Effect of cloud occurrences on tropospheric ozone over, Alipore (22.52°N, 88.33°E), India

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The paper presents the nature of annual cycles of tropospheric ozone, cloud occurrences, NO_2, rainfall, SO_2, SPM, CO, non-methane hydrocarbon and surface solar radiation for the period October 2004 to June 2009 over Alipore (22.52°N, 88.33°E), India. Annual cycle of low-level cloud occurrences depicts that the low-level cloud over Alipore had been noticed to occur for many days and nights, particularly from June to September. The low-level cloud occurrences were found in winter months and post-monsoon period. The effect of cloud occurrences on tropospheric ozone concentration has been critically analysed and explained. It has been observed that the concentration of ozone is oscillatory with cloud occurrences and has a slight linear decreasing trend with the increase of cloud occurrences and vice versa. The concentration of tropospheric ozone attained higher value at moderate cloud occurrences and comparatively lower value at both of the lower and higher cloud occurrences. The related possible chemical and physical explanation for role of cloud occurrences on tropospheric ozone has been offered.

1. Introduction

Ozone though a minor constituent is one of the dominant components that controls atmospheric environmental quality and atmospheric chemical processes. The concentration of ozone in the stratosphere is gradually declining, whereas its tropospheric counterpart displays the tendency to increase persistently due to human activities. Stratospheric ozone plays an important role in protecting mankind and the environment, but a very high amount of ozone in the troposphere is harmful to human beings and also to the environment. Tropospheric ozone, a key chemical constituent serves as a product and participant of the photochemical reactions therein. Variation in concentration and distribution in ozone exerts an immediate effect on the lifetime and distribution of other atmospheric chemical species such as SO_2, NO_2 and OH radicals, thereby influencing the composition and equilibrium of tropospheric chemistry.

Clouds are condensed atmospheric moisture in the form of minute water droplets or ice crystals. Condensed nuclei can be anything from dust to debris. Pratt *et al* (2009) detected that some mineral dusts and primary biological particles, such as bacteria, pollen and fungi, can act as ice nuclei and initiate ice-crystal formation in clouds. Once there is a large group of condensation nuclei, the cloud becomes visible. A cloud consists of water

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droplets. The liquid water content of a cloud can be defined as the mass of water in condensed state per unit volume. It is also referred to (Sarkar *et al* 2005) as the total water content and not only as water in droplet form. Several researchers (Gunn and East 1954; Staelin 1966; Slobin 1982; Feigelson 1984) have reported that the liquid water content in cloud varies from 0.10 to 1 g/m^3. Carrier *et al* (1967) and Slobin (1982) have reported that water droplet concentration varies from 70 to 465 per cm^3. It has been observed by Slobin (1982) that the average diameter of a water droplet in a cloud varies from 9 to 20 μm while Carrier *et al* (1967) reported that the drop size varies from 1 to 60 μm. Clouds contain saturated water vapour. Clouds occur at higher altitude also. A cloud has liquid water content between 0.1 and 1.0 g/m^3. The thickness of a cloud is usually between 1.5 and 2.5 km, depending on the type of cloud. Slobin (1982) reported that the thickness of a light cloud is around 0.2 km while the thickness of a medium cloud is 0.5 km and the thickness of a heavy cloud is 1 km and 1.5–2.0 km. Cloud occurrence morphology over Dumdum has been obtained from low-level cloud of about 2–6 km altitude.

Formation and destruction of ozone in the troposphere comprises a series of complex cycles in which atomic oxygen, molecular oxygen, carbon monoxide, oxides of nitrogen, water vapour, volatile organic compounds, etc. are involved. Ozone in the troposphere is produced by the addition of ground state oxygen atoms O (^{3}p) to molecular oxygen assisted by any third body M to ensure simultaneous momentum and energy conservation (Madronich 1993).

$$\mathrm{O}\left(^3\mathrm{p}\right) + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{O_3} + \mathrm{M}.$$

The primitive terrestrial atmosphere was oxygenic in nature and ozone was produced by photodissociation of water vapour as follows (Midya and Jana 2002):

$$\mathrm{H_2O} + h\nu \rightarrow \mathrm{OH} + \mathrm{H},$$
$$\mathrm{OH} + h\nu \rightarrow \mathrm{O} + \mathrm{H},$$
$$\mathrm{O} + \mathrm{O} + \mathrm{M} \rightarrow \mathrm{O_2} + \mathrm{M},$$
$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{O_3} + \mathrm{M}.$$

The source of oxygen atom in troposphere is not the same as in stratosphere where oxygen atoms are produced by the photodissociation of O_2 at UV wavelengths less than 240 nm. In the troposphere, only UV radiation with greater than 290 nm is available, because of essentially complete absorption of shorter wavelengths by O_2 and O_3 above the tropopause. Atomic oxygen in the troposphere is produced by photodissociation of NO_2 and tropospheric O_3 as follows:

i) $\mathrm{NO_2} + h\nu\,(\lambda = 424\ \mathrm{nm}) \rightarrow \mathrm{NO} + \mathrm{O}$
ii) $\mathrm{O_3} + h\nu\,(\lambda = 300{-}320\ \mathrm{nm}) \rightarrow \mathrm{O} + \mathrm{O_2}$

Tropospheric ozone is mainly formed by photochemical oxidation of carbon monoxide, methane and non-methane volatile organic compounds (NMVOCs) in the presence of nitrogen oxide radicals ($\mathrm{NOx} \equiv \mathrm{NO} + \mathrm{NO_2}$). Oxidation begins with the reaction of CO with OH radical. The hydrogen atom thus produced rapidly reacts with oxygen molecule to give peroxy radicals. Peroxy radicals then continue to react with NO to NO_2 that is photolysed to atomic oxygen which reacts with O_2 to produce a molecule of O_3.

$$\mathrm{OH} + \mathrm{CO} \xrightarrow{[\mathrm{O_2}]} \mathrm{H} + \mathrm{CO_2}$$
$$\mathrm{H} + \mathrm{O_2} \rightarrow \mathrm{HO_2}$$
$$\mathrm{HO_2} + \mathrm{NO} \rightarrow \mathrm{OH} + \mathrm{NO_2}$$
$$\mathrm{NO_2} + h\nu\,(\lambda = 424\ \mathrm{nm}) \rightarrow \mathrm{NO} + \mathrm{O}$$
$$\mathrm{O}\left(^3\mathrm{p}\right) + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{O_3} + \mathrm{M}.$$

The net effect of these reactions is:

$$\mathrm{CO} + 2\mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{O_3}.$$

The OH radical in the troposphere is produced by photodissociation of nitrous, and nitric acids, ozone (Tie *et al* 2003) and hydrogen peroxide (Tie *et al* 2003) as follows:

$$\mathrm{HONO} + h\nu\,(\lambda = 400\ \mathrm{nm}) \rightarrow \mathrm{OH} + \mathrm{NO}$$
$$\mathrm{HNO_3} + h\nu\,(\lambda = 350\ \mathrm{nm}) \rightarrow \mathrm{OH} + \mathrm{NO_2}$$
$$\mathrm{O_3} + h\nu\,(\lambda \leq 320{-}410\ \mathrm{nm}) \rightarrow \mathrm{O}\left(^1\mathrm{D}\right) + \mathrm{O_2}$$
$$\mathrm{O}\left(^1\mathrm{D}\right) + \mathrm{H_2O} \rightarrow 2\mathrm{OH}$$
$$\mathrm{H_2O_2} + h\nu \rightarrow 2\mathrm{OH}$$

