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RESEARCH ARTICLE

Trend and variability of atmospheric ozone over middle Indo-Gangetic Plain: impacts of seasonality and precursor gases

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Abstract Ozone dynamics in two urban background atmospheres over middle Indo-Gangetic Plain (IGP) were studied in two contexts: total columnar and ground-level ozone. In terms of total columnar ozone (TCO), emphases were made to compare satellite-based retrieval with ground-based observation and existing trend in decadal and seasonal variation was also identified. Both satellite-retrieved (Aura Ozone Monitoring Instrument-Differential Optical Absorption Spectroscopy (OMI-DOAS)) and ground-based observations (IMD-O_3) revealed satisfying agreement with OMI-DOAS observation over predicting TCO with a positive bias of 7.24 % under all-sky conditions. Minor variation between daily daytime ($r = 0.54$; $R^2 = 29$ %; $n = 275$) and satellite overpass time-averaged TCO ($r = 0.58$; $R^2 = 34$ %; $n = 208$) was also recognized. A consistent and clear seasonal trend in columnar ozone (2005–2015) was noted with summertime (March–June) maxima (Varanasi, 290.9 ± 8.8; Lucknow, 295.6 ± 9.5 DU) and wintertime (December–February) minima (Varanasi, 257.4 ± 10.1; Lucknow, 258.8 ± 8.8 DU). Seasonal trend decomposition based on locally weighted regression smoothing technique identified marginally decreasing trend (Varanasi, 0.0084; Lucknow, 0.0096 DU year^{-1}) especially due to reduction in monsoon time minima and summertime maxima. In continuation to TCO, variation in ground-level ozone in terms of seasonality and precursor gases were also analysed from September 2014 to August 2015. Both stations registered similar pattern of variation with Lucknow representing slightly higher annual mean (44.3 ± 30.6; range, 1.5–309.1 μg/m^3) over Varanasi (38.5 ± 17.7; range, 4.9–104.2 μg/m^3). Variation in ground-level ozone was further explained in terms water vapour, atmospheric boundary layer height and solar radiation. Ambient water vapour content was found to associate negatively ($r = -0.28$, $n = 284$) with ground-level ozone with considerable seasonal variation in Varanasi. Implication of solar radiation on formation of ground-level ozone was overall positive (Varanasi, 0.60; Lucknow, 0.26), while season-specific association was recorded in case of atmospheric boundary layer.

Keywords Boundary layer · Meteorology · Indo-Gangetic Plain · Ozone · OMI-DOAS · Varanasi

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Introduction

Atmospheric ozone (O_3) is a strong reactive oxidant which poses potential risk to human health (Zhang et al. 2004; Kumar et al. 2015a) and damages agricultural crops (Burney and Ramanathan 2014; Feng et al. 2016) as well as materials both on local and regional scale (Kambezidis and Kalliampakos 2013). Additionally, ozone has multiple impacts on the environment, particularly in forming photochemical smog (Geddes and Murphy 2012), global warming as a greenhouse gas (IPCC 2014), regulating oxidative potential of troposphere (Thompson 1992), affecting photosynthesis (Feng et al. 2016) and acting as a key precursor of hydroxyl radical (OH) (Seinfeld and Pandis 2006). Over India, ozone has been often linked with negative health impacts and reduction in crop yield (Burney and Ramanathan 2014; Debaje

2014). Debaje (2014) reported a relative loss of 5–11 % for winter wheat and 3–6 % for rabi rice in 2002–2007, while Burney and Ramanathan (2014) reported a 36 % of wheat losses due to ozone. Atmospheric ozone, in general, is explored in two contexts: total columnar and ground-level ozone. However, for practical purposes, stratospheric ozone corresponds to total columnar ozone (TCO) as it typically contributes over 90 % of columnar loading over a region. Ozone chemistry significantly varies at different atmospheric layers, e.g. in stratosphere, it is produced naturally because of photolytic decomposition of molecular oxygen by solar radiation (<242 nm), while in lower atmosphere, heterogeneous chemistry prevails (Wang et al. 2003; Seinfeld and Pandis 2006). Inter-annual variation in stratospheric ozone mostly driven by physical (temperature, radiation) and dynamical variability (transport, Seinfeld and Pandis 2006) has remain frequently under investigation (Monks 2000; Wang et al. 2003). There are few evidences on identifying spatio-temporal distribution of ground-level ozone over India like effects of precursors in urban (Singh et al. 1997; Londhe et al. 2008), rural (Londhe et al. 2008) and marine environment (Ali et al. 2009) and specifically over IGP (Beig and Ali 2006; Lal et al. 2008), while long-term trend and seasonality in TCO were less explored (Latha and Badarinath 2003; Londhe et al. 2003; Pal 2010).

Multiple factors potentially influence the inter-annual variation and amplitude of a pollutant cycle. Changes in precursors loading, meteorological variables and solar radiation potentially modify seasonal cycle of a pollutant in terms of timing of peaks/troughs, amplitude and seasonal trend (Banerjee et al. 2011, 2015; Sen et al. 2014). Carslaw (2005) hypothesised the necessity of identifying such seasonal trends of ozone concentrations as a mean of understanding possible involved mechanism. Columnar ozone is reported to be influenced by variations in solar radiation (Soukharev and Hood 2006; Londhe et al. 2003) and aerosol loading (Latha and Badarinath 2003 Ialongo et al. 2008). Globally, several researchers have highlighted the long-term statistical trend in columnar ozone using both ground-based (Londhe et al. 2003) and satellite-retrieved information (Pal 2010; Chehade et al. 2014; McPeters et al. 2015). Recently, IPCC concluded global stratospheric ozone has declined from pre-1980 values and remain fairly constant at about 3.5 % below the 1964–1980 level (Hartmann et al. 2013). However, there are limited evidences in identifying intra-season and long-term trend in TCO over India of which almost all recognize strong seasonality (Latha and Badarinath 2003; Londhe et al. 2003; Pal 2010). Londhe et al. (2003) reported a decreasing trend (−5 to −8 DU decade^{-1}) in Dobson spectrophotometer-measured TCO over four stations (Delhi, Varanasi, Pune and Kodaikanal) in Indian sub-continent over the period 1981–1998. Almost, 50 % of variability was associated with annual cycle, while the rest was reported to be influenced by Quasi-Biennial Oscillation (QBO) and the solar cycle. Pal (2010) using Total Ozone Mapping Spectrometer (TOMS) and Ozone Monitoring Instrument (OMI) data reported an average TCO decrease rate of −0.363 DU year within 1997–2008 for 15 stations spread across Indian sub-continent. However, scientific evidences on long-term changes of TCO concentrations over middle IGP with emphasis on seasonal components of ozone time series are largely unexplored. Additionally, specific factors that trigger such variability are mostly unidentified which increases the associated uncertainties in climate and air quality models. Triggered by such necessities, in the present analysis, an attempt has been made to compare satellite-retrieved TCO with ground-based measurement, and further, statistically significant trend both in terms of inter-annual (seasonal) and decadal timeframe was identified.

In contrast to stratospheric ozone, ground-level ozone is a short-lived trace gas that originates either through stratosphere −troposphere exchange or produced in situ through implications of precursor gases and solar radiation (Monks et al. 2009). In most of the cases, tropospheric ozone is regulated by various precursor gases like oxides of nitrogen, volatile organic compounds (VOCs), non-methyl hydrocarbons and CO, emitted either naturally or from industries, biomass burning and vehicular emissions (Badarinath et al. 2008; Lal et al. 2008) and topography/altitude (Aneja et al. 1991). There are some reports available on identifying effects of seasonality and precursor molecules on ground-level ozone over IGP which mostly concentrate on establishing prevalence of ozone precursors over the region (Lal et al. 2008) which is additionally forced by conducive synoptic condition and convergence of wind (Beig and Ali 2006). However, in urban agglomerates, photochemical ozone production and its precursor loading are often not linear depending on multiple factors like precursor concentrations, mass ratio of NOx to VOCs and meteorology (Zhang et al. 2004). Both emission profile and variation of ozone are poorly documented over South Asia which fundamentally limits its applications in air and climate models (Beig and Ali 2006). Therefore, efforts were also made to understand implications of meteorological variables and precursor gases in initiating variation of ground-level ozone at two urban stations over middle IGP. Implications of such analysis may well be in improving various climate and urban photochemical models for the concerned geographical region.

Experimental methods

Experimental sites

For the present analysis, two urban centres of middle IGP, namely, Varanasi and Lucknow, were specifically chosen for analysing spatio-temporal variability of ozone concentration (Fig. 1). Varanasi (25° 28′ N and 82° 96′ E; 82.2 m msl), the

Fig. 1 Geographical location of ozone monitoring stations

spiritual capital of India, is situated in the western bank of Gangetic Plain with an estimated area of 225 km^2 and population of 1.19 million (Census 2011). Although the city itself does not possess any significant industrial activity but road dust re-suspension, commercial activities and vehicular exhausts are considered as the dominant sources of pollutants (Murari et al. 2015, 2016). Lucknow, the state capital of Uttar Pradesh, is located at 26° 84' N and 80° 94' E (123 msl) with an estimated population of 2.8 million spread across 310 km^2 of area (Census 2011). Common air pollution in this region mainly constituted emissions from the domestic and vehicular sources, while industrial emissions were relatively less. Both sites characterize the middle IGP in terms of topography, regional climatology and aerosol type without having any specific localized effects of oceans or mountains. Further, regional climatology is mostly governed by synoptic weather pattern while comparatively flat topography simplifies the atmospheric boundary layer.

