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Four-year measurements of trace gases (SO_2, NO_x, CO, and O_3) at an urban location, Kanpur, in Northern India

Abhishek Gaur · S. N. Tripathi · V. P. Kanawade · Vinod Tare · S. P. Shukla

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Abstract In this study, we present long-term near-surface measurements of sulfur dioxide (SO_2), oxides of nitrogen (NO_x), carbon monoxide (CO), and ozone (O_3) carried out at an urban location, Kanpur (26.46°N, 80.33°E, 125 m amsl), in Northern India from June 2009 to May 2013. The mean concentrations of SO_2, NO_x, CO, and O_3 over the entire study period were 3.0, 5.7, 721, and 27.9 ppb, respectively. SO_2, NO_x and CO concentrations were highest during the winter season, whereas O_3 concentration peaked during summer. The former could be attributed mainly to the near-surface anthropogenic sources (e.g. automobiles, residential cooking, brick kilns, coal-burning power plants, agricultural land-clearing, and biomass burning) and low mixing height in winter, whereas the latter was clearly due to enhanced chemical production of O_3 during the pre-monsoon (i.e. summer) season. The lowest concentration of all trace gases were observed during the monsoon season, due to efficient wet scavenging by precipitation. The averaged diurnal patterns also showed similar seasonal variation. NO_x and CO showed peaks during morning and evening traffic hours and a valley in the afternoon irrespective of the seasons, clearly linked to the boundary layer height evolution. Contrarily, O_3 depicted a reverse pattern with highest concentrations during afternoon hours and lowest in the morning hours. The mean rate of change of O_3 concentrations (dO_3/dt) during the morning hours (08:00 to 11:00 h) and evening hours (17:00 to 19:00 h) at Kanpur were 3.3 ppb h^{-1} and −2.6 ppb h^{-1}, respectively. O_3 followed a positive linear relationship with temperature, except in post-monsoon season while the strong negative with the relative humidity in all seasons. The ventilation coefficient was found to be highest in the pre-monsoon season (15,622 m^2 s^{-1}) and lowest during winter (2564 m^2 s^{-1}), indicative of excellent pollution dispersion efficiency during the pre-monsoon season. However, the low ventilation coefficient during winter and post-monsoon seasons indicated that the high-pollution potential occurs at this site.

Keywords Surface ozone · Urbanization · Air quality · Seasonal variations

A. Gaur · S. N. Tripathi (✉) · V. P. Kanawade (✉) · V. Tare
Department of Civil Engineering, Indian Institute of Technology, Kanpur, India
e-mail: snt@iitk.ac.in
e-mail: vijaykanawade03@yahoo.co.in

A. Gaur · S. P. Shukla
Department of Civil Engineering, Institute of Engineering & Technology, Lucknow, India

1 Introduction

There is an increasing awareness in both the science and policy communities to the climate change, and predicted global warming due to changes in the atmospheric abundance of both the greenhouse and trace gases that alter the energy balance of the climate system (Houghton et al. 1992). For example, the radiative forcing for the tropospheric ozone (O_3) changes due to emission of O_3 precursors (e.g. oxides of nitrogen, NO_x and carbon monoxide, CO) is of the order of +0.25 to+0.65 W m^{-2} (with a mean value of +0.35 W m^{-2}) (Solomon et al. 2007).

Air pollution in urban areas is of serious concern in recent times, particularly for developing countries such as China and India, and it may further extend from local to global scale (Mage et al. 1996; Cohen 2006; Fenger 2009; Fang et al. 2009). Atmospheric trace gases are one of the challenging environmental issues in urban and industrial areas (Wang and Hao 2012). Amongst, nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) has the second and third highest exceedance rate in India, respectively, after particulate matter less than 10 μm (PM_{10}), as per the National Ambient Air Quality Monitoring Program (NAAQMP) (CPCB 2012). The expansion of industrialization and increasing population have inevitably resulted in an increased fossil- and bio-fuels combustion, prominent energy demand and higher agricultural land cultivation which caused enormous emission of pollutants into the atmosphere (Tie et al. 2009; Sharma et al. 2014); Combustion is one of the principal processes which emit trace gases and aerosols into the atmosphere (Khare 2012; Andreae and Merlet 2001), including several noxious pollutants such as SO_2, CO, NO_x, volatile organic compounds (VOCs), metal oxides, and particulate matter. Various meteorological parameters may also influence urban air pollution (Akpinar et al. 2008). For example, the ventilation coefficient, which is a product of mixing layer height and wind speed, can be considered as one of the factors determining pollution potential over a region (Goyal and Chalapati Rao 2007). While water vapor enhances the removal rate of free radical production, particularly in low-NO_x environments (Walcek and Yuan 1995), the linear relationship between temperature and O_3 leads to higher O_3 concentrations, with heat accelerating the chemical reactions in the atmosphere (Jacob et al. 1993a). However, the studies regarding meteorological influence on urban air pollution over Indian subcontinent are currently limited.

Tropospheric O_3 has two main sources, namely stratosphere intrusion affecting surface O_3 (Hocking et al. 2007; Lefohn et al. 2011) and in-situ production via photochemical oxidation of carbon-link compounds (i.e. CO, CH_4 and VOCs), in the presence of NO_x (Chameides and Walker 1973; Zhang et al. 2008). The net tropospheric O_3 production is a small difference (~10 %) between the two very large fluxes of O_3 production and destruction (Zahn and Brenninkmeijer 2003). Tropospheric O_3 is considered as a greenhouse gas as it absorbs radiation at 9.6 μm wavelength emitted from earth's surface (Akimoto 2003) and has a detrimental effect on human health and ecosystem productivity (Cooper et al. 2010). The residence time-scale of O_3 varies from season to season and with altitudes between a few days at the surface to a few weeks in the free troposphere (Finlayson-Pitts et al. 1986). The previous review report indicated that the O_3 concentration is rising with the rate of 0.5–2 % per year over the Northern Hemisphere due to the increased anthropogenic activities (Vingarzan 2004).

NO_x plays a major role in the oxidizing capacity of the lower atmosphere by its effect on the partitioning, formation and loss of free radical species (OH, HO_2 and RO_2) (Stroud et al. 2003; Sun et al. 2011; Mavroidis and Ilia 2012). The lifetime of NO_x can vary with the photochemical environment, but is typically on the order of hours to a day (Seinfeld and Pandis 1998) which further oxidizes into HNO_3 and peroxyacetyl nitrate (PAN) (Sun et al. 2011). NO_x and SO_2 can further affect the environment by acid rain and corrosions (Finlayson-Pitts et al. 1986). CO also plays an important role in controlling the oxidizing capacity of the troposphere,

by acting as a sink for a larger fraction of reactive hydroxyl (OH) radicals available in the lower atmosphere (Wayne 1991). The major sources of CO are emission from fossil- and bio-fuel combustion, biomass burning, and oxidation of methane (CH_4) and non-methane hydrocarbon (NMHC) (Logan et al. 1981; Crutzen and Andreae 1990). With its relatively longer lifetime of about 2 to 3 months, it can be used as a good tracer for long-range transport of pollutants (Jaffe et al. 2004; Jacob et al. 2003) and to identify the influence of anthropogenic emissions on the tropospheric O_3 (Chin et al. 1994; Suthawaree et al. 2008). Previous studies have inferred that the effectiveness of OH is sensitive to perturbations by widespread air pollution (Montzka et al. 2011; Lelieveld et al. 2004; Monks 2005). As a result, air pollution has become one of the serious environmental problems of the century which has severe health consequences as well as societal economic and climate impacts.

Trace gases observations caught the attention of scientists in India in the beginning of 1990's. Indian Space Research Organization-Geosphere Biosphere Programme (ISRO-GBP) took an initiative to increase the awareness and the understanding of atmospheric trace gases; their chemistry, transport pathways and modeling over the Indian subcontinent. To date, there exist several long-term studies based on near surface in-situ observations over Indian subcontinent (Table 1), but most studies reported O_3 data alone and, to the best of our knowledge, none of them reported SO_2. The use of space-borne measurements (Ghude et al. 2011b; Ghude et al. 2011a; Kar et al. 2010; Ghude et al. 2008; Lu et al. 2013; Kalita and Bhuyan 2011) and modeling results (Roy et al. 2008; Michael et al. 2014; Kumar et al. 2012) is also documented over Indian subcontinent. As a part of the ISRO-GBP project, the continuous measurement of trace gases (SO_2, NO_x, CO and O_3) were started at the Indian Institute of Technology Kanpur from June 2009 which is apparently the first-ever effort to record a long-term dataset of four simultaneous trace gases over this region. Here, our goal is to examine the temporal variations of these trace gases, relationship among them, and the role of meteorological variables.