Peroxy radical is also produced by the photolysis of formaldehyde (Tie *et al* 2003).

$$\mathrm{CH_2O} + h\nu + 2\mathrm{O_2} \rightarrow \mathrm{CO} + 2\mathrm{HO_2}$$

SO_2 injected into the atmosphere may also assist ozone formation by absorbing radiation. SO_2 absorbs radiation strongly between 180 and 235 nm, weakly between 260 and 340 nm and very weakly between 340 and 390 nm (Crutzen and Schmailzl 1983).

$$\mathrm{SO_2} + h\nu \rightarrow \mathrm{SO} + \mathrm{O}\,(\lambda < 220\ \mathrm{nm})$$
$$\mathrm{SO} + \mathrm{O_2} \rightarrow \mathrm{SO_2} + \mathrm{O}$$
$$2\,(\mathrm{O} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{O_3} + \mathrm{M})$$
$$\text{Net:}\ 3\mathrm{O_2} \rightarrow 2\mathrm{O_3}$$

The simplified form of tropospheric ozone formation from volatile organic compounds (VOCs) obeys the following steps:

$$\begin{aligned}
&\mathrm{VOC} + \mathrm{OH} + \mathrm{O_2} \rightarrow \mathrm{RO_2} + \mathrm{H_2O}\\
&\mathrm{RO_2} + \mathrm{NO} + \mathrm{O_2} \rightarrow \mathrm{NO_2} + \mathrm{HO_2}\\
&\quad + \mathrm{CARB}\,(\text{Secondary VOC})\\
&\mathrm{HO_2} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{OH}\\
&2\,(\mathrm{NO_2} + h\nu + \mathrm{O_2} \rightarrow \mathrm{NO} + \mathrm{O_3})\\
&\mathrm{Net}:\,(\mathrm{NOx} + \mathrm{OH}) + \mathrm{VOC} + 4\mathrm{O_2} \rightarrow 2\mathrm{O_3}\\
&\quad + \mathrm{CARB} + \mathrm{H_2O} + (\mathrm{NOx} + \mathrm{OH})\,,
\end{aligned}$$

where R denotes organic radicals and CARB stands for carbonyl compounds.

The loss of tropospheric ozone is mainly due to the following reaction (Tie *et al* 2003):

$$\mathrm{O_3} + h\nu\,(\lambda \leq 320{-}410\ \mathrm{nm}) \rightarrow \mathrm{O}\left(^1\mathrm{D}\right) + \mathrm{O_2}$$

OHx radicals are removed from the atmosphere by the formation of hydrogen peroxides, organic peroxides, nitric acids and other organic nitrates.

$$\begin{aligned}
\mathrm{HO_2} + \mathrm{HO_2} &\rightarrow \mathrm{H_2O_2} + \mathrm{O_2}\\
\mathrm{RO_2} + \mathrm{HO_2} &\rightarrow \mathrm{ROOH} + \mathrm{O_2}\\
\mathrm{OH} + \mathrm{NO_2} &\rightarrow \mathrm{HNO_3}
\end{aligned}$$

Stevenson *et al* (2006) proposed that the higher ozone production rates in the troposphere are due to higher NOx emission, higher isoprene emission, more detailed non-methane hydrocarbon (NMHC) scheme and improved parameterization of processes such as photolysis, convection and stratosphere–troposphere exchange. From the above mechanisms of tropospheric ozone production and loss, it is clear that solar radiation plays a key role. The main factors that affect the atmospheric radiative transfer at wavelengths important for tropospheric ozone budget are the solar zenith angle, absorption by stratospheric ozone, reflection from the surface, scattering and absorption by aerosol particles and clouds. From the observation of the short wave radiation effects of clouds on the tropospheric ozone, Voulgarakis *et al* (2009) found that clouds have a modest effect on ozone on global scale, but their role is much more significant on a regional scale. They observed that both the production and loss of ozone increase significantly above the cloudiest areas and decrease below these areas. The main cause of this feature is that the photolysis rates of NO_2 and O (^{1}D) decrease below the clouds because of attenuation of radiations by cloud particles and increase above the clouds due to backscattering. Solar zenith angles are small in the tropics and in such cases, the increase in photolysis rates starts in the lowest regions of the clouds.

2. Study of cloud chemistry

Cloud chemistry consists of gaseous phase chemistry, aqueous phase chemistry and scavenging of soluble gases (Zhu *et al* 2001). Clouds can bring about changes in solar radiation that are responsible for increasing or decreasing photochemical reaction in the troposphere and thus reduce or enhance the tropospheric ozone concentration. They can directly absorb ozone and its precursors (NOx, NMHC, free radicals, etc.) in cloud liquid water thereby decreasing the tropospheric ozone (Zhu *et al* 2001). Clouds are responsible for various aqueous phase chemical reactions in chemical species absorbed by clouds, leading to changes in the gaseous phase ozone concentration. Clouds provide surfaces for heterogeneous chemistry to take place (Jacob 2001). Precipitating clouds scavenge soluble trace gases and aerosols from troposphere (Liu *et al* 2001). Vertical motions associated with clouds result in substantial convective transport of chemical species. Particularly, deep convection can provide an important source of hydrogen oxide radicals in the upper atmosphere, leading to enhanced production of ozone (Prather and Jacob 1997). Lightning associated with deep convective clouds is an important source of nitrogen oxides in the middle and upper atmosphere (Pickering 1998). Clouds can also scatter and absorb incoming solar radiation, modifying the actinic flux and thus the photolysis frequencies of key chemical species. Enhanced photolysis frequencies have been observed above and in the upper level of clouds, while reduced frequencies were found below optically thick clouds and absorbing aerosols (Lefer *et al* 2003). Cloud reduction of solar radiation is wavelength-dependent in the UV-range. The longer wavelength UV-A is more strongly attenuated than UV-B wavelengths (Crawford *et al* 2003). Reduced photolysis frequencies occur underneath a cloud. UV radiation reflected up from the cloud can enhance the upwelling actinic flux by 50%–150% which results 30–40% increase in the total above-cloud photolysis frequencies (Pfister *et al* 2000). In addition, short-term local enhancement of photolysis frequencies of about 40% has been observed at the Earth's surface under some specific broken cloud conditions where the disc of the Sun is not occluded by a cloud and the cloudy portion of the sky is brighter than the clear sky portion (Lantz *et al* 1996).