Regional meteorology

The entire middle IGP is characterized by humid sub-tropical climate with relatively hot and dry summer and cold and humid winter with predominate rainfall only during monsoon. Both the locations ideally represent the characteristic climate variations of the middle IGP. The climate of Varanasi is characterized with high temperature (38.5 to 41.2 °C) during summer (April to June), intense rainfall during monsoon (July to September; 70 % of annual rainfall) and cold during winter (December to February, 8.4 to 15.0 °C). The daily sunshine (summer, 7.2–10.7 h; winter, 6.4–8.7 h) and relative humidity (annual mean, summer 50 %; monsoon 79 %; winter 82 %) profile denote marked seasonal variations while wind speed varied from 1.5 to 7.4 km h^{-1}. Lucknow also experiences wide variation in meteorological parameters with temperature varying from 45 °C in summer to 3 °C in winter with average annual rainfall of 100 cm.

For the current analysis, meteorological data on ambient temperature (*T*), relative humidity (RH), wind speed (WS) and solar radiation (SR) were obtained from Central Pollution Control Board real-time data inventory for Varanasi and Lucknow stations available at public domain (http://cpcb.nic.in/) and were validated with web-based meteorological database (wunderground.com) (Kumar et al. 2015 b, 2017). Atmospheric boundary layer depths (ABL) were obtained from Global Data Assimilation System (GDAS, 1°, 3 hourly) available at NOAA-ARL website (http://www.arl.noaa.gov/ready; Draxler and Rolph 2003; Kumar et al. 2016).

Satellite-retrieved columnar ozone (OMI-DOAS)

The TCO was routinely retrieved from the OMI on board Aura satellite. Launched on 2004 July into a sun-synchronous polar orbit, the OMI on board Aura measures direct and backscattered solar radiation in the UV−visible range and provides early afternoon (local time 13:00–14:30) TCO at a spatial resolution of 13 × 24 km^2 with daily global coverage. The nadir-viewing UV/visible spectrometer has a spectral resolution of 0.63 nm for visible channel (349–504 nm) and about 0.42 nm for the UV channel (307–383 nm) (Buchard et al. 2008). For the present analysis, TCO level 3e global data (OMDOAO3e, Version 003) gridded at 0.25°× 0.25° resolution were selectively retrieved for 11 years (2005–2015) both for Varanasi (25° 28′ N and 82° 96′ E) and Lucknow (26° 84′ N and 80° 94′ E) from the NASA Goddard Earth Sciences Data and Information Service Centre (http://www.esrl.noaa.gov/). TCO data were retrieved using algorithm based on Differential Optical Absorption Spectroscopy (OMI-DOAS) technique developed by Koninklijk Nederlands Meteorologisch Instituut (KNMI, Netherlands). Relative uncertainty on this OMI-DOAS-like product is about 3 % for cloudy days and 2 % for clear days (Veefkind et al. 2006).

Seasonal trend decomposition of OMI-DOAS

Preliminary analysis of temporal evolution of seasonal amplitude in OMI-DOAS ozone concentration exhibited a change over middle IGP which is supposed to be efficiently measured in terms of its decadal trend. The locally weighted regression smoothing technique (Loess) developed by Cleveland (1979) is therefore, used to compute the seasonal and linear trend components of OMI-DOAS ozone observations. The Loess technique has been successfully applied in estimating seasonal trend decomposition (STL, seasonal-trend decomposition using Loess) of a time series data consisting series of applications of Loess smoother with varied moving window widths selected to extract different frequencies within a time series (Carslaw 2005; Cleveland et al. 1990). STL is a versatile and robust method for decomposing time series data into three specific components: trend, seasonal and reminder. Two repetitive algorithms within STL, namely inner and outer loop, progressively apply seasonal smoothing to refine seasonal component followed by smoothing the trend to improve trend estimation. Further its non-parametric nature makes it even more appropriate for non-linear data series.

We used a regression model to understand both the seasonal and linear trend components in OMI-DOAS ozone observation. The time series of monthly averaged ozone concentrations (Ω) for 2005–2015 was assumed to be consisting of three sub-components: time-dependent seasonal component (α), a linear trend (β) and residual or noise (R):

$$\Omega(t) = \alpha(t) + \beta t + R(t) \quad (1)$$

where t represents time (month). Individual months were considered as sub-component of the fitted model; therefore, it appropriately computes variations in seasonal effects. Such advantages make STL essentially an effective statistical tool to estimate seasonality within large dataset. Application of STL has found to be successful in the works of Cleveland et al. (1990), Carslaw (2005) and Lamsal et al. (2015). In line with these methods, seasonal and linear trend components of OMI-DOAS ozone observations were identified and extracted for individual years for two urban stations at middle IGP.

Ground-based columnar ozone (IMD-O_3)

Ground-based columnar ozone (IMD-O_3) was routinely retrieved (only for Varanasi) from the Dobson spectrophotometer installed at Indian Meteorological Department within university campus. The Dobson spectrophotometer works on measuring the relative intensities of selected pairs of ultraviolet wavelengths emanating from the sun, moon or zenith sky. Absorption coefficient of ozone in the Huggins' band in near UV is a changing function of wavelength. The total amount of ozone present in atmosphere in centimetre is given by X.

$$X = \frac{(L_0 - L)}{\mu\,(a - a')} - \mathrm{AC} \quad (2)$$

$$L_0 = \log\left(\frac{I_0}{I'0}\right) \quad (3)$$

$$L = \log\left(\frac{I}{I'}\right) \quad (4)$$

where AC is atmospheric correction and I and I' are the observed intensities of the solar radiation at two UV wavelengths (λ, λ') at the earth surface, while I_0 and $I_0{}'$ are the undepleted intensities at the top of the atmosphere. α and α' are the decimal absorption coefficients per centimetre of ozone (at STP) for λ, λ'. The μ is the relative path length of the solar beam which is considered to be 1 for sun at zenith (Alexander and Chatterjee 1980).

Ground-based TCO data were only monitored at Varanasi and were used to study trend, seasonal variations and relative bias in the satellite observations. TCO has been continuously monitored for 2 years (May 2011−April 2013) for all clear sky conditions. Daily averaged ground-based ozone data for all-sky conditions (average ozone for the day) and specifically during satellite overpass time (13:00–14:30 local time) were computed against the OMI-DOAS-retrieved ozone concentrations. To quantify the agreement between OMI-DOAS and IMD-O_3, bias values were computed for i observation as:

$$\mathrm{Bias} = \frac{1}{n}\int_{i=1}^{n} \frac{\text{OMI-DOAS} - \text{IMD-O}_3}{\text{IMD-O}_3} \times 100 \quad (5)$$

Ground-level ozone and precursor gases

Near-surface concentrations of ground-based ozone and its precursor gases were collected both for Varanasi and Lucknow from Central Pollution Control Board (CPCB) real-time data inventory available at public domain (http://cpcb.nic.in/). The CPCB monitoring station in Varanasi was located at Ardhali bazaar, while for Lucknow, Lalbagh station was selected for data retrieval. For the current analysis, only 24-h average NO and NO_2 mass concentrations were selectively retrieved from September 2014 to August 2015 and daily loading of atmospheric NOx concentrations was computed in terms on NO and NO_2. Annual data coverage was above 78 % for both the stations, while summer (90 %) and monsoon (85 %) were best covered seasons. The 24-h averaged values of individual parameter were recorded, quality checked, sorted out for data unavailability/ abnormality and further used for analysis.

Results and discussion

Comparison of satellite- and ground-based columnar ozone

Both ground-based (IMD-O_3) and OMI-DOAS-retrieved TCO pose certain degree of instrumental errors, while OMI-DOAS is additionally affected by modelling uncertainties which therefore need to be validated (Buchard et al. 2008). However, such validation requires knowledge of atmospheric errors and scale calibration as OMI-DOAS-retrieved ozone represents interpolated information for a relatively larger area. For the current analysis, correlation between ground-based ozone (IMD-O_3) and OMI-DOAS-based TCO was determined for a time period of 24 months (May 2011–April

2013) for all-sky conditions specifically for Varanasi (Fig. 2). Ground-based ozone was typically time averaged one for an entire day while other specifically related to satellite overpass time. Correlation between IMD-O_3 and OMI-DOAS was found to be 0.58 (n = 208; R^2 = 34 %) for satellite overpass time (Fig. 2a) while 0.54 (n = 275; R^2 = 29 %) for daily daytime average ozone values (Fig. 2b). Interestingly, both daily and overpass-averaged ozone concentrations did not exhibit any differences possibly due to insignificant daytime variations of TCO. However, both scatter plots (Fig. 2a, b) indicate possible seasonal influences on interrelation of OMI-DOAS and IMD-O_3. In both instances, columnar ozone during post-monsoon supposed to relate more closely in respect to summer (March–June) and winter (December–February), while monsoon (July–September) was most distantly positioned. Seasonality in TCO comparison was also evidenced by Balis et al. (2007) for validating OMI-DOAS with ground-based Dobson and Brewer spectrophotometer observation. Such discrepancy requires further investigation for proper scientific understanding.

