DEPARTMENT OF PHYSICS
M. L. SUKHADIA UNIVERSITY, UDAIPUR – 313 001

Final Report of UGC Major Research entitled "Study of Surface Ozone and its Prominent Precursors over Semi Urban Tropical Region i.e., Udaipur"

(July, 2012 to December, 2015)

ज्ञान-विज्ञान विमुक्तये

Supported by

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Principal Investigator : Dr B. M. VYAS

Annexure – IX

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

THE FINAL REPORT OF THE WORK DONE ON THE PROJECT

1. Title of the Project: "Study of Surface Ozone and its prominent precursors over semi-urban tropical region, i.e., Udaipur".

2. NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR: Dr B.M.Vyas, Professor of Physics, Department of Physics, Mohanlal Sukhadia University, Udaipur-313 001(Rajasthan).

3. NAME AND ADDRESS OF THE INSTITUTION: M L Sukhadia University, Udaipur (Raj.).

4. UGC APPROVAL LETTER NO. AND DATE:UGC F.41-864/2012(SR)/ dated 23-07-2012

5. DATE OF IMPLEMENTATION 23 July, 2012.

6. TENURE OF THE PROJECT : 23 July, 2012 to 31 December, 2015

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10. TITLE OF THE PROJECT : Study of Surface Ozone and its prominent precursors over semi--urban tropical region i.e., Udaipur" .

11. OBJECTIVES OF THE PROJECT: -

It is a well a recognized fact from the classical theory of troposphere ozone chemistry that modulation of ground level ozone is primarily governed through a series of complex and mixed photo-ionization chemical reactions take place in presence of suitable incident solar radiations and variable anthropogenic source activities as the result of prominent precursor's emission of ozone trace gasses like as NOx(NO_2+NO),CO, VOC,NHMC, NH_3 etc., These prominent precursors such as numbers of atmospheric primary ambient atmospheric trace gaseous pollutants also chemically acted as catalysts for strengthening the photochemical production rate of ozone's amount as secondary ambient atmospheric pollutants under the suitable weather condition. Thus, the enhancement and reduction in ground level ozone variability is mainly affected by large number of local and regional factors like as several local weather parameters, atmospheric boundary layer thickness along with the availability of sufficient amount of the sun radiation intensity in the presence of their critical level of prescribed limit level of its prominent precursor gaseous surrounding observing location. And therefore, their fates and their dependence above considered several local and regional pathways are subject to both air pollution and earth climate changes influence aspects.

In view of the scientific importance about ozone at surface acts as air pollutant and detrimental effect to human, plant and agricultural health eco-system. While, in lower and middle troposphere, it served as greenhouse gas contributing to positive radiative forcing, thereby resulted impact on atmospheric and surface warming effects or climate responsive species. Nevertheless, response on ozone and its prominent pre-cursors gases levels through anthropogenic, biogenic, chemical and atmospheric dynamic process on various time scales have been unraveled from experimental measurements and modeling investigations.

Hence, consciously combined and systematic experimental efforts are realized to understand the contribution of the above specified some of known and unknown local and regional pathways and their several distinct roles of several regional scales and local meteorological and anthropogenic activity scale parameters in altering the surface ozone concentration along with other harmful ambient atmospheric air pollutant level specifically over tropical latitude, where there is sufficient and excess amount of incident solar radiation available relative to other latitude on the earth for favorable environment of modulation of several air pollutants due to completion of several series of complex photo ionization chemical reaction in the lower atmosphere. For this purpose, dense, long time regular and simultaneous concurrent and extensive measurement about the surface ozone, NOx, NO, NO_2, CO, PM2.5 and BC as

anthropogenic aerosols acting as atmospheric ambient air gas pollutants are being carried out under the time period of the project to achieve following main objectives. The main objectives of the proposed study are as follows:

i. Monitoring the long term, temporal, seasonal and diurnal variations in NO_X, O_3,, PM2.5 , BC and CO at Udaipur and also in different industrial location in surrounding regions during various environmental condition.

ii. To study the potential impact of anthropogenic in NO_X, CO, NMHC emissions on surface ozone content over Udaipur due to surface meteorological conditions and their individual regional and local contribution in ozone chemistry etc.

iii. With available MICROTOPS-II Sun photometer, the simultaneous measurement of UV- B radiation at 305 nm, total water vapor content, etc., would also be carried out at the site to identify the effect of UV-B radiation 320 nm, total water vapor content on the surface ozone. The average monthly variation of Ozone and its precursors obtain from in the present study period would be compared with the similar period of observations of tropospheric ozone, NOx, CO from satellite based observations.

12. WHETHER OBJECTIVES WERE ACHIEVED: Yes,

During the course of investigation of project tenure, main emphasis is principally focused on the investigations on the basis of simultaneous measurement and analysis of ground ozone's level and its related prominent precursors trace gases, i.e., CO, NO_X, PM 2.5, BC aerosols and gas particles, Total water vapour column content, incident solar radiation intensities in short wave length spectrum and their behavior of various time scales in normal conditions and abnormal anthropogenic emission phenomena within the lower troposphere at the semi-arid observing tropical station Udaipur. Over the Indian region, only very few such type of limited concurrent investigations about influence of meteorological activities, planetary boundary layer parameter, irradiation solar radiation intensity, total water vapour column content etc., on surface ozone and some of its prominent precursors chiefly CO, BC Aerosols, NOx and atmospheric particulate matters have been described earlier. Nevertheless, there were no systematic, continuous, planned and extensive simultaneous measurements of several ambient atmospheric trace gases and suspended materials, namely, surface ozone concentration and its prominent precursors over the Indian continent region during till recent years.

Understanding the importance of high priority atmospheric air pollutants scientific aspect in view of their nuisance role as health hazardous to the human body plants, animals and abrupt reduction in atmospheric local visibility and the definite atmospheric positive radiative forcing effect as earth's

climate changing impact in term of atmospheric and surface warming effects etc***.,. an attempt has been made in the course of investigation to summarized results based on collection of simultaneous measurement of atmospheric ambient air pollutant level by insitu measurement from online analysers of surface ozone, CO, NOx, BC aerosols along with the off line instrument as a high volume sampler for measurement of ambient fine size particulate matter below aerodynamic diameter size 2.5 micronmeter, short wavelength radiation intensity in broad spectrum from Complete Net Solar Radiometer (CNR-1) , at fixed wave lengths SW solar radiation measurement along with total water vapour column content employing MICROTOPS-II Sun photometer at semi-arid tropical observing site of Udaipur in India.*** From the analysis of three year data series of several atmospheric air pollutant levels, following main findings have been described briefly in various time scale evolution.

i) Diurnal distribution of O_3 and related prominent precursor trace gases and anthropogenic pollutants:

The maximum enhancement in ozone concentration values, especially around the afternoon hour interval (12-16hr, local time), was observed as the result of intense photo-ionization chemical activity with the coincidence of occurrence of higher ambient temperature in midday hours interval as well as with intrusion of free tropospheric ozone from the stratosphere through stratospheric-tropospheric ozone exchange phenomenon. The maximum amplitude in diurnal ozone variations was recorded within the ranges of 35-40 ppbv and 31-48 ppbv during the pre-monsoon and winter seasons, respectively. While the lower diurnal amplitude level in a range of 20-25 ppbv is clearly visible in post monsoon month, however, in rainy and monsoon month, strength of diurnal amplitude in ozone is almost very weak or negligible in a range of 5 to 8ppb only, as illustrated in left side of the upper blocks in Fig.1(a).In contrast to the above, the seasonal diurnal behavior of mixing ratios of NOx, CO and BC mass concentration has revealed a prominent and sharp peak value in the late evening hours of concerning of heavy vehicular traffic rush and human made domestic activities, whereas another secondary peaks are visible in morning hours linked to more bio-mass burning, fossil and bio-fuel of incomplete combustion activity duration, which are concurrent and coincided also with the interval of heavy rush vehicular traffic activity period as well as biomass burning event resulted to several types of the household of daily human life activity near the sampling site (Figs 1b-d). At the same time, the peak in late evening and morning hours and trough around after noon and midnight hours values of primary pollutants were greatly influenced with altering in nature of compression (about 2 meter) and rarefaction process (about 5000meter) of atmospheric boundary layer heights, respectively.

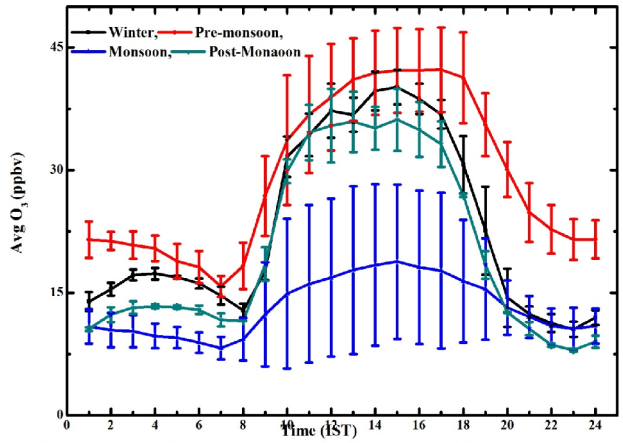


Fig.:1(a)

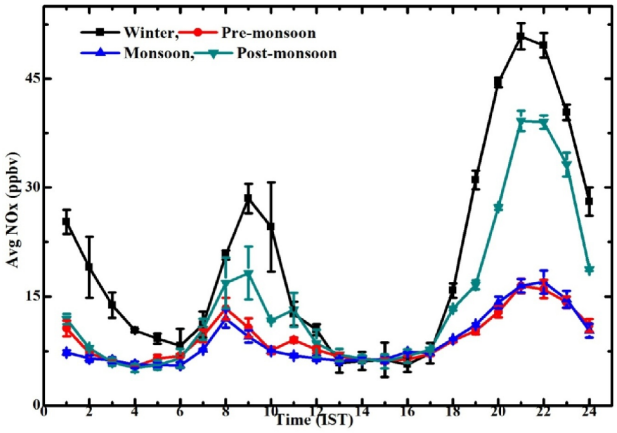


Fig.: 1(b)

Interestingly, the concentration levels of all kinds of atmospheric pollutants depict a prominent significant reduction during the monsoon season only, which attributes clearly unpolluted and clean with clear environmental condition period due to washing out effect of air pollutant in rainy events or in the presence of an excess abundance of OH radical as atmospheric ozone's detergent. Overall, the patterns of diurnal evolution of primary air pollutants like as NOx, CO and BC are seen to be entirely in reverse phase relative to as observed in the case of diurnal cycle behavior of secondary gaseous pollutants, i.e., O_3. Although, the strength of variability in each type of primary and secondary pollutant concentration varies strictly in accordance with changing season to season as well as with time also. This feature has been clearly demonstrated the confirmation about the influence of altering their source strength activities in such observation period according to their modulation of air pollutant emission loadings values together with their shifting in the occurrence timings of peak air pollutant level.

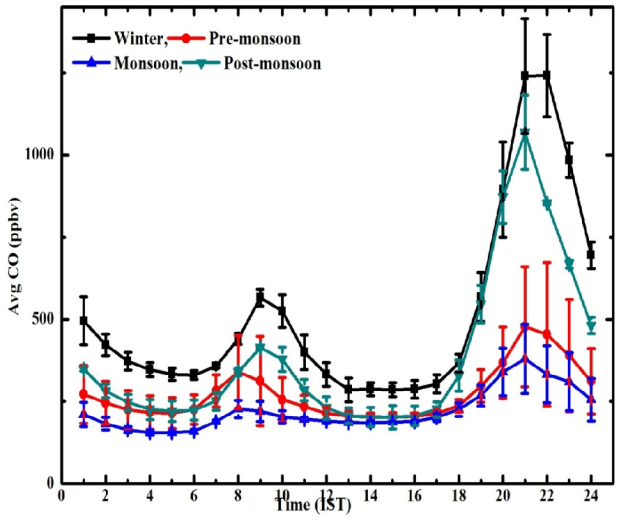


Fig.: 1 (c)

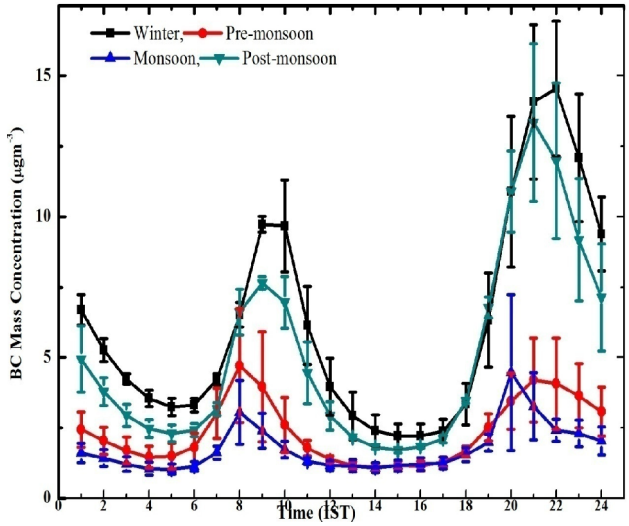


Fig.: 1 (d)

Figs.1(a-d): Seasonal Diurnal variation of surface ozone, NOx, CO and BC mass concentration at the semi-arid station of Udaipur for Winter and Pre-monsoon, monsoon and Post-monsoon seasons.

The strength of seasonal diurnal characteristic of primary as well as secondary air pollutants both showed the alike distinct following descending pattern, i.e., winter>post-monsoon> pre-monsoon> monsoon. The seasonal diurnal curves of several atmospheric ambient air pollutants at Udaipur are found to be in quite unique in a similar pattern to those reported at other urban and semi-arid sites of India with slight discrepancies in their corresponding magnitude only, which is expected in the account of alteration levels in the local air pollution source activity intensity level as well as fluctuation in local meteorological conditions and atmospheric boundary dynamics of particular experimental sites.

ii) Annual monthly behavior of an average day, night hours and 24 hourly values of surface ozone and related prominent trace gases and material pollutants:

The variation in monthly average mixing ratios of all these predominant precursor traces gases along with suspended fine size solid material pollutants depicted a well definite strong and distinct remarkable seasonal dependence feature at Udaipur, as shown in below Figs 2(a-e). The mixing ratios of daily averaged monthly ozone value were found to be the highest level of 29.1±9.6 ppbv and their lowest value of 13.2 ±3.5 ppbv during the pre-monsoon and monsoon months, respectively. However, their seasonal mixing ratios of primary pollutants CO, BC mass concentration and NOx were maximized at 515.2±289.6 ppbv, 20.2±14.3 ppbv and 6.2±3.8 μgm^{-3} respectively during the winter. While their respective minimum values of CO concentration at 221.6±61.5 ppbv and NOx at 8.8±3.5 ppbv and BC at 1.7± 0.8 μgm^{-3} were observed in rainy periods.

It is more worthwhile to be noticed from Fig.2(a) that the surface ozone values as secondary air pollutant levels are found to be maximized in sunlight hours relative to as observed their lower value in the nocturnal period of all months except in the rainy months ,i.e., July and August months. In such months, there deviation values from night hours to sunlight hours are appeared to be negligible.

In contrary to these, primary atmospheric air pollutant loadings are seen to be remained at the highest level in nighttime period relative to observed in the day hours levels, which clearly demonstrated the fact about the complete different nature of production mechanisms of primary and secondary pollutants, as seen from Figs 2(b-d). Hence, secondary pollutants, i.e., ground level ozone amount is not generated by natural processes, but it is mainly perturbed through the complex mixed photo-ionization chemical reactions of NOx, CO, VOC, CH_4, NHMC, produced caused by anthropogenic human made activities, under the presence of sufficient incident solar radiation levels. Whereas, ambient primary air pollutants are largely produced through the human made activity or anthropogenic processes. While, the such primary pollutants are chemically destroyed their level in the noon hours by complex mixed photochemical reactions along with the generation of maximum ground level as a harm full hazardous

ozone air pollutant. Therefore, the ground level ozone serves as chemical consumed gases for primary air pollutants for shorter duration, whereas, OH chemically reacted as a whole atmospheric detergent for both primary and secondary ambient air pollutants.

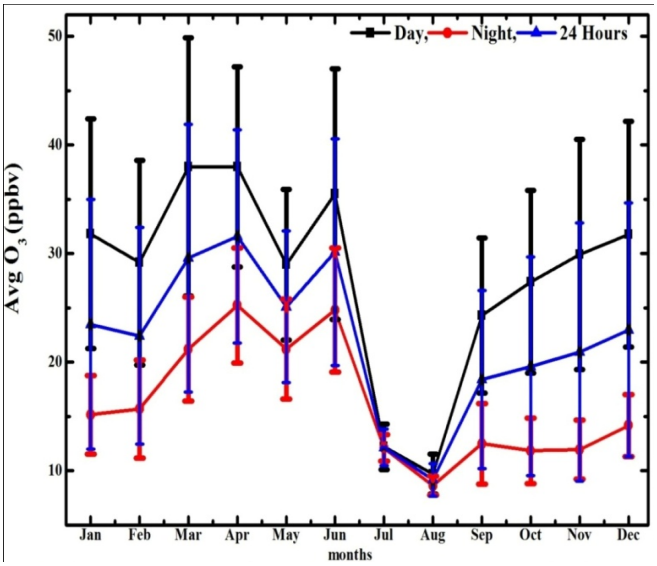


Fig.2(a)

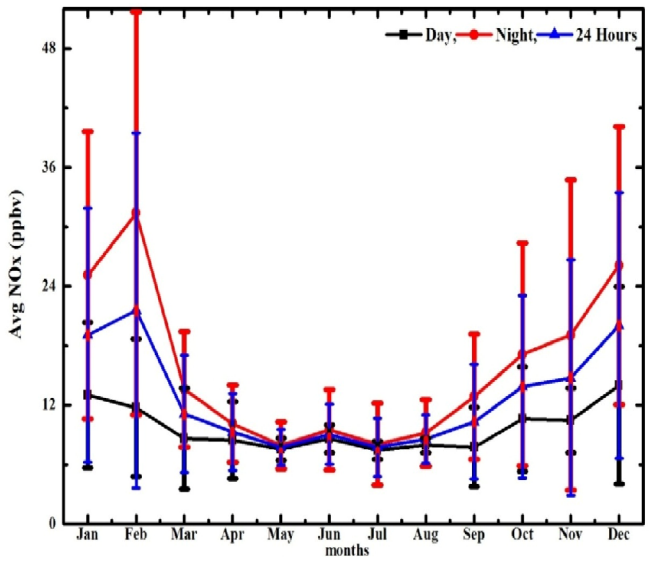


Fig. 2(b)

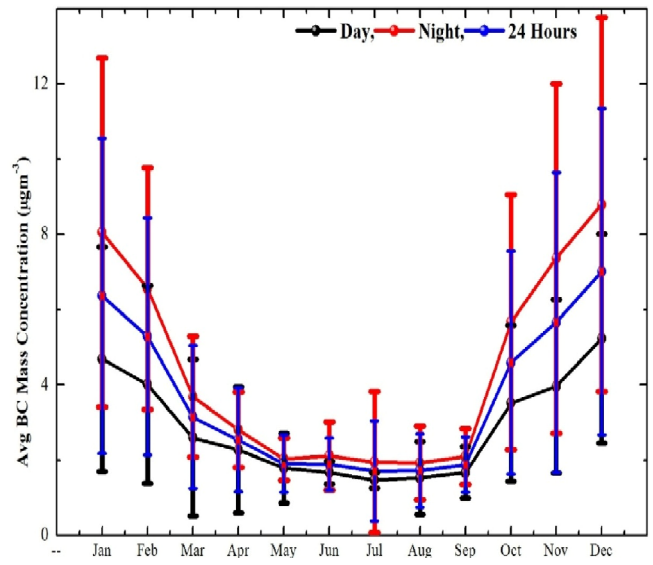


Fig. 2 (c)

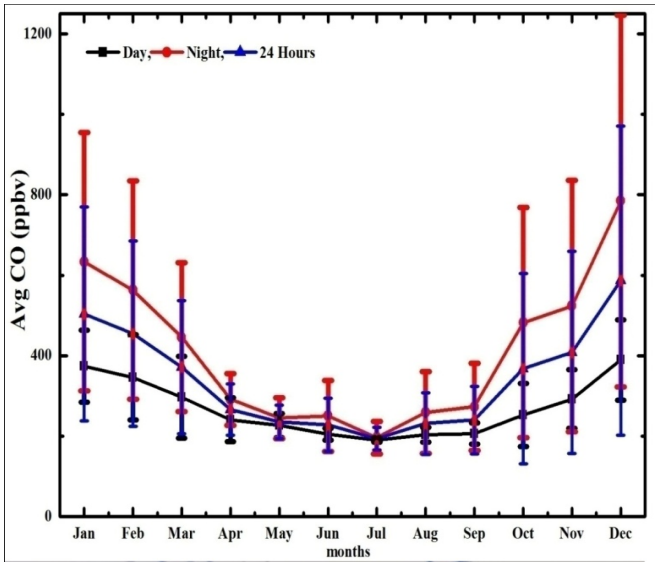


Fig . 2 (d)

Figs.2 (a-d): Annual monthly variation in average mixing ratio of O_3, NOx, CO and BC mass concentration during daytime, night time and 24 hours mean magnitude with their standard error bars.

In order to further more detailed investigation to access the nature and types of production and destruction mechanisms of PM 2.5 and BC aerosols, the overall combine annual monthly variation of

PM 2.5 and anthropogenic air pollutants as BC aerosols is illustrated in Fig. 2e. Their annual monthly curves show the almost identical pattern and illustrate the close resemblance with each other very well which clearly display one to one strong correlation between the PM 2.5 and BC level with observed their peak magnitude in winter and dip level in monsoon months along with intermediate levels in the rest of the month. Therefore, one can easily visualize that the dominant pathways of source mechanism of primary gaseous and solid air pollutants of PM and BC is predominantly governed by the same type of mechanism and nature of their sources mechanisms, which are furthermore linked to diverse and varieties of human made daily life activities. At the same time, in case of major sources of secondary air pollutant as ground level ozone is strongly generated through the photochemical ionization reaction only. However, the possible sink mechanism of all these major pollutant species seems to be controlled by meteorological processes and the availability of OH radical concentration in the earth atmosphere or excessive abundance of water molecules in the atmosphere.

