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Ozone distributions and urban air quality during summer in Agra – a world heritage site

Renuka Saini [1], Pradyumn Singh [1], Brij B. Awasthi [2], Krishan Kumar [3], Ajay Taneja [1]

[1] *Department of Chemistry, Dr. B.R. Ambedkar University, Agra, India*
[2] *Uttar Pradesh Pollution Control Board, Agra, India*
[3] *School of Environmental Studies, Jawaharlal Nehru University, New Delhi, India*

ABSTRACT

Unplanned urban and industrial growth and rise in population are the main factors that had led to air pollution problems. Surface ozone causes human health problems and environmental degradation and acts as a greenhouse gas. Surface ozone is the most significant key substance of photochemical smog. Dependence of air pollutants on meteorology is described with the objective of understanding the prevailing processes pollutants phase interaction. Rigorous measurements of gaseous materials (surface O_3, NO_2, CO, and SO_2) and particulate matter ($PM_{2.5}$) were carried out regularly during the summer season of 2012 at kerbsite of Agra to assess the characteristics of air pollutants. The air mass trajectories have been calculated using the HYSPLIT 4 and FLEXTRA model. The maximum hourly levels of these pollutants exceeded 116.5 ppb for O_3, 96.2 ppb for NO_2, 16 ppb for SO_2, 4.60 ppm for CO and 188 μg/m^3 for $PM_{2.5}$. There is obvious diurnal variation in the concentration of surface ozone which clearly follows the diurnal variation of atmospheric temperature. The joint application of principal component analysis and clustering techniques to data collected has led to the recognition of inherent relationships between variables that have been associated with governing processes related to surface O_3 formation. The effect of wind on pollutants appears to be noteworthy. We also found that, the maximum average concentrations of SO_2 and O_3 occurred at humidity ≤30% pinpointing for strong vertical mixing. For CO, NO_2 and $PM_{2.5}$ the maximum average concentrations occurred at humidity below 40%.

Keywords: *Surface ozone, diurnal variation, principal component analysis, cluster analysis, ozone transport*

Corresponding Author:
Renuka Saini
☎ : *+91-971-9338980*
✉ : *renukasaini@gmail.com*

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1. Introduction

Surface ozone is of scrupulous concern as an air pollutant since ozone the key oxidant in photochemical smog is acknowledged to have adverse effects on human health, vegetation and materials. Ozone is a key species of tropospheric chemistry, polluted or pristine (Crutzen, 1973; Fabian and Pruchniewz, 1977), and it is a greenhouse gas (IPCC, 2006). Ozone is a resultant pollutant formed in the atmosphere through a succession of photochemical reactions from natural and anthropogenic precursors (NO_X, CO, and volatile organic compounds) (Chan et al., 1998). Around 10% of the increased global warming potential of the atmosphere consequences from increases in surface ozone, however this value is very uncertain (Weikersheim, 2003). In polluted regions with heavy sources of NO_X and hydrocarbons, high concentrations of ozone in surface air stand for a major air pollution problem. Surface ozone over the continents has a marked seasonal cycle (Weikersheim, 2003; Zvyagintsev, 2004). The maximum can occur in winter/early spring (Gros et al., 1998; Oltmans et al., 2006; Oltmans et al., 2008), in spring, or in spring/summer (Ahammed et al., 2006; Felipe–Sotelo et al., 2006). A complex interaction of photochemical and dynamic processes controls the key features of surface ozone variations (Lelieveld and Dentener, 2000) and the shape of the seasonal cycle (Oltmans and Levy, 1992; Monks, 2000). The lifetime of O_3 in the lower troposphere varies from 4–5 days to 1–2 weeks depending on season (Wang et al., 2011). There is a lack of study related to the tropospheric chemistry in the tropical regions. NASA/GISS showed that depending on growing anthropogenic VOC emissions (by two and four times), O_3 production efficiency is greatest over the Indian region, followed by Japan and China, which is explained on the basis of increase in OH and peroxy radicals (Berntsen et al., 1996). The United Nations projected that over 600 million people worldwide in urban areas are exposed to harmful levels of traffic–generated air pollutants (Cacciola et al., 2002) and has been the issue of intensive study (Lelieveld and Dentener, 2000; Lamarque et al., 2005). Interest has more recently turned to the possible influence of climate change on future levels of ozone (Dawson et al., 2009; Langner et al., 2012; Wang et al., 2013).

Gaseous pollutants have major negative impacts on health. They also play significant role in environmental changes and changes in atmospheric chemistry. It is expected that the increasing load of atmospheric sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO), and ozone (O_3) will add to global climate change; therefore, it is necessary to quantify the emissions in the very near future. The linked issues of ozone and oxidant production as well as particulate matter pollution have been significant problems in the field of tropospheric chemistry for many years.