Clouds in the troposphere can influence the photolysis rates (J values) and hence concentrations of chemical species. Tie *et al* (2003) suggest that global mean OH concentration increases by about 20% due to the impact of clouds. Owing to clouds, the globally averaged photolysis rates of J [O_3], J [CH_2O] and J [NO_2] are enhanced in the

troposphere by about 12, 13, and 13%, respectively, that lead to an 8% increase in the tropospheric ozone. Liu*et al* (2006) proposed that the global mean change in OH concentration is insignificant (∼1%), but it shows much larger changes above (5–10%) and below (−5–20%) the tropical deep convective clouds and the mid-latitude low-level clouds, as well as near surface (approximately −20%). For O_3, the global mean effect is about 3–5% increase. O_3 increase in the tropical upper troposphere is ∼5–8%. They suggested that O_3 increase above the clouds is due to backscattering of solar radiation, whereas O_3 increase below the tropical deep clouds is due to the reduced net O_3 losses. Voulgarakis *et al* (2009) reported that the largest averaged change in chemical budgets of ozone was found in marine troposphere where cloud optical depths were high. Cloud effects were small on average in the middle troposphere because this is a transition region between reduction and enhancement in photolysis rates. Increases in boundary layer ozone due to clouds were driven by large-scale changes in downward ozone transport from higher in the troposphere rather than by decrease in *in situ* chemical loss rates. Increases in upper tropospheric ozone are caused by higher production rates due to back scattering of radiations and consequent increases in photolysis rates of mainly NO_2.

It is now well-established that different environmental parameters may influence the variation of ozone concentration in different layers in the atmosphere. Ozone layer in the atmosphere also plays an important role in controlling different events occurring in troposphere, stratosphere and mesosphere. Ozone is not equally distributed in the atmosphere. The concentration of ozone gradually increases from upper troposphere of about 10 km altitude, attains maximum value at an altitude of about 25 km and then gradually decreases. Dobson *et al* (1946) observed that the average temperature of the Earth is directly related to ozone concentration of stratosphere and fall in ozone concentration in the stratosphere takes place over England before the arrival of warm front at the ground surface. The rise in ozone content in the stratosphere occurs when cold front reaches the ground level. Mitra (1992) reported the close relation between barometric height, tropospheric weather and ionospheric parameters of the upper atmosphere. It was observed that the minimum height of F region and average E ionization tend to follow the variation of barometric height. Correlation was observed between the lowest virtual height of E region and ground temperature at Standford, California, USA. Bates (1981) and Mackay *et al* (1997) reported that the variation of solar UV radiation due to fall of stratospheric ozone concentration can influence tropospheric climate in several ways. Midya and Sarkar (2007) observed the correlation of the variation of stratospheric ozone with relative humidity and sharp depletion of absolute humidity related with Nor'wester over Kolkata. Mooley and Parthasarathi (1984) analysed all-India summer monsoon (June to September) rainfall for the period 1871 to 1978. They reported that the highest and lowest rainfall in the country was observed in the years 1961 and 1877, respectively. There was a continuous rise in 10-yr mean rainfall from 1899 to 1953. Rakecha and Soman (1994) observed that the annual extreme rainfall records of most of the stations over India were free from trend and persistence. The extreme rainfall series at stations over the west coast, north of 12°N and some stations to the east of the Western Ghats over the central parts of the peninsula showed a significant increasing trend at 95% level of confidence. Stations over the southern peninsula and the lower Ganga valley had been found to exhibit a decreasing trend at the same level of significance.

Monod and Carlier (1999) performed a box model study of the multiphase photochemistry (both gas and aqueous phases) of C_1 organic compounds within a non-precipitating cloud on a local scale. They found that in a situation where ozone accumulates in clear sky conditions, as soon as cloud is formed, the tropospheric ozone estimate changes drastically; the net production decreases by a factor of 2 or more and depending on the NOx concentration and the pH values, can actually lead to chemical destruction. Bremaud and Taupin (1998) investigated the influence of clouds on the diurnal cycle of ozone concentration in the Reunion Island marine boundary layer. They reported that the orographic cloud layer plays an important role in the chemistry of ozone through several ways. The two major ones are the enhancement of photodissociation processes in the interstitial air relative to clear sky conditions and the perturbation of the NOx photostationary state through the scavenging of HO_2 and CH_3O_2 radicals. They concluded that the greater destruction of the marine boundary layer ozone observed in Reunion Island relative to the mean 4 ppbv was due to clouds. Williams and Toumi (1999) reported that the inclusion of high cloud was found to bring about warming of the troposphere, resulting in a net heating in the lower stratosphere. It strengthened the circulation, leading to decrease in total tropical ozone. Jana *et al* (2010) reported the significant rise of total atmospheric ozone column density with increase in cloud occurrences not considering other meteorological parameters. In this paper, the nature of annual cycles of tropospheric ozone, cloud occurrences, NO_2, rainfall, SO_2, suspended particulate matter (SPM), CO, NMHC

and surface solar radiation for the period October 2004 to June 2009 has been shown and explained over Alipore (22.52°N, 88.33°E), India. The effect of these micro-meteorological parameters including cloud occurrences on tropospheric ozone has been critically analysed. Possible explanation based on physical considerations and chemical kinetics has been critically discussed. Alipore, an important site in the south of the megacity Kolkata is situated on the east bank of the river Hooghly. The sea (Bay of Bengal) is about 50 km away from it in the south. The population is approximately 46,00,000 over an area of 185 km^2 around it. The city is significantly polluted by a large number of small-scale industries, vehicular traffic, thermal power plants and very busy ports. At the west bank opposite to Kolkata, is Howrah city which is full of small and large industries of iron and jute mills.

3. Data and analysis

Total ozone mapping spectrometer (TOMS) version 8 monthly mean column density of tropospheric ozone in Dobson unit (DU) is derived by the convective cloud differential (CCD) method (Ziemke *et al* 1998) over Alipore station in India. Tropospheric column ozone can usually be determined from the following two well-known approaches using satellite data. In the first method, the stratospheric column ozone is derived by combining upper atmosphere research satellite (UARS) halogen occultation experiment (HALOE) and microwave limb sounder (MLS) ozone measurements. Tropospheric column ozone is then obtained by subtracting these stratospheric amounts from the total column. Total column ozone in this study includes retrievals from Nimbus 7 (November 1978 to May 1993) and Earth probe (July 1996 to present) TOMS. Data from HALOE are used in this first method to extend the vertical span of MLS (highest pressure level 46 hPa) using simple regression. This assimilation enables high resolution daily maps of tropospheric and stratospheric ozone which is not possible from solar occultation measurements alone, such as HALOE or Stratospheric Aerosols and Gas Experiment (SAGE). Ziemke *et al* (1998) provided another new and promising technique that yields tropospheric column ozone directly from TOMS high density footprint measurements in regions of high convective clouds. They defined this method as the CCD technique. The CCD method uses TOMS total ozone measurements over highly reflecting, high altitude clouds. In some regions, especially the tropical western Pacific, these high-reflectivity clouds are often associated with strong convection and cloud tops near the tropopause. The tropospheric column can be obtained at cloud-free pixels by subtracting the above-cloud stratospheric ozone amount from TOMS total ozone. Since cloud height information is not measured by TOMS, the primary assumption in the CCD method is that the high-reflectivity clouds often have cloud tops at the tropopause. The monthly mean ozone concentration in DU at Alipore has been obtained from the website http://jwocky.gsfc.nasa.gov, published by NASA, USA for the period October 2004 to June 2009.

The cloud data, concentration of NO_2, amount of rainfall, densities of CO, NMHC, SO_2 and SPM data over Alipore (22.52°N, 88.33°E) have been collected from the India Meteorological Department, Kolkata and belongs to the period October 2004 to June 2009. The cloud cover is estimated by the observer and expressed on a scale (Kumar *et al* 2001) ranging from 0 to 8 Octas. Hence, 0 Octas means clear sky, 4 Octas means that one-half (or four-eighths) of the sky is covered with cloud and 8 Octas implies fully covered (overcast).