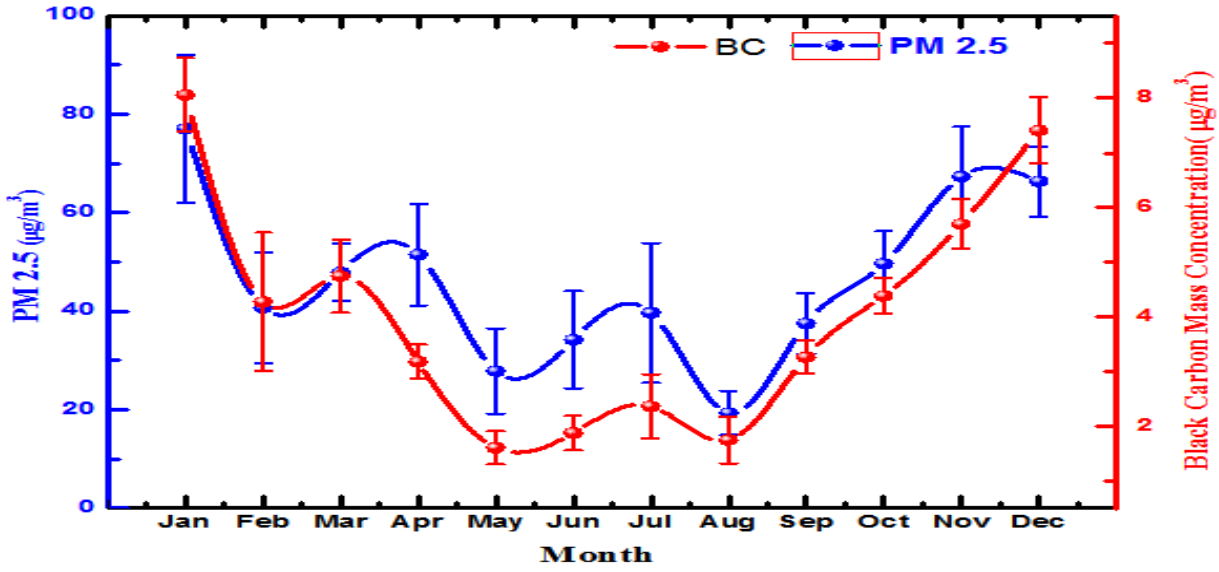


Fig . 2e: Annual mean monthly behavior of PM2.5 with BC mass concentration level.

Furthermore, in view of establish the source identification relation in PM2.5 with NOx, O_3, CO and BC as tracer of anthropogenic emission activity level, the seasonal scatter point plots along with their respective linear fit lines are plotted between NOx vs PM, O_3 vs PM, CO vs PM , BC vs PM, as seen in Figs 3(a-d). Their computed correlation coefficient (R) and slopes along with respective intercept values of linear fitted lines are displayed in the same plots. From the first glance of the plots, it is imperative to say at here that there is an excellent strong positive dependence between PM2.5 with each one selected air pollutant concentration level in all the season. All the atmospheric air pollutants such as BC, CO, Ozone and NOx vary in almost linearly in accordance with their respective PM values. But in

different rates, it is found to be highest in winter relative to rest of other seasons, which clearly demonstrated the evidence almost of similar types of their source mechanism for all mentioned considered ambient air pollutants generated principally by anthropogenic emission activity over measuring location.

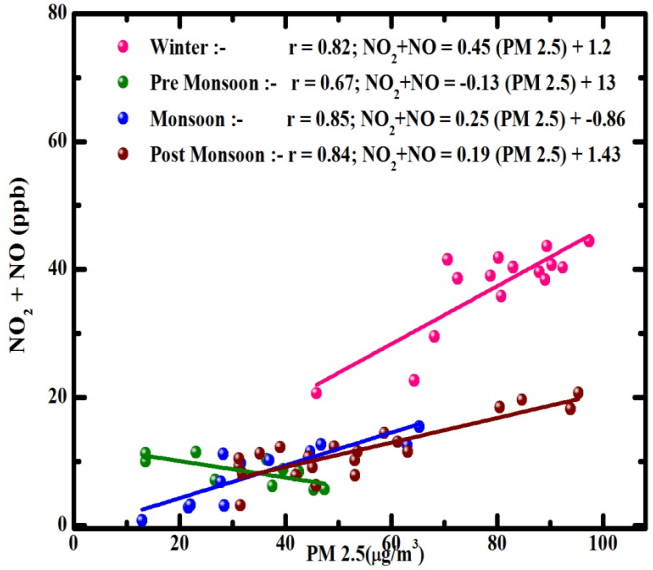


Fig. 3(a)

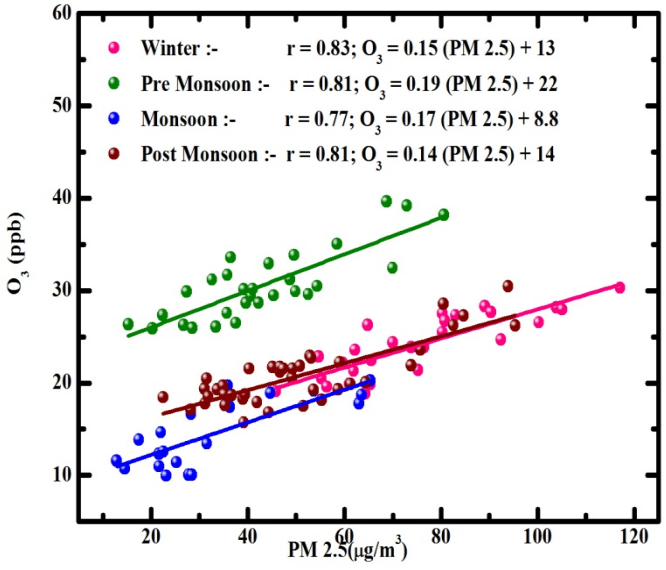


Fig. 3(b)

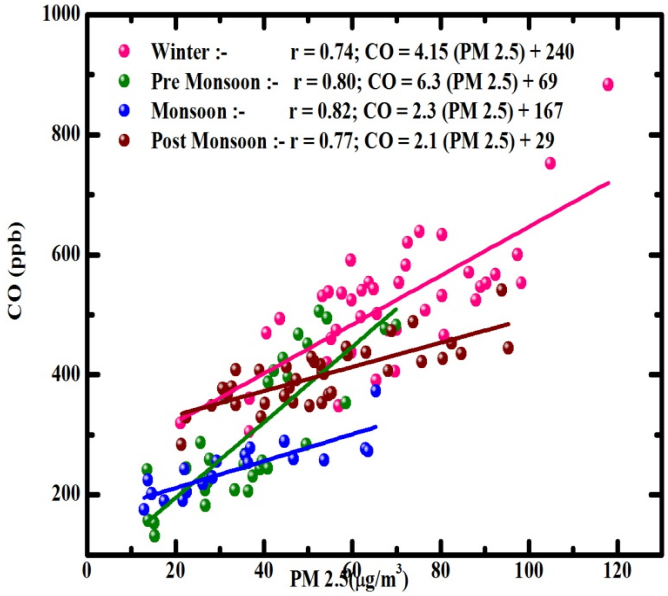


Fig 3(c)

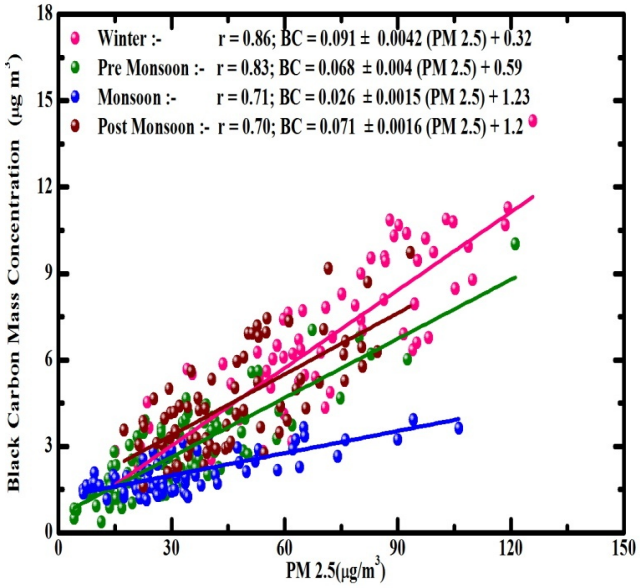


Fig. 3 (d)

Figs 3 (a-d): Seasonal scatter plots between measured ambient air pollutant particulate PM 2.5 levels with surface NOx, O_3, CO and BC aerosols air pollutant levels during period from October 2012 to November 2015 at Udaipur.

(iv) Influence of local meteorological, boundary layer dynamic activities, incident solar radiation intensity and NO2/NO on surface ozone concentrations

Among the several dominant pathways of local anthropogenic emission activity on surface ozone and its precursors gas levels as well as to varieties of atmospheric suspended fine size particulate matters and atmospheric aerosols of several kinds, namely, natural and anthropogenic aerosols at any site, modulated ozone and its pre-cursors species production and loss may also directly or indirectly perturbed through number of key metrological process parameters and boundary layer dynamics variables in term of i.e., rise or fall the values of ground level temperature (T, °C), relative humidity (RH, %), surface local wind speed (WS, m/s), local wind direction(WD, measured in degree from clock wise direction with respect to geographical North) and planetary boundary layer altitude (PBL, m).

Nevertheless, these contributed possible local source parameters are also very much meteorological/climate sensitive parameter and crucial chemical factor to understanding the processes of accumulation or dispersion of the air pollutants strength in several ways during the different months and in each seasons of years. Considering these such important aspects and their potential role of local prevailing meteorological processes and boundary layer dynamics phenomena through atmospheric solar heating, wind dispersion, accumulation, transportation phenomena on monthly in homogeneities characteristics of various atmospheric air pollutants loadings at any measuring site, the time series of both parameters at similar interval of mean hourly values along with their standard deviation values of mixing ratio of surface ozone along with their surface meteorological parameters such as T, RH, WS, WD and PBL values of particular day of specified months are synthesized on basis of available three hourly interval data on each day of surface meteorological parameters such as T, RH, WS, WD and PBL as well as their respective surface ozone concentration for the complete observation period.

(a) Seasonal dependence of Surface ozone with their ambient surface temperature

The surface ozone is predominantly generated through the anthropogenic emission processes instead of the natural phenomena. The diversified human made activities have been identified as the primary air pollutant sources of NOx, CO, VOC, CH_4 etc, which are produced by the industrial processes, vehicular emission, domestic activities, transportation sectors etc., The mixing ratio of these pre-cursor gases along with hydroxyl radical, as atmospheric detergent, play the pivotal role in enhancement and depletion in surface ozone through the series mixed photo-chemical reactions with sufficient amount of incident ground level sun radiation. Therefore, the production and loss of ground level ozone is directly linked to rate of photochemical ionization reactions in accessibility of sufficient

amount of incident solar radiation or ambient surface temperature itself. In this background, the mean hourly value of surface ozone plus standard deviation within specified group ranges is plotted with respect to their respective observed surface temperature plus standard deviation values in respective ranges for each season separately, as shown in the form of scatter diagrams in Fig.4.

The computed correlation coefficient values (R^2) between the seasonal Ozone with all chosen meteorological and atmospheric boundary layer parameters along with their corresponding significance level (P) are shown in tabular form of Table.1

Table 1 : Combine Correlation Table between O_3 Vs T, WS, Rh and PBL.

Season	Ozone vs T	Ozone vs WS	Ozone vs Rh	Ozone vs PBL
Winter	R^2= 0.49, P= 0	R^2= 0.059, P= 0.13	R^2= 0.32, P=0.02	R^2= 0.7, P= 0
Pre-monsoon	R^2= 0.74, P= 0	R^2= 0.55, P=0	R^2= 0.59, P=0	R^2= 0.78, P=0
Monsoon	R^2= 0.44, P= 0	R^2= 0.01, P=0.26	R^2= 0.5, P=0	R^2= 0.36, P= 0.001
Post-monsoon	R^2= 0.54, P= 0	R^2= 0.06, P=0	R^2= 0.2, P=0.01	R^2= 0.78, P= 0

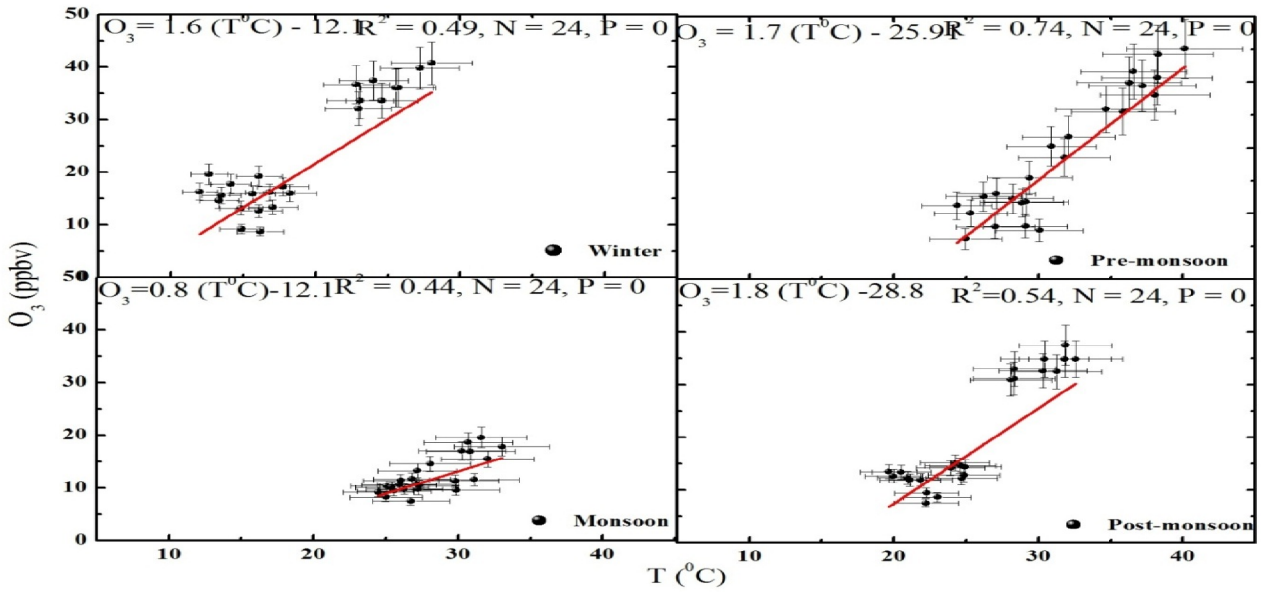


Fig. 4: Seasonally correlation between ambient temperature (T°C) and surface ozone level.

The square of correlation coefficient values (R^2) with their significance levels (p) is also computed from their respective surface ozone levels and ambient temperature values of the similar hours on the basis of season wise. The simple linear regression analysis is also performed to understand the role seasonal surface ozone amount with their seasonal dependence of surface temperature and their respective

computed straight line equation are also drawn and mentioned in respective graphs. It is clear from the computed statistical parameters, such as, R^2, p and N as well as linear regression lines for each season that the strong positive correlation values between ozone values with their corresponding surface temperature have been observed in all the seasons. The correction coefficient value is found to be systematically reduced after attaining their highest correlation value (r^2=0.74) in pre-monsoon to their lowest value of (r^2=0.44) in the monsoon months, with their intermediate correlation values of 0.54 and 0.49 in post-monsoon and winter months, respectively. A significant best correlation value (r^2=0.74, p=0) is found during the pre-monsoon. This can be well explained on the basis of the fact of decisive role of temperature on the formation of surface ozone through the intensity of photo-ionization chemical production mechanism as well as strength activity level of local emissions of precursors. Hence, the temperature factor solely plays the catalytic role of ozone formation in pre-monsoon season. As far as concerned with monsoon season, the minimum correlation values between surface ozone with temperature, indicating the less dominance and the lesser reaction rate of completion photochemical activity for surface ozone generation as the result of the major role of availability of high amount of OH radical in monsoon season. Furthermore, the positive slope values of 1.8, 1.7, 1.6 and 0.8 in post-monsoon, pre-monsoon, winter and monsoon period, respectively, for linear regression line also follow the similar ascending order as observed in case of their seasonal correlation coefficient values. Consequently, more strengthen the fact about of generation of surface ozone is primarily controlled by photochemical activities in each season. These observations have given clear support about the evidence that temperature plays a remarkable role in enhancing the formation of ozone in the tropical study area

(b)Correlation between PBL and surface ozone:

The seasonal inter relation between ozone concentration and PBL are also illustrated in the form of scattered point's plots in Fig.5 It is obvious from the Fig. 5 and several respective computed statistical parameters that the excellent positive correlation coefficient values of a higher magnitude are obtained between surface ozone and planetary boundary height in every season relative to observed in case of association with ozone with temperature also. The seasonal dependence of surface ozone with PBL also obeys the identical ascending pattern, i.e., pre-monsoon & post-monsoon>winter>monsoon as similarly to observed in the case of ozone vs Temperature. The highest positive R^2 values between 0.70 to 0.78 are seen in all three seasons, except in rainy season, when, the R^2 value is marginally found in lower side of 0.36, attribute the extra-influence of washout and scavenging effect on air pollutants loading in availability of surplus concentration of OH radical and water droplet. This significant positive correlation (R^2=0.36, p = 0.001) is also found during the monsoon season. Thus, only PBL is not solely

plays in helping the catalytic role of ozone formation in this season. Hence, the observed higher positive correlation coefficient value has explicitly demonstrated that ozone concentration reaches its peak value when the PBL and temperature both value is reached to their maximum level or vice versa.

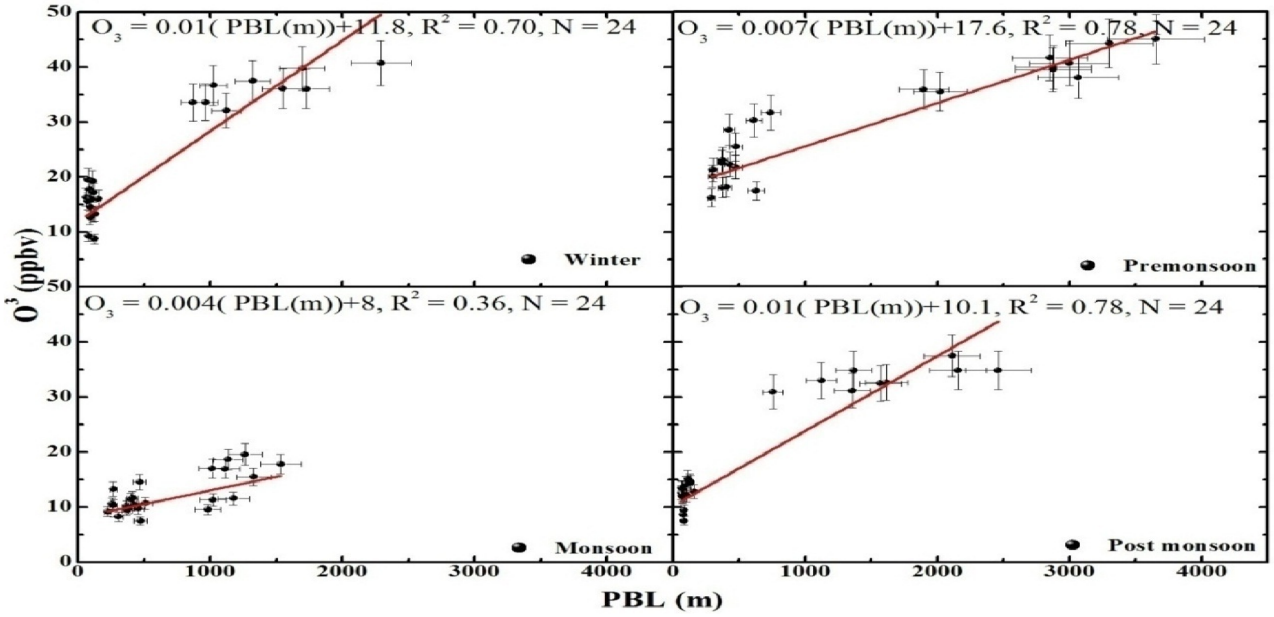


Fig. 5: Seasonally correlation between planetary boundary layer (PBL, m) and surface ozone level.

(c) Seasonal dependence of Surface ozone amount with their local relative humidity

. Fig. 6 shows the scatter point plots between their respective average hourly ground ozone levels and their observed hourly mean Rh values in same intervals. The necessary calculated statistical parameters and linear regression equations have been also mentioned in their respective Fig. 6

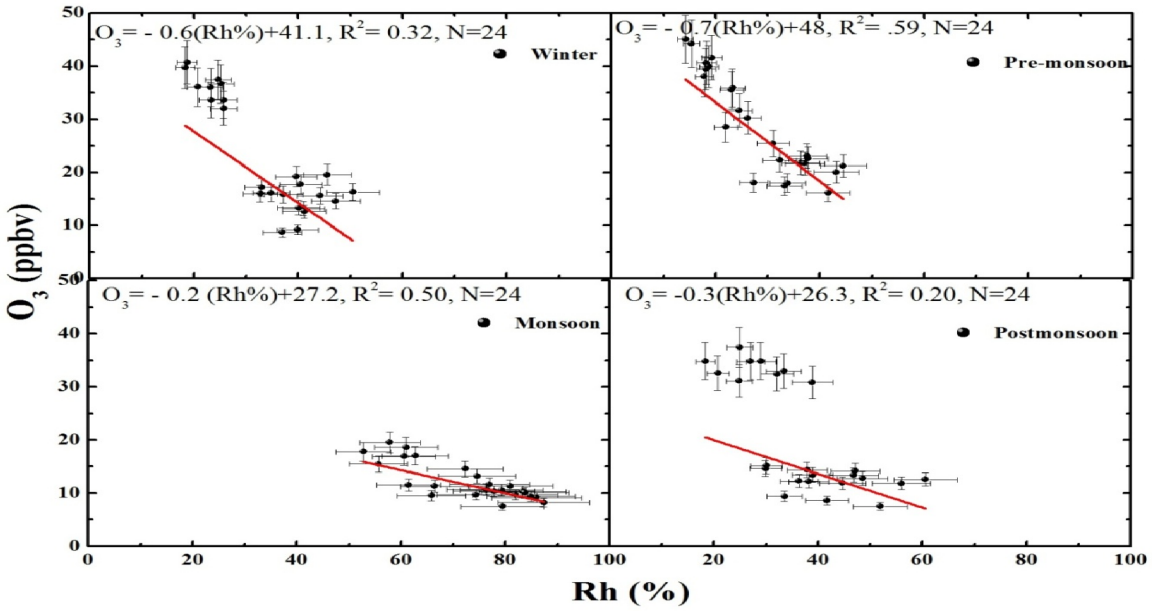


Fig. 6(a): Seasonally Correlation between Rh and Surface ozone.