Agra is located in north central part of India. Atmosphere of Agra is affected by emissions from vehicle exhaust, energy production and domestic heating (Kulshrestha et al., 2009; Masih et al., 2009; Pipal et al., 2011; Masih et al., 2012; Massey et al., 2013). High concentrations of surface ozone that predominantly arise during the summers have been shown to be detrimental to human health and destructive to vegetation (NRC, 1991). In view of

the above discussion, it is necessary to define the status of ambient air quality due to the presence of different pollutants in the environment of Agra. This paper examines the temporal relationship between meteorological parameters and urban air pollutants, helping to fill a void in research into the relationships between the atmospheric transport, local meteorology, and concentrations of tropospheric air pollutants.

2. Methodology

2.1. Experimental site

Agra, the city of Taj, a landlocked city is geographically located between 78°2' E and 27°11' N at 169 m above sea level (asl) with a tropical steppe climate influenced by the Thar Desert of Rajasthan in its South East, West and North West peripheries and is therefore, a semiarid area. The climate of Agra is divisible into three distinct seasons; summer, monsoon and winter (IMD, 2009). The weather at the experimental site during the summer season (April to June) is hot and dry with temperature ranging from 32 °C to 48 °C and winds are mostly gusty which is predominantly from west and northwest. The relative humidity during summer ranges between 30% and 48%. Large amount of windblown dust envelops the city during the summer months. The major industries in Agra are two thermal power stations, foundries, two railway marshalling yards (work on coal) industries like rubber, chemical, engineering, and brick. In spite of the above industries, Mathura Refinery and Firozabad Glass Industry are also very close to Agra, contributing to air pollution. The total population of Agra is 4 380 793 according to the Directorate of Census Operation in Uttar Pradesh showing a 21% increase in 2011 compared to the 2001 Census. The initial interim data suggest a population density of 1 084 in 2011 compared to 896 of 2001. Total area of Agra district is about 4 041 square kilometers. Agra has 580 396 motor vehicles registered, out of which 27 462 were transport vehicles (Census, 2011).

The study was performed in the summer period from April to June 2012 at a site located in an urban area of Agra near heavy traffic junction. Measurements were conducted on the roof of Agra Nagar Nigam building (78°00' E and 27°20' N), which is situated in the heart of the city. It is a major residential and commercial area. The monitoring site lies by the side of a road that carries mixed vehicular traffic. Traffic density is very high with a frequency of 10^5 vehicles per day. A major railway station (Raja Ki Mandi railway station) is also located at a distance of 1.3 km from the sampling site having a frequency of about 80 trains per day (Taneja et al., 2008) and is also surrounded with major urban activity centers, which include rubber–processing units, ferrous and non–ferrous metal casting units, chemical industries, tanneries and lime–processing units (Figure 1). These units emit major gaseous pollutants such as CO, hydrocarbons and NO_X (Saini et al., 2009).

2.2. Measuring instruments

Hourly concentrations of SO_2, NO_2, CO, O_3 and $PM_{2.5}$ were measured simultaneously with the instruments obtained from Ecotech, New Delhi, India and Met One Instruments, USA. SO_2 concentration was monitored by EC9850 with the precision and lower detection limit (LDL) of 0.5 ppb. The monitor (with an auto–range of 0–20 ppm) works on the principle of ultraviolet radiant excitation (fluorescence). NO_2 was monitored with an analyzer (EC 9841) with the precision and LDL of 0.5 ppb (auto–range of 0–20 ppm) runs on the principle of measurement of the chemiluminesence formed by the oxidation reaction of NO with O_3. The concentration of CO was monitored using non–dispersive infrared (NDIR) gas filter correlation technique based on the IR absorption (at 4.67 µm) by carbon monoxide molecules within its rotation–vibration absorption band by EC9830 monitor with the precision of 100 ppb and LDL of 50 ppb (auto–range of 0–200 ppm). The concentration of ozone was measured using Ecotech analyzer (EC9810) with the precision of 1.0 ppb (auto–range of 0–20 ppm). The instrument has lower detection limit of 0.5 ppb and works on the principle of absorption of UV radiation at 254 nm by ozone present in the sample air. The fine particulate matter ($PM_{2.5}$) concentrations were measured by Met One Instruments (USA) Model: BAM–1020 based on beta attenuation principle with the range of 1 mg (1 000 µg) default setting and settable from 0.1 mg to 10 mg with the lower detection limit of (2σ)<3.0 µg/m^3 (1 hour). Meteorological data were recorded through a weather station (Met One Instruments, USA) mounted on the roof of Nagar Nigam building, 12 m above the ground level. It records atmospheric temperature (AT) (range –50 °C to 50 °C), relative humidity (RH) (range 0 to 100 %), wind speed (WS) (range 0 to 55 mph), wind direction (WD) (range 0–360°), global solar radiation (SR) and rainfall (RF). It was programmed to collect data at 1 minute intervals and store them in memory to be downloaded to a computer. All the instruments were regularly calibrated, tested, and audited by standards with known traceability.