The relative difference between satellite-retrieved (OMI-DOAS) and ground-based (IMD-O_3) daily ozone was further studied through a scatter plot, and a time series depicting points of relative differences ((OMI-DOAS − IMD-O_3) / IMD-O_3, %) is presented in Fig. 3. Only daily averaged ozone data were considered over overpass-averaged value due to similarity of correlation and availability of larger data set. OMI-DOAS observations were found to overpredict the TCO (OMI-DOAS > IMD-O_3) with a positive bias of 7.24 %. In terms of identifying seasonal contribution in differentiating these two observations, bias within individual seasons was computed. Both winter (bias 4.9 %) and post-monsoon (5.5 %)-specific observations were found least deviated in contrast to summer (7.3 %) and monsoon (14.4 %). Validation of OMI TCO measurements using Brewer and Dobson spectrophotometer ground-based observations was made by various researchers. In most instances, TCO profile derived from OMI in comparison to ground-based measurement proved to be stable (Balis et al. 2007; Buchard et al. 2008; Chehade et al. 2014; McPeters et al. 2015; Veefkind et al. 2006; Ialongo et al. 2008), while having dependence on solar zenith angle (Balis et al. 2007; Buchard et al. 2008) and with extreme aerosol loading (Latha and Badarinath 2003; Chehade et al. 2014; Ialongo et al. 2008). An inter-comparison of OMI columnar ozone validation results is mentioned in Table 1, which signify the relative biases were within 2–3 %, while in some cases, it extends to 5–7 %. Overall, a positive bias of 7 % for IGP was computed which was consistent with previous observation (Buchard et al. 2008) while somewhat higher from the estimates reported by Ialongo et al. (2008) and Veefkind et al. (2006). For IGP, these discrepancies may be explained both in terms of boundary layer-absorbing aerosols, solar zenith angle and cloud effects for the region (Ialongo et al. 2008; Chehade et al. 2014). The middle IGP is supposed to be burdened with exceptionally high aerosol loading (AOD_{550} = 0.6 to 1.3; annual $PM_{2.5}$ = 100 ± 29 μg m^{-3}; Murari et al. 2015; Kumar et al. 2015b, 2017; Sen et al. 2016), significant proportions of which are absorbing aerosols with distinct seasonal and diurnal variations. Presence of absorbing aerosols is supposed to interfere on total columnar ozone measurement as observed by Latha and Badarinath (2003) for TOMS-retrieved ozone over Hyderabad, India. Presence of high aerosol loading and change in solar zenith angle may be partly attributed to relatively high bias over OMI-DOAS observation, while marginal seasonal dependency of TCO profile necessitates further understanding.

Trend of columnar ozone at middle IGP

The OMI-DOAS columnar ozone was selectively retrieved for 11 years (2005–2015) for the two urban sites at middle IGP. In the absence of long-term ground monitored data for multiple locations, we had to rely on retrieving TCO (OMDOAO3e, Version 003) gridded at 0.25°× 0.25° which is often proved to be stable (Buchard et al. 2008). With availability of around 88 %, daily TCO was categorized into different seasons and time series ozone concentration is plotted in Fig. 4. Both sites correspond to identical trend with a decadal average (2005–2015) of 276.1 ± 19.9 DU (Varanasi)

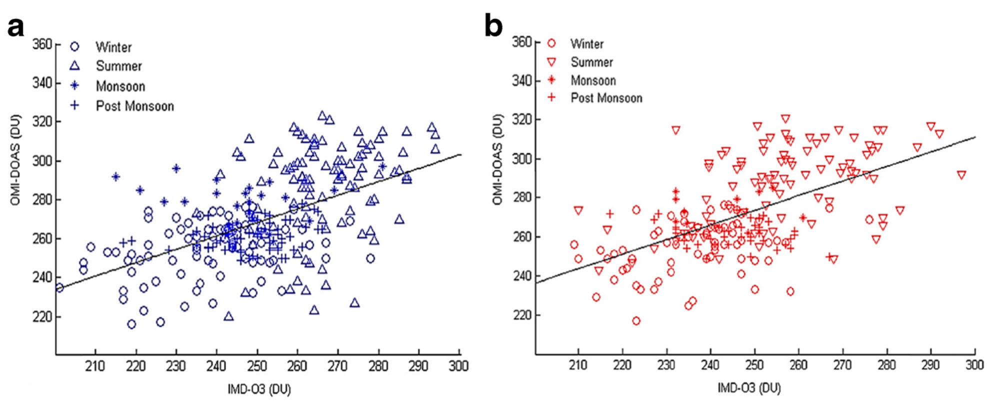
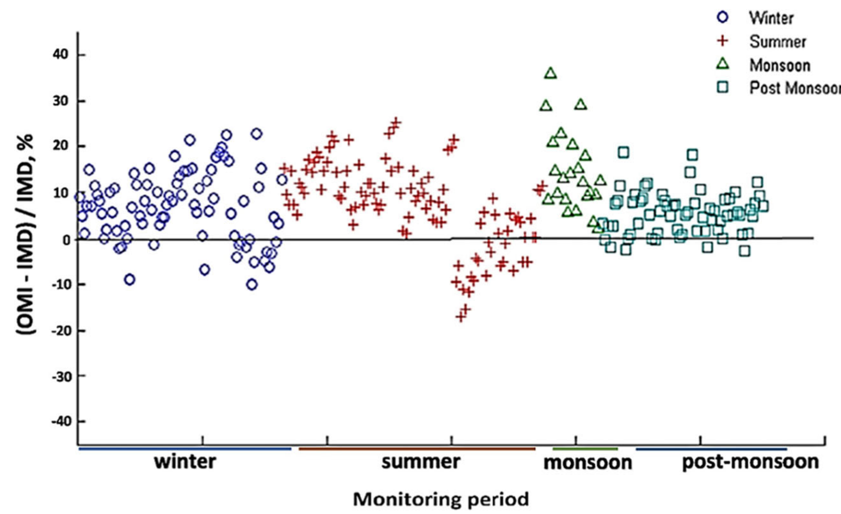


Fig. 2 Comparison of OMI-DOAS and IMD-O_3 in Varanasi. **a** Daily average. **b** Satellite overpass time average

Fig. 3 Relative differences between OMI-DOAS and IMD-O_3 in Varanasi



and 278.8 ± 21.3 DU (Lucknow) having maximum columnar ozone during 2007 (Varanasi, 281.0; Lucknow, 281.5 DU) closely followed by 2015 (Varanasi, 281.0; Lucknow, 283.7 DU) while minimum in 2013 (Varanasi, 269.1; Lucknow, 273.1 DU). Similar kind of observation was noted by Pal (2010) for Varanasi with 5-year seasonal ozone mean of 271.9 DU for 1997–2002 before being reduced to 270.6 DU over 2003–2008.

A consistent and clear seasonal trend in TCO was observed with summer time maximum (Varanasi, 290.9 ± 8.8; Lucknow, 295.6 ± 9.5 DU) which gradually dissipates during winter (Varanasi, 257.4 ± 10.1; Lucknow, 258.8 ± 8.8 DU). However, the rate of winter specific decrease was found to be slightly lower over autumn and monsoon because of variation in sun (zenith) angle. Due to low winter-specific sun zenith angle, most of the UV radiation was unable to destroy the low stratospheric ozone and thereby at lower altitude ozone remained safe from photochemical degradation. Further, ozone-rich air accumulates gradually from March as photolytic reactions starts to facilitate ozone formation in Northern Hemisphere and keeps on increasing till summer end. The decadal average of every single month specifically identifies the month of May (Varanasi, 301.1 ± 9.2; Lucknow, 307.2 ± 10.9 DU) having highest columnar ozone while December–January Varanasi, 301.1 ± 9.2; Lucknow, 307.2 ± 10.9 DU) as lowest (Fig. 5).

Spatial distribution of seasonally weighted OMI-DOAS observations for the year 2013–2015 is plotted in Fig. 6. The region corresponds to the Indian state of Uttar Pradesh (U.P.) which geographically represents major proportion of Indo-Gangetic Plain. Annual averaged OMI-DOAS observation (Fig. 6a) clearly establishes a gradual declining trend from north to south. Such trend corresponds to TCO as function of latitude where relatively high ozone was retrieved towards higher latitude with corresponding lower concentrations in the lower latitude. TCO is also function of solar zenith angle which results in higher ozone production in tropics before being transported towards pole.