2 Site description and general meteorology

The trace gas monitoring station was established inside the Indian Institute of Technology Kanpur campus (26.46°N, 80.33°E and 125 m amsl) in 2009. The trace gas analyzers are installed on the top of an existing over-head water tank of 25 m height from the ground level (Fig. 1). The Grand-Trunk (G-T) road, with a moderately heavy traffic, is located about 600 m to the east of the monitoring station. Kanpur city is ~16 km to the southeast and mostly in the downwind side of the station. Vehicular emissions, biomass burning (mostly in winter followed by early pre-monsoon for agricultural land-cleaning), residential cooking, and a thermal power plant are thought to be major sources of air pollution in this region (Tripathi et al. 2006; Dey and Tripathi 2007) . Kanpur is located in one of the biggest industrial hubs in Northern India, and a large number of coal-burning thermal power plants are clustered along this region. This site is also surrounded by vast agricultural fields. This region experiences four dominant seasons each year: winter (December-February), pre-monsoon (March-May), monsoon (June-August), and post-monsoon (September-November) (Singh et al. 2004). During the winter season, significant parts of northern India experiences western disturbances (a series of alternate low- and high-pressure areas), which move from west to east, leading to sudden winter rain accompanied by intense fog and haze events over this region (Pasricha et al. 2003). Kanpur gets an average rainfall of about 790 millimeters from the southwest monsoon winds. In the post-monsoon season, the weather is somewhat drier and is a transition period between wet and dry conditions. The shift of the monsoon winds to the west-northwest brings polluted air masses to the measurement site after September. During the winter season prevailing

Table 1 Comparison of trace gases concentrations at our site to that of other locations in India, where at least 1 year of continuous measurements are available

Location	Lat. [deg.]	Lon. [deg.]	Site type	Period [mm/year]	Concentration				Reference
					SO_2 [ppb]	NO_x [ppb]	CO [ppb]	O_3 [ppb]	
Kanpur	26.46	80.33	Urban	06/2009–05/2013	3.0±3.1	5.7±4.5	721±403	27.9±17.8	This study
Agra	27.18	78.02	Urban	01/2002–12/2002	–	–	–	21.0	(Satsangi et al. 2004)
Varanasi	25.28	82.96	Urban	11/2002–05/2006	–	–	–	41.5	(Tiwari et al. 2008)
New Delhi	28.61	77.23	Urban	01/2000–12/2009	–	–	2940±1729	31±19.7	(Chelani 2012)
Pune	18.53	73.86	Urban	01/2001–12/2005	–	9.6	–	30.1±7.8	(Debaje and Kakade 2009)
				06/2003–05/2004	–	9.6±5.9	–	30.9±14	(Beig et al. 2007)
Ahmedabad	23.03	72.58	Urban	06/2003–05/2004	–	9.5±2.7	–	20.7±55	(Beig et al. 2007)
				01/2002–12/2002	–	–	385±200	26.3±10	(Sahu and Lal 2006)
Anantapur	14.68	77.60	Rural	01/2001–12/2003	–	3.9±0.6	436±64	35.9	(Ahammed et al. 2006)
				01/2010-12/2010	–	5.1±0.7	–	40.7±3.7	(Reddy et al. 2013)
Gadanki	13.46	79.17	Rural	11/1993–12/1996	–	2.1±1.8	237±64	34±13	(Naja,Lal 2002)
Kannur	12.87	74.90	Coastal rural	11/2009–10/2010	–	2.5	–	18.4–44	(Nishanth et al. 2012)
Thumba	8.52	76.87	Coastal rural	04/1997–03/1998	–	–	–	23.0	(Nair et al. 2002)
Trivandrum	8.49	76.95	Coastal rural	11/2007–05/2009	–	–	–	11.5–28.1	(David and Nair 2011)
Nainital	29.23	79.27	High altitude	10/2006–12/2008	–	–	276±145	43.9±11.5	(Kumar et al. 2010)
Mt Abu	24.59	72.71	High altitude	01/1993–12/2000	–	1.5±1.4	131±36	39.9±10.8	(Naja et al. 2003)

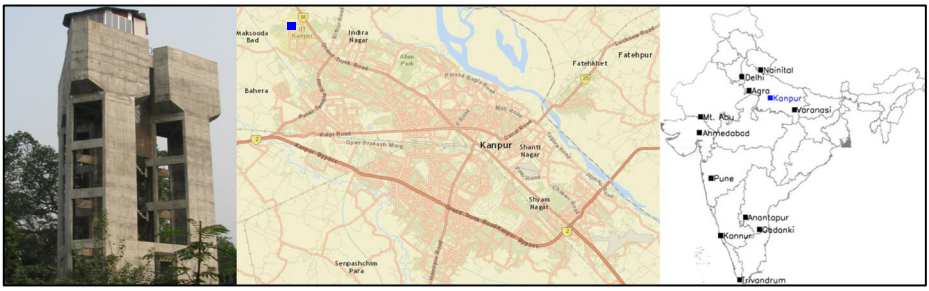

Fig. 1 Location of the measurement site. The *left panel* shows laboratory location on 25 m high over-head water tank, the *middle panel* shows a city-scale map showing location of measurement site (IITK, blue filled square), and the *right panel* shows location of the sites where long-term trace gas dataset available for at least one of the gases under investigation here

weather conditions are fair with calm wind speed from west, northwest direction. The dry season can subsequently be divided into two parts, the months of intense solar radiation from March to May (pre-monsoon) and another from September to November (post-monsoon).

Table 2 summarize monthly averaged meteorological parameters such as ambient air temperature, relative humidity, rainfall, solar radiation, wind speed and wind direction observed over the same time period. The monthly mean minimum (12.7±4.9 °C) and maximum (33.1±5.3 °C) temperature occurred in January and June, respectively. "±" indicates the one standard deviation. The monthly mean minimum (43.2±23.9 %) and maximum (87.5± 14.2 %) relative humidity was observed in May and August, respectively.

3 Instrumentation and data analysis procedures

Near-surface measurements of SO_2, NO_x, CO, and O_3 were started using online analyzers on 13 June 2009. The gas analyzers were installed in an air-conditioned laboratory located on the top of the over-head water tank. Teflon lines have been used as a sampling inlet to distribute ambient air, and to minimize the reactivity with monitoring species. The ambient air was passed through the distribution system where moisture is trapped before sample enters through the sample bulkhead of individual analyzers. The measurement principles and calibration procedure are standard and have already been discussed in several reports (Naja and Lal 1996; Lal et al. 2000; Beig et al. 2007) hence only a brief instrument details are summarized here in Table S1. Daily zero settings and weekly span checks have been conducted for the best performance of trace gas analyzers. The analog waveform trace gas data is converted into digital values through data acquisition system and stored in the computers by using ENVIDAS software. The averaged value over a time interval of 15 min has been recorded. The raw data files are then extracted and separated into individual time series. Note that the measurements of NO_x, CO, and O_3 presented in this study were available from June 2009 to May 2013 while SO_2 was available through September 2009 to May 2013. We used hourly averaged data to perform statistical analysis.

Based on hourly averaged data, the maximum observed concentration (90 % of the entire data) was found within 5 ppb for SO_2, 10 ppb for NO_x, 1200 ppb for CO, and 55 ppb for O_3, but several cases of high SO_2 (number of case, n=12 for SO_2>50 ppb), NO_x (n=28 for NO_x>

Table 2 Average monthly meteorological condition observed at the Kanpur site

Month	Temp. [°C]	RH [%]	Rainfall [mm]	Solar radiation [W m^{-2}]	Wind	
					Speed [m s^{-1}]	Direction
January	12.7±4.9	76.4±21.2	22±3	308	1.6±0.5	WNW
February	16.5±5.2	70.6±21.1	12±2	418	1.9±0.7	NW
March	22.1±6.2	60.8±22.2	9±2	499	2.2±0.7	ENE
April	28.3±6.5	43.6±20.6	5±2	510	2.7±0.7	S
May	32.9±5.6	43.2±23.9	9±3	491	3.2±1.1	SSW
June	33.1±5.3	47.3±23.8	98±22	451	3.0±1.0	SW
July	29.9±3.6	75.6±17.8	222±117	364	2.5±0.8	SW
August	28.6±2.8	87.5±14.2	262±26	371	2.1±1.0	WSW
September	27.4±2.1	86.9±14.7	208±118	396	2.0±0.6	SSW
October	25.1±4.8	72.5±22.4	19±30	429	1.7±0.4	WNW
November	19.8±5.3	77.7±21.7	5±8	337	1.4±0.4	NW
December	14.2±5.5	76.5±21.9	4±1	344	1.3±0.4	W

50 ppb), CO (n=81 for CO>3000 ppb), and O_3 (n=43 for O_3>90 ppb) were recorded. Note that hourly averaged SO_2 concentrations were also sometimes found lower than the minimum detection limit of the analyzer (n=3357 out of 34,775 data points over the entire study period). Since, the reason was unknown for such cases; we have discarded these data points in the analysis which have resulted in data gaps during the monsoon season for the year 2010 and 2011.

The meteorological parameters were also simultaneously measured at the same site (Table S2). Air mass backward trajectories were calculated with the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) PC version model (Draxler and Rolph 2010) and using gridded wind fields from the Global Data Assimilation System (GDAS), with a spatial resolution of 1°×1° and a time resolution of 1 h (Kanamitsu 1989). The mixing layer height at our site was obtained from the HYSPLIT calculations. The global monthly Fire Location Product (MCD14ML) from the MODIS was also used and obtained via University of Maryland ftp server ftp://fuoco.geog.umd.edu.

