J Atmos Chem (2015) 72:143–164
DOI 10.1007/s10874-015-9311-7

Trace gases at a semi-arid urban site in western India: variability and inter-correlations

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Received: 17 July 2014 / Accepted: 15 June 2015 /

Abstract Continuous measurements of O_3, CO, NO_x and SO_2 were made in Ahmedabad, a semi-arid, urban region in western India, during May-October, 2011 to study their levels, variability and inter-relationships during this period of changing meteorological conditions. The levels of CO and SO_2 observed in Ahmedabad were in general not very high compared to other major urban regions in India. On the other hand, NO_x levels, impacted by vehicular emissions, were found to be substantially elevated. However, these values are still lower than levels in megacities like Beijing, Hong-Kong, Mexico etc. A sudden increase in trace gas levels was observed during post-monsoon months due to a concurrent change in prevailing winds. The levels, variability as well as diurnal amplitudes for all the gases were particularly high during October. While the primary pollutants were negatively correlated with wind speed, O_3 interestingly showed a positive association. Low slope and relatively lower correlation between O_3 and CO in Ahmedabad indicate incomplete photochemical processes in the ambient air. Despite an overall inverse relationship between O_3 and NO_x, daytime O_3 was found to be positively correlated with night-time NO_x as well as night-time CO. Levels of CO, NO_x and SO_2 showed unique relationships with wind direction depending on source locations. Low CO-NO_x slope for Ahmedabad indicate relatively fresh emissions from local sources. SO_2 values as well as SO_2/NO_x ratios were higher when wind was from the eastern sector of the city, which contains a thermal power station and a few industrial clusters. The SO_2/NO_x slope for point sources in Ahmedabad is estimated to be 0.4 while for mobile sources, it is 0.026.

Highlights
1. Simultaneous study of O_3, CO, NO_x and SO_2 over Ahmedabad.
2. O_3 and CO relationships over Ahmedabad indicate incomplete photochemical processes.
3. High SO_2 and SO_2/NO_x in air masses in north-east of study site indicate coal burning.

Electronic supplementary material The online version of this article (doi:10.1007/s10874-015-9311-7) contains supplementary material, which is available to authorized users.

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Keywords Trace gases · Sulfur dioxide · Meteorology · Local emissions · Point sources

1 Introduction

Anthropogenic emissions of trace gases have been increasing during the last few decades, particularly over the Asian region (Ohara et al. 2007; Lu et al. 2011 and references therein), and are projected to increase further. These emissions are leading to local and regional air quality issues. Further, they have been associated with perturbation of regional and global climate (Jacob and Winner 2009) with potential impact on biogeochemical cycling of various elements, monsoon systems etc. The impacts of these emissions on air quality and climate can be direct as well as indirect (through formation of secondary species). Atmospheric levels of some of the climatically and biogeochemically important secondary species, ozone(O_3), secondary organic aerosols (SOA) etc. are influenced by primary emissions of carbon monoxide (CO), nitric oxide (NO), sulfur dioxide (SO_2), volatile organic compounds (VOCs), particulate matter (mainly $PM_{2.5}$) etc. Due to important consequences of these primary and secondary gases and aerosols to atmospheric chemistry, environment and climate, their monitoring has become necessary, over regions of different climatic regimes. In this perspective, trace gas and aerosol measurements over major urban regions assume significance because of potentially large fluxes and consequently more severe impacts on air quality and atmospheric chemistry. Studies estimate an increase in surface O_3 by 1–10 ppbv over urban areas due to climate change (Jacob and Winner 2009).

Despite being a pre-dominantly agricultural country, about 32 % of Indian population lives in urban areas (http://data.worldbank.org/indicator/SP.URB.TOTL.IN.ZS). Although the largest population densities in India are found along the Indo-Gangetic Plain (IGP) and eastern coastal regions, the western part of India (Gujarat and Maharashtra) is more industrialized (Table 2.1 of ASI 2008–09). A part of this region, the Golden corridor, contains the maximum number of large point sources (LPS) in India. At the national level, LPS are responsible for more than 65 % emissions of carbon dioxide (CO_2) as well as SO_2 (Garg et al. 2002). They also contribute significantly to nitrogen oxides (NO_x: $NO+NO_2$) emissions. The energy consumption in India is mainly attributed to four sectors: power, industries, residential and transport. The power and industry sectors are mainly driven by coal/lignite, the residential sector by biofuel/LPG and the transport sector by oil (petroleum products: diesel and gasoline/petrol) and natural gas (mainly LPG). The national consumptions of coal, lignite, LPG, gasoline, diesel and heavy fuel oil were 532, 38, 8, 26, 78 and 20 MT respectively during 2011. The SO_2 emissions in India were estimated at 8.8 Tg for 2010 with 5.8 Tg from power sector and 2.8 Tg from industries. Among this, coal and oil contributed 76 and 19 % respectively to the national SO_2 emissions (Lu et al. 2011). For NO_x emissions, the road and power sectors constitute 34 and 31 % respectively (Garg et al. 2006). Further, biomass burning accounts for 13 % of NO_x emissions in India. CO emissions in India are dominated by the residential sector, contributing about 86 % and constituted mainly by biofuel burning. The transport sector contributes about 13 % of CO emissions in India. Between 1971 and 2011, the energy production in India has compounded at a rate of more than 4 % per annum (pa) for coal, lignite and petroleum and more than 9 % pa for natural gas (Energy Statistics 2012). During this period, thermal power generating capacity has grown at a compounded rate of 6.45 pa, totaling 0.2 million MW in 2011. This energy scenario is the direct cause of increasing emissions of climatically and radiatively important trace gases over the Indian region. It also has implications to secondary species like O_3, which have direct impact on climate (greenhouse effect), environment (effects on vegetation and health) and atmospheric chemistry (budget of hydroxyl radical; OH).

In the present study, we are reporting simultaneous measurements of O_3, CO, NO_x and SO_2 over a semi-arid, urban region in western India during May to October, 2011. These measurements were made with a view to study levels and variability of these gases during this period of changing transport patterns (wind regimes) over a representative urban site in western India. Another important objective was to study emission characteristics of trace gases in this highly industrialized part of India. At this point, it is pertinent to mention that the seasonal and diurnal variations of O_3, CO and NO_x over Ahmedabad were also discussed in a previous study (Lal et al. 2000). However, the data is quite old: O_3 measurements were for the period 1991–95 while CO and NO_x were measured during 1993–96. Between then and now, there have been a lot of changes over Ahmedabad including vehicular and industrial growth. The population of Ahmedabad has increased from about 3.3 million in 1991 to about 6.3 million in 2011. Further, the CO data in Lal et al. (2000) were derived using gas chromatographic technique, hence the conclusions were based on limited data. Moreover, inclusion of SO_2 in the present study helps us to derive more information on emission sources in and around the city.

2 Methodology

2.1 The study location and general meteorology

The study was conducted at Ahmedabad (23.03°N, 72.58°E, 53 m AMSL), the fifth largest city of India with a population of 6.3 million (Fig. 1). Ahmedabad has more than 2 million

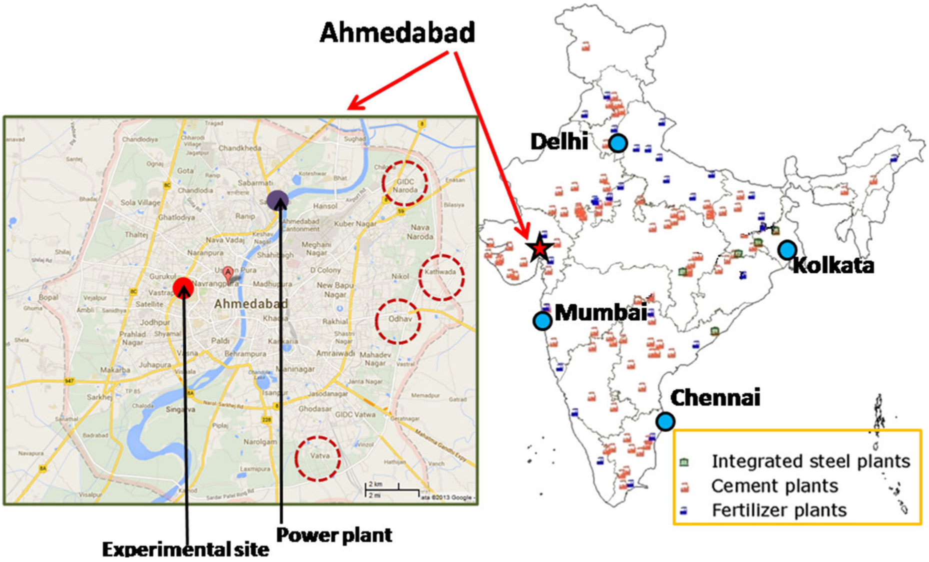

Fig 1 Right panel: Map of India showing major cities and industries. Left panel: The Ahmedabad city map shows industrial areas (dotted circles) to the east of the study location. The major power plant in Ahmedabad is the Sabarmati Thermal Power station (411 MW), about 10 km in the north-east of the study location (marked in Figure). Additionally, a Combined Cycle Dual Fuel Power Plant (100 MW) is located at Vatva (region encircled in the south-east of the Ahmedabad map)

registered motor vehicles which is growing at about 10 % per annum. The western part of Ahmedabad is developed as a residential area and the eastern part as an industrial area. The city has two power plants: the Sabarmati Thermal Power station (411 MW) and a Combined Cycle Dual Fuel Power Plant at Vatva (100 MW). The Sabarmati power plant is about 10 km in the north-east of the study location (Fig. 1). Major industrial clusters of Ahmedabad are located in the east of the city and include textiles, dye, casting and forging, power driven pumps etc.

