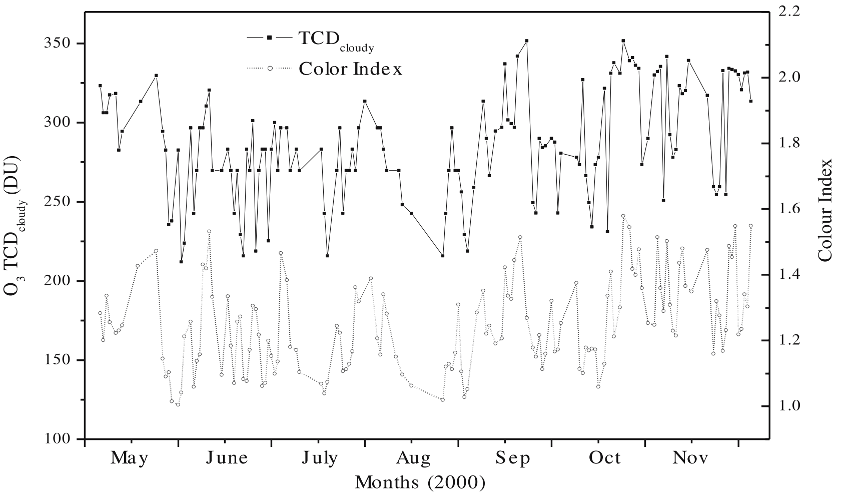

Figure 8. O_3 TCD_{cloudy} and colour index (CI) variations during cloudy days May–November 2000.

level, the absorption would become much larger than that for the clear sky condition. On the other hand, in the presence of high thin clouds, the tropospheric absorption can also be slightly decreased. Winterrath *et al* (1999) have noticed that slant optical thickness (SOT) enhancements of 62% for O_3 and up to 320% for NO_2 are found in a thunderstorm cloud. Sonde measurements carried out by Shlanta and Moore (1972) show O_3 values inside a cloud at 6 km that are 2.6 times higher than their pre-storm boundary layer level. If in cloudy conditions, the tropospheric AMF calculated under cloud-free assumption is used to retrieve the tropospheric density, large errors can occur. Without information about the location and extension of clouds, as well as the distribution of NO_2 inside clouds, it is difficult to correctly extract the tropospheric NO_2 density from zenith-sky measurement. For a trace gas with constant amount in the atmosphere, the observed diurnal SCD variation shows a smooth increase with the increasing SZA in clear sky condition (Meena *et al* 2006; Meena and Jadhav 2007; Chen *et al* 2009).

Figure 8 shows the TCD_{cloudy} of O_3 and colour index (CI) variations measured during cloudy days (May–November 2000). The TCD_{cloudy} of O_3 is a vertical columnar density derived using AMFs computed by RT model without considering cloud parameters. CI is a cloud sensitive parameter, which is defined as the ratio of the two different intensities of observed spectrum. CI for cloud free days is observed to be 1.2; small variations may be due to Rayleigh scattering and stratospheric aerosol. Under cloudy sky conditions the CI reaches values up to 1.6. Cloud enhances the scattered intensities relative to clear sky because of additional Mie-scattering in the zenith and light extension inside clouds reduces the measured intensity. The CI is observed to be high in the middle of May, last week in July and

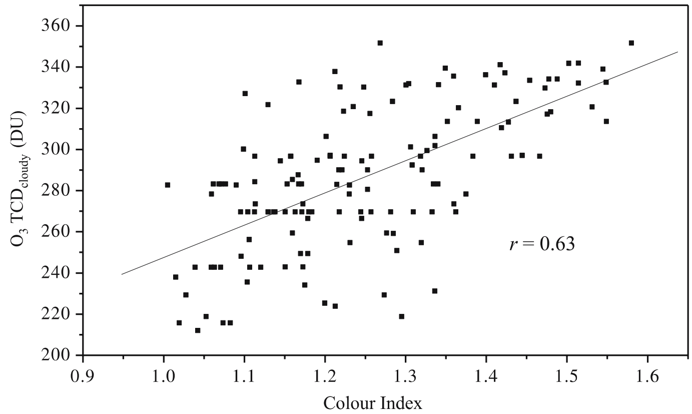

Figure 9. Correlation in O_3 TCD_{cloudy} and colour index (CI).

first week in August, middle of September, last week in October and November months. Similarly, TCD_{cloudy} of O_3 is also observed to be high in the same period. The TCD_{cloudy} and CI variations are well matched. These large enhancements and reductions observed in TCD_{cloudy} as well as in CI are associated with different types of clouds as discussed above. Figure 9 represents the correlation between TCD_{cloudy} of O_3 and cloud sensitive parameter CI. The TCD_{cloudy} varies between 210 and 350 DU while CI varies between 1 and 1.6. The linear fit line shows the increasing trend with correlation coefficient $r = 0.63$ between TCD_{cloudy} and CI, which are in good correlation. The CI has also been applied to scanning imaging absorption spectrometer for atmospheric chartography (SCIAMACHY) limb scattering measurements during 2003 to detect polar stratospheric cloud in the Southern Hemisphere (Savigny *et al* 2005). The relation between TCD_{cloudy} and CI has been observed, hence CI may be used as cloud correction factor for zenith sky measurements in RT model as well as satellite measurements of total column ozone.

4. Conclusions

In the present study, the considerable enhancements/reductions in TCDs of NO_2, O_3, H_2O and O_4 are noticed in cloudy sky conditions compared to clear sky conditions. A good agreement is observed between TCD_{model}, TCD_{clear}, TCD_{Dob} and TCD_{GOME}. Here, TCD_{model} is the cloud effect illuminated column density. Large enhancements and reductions are noticed in TCDs measured under cloudy sky conditions compared to TCDs of clear sky conditions. The TCD variations are discussed with total cloud cover (octas) of different types such as low clouds (C_L), medium clouds (C_M) and high clouds (C_H), which prevailed in pre-monsoon, monsoon and post-monsoon seasons. The large enhancements in TCD_{cloudy} of O_3 are observed in post-monsoon season as compared to pre-monsoon and monsoon seasons. In pre-monsoon season TCD_{cloudy} of O_3 is noticed to be 1.2 times higher than the TCD_{model} as well as TCD_{Dob} and in post-monsoon TCD_{cloudy} is noticed to be 1.3 times higher than TCD_{model}. The large enhancement observed in the TCDs of these trace gases may be attributed to multiple Mie-scattering or photon diffusion that can enhance the absorption in optically thick clouds (Cb) in the atmosphere. The decreases are noticed in the TCDs of trace species in thin high clouds (Ci) due to deceases in path length by transmitted diffused light through clouds.

It is also noticed that tropospheric gases such as O_4 and H_2O measurements are more affected by clouds than stratospheric gases NO_2 and O_3. The colour index (CI) is identified as cloud sensitive parameter, which may be used in RT model for cloud correction to retrieve total column ozone from ground-based zenith sky measurements as well as the satellite measurements. The TCD_{cloudy} and CI have been discussed in detail. The large enhancements and reductions are observed in TCD_{cloudy} of O_3, which vary between 210 and 350 DU while CI vary between 1 and 1.6. The TCD_{cloudy} and CI variations are found to be well matched. The linear fit line shows the increasing trend between TCD_{cloudy} and CI, which are found to be in good correlation. Cloud cover, types of cloud and CI are found to be useful parameters to compute the AMFs to illuminate the cloud effect in the TCDs in zenith sky measurements.

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