4 Results and discussion

This paper presents the four-years of continuous measurements of SO_2, NO_x, CO, and O_3. There are only a few minor missing data periods, due to instrument calibration and/or routine zero settings and span checks. The monthly data coverage over the entire study period was very high (Fig. 2), with more than 80 % of the data available. The winter was the best covered season, with data availability up to 98 %, and the data coverage was slightly lower during late monsoon and early post-monsoon season. Such data coverage is very useful to conduct statistical analysis of the time series. We present monthly, seasonal, and diurnal characteristics of these trace gases.

Figure 3 shows the average monthly variation of SO_2, NO_x, CO, and O_3 at the Kanpur site. As a measure of variability for individual month, the mean, median, 25th and 75th percentiles, and 10th and 90th percentiles were plotted. The hourly averaged mean SO_2, NO_x, CO, and O_3

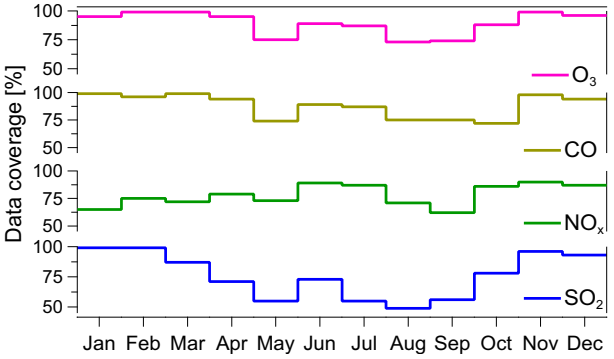

Fig. 2 Data coverage for trace gases (SO_2, NO_x, CO, and O_3) over the entire study period

concentrations over the entire study period ranged from 0.5 ppb to 98.7 ppb, 0.4 ppb to 96.8 ppb, 40 ppb to 5040 ppb, and 1.1 ppb to 106.8 ppb, respectively, with a mean and one standard deviation of 3.0±3.1 ppb, 5.7±4.5 ppb, 721±403 ppb, and 27.9±17.8 ppb, respectively. The highest monthly mean SO_2 concentration was observed during winter (4.6±4.1 ppb), while the lowest was recorded in the monsoon season (0.5±0.8 ppb). Based on 1-year data, the similar trend in SO_2 concentration was also observed at air quality monitoring stations over New Delhi, India (Datta et al. 2010). The second peak in the early pre-monsoon season could be attributed to the stable meteorological conditions (high temperature and dry period). NO_x and CO concentrations showed a very good correlation with maxima during

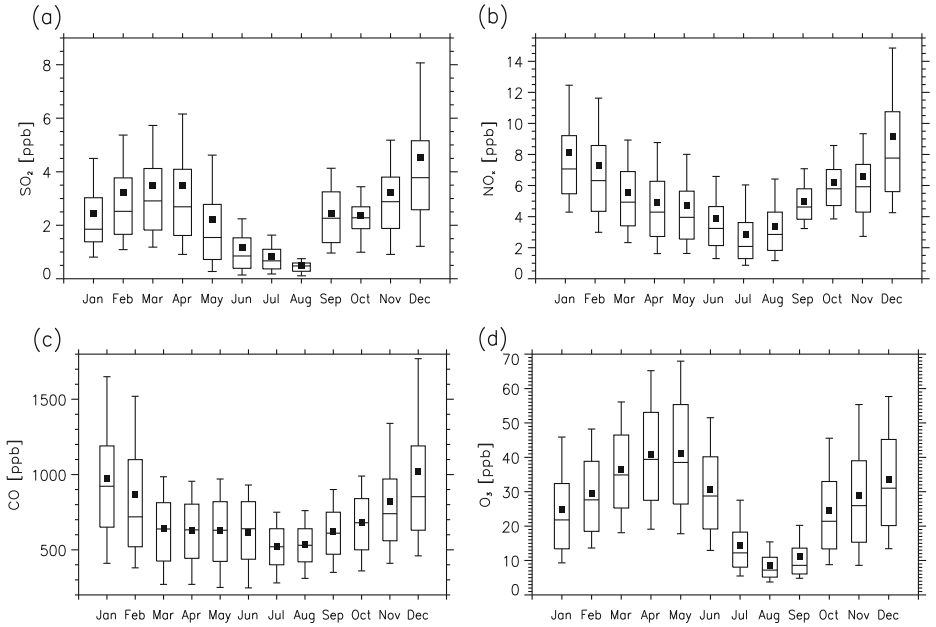

Fig. 3 Statistical analysis of (**a**) SO_2, (**b**) NO_x, (**c**) CO, and (**d**) O_3 at Kanpur for the entire study period. The horizontal solid line indicates the median, filled square indicates the mean, top and bottom of the box indicate the 75th and 25th percentile, respectively, top and bottom whiskers indicate the 95th and 5th percentile, respectively

winter and minima in the monsoon season (Fig. 3b and c), perhaps due to a combined effect of large near-surface anthropogenic emissions, boundary layer processes, retarded photochemical loss owing to lower solar intensity, as well as local surface wind pattern. A similar seasonal behavior was observed at other urban locations, Ahmedabad and Pune, in India (Beig et al. 2007). However, NO_x and CO did not show seasonal pattern at a rural site, Gadanki, in India (Naja,Lal 2002), which is not directly affected by local emission sources. Mean NO_x and CO concentrations at Kanpur were comparatively lower than those reported at other Indian urban locations, but much higher compared to rural/remote locations (Table 1).

In contrast, O_3 peaked during the pre-monsoon season (Fig. 3d), clearly due to its direct linear relationship with incoming solar radiation. The high solar radiation intensity (i.e. temperature) has a direct influence on chemical kinetic rates and the mechanism pathways for the O_3 production (Pudasainee et al. 2006; Han et al. 2011). Previous studies investigating the O_3-temperature relationship revealed O_3 formation from peroxyacetly nitrate (PAN) decomposition as temperature increases above ~310 K (Jacob et al. 1993b). The phot-oxidation of CO, CH_4, and NMHCs in presence of sufficient amount of NO_x may further lead to formation of O_3. The second peak during the winter season could be result of the long-range transport together with a shallow boundary layer height as during the winter season when temperature falls, the thermal decomposition of O_3 precursors (e.g. PAN and active hydrocarbons) also decreases and their atmospheric lifetime increases. O_3 concentrations were comparable to those reported at other urban locations in India (Chelani 2012; Debaje and Kakade 2009; Beig et al. 2007; Sahu and Lal 2006; Satsangi et al. 2004) as well as urban areas in China (Tu et al. 2007; Tang et al. 2009), but lower compared to rural and high altitude sites in India (24-36 %) (Kumar et al. 2010; Naja et al. 2003; Reddy et al. 2010) (Table 1).

Figure 4 shows the seasonally averaged diurnal variation of trace gases at the Kanpur site. The diurnal variation of SO_2 was the most pronounced in winter, with maxima during traffic hours. This could also be the effect of relatively shallow boundary layer height and less efficient oxidation to sulfate during winter. In the monsoon season, no diurnal variation in SO_2 was observed. During the pre-monsoon (i.e. summer) season, SO_2 showed a distinct diurnal

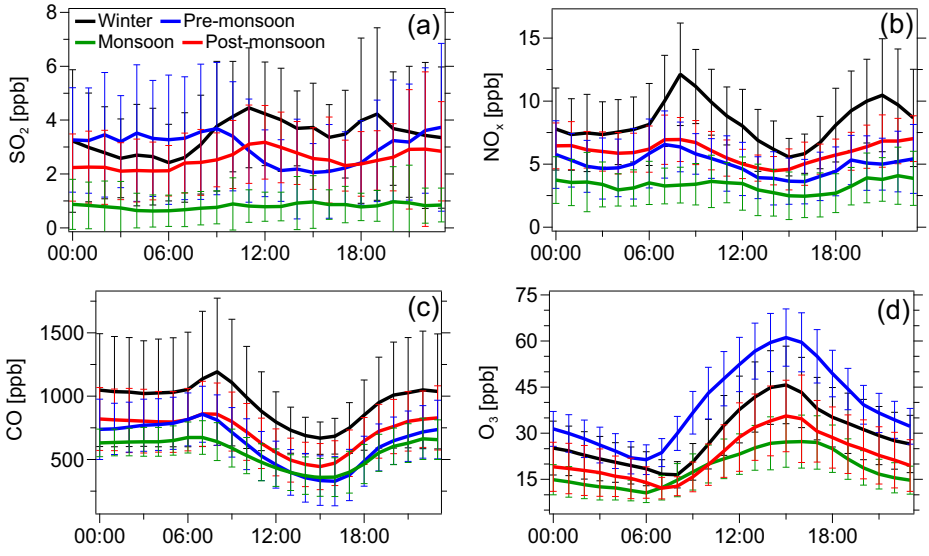

Fig. 4 Seasonally averaged diurnal variation of trace gases, (**a**) SO_2, (**b**) NO_x, (**c**) CO, and (**d**) O_3 at Kanpur

pattern, with a valley during afternoon hours. This could be explained by the increased boundary layer height (i.e. stronger dilution) and its loss to OH radicals, compared to the winter season. Further, the diurnal patterns of SO_2 were inconsistent with that of NO_x, except the winter seasons. The main source of gas-phase SO_2 is from the combustion of all sulfur-containing fuels (oil, coal and diesel). In India, about 60 % of SO_2 emissions may be due to the consumption of coal and oil products, mainly from industry (36 %) and transport (7.8 %), and others include biomass and non-energy consumption (Garg et al. 2001).