Figure 1. *Map of Agra city showing the sampling site.*

2.3. Multivariate analysis

The Principle Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) are the most common multivariate statistical methods applied in environmental studies. The SPSS software package (Portable–PASW–Statistics–18) was used for the multivariate analysis. The method of HCA helps to classify variables of different sources as a complementary analysis to PCA. As the variables have large differences in scaling, standardization was performed before computing proximities and can be done automatically by the HCA procedure. Further, the Ward's method of clustering was applied by the use of the Euclidean distance as a measure. The levels of various pollutants and meteorological parameters vary by different orders of magnitude and hence the PCA was applied to the correlation matrix. Likewise, each variable was normalized to unit variance and thus contributed equally. Further, skewness was applied to view whether the distribution of data is symmetric or asymmetric.

2.4. Back trajectory calculation

The back trajectory technique is a useful tool in tracing source regions of air pollution and determining transport patterns at receptor sites in general. Although they do not represent exactly the path of an air parcel, they are suitable for identifying particular synoptic situations (Stohl et al., 1995; Stohl, 1998). Considering the large uncertainty and limited significance of a single back trajectory (Stohl, 1998), a more reliable representation of the synoptic airflow in a given region can be achieved through the reconstruction and analysis of a large number of atmospheric trajectories.

To support the interpretation of chemical species behavior, backward trajectory analysis has been performed. The trajectories have been calculated online on the Web site of the FLEXTRA trajectory model (http://www.nilu.no/projects/ccc/trajectories/) (Stohl et al., 1995) hosted by the Norwegian Institute for Air Research (NILU). Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) (http://ready.arl.noaa.gov/HYSPLIT_traj.php) model (Draxler and Rolph, 2003; NOAA/ARL, 2005) was also used. On the basis of highest concentrations of ozone in the study period, back trajectories for 24th April 2012, 19th May 2012 and 22nd June 2012 were calculated using FLEXTRA and HYSPLIT models.

3. Results and Discussions

3.1. Diurnal variation and meteorological parameters

It is well known, meteorological parameters play a fundamental role in air pollution processes (Elminir, 2005) as they affect the rates of photochemical reactions. Meteorological conditions also affect the transport and mixing of precursor gases. Generally, raise in atmospheric temperature accelerates photochemical reaction rates in the atmosphere and increases the rate at which surface ozone and its oxidants are formed. Ground level ozone forms readily in the atmosphere, usually during hot summer weather conditions. Temperature, relative humidity, wind speed, wind direction and global solar radiation have been analyzed in order to get a better understanding of the daily behavior of air pollutants. Global solar radiation refers to the electromagnetic radiation that reaches the Earth from the Sun. It is commonly divided into various regions and bands on the basis of wavelength.

Unlike most studies we do include the diurnal cycle in our considerations, as this point is extremely significant as diurnal variations bear information on local pollution conditions. In particular, the rate of the afternoon ozone growth is defined by the local precursor levels, and the formation of the morning minimum is defined by the properties of the underlying surface and intensity of the temperature inversion. Moreover, the formation of the breeze–type (with morning diurnal maximum) or mountain type (with night diurnal maximum) shape of the diurnal cycle is defined. Thus the inclusion of diurnal variations in the analysis can help to distinguish more clearly the different regimes of the surface ozone variations and to identify the processes driven by sunlight.

Figure 2 presents the average hourly concentrations of O_3, NO_2, CO, SO_2, $PM_{2.5}$ and meteorological parameters in Indian Standard Time (IST) where temperature and global solar radiation have prominent diurnal variations. Dust storms and thunderstorms from the Asian subcontinent and the Thar Desert are frequently observed during the period from March to June (IMD, 2009). The wind speed varies from 2.6 to 6.9 km/h with a maximum during study period.