Ahmedabad has a hot, semi-arid climate. The city receives about 750 mm rainfall during June-August (monsoon) with maximum in July (average: 247 mm) and August (average: 288 mm). Among the pre-monsoon months (March-May), the climatologically hottest daytime temperature occurs during May (mean: 41.5 °C). During May 2011, the maximum temperature recorded was above 43 °C. Further, Ahmedabad receives maximum sunshine hours during May (>300 h). While average relative humidity (RH) during May and June, 2011 was below 50 %, it increased to above 85 % during July and August. The wind speed and direction during the study period are shown in Supplementary Fig. 1. In general, wind speeds are higher during pre-monsoon (>1.5 m/s during daytime) while they are lower during monsoon and post-monsoon (September-November). The wind direction is mainly westerly during pre-monsoon and monsoon. Reversal of winds takes place during late September when the north-east component increases. The wind becomes entirely north-easterly during October.

2.2 Experimental details

Continuous in-situ measurements of trace gases were conducted using on-line analyzers from Thermo Scientific [O_3 (49i), CO (48i-TLE), NO_x (42i-TL) and SO_2 (43i-TLE)]. Ambient air is drawn through a 2 m long perfluoroalkoxy (PFA) Teflon tubing (5 mm ID) into a glass manifold using a small pump. The O_3 instrument drew sample air directly from this manifold through a 3 m long heated inlet tube. The CO, NO_x and SO_2 analyzers drew the same air from the manifold through an additional Peltier-based moisture removal unit. This set-up was designed to prevent loss of O_3 in the peltier unit. PTFE (polytetrafluoroethylene) filters (5 μ; Sartorius AG, Germany) were placed at the inlet of each analyzer to remove dust and particles. The residence time in the manifold and tubing is assumed to be negligible due to a suction of about 2.5 l/min generated by the four analyzers.

The UV photometric O_3 gas analyzer works on the standard principle of absorption of radiation at 253.7 nm by atmospheric O_3. The CO analyzer is based on gas filter correlation technology and operates on the principle of infrared absorption at 4.67 μm vibration-rotation band of CO. The NO_x analyzer is based on the detection of chemiluminescence produced by the oxidation of NO by O_3 molecules, which peaks at 630 nm radiation. Since the method is specific to NO only, NO_2 is measured by the same instrument by converting it into NO using a molybdenum convertor and then measuring total NO_x as NO. Unfortunately, the reduction of NO_2 to NO is not specific for NO_2 and other nitrogen species viz. peroxyacyl nitrate (PAN), HNO_3 and organic nitrates/nitrites can also be reduced to NO and act as interferences in the NO_2 measurement. Nevertheless, the actual concentrations of NO_2 and therefore NO_x may be lower. The SO_2 analyzer is based on UV fluorescence wherein SO_2 is excited using 214 nm and a band pass filter centered around 350 nm is used to collect the fluorescence.

Calibration checks for zero and span (single point) for all the analyzers were performed on a regular basis. Zero air was produced from a Ecophysics zero air generator (PAG003), which is able to scrub the gases below detection limit of the analyzers. For span calibration checking, the respective calibration gases (1995 ppbv CO in N_2, 507 ppbv NO in N_2, 510 ppbv NO_2 in N_2 and 471 ppbv SO_2 in N_2) were directly passed (using a tee setup to maintain atmospheric pressure) through the respective analyzers for 15 min each. The span calibrations were done using National Physical Laboratory (UK) traceable calibration mixtures from Intergas (International Gases & Chemicals), UK. Multi-point calibrations were done fortnightly. Also, the O_3 instrument was calibrated periodically with a traceable O_3 generator (Sonimix 3001, LN Industries, Geneva, Switzerland).

3 Results and discussion

3.1 Diurnal and seasonal variations

Diurnal variations of O_3 in Ahmedabad are characterized by a distinct noon-time peak (Fig. 2a). The peak is attributed to photochemical formation and is a characteristic of urban regions. Immediately after sunrise, O_3 concentrations start to build up due to the photo-oxidation of the precursor gases such as CO, CH_4 and NMHCs in presence of sufficient amount of NO_x. Being an urban site, NO levels (>100 pptv) in Ahmedabad are above the threshold level for O_3 production (about 10 pptv, Lal et al. 2000). A typical reaction for O_3 formation in the atmosphere by photo-oxidation of CO is shown in Eq.1.

$$CO + 2O_2 + h\nu \rightarrow CO_2 + O_3 \tag{1}$$

During this process NO_x acts as a catalyst until it is permanently removed by various physical processes (e.g., surface deposition) or transformed to other NO_y compounds (sum of all oxidized nitrogen species, mainly comprised by NO_x, NO_3, N_2O_5, HNO_2, HNO_3, HNO_4, PAN and its analogs, non-peroxy organic nitrates, halogen nitrogen species and particulate nitrate). O_3 formation also takes place through CH_4, NMHCs etc. with about 3.5 -14 times higher O_3 yields per cycle compared to CO (Lal et al. 2000). Apart from photochemistry, dynamical and meteorological parameters also play crucial role in controlling O_3 diurnal variations. Lower O_3 during nighttime (the 50th percentile night-time O_3 is 15 ppbv) is attributed to inhibition of photochemical production, titration of O_3 by surface emissions of NO in a suppressed boundary layer (the 50th percentile of night-time NO_x is 7.9 ppbv) and loss due to surface deposition. The diurnal amplitudes (difference between maximum and minimum concentrations during a 24 h cycle) in O_3 are highest for October and lowest for August (Table 1). Suppressed diurnal variation during August is a result of lower sunshine hours implicated by cloudy conditions. The sharp increase in diurnal amplitude in O_3 during October is attributed to higher levels of precursors (CO, CH_4 and NMHCs) in the study location. Further, being in close proximity to the Thar desert, and itself being a semi arid region, mineral dust could play a major role towards O_3 losses. Interactions of N_2O_5, O_3, and HO_2-radicals with dust are found to affect the photochemical oxidant cycle, and can cause up to 10 % reductions in O_3 in and nearby the dust source areas (Dentener et al. 1996). Further, the increase rate of O_3 between its night-time minima (0000–0300 IST) and peak photochemical formation period (1300–1600 IST) is highest for October (Table 1). The increase rate is indicative of the O_3 formation potential during a day. The present rates are higher compared to the observations during 1991–95 (Table 1).