Table 1 Inter-comparisons of OMI total columnar ozone validation results

Sl. no.	Station	Parameter	Data period	Relative difference (%)	References
1.	Villeneuve d'Ascq and Briancon, France	OMI-TOMS	October 2004–September 2005	5	Buchard et al. (2008)
2.		OMI-DOAS	October 2004–September 2005	7	Buchard et al. (2008)
3.	Varanasi, India	OMI-DOAS	May 2011–April 2013	7.2	Present study
4.	Rome, Italy	OMI-TOMS	September 2004–December 2006	−1.8	Ialongo et al. (2008)
5.	Rome, Italy	OMI-DOAS	October 2005–December 2006	−0.7	Ialongo et al. (2008)
6.	Global Brewer networks	OMI-DOAS	January 2005−December 2006	2	Balis et al. (2007)
7.	Brewer stations in the Northern Hemisphere	OMI-DOAS	1–16 November 2004	2.9 ± 2.5	Veefkind et al. (2006)
8.	Smithsonian Astrophysical Observatory	OMI-DOAS	2005–2008	−1.22 to −1.75	Bak et al. (2015)
9.	Northern Hemisphere ground-based Dobson–Brewer instruments	OMI-TOMS	2004–2014	1.5	McPeters et al. (2015)

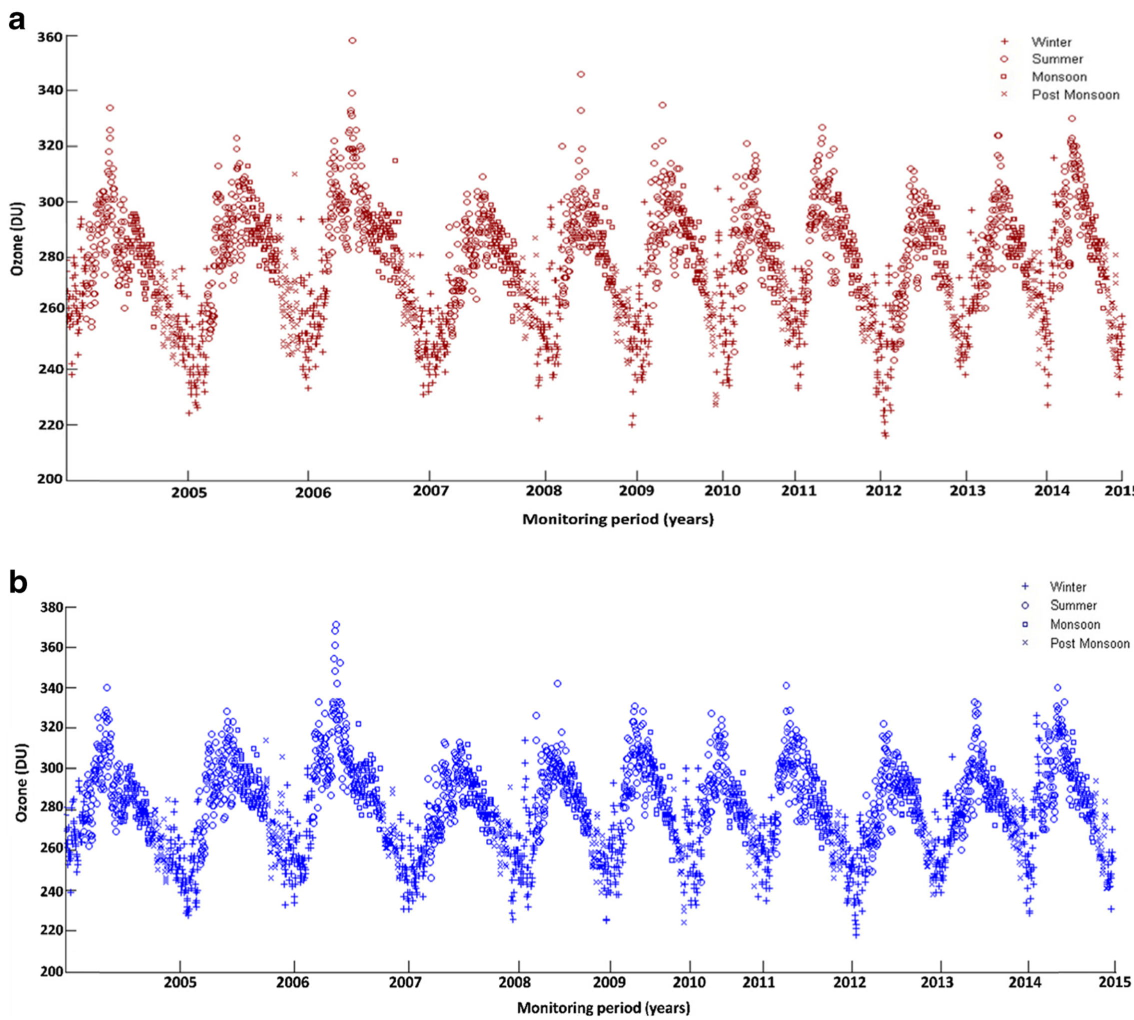


Fig. 4 **a**, **b** Time series of columnar ozone variation over middle IGP during 2005–2015. **a** Varanasi. **b** Lucknow

Interestingly, the trend was found to be valid in different seasons having relatively higher ozone during summer (Fig. 6b, March to June) and lower during winter (Fig. 6d, December to February).

Seasonal trend decomposition of columnar ozone

Temporal evolution of seasonal amplitude in OMI-DOAS monthly TCO was recognized through locally weighted

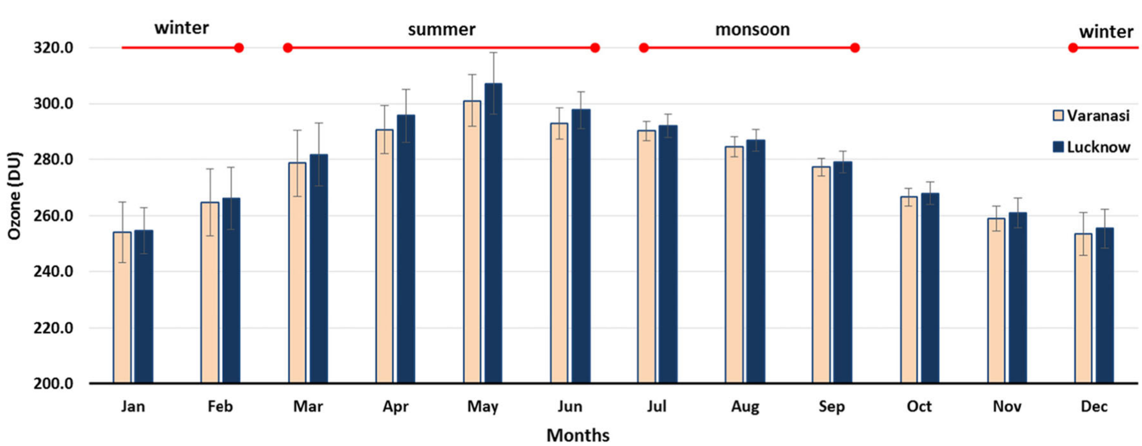


Fig. 5 Variation in 2005–2015 monthly average columnar ozone concentrations over middle IGP

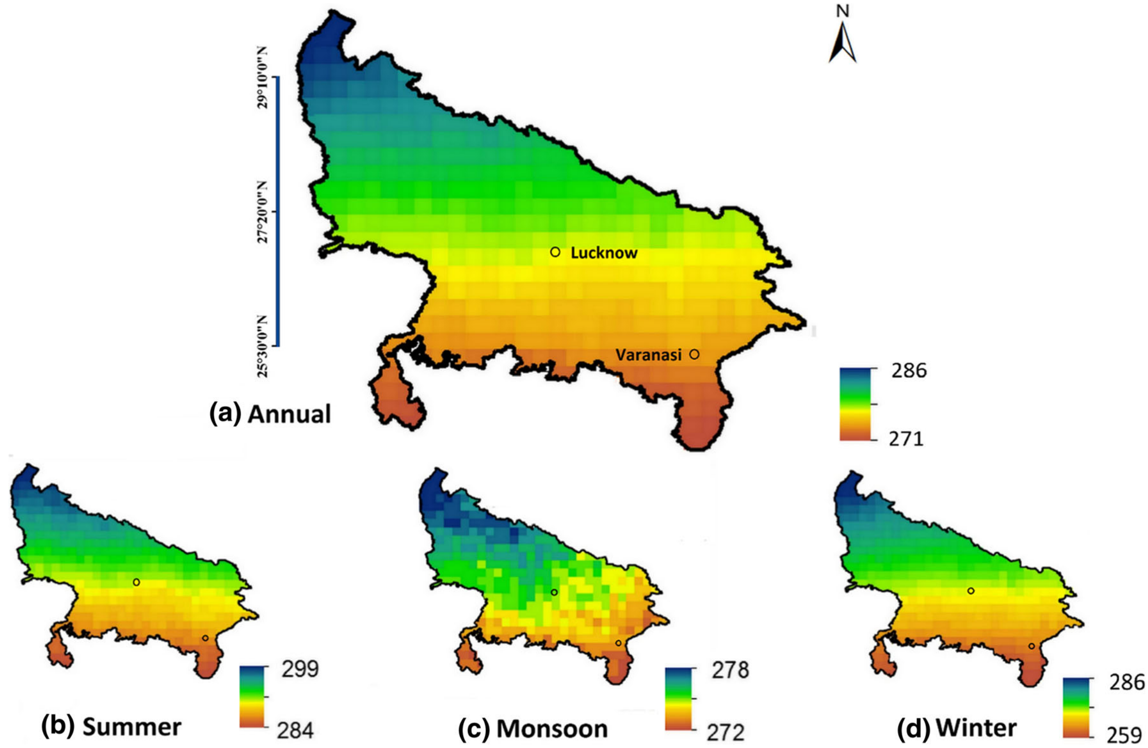


Fig. 6 Spatial distribution of seasonally averaged OMI-DOAS columnar ozone concentrations (DU)

regression smoothing technique. Figure 7a, b shows decomposed series of time-dependent seasonal amplitude, trend and remainder component of columnar ozone for both the sites. Non-linear plot depicts an identical trend for both sites with a moderate increase in TCO during 2005–2015. However, the magnitude of such increase is rather low for both the stations (Varanasi, 0.01; Lucknow, 0.004 DU year^{-1}). The seasonal component of OMI-DOAS ozone concentrations remains the same having a summertime peak around May and a valley during December. Seasonal amplitude was found to be marginally decreased (Varanasi, 0.0084; Lucknow, 0.0096 DU year^{-1}) especially due to reduction in monsoon time minima (Varanasi, 0.19; Lucknow, 0.20 DU year^{-1}) and summertime maxima (Varanasi, 0.02; Lucknow, 0.06 DU year^{-1}). The implications of winter and post-monsoon specific amplitude were rather low and did not overcome the declining trend of summer and monsoon. From all the comparisons, OMI-DOAS columnar ozone profile revealed a relative negative trend of 0.008 to 0.010 DU year^{-1} for the entire IGP. The trend was found to be relatively lower in comparison to values achieved by Pal (2010) (−0.363 DU year^{-1}) for various stations within India and adjoining regions for 1997–2008.