The density of carbon monoxide is measured by non-dispersive infrared (NDIR) gas filter correlation method based on the infrared absorption (at 4.67 μm) by CO molecules within its rotation–vibration absorption band. The analyser of CO (CO11M) has a lower detection limit of 0.4 ppbv (noise at 0.2 ppbv) with minimum response time of 20 s. The analyser was calibrated at regular intervals with reference standard CO gas in cylinders procured from Hydro Gas India Ltd. Concentration of NO_2 is monitored with a standard chemiluminescent analyser (AC 31M) based on measurement of chemiluminescence (at 630 nm) produced by the oxidation reaction of NO from the sample gas with ozone. The lower detection limit of the detector is 0.35 ppbv (noise at zero being 0.17 ppbv) with a response time of 20 s. The calibration was done with a reference standard of NO gas in cylinders procured from Hydro Gas India Ltd. The measurement of NMHC is carried out in reactive Hydrocarbon analyser (Model-HC 51M). The minimum detection limit of the analyser is 50 ppbv (noise at zero being 25 ppbv) at a response of time of about 120 s. The employed flame ionization detector is fired by hydrogen gas for quantization of hydrocarbons. The calibration was done with the help of reference standard propane gas in cylinders collected from Hydro Gas India Ltd. (Purkait *et al* 2009).

Isotropic ground reflected radiation has been computed by Katiyar and Panday (2010). Isotropic ground reflected daily radiation can be obtained by using the formula $Hr = H\rho\,(1 - \cos\beta)$, where H, ρ and β are the monthly mean daily total radiation on horizontal surface, albedo and tilt angle of 45°, respectively.

4. Results and discussion

Annual cycles of monthly mean tropospheric ozone concentrations, cloud occurrences, concentration of NO_2, amount of rainfall, densities of CO, NMHC, SO_2, SPM and solar radiation at Alipore (22.52°N, 88.33°E), for the period October 2004 to June 2009 are presented in figure 1. Amount of tropospheric ozone concentration gradually increased from January, attained maximum in May, then gradually decreased, achieved minimum value in August and then increased very slightly. This is due to the fact that the rates of the reactions which favour the tropospheric ozone formation from its precursors were enhanced by sharp increase of surface solar radiation from January to May. During August, the minimum amount of tropospheric ozone was a result of lower photolysis rates of ozone formation processes caused by lower surface radiation energy due to large occurrences of clouds in the monsoon time (JJAS) as well as lower concentration of ozone precursor, viz., CO, NMHC, SO_2, NO_2, etc. After August, the rate of increase in concentration of ozone was slow because of disappearance of clouds, mild fall of solar radiation and steady rise of ozone precursor amount.

Cloud occurrences show the number of days and/or nights, the sky is fully or partially covered with cloud during various times in each month. Cloud occurrence attained the lowest value in December, then gradually increased from January, attained its highest value in July and then

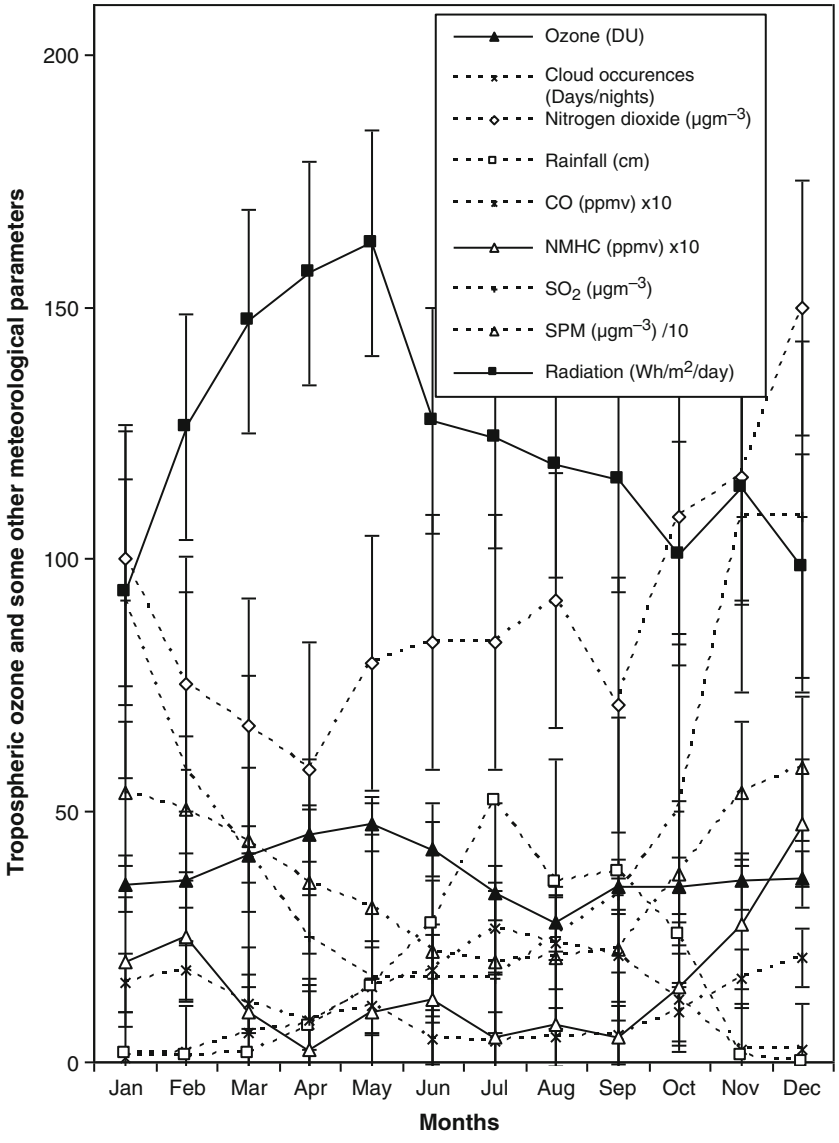

Figure 1. Annual cycles of tropospheric ozone and some other meteorological parameters over Alipore (22.52°N, 88.33°E) for the period October 2004 to June 2009.

gradually decreased. Amount of rainfall increased exponentially from January to July, attained the maximum value in July and then gradually decreased. Comparatively high rainfall was observed from June to September. Low occurrences of cloud and rainfall before and during pre-monsoon (MAM) had been attributed to occasional existences of Nor'wester that occurred usually 2–6 times in each month from February to May in every year. Large cloud occurrences and rainfall during monsoon (JJAS) were obviously due to the existence of monsoon wind from middle of June that carried huge amount water vapour from south oceans consisting of Bay of Bengal, Indian Ocean and Arabian Sea. Gradual fall of cloud occurrence and rainfall during post-monsoon was a result of dry-retreat monsoon or north-westerly wind comprising very less amount of water vapour entering from Bihar, Orissa, Assam including Bangladesh that might clash with wet wind of Bay of Bengal causing cyclone sometimes due to the high pressure and temperature difference.