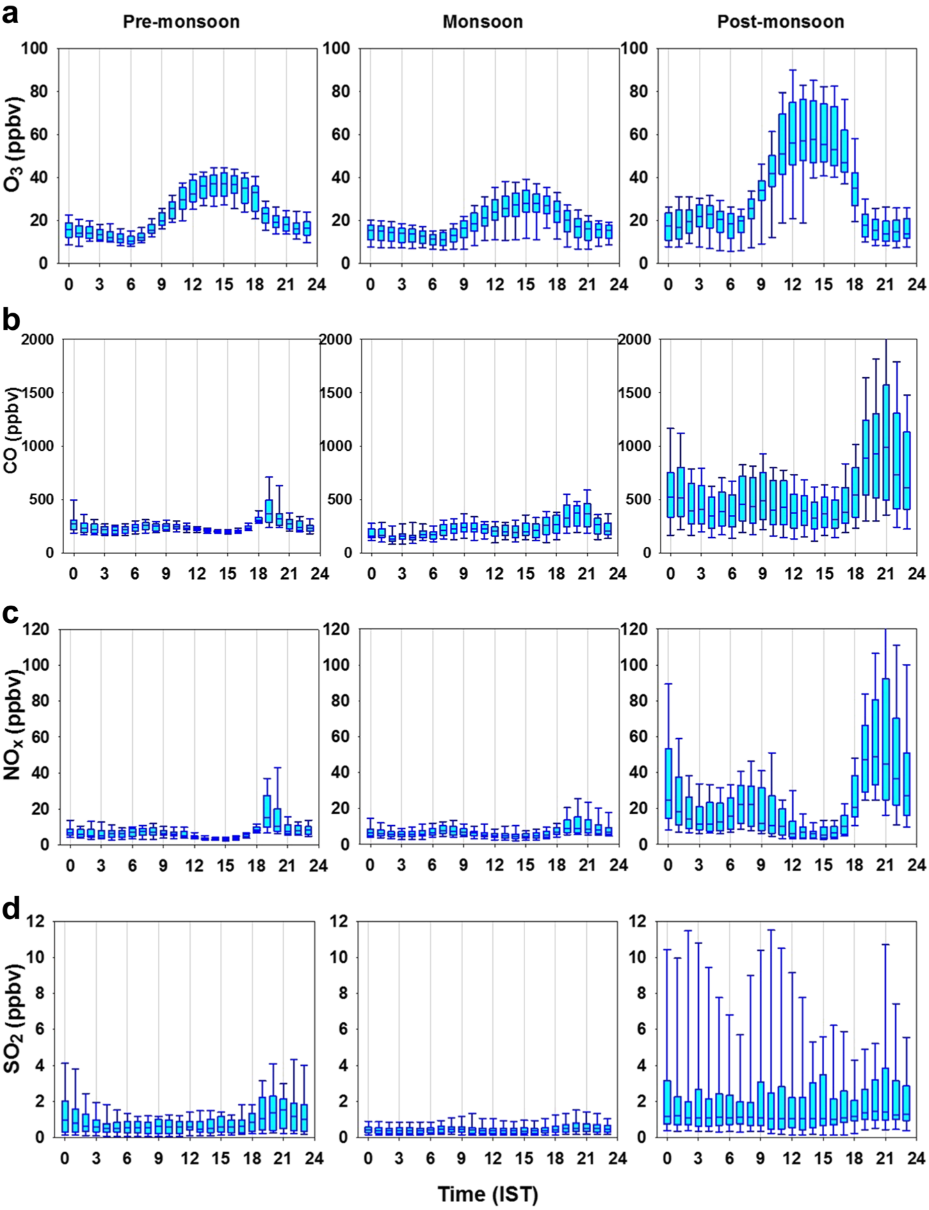

Fig. 2 Diurnal variations of surface (**a**) O_3, (**b**) CO, (**c**) NO_x and (**d**) SO_2 at Ahmedabad during pre-monsoon (May), monsoon (June-August) and post-monsoon (September-October) of 2011. The boxes represent the inter-quartile range while the whiskers are 5th and 95th percentiles

The diurnal variations of CO and NO_x during the study period are shown in Figs. 2b and c. These variations show a bimodal feature with peaks during morning and evening hours. Further, the peak of evening traffic emissions is always notably higher than the morning peak (Table 1). The increase in concentrations of these species during evening hours is attributed to the absence of photochemical consumption of NO_x and less dilution of vehicular emissions

Table 1 Mean values of O_3, CO, NO_x and SO_2 during May to October (2011) and their diurnal amplitudes are presented in ppbv units

	May	June	July	August	September	October
O_3	22.1	21.8	18.1	12.3	22.1	35.0
O_3 (2002)	15.9	13.2	16.8	19.0	17.9	26.0
O_3 (1991–95)	19.4	16.6	17.0	13.3	16.1	26.6
O_3 inc. rate	1.6	1.2	1.1	0.6	1.5	3.5
O_3 inc. rate (1991–95)	1.2	1.1	0.8	0.6	1.1	2.8
O_3 amplitude (Max-Min)	26.5	20.9	21.5	13.0	25.9	59.1
NO_x	7.2	5.2	7.3	8.2	9.7	26.0
NO_x (1991–95)	5.9	6.4	5.1	6.2	10.4	20.5
NO_x (morn.-aftnoon)	4.7	2.6	2.9	3.9	6.1	18.3
NO_x (even.-aftnoon)	12.9	2.8	6.4	10	26.4	56.5
NO_x amplitude (max-min)	19	6.2	11.7	15.8	31.2	73.0
CO	248	203	225	236	372	672
CO (2002)	225	158	169	171	238	303
CO (1991–95)	178	90	289	267	377	582
CO amplitude (Max-Min)	260.9	206.0	260.6	406.0	594.0	1275
SO_2	0.85	0.37	0.46	0.73	0.98	3.55
SO_2 amplitude (Max-Min)	0.8	0.5	0.3	0.9	0.5	5.6

Mean values of O_3, CO and NO_x during 1991–96 (Lal et al. 2000) and O_3 and CO during 2002 (Sahu and Lal 2006) are also presented for a comparison. O_3 increase rate (ppbv/h) for the present study is calculated between the morning minimum (0000–0300 IST) and daytime maximum (1300–1600 IST). Morning (0700–0800 IST), afternoon (1400–1500 IST) and evening (1900–2100 IST). Unless explicitly mentioned, the values in the table are for the present study i.e., for the year 2011

during evening rush hours accentuated by a lower boundary layer (Mallik et al. 2012). Further, evening traffic could be higher compared to morning traffic because the morning traffic is more dispersed in time. Lower values of CO and NO_x during afternoon occur due to lower emissions, higher boundary layer height (resulting in dilution) and loss due to OH chemistry. Further, in order to account for higher levels of O_3 in Ahmedabad during noon period, large amounts of precursors (like CO, NO_x, etc.) need to be consumed. Among the NO_x species, NO is mainly lost by titration with O_3 while NO_2 is mainly lost by photo-dissociation. The CO levels seem to be mainly controlled by various anthropogenic emissions (mainly biofuel burning, vehicular emissions, industries etc.), oxidation and loss due to OH. Unlike the bimodal features in the diurnal patterns of CO and NO_x (more prominent during post-monsoon), SO_2 does not exhibit peak like features during morning and evening, corresponding to traffic hours. This is because the major source of SO_2 is coal burning (in power plants and industries which occur throughout the day) rather than vehicular traffic. Further, there has been reduction in sulfur emissions from vehicles in India as a result of several regulations (Badami 2005; Lu et al. 2011; Mallik and Lal 2013).

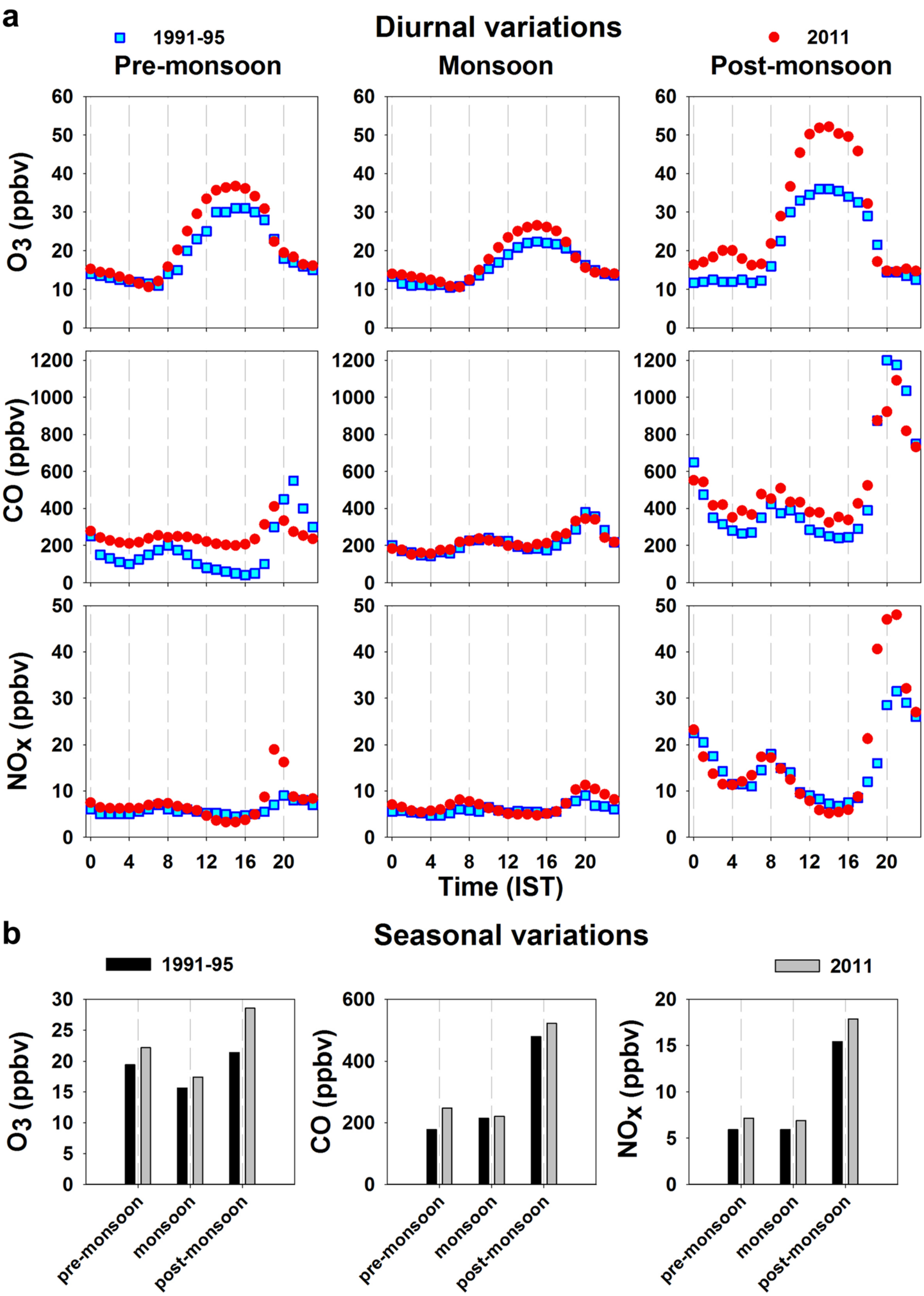

Fig. 3 Changes in the present level of trace gases at Ahmedabad using observations during 1991–96 (**a**) Diurnal variations (**b**) Seasonal variations