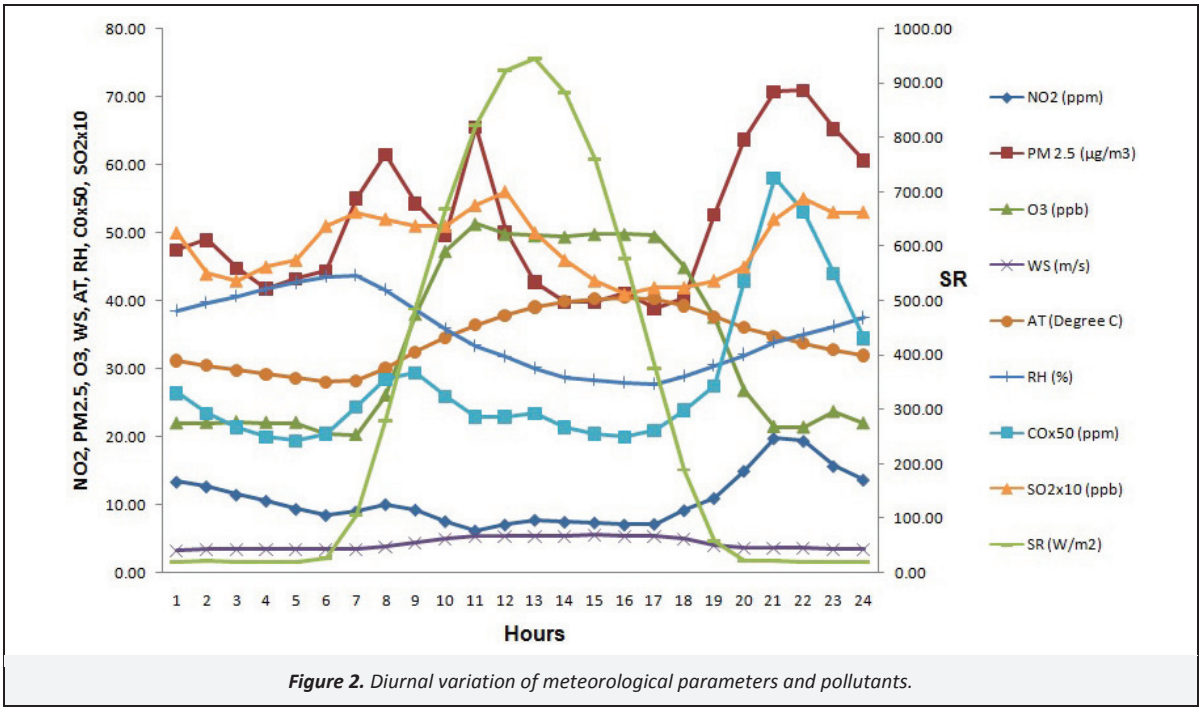

Figure 2. *Diurnal variation of meteorological parameters and pollutants.*

Diurnal variations in O_3 concentration show daytime photochemical production all through the study period. The diurnal average maximum is observed between 10:00 to 16:00 hours (51.7 ppb) whereas the minimum (20.5 ppb) appears at night. The decrease in night–time O_3 concentrations is mainly due to titration of O_3 by surface emissions of NO and ground level destruction of O_3 in a shallow boundary layer. In a dry season on sunny warm days large energetic turbulent mixing provides uniform mixing ratios throughout the depth of the convective boundary layer during the daytime (Sanhueza et al., 2000). The surface measurements on sunny and warm days during the hours of high solar radiance may be representative of the boundary layer concentrations.

Both NO_2 and CO start to build up from 16:00 hours (evening hours) and attains their maximum concentrations at 21:00 hours, which are different from the variation in ozone. Whereas the lowest values for both the species (NO_2, 6.45 ppb at 10:00 hours and CO, 0.39 ppm at 4:00 hours) were observed during the morning and afternoon hours. In order to sustain high levels of ozone during the noon period, large amounts of precursors (i.e., NO_2, CO) are needed. This leads to very low levels of these precursors during the noon period. Higher levels of NO_2 and CO all through the early morning and late evening hours are because of the combinations of boundary layer processes, chemistry and anthropogenic emissions. During night hours, the boundary layer descends and remains low till early morning, thereby resisting the mixing of the anthropogenic emissions with the upper layer. During these hours of maximum concentrations of NO_2 and CO, anthropogenic emissions are also prominent due to rush hours. It is important to note that the most important anthropogenic source of CO and NO_2 is fossil fuel combustion in motor vehicles. Traffic level in this intersection remains high from morning to late in the evening hours. But during peak office hours, traffic management becomes extremely difficult resulting in long wait at the traffic signals. During noon time, the higher height of boundary layer provides a larger mixing region and hence the pollutants get diluted (Lal, 2007).

As the monitoring site is surrounded by several industries (i.e., tanneries, smelting, shoe manufacturing, petha, rubber etc), use of fossil fuels for energy production could be the probable source of SO_2. The SO_2 concentration starts to increase in the morning hours (6:00 hours) and attains its maximum concentration at 12:00 hours than it decreases and again starts to rise up from 18:00 hours till 22:00 hours, than there is a sink at 22:00 hours to morning 5:00 hours. The average $PM_{2.5}$ concentration had the lowest value in early morning (39.7 μg/m^3) then, increased and remained almost unchanged from 9:00 hours till noon. After 12:00 hours it starts decreasing till 18:00 hours and then again increased up to the maximum value (68.9 μg/m^3 at 21:00 hours). The data for the site indicate that vehicular emissions have a clear influence on $PM_{2.5}$. In the morning and evening, a clear influence from the rush hour traffic on $PM_{2.5}$ is seen. During the other hours $PM_{2.5}$ seems to be influenced by wind and temperature inversion. In the afternoon (12:00 to 18:00 hours) there is a decrease in $PM_{2.5}$. It has to be noted that $PM_{2.5}$ decreases in the afternoon in spite of the fact that emissions from vehicles remain approximately constant (because the flux of vehicles does not decrease much). It was assumed that the lower concentration of $PM_{2.5}$ in afternoon hours was due to the non–working hours and less anthropogenic activities due to lunch hours and change in shifts of the workers in industries. $PM_{2.5}$ concentration at urban site is higher due to heavy vehicular traffic flow, emissions from nearby industries, emission from solid waste incineration from nearby hospitals, small restaurants and industries like rubber, shoe and petha industry (Indian confectionery sweet preparation made out of a vegetable of Cucurbitaceous family) around the area which contribute to aerosol loading through their solid waste dumping and incineration.