The annual cycle of the concentration of NO_2 reveals a sharp fall from January to April, then moderate rise up to August and the steep enhancement of NO_2 concentration up to December except September. Comparatively low concentration of NO_2 occurred in April and September. The density of CO gradually declined from January to June, then remained almost unaltered up to September and then gradually increased. The concentration of NMHC gradually fell from January to April, then remained almost steady up to September and then increased sharply. Comparatively, low concentration of NMHC was observed from May to September. The concentration of SO_2 steeply decreased from January to May, then attained minimum values for May to July and then steeply increased. The amount of SPM gradually reduced from January to June, attained comparatively low value from June to September and then sharply increased. The continuous fall of NO_2, CO and NMHC were because of increased photo-induced reaction producing tropospheric ozone due to rise in solar radiation during winter and pre-monsoon period, and increased absorption of these molecules and SPM by water vapour and clouds as follows:

$$\mathrm{NO_2} + h\nu\,(\lambda = 424\ \mathrm{nm}) \rightarrow \mathrm{NO} + \mathrm{O}.$$

$$\mathrm{CO} + 2\mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{O_3}.$$

$$(\mathrm{NOx} + \mathrm{OH}) + \mathrm{VOC} + 4\mathrm{O_2} \rightarrow 2\mathrm{O_3} + \mathrm{CARB} + \mathrm{H_2O} + (\mathrm{NOx} + \mathrm{OH}).$$

$$\mathrm{SO_2} + h\nu \rightarrow \mathrm{SO} + \mathrm{O}.$$

$$\mathrm{NO_2} + \mathrm{H_2O} \rightarrow \mathrm{HNO_2} + \mathrm{HNO_3}.$$

$$\mathrm{CO_2} + \mathrm{H_2O} \rightarrow \mathrm{H_2CO_3}.$$

$$\mathrm{SO_2} + \mathrm{H_2O} \rightarrow \mathrm{H_2SO_3}.$$

Moreover, westerly wind flow picked up above anthropogenically derived gases from Kolkata to eastern region of India during pre-monsoon. The lowest densities of NO_2 in September, CO, NMHC and SPM during monsoon were mostly due to wash out of these constituents from troposphere effect by huge rainfall. Gradual rise in concentration of NO_2 from April to August was mainly due to the reaction $N_2 + O_2 \rightarrow 2NO$ in presence of lightning that usually occurred during this period followed by the reaction $2NO + O_2 \rightarrow 2NO_2$. Steep building of these constituents during post-monsoon was due to comparatively low solar radiation, very little amount of rainfall and existence of north-westerly and mostly north-easterly

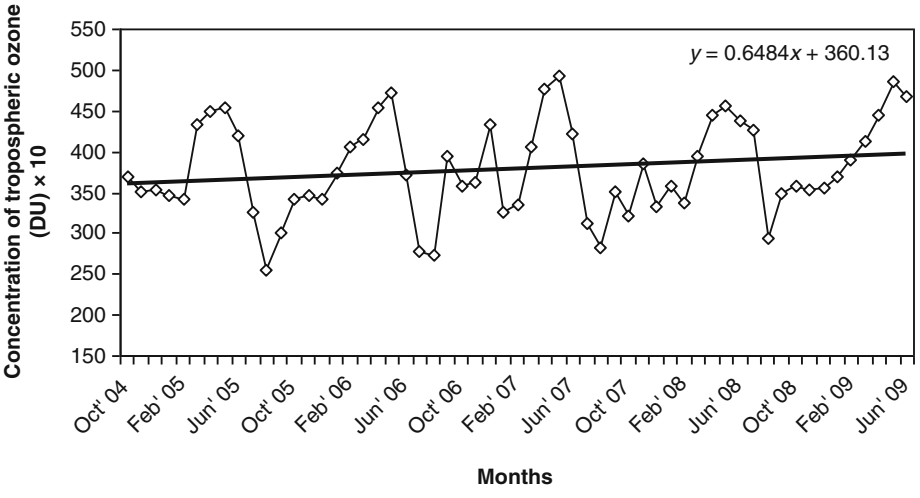

Figure 2. Variation of monthly mean tropospheric ozone concentration (DU) from October 2004 to June 2009 over Alipore (22.52°N, 88.33°E).

winds which entered from north-eastern and north western regions bringing significantly polluted air from the neighbouring cities to Kolkata (Purkait *et al* 2009).

Solar radiation exponentially increased from January to May, achieved maximum in May and then slowly decreased. The reason behind an enhancement in surface solar radiation from January to May is the gradual decrease in distance between the Earth and the Sun and increase in daytime from 21 December to 21 June. Sudden fall in surface solar radiation in the month of June was because of large occurrence of cloud appeared due to monsoon. Comparatively gradual lowering in solar radiation in monsoon and post-monsoon time was also due to large occurrence of cloud in monsoon, slow increase in distance between the Earth and the Sun, decrease in daytime and appearance of fog and smog during autumn and winter time.

Variation of monthly mean tropospheric ozone over Alipore from October 2004 to June 2009 has been depicted in figure 2. It reveals that though the nature of variation of tropospheric ozone was oscillatory, the concentration of tropospheric ozone had risen very slowly for this period probably due to slow increase in the amount of ozone precursors and surface temperature because of enhanced surface solar radiation.

Scattered variations of tropospheric ozone with cloud occurrence, rainfall, CO and SPM have been represented in figure 3. It clearly indicates that tropospheric ozone concentration attained higher value at moderate cloud occurrence, rainfall, CO and SPM, and comparatively lower tropospheric ozone at both lower and higher values of cloud occurrences, rainfall, CO and SPM. Tropospheric ozone concentration acquired the higher value during pre-monsoon and early monsoon time (MAMJ)