Figure 3 indicates that the diurnal levels of O_3 as well as its precursors are clearly higher during 2011 as compared to the 1991–95 period. For O_3, the difference in diurnal variation between the two periods is found to be extremely statistically significant (using a paired *t*-test) for each of pre-monsoon, monsoon, post-monsoon (two tailed P value<0.0001 at 95 % confidence interval). For CO diurnal variations, differences are statistically very significant during pre-monsoon (*P*=0.0059) but not during monsoon (*P*=0.2220) or post-monsoon (*P*=0.0694). Also, with respect to diurnal variations in NO_x using the paired *t*-test, the difference is significant for pre-monsoon (two-tailed P value equals 0.0461), extremely statistically significant during monsoon (*P*=0.0009), but not statistically significant during post-monsoon (*P*=0.1182). However, the diurnal changes in NO_x between the two periods during October is statistically significant (*P*=0.0180) while for the CO diurnal variations during October, the difference between the two periods is considered to be very statistically significant (*P*=0.0011).

The monthly variation of measured trace gases for the May-October period is shown in Fig. 4. Concentrations of O_3 gradually decrease from May (22.1±9.4 ppbv) to August (12.3±3.6 ppbv) and then build-up in September (22.1±9.3 ppbv) and October (35.0±20.3 ppbv), when precursor levels (CO and NO_x) also build-up. Similar to this study, observations of surface O_3 in Ahmedabad during 1991–95 had also revealed a 4 fold higher diurnal variation in October compared to August (Lal et al. 2000). The build-up in precursor levels is due to change in wind direction. Atmospheric transport (local, regional and long-range) plays a crucial role in determining background levels of O_3 as well as ozone precursors that impact

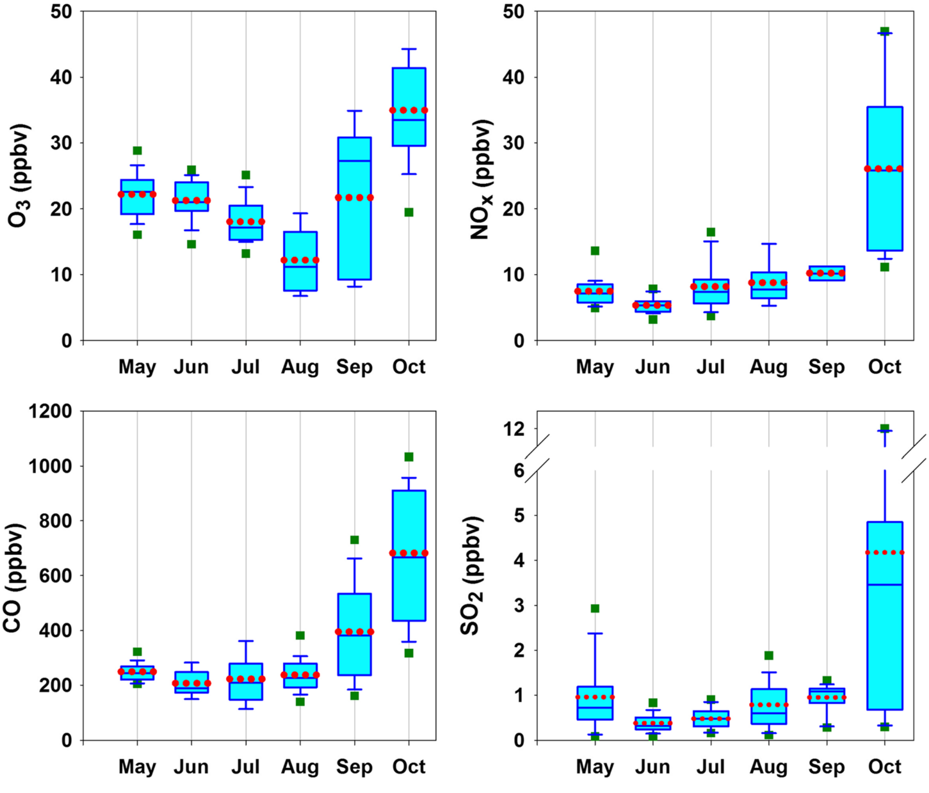

Fig. 4 Monthly averages of surface O_3, CO, NO_x and SO_2 at Ahmedabad during May-October, 2011. The boxes represent the inter-quartile range while the whiskers (green boxes) are 5th and 95th percentiles. Additionally, the mean line is shown by red dots

the final O_3 concentrations (Mallik 2014). Further, ozone-sonde measurements over Ahmedabad reveal that the background levels of O_3 over this region are minimum during summer-monsoon (~26.3±3.3 ppbv) and maximum during winter (~47.7±3.2 ppbv) within the boundary layer (Srivastava et al. 2012). Analysis of surface ozone data at Ahmedabad during noontime showed increase in ozone with residence time, attributed to local photochemistry (Srivastava et al. 2012). The authors suggest that mixing ratios of surface ozone are more influenced by local pollution of the city whereas boundary layer ozone is the regional representative of North West Indian region (this is explained further later during discussion of columnar O_3). Lower values of O_3 during monsoon occur as a result of lower photochemical activity and lower levels of precursors. The average rainfall over Ahmedabad in 2011 was 3.1, 254.2, 295.0 and 62.9 mm during June, July, August and September, respectively. Thus, relatively low O_3 during August coincides with maximum rainfall, indicating more cloudy conditions. Cloudy conditions result in inhibited photochemical formation of O_3. During the study period, a significant anti-correlation is noteworthy between O_3 concentrations and ambient relative humidity (Fig. 5). The monthly mean O_3 values during 2002 in Ahmedabad were lower than the present study (Table 1, Sahu and Lal 2006). Further, the monthly values of O_3 during May-October, 2011 are found to be significantly higher than the same months in 1995. The two-tailed P value for this difference equals 0.0453 (at 95 % confidence interval), which is statistically significant. The observed increases in O_3 in 2011 over 1991–95 are about 14, 10 and 34 % for pre-monsoon, monsoon and post-monsoon, respectively (Table 1, Fig. 3). Nevertheless, continuous long-term measurements are necessary to detect the trend (if any) in surface O_3 in Ahmedabad. However, for CO and NO_x, the two-tailed P values did not reveal statistically significant differences in monthly variations during the study period.

The CO levels decrease from May (248.2±47.9 ppbv) to July (224.5±46.0 ppbv) and show an enhancement from August (235.8±75.4 ppbv) to October (672.0±306.6 ppbv). CO values obtained by Sahu and Lal (2006) during 2002 were lower than the present observations. Combining the literature data with this study, it is clear that the monthly mean CO is lowest during July-August. NO_x concentrations in Ahmedabad generally show higher levels compared to other urban regions of India (Table 2). As mentioned in section 1, the study location has a predominant influence of NO_x from transport and power sectors.. The seasonal variation in NO_x

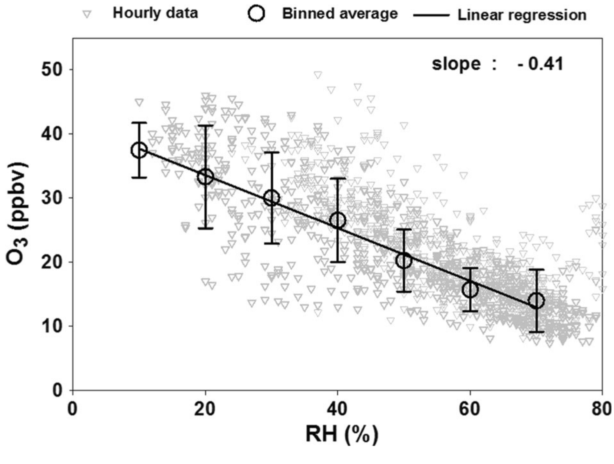

Fig. 5 Correlation of O_3 with RH during May-August, 2011

Table 2 Comparison of trace gas variations (in ppbv) in Ahmedabad with other regions in India and the world. s: summer/ pre-monsoon, m: monsoon, pm: post-monsoon, w: winter, a=annual