3.2. Backward trajectories analysis

Calculation of the backward trajectories was done using the boundary conditions obtained from European Centre for Medium–Range Weather Forecast (ECMWF) which are updated every 6 hours. The situations with medium–high ozone concentrations are useful to improve our understanding of both ozone dynamics and air quality. In order to show a typical and representative ozone event, we selected an event from the study period, with cases of incidence of human health protection limits (NAAQS, 2009). Using HYSPLIT and FLEXTRA model we have analyzed episodes with maximum ozone concentration in detail. Forty eight hours backward trajectories drawn from the HYSPLIT model shown in Figures 3a, 3c, and 3e and 60 hours backward trajectories drawn from FLEXTRA model are shown in Figures 3b, 3d, and 3f. The results of backward trajectories arriving to Agra for 24th April, (maximum hourly O_3 concentration 61 ppb) and 19th May (maximum hourly O_3 concentration 93.3 ppb) is presented in Figures 3a, 3b, 3c and 3d respectively. The analysis of trajectories for 24th April and 19th May showed that the trajectories were from northwestern direction, originating from Eastern Pakistan and crossing Indian states Punjab and Rajasthan. The air masses probably bring ozone and ozone precursors from the Arabian Sea during 24th April and 19th May which is indicative of gasoline combustion with possible origin from the Middle East, given the trajectory followed by the air mass.

Figure 3e and 3f shows air back trajectories for 22nd June (maximum hourly O_3 concentration 116.5 ppb). The analysis of trajectories for 22nd June showed that the trajectories were from western direction, coming from the Arabian Sea, crossing Indian states Gujarat and Rajasthan. The air masses probably bring ozone and ozone precursors passing from the Arabian Sea during 22nd June with a possible origin on the east coast of the Africa, given the trajectory followed by the air mass. This contribution of ozone and its precursors from these source areas result in a fast ozone rise in the early morning on these days, reaching a daily maximum higher than 100 ppb. Thus, it can be summarized that maximum ozone concentrations were probably the consequence of the transport effect of these directions. Therefore, it is possible that during the episode days, the pollutant concentrations in Agra may have been affected by the regional pollution as well.

3.3. Statistical analysis

Table 1 shows the summary of explorative statistical parameters calculated for pollutants. In the present study, the concentration of pollutants was found to vary from 0.09 to 4.6 ppm for CO, 0.5 to 16 ppb for SO_2, 0.3 to 96.2 ppb for NO_2 and 0.8 to 116.5 ppb for O_3 while $PM_{2.5}$ ranges from 12.0 to 188.0 μg/m^3. Large variation of CO, SO_2, NO_2, O_3 and $PM_{2.5}$ was observed throughout the study with positive skewness of 4.5, 0.9, 2.9, 0.6 and 0.6 at the present site respectively and median concentrations of all the pollutants are lower than their mean concentrations. The variation in pollutant concentrations throughout the study may be related to the combined effects of climatic factors and source strengths.

During the study period, more than 90% of valid data has been obtained for these pollutants. Figure 4 shows the Box and Whiskers summarizing the results obtained from the hourly values. These results reveal the existence of peaks although with a low frequency. Their origin can be regional due to the transport of air masses with aged pollutants or local too, which is in favor of weather conditions suitable for the formation (in the case of ozone) or accumulation of these species (Sansuddin et al., 2011). The upper box represents the 75th percentile, the lower box represents 25th percentile, and the line within each box represents median concentration. Awang et al. (2013) indicated that the mean values are very sensitive to large and small monitoring records and

at the same time they can represent the skewness of the data distribution. Results suggest that the distribution of data of these pollutants was skewed to the right (median<mean), which shows that there is a large amount of deviation present in the data. Furthermore, the standard deviation indicates the possibilities of extreme concentrations (when the standard deviation is high, the variability is likewise high, indicating extreme concentrations). The high concentrations of the pollutants are due to transport from several regions and from the trajectory analysis it is assumed that one of the reasons is trans–boundary pollution. Figure 1 clearly shows that the site is surrounded by many small scale industries and it is a major traffic junction too, so it is assumed that these local sources also increase the concentration of pollutants.

