Effect of some climatic parameters on tropospheric and total ozone column over Alipore (22.52°N, 88.33°E), India

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The paper presents the nature of variations of tropospheric and total ozone column retrieved from the Convective Cloud Differential (CCD) technique, Ozone Monitoring Instrument (OMI), and Total Ozone Mapping Spectrometer (TOMS) data, National Aeronautics and Space Administrations (NASA), USA, respectively; surface temperature, relative humidity, total rainfall, ozone precursors (non-methane hydrocarbon, carbon monoxide, nitrogen dioxide, and sulphur dioxide) that are collected from India Meteorological Department (IMD), Alipore, Kolkata; solar insolation obtained from Solar Geophysical Data Book and El-Niño index collected from National Climatic Data Center, US Department of Commerce, National Oceanic and Atmospheric Administration, USA. The effect of these climatic parameters and ozone precursors on ozone variations is critically analyzed and explained on the basis of linear regression and correlation. It has been observed that the maximum, minimum and mean temperature, relative humidity, solar insolation, tropospheric, and total ozone column (TOC) showed slight increasing tendencies from October 2004 to December 2011, while total rainfall and El-Niño index showed little decreasing tendencies for the same period. Amongst selected climatic parameters and ozone precursors, the solar insolation and the average temperature had a significant influence on both, the tropospheric ozone and total ozone column formation. The solar insolation had contributed more in tropospheric ozone than in total ozone column; while El-Niño index had played a more significant role in total ozone column build up than in tropospheric ozone. Negative correlation was observed between almost all ozone precursors with the tropospheric and total ozone. The tropospheric ozone and total ozone column were also significantly correlated. The level of significance and contribution of different climatic parameters are determined from correlation technique and Multiple Linear Regression (MLR) method. The related chemical kinetics for ozone production processes has been critically described.

1. Introduction

Tropospheric ozone, in spite of being less concentrated than stratospheric ozone, serves as an

important source of the hydroxyl radical, a powerful oxidant that breaks down various pollutants, readily reacts with other chemicals to produce several toxic oxides (Wayne 2000) and some

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greenhouse gases (Fowler *et al.* 2008). It is a pollutant and a constituent of smog. High concentrations of tropospheric ozone are toxic. Moreover, tropospheric ozone itself acts as an effective greenhouse gas and initiates the chemical removal of methane and other hydrocarbons from the atmosphere (Solomon *et al.* 2007).

Recent ozone assessments reveal that although the total ozone column is declining everywhere by a very small amount (Jana *et al.* 2012a, b, c, d), the dramatic decrease in TOC occurs at Antarctica during Antarctic spring-time causing an ozone hole (Farman *et al.* 1985). In our previous publication (Midya and Jana 2002), natural, dynamical, and chemical theories of intense stratospheric ozone depletion as well as stratospheric ozone formation processes have been described that are different from tropospheric ozone formation and depletion processes which are also shown in our publication (Jana *et al.* 2012a, b, c, d).

Several studies on ozone trends have been made over different places throughout the world (Kondratyev *et al.* 1994; Varotsos *et al.* 1994; Gernandt *et al.* 1995; Varotsos 2004). Varotsos (2002) exhibited that during September 2002, the ozone hole over the Antarctic was much smaller than in the previous six years and it was splitted into two separate holes due to the appearance of sudden stratospheric warming that had never been observed before in the southern hemisphere. Ozone showed a temporal variability over hourly, diurnal, synoptic, weekly, seasonal, and long-term time scales (Varotsos *et al.* 2004). 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 (Dobson *et al.* 1946). The rise in ozone content in the stratosphere occurred when cold front reached the ground level. Climatic impacts, especially temperatures, were strong enough to affect the tropospheric ozone distribution (Valero *et al.* 1992; Hsu 2007). Temperature and long term urban warming had a serious impact on urban pollution, resulting in higher ozone concentrations, as heat accelerates the chemical reactions in the atmosphere (Clark and Karl 1982; Walcek and Yuan 1999). The maximum surface temperature was directly related to stratospheric ozone concentration over Kolkata (Midya *et al.* 2003). The total ozone concentration had increased during pre-monsoon and winter periods. In pre-monsoon period, the rate of formation of ozone concentration was sharp with rise of temperature. The TOC had decreased during monsoon and post-monsoon periods. During monsoon period, rate of depletion of ozone was higher than post-monsoon with increased temperature (Midya

et al. 2011a, b). The ozone mixing ratio was negatively correlated with temperature at higher level (i.e., 40 km) and positively correlated at lower level (Barnett *et al.* 1975).