Location	O_3	CO	NO_x	SO_2	Period	Reference
Ahmedabad (Semi-arid, urban West India)	22.1 (s) 17.4 (m) 28.5 (pm)	248.2 (s) 221.2 (m) 521.7 (pm)	7.2 (s) 6.9 (m) 17.9 (pm)	0.85 (s) 0.52 (m) 2.26 (pm)	2011	This study
Delhi (Humid, urban North India)	66 (s) 54 (m) 66 (pm) 38 (w)			1.48 (s) 1.24 (m) 2.55 (w)	2003 (O_3) 2008 (SO_2)	Jain et al. (2005) Datta et al. (2011)
Agra (Semi-arid, sub-urban North India)	40 (s) 18 (m) 26 (pm) 23 (w)		24 (s) 28 (m) 25 (pm) 19 (w)	1.3 (s) 1 (m) 1.7 (w)	2009 (O_3, NOx) 1999–2001 (SO_2)	Singla et al. (2011) Kumar et al. (2004)
Kolkata (Urban, Humid, East India)	18 (s+w)	457 (s) 630 (m) 883 (w)	19 (s+w)	0.8 (s) 0.7 (m) 3.5 (pm) 6.4 (w)	2010–11 (O_3, NO_x) 2012–13 (SO_2, CO)	Ghosh et al. 2013; Mallik et al. 2014
Bhubaneshwar (Urban, Savana, East India)	38 (s) 28 (m) 29 (pm) 75 (w)				2010	Mahapatra et al. 2012
Hyderabad (Semiarid, urban, South-central India)	35 (s) 18 (m) 33 (w)		5.3 (s) 4.7 (m) 4.0 (w)		2010	Swamy et al. (2012)
Anatapur (Semi arid, rural South India)	28.5–56.1		3.2–13.1		2010	Reddy et al. 2012
Hong-Kong (Humid, urban China)	22.9 (s) 8.7 (m) 37.9 (pm) 21.1 (w) 20 (a)	376 (a)	91.6 (s) 82.0 (m) 96.5 (pm) 93.0 (w)	10.1 (s) 7.5 (m) 9.0 (pm) 7.5 (w) 6.4 (a)	2004 2002–03 (a)	Kwok et al. (2010) Guo et al. (2007)
Beijing (Humid, urban China)	46 (s) 10 (w)	2530 (s) 7330 (w)	34 (s) 52 (w)	5.7 (s) 60 (w)	2002–03	Sun et al. (2004)
Mexico city (Highland, urban Mexico)	140	1300	55	8	2009	Parrish et al. (2011)
Europe (surface sites)	32–40 (s) 25–38 (m) 20–28 (pm) 22–28 (w)		21(a)	<0.5	2004 (O_3, NO_2) 2000 (SO_2)	Chevalier et al. (2007) EEA 2007; Hanke et al. (2003)

is very similar to that of CO. The mean NO_x levels are 7.2. 5.2, 7.3, 8.2, 9.7 and 26.0 ppbv respectively during May, June, July, August, September and October. Among all measured trace gases, the SO_2 enhancement in October over September is by far the largest (262 %; Fig. 4). This can be explained as the major contributors to SO_2 are point sources (e.g., coal-fired power plant emissions), which are stationary sources, and hence, the role of wind direction in determining SO_2 levels at the receptor site becomes very important (discussed in Section 3.3).

A comparison of trace gas variations in Ahmedabad with other regions in India and the world are presented in Table 2. It may be noted that some of the values in the references were originally presented in μgm^{-3}. These have been converted to volume mixing ratios using the following conversion factors: O_3: 1ppbv=2.0 μgm^{-3}; CO: 1ppbv=1.145 μgm^{-3}; NO_2: 1ppbv= 1.88 μgm^{-3}; SO_2: 1ppbv=2.62 μgm^{-3}. O_3 values in Ahmedabad are found to be lower than the stations in the IGP (viz. Delhi, Agra) but comparable to urban regions in South India (viz. Hyderabad). It is interesting to note from Table 2 that very high levels of surface $O_3$are observed in Delhi (annual mean=56 ppbv) but the winter concentrations are low (mean=38 ppbv). In general, as observed from Table 2, in-situ measurements of CO in India are rather limited and more studies are required to understand its atmospheric chemistry with regard to heterogeneous surface process in aerosol particles. In absence of local comparisons, it is clearly observed that CO levels in Ahmedabad are generally very low when compared to several urban sites around the globe. These values are far below than those observed in Mexico and Beijing. This could be because of sources of elevated CO viz. biomass burning are not predominant in Ahmedabad. NO_x levels in Ahmedabad are lower than urban regions in IGP (viz. Agra). SO_2 levels in Ahmedabad as well as other Indian stations are lower than urban regions in China as well as Mexico. It is pertinent to mention that the sulfur content of Indian coals (0.51 % by weight) is lower than in many other regions of Asia (1–2.5 %) (Garg et al. 2001; Arndt et al. 1997).

In a previous study over Ahmedabad, Srivastava et al. (2012) suggested that mixing ratios of surface O_3 are more influenced by local pollution of the city whereas boundary layer ozone is the regional representative of North West Indian region. To investigate if there is any influence of O_3 and its precursor gases from higher altitudes to the surface concentrations, a comparison of surface measurements of trace gases in Ahmedabad during May-October, 2011 has been made with their columnar counterparts (Supplementary Fig. 2). Tropospheric NO_2 and boundary layer SO_2 have been obtained from the Ozone Monitoring Instrument (OMI) for the 22–23°N,72–73°E grid (gdata1.sci.gsfc.nasa.gov/daac-bin/G3/gui.cgi?instance_id=omil2g). Tropospheric O_3 from OMI/MLS (Microwave Limb Sounder) has been obtained for the grid centered at 23.5°N, 73.125°E (http://acdext.gsfc.nasa.gov/Data_services/cloud_slice/new_data.html). Tropospheric O_3 (1° latitude × 1.25° longitude) is obtained by using the difference of stratospheric column O_3 measurements (retrieved by MLS) and the total column O_3 measurements (retrieved by OMI) (Ziemke et al. 2006). The columnar CO data have been obtained from 1×1° MOPITT grids (ftp://l4ftl01.larc.nasa.gov/MOPITT/MOP03M.004). It is noteworthy that similar to surface O_3 in Ahmedabad, tropospheric O_3 also decreases from May to August and increases during September (Supplementary Fig. 2). This suggests influence of local and regional pollution to O_3 levels at higher altitudes. Ozone-sonde observations over Ahmedabad revealed that in the lower troposphere, a significant contribution of regionally polluted air is found during spring and summer-monsoon seasons (~9–12 %; Srivastava et al. 2012). The authors further claim that contribution of long range transport of O_3 in the lower troposphere amounts 9 and 27 % during spring and summer-monsoon seasons respectively. The large increase in surface O_3 during October is, however, not reciprocated by similar increase in tropospheric O_3, indicating lower influence of surface processes to tropospheric columnar O_3 values during October. This is supported by the fact that columnar CO in Ahmedabad also does not show sharp increase during October. In general, columnar CO in Ahmedabad starts to decrease during July-August and gradually increases during September-October. However, it seems that air mass changes in lower altitudes during post-monsoon does not significantly impact the tropospheric CO over Ahmedabad. For NO_2 and SO_2, there is no clear relationship between surface and columnar values. Due to the lower tropospheric lifetime of these species, vertical mixing and removal mechanisms could play a vital role in determining their tropospheric concentrations. Higher columnar SO_2 in Ahmedabad during monsoon, also observed for other Indian cities (Mallik and

Lal. 2013), needs to be further investigated for transport/transformation processes. Further, similar to SO_2, sulfate (SO_4^{2-}) concentrations in Ahmedabad have been observed to be higher during August compared to June-July (Rastogi and Sarin 2009).

3.2 Relationships of trace gases with wind speed and direction

From the above discussions, it is very clear that wind borne transport (on a local scale) plays a crucial role in controlling the observed trace gas levels in Ahmedabad. Variations of O_3, CO, NO_x and SO_2 with wind speed are shown in Fig. 6. It is observed that the primary pollutants viz. CO shows an inverse relationship with wind speed. Such features are characteristic of source regions. NO_x and SO_2 also show features similar to CO but the relationship is not as robust. The relationships imply that emissions of CO, NO_x and SO_2 are mostly within the city periphery and accumulation of pollutants takes place at lower wind speeds (i.e., mainly in calm conditions). Higher wind speed results in efficient dispersion of the anthropogenic emissions, causing the pollutants to be ventilated away from the measurement location. Since O_3 levels are influenced by photochemistry more than they are influenced by transport, hence O_3 and wind speed do not exhibit any direct relationship. It may be noted that O_3 values are higher