It can be noticed from Fig. 6a that even though negative correlation coefficient values with their best statistical relevance show a reverse dependence of surface ozone with relative humidity in all the seasons, which possess an almost opposite nature relative to as observed in the case of O3 vs T and O3 vs PBL. However, the correlation between O_3 with Rh is more pronounced in the pre-monsoon and monsoon months only with their R^2 values of 0.59 and 0.50, respectively. While in post-monsoon and winter period, their values are pretty lower by 0.20 and 0.32, respectively. Hence, the behavior of reduction of ozone with increasing of Rh values has clearly shown in the seasonal pattern in the following decreasing order, i.e., pre-monsoon> monsoon> winter> post-monsoon. It may be well explained in view of availability of excessive amount of total water vapour content or seasonal behavior of OH radical that when the humidity becomes higher, consequently, the major photochemical paths for removal of ozone will be enhanced as the result of enhancing the OH radical in the atmosphere. Moreover, due to higher atmospheric instability, the intensity of photochemical process is furthermore slowed down and the surface ozone is depleted by deposition on water droplets, hence the ozone concentration has a strong dependence on humidity owing the properties of OH as an atmospheric detergent.

It would be more appropriate at this juncture to explore the verification of seasonal relation between ground level ozone with Total Water Vapour Column Content (TWVCC, cm) on the basis of experimental measurements. In this direction, a hand held, microprocessor based and reliable, sophisticated and microprocessor based portable Sunphotometer MICROTOPS-II instrument has been extensively employed as standard and ground based instrument for regular instantaneous and continuous measurement of TWCVCC during project period. Seasonal temporal variation of mean hourly value of Total Water Vapour Column Content (TWVCC, cm) along with their corresponding average hourly surface ozone levels is illustrated with function of day hour time , as shown in Fig.6b. It is observed from figure and observed variation in TWVCC has been appeared to maximum levels (from 2.2 to 2.8 cm) in rainy season, followed by their intermediate range in between 0.8 to 1.73cm in post-monsoon, lower values in the range from 0.72 to 1.15 cm in pre-monsoon and their observed minimum range from 0.41 to 0.73cm in winter month. In reverse to this in the case of ozone levels, highest values from 10 to 46ppbv have been observed in winter, followed by their mid level values varying from 10 to 37 ppbv and 7 to 37ppbv in post-monsoon and pre-monsoon and their least range from 5 to 12ppbv in rainy periods. Thus, from the above discussion and nature of curve for ozone with water levels, it is appeared that there is a negative relation between surface ozone level and water level.

Similar fact is also confirmed about the statistically significant correlation coefficient values between ozone concentration and TWVCC parameter in all the season.

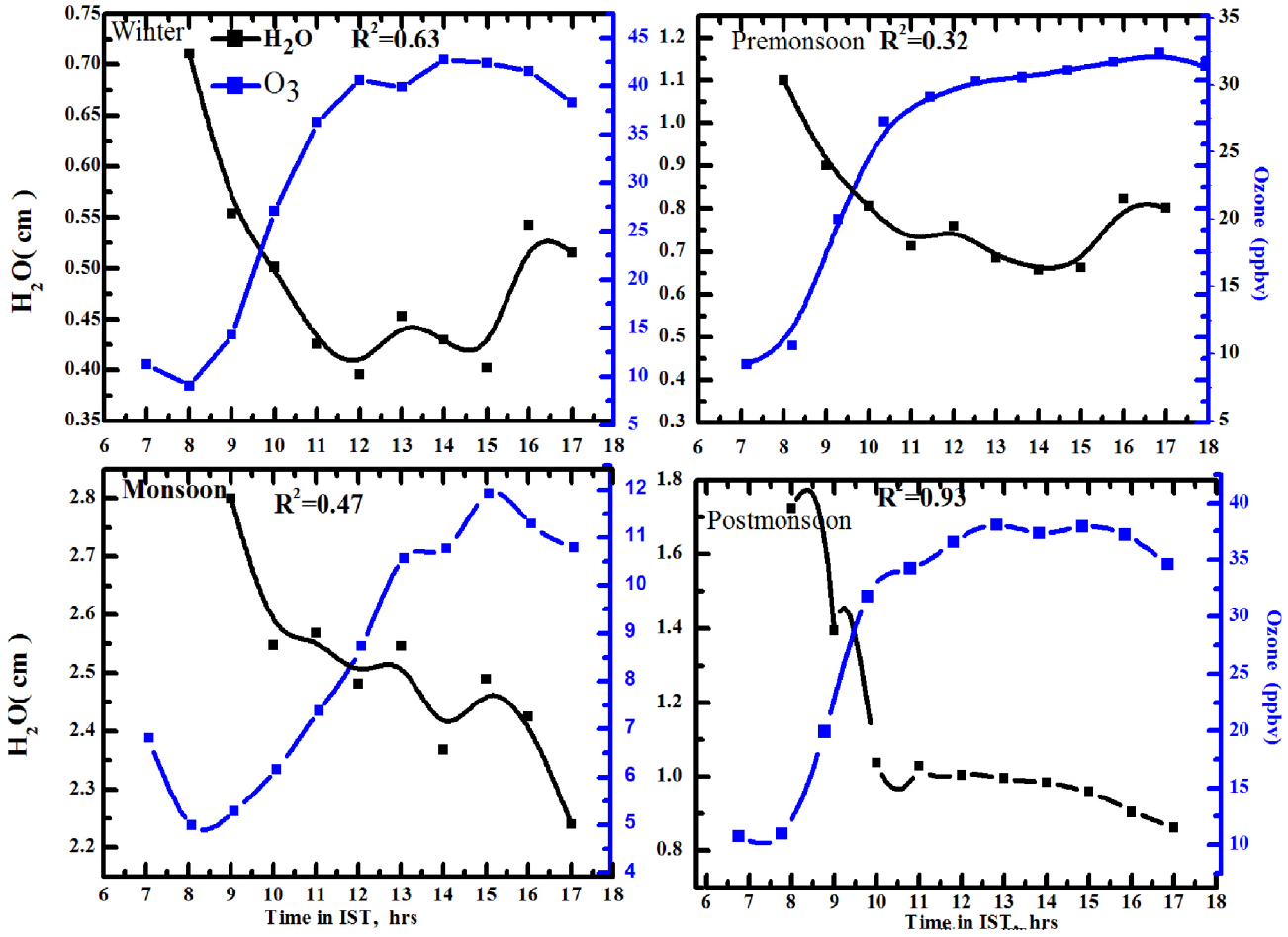


Fig.6(b): Seasonal temporal hourly average TWVCC and Surface Ozone variation during sunlight hours.

Hence, one can say that reduction of surface ozone and other pollutant is clearly seen owing to presence of excessive amount of water concentration as the result of the completion of following atmospheric chemical reactions

$$O_3 + h\nu \text{ (UV- B radiation)} \rightarrow O(^1D) + O_2 \quad (1)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (2)$$

$$OH + CO + O_2 \rightarrow CO_2 + HO_2 \quad (3)$$

$$HO_2 + NO \rightarrow NO_2 + OH \quad (4)$$

$$NO_2 + h\nu \rightarrow NO + O(3P) \quad (5)$$

$$O_2 + O(3P) + M \rightarrow O_3 + M \quad (6)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (7)$$

(d)Seasonal dependence of Surface ozone amount with their local wind speed and their direction

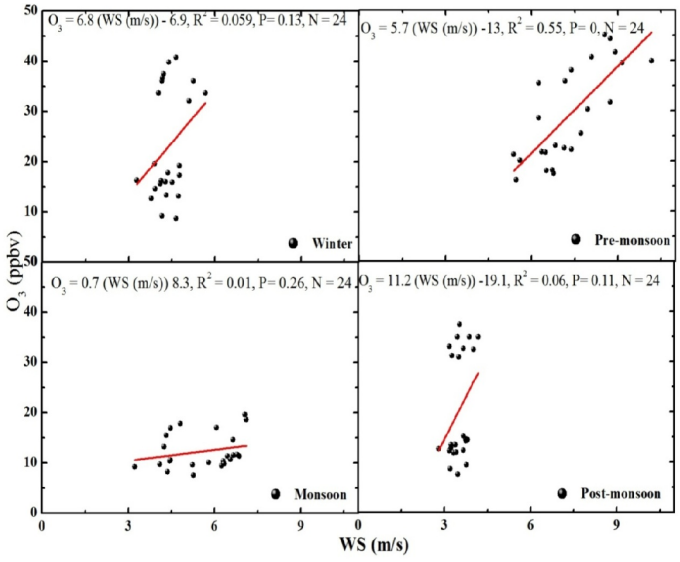


Fig. 7: Seasonally Correlation between Wind speed and surface ozone.

From the theoretical aspect, wind direction controls the pathway, nature of source region or tracks of pollutant dispersion, while wind speed decides the distance of the dispersion. Hence, spatial and temporal behavior of the major pollutants can be seriously affected by the coupled action of their corresponding variation in wind speed and wind direction both. It is seen from the Figure 7 as well with statistical analysis that at study place, wind speed does not contribute much more significantly with the ozone concentration ozone by dispersion or transportation mechanism in the seasons of clam condition, except in summer months associated with the strong wind condition. In the pre-monsoon season only, the remarkable negative statistical relevant correlation coefficient value (R^2=0.55, p=0) and slope of the linear regression line (5.7) is detected and further more attributed the explicit impact of prevailing the highest wind speed extend up to 12m/s in the hot climate period corresponding to the occurrences of highest surface ozone values. Whereas in case of rest of other season, the reason for this insignificant correlation may be attributed as the consequence of insufficient weak wind dynamics, i.e. clam and stagnation conditions and local wind circulation patterns that could not make any alteration in the dispersion and transportation of surface ozone.

Further more detail investigation in order to establish the close link between seasonal surface ozone with both wind speed and wind direction, firstly the seasonal polar diagrams of hourly wind speed along with their respective wind direction values are drawn in the form of the polar diagram to delineate the simultaneous seasonal features of wind speed values with their wind directions, as seen in Fig.8. It is clearly seen from the polar plots that the dominance of strong wind conditions are prevailing mainly southwesterly nature in pre-monsoon, in contrast to the above, the very weak condition is experienced primarily northeasterly behavior in post-monsoon. While in intermediate wind speed is noticed remarkable southwesterly characteristics in monsoon month, with the lower wind speed condition is found in northeasterly features during winter season. Thus, the wind speed along with wind direction both have displayed the distinct and consistent seasonal dependence with their maximum probability of

higher wind speed in pre-monsoon, middle level values in monsoon, lower values in winter and their lowest speed magnitude in post-monsoon.

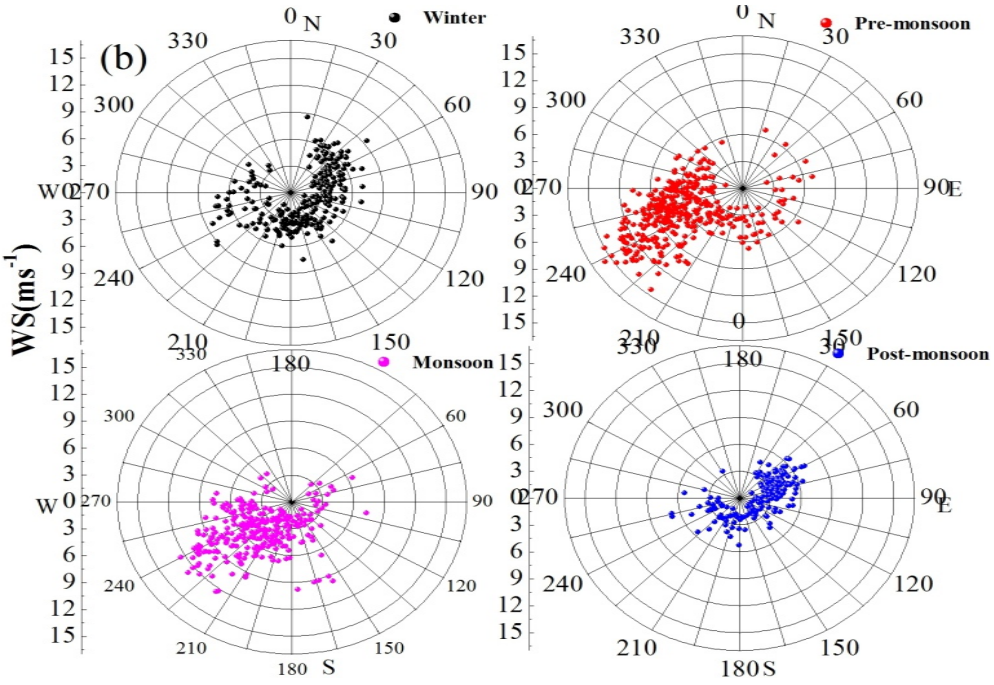


Fig.8: Seasonally Correlation between Wind direction and Wind speed.

In the similar analogy, seasonal behavior of wind directions also demonstrated from the same polar diagram about that most probable wind directions or air pollutants source regime are noticed to be toward north easterly in winter and post-monsoon and become south westerly in monsoon and pre-monsoon months. Hence, the strong seasonal wind speed is associated with wind flow from southwest to west direction regime from the observing site which has concerned to low density populated along with less industrialized activity and dust influenced of semi urban tropical regime in pre-monsoon. However, in monsoon season, the observed intermediate values of winds are travelled mainly from the oceanic clear environmental region along with also over to the mainland region before reaching to the experimental site. Consequently, wind is supposed to carry with their moisturized, clean sea breeze air together with the result of accumulation of low level air pollutants occurring at receptor areas.

But, in winter and post-monsoon season, the nature of local surface wind pattern is completely turned from south westerly & westerly in pre-monsoon and monsoon to become north-easterly and easterly during post-monsoon and winter months. Hence, in post-monsoon and winter period, the majority of wind speeds are seen to be varied in a lower range from 1 to 5m/s and it flowed across the heavily populated and polluted urban and industrialized sites of intense anthropogenic activities regions. As a result of this fact, during winter and post monsoon season, such types of winds are capable to bring

the excess amount of anthropogenic air pollutants from polluted site such as IGP region toward the monitoring region.

In addition to the above, the prevailing claim and stagnation wind conditions in such both season are also generated the suitable and favorable polluted environmental condition to accumulate more air pollutant burden at the experimental location. Thus, the seasonal variation of wind speed together their respective wind direction behaviors have played the decisive role in observed seasonal ozone dependence.Realizing the above perspective kept in mind, the seasonal polar plots of hourly surface ozone are also drawn with respect to their observed wind direction values, as depicted in Fig.9.

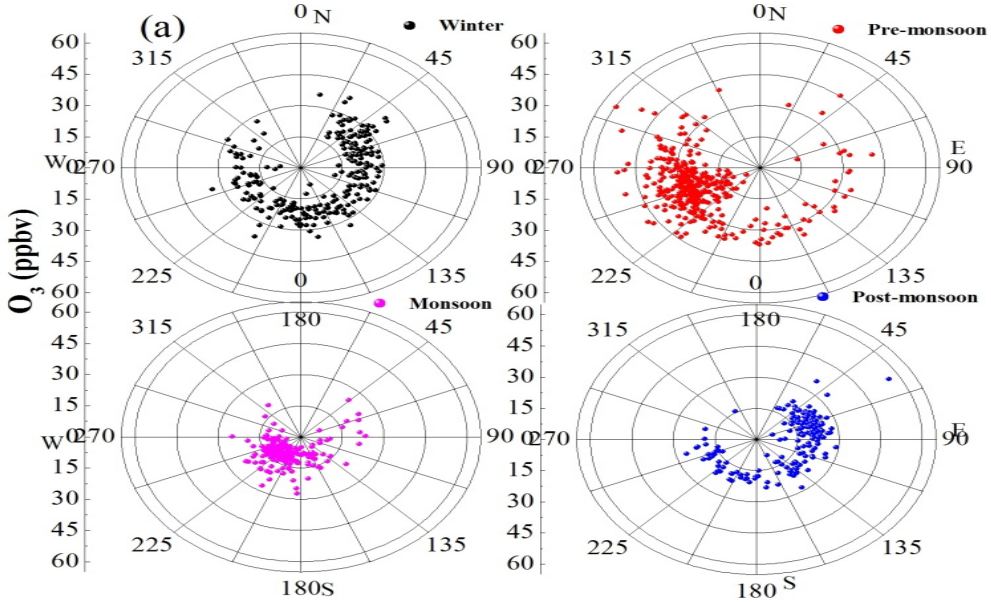


Fig. 9: Seasonally Correlation between Wind direction and surface ozone.

It is quite evident from the polar plots that during the pre-monsoon, the higher surface ozone values coincided with the occurrence of the strong wind condition along with south-westerly and westerly wind nature. But, in winter, the observed excessive amount of surface ozone loading is linked to the claim and the stagnation wind condition of predominantly north-easterly wind. The intermediate composite nature of seasonal wind speeds and wind directions together with seasonal ozone values have been observed in a transition period in monsoon and post-monsoon period.

(e) Role of long range transportation of atmospheric pollutants phenomena on observed monthly behavior of air pollutants strength as a contribution towards regional influence scale:

Among the several most possible identified explored factors related to local parameters on ambient air pollutants level, the regional air pollutants emission activities has been also recognized in recent years as one of another leading plausible factor in influencing the seasonal atmospheric pollutants characteristics even turn over less environmental polluted and low density populated sites. It is

attributable to the aspect of atmospheric pollutant outflows and long distance transports of air pollutants from remotely heavily polluted source regions over to less polluted and clean location, i.e., intercontinental air pollutants transportation phenomena. In the above prospective of understanding of regional air pollutant emission factor, it is, therefore, planned in this section to ascertain the effective role of daily air mass backward wind trajectory properties, i.e., travelled pathway regions of several air pollutants emission activities from various types of wind circulating source areas as well as on duration of air mass flow pattern on observed high degree variability in air pollutant loading characteristics and also with their alteration in types of atmospheric pollutant sources regions. Monthly statistical variable data set, i.e., mean plus sd with maximum and minimum values calculated on the basis of their hourly values of O_3, CO, NOx and BC mass concentration at Udaipur during entire measurement period i.e., 2012-2015 is shown in Table 2.

Table 2:.Monthly statistically variables data set, i.e., mean ± sd with minimum and maximum values computed on the basis of their hourly values of O_3, CO, NOx and BC mass concentration at Udaipur during entire measurement period , i.e., 2012-2015.

Months	O_3 in ppbv (mean ±Sd) Min, Max)	CO in ppbv (mean ±Sd) Min, Max)	NOx in ppbv (mean ±Sd) Min, Max)	BC μgm^{-3} (mean ±Sd) Min, Max)
January	23.49±11.5 (1, 60.1)	503.91±44.33 (103.4, 2364.8)	19.06±2.14 (0.5, 137.9)	6.37±4.18 (0.26, 49.1)
February	22.42±9.98 (1.29, 51.84)	454.69±38.37 (135.8, 2706.7)	21.55±2.99 (0.5, 147.6)	5.28±3.15 (0.18, 42.3)
March	29.59±12.33 (1.7, 64.5)	371.63±27.48 (146.9, 2280.3)	11.12±0.99 (0.5, 60.2)	3.14±1.9 (0.05, 23.9)
April	31.6±9.81 (4.7, 59.7)	266.25±10.62 (41.4, 1185.9)	9.3±0.65 (0.4, 56.5)	2.54±1.38 (0.12, 35.4)
May	25.09±6.99 (5.8, 66.3)	235.71±6.93 (106.8, 852.5)	7.74±0.3 (1, 42.9)	1.91±0.76 (0.087, 16.9)
June	30.13±10.44 (1.2, 96.7)	227.87±11.02 (128.7, 795.9)	9.06±0.5 (0.5, 52.9)	1.89±0.69 (0.147, 18.6)
July	12.15±1.69 (6.7, 21.9)	193.67±4.69 (112.5, 369.5)	7.75±0.49 (0.4, 32.1)	1.71±1.33 (0.05, 11.1)
August	9.16±1.51 (3.3, 17.4)	231.36±12.84 (53.2, 654.8)	8.58±0.41 (0.5, 29.9)	1.73±0.97 (0.07, 30.4)
September	18.4±8.22 (5.9, 47.3)	239.96±14.05 (89.5, 778)	10.33±0.96 (0.5, 58.2)	1.88±0.73 (0.1, 24.5)
October	19.62±10.07 (2.1, 50.2)	367.66±39.42 (100.5, 2037.9)	13.86±1.53 (2.6, 71.8)	4.59±2.96 (0.48, 40.8)
November	20.92±11.89 (1.1, 59.5)	408.03±41.86 (103.7, 2364)	14.76±1.98 (2.6, 97)	5.66±3.99 (0.53, 47.6)
December	22.97±11.69 (1.3, 62.9)	587.08±64.06 (135.5, 3048.6)	20.05±2.24 (0.8, 106.2)	7.01±4.34 (0.15, 39.2)

Fig. 10 show mixed average monthly behavior of isentropic air mass backward wind trajectories patterns arriving on measurement site at three height levels of 500m AGL, 1500m AGL and 4000m AGL(above ground level) depicting by their individual colors curves lines to provide experimental evidence about the role of long range transportation of air pollutant phenomena on mean monthly behavior of surface ozone, NOx, CO and BC through the altering the monthly air mass flow pattern characteristics before reaching to the receptor side by various advection altitude levels.