A close relation existed between barometric height, tropospheric weather, and ionospheric parameters of the upper atmosphere (Mitra 1992). 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 Stanford, California, USA. The variation of solar UV radiation due to fall of stratospheric ozone concentration had a pronounced influence on tropospheric climate (Bates 1981; Mackay *et al.* 1997). The variation of stratospheric ozone was also correlated with relative humidity, e.g., sharp depletion of absolute humidity occurs during Nor'wester over Kolkata (Midya and Sarkar 2007). Ozone production decreased with increase in humidity in air contaminated by *n*-heptane (Pekarek 2008). Analyzing all-India summer monsoon (June–September) rainfall for the period 1871–1978, Mooley and Parthasarathy (1984) noticed a continuous rise in 10-yr mean rainfall from 1899 to 1953. Rakhecha and Soman (1994) observed that the annual extreme rainfall records of most stations over India were free from trend and persistence. From the study of the surface ozone data over Trivandrum (8.5°N, 76.9°E) together with temperature and rainfall, Muralidharan *et al.* (1989) reported that the day-time rainfall brought a decrease in surface ozone, while night-time rainfall produced an increase. Long term changes of seasonal and annual surface temperatures and precipitation (Govindo Rao 1993) of the Mahanadi river basin in India showed a highly significant warming trend in the mean maximum, mean minimum, and average mean temperature of the basin for the period 1901–1980. But rainfall for monsoon and annual series did not show any significant trend for the same period. A spring time ozone maximum and summer minimum had been observed in the marine boundary layer over the northern North Pacific Ocean (Watanabe *et al.* 2005). Rainfall showed an increasing trend with the increases of rate of change of TOC during all seasons from the study over Dibrugarh, India (Midya *et al.* 2012a, b). Rain occurred only when ozone concentration achieved a certain concentration level (Midya *et al.* 2011a, b). Rainfall rates in most of the urban areas were higher than the corresponding subdivision rates in the later part of the last century but reverse trends are being seen in some cities. Subdivision rainfall, monsoon as well as annual are showing a decreasing trend (Ganda and Midya 2012). The pre-monsoon rate of change of TOC is highly correlated with monsoon

rainfall of same year but TOC of other seasons are independent of monsoon rainfall over Gangetic West Bengal, India. A statistical analysis of TOC showed that annual co-efficient of relative variability (ACRV) of ozone in West Africa over a period of 48 months increased gradually from 3.5% at latitudinal zone 0–5°N to 6.1% at zone 20–25°N. A strong positive correlation of 0.99 was observed between the ACRV of ozone and average annual temperature, while a negative correlation of –0.99 was observed between the ACRV of ozone and average annual precipitation in the same region (Akinyemi 2010).

El Niño Southern Oscillation (ENSO) played a dominant role in interannual variability of tropospheric climate and chemistry of the troposphere (Doherty *et al.* 2006). From analysis of 20 years of TOMS TCO, Ziemke and Chandra (1999) reported annual average positive and negative anomalies both of 3–4 DU, associated with El Niño events over the 1979–1999 period, which explained about 40% of the interannual variability. Chandra *et al.* (2009) reported that the 2006 El Niño-induced drought caused forest fires to burn out of control during October and November in the Indonesian region. During that time biomass burning and meteorological changes had contributed almost equally to the observed increase in tropospheric ozone. By December 2006, the effect of biomass burning was reduced to zero and the observed 2–3% in the global burden of tropospheric ozone was mostly due to dynamical effects. A strong interrelation between El Niño index with solar flare index during the pre-monsoon season and with surface temperature of Kolkata (22.5°N, 88.4°E) for other seasons existed for the period 1997–2005 (Midya *et al.* 2012a, b).

A relation existed among ozone concentration, solar radiation, and associated meteorological parameters (Cracknell and Varotsos 1994, 1995; Varotsos *et al.* 1995; Kondratyev and Varotsos 1996; Katsambas *et al.* 1997). A correlation existed between weather conditions in the troposphere and the ozone content in the stratosphere. The long-term coupling occurred between TOC and tropopause properties (Varotsos *et al.* 2001a, b). The passage of a warm front might be accompanied by a fall in TOC, while that of a cold front might be accompanied by a rise in TOC, when the fronts influenced the stratosphere well (Mitra 1952). Seasonal variation of surface ozone over Athens, Greece was studied (Varotsos *et al.* 2000, 2001a, b). Ground and satellite-based measurements revealed an overall global decline in ozone concentration (Stolarski *et al.* 1992). Ozone studies over India have also clearly been done by different investigators (Chiplonkar 1939; Ramanathan and Karandikar 1949; Mani 1990). Ozone, one of the

most important radiative gases in the stratosphere and the upper troposphere is not only able to absorb the incoming solar ultraviolet radiation, but also part of the visible radiation, as well as re-emit and absorb the outgoing terrestrial infrared (IR) radiation. Consequently, changes in ozone concentrations affect climate, with the effect depending on the altitudes where the changes occur (Bojkov and Fioletov 1995; Orsoline *et al.* 1998). Two recent reference atmosphere models for ozone and temperature, which were deduced from satellite data, had been employed to detect the existence and the behaviour of a terannual wave both in ozone and temperature. Through the photochemical and radiative processes, physical considerations had been given in an attempt to explain the cause of the formation of the terannual wave (Varotsos *et al.* 1992). The large magnitude of aerosol loading and its impact on land–atmosphere interaction could significantly influence the mesoscale monsoonal characteristics in the Indo-Ganges Basin (Niyogi *et al.* 2007).