Figure 4b and c show the seasonally averaged diurnal patterns of NO_x and CO, respectively. The diurnal cycles show two peaks during morning and evening traffic hours and valley during the afternoon hours. The nighttime concentrations stayed relatively flat between the peak and valley concentrations. This phenomenon can be attributed to the day-night differences in the chemical removal of NO_x and CO via photo-oxidation reactions and the height of the mixing layer. Earlier studies also suggested that the chemical sources of CO are smaller than anthropogenic emissions and during nighttime formaldehyde (HCHO) accumulates which undergo chemical reaction and photo-dissociation during morning hours resulting into the production of more CO (Monks 2005; Finlayson-Pitts et al. 1986). The diurnal variation of NO_x did not show a clear fluctuation during the monsoon. Further, the difference in peak magnitude of NO_x and CO between winter and pre-monsoon season was about two-fold, possibly indicating that the vertical mixing may be an important factor for the observed diurnal variations as photo-chemical loss is much lower in winter than that of the pre-monsoon season. The concentrations of NO_x and CO showed the highest magnitude in winter season followed by post-monsoon, pre-monsoon and monsoon season. The diurnal peaks of NO_x and CO in pre-monsoon (6.5 ppb and 857 ppb, respectively) were smaller than those in winter (12.2 ppb and 1192 ppb, respectively).

NO_x and CO are the main precursors of O_3, and followed a reverse diurnal pattern (Fig. 4d). Lowest concentration of NO_x and CO was observed during afternoon hours when O_3 showed a peak. This clearly illustrates the production of O_3 via photo-chemical oxidation of carbon-like compounds such as CO, CH_4, and NMHCs by their reaction with OH radicals in the presence of NO_x. The daytime O_3 concentration buildup is a pronounced feature of urban polluted sites (Lal et al. 2000). The largest diurnal peak concentration observed in pre-monsoon (i.e. summer) (61.1 ppb), followed by winter (45.7 ppb), post-monsoon (35.6 ppb), and monsoon (27.1 ppb), respectively. This seasonal diurnal pattern is similar to that of other locations in India (Pulikesi et al. 2006; Reddy et al. 2010; Ahammed et al. 2006; Beig et al. 2007), but unlike to that of in Northern China (Meng et al. 2009) where O_3 concentration were lowest in winter season. The larger variability in monthly averaged SO_2,NO_x, and CO were noticed during the winter season, indicative of larger near-surface anthropogenic sources and boundary layer height evolution, whereas O_3 shows higher variability in the pre-monsoon season when the photochemistry is at its peak. A positive correlation among SO_2, NO_x, and CO can be seen irrespective of the season of the year (Table 3), indicative of similar anthropogenic sources (e.g. mobile as well as stationary). Further, a negative correlation of NO_x and CO with O_3 clearly indicates the O_3 production via photochemical oxidation of carbon-link compounds (CO, CH_4, NMHC) in presence of NO_x, with a highest value being in pre-monsoon (i.e. summer) when ample sunlight is available.

Figure 5 shows the seasonally averaged diurnal variation of the rate of change of O_3 concentrations (dO_3/dt) at Kanpur. The rate of change of O_3 can be used as an indicator of urban and rural chemical environment (Naja,Lal 2002). Urban environments commonly show similar morning and evening rates of change in O_3, while rural sites are characterized by asymmetric diurnal pattern i.e. higher build up rates in the morning and lower loss rates in the evening hours. The highest seasonal positive rate of change was +6.77 ppb h^{-1} in pre-monsoon

Table 3 Correlations coefficients for measured trace gases

x\y	SO_2	NO_x	CO	O_3
Winter				
SO_2	1	0.20	0.18	0.17
NO_x		1	0.32	−0.27
CO			1	−0.28
O_3				1
Pre-monsoon				
SO_2	1	0.39	0.26	0.10
NO_x		1	0.33	−0.24
CO			1	−0.47
O_3				1
Monsoon				
SO_2	1	0.11	0.09	0.11
NO_x		1	0.15	0.04
CO			1	−0.12
O_3				1
Post-monsoon				
SO_2	1	0.32	0.13	0.07
NO_x		1	0.42	−0.10
CO			1	−0.03
O_3				1

while the negative rate of change was −5.67 ppb h^{-1} in winter, which can be attributed to the diminished photochemistry and shallow mixing layer height. The lowest positive and negative rate of change +2.56 ppb h^{-1} and −2.76 ppb h^{-1}, respectively, was observed during the monsoon season, which is attributed to washout effect and reduced availability of precursors and active radicals for the production of O_3. The nighttime rate of change was found almost steady and slightly negative, perhaps due to O_3 loss to surface deposition. The mean rate of change of O_3 concentration was also compared with a few other urban to rural sites in India (Table 4). The mean rate of change of O_3 at Kanpur found similar to that of at Agra whereas it was lower compared to other urban locations, Delhi, Ahmedabad and Pune, in India. Urban

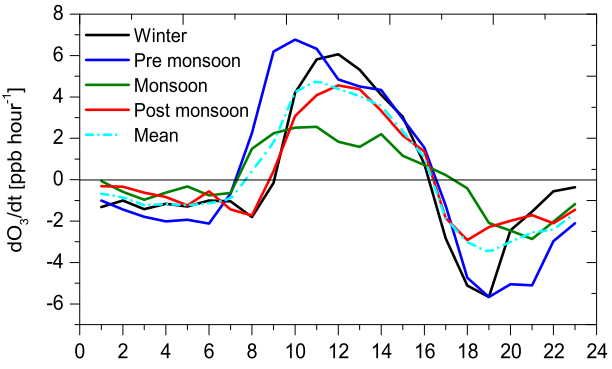

Fig. 5 Seasonally averaged diurnal variation of the rate of change of O_3 (dO_3/dt) at Kanpur. The dotted cyan color line indicates the mean over all seasons

Table 4 Rate of change of O_3 concentration (dO_3/dt) at Kanpur and other sites in India

Location	Site type	Rate of change of O_3 [ppb h^{-1}]		Reference
		(08:00–11:00 h)	(17:00–19:00 h)	
Kanpur	Urban	3.3	−2.6	This study
Agra	Urban	2.5	−2.4	(Singla et al. 2011)
Delhi	Urban	4.5	−5.3	(Ahammed et al. 2006)
Ahmedabad	Urban	5.9	−6.4	(Lal et al. 2000)
Pune	Urban	4.8	−2.6	(Shende et al. 1992)
Anantapur	Rural	4.6	−2.5	(Reddy et al. 2010)
Gadanki	Rural	4.6	−2.6	(Naja,Lal 2002)
Thumba	Coastal rural	5.5	−1.4	(Nair et al. 2002)
Kannur	Coastal rural	4.9	−6.4	(Nishanth et al. 2014)

locations showed comparable magnitude in the morning and evening rates of change in O_3 concentrations while this was not true in case of rural/remote sites. The morning time O_3 formation is strongly dependent on the available amount of precursors, while the evening time loss rate largely depends on nitrous oxide (NO) concentration which participates in O_3 titration processes. Generally, NO levels are found comparatively lower at rural sites than urban areas, which lead to slower O_3 titration in evening hours (Naja,Lal 2002). The evening time loss rate at Indian rural sites was generally found lower which supports relatively strong O_3 titration via NO, except at Kannur site (Table 4).