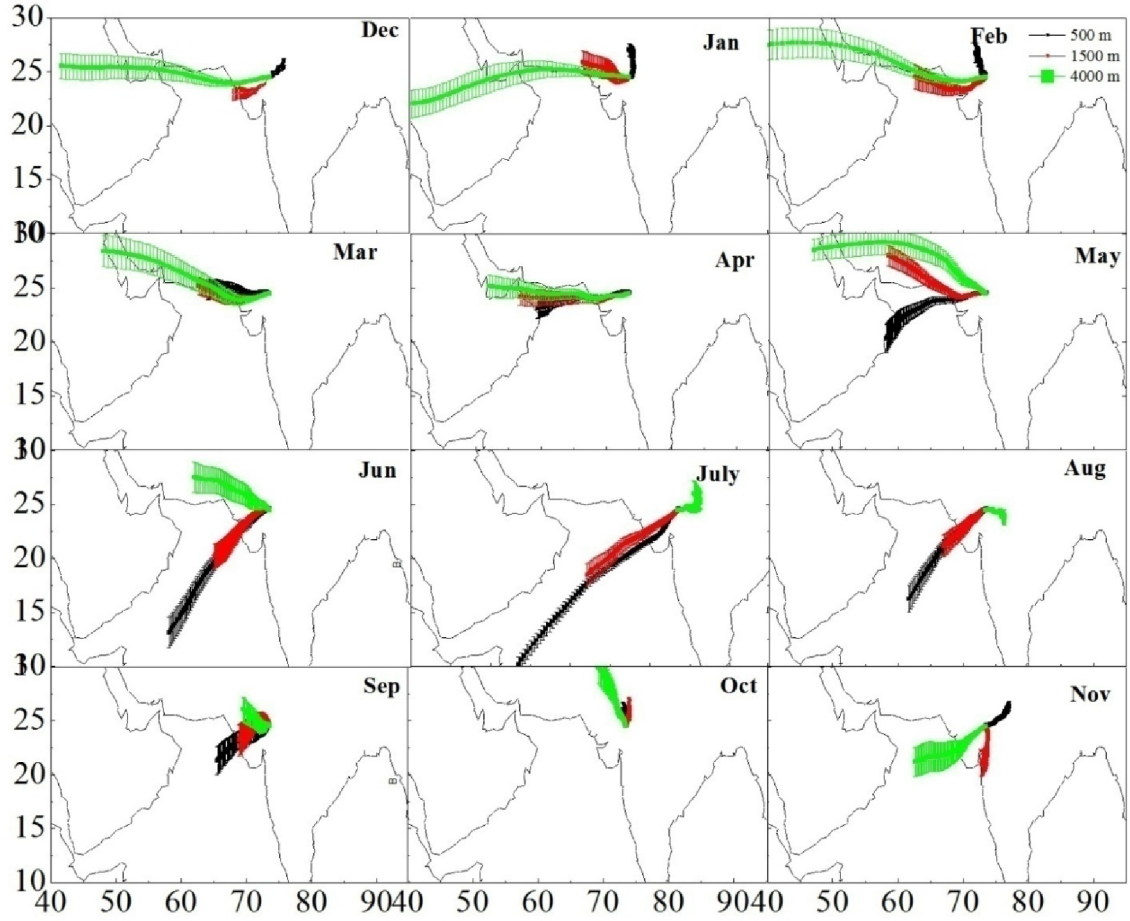


Fig.10: Long range transportation phenomena of monthly mean backward air mass wind trajectory observed over observing site at 500m, 1500m and 4000m amsl.

It is clearly observed from the Fig. 10 that average air mass trajectories paths spread over the larger covered areas depicted in term of longitude along with their sd values as drawn by vertical bar lines with the latitude on respective same points has shown their special travelled path area as well as their transverse path direction on the map.

In the more concise, the average monthly behavior of backward air mass trajectories has shown the strong and well distinct consistent seasonal characteristics of possessing diverse nature for only two selected advection height levels. Only strong westerly/north westerly wind was predominant in most of

each season in case of back ward trajectories group of 4000m AGL. Whereas in case of back trajectory air mass clusters of 1500m AGL, westerly/ north westerly winds flow was more pronounced and dominated in both winter and pre-monsoon and became the southwesterly in rainy season with almost mixed nature in post-monsoon. However, in case of backward trajectories class of 500m AGL, the northerly and westerly winds were more predominant in winter and pre-monsoon and then again became as southwesterly in monsoon with their composite and mixed nature seen in post-monsoon.

Hence, only atmospheric backward wind trajectories of below the atmospheric boundary and within the atmospheric boundary layer region of 500m AGL and 1500 m AGL, respectively, has shown the definite and consistent, systematic seasonal dependence pattern, as compared to observed in case of atmospheric air mass flow in the free aerosols troposphere region, i.e. 4000m AGL. In light of observed evidence of higher and intermediate values of surface ozone in pre-monsoon and winter month may also be well explained on basis of the argument of the condition of westerly and northwesterly wind flow pattern in such similar period. Consequently, westerly and northwesterly flow from arid to semi arid region part of northern and western Indian subcontinent may be anticipated to bring more natural types and anthropogenic air pollutants in pre-monsoon and winter season, respectively..

In contrast to this, prevailed very strong southwesterly originated from clean and marine oceanic region may also carry out the marine aerosols with lesser pollutants at the observing site by both air mass trajectories of low and middle advection level of 500m and 1500m AGL.As result of this, wind also brings moisturized pollutants with excessive amount of water droplet which will further more depleted the surface ozone and other pollutants in monsoon. Hence, from the above discussion, it may be clearly visualized that backward trajectory analysis that their nature of path region and area covered by air mass parcel conduits would also be served as a tracer of transport air pollutants. Besides these facts, it is also evident that alteration in monthly air mass flow pattern, i.e., their air mass backward winds directions and travelled pathways in various transported source regions has also contributed as one of the leading significant and sensitive factor in changing the monthly behavior of several air pollutants burdens at Udaipur.

Among of all these, some of interesting, spectacular facts have emerged from the above analysis that more strong wind condition is explicitly visible in higher levels of air mass trajectories and than their intermediate level in a middle level group of both 500m and 1500m AGL. From this, it is understandable that the air mass movements during winter months and post monsoon months are reaching from north and northeast of this site and confined from south during pre-monsoon months and south west in monsoon months. Thus, during the winter month, long range transport of air mass

contributes to the observed extra abundance of surface ozone levels in addition to its photochemical formation. It is further observed that air masses appear to be originated from the eastern part of Udaipur that is greater affected by the transport of pollutants from nearby industrialized and heavy populated land during winter. Under such conditions NO_2 undergoes photochemical reactivity at a faster rate, thereby resulting, in an excessive amount of ground level ozone concentration.

During summer and monsoon seasons, the movement of air mass trajectories originated over the Arabian Sea and traversed through a smaller area of landmass before reaching observing site Udaipur. Since, these air masses have a strong land mass region area; the observed enhancement of surface ozone is only at the expense of photo ionization chemical reaction activity rather than the transportation of air pollutants. Marine air mass was relatively clean air in monsoon season. Owing to this oceanic influence, the air mass enriched with hydroxyl radicals (OH) may trigger the removal of surface ozone to a larger extent. This may be one of the great possible reasons for the reduction of surface ozone mixing ratio observed during monsoon and late summer season at this location in spite of high solar flux. During post monsoon, short range air masses at low altitude (500m) appear to originate from the east of this site inducing the transport of precursors which, seems to have little contribution. Hence, during post-monsoon, in addition to photochemical production, inventories within short range air pollutant transportation may lead effectively contribute to O_3 formation at this location.

(f) Mean monthly diurnal variations of Surface ozone along with SW down welling and NO_2/NO ratio concentration:

Considering several local and regional air pollution governing factors to influencing the surface ozone level and associated other air pollutants by meteorological, atmospheric boundary layer dynamics variables, transportation phenomena etc., one of the other extra crucial direct sensitive factor is also realized and considered, which is based absolutely on photochemical ionization process feature. In addition to above line, the other plausible related parameters are incident short wave (SW) solar radiation and NO_2/NO value due to consequence of intensity of photo-chemical ionization reactions rates actively participate prominent roles in several physical and chemical processes in the atmospheric air pollutants formation. It affects both on the oxidation processes in the troposphere and consequently the budgets of photo-oxidant reactive trace gases as well as generation and reduction in air pollutant levels. For this purpose, the SW solar radiation intensity parameter have been continuously monitored on real time measurement in interval of one minute sampling interval by using a well known popular

and commercial calibrated CNR-1 Net Radiometer which is installed in free space condition at Udaipur station.

In order to demonstrate the contribution of photochemical sensitive feature along with justification of effective roles in the completing these photo-chemical reactions with photo oxidant reactive gases with hydroxyl-radicals etc. with concerning to shortwave solar radiation intensity in affecting the surface ozone level, the monthly diurnal hourly variation of shortwave radiation (SW, Wm^{-2}) intensity as well as respective [NO_2/NO] diurnal mean hourly magnitude are inter-correlated with their recorded similar monthly diurnal ozone variation for the same study period, as depicted in same Fig. 11. It is observed a common salient feature that for each particular month, mean diurnal curves of surface ozone and SW intensity exhibit the almost identical shape of diurnal curve of possessing single peak ozone value and also SW intensity's peak magnitude around afternoon. Later on, both parameters displayed the steadily decreasing trend around on both sides with their respective noon time peak values around early morning hours and late evening hours to complete night period. However, the peak recorded ozone values around late afternoon hours are not coincided with the maximum SW intensity level in noon hours, but in a definite certain time delay about two to three hours between the timing of peak production ozone and highest prevailed value of SW intensity in noon hours. It is reasonable expected to certain time delay required in sustaining the complete effect of photo-ionization chemical activities to observed peak surface ozone interval in noon to late noon hours.

Some typical similar characteristics are notable also from their close look to statistical analysis performed on basis of monthly diurnal pattern of ozone and SW intensity that there is best statistical significance with slightly higher positive correlation values between their diurnal variation of ozone and SW intensity, as noticed from their calculated correlation coefficient (R) values (ranging from 0.55 in July to 0.84 December along with their p values always remain below 0.05) in case of sun light hours for all the months. Therefore, from the above discussion about the experimental verification from simultaneous variation in monthly diurnal behavior of ozone and SW intensity, it may be concluded that photo-ionization mechanism factor may be played as one of essential deciding leading factor for controlling the monthly diurnal evolution of ozone. The diurnal cycles of O_3 and SW are fairly similar, with O_3 maximum occurring at 15:30 hr, which is about 2.5 hrs after the solar irradiance, becomes the highest.

In more detail in reference their prevailing peak monthly values, daytime solar radiation is most intense during all seasons except in cloudy and rainy days with daytime average values as high as 536±317 W/m^2 in May and least intense or weakest during monsoon with daytime average value of

289±189 W/m^2 in August. At this stage, it is interesting to be noticed at here that the seasonal variations in average Ozone are characterized by a broad pre-monsoon maximum with highest values 38.02 (ppbv) in April and lowest values 9.76 (ppbv) in August similar to as observed the highest ground level sun radiation level with the broad peak nature in April or vice versa, which also gave a excellent support and clear observational evidence of influence due to broad peak of SW radiation intensity with corresponding the prevailed broad peak of ozone with their maximum ozone values in similar duration through the photo ionization chemical process etc.

As discussed from the above, monthly diurnal curves of ozone and SW intensity both display the highest concentration around the afternoon and noon hours, respectively, whereas their minimum values occur during early morning as well as in complete night hours. Such daytime increase trend in O_3 mixing ratio is principally allied from the photo-oxidation chemical reactions along with industrial and anthropogenic hydrocarbons, carbon monoxide, and methane in the existence of sufficient amount of NOx. With the onset of sunshine hours, O_3 concentration gradually raises and it attains a maximum value around after noon hours time, through the photolysis of NO_2 following reactions:

$$NO_{2+}hv(\lambda < 420nm) \rightarrow NO + O \quad (8)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (9)$$

At this juncture, it is more worthwhile to be noticed at here that certain delay time period required for effective completion of photo-chemical ionization process is required about two to three hours in order to complete the above photo-ionization chemical reactions for attaining the broad maximum ozone values around late afternoon hours in each month. As the result of this that delay in declining trend of the mixing ratio surface O_3 initiated after 17:00 hr in the evening hours on all days with coincidence of abruptly decreasing nature of the incident solar radiation level. The minimum concentration of surface O_3 during nighttime is attributed due to the absence of photolysis of NO_2 and loss of O_3 by NO via the following titration reaction and surface deposition.

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (10)$$

To understand, prove the above chemical process and furthermore check the role of monthly diurnal ozone with NO_2/NO in reference to the above atmospheric chemical reactions, the diurnal monthly average diurnal variations of NO_2/NO and their surface ozone is also plotted in the same figure. It was seen that in contrast to nature of monthly diurnal ozone curves with their SW intensity, the monthly diurnal curves of NO_2/NO mixing ratio showed remarkably opposite trend relative to the monthly diurnal evolution of ozone with SW intensity, attributing the higher NO_2/NO values of during nighttime in absence of photo ionization chemical activities and lower NO_2/NO values during daytime

in occurring the various higher rates of photochemical reaction activities strictly in accordance with diurnal hourly variation of SW level. During night hours, the boundary layer also gets down, contracts and remains low till early morning hours, therefore pollutants gets trapped in the shallow surface layer condition, and, hence, the air pollutants level are observed at high concentrations in such period due to both reason of cease of photochemical reaction along with boundary layer dynamics process too.

In order to attain greatest levels of surface ozone towards noon hours, large amounts of precursors are involved, this may cause to attain the lowest levels of NO_2/NO during day time as suggested from the photochemical mechanism with their suggested chemical reactions (1 to 3)

To prove the daytime production of O_3 via the photolysis mechanism of NO_2/NO in the presence of sunlight, the diurnal variations of NO_2/NO and O_3 mixing ratios are depicted in Fig. 11. It is clearly seen from monthly diurnal averaged curves of O_3 and NO_2/NO that during sunlight hours, higher hourly average O_3 concentration and SW intensity both are found more compatible at smaller values of [NO_2]/[NO] in before afternoon hours and slightly higher values around sunset hours, attributed to more production ozone with the help of completion of well known photochemical reaction of conversion of NO_2 to NO in presence of changing the solar radiation level in that duration. However, lower day hour values of [NO_2]/ [NO] with corresponding higher ozone level day noon hour values are visualizing the quite clear verification of argument suggested the photochemical reaction mechanisms.

Based on this three year analysis period, among in the different seasonal months, seasonal monthly hourly values of O_3 and NO_2/NO concentrations, as depicted in bracket only, were found to be higher value of NO_2/NO ratio in Post-monsoon [23.29±12.89] than [16.39±7.33] in pre-monsoon months with their minimum values occurred in monsoon and winter season [15.79 ± 10.67] and [14.03±5], respectively. From the Fig.11, it may be quite evident that enhancement of day hourly values of surface O_3 production is more pronounced in comparison with reduction of NO_2/NO occur lower values in the same interval at measuring site. The higher values of NO_2/NO reduce the O_3 production rate which is a fairly good agreement with the atmospheric chemistry involving NO_2, NO and O_3. The degree of diurnal variability in NO_2/NO ratio were recorded to be in diverse nature from month to month in conjunction with their strong variability in the pre-monsoon, post-monsoon and winters seasons, while as usual weaker diurnal dependency registered in the monsoon season. The mixing ratios of NO_2/NO ratio show a sharp peak in the morning hours between 07:00 hr and 10:00 hr, with coincidence of timing with more anthropogenic activities sources of ozone's pre-cursors.

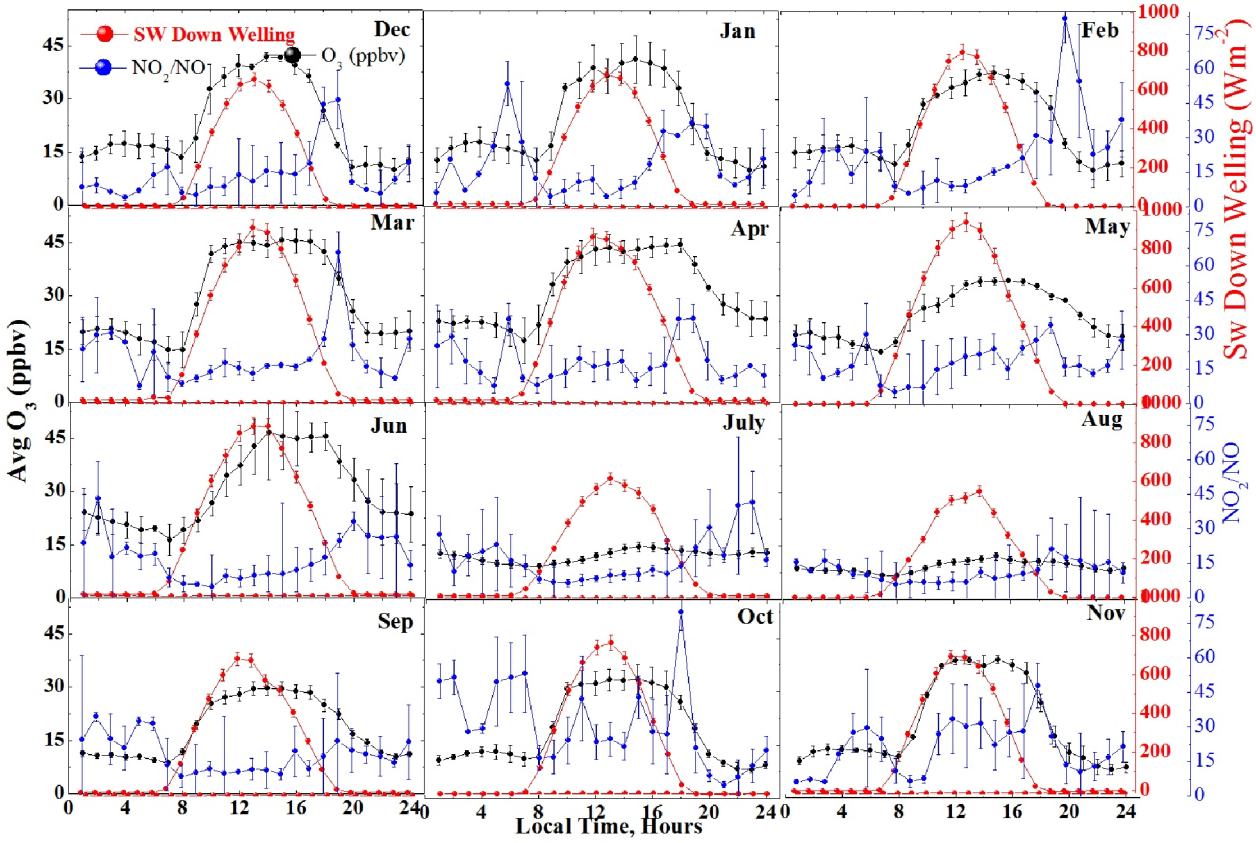


Fig. 11: Diurnal variation of average ozone mixing ratios, SW down Welling, NO_2/NO and Surface ozone concentration during Dec., 2012 to Nov., 2015 observed at Udaipur.

Their lowest mixing NO_2/NO ratios were observed in the afternoon hours (12-16 hr).Subsequently, the observation between 17 hr and 19 hr, their values showed increasing tendency as the elevated mixing ratios were observed from evening to whole night hour period till early morning hours .In the pre-monsoon and post-monsoon months, the morning peak amplitudes of NO_2/NO ratio varied in the ranges of 8-19. In the monsoon months, the morning peak amplitudes of NO_2/NO ratio were in the range only of 8-10. While in winter season, the morning peaks in NO_2/NO values occurred in a higher range at 20-27, which were noticed to be most prominent in winter compared to rest of other seasons.

The afternoon values of lower NO_2/NO ratio also show some seasonality dependence. The average seasonal values of NO_2/NO in the afternoon hours were found to highest at 27.6±13.3 in post-monsoon and at 17.1±13.4 in winter, with their lower values of 14.6±8 and 10.5±4 during the pre-monsoon, monsoon, respectively. The elevated levels of NO_2/NO ratio during morning and evening hours at Udaipur coincide with peak emission NOx activities attributed to vehicular, industrial and domestic emission exhausts etc. along with altering the characteristic of local atmospheric dynamics conditions around surrounding the monitoring site.

On the other hand, the observations from night to till early morning hours illustrated higher values mainly due to absence of titration photo chemical reaction of conversion NO_2 to NO, consumption of nighttime ozone values with available NO in to formation of NO_2, i.e., $O_3 + NO \rightarrow NO_2 + O_2$ (3.19) and also a shallow nocturnal boundary layer depth resisting the mixing of local emissions with the free tropospheric air. In concise during monsoon months, in after noontime, the higher chemical rate of photochemical reaction and also PBL depth provides a unique favorable situation for sustaining the slightly larger mixing volume region and hence the air pollutants NO_2 get diluted. The morning and evening peaks are almost absent during monsoon months and lower concentrations of both NO_2/NO ratio were observed with no significant differences between day and night. In the months of July and August, at the same time, the amount of rainfall at Udaipur is highest in the month of August and September. During this season, observational site experiences the highest total annual rainfall about 480nm of the year in such two months only. Monthly Correlation O_3 Vs SW radiation and NO_2/NO are shown in Table 3 for further justification of above discussion.

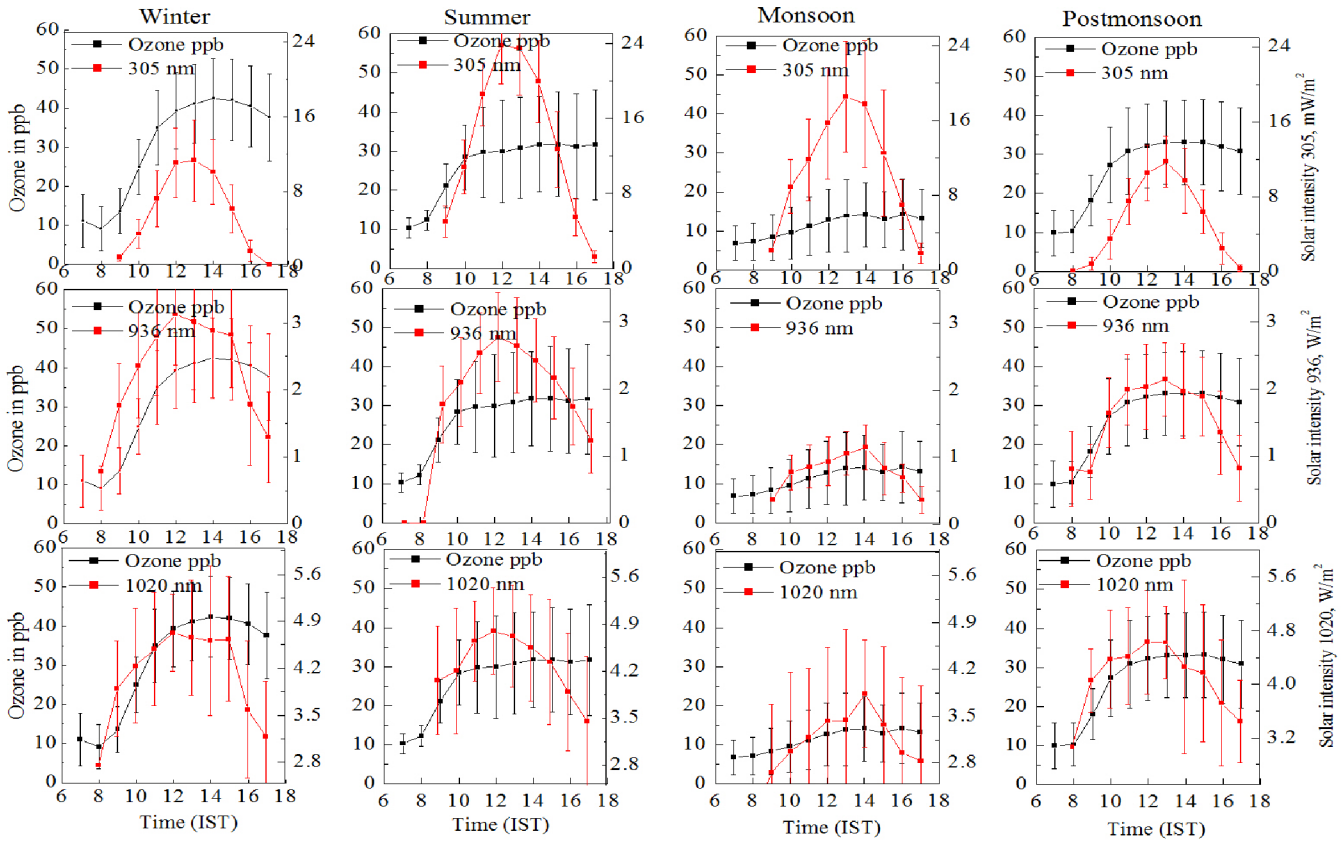


Fig. 11(b): Seasonal average hourly variation of surface ozone level with incident SW solar radiation intensity at three wave length of 305nm, 930nm and 1020nm for only sun light hours period.