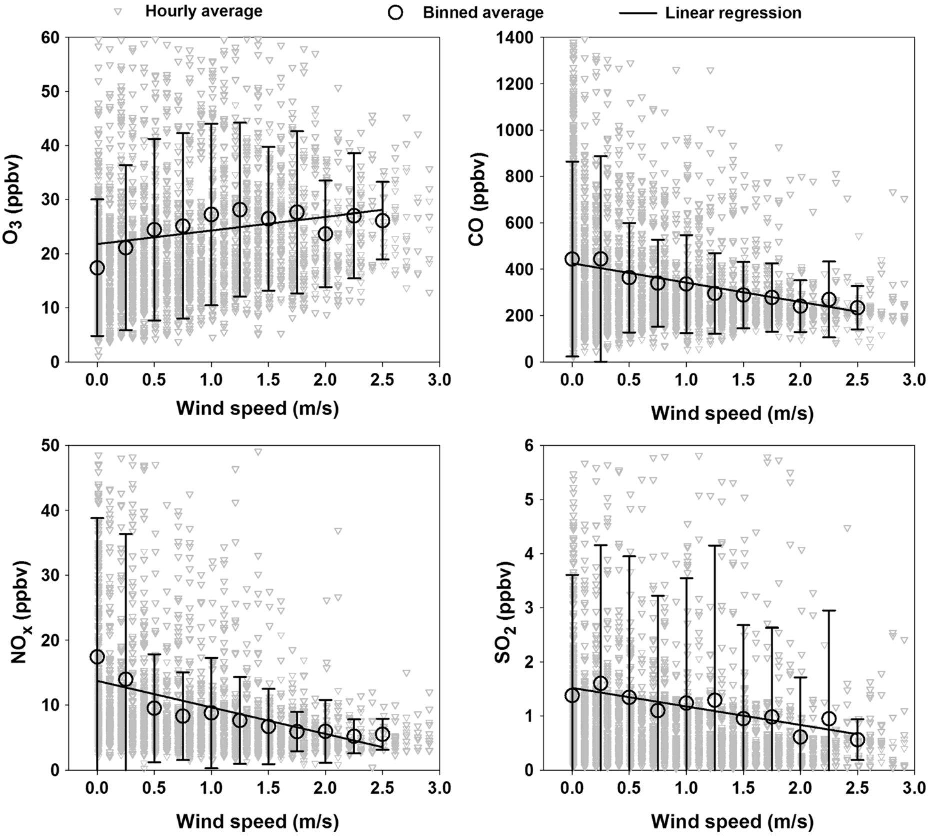

Fig. 6 Variation of surface O_3, CO, NO_x and SO_2 with wind speed in Ahmedabad during May-October, 2011. The data has been averaged into 0.25 m/s wind speed bins between 0 and 2.5 m/s for regression analysis

during daytime (result of photochemistry) when wind speeds are also higher (impact of higher daytime temperatures).

Figure 7 shows the variation of O_3, CO, NO_x and SO_2 with wind speed as well as direction. It is observed that most of the data points lie between 135 and 315°. These data points mostly belong to the pre-monsoon and monsoon period (May to early September), when wind direction varies between south-westerly to south-easterly (also see Supplementary Fig. 1). The points lying between 45–135° mostly represent the late September-October period, when a change in prevailing winds occur. Figure 7 further shows that wind speeds are lower during this period (October mean: 0.5 m/s vs. May mean: 1.3 m/s), allowing accumulation of primary pollutants. Surface O_3 concentrations are scattered in all directions because O_3 is a secondary pollutant and in-situ production of O_3 occurs on a local scale in Ahmedabad. While CO and NO_x show higher values in the 45–135° sector i.e., during October; their values are also higher in west, very close along the 45–135° axis, indicating accumulation during calm (very low wind speed conditions) in this sector. The pattern in SO_2 is very different from the two other primary pollutants viz. CO and NO_x. The high SO_2 values are almost entirely restricted in the 30–145° sector. It was shown in Fig. 1 that a major thermal power plant and several industries lie in this sector. Coal burning in these industries and the power plant is likely to be responsible for the observed high SO_2. Further, on a finer scale, SO_2 concentrations are higher irrespective of wind speed in the 45–90° sector. It seems that these values are mostly influenced by

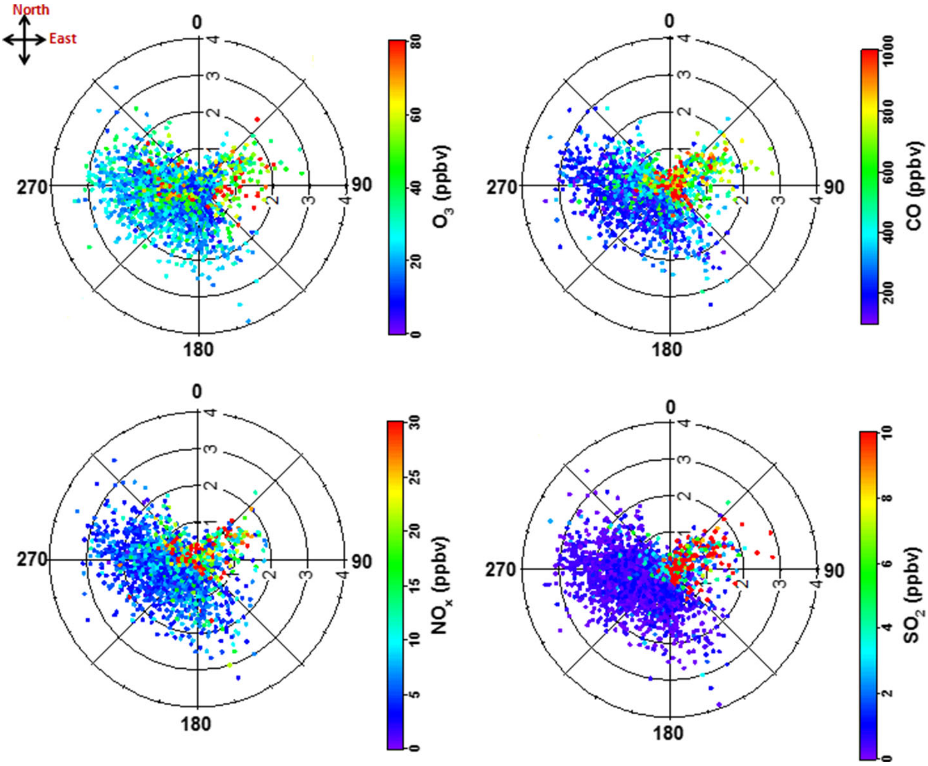

Fig. 7 Variation of hourly averaged O_3, CO, NO_x and SO_2 in Ahmedabad with wind direction and speed during May-October, 2011. The angle represents wind direction; the radius represents wind speed while the trace gas concentrations are color coded

transport of SO_2 from the local thermal power station in the east and to some extent by the industrial clusters in the east of Ahmedabad, which houses several manufacturing units (Fig. 1). The atmospheric abundance ratios of trace gases are informative indicators of source signatures rather than individual trace gases as the impact of common processes is minimized in ratio analysis. Supplementary Fig. 3 shows higher SO_2/NO_x values in the 30-150° sector, clearly relating these values to the point sources present in this sector (Fig. 1). It is observed that most of these data also lie between 135 and 315°. CO/NO_x values (<100) are more skewed towards west, indicating impact of vehicular emissions. However, some high values towards east indicate transport of CO from coal burning in power plants/ industries in that sector. Again, O_3/NO_x does not show preference to any direction and these values are governed by the O_3-NO_x chemistry. The same rationale also applies to O_3/CO values.

3.3 Inter-correlations

CO, NO_x and SO_2 over urban areas are supposed to be mainly impacted by anthropogenic emissions (barring influence of volcanic emissions for SO_2 in certain areas (Mallik et al. 2013) or biomass burning for CO in some regions). In general, CO is produced from the incomplete combustion of fossil fuels and biomass/biofuel while NO_x is produced during high-temperature combustion of fossil fuels. On the other hand, SO_2 is mainly produced during combustion of coal (which contains sulfur) in power plants and industries. The relationships among various trace gases measured during this study has been investigated in order to understand the processes/sources controlling their levels and variability. For regression analysis, the data was separated into two sets viz. $NO_x < 10$ ppbv and $NO_x \geqq 10$ppbv, since more than 72 % of data points belong to $NO_x < 10$ppbv. In general, we will focus more on the slopes obtained for NO_x below 10 ppbv, as this explains larger part of the data. Figure 8 shows that the relationship of O_3 and CO with NO_x is similar for both the data sets.

Although the amount of O_3 produced due to each molecule of NO_x consumed is controlled by a complex nonlinear chemistry (involving VOCs), the O_3 to NO_x slopes can be used as rough indicators for the production efficiency of O_3 (Trainer et al. 1995). Fig. 8 shows that O_3 concentrations decrease with increasing NO_x values for both the data sets. The negative relationship is governed by two processes, both achieving similar results. During daytime, O_3 increases due to photochemical production while NO_x decreases due to being consumed by photochemical reactions and also due to boundary layer dilution. In a previous study, the daytime convective boundary layer height over western part of India was shown to rise above 3 km during May-October (Kumar et al. 2010). Further, during evening, O_3 is slowly lost to various physical processes e.g., deposition in a subsiding mixed layer and inhibition of production while NO_x values are higher due to traffic emissions and inhibition of photochemical consumption. For $NO_x < 10$ppbv, the slope is −1.04 and the intercept is 29.2. Compared to several studies over the Indian region, the intercept value seems to be on the lower side which could be attributed to less active photochemistry during monsoon months. Negative O_3-NO_x slopes of −1.0 and −6.4 during monsoon and post-monsoon were obtained for Gadanki, a rural site, and were attributed to partially processed air masses with lower O_3 production potential (Naja and Lal 2002). Less negative slopes in Ahmedabad indicate more fresh air masses. An extensive study of O_3-NO_x relationships over Trivandrum (a coastal urban site in Southern India) also showed negative slopes, with values in the range of −2.1 to −6.8 during May-August, 2008 (David and Nair 2011). Among these, the slopes were higher for morning data as compared to evening data indicating production processes are faster than processes of