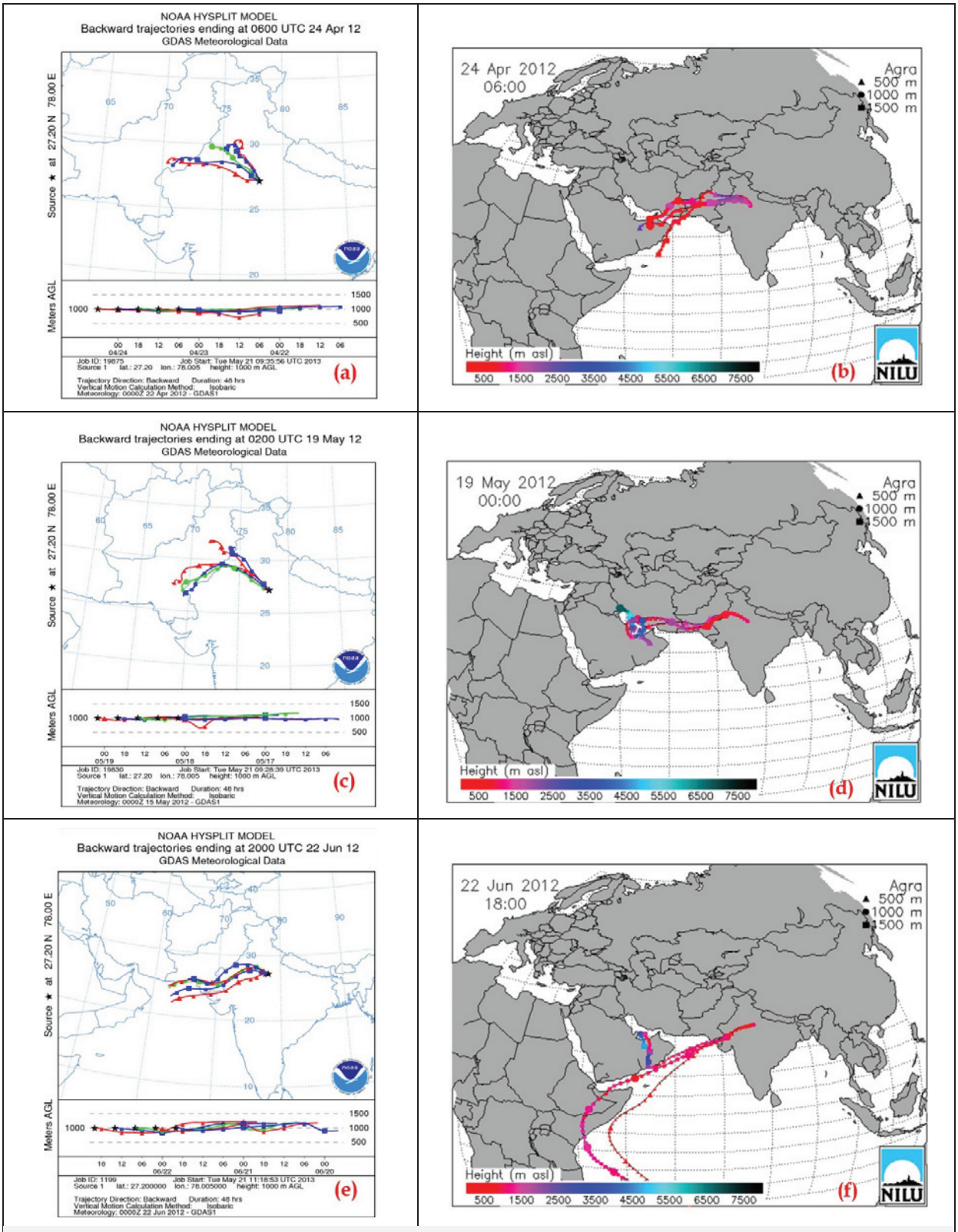

Figure 3. (a), (b), (c), (d), (e), *and* ***(f):*** *Backward trajectories originated from Agra starting at 24th April, 19th May and 22nd June, 2012, respectively.*

Table 1. *Descriptive statistical parameters for daily pollutant concentrations*

	CO (ppm)	SO_2 (ppb)	NO_2 (ppb)	O_3 (ppb)	$PM_{2.5}$ ($\mu g/m^3$)
No. of samples	1 910	1 910	1 910	1 910	1 910
Mean	0.50	4.80	10.60	33.80	51.40
Median	0.40	4.50	7.80	31.80	47.0
Standard Deviation	0.45	2.20	10.50	19.80	24.40
Variance	0.20	4.90	111.30	393.00	596.10
Skewness	4.50	0.90	2.90	0.80	1.20
Minimum	0.09	0.50	0.30	0.80	12.0
Maximum	4.60	16.0	96.20	116.50	188.0

3.4. Principal component and cluster analysis

In order to identify the pollutant sources, PCA with Varimax rotation was applied. All principal components with eigenvalues >1 were retained as suggested by the Kaiser criterion. Table 2 displays that PCA produced three factors explaining about 80% of the total variance and factor loadings for those three extracted components after rotation. The first factor was composed of O_3, atmospheric temperature (AT), solar radiation (SR) and wind speed (WS) and this explains 38.5% of the data variance. The second factor, formed from NO_2, CO and SO_2 explained 21.7% of the variance. This factor is indicative of fossil fuel combustion. The third factor extracted explained 19.8% and it was made up of wind direction (WD) and barometric pressure (BP). The principal component analysis reveals that the ozone formation is governed equally by meteorological parameters (temperature, solar radiation, wind speed) and ozone precursors (NO_2 and CO). In addition to this, a factor loading on principal components also confirms that ozone and meteorological parameters follow an inverse relationship with ozone precursors, i.e. NO_2 and CO.