In mesospheric region, a correlation exists between mesospheric ozone and intensities of various airglow emissions. The effects of long-term variation of total column ozone on seasonal, annual cycle and yearly variation of airglow emissions of Na 5893 Å, Li 6708 Å and OH (8, 3) band over different stations in India and Halley Bay, a British Antarctic Survey station had been compared (Jana and Nandi 2006; Jana *et al.* 2011, 2012a, b, c, d).

Figure 1. Location of Alipore (22.52°N, 88.33°E) in India.

In this paper, the nature of variation of temperature, relative humidity, rainfall, ozone precursors, and atmospheric ozone over Alipore (22.52°N, 88.33°E), India (figure 1), an important site in the south of the megacity Kolkata, situated on the east bank of river Hooghly and significantly polluted by a large number of small scale industries, vehicular traffic, thermal power plants, very busy ports, small and large industries of iron and jute mills of Howrah city on the west bank opposite to Kolkata has been shown for the period 2005–2011. The effect of these climatic parameters, solar insolation, El-Niño index, and ozone precursors on atmospheric ozone has been critically analyzed. Possible explanation based on physical considerations and chemical kinetics has been discussed.

2. Data and methodology

Daily average value of TOC over Alipore (22.52°N, 88.33°E), India measured by the Ozone Monitoring Instrument (OMI), a nadir-viewing wide-field-imaging spectrometer, giving daily global coverage that continues the Total Ozone Mapping Spectrometer (TOMS) record for total ozone and other atmospheric parameters related to ozone chemistry and climate has been obtained from <http://jwocky.gsfc.nasa.gov>. OMI measurements are highly synergistic with the other instruments on the Aura platform. The OMI instrument employs hyperspectral imaging in a push-broom mode to observe solar backscatter radiation in the visible and ultraviolet. The hyperspectral capabilities improve the accuracy and precision of the total ozone amounts and also allow for accurate radiometric and wavelength self calibration over the long term. The instrument observes Earth's backscattered radiation with a wide-field telescope feeding two imaging grating spectrometers. Each spectrometer employs a convective cloud differential (CCD) detector. Onboard calibration includes a white light source, light emitting diodes (LEDs), and a multi-surface solar-calibration diffuser. A depolarizer removes the polarization from the backscattered radiation. It can measure many more atmospheric constituents than TOMS and provides much better ground resolution than GOME (Global Monitoring Experiment) (13×25 km for OMI *vs.* 40×320 km for GOME). TOMS instruments were flown on three National Aeronautics and Space Administrations (NASA)/Goddard Space Flight Center spacecrafts: Nimbus 7 (November 1978–May 1993), Meteor 3 (August 1991–December 1994), and Earth Probe (January 1997–2005). It uses the ratio of backscattered earth radiance to solar irradiance at specific wavelengths to infer TOC. In this ratio,

all instruments related reflect diffused solar light into instrument optics. The degradation of diffuser plate is related to the exposure to sunlight. A non-diffusion based technique termed spectral discrimination was used to calibrate the TOMS data. For this work, TOC data were collected from the OMI instrument, which provides total ozone data from October 2004 to December 2011. OMI data are gridded into one degree latitude and 1.25 degree longitude, latitude ranging from +90° (North Pole) to −90° (South Pole).

Tropospheric column ozone can usually be determined from the following two well-known techniques using satellite data. Firstly, the stratospheric column ozone is derived by combining upper atmospheric research satellite (UARS) halogen occultation experiment (HALOE) and microwave limb sounder (MLS) ozone measurements. Tropospheric column ozone is then calculated by subtracting these stratospheric amounts from the TOC. Data from HALOE are used 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 Aerosol and Gas Experiment (SAGE). Secondly, 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 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.

Data for surface maximum and minimum temperature in degree centigrade, maximum and minimum relative humidity in percentage, rainfall in mm, concentrations of non-methane hydrocarbon (NMHC) and carbon monoxide (CO) in ppmv; and nitrogen dioxide (NO₂) and sulphur dioxide (SO₂) in μgm^{-3} have been collected from India Meteorological Department, Alipore, Kolkata for the above period. Daily mean temperatures and daily relative humidity have been calculated from its maximum and minimum values. Monthly mean values have been computed from their daily mean values.

Solar insolation is taken from Solar Geophysical Data Book (<ftp://ftp.ngdc.noaa.gov>). El Niño index has been collected from National Climatic Data Center (<http://www.ncdc.noaa.gov/enso>).

Trends of climatic parameters and ozone precursors are deduced from linear trend line of their monthly mean values obtained by least square principle. The dependence of tropospheric ozone and TOC on different climatic parameters and ozone precursors has been depicted by scattered plot of tropospheric and total ozone with every climatic parameter. Significance of dependence is inferred from their coefficient of correlation values and multiple linear regression technique.