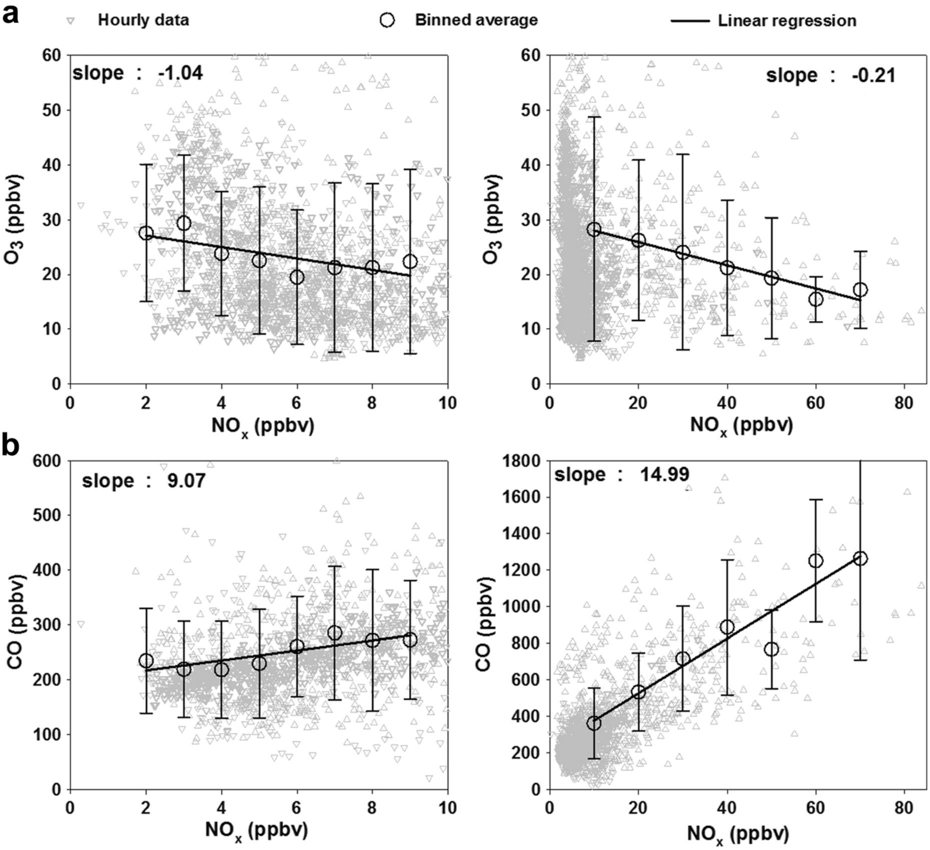

Fig. 8 Correlation of (**a**) O_3 and (**b**) CO with NO_x in Ahmedabad during May-October, 2011. The left panels show variations until 10 ppbv of NO_x and contain most of the data points. The right panels indicate the relationships at higher NO_x concentrations. It may be noted that the regression line represents the mean values in subsequent NO_x bins

destruction in Trivandrum. In the present study, daytime O_3 shows a positive association with nighttime NO_x (Supplementary Fig. 4; slope: 1.4, $r^2=0.56$). The relationship indicates that 1 molecule of NO_x is responsible for formation of 1.4 molecules of O_3. The value is quite low compared to other sites in India and China (Cheung and Wang; 2001; David and Nair 2011).

The covariance of O_3 and CO concentrations offers a valuable constraint for quantifying anthropogenic sources of O_3 (Chin et al. 1994). O_3-CO relationship can be used to investigate O_3 photochemistry over polluted regions and study evolution of polluted plumes. Increasing O_3-CO ratios in a plume suggest photochemical formation of O_3. During the East Asian Regional Experiment, the O_3-CO slopes at Gosan (Korea) varied between 0.03 and 0.07 but increased with increasing transport time due to O_3 production (Tanimoto et al. 2008). The observed O_3-CO slopes varied between 0.15 and 0.32 for various sites in northern United States during summer (Chin et al. 1994 and references therein). Fig. 9a shows that until about 500 ppbv of CO, the O_3-CO shows a large scatter in Ahmedabad despite a small positive slope. It indicates that a linear relationship does not explain the variation of O_3 with CO. One of the major causes could be high levels of NO_x that controls O_3 chemistry. Positive slopes

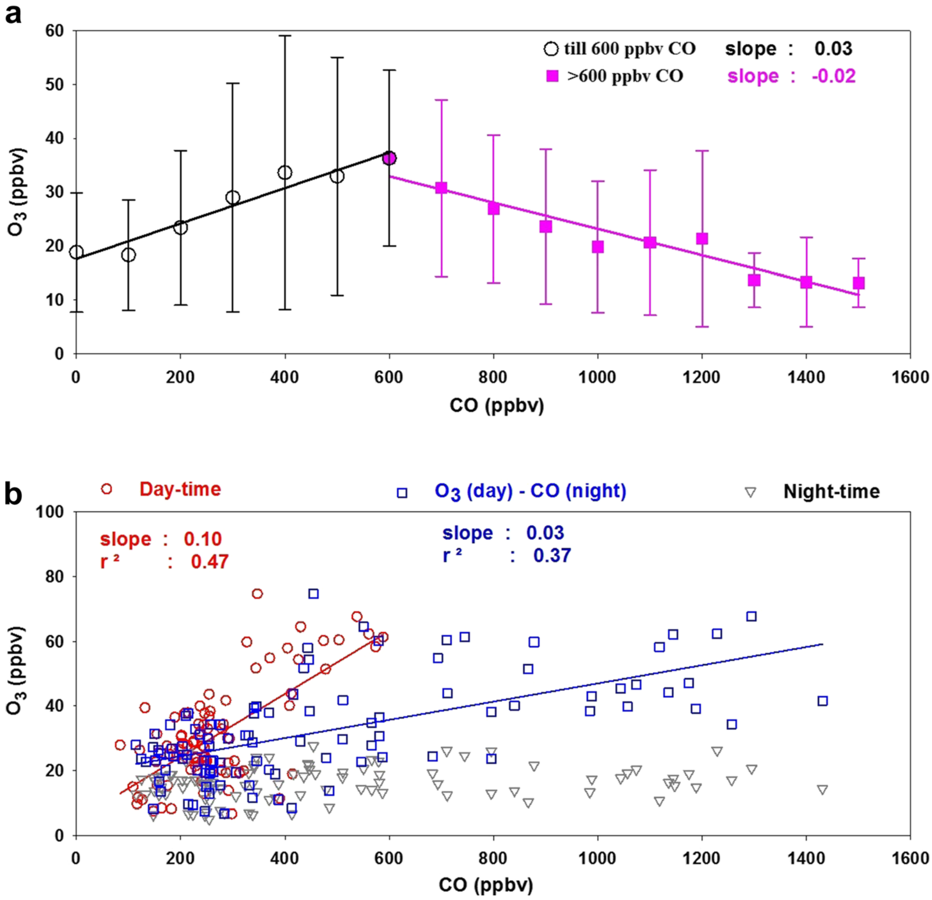

Fig. 9 Relationships between O_3 and CO in Ahmedabad during May-October, 2011 (**a**) using all available hourly data (**b**) using day-time and night-time data

(0.16 ppbv/ppbv) between O_3 and CO have been previously observed in Ahmedabad, which were however; lower than some other non-urban sites (0.24-0.33 ppbv/ppbv; Lal et al. 2008a). At very high CO concentrations (500 ppbv), the slope becomes negative. Negative O_3-CO slopes were found in Hissar, a semi-urban site in India (Lal et al. 2008b). Negative O_3/CO slopes over source regions generally occur due to large short-term variability in CO emitted by the surface sources. Further, during night-time, O_3 would be gradually lost due to deposition and result in a negative association with CO (Chin et al. 1994).

The O_3-CO and O_3-NO_x relationships suggest that not only photochemistry but also mixing of different emissions might be responsible for the observed O_3-CO relationship for Ahmedabad. Positive correlation is observed between daytime O_3 and daytime CO (Fig. 9b), suggesting O_3 production due to sufficient levels of precursors. No correlation is observed between night-time O_3 and night-time CO as they are controlled by different processes during this period and absence of photochemical reactions which link O_3 and CO. However, there seems to be a weak association between day-time O_3 and night-time CO (R^2= 0.37), indicating the role of night-time reservoir of CO in O_3 photochemistry. This night-time reservoir of CO (depending on its levels) will participate in chemical reactions during the day and serve as the background value of CO. Further, lack of correlation between O_3 and CO indicates that there are number of points with elevated CO but low O_3, representing air parcels containing fresh emissions that have not still realized their O_3 production potential (Chin et al. 1994). Overall, lower slope and relatively lower correlation between O_3 and CO in Ahmedabad indicate incomplete photochemical processes in the ambient air. However, due to two major complications (a. accounting for the chemical sources and sinks of CO b. accounting for O_3 advection from outside the city), the interpretation of O_3-CO relationships must be supplemented by model studies.