Further, the meteorological parameters (temperature and relative humidity) influence on trace gases was also examined. Figure 6 shows the scatter plot of temperature versus relative humidity as a function of trace gases for each season. Here, daily mean data was used instead of hourly mean data, to avoid the influence of the diurnal variations on the correlations. The association between temperature and SO_2, NO_x, and CO was found to be weak or insignificant (Table S3, Fig. 6). Although a fair correlation was found between temperature and NO_x in monsoon. The correlation coefficient between relative humidity and SO_2, NO_x, and CO was also found to be negative or weak (Table S3). The comparatively similar association between SO_2, NO_x, and CO and meteorological parameters (temperature and relative humidity) was also found at other urban site (Marković et al. 2008). Contrarily, O_3 followed a positive linear relationship with temperature, except in post-monsoon season while the strong negative with the relative humidity in all seasons. The highest O_3 concentrations were observed in the pre-monsoon season and lowest concentrations were found during middle of monsoon to early post-monsoon season. The persistent cloudy conditions with lower solar radiation and wet scavenging of pollutants result in near absence of photochemical O_3 production during monsoon season. Relative humidity is also an important factor because of its role in the overall reactivity of the system by affecting chain termination reactions. Major photochemical paths for O_3 sink are photolysis followed by the reaction of $O(^1D)$ with water vapor and via its reaction with hydrogen oxide radicals (HO_x) (Monks 2005; Wayne 2000). While, the previous global modeling study predicted decrease in global O_3 due to increased water vapor, mostly in remote areas, but also predicted summertime O_3 increase in polluted areas (Racherla and

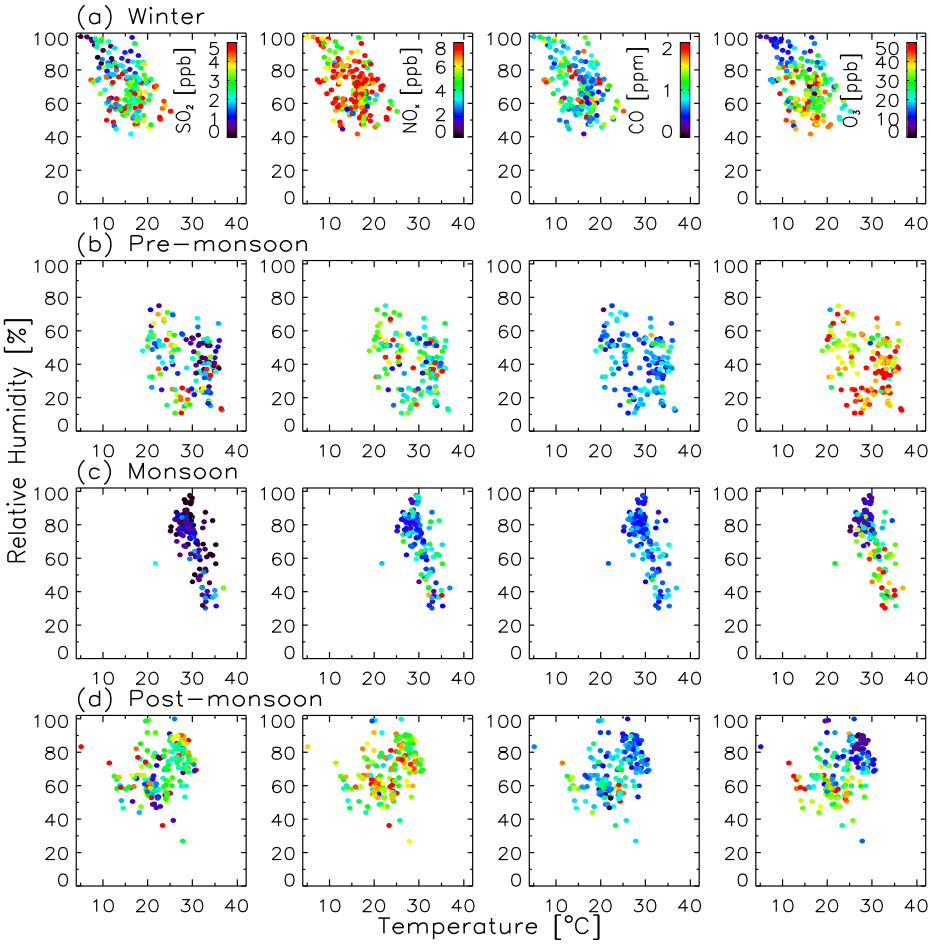

Fig. 6 Scatter plot of temperature versus relative humidity as a function of trace gases (SO_2, NO_x, CO, and O_3) for (**a**) winter (**b**) pre-monsoon, (**c**) monsoon, and (**d**) post-monsoon seasons at Kanpur. Each datapoint represents daily mean value

Adams 2006). A more recent study, however, suggested that the negative O_3-relative humidity correlation attributed to several other meteorological factor directly influencing O_3 production (Tawfik and Steiner 2013). Further investigation revealed that West-Northwest winds during post-monsoon and winter season brings long-range transported polluted air masses at the site (Fig. S1), leading to secondary peak in O_3 concentrations.

Further, we also examined ventilation coefficient which defines the atmospheric efficiency to disperse the air pollution. The ventilation coefficient is a product of wind speed (i.e. horizontal ventilation) and mixing layer height (i.e. vertical dilution of pollutants) (Goyal and Chalapati Rao 2007; Rama Krishna et al. 2004). The diurnal variation of wind speed, mixing layer height and ventilation coefficient for each season at Kanpur is shown in Fig. 7. The ventilation coefficient shows a similar pattern in all seasons. Low values of the ventilation coefficient during night indicate

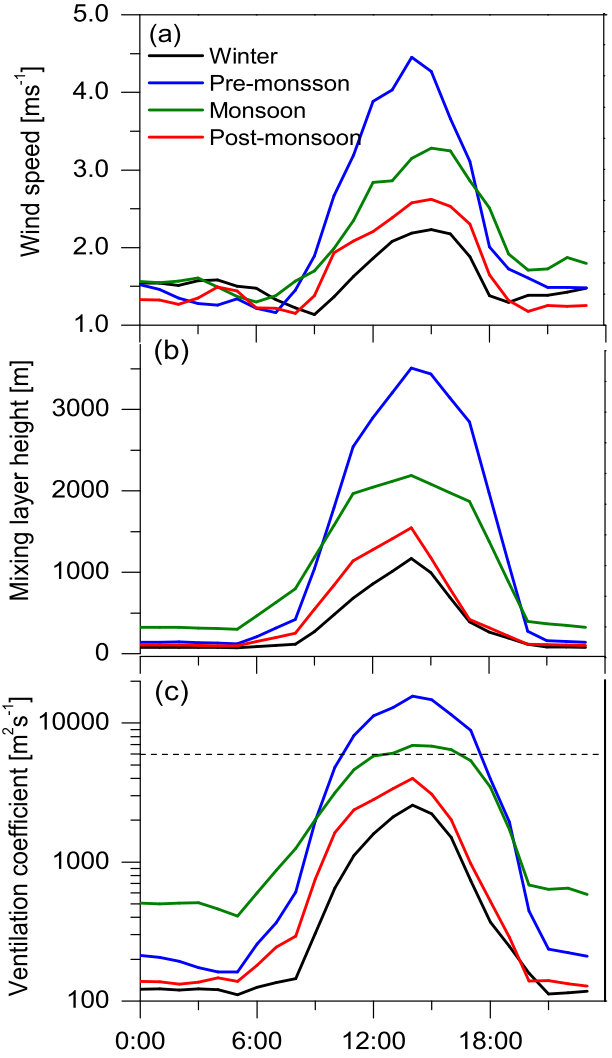

Fig. 7 Seasonally averaged diurnal variation of (**a**) wind speed, (**b**) mixing layer height, and (**c**) ventilation coefficient at Kanpur. The dotted line indicates the ventilation coefficient of 6000 m^2 s^{-1}, above which excellent pollutants dispersion efficiency occurs

the high pollution potential (Fig. 7c). The ventilation coefficient starts increasing after sunrise reaching a maximum during afternoon hours. The maximum value of ventilation coefficient in winter, pre-monsoon, monsoon, and post-monsoon was 2564 m^2 s^{-1}, 15,622 m^2 s^{-1}, 6895 m^2 s^{-1}, and 3991 m^2 s^{-1}, respectively, at 14:00 h. Eagleman (1991) proposed that low-pollution potential (i.e. excellent pollutants dispersion efficiency) occurs when the ventilation coefficient is >6000 m^2 s^{-1}. This criterion was met during 11:00–17:00 h in pre-monsoon and 12:00–16:00 h in monsoon making them efficient hours of pollution dispersion in the atmosphere. However, this criterion was not met at all during winter and post-monsoon.

Nevertheless, the high-pollution potential occurs at this site, indicates that air pollution is actually a regional issue and not limited to city-scale.

5 Conclusions

Here, we presented continuous measurements of SO_2, NO_x, CO and O_3 from an urban site, Kanpur, in India during June 2009 to May 2013. The data coverage over the entire study period was exceptionally good, with more than 80 % of the data available. We have performed statistical analysis of SO_2, NO_x, CO and O_3 to characterize their monthly as well as diurnal patterns together with meteorological parameters influence on these trace gases.

The hourly averaged mean SO_2, NO_x, CO, and O_3 concentrations over the entire study period ranged from 0.5 ppb to 98.7 ppb, 0.4 ppb to 96.8 ppb, 40 ppb to 5040 ppb, and 1.1 ppb to 106.8 ppb, respectively, with a mean and one standard deviation of 3.0±3.1 ppb, 5.7± 4.5 ppb, 721±403 ppb, and 27.9±17.8 ppb, respectively. Mean NO_x and CO concentrations at Kanpur were comparatively lower than those reported at New Delhi, India (40 % and 70 %, respectively). However, mean O_3 concentrations were comparable to those reported at other urban locations, but lower compared to rural and high altitude sites in India (24-36 %). SO_2, NO_x, and CO concentrations were highest during the winter season, perhaps due to a combined effect of large near-surface anthropogenic emissions, boundary layer processes, retarded photochemical loss owing to lower solar intensity as well as local surface wind patterns. Contrarily, O_3 concentrations were observed highest during pre-monsoon season, with its direct linear relationship with incoming solar radiation. The lowest concentrations for all trace gases were observed during the monsoon season, mainly due to relatively lower near-surface emissions (other than traffic and industrial) and wet scavenging of pollutants.