3. Results and discussion

Variations of monthly mean tropospheric ozone concentration and TOC from October 2004 to December 2011 and January 2005 to December 2011, respectively, over Alipore, India are depicted in figure 2(a and b), respectively. The nature of both the variations of tropospheric ozone and TOC, though oscillatory, had revealed a slight increasing tendency from October 2004 to December 2011 and January 2005 to December 2011, respectively. The concentrations of tropospheric ozone and total ozone had enhanced by about 0.01 DU and 0.02 DU per month, respectively. The variation of tropospheric ozone agrees fairly well with our previous observation (Jana *et al.* 2012b) that

showed an increasing trend in tropospheric ozone over most of the places in India from October 2004 to June 2009. But, the variation of TOC disagrees with our previous observations of total ozone over several stations, viz., Thumba (8.5°N, 77°E) and Bangalore (13°N, 77.5°E) (Jana *et al.* 2012a), New Delhi (29°N, 77°E) (Jana *et al.* 2012c), Dum Dum (22.5°N, 88.5°E) (Jana and Nandi 2006), etc., in India before, during and after Montreal Protocol and Kyoto agreement for different periods from 1979 to 2005, which represented a decreasing trend in TOC. Variations of monthly mean maximum, minimum, and average temperature from October 2004 to December 2011 are represented in figure 3, which clearly indicates oscillatory nature of these temperatures with a slight enhancing tendency from October 2004 to December 2011. The enhancement in the mean temperature per month was approximately 0.0078°C. Figure 4 shows the variations of maximum, minimum, and average relative humidity for the period October 2004–December 2011. In spite of oscillatory nature, maximum, minimum, and average relative humidity had enhanced slowly from October 2004 to December 2011. But the nature of variation of monthly total rainfall was oscillatory and revealed a slow decrease from October 2004 to December 2011 as shown in figure 5. Interannual variability had been revealed both in solar insolation and El-Niño index from January 2005 to December 2011, but solar insolation had shown an increasing tendency of 0.0043 kWhr/m²/month while El-Niño index had shown a slight decreasing tendency by 0.0169 per month as depicted in figures 6 and 7, respectively.

Annual cycles of monthly mean densities of non-methane hydrocarbon (NMHC), carbon monoxide (CO), nitrogen dioxide (NO₂), and sulphur dioxide (SO₂) over Alipore are represented in figure 8 for the period January 2005 to December 2011. The density of NMHC gradually fell from January to April, then remained almost steady up to September and then increased sharply. Comparatively, lower concentration of NMHC was noticed from May to September. The concentration of CO smoothly declined from January to June, then remained almost unaltered up to September and then gradually built up. The annual cycle of the density of NO₂ revealed a sharp fall from January to April, then moderate rise up to August, and steep enhancement up to December except in September. The concentration of SO₂ steeply decreased from January to May, then attained minimum values for the months of May to July and then steeply increased. The continuous fall of concentration of NMHC, CO, NO₂, and SO₂ were because of increased photo-induced reaction producing tropospheric ozone due to rise in solar radiation during winter and pre-monsoon period,

Figure 2. Variation of (a) tropospheric ozone (DU) from October 2004 to December 2011 and (b) total ozone column (DU) from January 2005 to December 2011 over Alipore (22.52°N, 88.33°E), India.

Figure 3. Variations of surface maximum, minimum and mean temperature (°C) over Alipore (22.52°N, 88.33°E), India from October 2004 to December 2011.

Figure 4. Variations of maximum, minimum and mean relative humidity (%) over Alipore (22.52°N, 88.33°E), India from October 2004 to December 2011.

and increased absorption of these molecules by water vapour as follows:

Figure 5. Variations of total rainfall (mm) over Alipore (22.52°N, 88.33°E), India from October 2004 to December 2011.

where VOC denotes volatile organic compound and CARB stands for carbonyl compounds.

Moreover, westerly wind flow picked up the above anthropogenically derived gases from Kolkata to eastern region of India during pre-monsoon. The lowest densities of NO_2 in the month of September, CO and NMHC during monsoon were mostly due to washed out effect of these constituents from troposphere by huge rainfall. Gradual rise in concentration of NO_2 from April to August was mainly due to the reaction $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ in presence of lightning that usually occurred during this period followed by the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$. Steep building of these constituents during post-monsoon time was due to comparatively low solar radiation, very little rainfall and existence of northwesterly and mostly northeasterly winds entering from northeastern and northwestern region bringing significantly polluted air from the neighbouring cities to Kolkata (Purkait et al. 2009).

Annual cycles of tropospheric and TOC for the above period showed a gradual increase from

Figure 6. Variation of solar insolation (kwhr/m^2) over Alipore (22.52°N , 88.33°E), India from January 2005 to December 2011.

Figure 7. Variation of El-Niño index over Alipore (22.52°N , 88.33°E), India from January 2005 to December 2011.