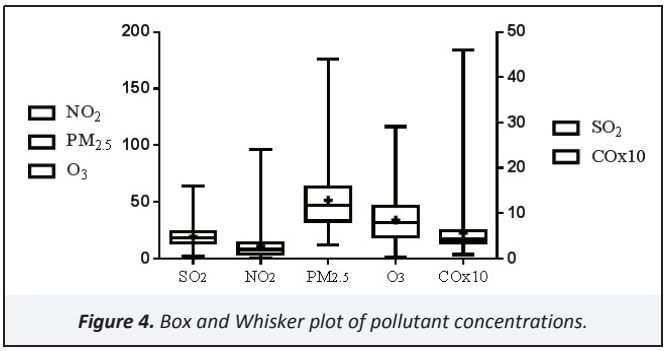

Figure 4. *Box and Whisker plot of pollutant concentrations.*

The hierarchical cluster analysis was used further to identify relatively homogeneous groups of variables. The objects which belong to the same cluster are similar with respect to the predetermined selection criterion. The resulting clusters exhibit high internal (within a cluster) and external (between–cluster) homogeneity. A cluster analysis was applied using Ward's method with Euclidian distances as the criterion for clusters forming. This form of cluster analysis is regarded as very resourceful, even though it tends to create small clusters. As the variables have large amount of differences in scaling, standardization was done before computing. Figure 5 displays three clusters: (1) SO_2–WS–CO–NO_2; (2) O_3–AT–$PM_{2.5}$–RH; (3) BP–SR. It is observed, however, that clusters 1 and 2 group together at implying probably their common source.

3.5. Correlation matrix

The bivariate Pearson correlation coefficients within measured meteorological parameters and air pollutants are presented in Table 3. The results indicate that O_3 has positive correlation with solar radiation, atmospheric temperature, and wind speed and negative correlation with relative humidity. It is evident that the surface ozone variation is directly correlated to atmospheric temperature and is inversely related to humidity. The positive correlation between ozone and atmospheric temperature is due to the fact that the radiation controls the temperature and therefore the photolysis efficiency will be higher. Negative correlation between the surface ozone and humidity lies in the fact that when humidity increases the major photochemical paths for removal of ozone (i.e., photolysis of ozone followed by the reaction of O (^{1}D) with water vapor and reaction of H_2O with ozone) becomes effective. Secondly, higher humidity levels slow down photochemical process due to its association with greater cloud abundance, atmospheric instability and low incoming solar radiation. Also the surface ozone is depleted through deposition of its molecules on water droplets (Londhe et al., 2008). Temperature and solar radiation have negative correlation with CO, NO_2 and $PM_{2.5}$. The negative correlation between wind speed and CO, NO_2, SO_2 and $PM_{2.5}$ indicate dilution of these air pollutants by wind. The positive correlation between O_3 and wind speed points out to O_3 transport. The increase of wind speed implies the increasing transport of air, thus the influence of wind speed on primary and secondary pollutants may differ. In case of primary pollutant, it acts as diluting agent, while O_3 concentration increased due to its transport from other regions (Dragan, 2008).

Projections for future O_3 precursor emissions suggest that at least over the next few decades O_3 concentrations are likely to increase, especially across the parts of South and East Asia. The extent of these changes will strongly depend on global and regional O_3 precursor emission pathways. Some additional sources for O_3 is required to account for the theoretical estimates which could be by downward transport of stratospheric O_3 through the free troposphere to near ground level (Gupta et al., 2007).

4. Conclusions

These observations are helpful in understanding the ambient air quality of a place with high population density and the enhanced anthropogenic activities that lead to worsening of the air quality. The results indicate that maximum O_3 concentration was observed during the daytime due to photo–oxidation of the precursor gases originated from anthropogenic sources. The average diurnal maximum of ozone varied from 44–51 ppb during 10:00 to 16:00 hours and the average diurnal minimum varies from 20–26 ppb during nighttime and early morning hours. During the study period, diurnal variation of O_3 is different from that of CO and NO_2 exhibiting an anti–correlation. For CO and NO_2, distinct diurnal variations are found with minimum values during daytime and maximum values around midnight. Photochemical processes are predominant during summer period. It appears that when NO_2 value is low, O_3 value is high as observed and when NO_2 value is high O_3 value is low. Measurements also show the important relationship between changes in meteorology and O_3 concentrations. The calculated and analyzed characteristic backward

trajectories for the days with maximum O_3 concentrations clearly pointed out the transport from the NW and W directions. Statistical analysis showed that formation of O_3 is equally depend on ozone precursors and meteorological parameters what was also indicated by PCA and cluster analysis and also shows that the variation of pollutant at the site was strongly influenced by regional emission and chemical and transport processes. Our analysis has also described some of the complexities of the relationships among air pollutants like $PM_{2.5}$ and SO_2 with other gaseous pollutants and weather variables. Finally, tropospheric study of ozone and related trace gases as well as aerosols are becoming increasingly important because deteriorating air quality may exert negative impacts on human health and vegetation. Therefore, control measures should be taken to avoid further exacerbation of air pollution.