The above findings are also furthermore validated from the individual SW solar radiation measurement at 305nm, 936nm and 1020 nm using by factory calibrated MICROTOPS-II Sun photometer and ground level ozone measurement. In this context, mean hourly variations of SW sun radiation intensities at above three specified wavelengths along with ground level ozone with function of day hours are plotted for each season separately. It is found that hourly ozone also shows the similar pattern to as observed hourly variation of SW intensity at three wavelengths, indicating the confirmation of modulated surface ozone production and loss due to completing the photo-ionization chemical reactions as described in this report.

Table 3: Monthly Correlation O_3 Vs SW radiation and NO_2/NO

Months	O_3 Vs SW 24 Hours	O_3 Vs NO_2/NO 24 Hours	O_3Vs SW Day Hours	O_3 Vs SW Night Hours	O_3 Vs NO_2/NO Day Hours	O_3 Vs NO_2/NO Night Hours
Dec	R=0.91, P=0	R= 0.12, P=0.55	R=0.84, P=0	R=0.2, P=0.51	R=0.03, P=0.9	R=0.2, P=0.52
Jan	R=0.88, P= 0	R=-0.13, P= 0.5	R=0.78, P=0.002	R=0.4, P=0.13	R= - 0.02, P=0.93	R= 0.38, P=0.21
Feb	R=0.85, P= 0	R=-0.27, P= 0.19	R=0.77, P=0.003	R=0.84, P=0	R= 0.12, P=0.69	R= 0.03, P=0.92
Mar	R=0.87, P= 0	R= 0.03, P= 0.87	R=0.78, P=0.002	R=0.73, P=0.006	R= 0.59, P=0.04	R= 0.86, P=0
Apr	R=0.81, P=0	R=0.12, P= 0.56	R=0.78, P=0.002	R=0.78, P=0.002	R= 0.49, P=0.09	R= 0.25, P=0.42
May	R=0.71, P= 0	R= 0.27, P= 0.20	R=0.60, P=0.03	R=0.62, P=0.02	R= 0.82, P=0.001	R= 0.15, P=0.62
Jun	R=0.70, P= 0	R=-0.20, P= 0.34	R=0.61, P=0.03	R=0.77, P=0.003	R=0.72, P=0.007	R= 0.30, P=0.33
Jul	R=0.31, P= 0.13	R=0.15, P= 0.47	R=0.55, P=0.05	R=0.34, P=0.27	R= 0.36, P=0.24	R= 0.36, P=0.24
Aug	R=0.66, P= 0	R= 0.06, P= 0.77	R=0.72, P=0.007	R=0.63, P=0.02	R= 0.52, P=0.08	R= 0.78, P=0.002
Sep	R=0.86, P= 0	R=-0.58, P=0.002	R=0.75, P=0.004	R=0.81, P=0.001	R= 0.13, P=0.68	R=-0.22, P=0.47
Oct	R=0.86, P= 0	R= 0.12, P=0.55	R=0.72, P=0.007	R=-0.22, P=0.48	R=- 0.06, P=0.85	R= 0.21, P=0.5
Nov	R=0.87, P= 0	R= 0.54, P=0.006	R=0.74, P=0.005	R=-0.17, P=0.58	R= 0.46, P=0.13	R= 0.27, P=0.38

iv). Study of short term perturbation in various gases and material pollutants during major firework festival event i,e., Diwali :-

Influences of local and regional scale source emission activities on several air pollutants levels i.e., Surface ozone (O_3), Nitrogen Oxides (NO_X), Carbon monoxide (CO), Particulate matters of size less than 2.5 μm ($PM_{2.5}$), during fireworks display activity, have been described from their diurnal variation and day to day averaged level fluctuations during pre, post-Diwali and on Diwali festival period, i.e., from 27th Oct to 13th Nov, 2010 over a western tropical semi-arid location of Udaipur over India. Besides this, the altering in types of air pollutant emission source materials in various types of fire work episode take place in such specific Diwali festival, as prime anthropogenic event, has been described first time by adopting the standard criteria based on the magnitudes of the identification parameters namely, angstrom absorption coefficient of Black Carbon (BC) (α_{abs}) and CO/NOx.

On the basis of their both day as well as night hours temporal evolution analysis of the atmospheric pollution loadings as well as their relative change in air pollutant source identification variables concerning to a large scale induced firework emission episode take place around festival and non-festival period, the following main salient interesting facts are emerged (i) a significant enhancement by three to four time folds in the average daily $PM_{2.5}$ levels is unusually observed especially in the Diwali event, when compared to their respective normal days values. On Diwali festival, an unusual change in 24 hourly average $PM_{2.5}$ concentration registered as high as values at their peak level of 165 μg m^{-3}, i.e., exceeding by four time values above from the healthy NAAQSL of $PM_{2.5}$, as seen in Fig 12.

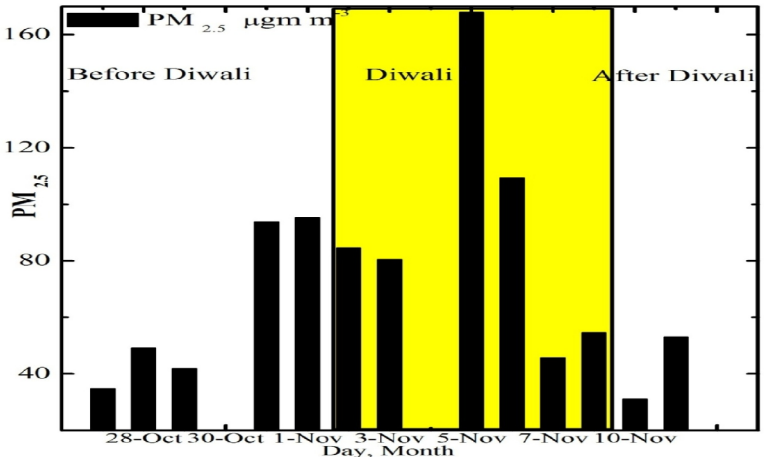
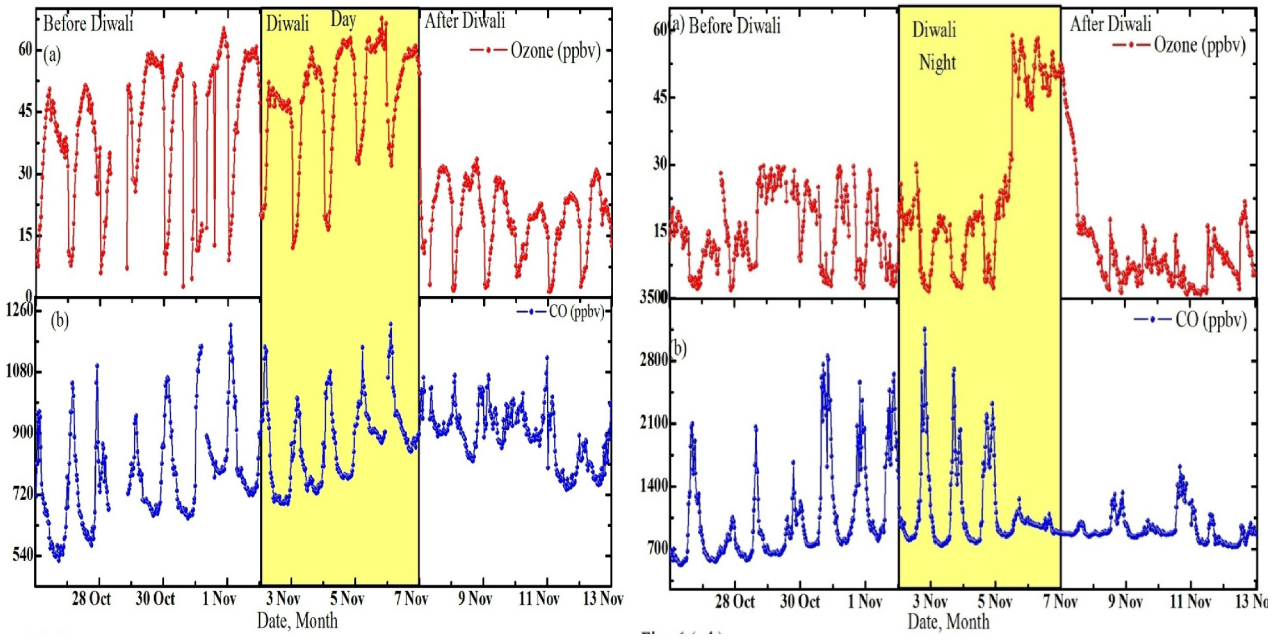


Fig 12.: Day to day changes in 24 hourly average PM $_{2.5}$ levels from pre-Diwali to post-Diwali through main festival days.

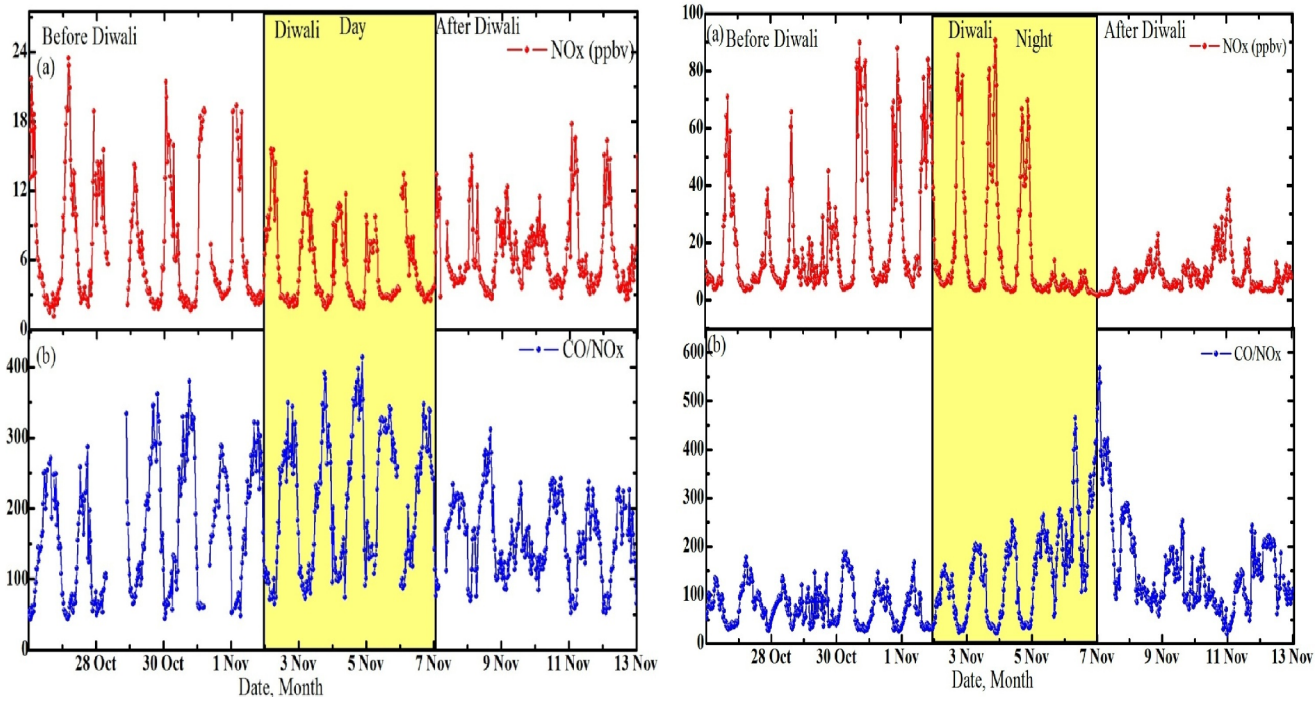
(ii) On the whole, during after sunset to pre mid-night hours of matching the peak interval with the main Diwali celebration event of fireworks and light display activities, the ground level of average fifteen

minute interval values of NOx, CO and O_3 along with the source emission identification parameters, i.e., α_{abs} and ratio of CO to NOx values illustrated an appreciable amount of enhancement by 1.5 to 3 times above relative to those of their normal day level in the same duration. It obviously gives an indication about the variation in origin as well as changes in the types of anthropogenic source strength, as a direct manifestation of an extra anthropogenic pollutants emission effect takes place by a widespread burning of crackers, sparklers and other firework activities, etc., in Diwali celebration. But, their prevailed maximum amount of air pollutants gas species and materials do not reach to go beyond above from the prescribed limit of NAAQSL values, (iii) unlike to this, during sunlight hours, the elevated level of fifteen hourly averaged O_3 value is also registered as high as the peaked value of 67.5ppbv in Diwali eve period only, which is greater than double value in comparison to their observed values on the similar interval on non-festival days, (iv) the relative remarkable altering in rising of air pollutants loading levels deviation from their reference level by more than 150 % on celebration event are more visible, which is expected to be more prominent in the night hours Diwali festival celebration period relative to their corresponding day hour levels. These results, therefore, confirmed the argument about the unusual degradation of the ambient air quality condition noticed, especially on night festival event in reference to their prevailed clear earth's environmental circumstance in post-Diwali period, as depicted in Fig 13 and 14.



Figs. 13 (a-b): Temporal day hours and nighttime hourly variations of surface ozone and carbon monoxide measured on before Diwali, Diwali and after Diwali festival dates.

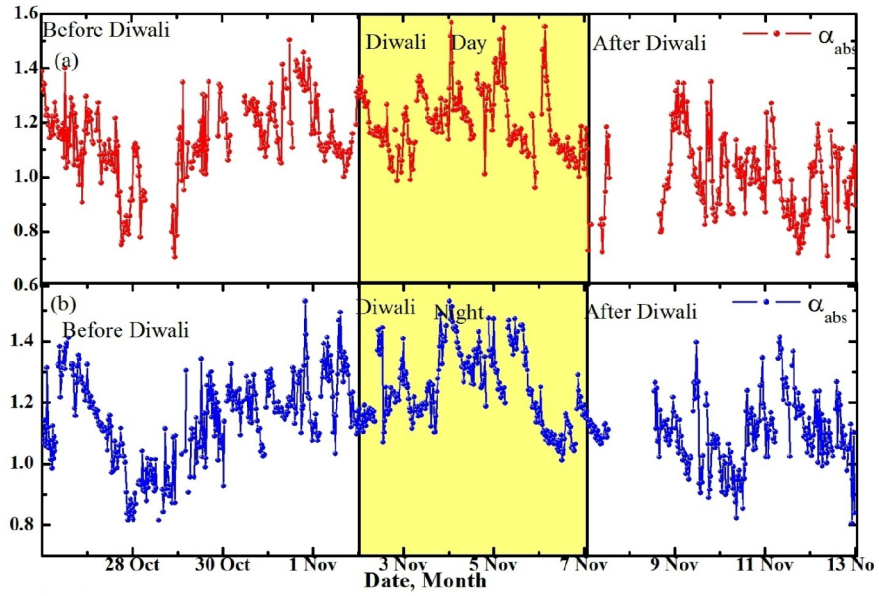
(v) This study furthermore demonstrated a close consistent in nature, except that, there discrepancies are seen in their amplitude levels when compared to the other similar investigations reported on Diwali festival over other major Indian air polluted cities.



Figs. 14 (a-b): Temporal day hours and nighttime hourly variations in NOx and CO/NOx measured on before Diwali, Diwali and after Diwali festival dates.

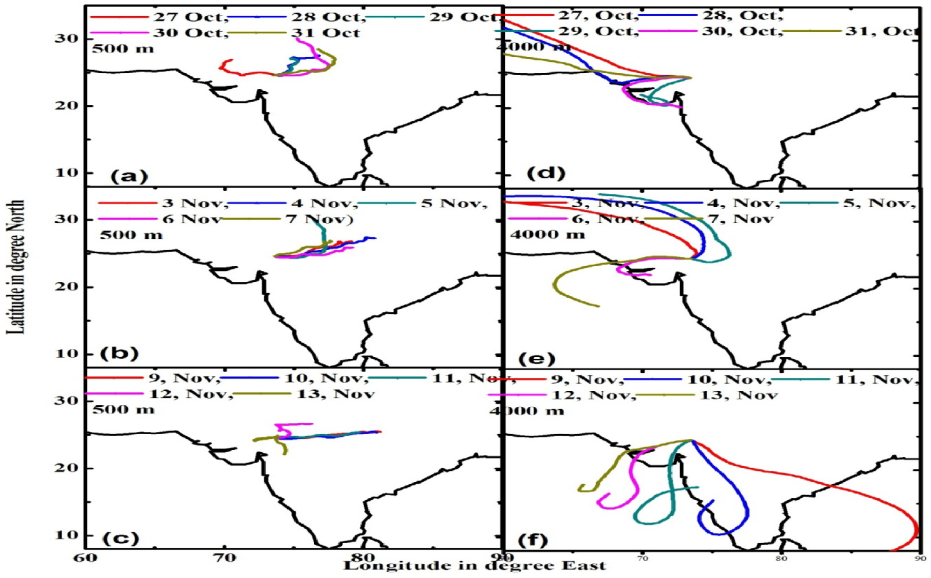
Although, monitoring of firework induced impacts on atmospheric air pollutants deterioration level over other major urban polluted cities are found to be enhanced abnormally exceeding by three to five time greater than their respective normal days levels, when compared to observed a lower change in air pollutant level by its doubles magnitude only, from their normal day levels at the measuring site.

(v)A wide temporal variations in air pollutant source discrimination parameter values, such as α_{abs} and CO/NOx segregated based on above 1.1 and 150, respectively, have given an evidence and clear insight in changing the potential origin of air pollutant source emission of burning materials types in the night and day-time festival celebration. The majority observed α_{abs} values above 1.1 and CO /NOx exceeding of 150 gave an explicit confirmation and support of predominant nature of production of atmospheric pollutants due to bio-mass and bio-fuel activity emission activity in Diwali episode relative to non-festival period, while in non festival period, their calculated values are found to be lower than above the prescribed limit magnitude and, therefore, present the scientific verification of the predominance nature of the burning of fossil fuel ignition materials.(Figs 14 & 15).



Figs. 15 **(a-b):** Temporal day and nighttime hourly variations in α_{abs} calculated on before Diwali, Diwali and after Diwali festival dates.

(vi)During the festival and non-festival episode, the impact of atmospheric pollutants outflow and long range transportation of the these key pollutants loadings as regional scale emission contribution have been discussed in light of altering in the nature of travelled source path areas and duration of backward air mass wind trajectories originating from varieties of air pollutants sources regions before reaching to measurement location at two advection level heights as an estimation of regional air pollutant emission contributed factor as seen in Fig. 16.



Figs.16 (a-f): Air Mass Backward Trajectories using NOAA Hysplit Model for 500m AGL and 4000m AGL observed over Udaipur on pre-Diwali, post Diwali as well as on main Diwali dates.

e). The following three objectives are also completed (i) the general morphology based on satellite derived total tropospheric, nitrogen oxide and carbon monoxide column content and their annual, seasonal and inter-annual monthly averaged value variations over eleven cities of Rajasthan state. (ii) Assessment of seasonal and monthly scale of Ambient Air Quality based parameters derived from the ground level ozone, NOx and CO measurement in view of human and plant and vegetation health system aspect. (iii) Multi-year behavior of total ozone column content over western tropical site i.e., Udaipur.