January, attaining the maximum value during May (figure 9a and b) and June, and then gradual decrease in case of TOC; while after May and June tropospheric ozone declined and attained the minimum value in the month of August and September, and then slowly enhanced as shown in figure 9(a). Annual cycle of the maximum, minimum, and average surface temperature steeply and gradually increased from January, attained the highest value from May to September and then gradually decreased. In case of the maximum temperature, comparative lowering of temperature was observed during monsoon season. Annual cycles of the maximum, minimum, and average relative humidity reveal that the relative humidity slightly decreased from January, attained the minimum during March, then gradually enhanced, achieved the maximum value during August, and then gradually declined. Annual cycle of total rainfall depicted very slow rise from January to June, comparatively much higher value of total rainfall during the monsoon (June to September) and then slow decline. Annual cycle of solar insolation showed gradual rise from January to April and May, comparatively lower values during monsoon season and then slightly increasing tendency in the post-monsoon period. El Niño index revealed mild increasing tendency from January to July and steep decreasing tendency from July to December.

Figure 8. Annual cycles of concentrations of NMHC, CO, NO_2 and SO_2 over Alipore (22.52°N , 88.33°E), India for the period January 2005 to December 2011.

Figure 9. Annual cycles of (a) tropospheric and (b) total ozone column (DU) over Alipore (22.52°N , 88.33°E), India for the period October 2005 to December 2011.

The scattered variation of tropospheric ozone with average temperature (figure 10) indicates

Figure 10. Scattered diagram of tropospheric and total ozone (DU) with surface (a) maximum, (b) minimum and (c) mean temperature (°C).

significant rise of tropospheric ozone with the rise in temperature by 0.47 DU/°C. Though the correlation coefficients between the tropospheric ozone with the average temperature (0.32) was comparatively low (table 1), the scattered variations of TOC with the maximum, minimum, and average temperature indicated the growth of TOC with the increase in temperature by 3.4, 2.1 and 2.75 DU/°C, respectively. The correlation coefficients between the TOC with the maximum, minimum, and average temperature were comparatively higher and varied from 0.85 to 0.95. The low value of coefficient of correlation between tropospheric ozone and surface temperature indicated that the variation of tropospheric ozone was controlled largely by other parameters

such as increasing concentrations of ozone precursors, variations of solar insolation, total ozone, and tropospheric/stratospheric exchange of ozone. Favourable meteorological conditions, viz., clear sky, warm temperatures, soft winds had a great contribution on ozone concentrations (Vacchi and Valli 1999). At the same time, higher temperatures caused convection to develop, which in turn could develop vertical ozone transport. On the other hand, wet, rainy weather with high relative humidity was associated with low ozone levels provided by less intensive photochemical production and possibly, by ozone deposition on water droplets (Lelieveld and Crutzen 1990). Strong wind increased the intensity of vertical transport. If the boundary layer acts as a source of ozone due to

Table 1. Coefficient of correlation.

	Tropospheric ozone	Total ozone	Max. temp.	Min. temp.	Mean temp.	Rainfall	Max. humidity	Min. humidity	Mean humidity	Solar insolation	El-niño index	NMHC	CO	NO ₂	SO ₂
Tropospheric ozone	1	0.6	0.53	0.18	0.32	-0.38	-0.83	-0.42	-0.51	0.9	0.26	-0.17	0.05	-0.4	-0.25
Total ozone	0.6	1	0.95	0.85	0.91	0.39	-0.39	0.31	0.2	0.65	0.72	-0.77	-0.69	-0.72	-0.86
Max. temp.	0.53	0.95	1	0.9	0.96	0.38	-0.3	0.31	0.22	0.63	0.72	-0.77	-0.68	-0.73	-0.84
Min. temp.	0.18	0.85	0.9	1	0.98	0.72	0.13	0.68	0.62	0.24	0.66	-0.79	-0.88	-0.57	-0.88
Mean temp.	0.32	0.91	0.96	0.98	1	0.6	0.56	0.48	0.48	0.4	0.72	-0.81	-0.83	-0.65	-0.89
Rainfall	-0.38	0.39	0.38	0.72	-0.03	1	0.61	0.95	0.93	-0.88	-0.15	-0.6	-0.87	-0.23	-0.68
Max. humidity	-0.83	-0.39	-0.3	0.13	0.56	0.95	1	0.73	0.99	-0.49	0.31	-0.01	-0.34	0.39	0.04
Min. humidity	-0.42	0.31	0.31	0.68	0.48	0.95	0.73	1	0.93	0.4	0.25	-0.47	-0.8	0.05	-0.54
Mean humidity	-0.51	0.2	0.22	0.62	0.6	0.93	0.99	0.93	1	-0.57	0.45	-0.41	-0.75	0.02	-0.47
Solar insolation	0.9	0.65	0.63	0.24	0.4	-0.4	-0.49	0.4	-0.57	1	0.42	-0.32	0.01	-0.59	-0.35
El-niño index	0.26	0.72	0.72	0.66	0.72	0.45	0.31	0.25	0.25	0.42	1	-0.9	-0.86	-0.83	-0.84
NMHC	-0.17	-0.77	-0.77	-0.79	-0.81	-0.6	-0.01	-0.47	-0.41	-0.32	-0.9	1	0.86	0.84	0.85
CO	0.05	-0.69	-0.68	-0.88	-0.83	-0.87	-0.34	-0.8	-0.75	0.01	-0.69	0.86	1	0.56	0.85
NO ₂	-0.4	-0.72	-0.73	-0.57	-0.65	-0.23	0.39	-0.05	0.02	-0.59	-0.83	0.84	0.56	1	0.76
SO ₂	-0.25	-0.88	-0.84	-0.88	-0.89	-0.68	0.04	-0.54	-0.47	-0.35	-0.84	0.85	0.85	0.76	1