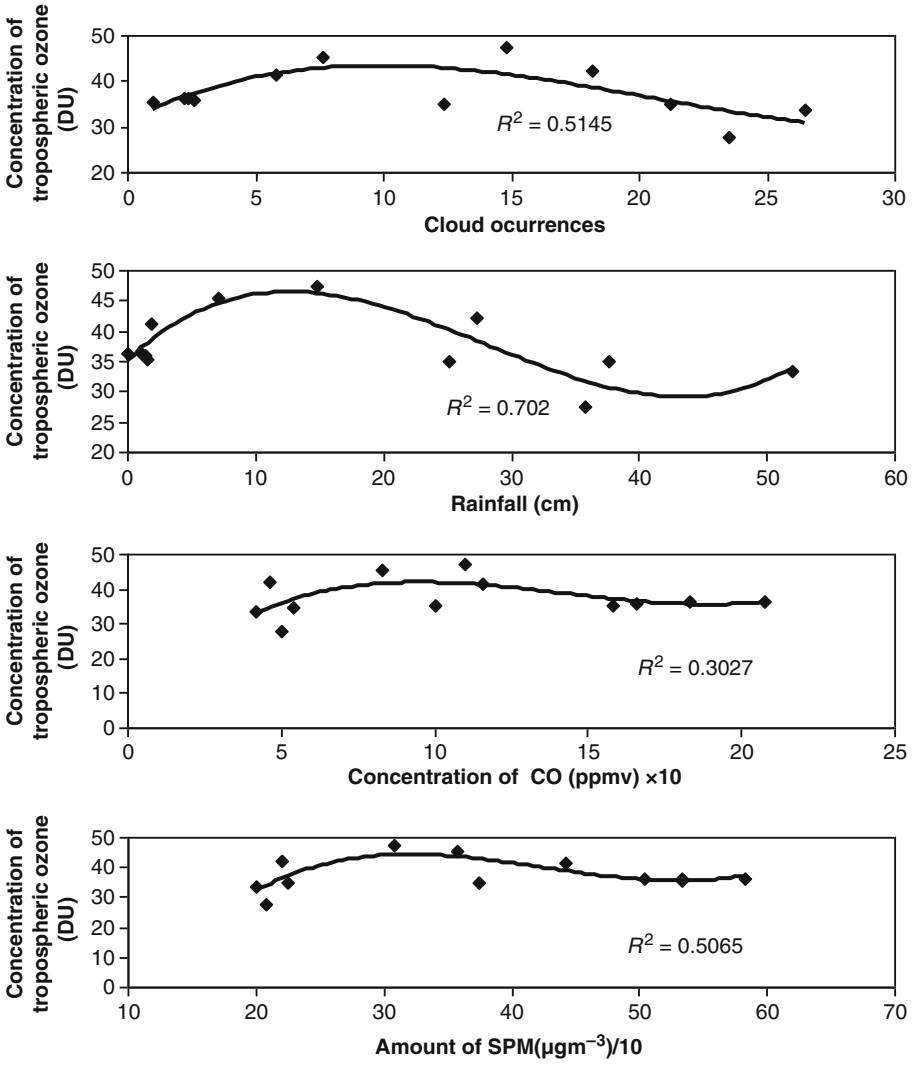

Figure 3. Scattered diagram of tropospheric ozone (DU) with cloud occurrences, rainfall (cm), CO (ppmv) and SPM (μgm^{-3})/10.

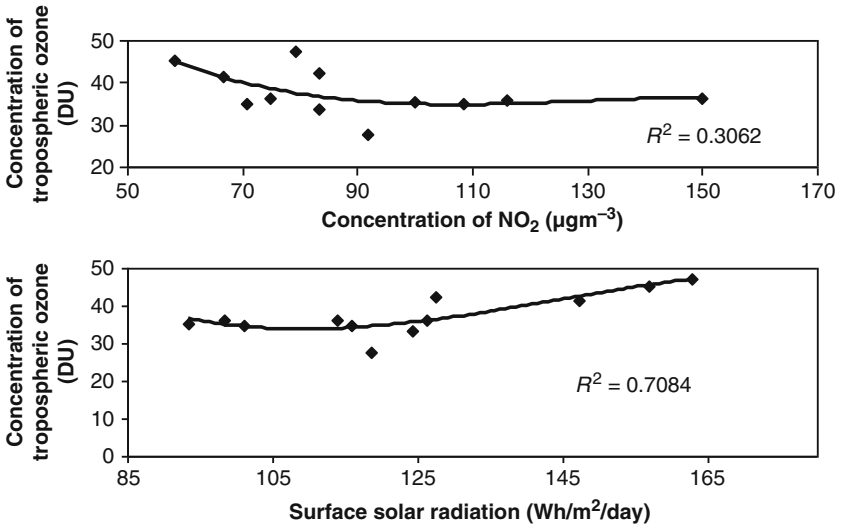

Figure 4. Scattered diagram of tropospheric ozone (DU) with NO_2 (μgm^{-3}) and surface solar radiation (Wh/m^2/day).

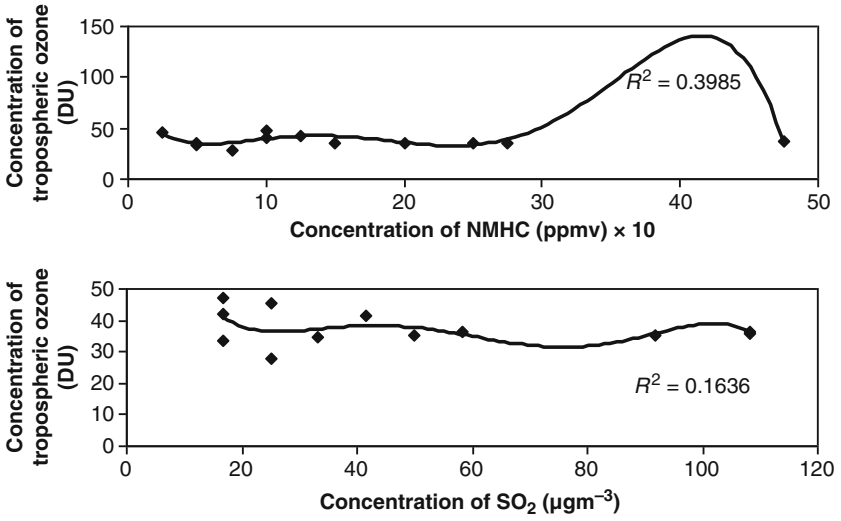

Figure 5. Scattered diagram of tropospheric ozone (DU) with NMHC (ppmv) ×10 and SO_2 (μgm^{-3}).

when cloud occurrences, rainfall, CO and SPM; all had moderate values, but surface solar radiation attained higher and some moderate values. These observations clearly indicate that photo-oxidation processes took place at the maximum rate leading the optimum net tropospheric ozone formation because of moderate amount of reactant molecules and higher surface solar radiation. Tropospheric ozone concentration acquired minimum value during the months of July and August when cloud occurrences and rainfall had occurred higher values, but CO, SPM and solar radiation achieved the lower values which indicate the slower rate of photo-oxidation reactions. Again at lower values of cloud occurrence, rainfall, CO and SPM; solar radiation is either lower or somewhat moderate that lowers ozone formation rates. At higher values of these micro-meteorological parameters, solar radiation is also low which again reduces the rate of ozone formation.

Scattered variations of tropospheric ozone with NO_2 and solar radiation have been shown in figure 4. The nature of tropospheric ozone variation with NO_2 and solar radiation though oscillatory has slight decreasing trend and increasing trend with increase in NO_2 and solar radiation, respectively. At low concentration, oxides of nitrogen instead of ozone formation favour the depletion of ozone as follows (Bekki *et al* 1993):

$$NO_2 + h\nu\,(\lambda = 424\text{ nm}) \rightarrow NO + O$$

$$NO + O_3 \rightarrow NO_2 + O_2.$$

As a result of the increase in NO_2 concentration, the decline rate of ozone increases reducing the

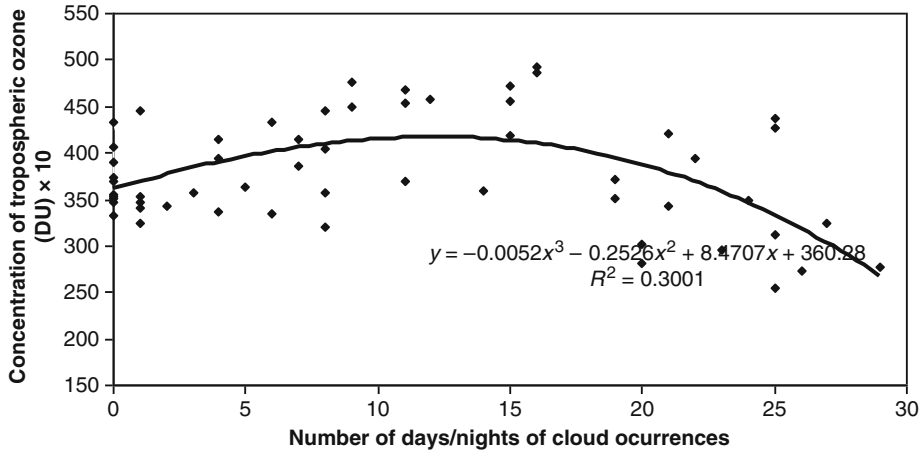

Figure 6. Scattered diagram of monthly mean tropospheric ozone (DU) × 10 with cloud occurrences from October 2004 to June 2009 over Alipore (22.52°N, 88.33°E).