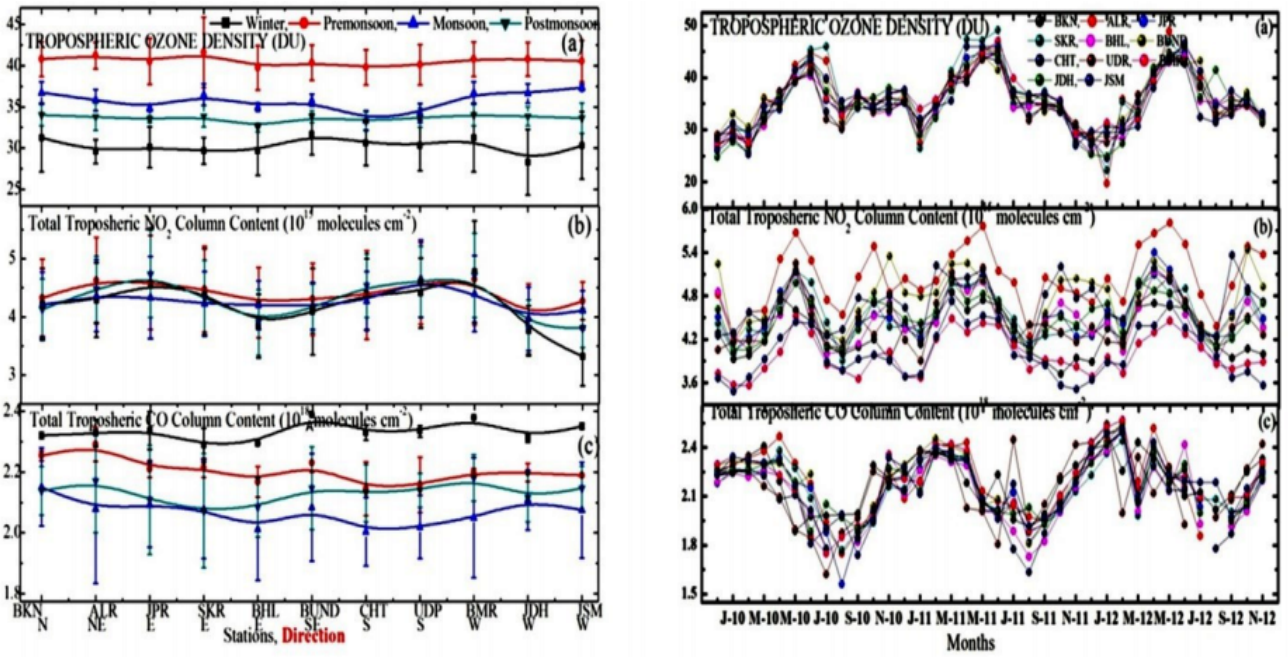
e(i) Tropospheric Ozone

The combined annual monthly mean tropspheric ozone values vary between from their minimum value of 34.7±4.6 DU at CHT (semi-urban site) and maximum value of 36.8±6.1 DU at BKN and BMR (Desert arid and rural site) with their annual monthly mean value of 35.62±5.4 DU for the complete observation period. Seasonal tropospheric ozone patterns have also displayed the definite and distinct seasonal dependence with observing the highest range from 39.7±2.7 DU to 41.7±4.3 DU in pre-monsoon, followed by their slightly lower values range of 33.3±1.15 to 37.3 DU in monsoon, lower range of 32.5±0.52 DU to 34.02±1.29 DU in post-monsoon and their lowest range of 28.2±4.0 DU to 31.6±2.5 DU in winter. Thus, maximum monthly values have been also observed in pre-monsoon, followed by their lower values in monsoon, post-monsoon months and their minimum values in winter months. Such typical annual monthly cyclic pattern has been observed over all the selected years with marginally different in their annual monthly amplitude variability.

e (ii) Tropospheric Carbon monoxide

Over the Rajasthan region, the all annual mean total troposheric CO column content values spread from their lowest value of $2.17x10^{18} \pm 1.55x10^{17}$ molecules/cm^2 at JSM (rural desert arid site) and their highest value of $2.26x10^{18} \pm 1.37x10^{17}$ molecules/cm^2 at ALR (semi-urban industrial site) with their annual mean value of $2.21\times10^{18} \pm 3.49\times10^{16}$ molecules/ cm^{-2} for the whole data set of Total Troposheric CO column content. seasonal total troposheric CO column content patterns have displayed the definite seasonal characteristics with observing the highest range from $2.29\times10^{18} \pm 2.27 \times10^{15}$ molecules/cm^2 to $2.38\times10^{18} \pm 1.05\times10^{18}$ molecules/cm^2 in winter, followed by their mid way range of $2.14\times10^{18} \pm 8.8\times10^{16}$ to $2.29\times10^{18} \pm 5.48\times10^{18}$ molecules/cm^{-2} in pre-monsoon, lower range of $2.07\times10^{18} \pm 1.88\times10^{17}$ to $2.18\times10^{18} \pm 7.6\times10^{18}$ molecules/cm^2 in post-monsoon and their lowest range of $2.00\times10^{18} \pm 1.11\times10^{17}$ molecules/cm^2 to $2.15 \times10^{18} \pm 1.28\times10^{17}$ molecules/cm^2 in monsoon. Hence, annual monthly cycle

exhibits a consistence seasonal feature with their observed peak value during pre-monsoon months and their dip level in monsoon months with their marginally variability with respect to their location. This same seasonal feature repeats year to next year also.



e(iii) ***Tropospheric Nitrogen Oxide***

The annual averaged total tropospheric NO_2 column content values change from their minimum value of $3.88\times10^{15}\pm 5.24\times10^{14}$ molecules/cm^2 at JDH (Desert semi-urban site) and its maximum value of $4.62\times10^{15}\pm 7.64\times10^{14}$ molecules/cm^2 at BMR (Desert semi-rural hot climate site) with an annual mean value of $4.29\times10^{15}\pm2.54\times10^{14}$ molecules/cm^2. The total tropospheric NO_2 column content patterns have displayed the definite seasonal dependence in the course of this study. Their seasonal variation in their ranges have been systematically declined and obeyed the following order i.e., winter>post-monsoon>pre-monsoon>monsoon seasons. Their seasonal range values have been noticed to maximized over two close site i.e., from $3.31\times10^{15}\pm 5.04\times10^{14}$ molecules/cm^2 at JSM to $4.77\times10^{15}\pm 8.71\times10^{14}$ molecules/cm^2 at BMR in winter, followed by their intermediate range between $3.80\times10^{15}\pm 3.34\times10^{14}$ at JSM (desert rural site) to $4.74\times10^{15}\pm 7.51\times10^{14}$ molecules/ cm^2 at JPR (urban and capital city) in post-monsoon, $3.96\times10^{15}\pm6.03\times10^{14}$ molecules/cm^{-2} at JDH to $4.64\times10^{15}\pm 7.85\times10^{14}$ molecules/cm^{-2} at BMR in pre-monsoon and their minimum range of $3.96\times10^{15}\pm5.48\times10^{14}$ at JSM to $4.65\times10^{15}\pm6.65\times10^{14}$ molecules/cm^2 at UDP in monsoon. Therefore, it also exhibits almost similar monthly cyclic pattern with their maxima in winter months and minima in monsoon months with their slight variability with their locations.

More details of further results have been discussed in the published paper which is attached.

e(iv) Assessment of Air Quality level from various computed AOI at Udaipur

The AQI (Air Quality Index) of ozone (ozone, 8 hr. avg.), Carbon monoxide (CO, 8 hr. avg.) and Nitrogen dioxide (NO_2, 24hr. avg.) depicted the mean mixing ratio of ozone were observed that in the year 2012-13 the mixing ratio of ozone varies between maximum 96.6 ppbv to minimum 1 ppbv, in 2013-14 it was found between 54.6 ppbv to 1 ppbv, in 2014-15 it was found in the range of 57.9 ppbv maximum and 1 ppbv minimum, with average concentrations of 25.5 ppbv, 25.9 ppbv, and 25.7 ppbv respectively, indicating similar concentrations in all year. Therefore, it could be seen very little higher mean mixing ratio of O_3 during 2013-14 as compared to other years due to higher levels of precursor's gases, rapidly urbanization, and transportation. During 2012, 2013, 2014, it has been observed that the level of Ozone exceeds the National Ambient Air Quality Standard (NAAQS) of 50 ppbv during arious periods of the year. On an average it has been found that the average concentration of ozone was more or less similar during 2012 to 2015 and there is no increasing or decreasing trend observed. The detailed analysis showed that in Udaipur there is no associated health risk related to CO and NO_2 levels, during 2012-2013 to 2013-2014, it has been found in Good range of AQI, whereas, there is a little health risk linked with surface ozone mixing ratios during some days of the year specifically in the months of March, April, May, November and December, when its concentration found in Moderate range indicating no health risk for healthy persons but little to moderate health risk for sensitive group of people including persons already having respiratory or cardiovascular diseases, children's having maximum outdoors and adults with depressed immunity. During other months of the year ozone mixing ratios were detected in Good range suggesting no related health risk.

e(v) ***Multiyear behavior of Total Ozone Column Content over measuring site***

This study focuses on multi-year change in Total Ozone Content (TOC) values measured simultaneously by ground based instrument, i.e., MICROTOPS-II sun photometer and space based TOMS satellite experiment during the last decade, i.e., the period from 2002 to 2009 in the outskirts of the semi-arid and semi-urban tropical region of Udaipur (24.6˚N, 73.7˚E; 580 m asl), India.

The negative declining trend in TOC value has been detected about 2 DU/decade by using Linear Regression Analysis (LRA) of the monthly averaged TOC levels. The LRA presents the best statistically significant percentage level (p) of greater than 99%. From the comparison of present result with the observations reported over mid, high and polar latitude sites, long-term TOC variability from tropical site is found to be the lowest, followed by their intermediate range from 10 to 30 DU/ decade over mid

latitude sites and the highest range from 30 to 50 DU/decade over high to polar latitude. In order to establish the possible linking of reduction in TOC level per decade with other stratospheric dynamic parameters and atmospheric UV aerosols parameter, inter-annual change in average monthly TOC level has shown a strong correlation coefficient (r) of the order of 0.73 (p>99.9990) with the stratospheric temperature, followed by its observed lower r value of 0.25 (p = 99%) for stratospheric zonal wind and then a significant correlation (r = 0.17; p = 95%) for AI 300 nm (Aerosols Index 300 nm) parameter. The variation of monthly mean meridional wind component does not illustrate a statistically significant correlation (r = 0.13; p<80%) with their respective multi-year change in mean monthly TOC values. The consequence of such reduction of TOC per decade may be identified as the result of expected enhancement in incident ground UV-radiation level. At the same time, the harmful influence of increasing the UV level seems to be counteracted and reduced with the evidence of observed higher level of AI at 300 nm as high as 3 in the summer months over selected tropical environmental site.
More detail about important findings are discussed in published which is attached with this report.

13. ACHIEVEMENTS FROM THE PROJECT : **Presentations of following research papers:**

(i) **Papers is presented** in 18th National Space Science Symposium- 2014 (NSSS-2014), held at Dibrugarh University, Dibrugarh from 29th Jan., to 1st February, 2014, paper entitled "*Surface ozone its prominent precursors gases and its behavior with BC aerosols in western Indian region i.e., Udaipur"* as PS-1 (52) for Poster presentation.

(ii) **Paper is presented** in 18th National Space Science Symposium- 2014 (NSSS-2014), held at Dibrugarh University, Dibrugarh from 29th Jan., to 1st February, 2014, paper entitled "Multiyear behavior of Fine Particulates Matter, Black Carbon Aerosols Mass Concentration and its Percentage of Mass Concentration Fraction over Udaipur" as PS-1 (50) for Poster presentation.

(iii) Invited review talk on "*Interaction of UV to IR solar radiation among the air pollutants with special emphasis on atmosphere radiative forcing" is presented in* **National Symposium on Emerging Trends in Physics for Ionizing Radiations, Aerosols and Material Science (ETPRAM-13)** held at Department of Physics, Punjabi University, Patiala from 13 and 14th December, 2013.(IT-08).

Published papers:

(i) Abhishek Saxena & **B.M. Vyas**, (2016), "Total Ozone Content Trend During the Last decade over Western Indian Tropical Station i.e., Udaipur", *American J Climate Change,* **5(2),**193-201.

(ii) **B. M. Vyas,** Abhishek Saxena, and M. S. Shekhawat; "Behavior of total tropospheric ozone, nitrogen oxide and carbon monoxide column over western Indian region by exploring space based satellite observations" *AIP Conference Proceedings* 1953, 140078 (2018); doi: 10.1063/1.5033253.

13. SUMMARY OF THE FINDINGS (IN 500 WORDS) : Atmospheric air pollutant levels, such as, surface ozone with its prominent precursors NOx, CO and BC aerosols concentration are not only adversely influenced to human health, natural environmental eco-system, atmospheric visibility, earth- climate changing by local anthropogenic activities which are observed over the surrounding location of sampling side. The influence of reverse character of local weather parameters on these traces gaseous pollutants also showed that low wind speed and low relative humidity and deepen boundary layer height also favour to enhancement in the above atmospheric air pollution levels at the sampling site. In addition to this, air pollutants emission activities occurred over far ways from the observing site, such as over IGP region belt are also influenced to air pollutant levels at the sampling site of clean environmental through the favourable mechanism of long range transportation of air pollutants. The contribution of regional source of air pollutant level is investigated and demonstrated from variation in their direction of mean monthly backward air mass trajectories and its area concerned. The various measured atmospheric pollutants are seen with higher loading in winter and lower air pollutant burden in monsoon months.

Study also focuses on multi-year change in Total Ozone Content (TOC) values measured simultaneously by ground based instrument, i.e., MICROTOPS-II sun photometer and space based TOMS satellite experiment during the last decade, i.e., the period from 2002 to 2009 over Udaipur (24.6˚N, 74˚E; 580 m asl), India. The negative declining trend in TOC value has been detected about 2 DU/decade by using Linear Regression Analysis (LRA) of the monthly averaged TOC levels. The LRA presents the best statistically significant percentage level (p) of greater than 99%. From the comparison of present result with the observations reported over mid, high and polar latitude sites, long-term TOC variability from tropical site is found to be the

lowest, followed by their intermediate range from 10 to 30 DU/decade over mid latitude sites and the highest range from 30 to 50 DU/decade over high to polar latitude. In order to establish the possible linking of reduction in TOC level per decade with other stratospheric dynamic parameters and atmospheric UV aerosols parameter, inter-annual change in average monthly TOC level has shown a strong correlation coefficient (r) of the order of 0.73 ($p > 99.9990$) with the stratospheric temperature, followed by its observed lower r value of 0.25 ($p = 99\%$) for stratospheric zonal wind and then a significant correlation ($r = 0.17$; $p = 95\%$) for AI 300 nm (Aerosols Index 300 nm) parameter. The variation of monthly mean meridional wind component does not illustrate a statistically significant correlation ($r = 0.13$; $p < 80\%$) with their respective multi-year change in mean monthly TOC values. The consequence of such reduction of TOC per decade may be identified as the result of expected enhancement in incident ground UV-radiation level. At the same time, the harmful influence of increasing the UV level seems to be counteracted and reduced with the evidence of observed higher level of AI at 300 nm as high as 3 in the summer months over selected tropical environmental site.

Monthly, seasonal and annual variation of major atmospheric pollutant levels, such as Total Tropospheric Ozone (TO), Total NO_2 columnar content (TNO_2) and Total CO columnar content (TCO) have been presented first time for eleven district sites of Rajasthan state located in the western tropical Indian region.

14. CONTRIBUTION TO THE SOCIETY (GIVE DETAILS): Since this research project is directly concerned with investigation of primary and secondary atmospheric ambient air pollutants level over semi-urban and semi-tropical arid station. The seasonal trend of secondary air pollutants such as ground level ozone concentration level over Udaipur is found to be higher than exceeding level of standard ozone 40 ppbv, which is really harmful for good agricultural activity condition level specifically in winter and pre-monsoon, The air quality degradation level at measuring site follows the following decreasing trend: winter> pre-monsoon>post-monsoon> monsoon. It is very interesting to note at here that even then prevailing cool and dry weather conditions in the winter months of lesser photochemical reaction activity, monthly and its diurnal behavior of ozone showed the excessive ozone loading in the winter period relative to their observed variation in pre-monsoon or summer months. The cause of enhancement in secondary and primary air pollutant levels are also identified on the basis of regional scale anthropogenic air pollutant activities occurring far away location, such as highly polluted, densely populated

and rapidly industrialized urban city centers near by surrounding the monitoring site. The monthly diurnal behavior of secondary air pollutant i.e., ozone showed one major peak around noon hours and a broad dip around late evening to early morning hours. In contrary to this, monthly and seasonal variation of NOx, CO and BC as primary air pollutants display two maxima, first primary peak at late evening hours and morning hours of concerning heavy traffic and human made activity period, whereas, two minima are seen around noon hours and late midnight to early morning hours. In view of the different shape of their diurnal curves, one can conclude that there is different source mechanisms of primary air pollutants relative to secondary air pollutants concentration which are quite clear from the reverse and different nature of diurnal curves of primary and secondary pollutants.

The diurnal peak values of primary and secondary pollutant level also exhibit a distinct seasonal dependence with their maximum value in winter, followed by post-monsoon, minimum values in hot and dry season with their least value in rainy season. An identification of the inverse character of weather parameters on atmospheric air pollutant level is also observed through the interdependence of surface meteorological parameters as a local scale influence level with all types of air pollutants. The impact of regional air pollution activity on various monthly air pollutant levels at observing location are also conducted through the backward air mass trajectories at 500m, 1500 m and 4000m level at the sampling side which are developed by HYsplit model. It is clearly evident that monthly mean air pollutant level vary in accordance of turning with monthly most probable air mass flow pattern.

The consequence of reduction of TOC per decade over Udaipur may be identified as the result of expected enhancement in incident ground UV-radiation level. At the same time, the harmful influence of increasing the UV level seems to be counteracted and reduced with the evidence of observed higher level of UV aerosol index AI at 300 nm as high as 3 in the summer months over selected tropical environmental site.

Monthly, seasonal and annual variation of major atmospheric pollutant levels, such as Total Tropospheric Ozone (TO), Total NO_2 columnar content (TNO_2) and Total CO columnar content (TCO) have been presented first time for eleven district sites of Rajasthan state located in the western tropical Indian region. The study is based on collection of above air pollutant data retrieved from space based satellite measurements by exploring OMI and MOPITT data for a three year period from Jan 2009 to December 2012. A clear, distinct seasonal dependence in TO, TCO and TNO_2 column content values have been noticed all over selected measuring locations. The maximum

average seasonal TO is observed in pre-monsoon and their minimum value in the monsoon months. However, in TCO and TNO_2 case, the highest TCO and TNO_2 level is seen rather in the winter and their respective lowest value in monsoon season. Thus, their seasonal variability of TNO_2 and TCO in their ranges have been systematically found to be reduced and obeyed the following descending order, ,i.e., winter> post-monsoon> pre-monsoon> monsoon seasons. As far as concerned with their annual values, the observed values of all considered atmospheric pollutants are almost found in the same levels with slight discrepancies over their lower air pollutant levels recorded in hot, arid, rural as compared to the prevailing elevated value at other Indian urban regions.

15. WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT: No

16. NUMBER OF PUBLICATIONS OUT OF THE PROJECT: Two papers are published.

(i) Abhishek Saxena & **B.M. Vyas**, (2016), "Total Ozone Content Trend During the Last decade over Western Indian Tropical Station i.e., Udaipur", *American J Climate Change*, **5(2),**193-201.

(ii) **B. M. Vyas,** Abhishek Saxena, and M. S. Shekhawat; "Behavior of total tropospheric ozone, nitrogen oxide and carbon monoxide column over western Indian region by exploring space based satellite observations" *AIP Conference Proceedings* 1953, 140078 (2018); doi: 10.1063/1.5033253.

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Annexure – X

UNIVERSITY GRANTS COMMISSION
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ASSESSMENT & EVALAUTION CERTIFICATE

It is certified that the research project entitled" "Study of Surface Ozone and its prominent precursors over semi-urban tropical region i.e., Udaipur" sanctioned to Dr B M. Vyas. Deptt. of Physics has been assessed and evaluated by the committee consisting of the following members:

Report and Details of Expert Committee:

The Report of Committee is as follows:

The Committee evaluated the academic progress made under the project and found it satisfactory.

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(2) (Prof A K Nagwat, External Member)
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3.8.2018

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American Journal of Climate Change, 2016, 5, 193-201
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Total Ozone Content Trend during the Last Decade over Western Indian Tropical Station *i.e.* Udaipur

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Abstract

This study focuses on multi-year change in Total Ozone Content (TOC) values measured simultaneously by ground based instrument, *i.e.*, MICROTOPS-II sun photometer and space based TOMS satellite experiment during the last decade, *i.e.*, the period from 2002 to 2009 in the outskirts of the semi-arid and semi-urban tropical region of Udaipur (24.6˚N, 74˚E; 580 m asl), India. The negative declining trend in TOC value has been detected about 2 DU/decade by using Linear Regression Analysis (LRA) of the monthly averaged TOC levels. The LRA presents the best statistically significant percentage level (p) of greater than 99%. From the comparison of present result with the observations reported over mid, high and polar latitude sites, long-term TOC variability from tropical site is found to be the lowest, followed by their intermediate range from 10 to 30 DU/decade over mid latitude sites and the highest range from 30 to 50 DU/decade over high to polar latitude. In order to establish the possible linking of reduction in TOC level per decade with other stratospheric dynamic parameters and atmospheric UV aerosols parameter, inter-annual change in average monthly TOC level has shown a strong correlation coefficient (r) of the order of 0.73 (p > 99.9990) with the stratospheric temperature, followed by its observed lower r value of 0.25 (p = 99%) for stratospheric zonal wind and then a significant correlation (r = 0.17; p = 95%) for AI 300 nm (Aerosols Index 300 nm) parameter. The variation of monthly mean meridional wind component does not illustrate a statistically significant correlation (r = 0.13; p < 80%) with their respective multi-year change in mean monthly TOC values. The consequence of such reduction of TOC per decade may be identified as the result of expected enhancement in incident ground UV-radiation level. At the same time, the harmful influence of increasing the UV level seems to be counteracted and reduced with the evidence of observed higher level of AI at 300 nm as high as 3 in the summer months over selected tropical environmental site.

Keywords

Total Ozone Content, AI 300 nm, Stratospheric Parameters, Tropical Latitude

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1. Introduction

Atmospheric ozone is one of the leading minor Earth chemical constituents as well as positive Earth's atmospheric radiative forcing active species [1] [2]. It absorbs completely solar ultraviolet (UV-A) radiation below 280 nm and partially attenuates UV-B (Ultra-Violet-Biological Radiation) solar radiation between 290 - 320 nm along with absorbing the on-going reflected terrestrial Infrared (IR) radiation, *i.e.*, perturbs the radiative energy balance of the upper troposphere and lower stratosphere [3]. Therefore, the stratospheric ozone generated through photochemical processes provides a protective layer shielding to the Earth environment against the attenuation of harmful solar UV-B radiation in stratospheric height from 15 to 40 Km and saves the public health as well as an eco-vegetations of the surrounding region around observing location. It, further, influences the atmospheric stability of thermal structure, *i.e.*, cooling and warming effect in accordance with depletion and enhancement of TOC [4]-[7]. At the same time, ozone available over the Earth's surface to 10 Km (Troposphere) is produced mainly by anthropogenic activities and exhibits harmful effect on natural vegetation, air quality, human health, Earth's atmospheric climate change, etc., even their availability of small concentration in parts per billion levels [1]. As a result, atmospheric ozone, available at various altitudes from Earth's surface to troposphere and stratosphere, behaves as the dual nature like as either a bad or a good ozone, respectively [7]-[9].

Since stratospheric ozone concentrations share about more than 90% of the Total Ozone Content (TOC) amount in the Earth's atmosphere, and it shields from dangerous solar incident UV radiation to our human being life on the Earth system. It has furthermore implication to global environmental and Earth climate issue, *i.e.*, radiative forcing of climate [3] [9]. In addition to this, recent studies have also given the evidence about the consequences of the reduction of TOC in term of enhancement of ground level solar UV radiation intensities. Their findings highlighted that about 1% decrease TOC in DU (Dobson Unit, a unit of TOC) could cause about 2% increment in the UV-B radiation [10]-[15].

With views of the above importance of perturbation on ground level reaching to the net solar UV radiation irradiation intensity and their serious impact on the human health and environmental change assessment, stratospheric ozone or TOC investigations have been the cynosure for atmospheric scientists and common person's life. Thus, numerous kinds of atmospheric ozone studies were conducted in past decades to elucidate the TOC variability over the distinct geographical and environmental locations along with in special time scales ranging from solar cycle (11 years) to planetary wave scale (few days) etc. [16]-[24]. Since after motivation from the greatest scientific discovery of the present century, *i.e.*, the "Ozone Hole" over Antarctica by Farman [10], the assessment of year to year change in TOC over various parts of the world has been further motivated. Therefore, now it becomes a frontier research topic, which is seriously concerned with global environmental warming issue [17] [18] [21] [25]-[30]. In the past one decade, several investigations over various parts of the world as well as also over Indian sites, based on both ground and satellites based TOC measurements, have been reported with emphasis on investigating the long term change in TOC over tropical sites. Their investigations bring out an overall declining trend of the TOC with various variability levels as high as 30 DU/decade to a minimum level of 2 DU/decade over northern high, mid and low latitude stations [16] [17] [21] [31]-[36].