chemical generation, the increase in wind speed leads to fall in ozone concentration because of the vertical mixing. Conversely, if the ozone chemical budget in the boundary layer is negative, vertical transport transfers ozone-rich air from aloft downward, and surface ozone concentrations correlate positively with wind speed. The scattered variations of tropospheric ozone and TOC with relative humidity (figure 11) and total rainfall (figure 12) revealed insignificant trends. Scattered variations of tropospheric and TOC with the concentrations of NMHC (figure 13), CO (figure 14), NO₂ (figure 15), and SO₂ (figure 16) clearly revealed the gradual decline of both the tropospheric and TOC except CO. The concentration of tropospheric ozone had a slight increasing tendency with increase in CO. The correlations and dependence among them were also very poor as depicted in tables 1 and 2. These observations clearly indicate that concentrations of both the tropospheric and total ozone were not only controlled by ozone precursors but also greatly by other climatic parameters. Scattered variations of tropospheric and TOC with solar insolation (figure 17), and with El-Niño index (figure 18) clearly showed the gradual significant build-up of both tropospheric and total ozone by 0.53 and 0.11 DU (tropospheric ozone), and 7.9 and 4.8 DU (total ozone) with the enhancement of both of solar insolation and El-Niño index (table 2). Correlation coefficients were comparatively high and also significant between solar insolation with tropospheric ozone (0.9), total ozone (0.63), and maximum temperature (0.63). In case of El-Niño, the correlation coefficient of El-Niño with tropospheric ozone was poor (0.26), while with total ozone and temperature it was high and significant (0.72). Figure 19 depicts the scattered diagram between tropospheric and total ozone column that indicated the existence of the proportionality relation between them. Correlation coefficient between them was 0.6 which is significant. According to multi-regression analysis, the concentrations of tropospheric ozone and total ozone were governed by the above climatic parameters and ozone precursors as follows:

$$[\text{Tropospheric O}_3] = -255.4 + 0.36 [\text{Total O}_3] - 6.86 \text{ Min. Temp.} + 7.3 \text{ Mean Temp.} + 0.09 \text{ Max. Humidity} + 0.05 \text{ Rainfall} + 0.07 [\text{NMHC}] - 0.101 [\text{CO}] - 0.05 [\text{NO}_2] + 0.02 [\text{SO}_2] + 10.7 \text{ Solar Insolation} + 4.5 \text{ El Niño Index.}$$

$$[\text{Total O}_3] = 624 - 0.06 [\text{Tropospheric O}_3] + 0.29 \text{ Min. Temp.} - 4.3 \text{ Max. Humidity} + 1.5 \text{ Min. Humidity} - 0.08 \text{ Rainfall} - 0.004 [\text{NMHC}] - 0.04 [\text{CO}] - 0.08 [\text{NO}_2] - 0.15 [\text{SO}_2] + 2.2 \text{ Solar Insolation} - 7.4 \text{ El Niño Index.}$$

The above equations also vividly reveal that tropospheric ozone had increased by total ozone by very little amount which supports the downward transport of stratospheric ozone causing the decline of total ozone and the build up of tropospheric ozone. Tropospheric ozone had greatly enhanced by mean temperature, while total ozone by minimum temperature by smaller amount. Though, solar insolation had influenced the growth of both tropospheric and total ozone column, it contributed more to tropospheric ozone. El Niño index played a positive role for the growth of tropospheric ozone, but a negative role for total ozone according to above equations.

The oscillatory nature and slow rise in monthly mean tropospheric ozone from October 2004 to

December 2011 (figure 2a) was due to the oscillatory nature and slow increase in the amount of ozone precursors such as oxides of nitrogen (NO_x), non-methane hydrocarbon (NMHC), oxides of sulphur (SO_x), carbon monoxide (CO), etc. and surface temperature because of enhanced solar radiation (Jana et al. 2012d) and global warming (Jana et al. 2011) which catalyzed more tropospheric ozone formation processes that had been critically discussed in our previous publications (Jana et al. 2012a, b, c). Downward transport of elevated TOC also had an influence on the rise of tropospheric ozone (Jana et al. 2012a). The slow building of TOC over Alipore from January 2005 to December 2011 (figure 2b) had been noticed as a result of the implementation of Montreal protocol (1987)

Figure 11. Scattered diagram of tropospheric and total ozone (DU) with (a) maximum, (b) minimum and (c) relative humidity (%).