amount of tropospheric ozone. But, with enhancement of surface solar radiation, photodissociation rates of ozone formation from its precursors predominated over depletion processes that led to net tropospheric ozone rise. Scattered variations of tropospheric ozone with NMHC and SO_2 depicted in figure 5 reveal oscillatory nature because of comparable rates of their catalysed ozone formation and depletion processes. Figure 6 represents the scattered diagram of monthly mean tropospheric ozone concentrations with the monthly mean cloud occurrences for the period October 2004 to June 2009 at Alipore. It clearly depicts that the concentration of ozone was oscillatory with occurrences of cloud and had decreased very slowly with increase in cloud occurrence because of larger rate of absorption of solar radiation reflected from Earth and prevention of solar radiation entering through the cloud. Ozone concentration attained higher value at moderate cloud occurrences and lower value at both lower and higher cloud occurrences due to higher solar radiation and moderate concentration of ozone precursors at moderate cloud occurrences and comparatively lower solar radiation energy at both the lower and higher range of cloud occurrences.

The correlation coefficient between the tropospheric ozone and other micro-meteorological parameters including cloud occurrences shows very poor positive or negative imperfect correlations between them except with solar surface radiation that supports oscillatory nature of ozone variation to the rise in other parameters. The correlation coefficient between tropospheric ozone with surface solar radiation reveals high positive correlation between them that supports the build-up in tropospheric ozone with rise in surface solar radiation as represented in figure 4. According to multiregression analysis, the formation of tropospheric ozone was governed by the above parameters as follows:

$$\begin{aligned}[\mathrm{O_3}] \;=\; & 43.835 - 4.003\ \mathrm{Cloud} + 0.781\mathrm{NO_2} \\ & + 01.482\ \mathrm{Rainfall} - 0.096\,[\mathrm{SO_2}] \\ & - 2.627\,[\mathrm{SPM}] + 0.149\,[\mathrm{CO}] \\ & + 0.095\,[\mathrm{NMHC}] + 1.135\ \mathrm{Radiation}.\end{aligned}$$

The above equation also reveals the build-up of tropospheric ozone with increase in surface solar radiation as obtained in figure 4 and declining of tropospheric ozone with increase in cloud as depicted in figures 3 and 6.

5. Conclusions

Clouds can not only influence the Earth's climate through modulation of the Earth's energy and hydrological cycles, but also tropospheric photochemistry through modification of solar radiation that determines photolysis rates for ozone production and loss. Annual cycles of tropospheric ozone, cloud occurrences, surface solar radiations and other meteorological parameters during the period October 2004 to June 2009 revealed a gradual rise in tropospheric ozone from January to May because of increasing rates of ozone formation reactions by the enhanced surface solar radiation, the minimum amount of tropospheric ozone in August due to lower photolysis rates of ozone formation processes caused by lower surface radiation energy due to large occurrences of clouds in the monsoon time (JJAS) as well as lower concentration of ozone precursor viz., CO, NMHC, SO_2, NO_2, etc., and then slow increase in the concentration of ozone due to disappearance of cloud, mild fall in solar radiation and steady rise in ozone precursors.

Low occurrences of cloud and rainfall before and during pre-monsoon (MAM) had been observed for the occasional existences of Nor'wester usually occurred 2–6 times in each month from February to May in every year. Large cloud occurrences and rainfall during monsoon (JJAS) had been seen obviously as a result of the existences of monsoon wind from middle of June that brought huge amount of water vapour from south oceans and gradual fall of cloud occurrence and rainfall during post-monsoon due to dry-retreat monsoon or north-westerly wind comprising very less amount of water vapour entering from Bihar, Orissa, Assam including Bangladesh that might clash with wet wind of Bay of Bengal causing cyclone sometimes because of the high pressure and temperature difference. Slow rise of monthly mean tropospheric ozone over Alipore from October 2004 to June 2009 was probably due to slow increase in the amount of ozone precursors and surface temperature because of enhanced surface solar radiation as a result of declining cloud occurrences.

The gradual decline of NO_2, CO and NMHC from winter to pre-monsoon might be a result of enhanced photo-induced reaction producing tropospheric ozone due to rise in solar radiation during winter and pre-monsoon periods, and increased absorption of these molecules and SPM by water vapour and clouds and westerly wind flow that picked up above anthropogenically derived gases from Alipore, Kolkata to eastern region of India during pre-monsoon. The lowest densities of NO_2 in September, CO, NMHC and SPM during monsoon were mainly due to washing out of these constituents from troposphere by heavy rainfall; while gradual rise in concentration of NO_2 from April to August was mainly due to the formation of NO and NO_2 in presence of lightning usually occurred during this period from atmospheric nitrogen and oxygen molecules. The steep building up of these constituents was observed during post-monsoon because of comparatively low solar radiation, very little amount of rainfall and existence of north-westerly and mostly north-easterly winds entered from north-eastern and north western regions which carried significantly polluted air from neighbouring cities to Alipore.

The nature of variation of tropospheric ozone was oscillatory with occurrences of cloud for the period October 2004 to June 2009 at Alipore and had very little declining tendency with increase in cloud occurrence because of larger rate of absorption of solar radiation reflected from Earth and prevention of solar radiation entering through the cloud. Ozone concentration attained higher value at moderate cloud occurrences and lower value at both lower and higher cloud occurrences due to higher solar radiation and moderate concentration of ozone precursors at moderate cloud occurrences and comparatively lower solar radiation energy at both the lower and higher range of cloud occurrences. Again very low negative correlation coefficient value of cloud occurrences (-0.25) and high correlation coefficient value of surface solar radiation (0.73) signifies insignificant contribution of cloud occurrences and significant contribution of surface solar radiation on tropospheric ozone formation processes over Alipore, though cloud occurrences play a significant role in total ozone column density over Kolkata (Jana *et al* 2010).

References

Bates J R 1981 A dynamical mechanism through which variations in solar ultraviolet radiation can influence tropospheric climate; *Solar Phys.* **74(2)** 399–415.

Bekki S, Toumi R, Pyle J A and Jones A E 1993 Future aircraft and global ozone; *Nature* **354** 193–194.

Bremaud P J and Taupin F 1998 Cloud influence on ozone diurnal cycle in the marine boundary layer at Reunion Island; *Atmos. Res.* **47–48** 285–298.

Carrier L W, Cato G A and Von Essen K J 1967 The back scattering and excitation of visible and infrared radiation by selected major cloud models; *Applied Optics* **6(7)** 1209–1216.