The seasonally averaged diurnal variation of SO_2 was most pronounced in winter, with maxima during traffic hours, due to relatively low mixing height and less efficient oxidation to sulfate during winter. The diurnal variation of SO_2 in other seasons did not show significant variability, with lowest in the monsoon seasons. The seasonally averaged diurnal cycles of NO_x and CO showed similar pattern with peaks during traffic hours and a valley during afternoon hours. O_3 depicted a reverse pattern with highest concentrations during afternoon hours and lowest in early morning before the sunrise. The mean rate of change of O_3 concentrations during the morning hours (08:00 to 11:00 h) and evening hours (17:00 to 19:00 h) at Kanpur were 3.3 ppb h^{-1} and −2.6 ppb h^{-1}, respectively. This feature in the rate of change of O_3 itself indicates that this site is a typical urban chemical environment. The association between meteorological variables (temperature and relative humidity) and SO_2, NO_x, and CO were found to be weak or insignificant, with a few exceptions. However, O_3 followed a positive linear relationship with temperature, except in post-monsoon season while the strong negative with the relative humidity in all seasons. The ventilation coefficient was found to be highest in the pre-monsoon season and lowest during winter. The low value in winter indicated the high-pollution potential occurs at this site. Thus further suggests that air pollution is actually a regional issue and not limited to local-scale.

Nevertheless, such long-term continuous measurements of trace gases and meteorological variables are crucial to better understand the characterization of air pollutants at diverse locations, including urban areas which are at high health and economical risk in developing nations such as India and China.

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References

Ahammed, Y.N., Reddy, R.R., Gopal, K.R., Narasimhulu, K., Basha, D.B., Reddy, L.S.S., Rao, T.V.R.: Seasonal variation of the surface ozone and its precursor gases during 2001–2003, measured at Anantapur (14.62°N), a semi-arid site in India. Atmos. Res. **80**(2–3), 151–164 (2006). doi:10.1016/j.atmosres.2005.07.002

Akimoto, H.: Global Air quality and pollution. Science **302**(5651), 1716–1719 (2003). doi:10.1126/science.1092666

Akpinar, S., Oztop, H., Kavak Akpinar, E.: Evaluation of relationship between meteorological parameters and air pollutant concentrations during winter season in Elazığ, Turkey. Environ. Monit. Assess. **146**(1–3), 211–224 (2008). doi:10.1007/s10661-007-0073-9

Andreae, M.O., Merlet, P.: Emission of trace gases and aerosols from biomass burning. Glob. Biogeochem. Cy. **15**(4), 955–966 (2001). doi:10.1029/2000gb001382

Beig, G., Gunthe, S., Jadhav, D.B.: Simultaneous measurements of ozone and its precursors on a diurnal scale at a semi urban site in India. J. Atmos. Chem. **57**(3), 239–253 (2007). doi:10.1007/s10874-007-9068-8

Chameides, W., Walker, J.C.G.: A photochemical theory of tropospheric ozone. J. Geophys. Res. **78**(36), 8751–8760 (1973). doi:10.1029/JC078i036p08751

Chelani, A.B..: Persistence analysis of extreme CO, NO_2 and O_3 concentrations in ambient air of Delhi. Atmos. Res. **108**, 128–134 (2012). doi:10.1016/j.atmosres.2012.02.001

Chin, M., Jacob, D.J., Munger, J.W., Parrish, D.D., Doddridge, B.G.: Relationship of ozone and carbon monoxide over North America. J. Geophys. Res. **99**(D7), 14565–14573 (1994). doi:10.1029/94jd00907

Cohen, B.: Urbanization in developing countries: current trends, future projections, and key challenges for sustainability. Technol. Soc. **28**(1–2), 63–80 (2006). doi:10.1016/j.techsoc.2005.10.005

Cooper, O.R., Parrish, D.D., Stohl, A., Trainer, M., Nedelec, P., Thouret, V., Cammas, J.P., Oltmans, S.J., Johnson, B.J., Tarasick, D., Leblanc, T., McDermid, I.S., Jaffe, D., Gao, R., Stith, J., Ryerson, T., Aikin, K., Campos, T., Weinheimer, A., Avery, M.A.: Increasing springtime ozone mixing ratios in the free troposphere over western North America. Nature **463**, 344–348 (2010). doi:10.1038/nature08708

CPCB: National ambient air quality status and trends in India-2010. In: Central pollution control board, ministry of environment and forests, NAAQMS/ 35 /2011-2012. (2012)

Crutzen, P.J., Andreae, M.O.: Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. Science **250**(4988), 1669–1678 (1990). doi:10.1126/science.250.4988.1669

Datta, A., Saud, T., Goel, A., Tiwari, S., Sharma, S.K., Saxena, M., Mandal, T.K.: Variation of ambient SO_2 over Delhi. J. Atmos. Chem. **65**(2–3), 127–143 (2010). doi:10.1007/s10874-011-9185-2

David, L.M., Nair, P.R.: Diurnal and seasonal variability of surface ozone and NO_x at a tropical coastal site: association with mesoscale and synoptic meteorological conditions. J. Geophys. Res. **116**(D10), D10303 (2011). doi:10.1029/2010jd015076

Debaje, S.B., Kakade, A.D.: Surface ozone variability over western Maharashtra, India. J. Hazard. Mater. **161**(2–3), 686–700 (2009). doi:10.1016/j.jhazmat.2008.04.010

Dey, S., Tripathi, S.N.: Estimation of aerosol optical properties and radiative effects in the Ganga basin, northern India, during the wintertime. J. Geophys. Res. **112**(D3), D03203 (2007). doi:10.1029/2006jd007267

Draxler, R.R., Rolph, G.D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://ready.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, Silver Spring, MD (2010)

Eagleman, J.R.: Air pollution meteorology. Lenexa, KS : Trimedia, (1991)

Fang, M., Chan, C.K., Yao, X.: Managing air quality in a rapidly developing nation: China. Atmos. Environ. **43**(1), 79–86 (2009). doi:10.1016/j.atmosenv.2008.09.064

Fenger, J.: Air pollution in the last 50 years – from local to global. Atmos. Environ. **43**(1), 13–22 (2009). doi:10.1016/j.atmosenv.2008.09.061

Finlayson-Pitts, B.J., Pitts, J.N.: Atmospheric Chemistry: Fundamentals and Experimental Techniques, John Wiley & Sons; 1 edition (April 1986) ed. Chemical analysis: a series of monographs on analytical chemistry and Its applications, New York: John Wiley (1986)

Garg, A., Shukla, P.R., Bhattacharya, S., Dadhwal, V.K.: Sub-region (district) and sector level SO_2 and NO_x emissions for India: assessment of inventories and mitigation flexibility. Atmos. Environ. **35**(4), 703–713 (2001). doi:10.1016/S1352-2310(00)00316-2

Ghude, S.D., Fadnavis, S., Beig, G., Polade, S.D., van der, A.R.J.: Detection of surface emission hot spots, trends, and seasonal cycle from satellite-retrieved NO_2 over India. J. Geophys. Res. **113**(D20), D20305 (2008). doi:10.1029/2007jd009615

Ghude, S., Kulkarni, S., Kulkarni, P., Kanawade, V., Fadnavis, S., Pokhrel, S., Jena, C., Beig, G., Bortoli, D.: Anomalous low tropospheric column ozone over Eastern India during the severe drought event of monsoon 2002: a case study. Environ. Sci. Pollut. R. **18**(8), 1442–1455 (2011a). doi:10.1007/s11356-011-0506-4

Ghude, S.D., Beig, G., Kulkarni, P.S., Kanawade, V.P., Fadnavis, S., Remedios, J.J., Kulkarni, S.H.: Regional CO pollution over the Indian-subcontinent and various transport pathways as observed by MOPITT. Int. J. Remote. Sens. **32**(21), 6133–6148 (2011b). doi:10.1080/01431161.2010.507796

Goyal, S.K., Chalapati Rao, C.V.: Assessment of atmospheric assimilation potential for industrial development in an urban environment: Kochi (India). Sci. Total Environ. **376**(1–3), 27–39 (2007). doi:10.1016/j.scitotenv.2007.01.067

Han, S., Bian, H., Feng, Y., Liu, A., Li, X., Zeng, F., Zhang, X.: Analysis of the relationship between O_3, NO and NO_2 in Tianjin, China. Aerosol. Air. Qual. Res. **11**, 128–139 (2011). doi:10.4209/aaqr.2010.07.0055

Hocking, W.K., Carey-Smith, T., Tarasick, D.W., Argall, P.S., Strong, K., Rochon, Y., Zawadzki, I., Taylor, P.A.: Detection of stratospheric ozone intrusions by windprofiler radars. Nature **450**(7167), 281–284 (2007). doi:10.1038/nature06312