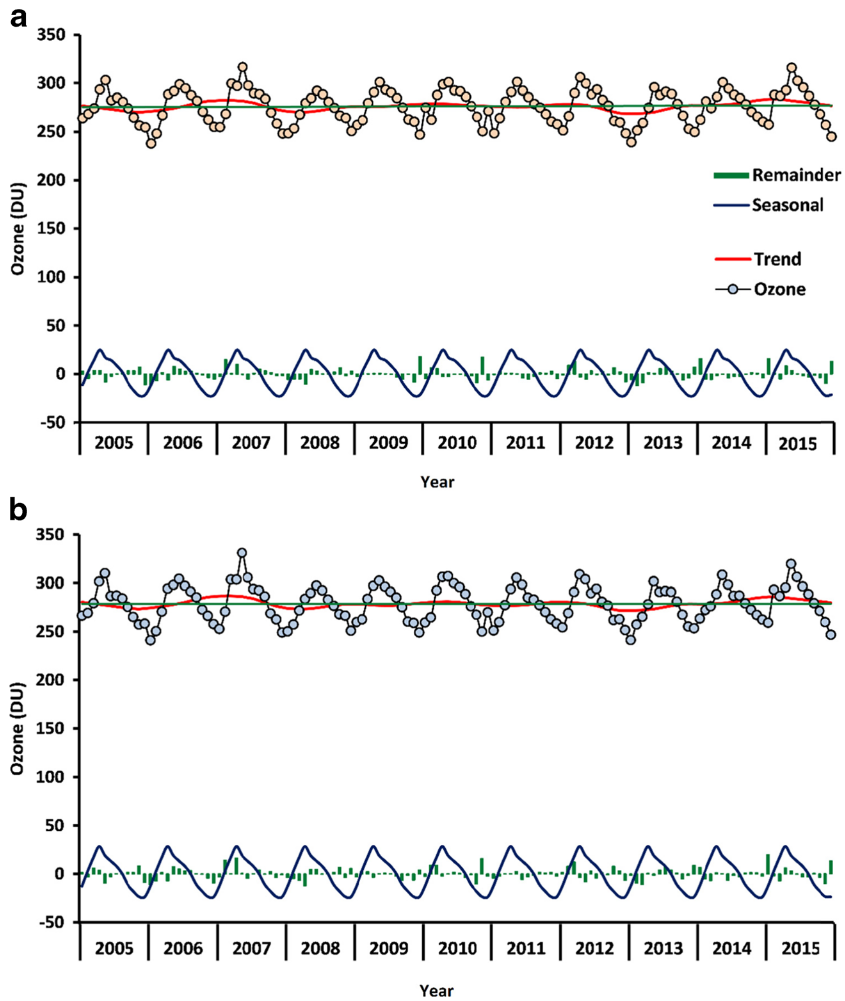
Remainder components or outliers are generally expressed as irregularity, neither explained by trend nor by seasonality. However, certain outliers may be associated with natural or anthropogenic processes which induce chemical and dynamical changes in total ozone (Chehade et al. 2014). For instance, during 2007, summertime TCO peaks over Varanasi (2007 summer, 302.7; decadal summertime average, 290.9 DU) and Lucknow (2007 summer, 311.2; decadal summertime average, 295.6 DU) possibly associated to El Niño–Southern Oscillation (ENSO)-induced air quality changes. El Nino's are well known for causing inter-annual variability of tropical climate and potentially modify the chemistry of trace gases (Chehade et al. 2014). It drives large-scale modification in ocean–atmosphere dynamics causing ozone-rich air to transport from stratosphere to troposphere, causing large-scale increase in ozone concentration. Similar hypothesis was proposed for large-scale increase in columnar ozone (increase of 25 DU) in the tropics during 1997–1998 El Niño event (Fujiwara et al. 1999; Thompson et al. 2001).

Seasonal variations of ground-level ozone

Variations of ground-level ozone with respect to precursor gases (NO_2 and NO) and meteorological parameters (RH, WS and SR) were analysed over middle IGP from September 2014 to August 2015. The entire period was divided into summer (March–June), monsoon (July–September), post-monsoon (October–November) and winter (December–February) to identify seasonal deviation.

Ground-level ozone concentrations over both the stations were identical, while Lucknow represents higher annual mean (44.3 ± 30.6; range, 1.5–309.1 μg m^{-3}) compared to Varanasi (38.5 ± 17.7; range, 4.9–104.2 μg m^{-3}) (Fig. 8). Both the

Fig. 7 **a**, **b** Seasonal decomposition of monthly OMI-DOAS columnar ozone measured in **a** Varanasi and **b** Lucknow (2005–2015). Note: The *circles and green line* represent original time series and linear regression fit, respectively



stations represent seasonal variations with summertime high (Varanasi, 50.1 ± 16.9; Lucknow, 48.5 ± 20.42 μg m^{-3}) and monsoonal low in Varanasi (22.0 ± 6.9) with post-monsoon specific low in Lucknow (30.1 ± 26.3 μg m^{-3}). This signifies the considerable intra-seasonal variation of ground-level ozone over the middle IGP possibly influenced by varying meteorology and precursor concentrations. Likewise, in Varanasi, ozone concentration attained its peak around November (monthly mean, 49.1 ± 8.8 μg m^{-3}) before decline to a lowest during winter (seasonal average, 32.6 ± 14.1 μg m^{-3}) (Fig. 8a). Further, ozone reached its highest during mid-summer around May (63.9 ± 13.7 μg m^{-3}; summertime mean, 50.1 ± 16.9 μg m^{-3}) before declining to a lowest in monsoon (22.0 ± 6.9 μg m^{-3}). In contrast, ozone level at Lucknow revealed pre-winter-specific decline trend (November–December; mean, 14.9 ± 1.3 μg m^{-3}) before increasing to its maximum in winter (January–February; mean, 52.4 ± 53.5 μg m^{-3}) (Fig. 8b). However, for the rest of the seasons, ozone in Lucknow did not correspond to a significant seasonal variation as evidenced over Varanasi. Except post-monsoon-specific low (30.1 ± 26.3 μg m^{-3}), ozone mass ratios were relatively stable both during summer and monsoon. Both stations over middle IGP characterize elevated O_3 levels during summer which may be attributed to higher precursor loading coupled with solar radiation which favours mixing of precursor gases within boundary layer to induce photochemical reactions. Except summer, there were considerable deviations in season-specific ozone level for both the stations. This potentially indicates the significance of conducive micro-environment in regulating heterogeneous chemistry in forming tropospheric ozone over a region. Such observations of ozone formation were well in line of finding as reported by Gopal et al. (2014), Londhe et al. (2008) and Lal et al. (2008).

Influence of precursor gases and meteorology on ground-level ozone

Variations in tropospheric ozone were further analysed in terms of precursor loading and existing meteorology. For both stations, ground-level ozone revealed diverse associations