In extended to such studies in more details, large numbers of researchers have proposed hypothesis and possible causes of negative trend of the TOC on the basis of several new pathways contributing to atmospheric ozone depletion phenomena time to time. They have made an attempt to establish the inter link between long-term change in TOC with atmospheric dynamics and chemistry coupled processes parameters like emission of Ozone Depleted Substance (ODS) as chemical catalyst Chlorofluorocarbons (CFCs), etc., stratospheric temperature, stratospheric cooling, El-Nino phenomena, planetary wave activity, tropopause height, cosmic ray, thunderstorm activities [19] [28] [37]-[43].

In this context, over Indian site, the first ever observation about the reducing trend of TOC per decade was reported by Chakrabarty [5]. Subsequently, long-term trend analysis of TOC was also discussed by Indian researchers [5] [6] [21] [23] [36]. Such findings have been creating a lot of attention and interest to motivate to carry out further more in depth investigation of long-term changes in TOC along with special highlighting on their identifications of their possible causes. Most of such past studies over Indian region have been focused on the negative trend of TOC per decade with varying amount depending upon the locations. Their results have given the indication about the greater rate of annual TOC declining of 9 DU/decade over the Northern Indian zone, when compared to the central Indian region, where the annual declining trend is found of the 3 - 5 DU/decade. However, the statistically insignificant long-term TOC declining trend less than 1 DU/decade is ob-

served over the southern Indian region.

It is more worthwhile to be noticed at this stage that, in the special reference to the tropical climate region, where nearly 40% of global atmospheric ozone is generated through the photochemical reactions due to the accessibility of a large plenty of incident solar radiation over the edges of this specific tropical region. But, it is transported towards higher latitudes by atmospheric transport dynamic mechanisms (e.g. Brewer-Dobson circulation). Thus, an excessive amount of ozone accumulates at higher latitudes relative to the lower latitudes, where it is created [28].

Above and beyond this, net TOC over tropical latitudes is affected not only by the absorption of UV-B radiation, but all together it is also affected by clouds, aerosols, large-scale atmospheric transportation or stratospheric dynamics phenomena (*i.e.*, Brewer-Dobson circulation) as well as reactions to long-lived chemicals in the atmosphere acting as catalysts, such as chlorine, bromine, hydrogen, and nitrogen (chlorofluorocarbons), especially at low temperatures [2] [14] [44].

Realizing the above facts kept in mind, there are either very few or rare investigations on its identification of its possible causes of the declining TOC trend over Indian tropical zone, except by Vyas and Saraswat [23]. Thus, in order to capture the most possible causes of the ozone depletion level and their consequences on feasible enhancing of ground level reaching the dangerous solar UV-A and UV-B radiation band for human health, controlling the role of affecting the thermal structure of atmosphere etc., an attempt has been made in this paper to quantify the trend analysis of TOC variability on basis of averaged multiyear monthly TOC values over tropical station like Udaipur (24.6˚N, 74˚E; 580 m asl) along with to ascertain their inter-correlation between the declining trend of TOC with other new most relevant atmospheric parameters like Aerosols Index at 300 nm (AI 300 nm), stratospheric air temperature (AT, T˚C) at 30 mb, zonal wind velocity (V, m/s) and meridional wind velocity component (U, m/s). As such these atmospheric dynamics and UV absorption aerosol index parameters are especially considered in the course of the work in views of that tropical ozone concentration is predominantly governed through several mechanisms, *i.e.*, photochemical, chemical and atmospheric dynamic transport processes or incident ground UV radiation level, aerosols, cloud and meteorological parameters, etc. [11] [23] [24].

2. Data Analysis

The basis of the present study is comprised of daily value data set of TOC and AI300 nm collected by Total Ozone Mapping Spectrometer (TOMS) and Ozone Monitoring Instrument (OMI) on-board flown on the Earth Probe (NASA) during the period 2002 to December 2003 and the Dutch-Finnish Aura satellite during 2004 to 2009. These day to day values of TOC and AI300 nm data over Udaipur site are accessed from their websites at http://toms.gsfc.nasa.gov and http://aura.gsfc.nasa.gov. Several other concerned atmospheric parameters at stratospheric height for each monthly value have been downloaded for the similar geographical coordinate systems from NOAA website *i.e.*, http://www.ready.noaa.gov. From the available such daily values of the TOC of the complete study period, the monthly mean values are calculated for their respective months of the years. The variations in monthly mean values of TOC have been plotted with function of months depicted for the entire study period. In order to quantify the trend analysis of change in TOC and to identify their possible causes, variations of monthly mean values of other atmospheric parameters like AI300 nm, U, V wind components and AT at 30 mb over the same study period along with their corresponding monthly TOC variations are illustrated in the same figures to correlate the declining trend of the TOC with selected parameters. Furthermore, for statistical analysis of inter-annual yearly change in the TOC, the linearly fitted line has been also plotted on the basis of its statistical linear regression analysis. The statistically linearly regression fit line is illustrated along with their observed trend in the respective figures (**Figure 1(a)**, **Figure 1(b)**). The slope, correlation coefficient (in term of r) values and number of data points (N) are depicted in each respective figure, which gives the inference about multi-year TOC variable and its statistical significance relevance level, respectively (**Figure 1(a)**, **Figure 1(b)**) represent the monthly change in TOC derived from TOMS and as well as from the measurement of TOC values obtained from MICROTOPS-II Sun Photometer Ozonometer (M/s Solar Light Co. USA, Model-541) at Udaipur for selecting study years from 2002-2009. Likewise, the monthly multi-year variations in TOC measured from TOMS along with retrieved stratospheric parameters, *i.e.*, U, V, AT at 30 mb and AI 300 nm have been also displayed in **Figures 2(a)-(d)**.

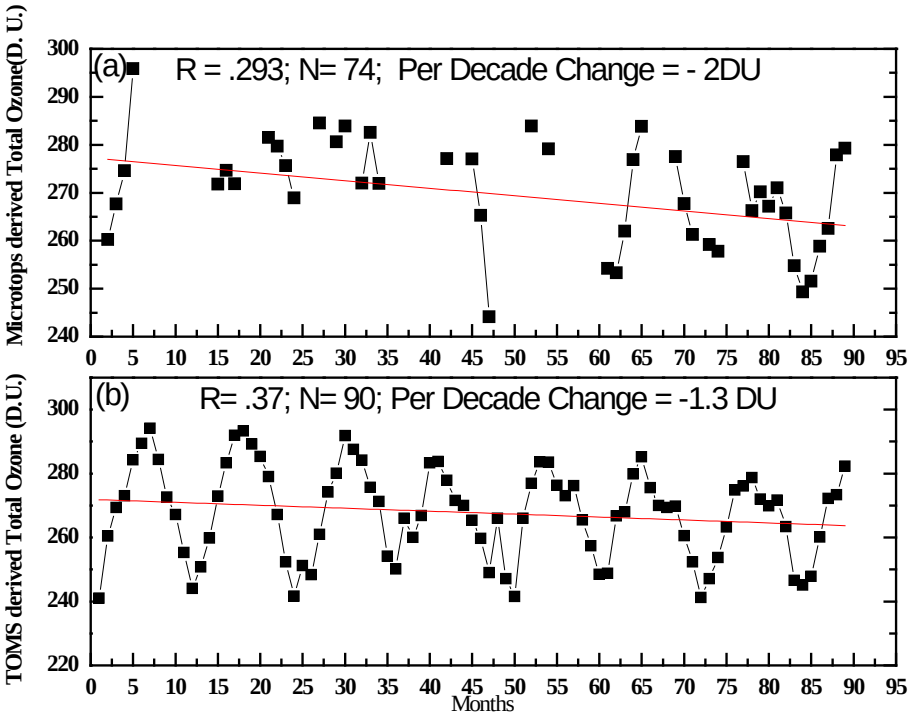

Figure 1. (a) (b) Monthly averaged variation of micro tops II derived total ozone content & TOMS derived during year from 2002 to 2009 over Udaipur.

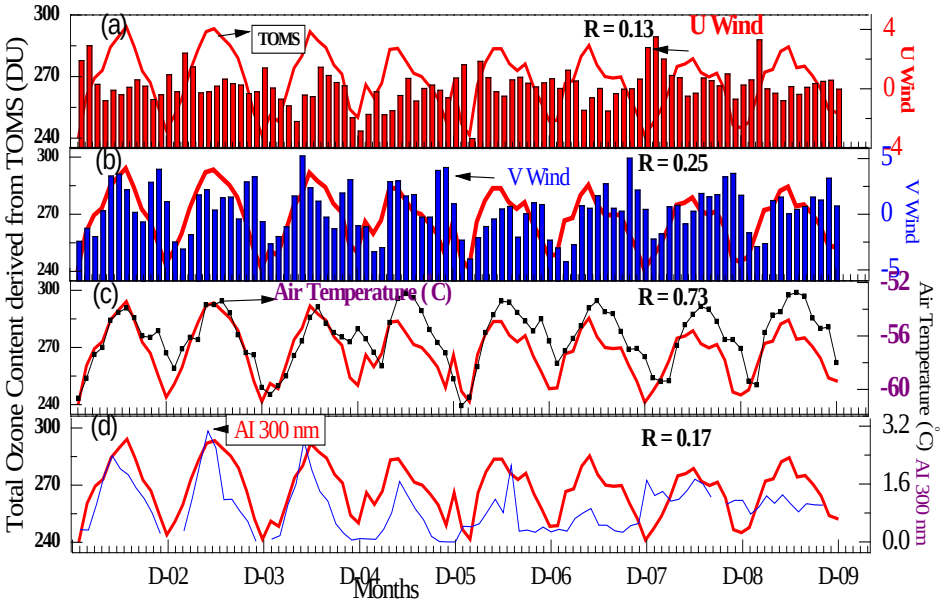

Figure 2. (a)-(d) Comparative average monthly behavior of Total Ozone Content (TOC) derived from TOMS along with merdional wind velocity (U-wind(m/sec)), (V-wind(m/sec)), Air Temperature at 30 mb & AI 300 nm during period from Jan., 2002 to Dec.,2009 over Udaipur.

3. Results

Figure 1(a) and **Figure 1(b)** represent year to year variations in averaged monthly TOC values measured from MICROTOPS-II and the satellite observations during the selected study period. It is observed from the figures that monthly TOC value is found to be highest in all the June months of each year. However, such highest

monthly TOC observed from MICROTOPS-II is showing a good systematic decreasing trend from 297 to 283 DU or 14 DU during 2002-2009. Likewise, from satellite observations, the corresponding highest monthly average TOC magnitudes are also seen in June months, which vary from 294 to 283 DU for the same observation period. Moreover, the lowest monthly TOC levels always appearing in December months, which are in a lesser range from 240 to 245 and 245 to 259 DU derived from satellite technique and MICROOPS-II, respectively. Thus, there is a distinct declining change in the highest TOC level of 14 to 11 DU in nine years, but, in case of the lowest TOC monthly levels alter from 5 to 14 DU in nine year period. From the linear regression analysis and its related estimated parameters such as slope and correlation coefficient value, it is observed as a quite statistically relevant fact that the best statistically significant declining trend in the TOC of about 2 DU/decade is estimated from Ground Based measurements *i.e.*, MICROTOPS-II Sun photometer with it a strong significance level 99% ($p < 0.01$). However, measurements of TOC from the satellite based technique, a similar appreciable variation of negative decadal change in TOC value of 1.3 DU/decade is also found along with also better significance of confidence level 99.9% ($p < 0.001$). Thus, it is imperative to say that the average monthly variation of TOC values during the observation period from ground based as well as spaced based experiment displays the decreasing behaviour in TOC magnitude in almost of the same order of about 2 DU/decade during the selected observation period over observing site.

The investigations of long-term change in TOC have been reported in the past many years by earlier researchers from the Arctic, high latitude stations [32] [45] as well as mid latitude sites [27] [31] [33] [46]. However, on the basis of their observations about the long-term change in TOC values over 13 Antarctic stations, Bojkov [26] has documented the maximum decadal change in TOC value from 35 to 50 DU/decade. Yet, Goodson (1960) has also demonstrated about the negative trend of TOC magnitude 50 DU/decade on the basis of average monthly TOC over the Arctic region. On the other hand, the ozone depletion trend is also described in range between 25 and 30 DU per decade over mid latitude stations [1] [6] [33]. The negative reducing changes in TOC are also documented in the inferior range from 3 to 10 DU/decade along with a variable rate of decreasing levels in TOC/decade over several Indian-subcontinent regions [16] [21] [22] [42]. Such depletion in ozone trend has been detected to be the highest magnitude varying from −7 to −15 DU/decade over Northern Indian region locations, at lower values from −2 to −5 DU/decade over the central Indian part and an insignificant trend about less than −1 DU/decade over the equatorial region or southern Indian site [21] [34]-[36]. Referring to the above results over varieties of distinct geographical locations and environmental conditions region, it is rather imperative to say from the previously reported results and present observations that rate of decreasing the decadal change in TOC level systematically reduces, as we shift from polar to low latitude region and furthermore toward equatorial latitude zone. However, in the present work, the estimated decadal declining trend of TOC value is reported to be the minimum of the order 2 DU per decade, which is lower than observed declining the change in TOC value of the order 7 to 15 DU per decade over other northern Indian tropical stations. However, it is comparable and consistent with the value of observing central Indian sites. Hence, the about the present reported findings concerning the order of reducing the TOC magnitude about 2 DU/decade is corroborated and matched with the earlier reported results over the central part of Indian region and lower than they observed TOC declining trend over northern Indian regions.

In order to establish possible linkage of present lower declining long term TOC trends along with the similar variation of monthly mean wind components, *i.e.*, U, V and AT at 30 mb, AI 300 nm, the average monthly behaviour of TOC are also illustrated by different color lines along with the average monthly variations in U, V, AT at 30mb and AI300 nm for the entire experimental period for similar geographical location in **Figures 2(a)-(d)**. From the close look to **Figure 2(a)**, it is noticed that meridional wind is mainly weak, *i.e.*, less than ±4 m/s, in general the northward meridional wind coincides with the occurrence of a lower TOC value. Unlike to this, the peak TOC value may be noticed during observing southward meridional wind. Nevertheless, on the basis of statistical analysis inferences, a very poor correlation coefficient value (0.13) with insignificant statistical level is seen in the case of the correlation of the TOC with U. This month to month change in TOC magnitudes didn't show any much dependence with the U.

The year to year variation of monthly average TOC level along with their mean monthly zonal wind velocity component is depicted in **Figure 2(b)**. The zonal wind is primarily found westward in the winter month with the concurrence of observing lower TOC values and, then it turns systematically from westward to eastward during April to November of yielding with their higher TOC level. Therefore, zonal wind shows close resemblance with the average monthly TOC parameter (**Figure 2(b)**). It is interesting to be noticed from the first look to plots

that the average TOC magnitudes and zonal wind speed both change in accordance with almost in their same phase. The lowest TOC values correspond to prevailing higher westward wind component, in contrary to this, the higher TOC values are seen in June month, when the zonal wind remains mainly toward east. Hence, the monthly TOC amount increases in accordance with the decreasing of westward or increasing eastward wind speed or vice versa. On the basis of computing statistical parameters, such as r and p, the good statistical correlation coefficient value of 0.25 with the percentage of significance level above 95% is noted between the their TOC and zonal wind component, which further support the confirmation the positive relation with their observed monthly TOC and the zonal wind velocity.

Figure 2(c) gives the comparative views of observed monthly average TOC values vary with their respective stratospheric atmospheric temperature (AT at 30 mb) for the entire selected study period. The monthly behaviour of TOC is seen to be varied exactly in similar fashion with their month to month change in the AT. The mean monthly TOC and AT values both increases in the same phase after attaining their minimum values of about 241 DU and −61˚C in January. After that their values showed to begin their growing level and, attained their peak values about 297 DU and −53˚C in June month. Subsequently, their levels go down onward July to attain their original values around 241 DU and −61˚C in December. It is more worthwhile to be noticed at this junction that the monthly values of AT at 30 mb are also found to be the highest in June and the lowest in December, which trend is quite comparable in nature to mean monthly behaviour of TOC. But, the reduction in the highest TOC values from 297 to 283 DU has coincided with a similar period of more enhancements in AT at 30 mb from −52˚C to −56˚C (**Figure 2(c)**). Therefore, the increase or decrease in highest TOC values fluctuates accordingly to corresponding increases or decreases in the air temperature. It gives clearest indication about the warming of the stratosphere in summer months. It may attribute to perturbation in photochemical activity of ozone destruction in atomic oxygen and molecular oxygen under the presence of incident solar UV-B radiation and ODS substances. It is, therefore, further responsible for altering the thermal structures of stratosphere. Thus, the consequence of such reduction of TOC value seems to be in two folds *i.e.*, (1) observed in term of increase in air temperature at a stratospheric height, which is quite expected from one of the causes by more consumption of incident UV-radiation in the destruction of ozone into atomic oxygen and molecular oxygen with incident solar UV solar radiation and (2) by the presence of UV absorbing aerosol type (AI 300 nm value above 1.5) in the summer months [18] [43] [44]. At this juncture, it is interesting to be noted that one of strong correlation coefficient value of 0.73 along with best significance level above 99.999% is appearing between their observed monthly averaged variation of both the TOC and AT. Thus, in among of all of these chosen parameters such as U, V and AI 300 nm also, the computed correlation coefficient between the TOC and the AT at 30 mb showed their highest value along with their possessing strong statistical confidence significance level above 99.99% as compared to other remaining parameters.

The month to month change in mean TOC and AI 300 nm is depicted in **Figure 2(d)**. It is observed from the figure that the monthly values also vary in similar fashion with the monthly variation of AI 300 nm. Moreover, it can also be seen from **Figure 2(d)** that monthly variation of AI 300 nm occurs the minimum value as low as 0.2 to 0.3 in December and January or presence of lower UV absorbing aerosol type (winter months), afterward it shows the continuously increasing behaviour onward and attains its peak value as high as 1.2 to 2.6 during May and June or more occurrence of highly UV absorbing nature of aerosols. Subsequently, its value continuously decreases from summer month onward till winter months during the study period. The average monthly behaviour of AI 300 nm and TOC are quite analogous to each other. The occurrences of the lower value of TOC coincide with the occurrence of lower value of AI 300 nm or vice versa. On the basis of statistical inferences, a slightly lower correlation coefficient value of 0.17 with the computed the significance level above 95% is observed between their monthly behaviour of the TOC and AI 300 nm

4. Conclusions

In this paper, the multi-year behaviour of TOC over Udaipur has been described for the period from 2002 to 2009 by using the ground based and satellite based experiment. An attempt has also been made to associate the long-term declining trend in TOC with various stratospheric dynamic and aerosol parameters like AT 30 mb, V and U wind component and also to AI at 300 nm and their interrelation with the declining trend of TOC. Based on above results with multi-year analysis of TOC and its interrelationship with stratospheric and aerosol parameters, the following main conclusions are summarised as below over the Indian tropical station.

1) The overall declining trend in TOC value finds the order about 2 DU per decade, which is the lowest value as compared to previously reported results of high, mid and low latitude stations during past decades. On the basis of this fact, the present study suggests the consequence of declining in TOC about 2 DU/decade over tropical station may lead to perturbation in the increasing of ground level UV radiation level above 4% decade.

2) The strong negative correlation coefficient value between monthly variation of TOC and stratospheric air temperature supports the view of destruction of ozone with increase in temperature or thermal unbalance of the stratosphere. The occurrences of the lower value of TOC are also coinciding with more northward and westward wind or vice-versa. It gives further more support to the argument of TOC variability due to varying the atmospheric dynamics or transport variables over the tropical site.

3) The lower monthly TOC values are linked to the respective lower values of AI at 300 nm or more dominance of non-absorbing UV aerosol type. And, higher monthly TOC concentrations are associated with more presence of absorbing UV-aerosols type or higher AI 300 nm values. It may also be pointed out that the implication of decreasing of TOC level in summer months with corresponding increasing ground level UV-B radiation level in summer months may further coincide with the increase of availability of higher values of AI 300 nm or UV absorbing aerosols type.

Referring to above discussions, it may be summarised that some of the main responsible factors of declining of TOC may be linked with the coincidence of enhancement in stratospheric temperature, AI 300 nm and transportation of TOC due to changing in meridional and zonal wind circulation pattern during the study period along with presence of longer life ODS chemical substance as a catalyst in the stratosphere for destruction of ozone concentration.

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Behavior of total tropospheric ozone, nitrogen oxide and carbon monoxide column over western Indian region by exploring space based satellite observations

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Behavior Of Total Tropospheric Ozone, Nitrogen Oxide And Carbon Monoxide Column Over Western Indian Region By Exploring Space Based Satellite Observations

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Abstract. Monthly, seasonal and annual variation of major atmospheric pollutant levels, such as Total Tropospheric Ozone (TO), Total NO_2 columnar content (TNO_2) and Total CO columnar content (TCO) have been presented first time for eleven district sites of Rajasthan state located in the western tropical Indian region. The study is based on collection of above air pollutant data retrieved from space based satellite measurements by exploring OMI and MOPITT data for a three year period from Jan 2009 to December 2012. A clear, distinct seasonal dependence in TO, TCO and TNO_2 column content values have been noticed all over selected measuring location.The maximum average seasonal TO is observed in pre-monsoon and their minimum value in the monsoon months. However, in TCO and TNO_2 case, the highest TCO and TNO_2 level is seen rather in the winter and their respective lowest value in monsoon season. Thus, their seasonal variability of TNO_2 and TCO in their ranges have been systematically found to be reduced and obeyed the following descending order, i.e., winter> post-monsoon> pre-monsoon> monsoon seasons. As far as concerned with their annual values, the observed values of all considered atmospheric pollutants are almost found in the same levels with slight discrepancies over their lower air pollutant levels recorded in hot, arid, rural as compared to the prevailing elevated value at urban region. The more detail investigation of comparison of present observations with earlier reported similar studies over other Indian regions and their possible explanation is also discussed.