Figure 12. Scattered diagram of (a) tropospheric and (b) total ozone column (DU) with total rainfall (mm).

Figure 13. Scattered diagram of (a) tropospheric and (b) total ozone column (DU) with non-methane hydrocarbon (ppmv).

Figure 14. Scattered diagram of (a) tropospheric and (b) total ozone column (DU) with carbon monoxide (ppmv).

Figure 15. Scattered diagram of (a) tropospheric and (b) total ozone column (DU) with nitrogen dioxide (µgm⁻³).

Figure 16. Scattered diagram of (a) tropospheric and (b) total ozone column (DU) with sulphur dioxide (μgm^{-3}).

that facilitated the reduction of production of ODS (viz., CFC-11, CFC-12, CFC-113, CH_3Cl , CH_3Br , CCl_4 , halons, WMO (World Meteorological Organization) minor constituents, etc.) from 1996 to 2010, gradual reduction of consumption of ODS from 1996 to 2010, and production of ODS substitute (HCFC 22, other refrigerants, LPG) requirements from 1996 to 2010 facilitated the phase out programme of these substances and evolved the path of conversion from ODS to non-ODS (viz., HCFC-22 (CHF_2Cl), HCFC-123 ($\text{C}_2\text{HF}_3\text{Cl}_2$), CO_2 , Propane, Butane, etc.) (Midya and Jana 2002), and Kyoto Protocol (1997) that limited emissions of greenhouse gases (GHGs) (Jana et al. 2013). Upward transport of elevated tropospheric ozone also had an influence on the rise of tropospheric ozone (Jana et al. 2012a, b, c, d).

Oscillatory and mild increase of monthly mean maximum, minimum, and average temperature from October 2004 to December 2011 (figure 3) had been attributed to the fluctuation and gradually low increase in greenhouse molecules and surface radiation for the above period. Jana and Saha (2011) also reported gradual increase in global and surface temperature with the increase of the amounts of H_2O , CO_2 , N_2O , CH_4 , CFC-11, and CFC-12 from 1979 to 2005. Feeble enhancement of maximum, minimum, and average relative humidity for the period from October 2004 to December 2011 (figure 4) was due to slow rise in surface temperature, which caused more evaporation of water from water bodies. Gradual enhancement in the amount of tropospheric ozone from January to May, then its reduction in amount, attainment of minimum amount during the month of August and September; and slow build-up of tropospheric ozone afterwards were due to the fact that the rates of reactions which favour the tropospheric ozone from its precursors were enhanced by sharp increase of solar radiation and its precursors from January to May. During August and September, 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 occurrence of clouds in the monsoon time (JJAS), as well as lower concentrations of ozone precursors because of washing down by the rain. After September, the rate of rise in concentration of tropospheric ozone was slow due to disappearance of clouds, mild fall in solar radiation, and steady enhancement of ozone precursor as depicted in figure 8(a) (Jana et al. 2012a, b, c, d). While the gradual increase of TOC from January, attainment of its maximum concentration during May and June, and then gradual steady decrease (figure 8b) was because of steady increase in solar radiation due to gradual decrease in distance between the Earth and the Sun from January to May. It caused gradual enhancement of rates of ozone formation processes mostly in stratospheric region and steady decrease in solar radiation from June to December due to gradual increase in distance between the Earth and the Sun that caused less production of stratospheric ozone. The steep and gradual increase in maximum, minimum, and mean temperature had been attributed to the steep and gradual increase in solar radiation and daylight duration from January to May, as well as due to the steady enhancement of pollutants and greenhouse molecules in the atmosphere (Jana and Saha 2011). The comparatively lower value of maximum temperature during monsoon time from June to September (JJAS) was due to the rainfall, high occurrence of clouds that prevented the entry of solar radiation and also because of lower amount of pollutants and greenhouse gases in the atmosphere. The lower value of relative humidity in the months January to March is due to the lower rate of evaporation of water from water bodies caused by lower temperature. Gradual rise in relative humidity from March to August was accompanied by the steady increase of temperature that caused more evaporation and the occurrence of monsoon winds that carried more water vapour from the Indian Ocean, the Arabian Sea, and the Bay of Bengal to the atmosphere of West Bengal. The maximum relative humidity in the month of August was obviously a result of the high

Table 2. Trends of some climatic parameters, atmospheric constituents, tropospheric ozone and total ozone column over Alipore (22.52°N, 88.33°E), India.