Since CO and NO_x have many anthropogenic sources in common, it is of interest to investigate their relationships. The CO/NO_x value in a polluted air parcel is impacted by (a) the ratio of the emissions of CO and $NO_{x(y)}$ (b) the levels of CO and $NO_{x(y)}$ in the background air (valid more in cases where regional transport plays substantial role) and (c) the photochemical transformation of the air parcel, which removes a different fraction of each pollutant in the time between emission and measurement (Parrish et al. 1991). In general, very low values imply dominance of NO_x and hence vehicular emissions. On the other hand, very high values should indicate biomass/biofuel combustions, which emit large amount of CO e.g., high CO/NO_x obtained for Linan (Table 3) were attributed to dominance of biofuels (Wang et al. 2002). High CO/NO_x also indicate longer transport time with aging of an air parcel as NO_x levels will gradually decline due to its shorter lifetime. The CO-NO_x slope for Ahmedabad is very low (Table 3; 9.1 ppbv/ppbv with an intercept of 199.1 and $r^2=0.70$) indicating very fresh emissions from area sources. The slope can be interpreted as the emission ratio, assuming that CO is not produced in significant amount through oxidation of hydrocarbons and that NO_x is not removed from the atmosphere between emission and sampling. The assumption is highly valid because of nearby sources. The intercept may be interpreted as the regional background of CO.

In general, mobile sources, characterized by diesel and gasoline consumption, are rich in CO and NO_x, while point sources, mainly characterized by coal consumption, are rich in SO_2 and

Table 3 Comparison of trace gas ratios with NO_x (ppbv/ppbv) obtained over Ahmedabad with other studies. s: pre-monsoon, m: monsoon, pm: post-monsoon, w (winter)

Location	Source	CO/NO_x	SO_2/NO_x	Reference
Ahmedabad	All data	9.07	0.08	This study
	Mobile		0.026	–
	Point		0.41	–
North China	Power	0.42	1.39	Zhang et al. (2009)
	Industry	27.49	0.99	–
	Residential	82.48	1.29	–
	Transport	16.16	0.02	–
Linan, China	Biofuel Coal	36–39	0.83–1.26	Wang et al. (2002)
Western US	Point sources	1.2	1.1	Parrish et al. (1991)
	Mobile sources	10.2	0.05	–
Dhaka, Bangladesh	Area sources	12.2–14.6 (w, pm) 19.5–22.6 (s, m)	0.02–0.6 (w, pm) 0.1 (s, m)	Sikder et al. (2013)

NO_x. Thus, mobile sources are characterized by high CO/NO_x but low SO_2/NO_x, as these emissions are dominated by NO rather than SO_2. On the other hand, point sources mainly comprising coal combustion in industries and power plants are rich in SO_2 emissions because of the sulfur content in coal. Hence, point sources exhibit higher SO_2/NO_x but lower CO/NO_x. A comparison of CO/NO_x and SO_2/NO_x values obtained in this study with other regions of the world is presented in Table 3. The study of SO_2/NO_x and CO/NO_x values by several authors alludes to their importance in differentiating emissions from point sources and mobile sources. The use of these relationships as source signatures is clearly corroborated by studies of Zhang et al. 2009 (Table 3). The authors found that SO_2/NO_x values from the power sector (coal burning) is 1.39 while these ratios are only about 0.02 for the transport sector in China. Similar conclusions were also derived from studies by Parrish et al. 1991 over Western US. For the Indian region, using emission estimates from Garg et al. (2001), the emission factors from coal are 549 T/PJ and 300 kg/TJ for SO_2 and NO_x respectively. This gives a SO_2/NO_x for coal of about 1.83 by weight. The emission factors provided by Streets et al. (2003) for coal burning in power plants are 8.38–16 g/kg SO_2 and 4.59–11.8 g/kg NO_x. Thus, for power plants, the SO_2/NO_x ratio can vary between 0.68 and 3.49 by weight. To convert into concentration ratio, we need to normalize by molecular weights i.e., (30+46)/64=1.19. This gives a volumetric SO_2/NO_x ratio of 0.81–4.15.

In Ahmedabad, SO_2 shows weak correlations with both CO and NO_x, suggesting that the SO_2 is emitted from sources different from those for CO and NO_x. To separate the effect of point and mobile sources in SO_2/NO_x ratios, we segregate the hourly averaged data with respect to wind direction and time. To estimate impact of mobile sources, we take all the data during 1800–2100 IST when effect of mobile sources is dominant. The average NO_x and SO_2 concentrations for this dataset are 21 and 1.2 ppbv respectively. For estimating point sources, we take all data in the 0–90° sector (Fig. 7). Further, from this subset, we select data with SO_2 concentrations greater 1.2 ppbv to remove the impact of vehicles (as vehicular emissions are unlikely to raise SO_2 levels so much). This final dataset is used as an indicator of point sources. The slopes obtained for mobile and point sources from this analysis are 0.026 and 0.4 (Fig. 10). However, it is pertinent to mention here that due to plethora of sources and mixing of air parcels, it is very difficult to entirely isolate these impacts in an urban region like Ahmedabad.

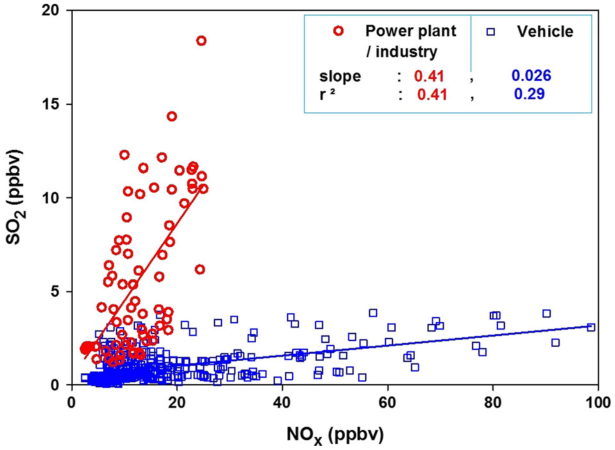

Fig. 10 Relationships between SO_2 and NO_x in Ahmedabad during May-October, 2011

4 Conclusions

Measurements of O_3, CO, NO_x and SO_2 were conducted in Ahmedabad during May-October 2011 to study their levels, variability and inter-relationships during this period of changing meteorological conditions. All the gases exhibited diurnal patterns typical of urban regions during the study period consisting of one pre-monsoon, three monsoon and two post-monsoon months. While O_3 showed a daytime maximum due to photochemical production, CO and NO_x showed morning and evening peaks coinciding with traffic rush hours. The seasonal variations show primary trace gas levels to increase suddenly (by more than a factor of two) during post-monsoon when the prevailing air mass changes. The levels, variability as well as diurnal amplitudes for all the gases are particularly high during the month of October, when the air mass over Ahmedabad becomes almost entirely north-easterly.

A clear negative relationship of primary pollutants with wind speed shows minimal role of advection from outside Ahmedabad and more predominant role of local emissions. However, this argument does not hold for a secondary pollutant like O_3. CO, NO_x and SO_2 show unique relationships with wind direction depending on source locations. NO_x levels are mostly controlled by vehicular emissions in the western side of the city. Very good correlations are observed between CO and NO_x(R^2=0.7–0.9) indicating co-emissions/ co-locations. Low CO-NO_x slopes (9–15 ppbv/ppbv) for Ahmedabad indicate relatively fresh emissions from area sources and dominance of vehicular emissions. Low CO-NO_x slopes in Ahmedabad are characteristics of urban regions (Hong-Kong: 3 ppbv/ppbv, Denver: <10 ppbv/ppbv) and in sharp contrast to slopes greater than 30 ppbv/ppbv observed for areas such as Linan which are influenced by combustion processes. SO_2 values as well as SO_2/NO_x ratios are higher when wind is from the eastern sector of the city which contains a thermal power station and a few industrial clusters. The SO_2/NO_x slope for point sources in Ahmedabad is found to be 0.4 while it is 0.026 for mobile sources.

Low slope and relatively lower correlation between O_3 and CO in Ahmedabad indicate incomplete photochemical processes in the ambient air. Overall, O_3 and NO_x show an inverse association resulting from competing photochemical, dynamical and physical processes in the atmosphere. Interestingly, however, daytime O_3 is found to be positively correlated with night-time NO_x as well as night-time CO. This suggests daytime photochemistry over Ahmedabad is also influenced by night-time reservoir of precursors. Overall, the study explores various processes occurring in an urban site and the results derived may be used as representative for western India urban scenario.

Acknowledgments We thank Physical Research Laboratory for facilities and support. We acknowledge ISRO-ATCTM for funding. We thank Mr. T.K. Sunil Kumar for his co-operation in the laboratory. CM thanks Dr.L.K. Sahu for fruitful discussions regarding this MS. We thank the editor for his efforts in getting the paper reviewed. The comments from anonymous reviewers have greatly improved this MS to its present form. We are grateful to them.

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