INTRODUCTION

Atmospheric O_3, NOx and CO are some of crucial atmospheric chemical trace constituent of the troposphere, and they did serve as a strong global climate change sensitive agent, deciding oxidizing factor of the cleaning atmospheric pollutants through its reaction with OH radical as well as also human health hazard toxic species which are known as primary and secondary air pollutant. [Crutzen, et al., 1999; Vingarzan, 2004; Jana, et al., 2012 (a,b)]. Among the such various atmospheric positive radiative forcing climate drivers as the atmospheric pollutants such as carbon dioxide (CO_2), surface ozone (O_3), Black carbon aerosols (BC), methane (CH_4) and other several kinds of atmospheric aerosols etc., the secondary air pollutant i.e., ozone is an important candidate which possess it third rank after the another primary atmospheric pollutant CO_2 as a definite primary positive radiative forcing agent [Mohankumar, 2008; Senfeld and Pandis, 2016].The ozone shares to about 16% of their total contribution in global warming, environmental impact,as per the IPCC report [Staehelin et al., 2001; Lal, et al., 2008; IPCC, 2013].

Furthermore, ozone also behaves as a greenhouse trace gas, owing to their unique, absorbing property at the infrared solar–terrestrial long wave radiation of the earth's surface as well as also to the incident solar ultraviolet radiation in the stratosphere. As a result of this fact, it directly perturbs the thermal unbalance of the earth's atmosphere at various altitudes [IPCC, 2007, Ojha et al., 2015]. The majority of tropospheric ozone formation takes place, when sufficient amount of NOx, CO and volatile organic compounds (VOCs), such as xylene, chemically react in the atmosphere in existence of sufficient amount of solar radiation with suitable meteorological and boundary layer

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dynamics activities [Ramanathan et al., 1985]. Whereas, motor vehicle exhausts, industrial emissions, atmospheric lightening and chemical solvents are the huge anthropogenic origins of NOx as ozone precursors. While these chemicals of health hazard and toxic elements often produced in urban sites, but at the same time, winds can carry and transport those hundreds of kilometers far away from their source region, causing ozone formation to occur in less populated regions also [Collins et al., 1997; Jenkin et al., 2000; Oltmans et al., 2006; Beig and Brasseur 2006; Patil and Revadekar 2009; Kalita and Bhuyan, 2011].

Carbon monoxide (CO) is one more vital candidate as prominent trace gas as well as pre-cursors of ozone. Its main production sources are low temperature, bio-mass and bio-fuel activities materials. The CO is removed from the troposphere primarily by reaction with the OH radical, which further acts as atmospheric detergent, and this reaction in turn controls the tropospheric OH amount [Mohankumar, 2008; Senfeld and Pandis, 2016]. Hence, OH radical is recognized as one of the main "cleaning and detergent agent" factor of several kind air pollutants in the troposphere [Lelieveld et al., 2004; Beig and Brasseur 2006; Ojha et al., 2015]. Large-scale changes in CO thus affect the self cleaning capacity of the troposphere. Thus, CO also acts as a precursor of tropospheric O_3, a prominent greenhouse gas, in the presence of sufficient nitrogen oxides and sunlight.

Regarding the measurements of O_3, NO_2 and CO in the troposphere, there are no such dense observations reported for specific location over western Indian region i.e., Rajasthan state. Realizing the above perspectives such as global warming, environmental air pollution aspects etc., monthly, seasonal and annual temporal variability in tropospheric ozone along with its prominent precursors i.e., NOx and CO over eleven locations of unusual environmental climatic condition and geographical topography within Rajasthan state have been described in this paper.

OBJECTIVES

The present study has been mainly focused on quantification of topological studies of several direct positive earth's climate radaitive forcing agent as the atmospheric air pollutants such as TO, TNO_2 and TCO column content over the least explored regions i.e., Rajasthan state of western Indian parts. The primary dataset of this investigation is based on collection of monthly values of TO, TNO_2 and TCO column content for an entire three year period from 2009 to 2012. Such measured monthly values of space based satellite measurements have been retrieved from their respective websites.

As tropospheric ozone and its precursors gases are mainly governed by several anthropogenic emission activities instead of natural activities which have been closely linked with urgent requirements for sustainable development of human life in way of rapid urbanization, higher need of energy consumption, deforestation etc. Therefore, in the course of present investigation, considerable attentions on analysis of simultaneous measurements of tropospheric ozone with its precursors gases i.e., NOx and CO have been undertaken in view of their importance as direct role as greenhouse gases, air pollutant gases, human health hazard and air toxic gases for plants, trees as well as for earth's weather, climate change issues, etc. Hence, this study would be strengthened our knowledge in the era of atmospheric air pollutant assessment levels over the least explored western Indian region i.e., over Rajasthan state, where the ground based air pollutants dataset are unavailable.

DATA SET

With unique advent of satellite based technology, space-based continuous ongoing monitoring of monthly TCO was started with the MOPITT (Measurement of Pollution in the Troposphere) remote sensing instrument. MOPITT has furnished global tropospheric carbon monoxide (CO, 10^{18} mole/cm^2) at several tropospheric altitude levels from March 2000 onward (Rodgers and Connor, 2003; Deeter et al., 2004). Whereas, all these major three air pollutants measurements from various satellites based space observations, i.e., TO column content (O_3, Dobson Unit, DU), TNO_2column content (NO_2, 10^{15} molec/cm^2) and TCO (CO, 10^{18} molec/cm^2) parameters by various sun synchronized polar satellites have been also accessed from their respective websites [Kar et al., 2008; Ojha, et al., 2015].

RESULTS AND DISCUSSION

Temporal behavior of various scales in Tropospheric ozone (TO) column content:

Fig 1 (a) shows the complete annual mean variation of TO observed over various specified locations of Rajasthan state for the whole observation data set of present study period. It is observed from the plot that over the monitoring

regime, the combined monthly mean TO values vary between, from their minimum value of 34.7± 4.6 DU at Chitorgarh (semi-urban site) and maximum value of 36.8 ± 6.1 DU at Bikaner and Barmer (Desert arid and rural site) with their annual monthly mean value of 35.62 ± 5.4 DU for all the selected sites in Rajasthan for the entire observation period.

The average seasonal behaviors of TO over individual sites are represented in Fig. 2 (a). It is may be seen that seasonal ozone patterns have also displayed the well-known definite and distinct changes in each season with observing the highest range from 39.7 ± 2.7 DU to 41.7 ± 4.3 DU in pre-monsoon, followed by their slightly lower values range of 33.3± 1.15 to 37.3 ± 1.35 DU in monsoon, lower range of 32.5±0.52 DU to 34.02 ± 1.29 DU in post-monsoon and their lowest range of 28.2 ± 4.0 DU to 31.6 ± 2.5 DU in winter. It is interesting fact to be noticed at here that maximum seasonal TO values are noticed in pre-monsoon months and their respective minimum values in winter season, clearly demonstrated a fact of dominance of production of TO due to photochemical processes in presence of other prominent pre-cursor gases of ozone its self such as NOx, CO , VOC etc., At the same time, the observed higher standard deviation values of ozone in winter season relative to as observed their lower values in the rest of sesaons has given clear inference of one of the possible leading factor of excessive anthropogenic activities in cold and dry climatic conditions over measurement regime.

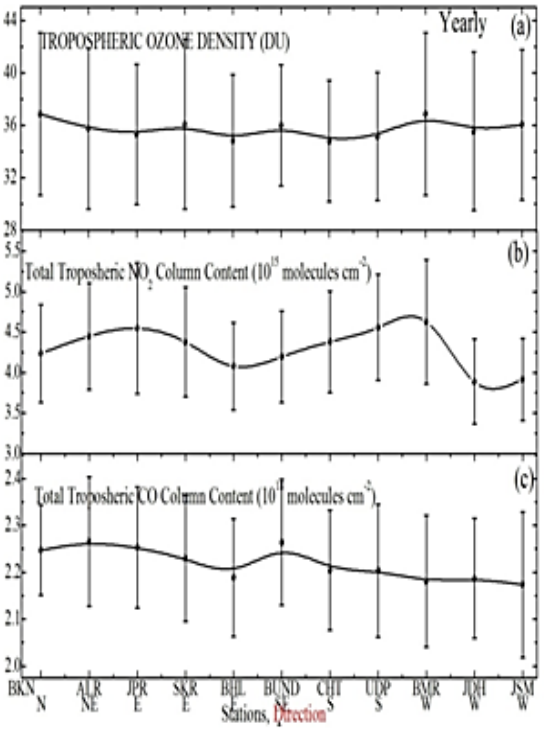

FIGURE.1(a-c): Annual Variation of with tropospheric columnar ozone content (a),Total Tropospheric NO_2 column content (b) and Total Tropospheric CO column content (c).

While comparing the present observation with other Indian sites' result, their monthly characteristics about as observed over Delhi, the peak values of 49DU in pre-monsoon and the dip level at 22 DU in January have been noticed to be in similar seasonal dependence as reported to present study over Rajasthan region, but their discrepancy is noticed in their magnitude part, which are found to be in lower side in Rajasthan region. However, the present observed trend with their values are quite a resemblance with reported values over some of southern Indian cities (Nishta et al., 2012).

The inter-annual, monthly averaged TO behaviors over selected places is also exhibited in Fig 3 (a). It may be evident from the figures that a distinct and consistent annual, monthly variation of TO values has been seen over all the places and identical annual monthly cycle trend also repeat year to next year. The maximum monthly values have been also recorded in pre-monsoon, followed by their intermediate values in monsoon, post-monsoon months and their minimum values in winter months. Such typical annual, monthly cyclic pattern has been observed for all the selected years with marginal differences in their annual monthly amplitude variability in other years.

Temporal behavior of Troposheric total CO column content:

The overall annual mean behavior of TCO column content over diverse specified locations of Rajasthan state is illustrated for the complete studied period in Fig.1(c). It can be seen from the figure that over the Rajasthan region, the combine annual mean TCO column content values spread from their lowest value of 2.17 10^{18}± 1.55 10^{17} molecules/ cm^2 at Jaisalmer (rural desert arid site) and their highest value of 2.26×10^{18}± 1.37 10^{17} molecules/cm^2 at Alwar (semi-urban industrial site) with their annual mean value of $2.21\times10^{18}\pm3.49\times10^{16}$ molecules cm^{-2} for the whole data set of TCO column content. The average seasonal behaviors in TCO column content over specified sites are represented in Fig. 2 (c). It is obvious that seasonal TCO column content patterns have displayed the definite seasonal characteristics with observing the highest range from $2.29\times10^{18}\pm2.27\times10^{16}$ molecules/cm^2 to $2.38\times10^{18}\pm 1.05\times10^{18}$ molecules/cm^2 in winter, followed by their mid way range of 2.14×10^{18} ± 8.8×10^{16} to 2.29×10^{18} ± 5.48×10^{18} molecules.cm^{-2} in pre-monsoon, lower range of 2.07×10^{18} ±1.88×10^{17} to 2.18×10^{18} ±7.6×10^{18} molecules cm^2 in post-monsoon and their lowest range of $2.00\times10^{18}\pm1.11\times10^{17}$ molecules/cm^2 to $2.15\times10^{18}\pm1.28\times10^{17}$ molecules/cm^2 in

the monsoon months. It is interesting fact to be noticed at here that maximum TCO column content is registered in the winter and their corresponding minimum value in monsoon season clearly demonstrated a fact of dominance of production of TCO column content due to primarily increasing the bio-mass and bio-fuel emission activities in colder season and significantly lesser anthropogenic emission process along with mitigation of the washout effect of rainfall event in the monsoon months.

This seasonal pattern of TCO has clearly shown the reverse nature relative to as observed in the case of seasonal variation of TO, indicating the role of generation and loss of the tropospheric CO level in accordance with depletion and enhancement of tropospheric ozone as pre-cursors behaviors of ozone gas. The observed higher standard deviation values of ozone in the winter season as similar to observed in the TCO column content relative to observed their lower values in the remaining season has given clear support an evidence of one of the possible leading effect of surplus anthropogenic bio-emission and fossil fuel activities in TCO column content and dry climatic regime.

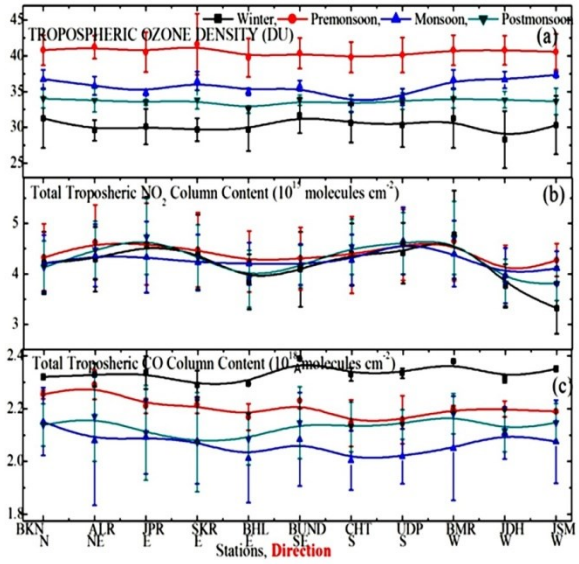

FIGURE 2 (a-c) Seasonal behavior of (a) TO, (b) TNO_2 and TCO

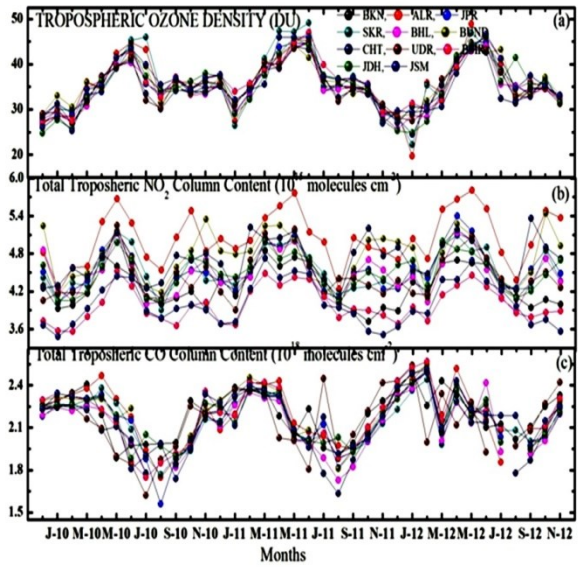

FIGURE 3 (a-c) Monthly Variation of (a) TO, (b) TNO_2 and TCO

The inter-annual monthly averaged TCO column content behaviors over selected places are also drawn with the function of months in Fig. 3 (c). It is clear from a plot that annual monthly cycle exhibits a consistent seasonal feature with their observed peak value during pre-monsoon months and their dip level in monsoon months with their marginally variability with respect to their location. This same seasonal feature repeats year for next year too.

From the close look to both figures of TCO and TO, it can be seen that mean monthly TCO amount starts to exhibit the rising behavior after acquiring their lower value of the CO in August and then gradually display increasing trend with the progress of the month from September onward to attain the peak value in March and April, after that its value again reduces to retain their original level in the next months. In contrast to this, the monthly TO values begin to acquire the lowest value in December and January month, subsequently, their average monthly values again to display their increasing behavior to reach their peak level in June and later on that it showed the gradual declining pattern in the next months. Thus, the coincidence of minimum monthly ozone level with the intermediate CO level in winter season and certain delay in the peak monthly value of the CO and ozone has given clear support of possible evidence of generation and losing of ozone at the tropospheric height in accordance with depletion and enhancement of CO with the possible series of photochemical reactions given in equations as the property of CO as pre-cursors gases of ozone as mentioned in chemical equations (1 to 6).

When the tropospheric ozone precursor gases are emitted into the atmosphere through anthropogenic source activities instead their natural emission phenomena, they are bound to enter into the chemistry of ozone. The emitted CH_4 and CO would enter into the oxidation chain started by them with OH, and emission of NOx will enhance the photochemical production of ozone. NO_2 is known to be the primary precursor of ozone and mainly involved in balancing the ozone concentration. The excess amount of CO, CH_4 and NO leads to the photochemical production of ozone, which are as follows (Ojha, et al., 2015; Ganguly and Iyer 2006)

$$OH + CO + O_2 \rightarrow CO_2 + HO_2 \quad (1)$$

$$HO_2 + NO \rightarrow NO_2 + OH \quad (2)$$
$$OH + CH_4 + O_2 \rightarrow CH_3O_2 + HO_2 \quad (3)$$
$$CH_3O_2 + NO \rightarrow NO_2 + CH_3O \quad (4)$$
$$NO_2 + h\nu \rightarrow NO + O \quad (5)$$
$$O + O_2 + M \rightarrow O_3 + M \quad (6)$$

Temporal behavior of Total tropospheric NO_2 column content:

Fig. 1 (b) displayed combined annual mean level of TNO_2 column content over various particular locations of Rajasthan state for the whole data set of observation period. It is observed from the plot that the annual averaged TNO_2 column content values change from their minimum value of $3.88\times10^{15}\pm 5.24\times10^{14}$ molecules/ cm^2 at JDH (Desert, semi-urban site) and attains its maximum value of $4.62\times10^{15}\pm 7.64\times10^{14}$ molecules/ cm^2 at BMR (Desert semi-rural hot climate site) with an annual mean value of $4.29\times10^{15}\pm2.54\times10^{14}$ molecules/ cm^2.

The mean seasonal behaviors of TNO_2 column content over specified sites are represented in Fig. 2 (b). It appears from the figure that the TNO_2 column content patterns have displayed the specific seasonal dependence in the course of this study. Their seasonal variation in their ranges have been systematically declined and obeyed the following order, i.e., winter> post-monsoon> pre-monsoon > monsoon seasons. Their seasonal range values have been seen to maximized over two close site i.e., from $4.31\times10^{15}\pm5.04\times10^{14}$ molecules/cm^2 at JSM to $4.77\times10^{15}\pm 8.71\times10^{14}$ molecules/cm^2 at BMR in winter, followed by their intermediate range between $3.80\times10^{15}\pm 3.34\times10^{14}$ at JSM (desert rural site) to $4.74\times10^{15}\pm 7.51\times10^{14}$ molecules/ cm^2 at JPR (urban and capital city) in post-monsoon, $3.96\times10^{15}\pm6.03\times10^{14}$ molecules.cm^{-2} at JDH to $4.64\times10^{15}\pm 7.85\times10^{14}$ molecules.cm^{-2} at BMR in pre-monsoon and their minimum range of $3.96\times10^{15}\pm 5.48\times10^{14}$ at JSM to $4.65\times10^{15}\pm6.65\times10^{14}$ molecules/cm^2 at UDP in monsoon. Hence, the highest TNO_2 column content has been recorded in winter and their respective lowest values in monsoon season with their middle range levels in post-monsoon and pre-monsoon. It is clearly visualized the dominance of fossil fuel emission activities of production along with long range transportation of pre-cursors of ozone nearby polluted sides of Punjab, Harayana, Delhi etc., in total tropospheric NO_2 column content due to increasing the their source strength in winter and post- monsoon relative to other season. Such seasonal TNO_2 trend follows the identical pattern as seen in the case of TCO seasonal behavior over the western Indian region. The inter-annual, monthly averaged TNO_2 column content behaviors over selected places are also depicted in Fig 3 (b). It is clear from diagram that it also displayed almost similar consistent monthly cyclic pattern with their maxima in winter months and minima in the monsoon month with their slight spatial variability with their locations.

CONCLUSION

- Annual monthly mean tropospheric ozone values vary between, from their minimum value of 34.7± 4.6 DU at Chitorgarh (semi-urban site) and maximum value of 36.8 ± 6.1 DU at Bikaner and Barmer (Desert arid and rural site) with their annual monthly mean value of 35.62 ± 5.4 DU for all the selected sites in Rajasthan for the whole observation period. The combine annual mean total tropospheric CO column content values spread from their lowest value of 2.17 $10^{18}\pm$ 1.55 10^{17} molecules/ cm^2 at Jaisalmer (rural desert arid site) and their highest value of $2.26\times10^{18}\pm$ 1.37 10^{17} molecules/cm^2 at Alwar (semi-urban industrial site) with their annual mean value of $2.21\times10^{18}\pm3.49\times10^{16}$ molecules.cm^{-2} for the whole data set of Total Troposheric CO column content. The annual averaged total tropospheric NO_2 column content values change from their minimum value of $3.88\times10^{15}\pm 5.24\times10^{14}$ molecules/ cm^2 at JDH (Desert, semi-urban site) and its maximum value of $4.62\times10^{15}\pm 7.64\times10^{14}$ molecules/ cm^2 at BMR (Desert semi-rural hot climate site) with an annual mean value of $4.29\times10^{15}\pm2.54\times10^{14}$ molecules/ cm^2. These values are slightly found lower than as observed their respective annual values over the Indian Gangetic region and comparable to the South Indian region.
- A well defined and distinct seasonal characteristics the tropospheric ozone has been observed by observing the highest magnitude in pre-monsoon, followed by their slightly lower values in monsoon, lower magnitude in post-monsoon and their lowest level in winter. In contrary to the above, in case of both the CO and NO_2, seasonal total tropospheric CO and NO_2 column content patterns have displayed the definite seasonal characteristics with prevailing the highest magnitude in winter, followed by their mid way values in pre-monsoon, lower magnitude in post-monsoon and their lowest level in monsoon. While comparing the present investigation, seasonal values recorded over the Rajasthan region are found to be lower than as observed

their respective values over the Indian Gangetic region of highly polluted sites. However, their respective nature of monthly and seasonal characteristics are observed to be similar in the entire study region.

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मोहनलाल सुखाड़िया विश्वविद्यालय, उदयपुर
MOHANLAL SUKHADIA UNIVERSITY : UDAIPUR
NAAC ACCREDITED 'A' GRADE STATE UNIVERSITY

No.F. /Gen/MLSU/2019/५१८९ Dated: 14.03.2019

ORDER

In continuation to office order No. F./ Gen/ MLSU/ 2018/3994 dt. 19.12.2018, the Vice Chancellor is pleased to reconstitute a Committee consisting of the following members, regarding final assessment and evaluation of project entitled "Study of Surface Ozone and its prominent precursors over semi-urban region i.e., Udaipur." under Prof. B.M. Vyas Retd. Prof., University College of Science, MLSU, Udaipur.

1. Prof. B. L. Ahuja, Dean, UCS	Convener
2. Prof. A.K. Nagawat, University of Rajasthan, Jaipur	Member
3. Prof. M.L. Kalra, Udaipur	Member
4. Prof. M.Roy, Physics	Member

The Convener of the Committee is requested to submitt report at the earliest.

REGISTRAR

Copy to :-
1. All members concerned
2. Prof. B.M. Vyas, Retd. Prof., University College Of Science, MLSU, Udaipur
3. P.S. to Vice Chancellor/ Addl. P.S. to Registrar, MLSU, Udaipur

DY. REGISTRAR