Houghton, J., Callander, B., Varney, S.: Climate change 1992: the supplementary report to the IPCC scientific Assessment', intergovernmental panel on climate change. In. Cambridge University Press, Cambridge (1992)

Jacob, D.J., Logan, J.A., Gardner, G.M., Yevich, R.M., Spivakovsky, C.M., Wofsy, S.C., Sillman, S., Prather, M.J.: Factors regulating ozone over the United States and its export to the global atmosphere. J. Geophys. Res. **98**(D8), 14817–14826 (1993a). doi:10.1029/98jd01224

Jacob, D.J., Logan, J.A., Yevich, R.M., Gardner, G.M., Spivakovsky, C.M., Wofsy, S.C., Munger, J.W., Sillman, S., Prather, M.J., Rodgers, M.O., Westberg, H., Zimmerman, P.R.: Simulation of summertime ozone over North America. J. Geophys. Res. **98**(D8), 14797–14816 (1993b). doi:10.1029/93jd01223

Jacob, D.J., Crawford, J.H., Kleb, M.M., Connors, V.S., Bendura, R.J., Raper, J.L., Sachse, G.W., Gille, J.C., Emmons, L., Heald, C.L.: Transport and chemical evolution over the pacific (TRACE-P) aircraft mission: design, execution, and first results. J. Geophys. Res. **108**(D20), 9000 (2003). doi:10.1029/2002jd003276

Jaffe, D., Bertschi, I., Jaeglé, L., Novelli, P., Reid, J.S., Tanimoto, H., Vingarzan, R., Westphal, D.L.: Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America. Geophys. Res. Lett. **31**(16), L16106 (2004). doi:10.1029/2004gl020093

Kalita, G., Bhuyan, P.K.: Spatial heterogeneity in tropospheric column ozone over the Indian subcontinent: long-term climatology and possible association with natural and anthropogenic activities. Adv. Meteorol. 2011 (2011). doi:10.1155/2011/924516

Kanamitsu, M.: Description of the NMC global data assimilation and forecast system. Weather. Forecast. **4**, 335–342 (1989). doi:10.1175/1520-0434(1989)

Kar, J., Deeter, M.N., Fishman, J., Liu, Z., Omar, A., Creilson, J.K., Trepte, C.R., Vaughan, M.A., Winker, D.M.: Wintertime pollution over the eastern indo-Gangetic plains as observed from MOPITT, CALIPSO and tropospheric ozone residual data. Atmos. Chem. Phys. **10**(24), 12273–12283 (2010). doi:10.5194/acp-10-12273-2010

Khare, M.: Air pollution – monitoring, modelling, health and control. InTech Janeza Trdine 9, 51000 Rijeka, Croatia, (2012)

Kumar, R., Naja, M., Venkataramani, S., Wild, O.: Variations in surface ozone at Nainital: a high-altitude site in the central Himalayas. J. Geophys. Res. **115**(D16), D16302 (2010). doi:10.1029/2009jd013715

Kumar, R., Naja, M., Pfister, G.G., Barth, M.C., Wiedinmyer, C., Brasseur, G.P.: Simulations over south Asia using the weather research and forecasting model with chemistry (WRF-Chem): chemistry evaluation and initial results. Geosci. Model. Dev. **5**(3), 619–648 (2012). doi:10.5194/gmd-5-619-2012

Lal, S., Naja, M., Subbaraya, B.H.: Seasonal variations in surface ozone and its precursors over an urban site in India. Atmos. Environ. **34**(17), 2713–2724 (2000). doi:10.1016/S1352-2310(99)00510-5

Lefohn, A.S., Wernli, H., Shadwick, D., Limbach, S., Oltmans, S.J., Shapiro, M.: The importance of stratospheric–tropospheric transport in affecting surface ozone concentrations in the western and northern tier of the United States. Atmos. Environ. **45**(28), 4845–4857 (2011). doi:10.1016/j.atmosenv.2011.06.014

Lelieveld, J., Dentener, F.J., Peters, W., Krol, M.C.: On the role of hydroxyl radicals in the self-cleansing capacity of the troposphere. Atmos. Chem. Phys. **4**(9/10), 2337–2344 (2004). doi:10.5194/acp-4-2337-2004

Logan, J.A., Prather, M.J., Wofsy, S.C., McElroy, M.B.: Tropospheric chemistry: a global perspective. J. Geophys. Res. **86**(C8), 7210–7254 (1981). doi:10.1029/JC086iC08p07210

Lu, Z., Streets, D.G., de Foy, B., Krotkov, N.A.: Ozone monitoring instrument observations of Interannual increases in SO_2 emissions from Indian coal-fired power plants during 2005–2012. Environ. Sci. Technol. **47**(24), 13993–14000 (2013). doi:10.1021/es4039648

Mage, D., Ozolins, G., Peterson, P., Webster, A., Orthofer, R., Vandeweerd, V., Gwynne, M.: Urban air pollution in megacities of the world. Atmos. Environ. **30**(5), 681–686 (1996). doi:10.1016/1352-2310(95)00219-7

Marković, D., Marković, D., Jovanović, A., Lazić, L., Mijić, Z.: Determination of O_3, NO_2, SO_2, CO and PM_{10} measured in Belgrade urban area. Environ. Monit. Assess. **145**(1–3), 349–359 (2008). doi:10.1007/s10661-007-0044-1

Mavroidis, I., Ilia, M.: Trends of NO_x, NO_2 and O_3 concentrations at three different types of air quality monitoring stations in Athens, Greece. Atmos. Environ. **63**, 135–147 (2012). doi:10.1016/j.atmosenv.2012.09.030

Meng, Z.Y., Xu, X.B., Yan, P., Ding, G.A., Tang, J., Lin, W.L., Xu, X.D., Wang, S.F.: Characteristics of trace gaseous pollutants at a regional background station in Northern China. Atmos. Chem. Phys. **9**(3), 927–936 (2009). doi:10.5194/acp-9-927-2009

Michael, M., Yadav, A., Tripathi, S.N., Kanawade, V.P., Gaur, A., Sadavarte, P., Venkataraman, C.: Simulation of trace gases and aerosols over the Indian domain: evaluation of the WRF-Chem model. Geosci. Model. Dev. Discuss. **7**(1), 431–482 (2014). doi:10.5194/gmdd-7-431-2014

Monks, P.S.: Gas-phase radical chemistry in the troposphere. Chem. Soc. Rev. **34**(5), 376–395 (2005). doi:10.1039/b307982c

Montzka, S.A., Krol, M., Dlugokencky, E., Hall, B., Jöckel, P., Lelieveld, J.: Small Interannual variability of global atmospheric hydroxyl. Science **331**(6013), 67–69 (2011). doi:10.1126/science.1197640

Nair, P.R., Chand, D., Lal, S., Modh, K.S., Naja, M., Parameswaran, K., Ravindran, S., Venkataramani, S.: Temporal variations in surface ozone at Thumba (8.6°N, 77°E)-a tropical coastal site in India. Atmos. Environ. **36**(4), 603–610 (2002). doi:10.1016/S1352-2310(01)00527-1

Naja, M., Lal, S.: Changes in surface ozone amount and its diurnal and seasonal patterns, from 1954 to 55 to 1991–93, measured at Ahmedabad (23 N), India. Geophys. Res. Lett. **23**(1), 81–84 (1996). doi:10.1029/95gl03589

Naja, M., Lal, S.: Surface ozone and precursor gases at Gadanki (13.5°N, 79.2°E), a tropical rural site in India. J. Geophys. Res. 107 (D14), ACH 8-1-ACH 8–13 (2002). doi:10.1029/2001jd000357

Naja, M., Lal, S., Chand, D.: Diurnal and seasonal variabilities in surface ozone at a high altitude site Mt Abu (24.6°N, 72.7°E, 1680m asl) in India. Atmos. Environ. **37**(30), 4205–4215 (2003). doi:10.1016/S1352-2310(03)00565-X

Nishanth, T., Satheesh Kumar, M.K., Valsaraj, K.T.: Variations in surface ozone and NO_x at Kannur: a tropical, coastal site in India. J. Atmos. Chem. **69**(2), 101–126 (2012). doi:10.1007/s10874-012-9234-5

Nishanth, T., Praseed, K.M., Satheesh Kumar, M.K., Valsaraj, K.T.: Observational study of surface O_3, NO_x, CH_4 and total NMHCs at Kannur, India. Aerosol. Air. Qual. Res. **14**, 1074–1088 (2014). doi:10.4209/aaqr.2012.11.0323

Pasricha, P.K., Gera, B.S., Shastri, S., Maini, H.K., John, T., Ghosh, A.B.., Tiwari, M.K., Garg, S.C.: Role of the water vapour greenhouse effect in the forecasting of fog occurrence. Bound.-Lay. Meteorol. **107**(2), 469–482 (2003). doi:10.1023/a:1022128800130

Pudasainee, D., Sapkota, B., Shrestha, M.L., Kaga, A., Kondo, A., Inoue, Y.: Ground level ozone concentrations and its association with NO_x and meteorological parameters in Kathmandu valley, Nepal. Atmos. Environ. **40**(40), 8081–8087 (2006). doi:10.1016/j.atmosenv.2006.07.011