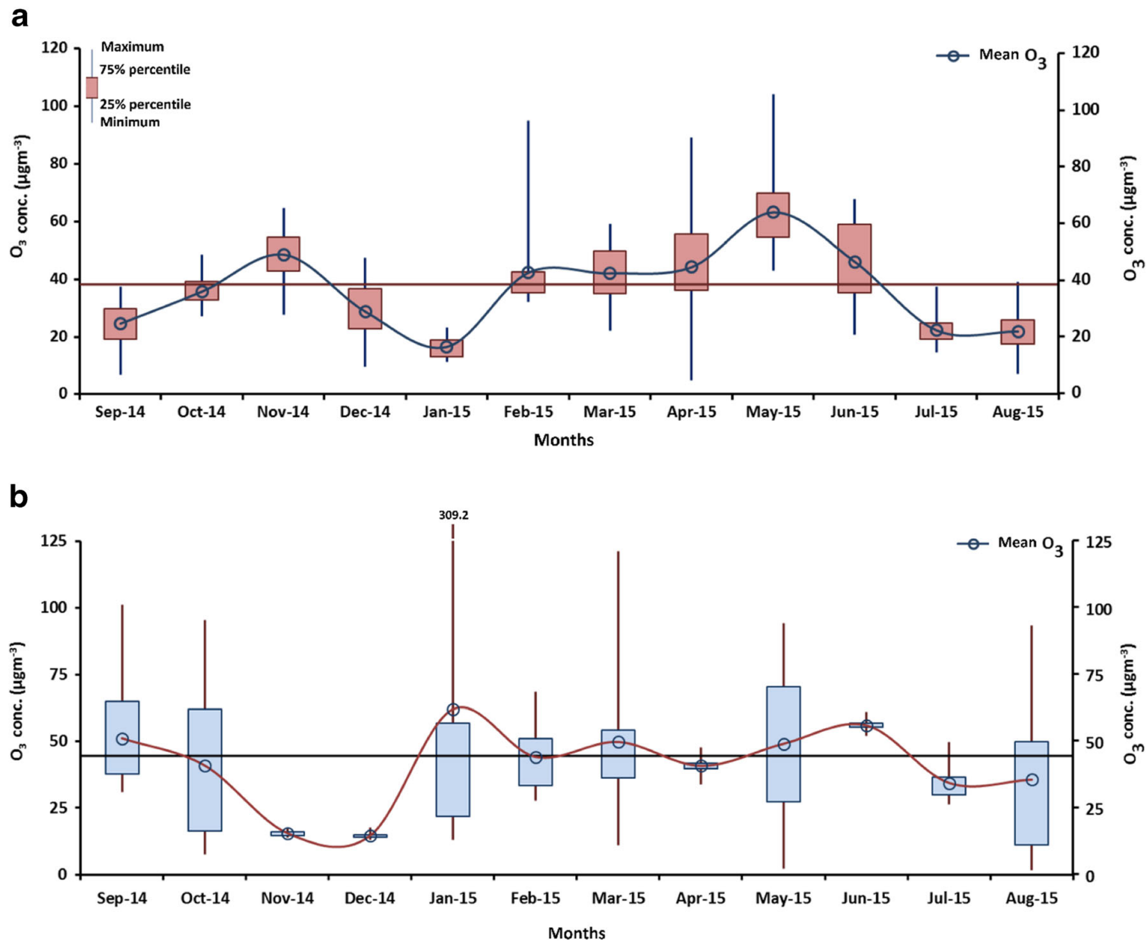


Fig. 8 Monthly variation of ground-level ozone mass ratio in **a** Varanasi and **b** Lucknow

with precursor gases. In principal, generation of tropospheric ozone is a function of precursor loading, intensity of solar radiation, water vapour content and boundary layer height (Gopal et al. 2014; Han et al. 2011). Therefore, changes in any factor may significantly contribute variation in ozone level.

Figures 9 and 10 depict the variations of tropospheric ozone in reference to precursor gas (NOx) and meteorology (ρv, RH, WS, ABL and *T*). During post-monsoon (October–November) in Lucknow, ozone concentration (mean, 30.1 ± 26.3 μg m^{-3}) mostly persists below annual average (44.3 ± 30.6 μg m^{-3}) despite having relatively higher background NOx concentration (mean, 25.1 ± 28.8; annual average, 23.7 ± 16.9 μg m^{-3}). Such abnormalities in ozone concentration may be influenced by periodical rain and high amount of water vapour (mean, 14.3 ± 6.6 g mm^{-3}). Water vapour acts as catalysts for reducing ozone to its surface reactions with OH radicals while simultaneously reacting precursor NOx molecules to convert it into water-soluble HNO_3. In such condition, limited photolytic reactions could take place thus generating less ground-level ozone. In contrast, Varanasi revealed an elevated ozone concentration during post-monsoon (mean, 42.5 ± 9.8 μg m^{-3}) possibly contributed by higher ambient NOx concentrations (average, 71.9 ± 21.6; annual average, 58.0 ± 21.3 μg m^{-3}), increasing boundary layer height (mean, 471.8 ± 121.2 m) and temperature (mean, 23.3° ± 3.3 C) creating conducive environment in building higher ozone concentration (Fig. 9).

As winter approach, ground-level ozone gradually reduced both in Varanasi and Lucknow specifically due to reduced solar intensity and thereby, ambient temperature. In Varanasi, ozone concentration declines from pre-monsoon to form a valley during winter (seasonal mean, 32.6 ± 14.1 μg m^{-3}) despite having relatively high precursor loading (NOx; wintertime mean, 71.5 ± 26.4 μg m^{-3}) possibly due to a decrease in solar intensity (mean, 131.7 ± 49.8 W m^{-2}), temperature (18.4 ± 4.4 °C) and ABL (385.6 ± 120.9 m). Lucknow to an extent resembles the trend of Varanasi having relatively higher ozone values (seasonal mean, 46.2 ± 16.5 μg m^{-3}) with significant level of temporal variation. Such variations are true characteristics of an urban region specifically induced by regional air circulations and short-term meteorological effects (Pudasainee et al. 2006).

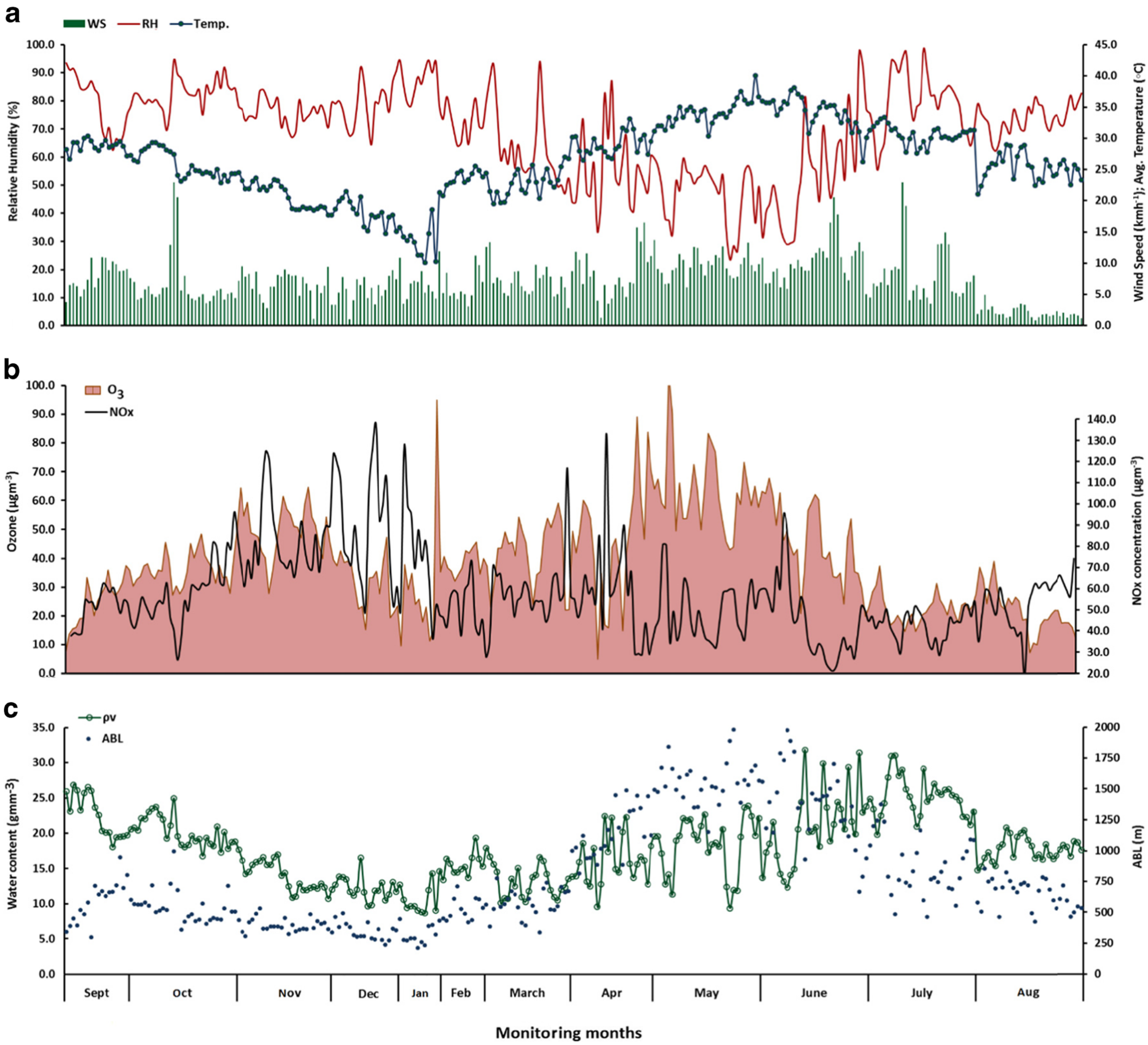


Fig. 9 **a**–**c** Time series of ground-level ozone and precursor gases with meterological variables in Varanasi

Over middle IGP, summers were relatively dry (mean RH; Varanasi, 54.8 ± 15.4 %; Lucknow, 50.8 ± 14.1 %) with comparatively high ambient temperature (Varanasi, 30.6 ± 5.1; Lucknow, 27.8 ± 6.1 °C) favourable for initiating photochemical reactions. Additionally, an increase in boundary layer height (ABL; Varanasi, 1195.4 ± 426.4; Lucknow, 1153.1 ± 434.4 m) facilitates mixing of various precursor gases and thereby, increases the possibilities in ozone formation. Incidentally, such pre-assumptions appeared to be valid for the entire summer over middle IGP as ground-level ozone recorded exceptionally high concentrations for both Varanasi (50.1 ± 16.9 μg m^{-3}) and Lucknow (48.5 ± 20.42 μg m^{-3}). Interestingly, such abruptly high ozone concentrations were evident despite having relatively lower precursor gases in Lucknow (summertime mean, 20.2 ± 7.2 μg m^{-3}) compared to Varanasi (51.9 ± 18.6 μg m^{-3}). This clearly establishes the significance of micro-environment (like meteorology) over precursor gases in generating ground-level ozone. Such observation was in line of finding of Gopal et al. (2014) and Lal et al. (2008).