Climatic parameters/ atmospheric constituents	Rate of variation of tropospheric ozone (DU) w.r.t. climatic parameters/ atmospheric constituents		Correlation coefficient with tropospheric ozone	Significance of variation trend	Rate of variation of TOC (DU) w.r.t. climatic parameters/ atmospheric constituents		Correlation coefficient with TOC	Significance of variation trend
Max. temperature (°C)	0.86		0.53	Insignificant	3.4		0.95	Significant
Min. temperature (°C)	0.21		0.18	Insignificant	2		0.85	Significant
Mean temperature (°C)	0.47		0.32	Significant	2.8		0.91	Significant
Rainfall (mm)	-0.01		-0.38	Insignificant	0.01		0.39	Insignificant
Max. humidity (%)	-1.2		-0.83	Insignificant	-0.9		-0.39	Insignificant
Min. humidity (%)	-0.2		-0.42	Insignificant	0.2		0.31	Insignificant
Mean humidity (%)	-0.34		-0.51	Insignificant	0.36		0.2	Insignificant
Solar insolation (per kwhr/m ²)	5.3		0.9	Significant	7.9		0.65	Significant
El-niño index	0.11		0.26	Significant	4.8		0.72	Significant
Tropospheric ozone (DU)	1		1		4.5		0.6	Insignificant
TOC (DU)	0.23		0.8	Significant	1		1	
NMHC (ppmv)	-0.07		-0.17	Insignificant	-0.69		-0.77	Insignificant
CO (ppmv)	0.05		0.05	Insignificant	-1.4		-0.69	Insignificant
NO ₂ (µgm ⁻³)	-0.09		-0.4	Insignificant	-0.33		-0.72	Insignificant
SO ₂ (µgm ⁻³)	-0.04		-0.25	Insignificant	-0.29		-0.86	Insignificant

Figure 17. Scattered diagram of (a) tropospheric and (b) total ozone column (DU) with solar insolation (kwhr/m²).

Figure 18. Scattered diagram of (a) tropospheric and (b) total ozone column (DU) with El-Niño index.

Figure 19. Scattered diagram of tropospheric ozone (DU) with total ozone column (DU).

occurrence of monsoon winds. Afterwards, relative humidity decreased with the absence of monsoon winds, occurrence of westerly wind and gradual fall of temperature. Low rainfall in pre-monsoon time from March to May (MAM), huge rainfall in monsoon time from June to September (JJAS), and very low rainfall in post-monsoon from October to November (ON) and winter period from December to February (DJF) had been attributed to occasional existence of Nor'wester that occurred usually 2–6 times in each month from February to May in every year, high prevalence of monsoon wind during the monsoon period and appearance of dry-retreat monsoon or northwesterly wind consisting very low amount of water vapour entering from Bihar, Orissa, and Assam including Bangladesh that might clash with the wet winds of Bay of Bengal, causing cyclones, sometimes due to high pressure and temperature difference in post-monsoon

and winter season, respectively. The temperature dependence of tropospheric and TOC (figure 10) and their high correlation were due to the fact that ozone formation reaction from oxygen is a reversible and endothermic process. So, the formation of atmospheric ozone had been favoured comparatively by higher temperature. Thus the variation of maximum temperature had played a major role in the formation of tropospheric and TOC. Again comparatively lower correlation coefficient value in case of tropospheric ozone indicates that not only the surface temperature plays a major role in tropospheric ozone formation processes, but also the concentrations of ozone precursors have a comparable influence on the tropospheric ozone formation. Total ozone column mostly comprises of stratospheric ozone in the layer of stratosphere where temperature is very low. So increase in surface temperature has a greater influence on

stratospheric ozone formation than tropospheric ozone formation. As a result, higher correlation coefficient has been obtained for TOC with maximum temperature. The concentration of tropospheric ozone slowly decreased with increase in rainfall (figure 12) due to removal of pollutants and ozone precursors by absorption and washing down by rain. Tropospheric ozone increased with increase in TOC because of downward transport of stratospheric ozone (figure 19). Again increase in tropospheric ozone contributed more to the TOC and *vice versa*.

4. Conclusions

The concentration of tropospheric ozone had increased slowly over Alipore, India from October 2004 to December 2011 due to the oscillatory nature and slow increase in the amount of ozone precursors such as oxides of nitrogen (NO_x), non-methane hydrocarbon (NMHC), oxides of sulphur (SO_x), carbon monoxide (CO), etc., and surface temperature because of enhanced solar radiation and global warming, which catalyzed more tropospheric ozone formation processes and downward transport of stratospheric ozone. The concentration of TOC had risen slightly from January 2005 to December 2011 as a result of the implementation of Montreal protocol (1987) that controlled the production and emission of ozone depleting substances (ODS), facilitated the phase out programme of these substances and evolved the path of conversion from ODS to non-ODS. Kyoto Protocol (1997) limited emissions of greenhouse gases (GHGs) and upward transport of elevated tropospheric ozone. Among surface temperature, relative humidity, total rainfall, ozone precursors, solar insolation and El Niño index, solar insolation, surface temperature and El Niño index played a major role in controlling the amount of tropospheric and TOC. The concentration of tropospheric ozone was significantly controlled by the variations of solar insolation, total O₃ and mean surface temperature and El Niño index; while total O₃ by solar insolation and El-Niño index from 2005 to 2011.

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