Table 2. *Factor loading after Varimax rotation and Eigenvalues of PCA of the data sets*

Factor loading after Varimax rotation			
	Factor 1	Factor 2	Factor 3
O_3	**0.928**	–0.217	–0.091
AT	**0.887**	0.151	–0.237
WS	**0.881**	–0.341	–0.085
SR	**0.810**	–0.171	0.278
RH	–0.784	–0.504	–0.053
$PM_{2.5}$	–0.500	0.170	0.005
NO_2	–0.348	**0.839**	0.320
CO	–0.340	**0.818**	0.139
SO_2	0.123	**0.712**	–0.235
WD	–0.162	–0.039	**0.967**
BP	0.139	0.123	**0.960**
Variance Explained (%)	38.57	21.77	19.86
Eigenvalues of PCA of the data sets			
Component	Eigenvalues	Variance (%)	Cumulative (%)
1	**4.517**	**41.062**	**41.062**
2	**2.333**	**21.212**	**62.274**
3	**1.973**	**17.939**	**80.213**
4	0.956	8.688	88.901
5	0.675	6.135	95.036
6	0.205	1.859	96.895
7	0.135	1.231	98.126
8	0.082	0.745	98.871
9	0.078	0.705	99.576
10	0.034	0.307	99.883

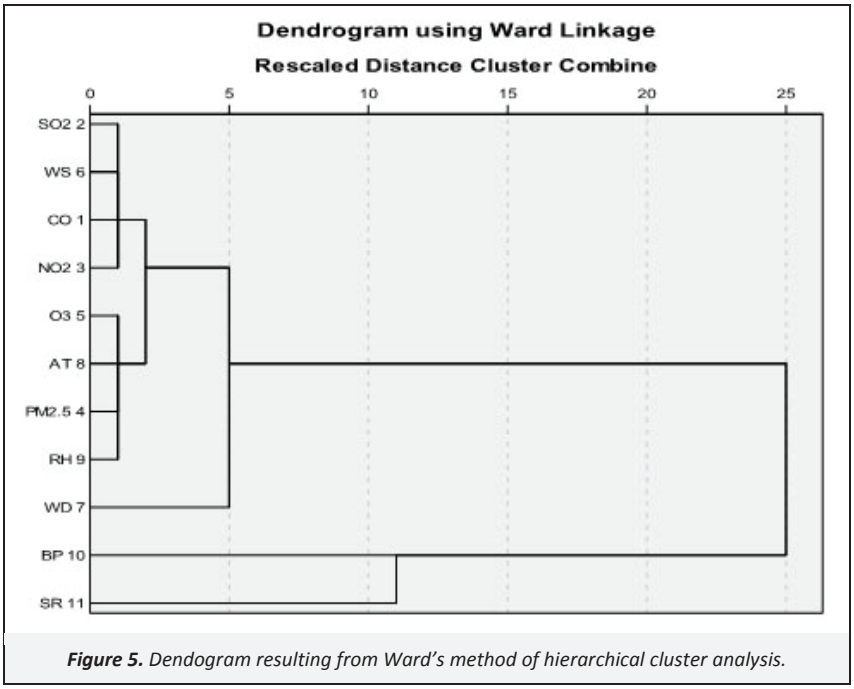

Figure 5. *Dendogram resulting from Ward's method of hierarchical cluster analysis.*

Table 3. *Bivariate Pearson correlation coefficient among different pollutants and meteorological parameters in Agra*

	CO	SO_2	NO_2	$PM_{2.5}$	O_3	WS [a]	WD [b]	AT [c]	RH [d]	BP [e]	SR [f]
CO	1										
SO_2	0.349	1									
NO_2	**0.806**	0.444	1								
$PM_{2.5}$	0.494	–0.046	0.207	1							
O_3	–0.461	–0.013	–0.549	–0.380	1						
WS [a]	–0.526	–0.126	–0.626	–0.350	**0.925**	1					
WD [b]	0.158	–0.255	0.307	0.122	–0.236	–0.198	1				
AT [c]	–0.144	0.073	–0.264	–0.282	**0.812**	**0.763**	–0.373	1			
RH [d]	–0.131	–0.298	–0.179	0.356	–0.568	–0.470	0.081	–0.837	1		
BP [e]	0.150	–0.087	0.370	–0.074	0.033	–0.012	**0.879**	–0.092	–0.209	1	
SR [f]	–0.342	0.064	–0.373	–0.330	**0.765**	**0.764**	0.141	**0.535**	–0.449	0.321	1

[a] *wind speed,* [b] *wind direction,* [c] *atmospheric temperature,* [d] *relative humidity,* [e] *barometric pressure,* [f] *solar radiation*
Correlation coefficients significant at 0.05 level are marked in bold

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