During monsoon, tropospheric ozone reached its lowest over middle IGP (seasonal mean; Varanasi, 22.0 ± 6.9; Lucknow, 41.1 ± 19.8 μg m^{-3}) due to influence of reduced solar radiation associated with high humidity (Varanasi, 77.1 ± 9.3 %; Lucknow, 76.3 ± 8.1 %). Over both the stations, increased water vapour content (Varanasi, 21.7 ± 4.1; Lucknow, 22.7 ± 4.1 g mm^{-3}) enhanced removal rate of free radical production (wet scavenging), particularly in low NOx environments.

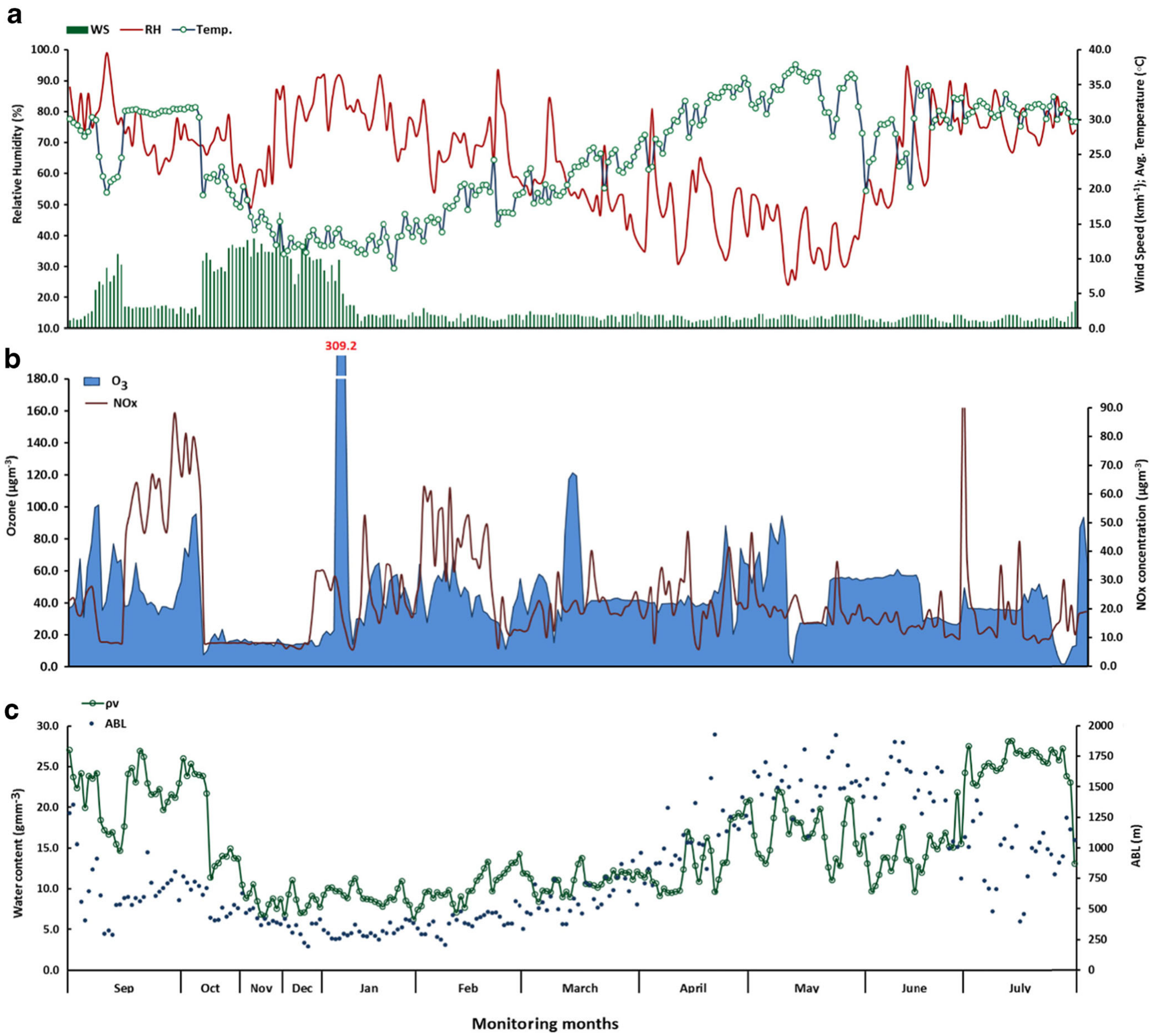


Fig. 10 **a**–**c** Time series of ground-level ozone and precursor gases with meterological variables in Lucknow

Effect of water vapour on ground-level ozone

In lower troposphere, OH molecules play a dominant role in formation and destruction of ground-level ozone. Photolysis of ozone creates $O(^1D)$ which reacts with water vapour to generate OH radicals and causes depletion of O_3 (Pitts and Pitts 2000). Generation of OH radicle in lower atmosphere depends on atmospheric absolute water vapour content (ρv), a function of RH, T and P. The absolute ρv was estimated by the empirical formula given by Nair et al. (2011):

$$\rho s = A\exp\left(18.9766-14.9595A-2.4388A^2\right) \tag{6}$$

where,

$$A = {}^{T_0}/_{(T_0+t)} \tag{7}$$

$$T = T_0 + t \tag{8}$$

$$\rho v = \rho s\left(\frac{\mathrm{RH}}{100}\right)\left[1-\left(1-\frac{\mathrm{RH}}{100}\right)\left(\rho s\, R_v \frac{T}{P}\right)\right]^{-1} \tag{9}$$

Here, ρs is the saturation density of water vapour at ambient temperature, T^0 is 273.15 K, t is temperature in degrees Celsius, R_v is the gas constant for water vapour (4.615×10^{-3} mbar g m^{-3} K^{-1}) and P is atmospheric pressure (mbar).

In heterogonous chemistry, water vapour behaves as a catalyst, which facilitates destruction of ground-level ozone concentration through generation of OH radicles. However, implications of water vapour in regulating ozone depends on multiple factors, like boundary layer height, solar radiation and loading of precursor gases. In a controlled environment, water vapour and ground-ozone develop contrasting pattern having considerable diurnal variation (Fig. 11a, b). In the current analysis, annual mean water vapour for both the stations was identical (Varanasi and Lucknow 17.8 ± 5.0 and 15.3 ± 6.1 g mm^{-3}, respectively) with considerably high loading during monsoon (21.7 ± 4.1 and 22.7 ± 4.1 g mm^{-3}) before being reduced to a minimum in winter (12.7 ± 2.7 and 9.5 ± 1.7 g mm^{-3}). In Varanasi, considerable negative correlation (−0.24, n = 284) was found between water vapour and ozone with high level of seasonality (post-monsoon, −0.67; monsoon, −0.12; summer, −0.06). For all the instances, correlation was found to be negative signifying implications of water vapour in destroying tropospheric ozone which is identical as recorded by Gopal et al. (2014) for ground-level ozone at Anantapur, India. Photolysis of ozone generates O(^{1}D) which subsequently reacts with water vapour to produce OH radicle, thus causing depletion of ozone.

Water vapour also denotes negative association (r = −0.52, n = 284) with precursor NOx concentrations which suggest the contribution of OH radicle in regulating NOx in lower atmosphere. Presence of significant amount of OH molecule in lower atmosphere possibly transforms NO_2 to HNO_3 and thereby facilitates its wet removal from atmosphere (Seinfeld and Pandis 2006). However, the level of association was poor for Lucknow.

Effect of boundary layer on ground-level ozone

Boundary layer is a function of solar radiation, temperature, topography and local wind, and therefore, variation in any parameter may consequently modify the ABL. For the current analysis, relatively flat topography within middle IGP simplified the planetary boundary layer structure (Kumar et al. 2016; Sen et al. 2016). For both stations, ABL denoted significant seasonal variations with very low ABL during winter (Varanasi, 385.6 ± 120.9; Lucknow, 353.9 ± 79.3 m) and post-monsoon conditions (Varanasi, 471.8 ± 121.2; Lucknow 516.1 ± 126.0 m) before gradually alleviated during summer (Varanasi, 1195.4 ± 426.4; Lucknow, 1153.1 ± 434.9 m) (Fig. 11a, b).