Pulikesi, M., Baskaralingam, P., Rayudu, V.N., Elango, D., Ramamurthi, V., Sivanesan, S.: Surface ozone measurements at urban coastal site Chennai, in India. J. Hazard. Mater. **137**(3), 1554–1559 (2006). doi:10.1016/j.jhazmat.2006.04.040

Racherla, P.N., Adams, P.J.: Sensitivity of global tropospheric ozone and fine particulate matter concentrations to climate change. J. Geophys. Res. **111**(D24), D24103 (2006). doi:10.1029/2005jd006939

Rama Krishna, T.V.B.P.S., Reddy, M.K., Reddy, R.C., Singh, R.N.: Assimilative capacity and dispersion of pollutants due to industrial sources in Visakhapatnam bowl area. Atmos. Environ. **38**(39), 6775–6787 (2004). doi:10.1016/j.atmosenv.2004.09.014

Reddy, B.S.K., Kumar, K.R., Balakrishnaiah, G., Gopal, K.R., Reddy, R.R., Ahammed, Y.N., Narasimhulu, K., Reddy, L.S.S., Lal, S.: Observational studies on the variations in surface ozone concentration at Anantapur in southern India. Atmos. Res. **98**(1), 125–139 (2010). doi:10.1016/j.atmosres.2010.06.008

Reddy, B.S., Kumar, K.R., Balakrishnaiah, G., Gopal, K.R., Reddy, R.R., Sivakumar, V., Lingaswamy, A.P., Arafath, S.M., Umadevi, K., Kumari, S.P., Ahammed, Y.N., Lal, S.: Analysis of diurnal and seasonal behavior of surface ozone and its precursors (NO_x) at a semi-arid rural site in southern India. Aerosol. Air. Qual. Res. **12**, 1081–1094 (2013). doi:10.4209/aaqr.2012.03.0055

Roy, S., Beig, G., Jacob, D.: Seasonal distribution of ozone and its precursors over the tropical Indian region using regional chemistry-transport model. J. Geophys. Res. **113**(D21), D21307 (2008). doi:10.1029/2007jd009712

Sahu, L.K., Lal, S.: Distributions of C_2–C_5 NMHCs and related trace gases at a tropical urban site in India. Atmos. Environ. **40**(5), 880–891 (2006). doi:10.1016/j.atmosenv.2005.10.021

Satsangi, G., Lakhani, A., Kulshrestha, P.R., Taneja, A.: Seasonal and diurnal variation of surface ozone and a preliminary analysis of exceedance of its critical levels at a semi-arid site in India. J. Atmos. Chem. **47**(3), 271–286 (2004). doi:10.1023/B:JOCH.0000021156.04126.3b

Seinfeld, J.H., Pandis, S.N.: Atmospheric chemistry and physics. From Air Pollution to Climate Changes, Wiley, New York (1998)

Sharma, A.P., Kim, K., Kim, K., Ahn, J., Shon, Z., Sohn, J., Lee, J., Ma, B.R.J.C.: Ambient particulate matter (PM_{10}) concentrations in major urban areas of Korea during 1996–2010. Atmos. Poll. Res. **5**, 161–169 (2014). doi:10.5094/APR.2014.020

Shende, R.R., Jayaraman, K., Sreedharan, C.R., Tiwari, V.S.: Broad features of surface ozone variations over Indian region. paper presented at the quadrennial ozone symposium, Intl. Ozone Comm, Charlottesville (1992)

Singh, R.P., Dey, S., Tripathi, S.N., Tare, V., Holben, B.: Variability of aerosol parameters over Kanpur, northern India. J. Geophys. Res. **109**(D23), D23206 (2004). doi:10.1029/2004jd004966

Singla, V., Satsangi, A., Pachauri, T., Lakhani, A., Kumari, K.M.: Ozone formation and destruction at a sub-urban site in North Central region of India. Atmos. Res **101**(1–2), 373–385 (2011). doi:10.1016/j.atmosres.2011.03.011

Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L.: Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change. In. Cambridge University Press, Cambridge (2007)

Stroud, C., Madronich, S., Atlas, E., Ridley, B., Flocke, F., Weinheimer, A., Talbot, B., Fried, A., Wert, B., Shetter, R., Lefer, B., Coffey, M., Heikes, B., Blake, D.: Photochemistry in the arctic free troposphere: NO_x budget and the role of odd nitrogen reservoir recycling. Atmos. Environ. **37**(24), 3351–3364 (2003). doi:10.1016/S1352-2310(03)00353-4

Sun, Y., Wang, L., Wang, Y., Quan, L., Zirui, L.: In situ measurements of SO_2, NO_x, NO_y, and O_3 in Beijing, China during august 2008. Sci. Total Environ. **409**(5), 933–940 (2011). doi:10.1016/j.scitotenv.2010.11.007

Suthawaree, J., Kato, S., Takami, A., Kadena, H., Toguchi, M., Yogi, K., Hatakeyama, S., Kajii, Y.: Observation of ozone and carbon monoxide at Cape Hedo, Japan: seasonal variation and influence of long-range transport. Atmos. Environ. **42**(13), 2971–2981 (2008). doi:10.1016/j.atmosenv.2007.12.053

Tang, G., Li, X., Wang, Y., Xin, J., Ren, X.: Surface ozone trend details and interpretations in Beijing, 2001–2006. Atmos. Chem. Phys. **9**(22), 8813–8823 (2009). doi:10.5194/acp-9-8813-2009

Tawfik, A.B.., Steiner, A.L.: A proposed physical mechanism for ozone-meteorology correlations using land–atmosphere coupling regimes. Atmos. Environ. **72**, 50–59 (2013). doi:10.1016/j.atmosenv.2013.03.002

Tie, X., Geng, F., Peng, L., Gao, W., Zhao, C.: Measurement and modeling of O_3 variability in Shanghai, China: application of the WRF-chem model. Atmos. Environ. **43**(28), 4289–4302 (2009). doi:10.1016/j.atmosenv.2009.06.008

Tiwari, S., Rai, R., Agrawal, M.: Annual and seasonal variations in tropospheric ozone concentrations around Varanasi. Int. J. Remote. Sens. **29**(15), 4499–4514 (2008). doi:10.1080/01431160801961391

Tripathi, S.N., Tare, V., Chinnam, N., Srivastava, A.K., Dey, S., Agarwal, A., Kishore, S., Lal, R.B., Manar, M., Kanwade, V.P., Chauhan, S.S.S., Sharma, M., Reddy, R.R., Gopal, K.R., Narasimhulu, K., Reddy, L.S.S., Gupta, S., Lal, S.: Measurements of atmospheric parameters during Indian space research organization Geosphere biosphere programme land campaign II at a typical location in the Ganga basin: 1. physical and optical properties. J. Geophys. Res. **111**(D23), D23209 (2006). doi:10.1029/2006jd007278

Tu, J., Xia, Z.-G., Wang, H., Li, W.: Temporal variations in surface ozone and its precursors and meteorological effects at an urban site in China. Atmos. Res. **85**(3–4), 310–337 (2007). doi:10.1016/j.atmosres.2007.02.003

Vingarzan, R.: A review of surface ozone background levels and trends. Atmos. Environ. **38**(21), 3431–3442 (2004). doi:10.1016/j.atmosenv.2004.03.030

Walcek, C.J., Yuan, H.-H.: Calculated influence of temperature-related factors on ozone formation rates in the lower troposphere. J. Appl. Meteorol. **34**(5), 1056–1069 (1995). doi:10.1175/1520-0450(1995)034<1056:ciotrf>2.0.co;2

Wang, S., Hao, J.: Air quality management in China: issues, challenges, and options. J. Environ. Sci. **24**(1), 2–13 (2012). doi:10.1016/S1001-0742(11)60724-9

Wayne, R.P.: Chemistry of atmospheres: an introduction to the chemistry of the atmospheres of earth, the planets, and their satellites. Oxford University Press, New York (2000)

Wayne, P.: Chapter 5: the earth's troposphere, chemistry of atmospheres, an introduction to the chemistry of atmospheres of earth, the planets and their satellites. Oxford Clarendon Press, (1991)

Zahn, A., Brenninkmeijer, C.A.M.: New directions: a chemical tropopause defined. Atmos. Environ. **37**(3), 439–440 (2003). doi:10.1016/S1352-2310(02)00901-9

Zhang, L., Jacob, D.J., Boersma, K.F., Jaffe, D.A., Olson, J.R., Bowman, K.W., Worden, J.R., Thompson, A.M., Avery, M.A., Cohen, R.C., Dibb, J.E., Flock, F.M., Fuelberg, H.E., Huey, L.G., McMillan, W.W., Singh, H.B., Weinheimer, A.J.: Transpacific transport of ozone pollution and the effect of recent asian emission increases on air quality in North America: an integrated analysis using satellite, aircraft, ozonesonde, and surface observations. Atmos. Chem. Phys. **8**(20), 6117–6136 (2008). doi:10.5194/acp-8-6117-2008