Crawford J, Shetter R E, Lefer B, Cantrell C A, Jukerman W, Madronich S and Calvert J 2003 Cloud impacts on UV spectral actinic flux observed during IPMMI; *J. Geophys. Res.* **108(D16)** 8545, doi: 10.1029/2002JD002731.

Crutzen P J and Schmailzl U 1983 Chemical budgets of the stratosphere; *Planet Space Sci.* **31** 1009.

Dobson G M B, Brewer A W and Cwilong B M 1946 Meteorology of the lower stratosphere; *Proc. Roy. Soc. London A* **185** 144–175.

Feigelson E M F 1984 *Radiation in a cloudy atmosphere* (Reidel, Dordrecht: Atmospheric Science Library).

Gunn K L S and East T W R 1954 The microwave properties of precipitation particles; *Quart. J. Roy. Meteorol. Soc.* **80(346)** 522–545.

Jacob D J 2001 Heterogeneous chemistry and tropospheric ozone; *Atmos. Environ.* **34** 2131–2159.

Jana P K, Saha D K and Midya S K 2010 Effect of cloud on atmospheric ozone formation over Kolkata; *Indian J. Phys.* **84(4)** 367–375.

Kumar R, Sarkar S K and Mali P 2001 Cloud characteristics and cloud attenuation over Kolkata; *Indian J. Phys.* **75B(5)** 403–406.

Katiyar A K and Panday C K 2010 Study of ground reflected component and its contribution in diffused solar radiation incident on inclined surfaces over India; *Int. J. Energy Environ.* **1(3)** 547–554.

Lantz K D, Shetter R E, Cantrell C A, Flocke S J, Calvert J G and Madronich S 1996 Theoretical, actinometric and radiometric determinations of the photolysis rate coefficient of NO_2 during the Mouna Loa Observatory photochemistry experiments; *J. Geophys. Res.* **101(D9)** 14,613–14,630.

Lefer B, Shetter R E, Hall S R, Crawford J H and Olson J R 2003 Impacts of clouds and aerosols on

photolysis frequencies and photochemistry during TRACE-P Part I: Analysis using radiative transfer and photochemical box models; *J. Geophys. Res.* **108(D21)** 8821, doi: 10.1029/2002JD003171.

Liu H, Crawford J H, Pierce R B, Norris P, Platnic S E, Chen G, Logan J A, Yantosca, R M, Evans M J, Kittaka C, Feng Y and Tie X 2006 Radiative effect of clouds on tropospheric chemistry in a global three-dimensional chemical transport model; *J. Geophys. Res.* **111(D20303)**, doi: 10.1029/2005JD006403.

Liu H, Jacob D J, Bey I and Yantosca R M 2001 Constraints from ^{210}Pb and ^{7}Be on wet deposition and transport in a global three dimensional chemical tracer model driven by assimilated meteorological fields; *J. Geophys. Res.* **106** 12,109–12,128.

Mackay R M, KoMalcom K W, Shia R-L and Yang Y 1997 An estimation of the climatic effects of stratospheric ozone losses during the 1980s; *J. Climatol.* **10** 774–788.

Madronich S 1993 *Tropospheric photochemistry and its response to UV changes. In the role of the stratosphere in global change*; Vol. 18, NATO-ASI series, (ed.) Chanin, M L 437 (Amsterdam: Springer-Verlag).

Midya S K and Jana P K 2002 Atmospheric ozone depletion and its effect on environment; *Indian J. Phys.* **76(B)** 107–138.

Midya S K and Sarkar H 2007 Variation of stratospheric ozone with relative humidity and sharp depletion of absolute humidity associated with Nor'wester over Kolkata; *Indian J. Phys.* **81(2)** 217–224.

Mitra S K 1992 *The upper atmosphere* (Kolkata, India: Asiatic Society), pp. 351.

Monod A and Carlier P 1999 Impact of clouds on the tropospheric ozone budget: Direct effect of multiphase photochemistry of soluble organic compounds; *Atmos. Environ.* **33(27)** 4431–4446.

Mooley D A and Parthasarathi B 1984 Fluctuations in all-India monsoon rainfall during 1871–1978; *Climate Change* **6(3)** 287–301.

Pfister G, Baumgartner D, Maderbacher R and Putz E 2000 Aircraft measurements of photolysis frequencies for ozone and nitrogen dioxide under cloudy conditions; *Atmos. Environ.* **34** 4019–4029.

Pickering K E 1998 Vertical distribution of lightning NOx for use in regional and global chemical transport models; *J. Geophys. Res.* **103(D23)** 31,203–31,216.

Pratt K A, Demott P J, French J R, Wang Z, Westphal D L, Heymsfield A J, Twohy C H, Prenni A J and Prather K A 2009 *In-situ* detection of biological particles in cloud ice crystals; *Nature Geosci.* **2** 398–401.

Prather M and Jacob D 1997 A persistent imbalance in OH and NO photochemistry of the upper troposphere driven by deep tropical convection; *Geophys. Res. Lett.* **24** 3189–3192.

Purakait N N, De S, Sen S and Chakrabarty D K 2009 Surface ozone and its precursors at two sites in the northeast coast of India; *Indian J. Radio Space Phys.* **38** 86–97.

Rakecha P R and Soman M K 1994 Trends in the annual extreme rainfall events of 1 to 3 day duration over India; *Theor. Appl. Climatol.* **48(4)** 227–237.

Sarkar S K, Ahmad I and Gupta M M 2005 Statistical morphology of cloud occurrences and cloud attenuation over Hyderabad, India; *Indian J. Radio Space Phys.* **34** 119–124.

Slobin S D 1982 Microwave noise temperature and attenuation of clouds: Statistics of these effects at various sites in the United States, Alaska and Hawaii; *Radio Sci.* **17(6)** 1443–1454.

Staelin D H 1966 Measurements and interpretation of the microwave spectrum of the terrestrial atmosphere near 1-centimeter wavelength; *J. Geophys. Res.* **71(12)** 2875–2881.

Stevenson D S, Dentener F J, Schultz M G, Ellingsen K, Van-Noije T P C and Wild O 2006 Multi-model ensemble simulations of present-day and near-future tropospheric ozone; *J. Geophys. Res.* **111(D08301)**, doi: 10.1029/2005JD006338.

Tie X, Madronich S, Walters S, Zhang R, Rash P and Collins W 2003 Effects of clouds on photolysis and oxidants in the troposphere; *J. Geophys. Res.* **108(D20)** 4642, doi: 10.1029/2003JD003659.

Voulgarakis A, Wild O, Savage N H, Carver G D and Pyle J A 2009 Clouds, photolysis and regional tropospheric ozone budget; *Atmos. Chem. Phys.* **9** 8235–8246.

Williams V and Toumi R 1999 The radiative-dynamical effects of high cloud on global ozone distribution; *J. Atmos. Chem.* **33** 1–22.

Zhu B, Xiao H, Huang M and Li Z 2001 Numerical study of cloud effects on tropospheric ozone; *Water Air Soil Pollut.* **129** 199–216.

Ziemke J R, Chandra S and Bharatia P K 1998 Two new methods for deriving tropospheric column ozone from TOMS measurements; the assimilated UARS MLS/HALOE and convective-cloud differential techniques; *J. Geophys. Res.* **103** 22,115–22,127.

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