The implication of boundary layer height on ozone variation was found to be high for both the stations (r; Varanasi, 0.59; Lucknow, 0.32). Analysis reveals that the interaction was overall positive suggesting an increase in formation of ground-level ozone with corresponding increase in ABL. That was according to expectations as relatively high ABL

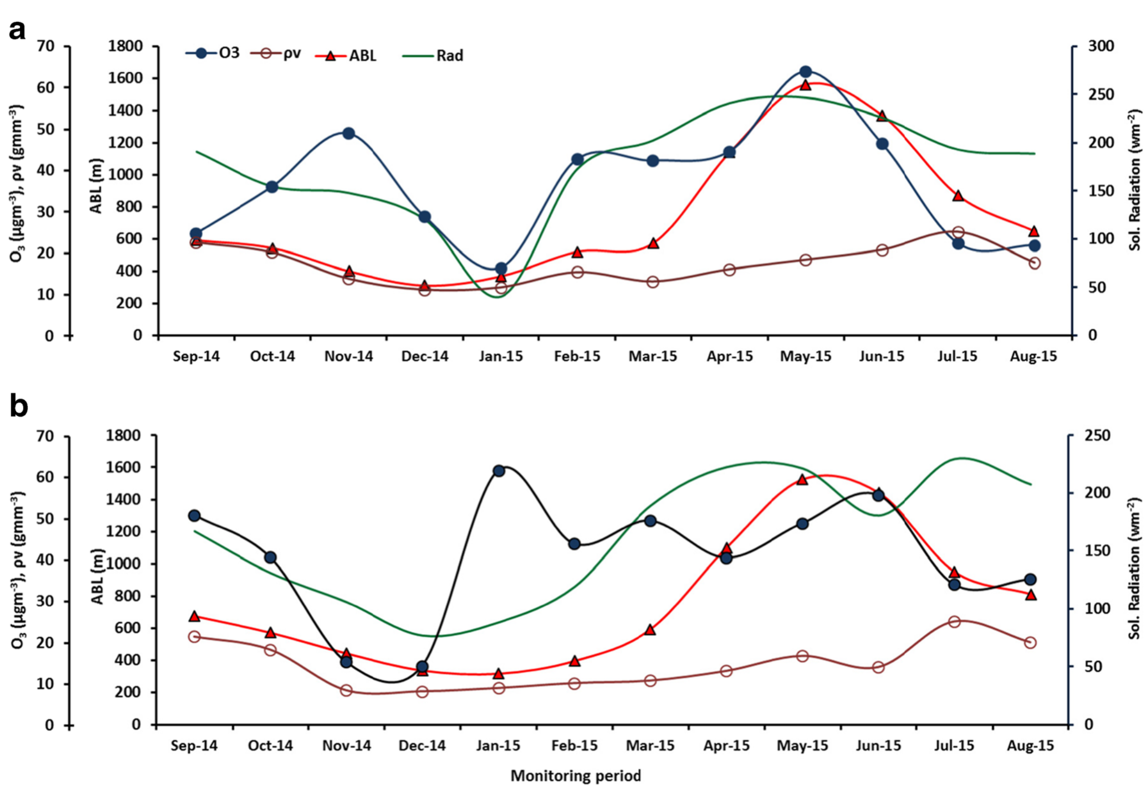


Fig. 11 Implications of meteorological variables on ground-level ozone in **a** Varanasi and **b** Lucknow

is generally associated with more intense solar radiation and light wind, which facilitate proper mixing of ozone precursors and thereby develop conducive environment for generation of ground-level ozone. Likewise during summer, very high ABL within the region was associated with considerably high ground-level ozone (Varanasi, 50.1; Lucknow, 48.6 μg m^{-3}) concentrations. However, this association is not universal as ABL is not supposed to solely regulate ozone formation and variation in ABL possibly induce diverse implications in tropospheric chemistry. Thereby, despite having minimum ABL heights during winter, both locations exhibited considerably high ground-ozone concentrations (Varanasi, 32.6; Lucknow, 46.2 μg m^{-3}). Implication of boundary layer on ozone was also identified by Gopal et al. (2014), where higher ABL corresponding with high ozone was found during summer and pre-winter months.

Interestingly, despite having relatively shallow ABL heights (Varanasi, 400.4; Lucknow, 315.5 m) and identical meteorological conditions, two distinct sharp peaks in ground-level ozone were observed, one during November (for Varanasi, O_3 49.1 μg m^{-3}) and other in January (for Lucknow, O_3 61.8 μg m^{-3}). Such abnormalities may well be explained by corresponding increase in precursor gas concentrations (NOx; Varanasi, 85.0; Lucknow, 24.4 μg m^{-3}), which consequently generate elevated levels of ozone over the region.

Effect of solar radiation on ground-level ozone

Stratospheric ozone is formed through UB-B (280–315 nm)-induced photolytic decomposition of oxygen molecule, especially in tropical stratosphere, while ground-level ozone is the function of precursor gases facilitated through local meteorological conditions.

Solar radiation intensity has a direct impact on dynamics of precursor gases and pathways for the ozone formation (Pudasainee et al. 2006; Han et al. 2011). Annual average solar radiation in Varanasi and Lucknow was 189.0 ± 62.8 and 171.5 ± 63.5 W m^{-2}, respectively. Solar radiation denoted seasonal variations (Fig. 11) with minimum insolation during winter (Varanasi, 131.7 ± 49.8; Lucknow, 100.1 ± 33.1 W m^{-2}) and post-monsoon (Varanasi, 151.2 ± 42.5; Lucknow, 120.4 ± 45.5 W m^{-2}) before gradually increased in summer (Varanasi, 229.7 ± 52.9; Lucknow, 204.0 ± 40.5 W m^{-2}). Monthly means of ground-level ozone were found to be positively correlated with solar radiation (Varanasi, 0.60; Lucknow, 0.26) with level of association varying according seasons. Maximum insolation was found within the summer months which also corresponded to maximum ground-level ozone (Varanasi, 50.1; Lucknow, 48.6 μg m^{-3}). Exemplifying summer in Varanasi, intense solar radiation, elevated ABL (ABL, 1195.4 m) and high background NOx loading (NOx, 51.9 μg m^{-3}) promote photo-oxidation of precursor molecules which subsequently enhanced ozone formation. Further, elevated insolation reduces the relative humidity of the atmosphere, thereby increasing residence time of ozone. In contrast during winter, solar radiation gradually declines (Varanasi, 131.0; Lucknow, 100.1 W m^{-2}) so the formation of tropospheric ozone (Varanasi, 32.6; Lucknow, 46.2 μg m^{-3}). A strong and significant positive correlation was accounted between insolation and ozone formation for both summer (r = 0.30) and winter (r = 0.48) seasons in Varanasi, while the levels of association were poor for Lucknow.

Conclusions

Ozone concentrations both in terms of columnar and at ground level over the middle Indo-Gangetic Plain were analysed. Initially, satellite-retrieved columnar ozone was validated using measured ground-based dataset (2011–2013) and bias associated with satellite observation was measured in terms of seasonality. Both daily daytime and satellite overpass time-averaged TCO for all-sky conditions were compared with ground-based observations. The seasonal trend decomposition technique was further applied to monthly TCO (2005–2015) which provided insight into the regulating factors of seasonal ozone cycle and trends over middle IGP. Further, spatio-temporal variation in ground-level ozone concentrations in reference to regional meteorology and precursor gases was analysed. Implications of such analysis may well be in improving various climate and urban photochemical models for the concerned geographical region. Specific scientific findings of the investigation may be summarized as follows:

1. The comparison between satellite-retrieved (OMI-DOAS) and ground-based (IMD-O_3) TCO revealed agreement with minor variation between daily daytime (r = 0.54; R^2 = 29 %; n = 275) and satellite overpass time (r = 0.58; R^2 = 34 %; n = 208) averaged value. This signifies insignificant daytime variations of TCO within the region.
2. OMI-DOAS observations were found over predicting TCO (OMI-DOAS > IMD-O_3) with a positive bias of 7.24 % under all-sky conditions with varying seasonal influences.
3. A consistent and clear seasonal trend in columnar ozone for baseline air from 2005 to 2015 was observed with summertime maxima and minima during winter. Columnar ozone was also found as a function of latitude where consistently high ozone values were retrieved towards higher latitude.

4. Seasonal component of OMI-DOAS TCO was found to be marginally decreased throughout the time series (Varanasi = 0.0084; Lucknow = 0.0096 DU year^{-1}) especially due to reduction in monsoon time minima and summertime maxima.
5. During 2007 summer, an increase in TCO (11.8–15.6 DU) was associated to ENSO which induce large-scale modification in atmospheric trace gas chemistry and in ocean–atmosphere dynamics.
6. Ground-level ozone (September 2014 to August 2015) registered considerable variation in both sampling locations over middle IGP with Lucknow representing slightly higher annual mean over Varanasi.
7. Ground-level ozone also represents significant seasonal variation with summertime high and monsoonal low. However, the trend was varied in terms of its peaks/troughs.
8. Variation in ground-level ozone was further explained in terms water vapour, atmospheric boundary layer height and solar radiation. Presence of conducive meteorology was found a limiting factor in ozone formation as there were evidences in high ozone formation despite of low NOx and low ozone formation in spite of high NOx conditions.
9. Implication of boundary layer on ground-level ozone was found high for both the stations (*r*; Varanasi, 0.60, Lucknow, 0.32). However, association of ABL with ozone poses low level of uncertainty under varying meteorological conditions and therefore requires further investigation. Solar radiation intensity revealed positive association with ground-level ozone at both the stations.

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