

Study of a High SO₂ Event Observed over an Urban Site in Western India

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(Manuscript received 21 October 2011; revised 21 December 2011; accepted 27 December 2011)

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Abstract: Continuous measurements of SO₂, NO_x and O₃ along with sampling based measurements of CO, CH₄, NMHCs and CO₂ were carried out during May, 2010 at Ahmedabad. The diurnal variations of SO₂ in ambient air exhibited elevated values during the night and lower levels during the sunlit hours. The mean concentration of SO₂ during the study period was 0.95 ± 0.88 ppbv. However, the ambient SO₂ exceeded 17 ppbv in the night of 20 May, 2010. On the same day, tropospheric columnar SO₂ from OMI showed almost 350% increase corroborating the surface observations over an extended height regime. This was also the highest columnar value of SO₂ during the summer of 2010. Columnar loadings were also found to be high for formaldehyde, precipitable water vapor and aerosol optical depth on 20 May. Elevated concentrations were also recorded for other trace gases like NO₂ and O₃. Analysis of related data of trace gases indicated characteristics of fresh emissions with dominant contributions from mobile sources during the study period. However, SO₂/NO₂ ratio of 0.36 during the event period on 20th May connotes non-local influences. Analyses of meteorological parameters suggest combined impacts of transport and inversion causing higher levels of SO₂ and other pollutants during 20-21 May. Episodes of such enhancements may perturb chemical and radiative balance of the atmosphere.

Key words: SO₂, trace gases, pollution event, satellite observations, transport, inversion

1. Introduction

Rapid economic and social developments in India have repercussions in a surging need in power, steel and other industrial products requiring burning of more and more fossil fuel like coal and petroleum. The intensification of agricultural practices including the extensive use of fertilizers and the spurt in the number of vehicles also engenders soaring levels of various pollutants (Chameides *et al.*, 1994; Lal, 2007). All of these processes release a plethora of trace gases like sulfur dioxide (SO₂), carbon monoxide (CO), nitrogen oxides (NO_x) and volatile organic compounds (VOCs) including methane (CH₄) and non-methane hydrocarbons (NMHCs), contributing to air pollution and its associated hazards. Inventories reporting the budget estimates of these species over the Indian subcontinent are still inadequate to make policy decisions and to determine their impacts on the environment, climate, health

and crops (Streets *et al.*, 2003; Gurjar *et al.*, 2010).

SO₂ is a primary criteria pollutant; the short-term exposures to elevated SO₂ levels can have significant health effects (WHO, 2005). The chemistry of SO₂ is mainly controlled by the formation from reduced sulfur compounds (hydrogen sulfide, dimethyl sulfide etc.) and its oxidation into sulfate (single scattering albedo of 0.97). The direct radiative forcing of sulfate is estimated to be around -0.4 ± 0.2 W m⁻² while the total direct forcing of aerosols is -0.5 ± 0.4 W m⁻² (IPCC, 2007). The unconverted SO₂ is responsible for local air pollution and can exacerbate smog formation and acid rain. Though global SO₂ emissions have stabilized since 1990, Indian emissions continue to increase from 2.85 Tg-SO₂ in 1990 to 4.26 Tg-SO₂ in 2000 (Garg *et al.*, 2006) to a staggering 8.8 Tg-SO₂ in 2011 (Lu and Streets, 2011).

Though knowledge of SO₂ levels is very crucial in the understanding of the global sulfur cycle and the radiation budget, its precise in-situ measurements are still very limited in India. The emissions of SO₂ in the Indian subcontinent are found to be high in north India along the Indo-Gangetic plains (Adhikary *et al.*, 2007). A recent study at New Delhi reported SO₂ mixing ratio of the order of 1.48 ppbv during summer, 1.24 ppbv during monsoon and 2.55 ppbv during winter (Datta *et al.*, 2011). Its concentration was measured to be 1.35 ± 0.54 ppbv over Agra for the period from July 1999 to June 2001 (Kumar *et al.*, 2004). An increase in its concentrations from 7.2 ppbv in 1997 to 12.8 ppbv in 2000 was observed at Mumbai (Gupta *et al.*, 2003). SO₂ concentrations of the order of 3-5 ppbv were reported in the southern part of India during the February 2004 phase of ISRO-GBP land campaign-1 (Reddy *et al.*, 2008).

In-situ measurements of SO₂ at Ahmedabad enabled detection of a pollution event that culminated during 20-21 May, 2010. In this paper, this occurrence is explored in detail and documented in terms of trace gas variations and dynamics.

2. Material and methods

a. The study region

The observational site is located in the main campus of Physical Research Laboratory (PRL), Ahmedabad (23N, 72.6E and 49 m above sea level) in Gujarat state of India. It is situated in the western region of the Ahmedabad city (right panel of

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Fig. 1). Ahmedabad is an urban region in western India, having numerous chemical and pharmaceutical industries and a thermal power station. It has a hot semi-arid climate with three main seasons: summer, monsoon and winter. Apart from the monsoon season, the climate is dry. The population of Ahmedabad is around 5 million and like any other urban center, it also has considerable vehicular traffic, which is growing at about 10% per annum.

b. SO₂ sources in and around the study region

Power sector has been reported to contribute ~46% of SO₂

emissions in India. Industries (steel, cement, fertilizer and oil refinery) contribute ~36% and transport contributes ~8% to SO₂ emissions in India (Garg *et al.*, 2001). Ambient SO₂ mixing ratio may also be influenced by the burning of crop stubbles (Mittal *et al.*, 2009). Many other trace gases have emission sources common to SO₂; however, their volume mixing ratios in ambient air may vary depending on the type of emission dominating in that region. O₃ precursors, such as CO, NO_x, NMHCs and CH₄, have both anthropogenic as well as natural sources though there are large uncertainties in their budgets also (Streets *et al.*, 2003). Among NMHCs, ethene (C₂H₄), acetylene (C₂H₂), propene (C₃H₆) and butanes (C₄H₁₀)



Fig. 1. Left panel: Map of India showing location of Ahmedabad. Right panel: Ahmedabad and the measurement location (PRL). Indian Fertilizer of Farmer Co-operation Kalol Plant (IIFCO) and Thermal Power House (Sabarmati) are two large emitters of SO₂ near the measurement site. IIFCO is ~30 km from PRL and Power House is ~10 km.

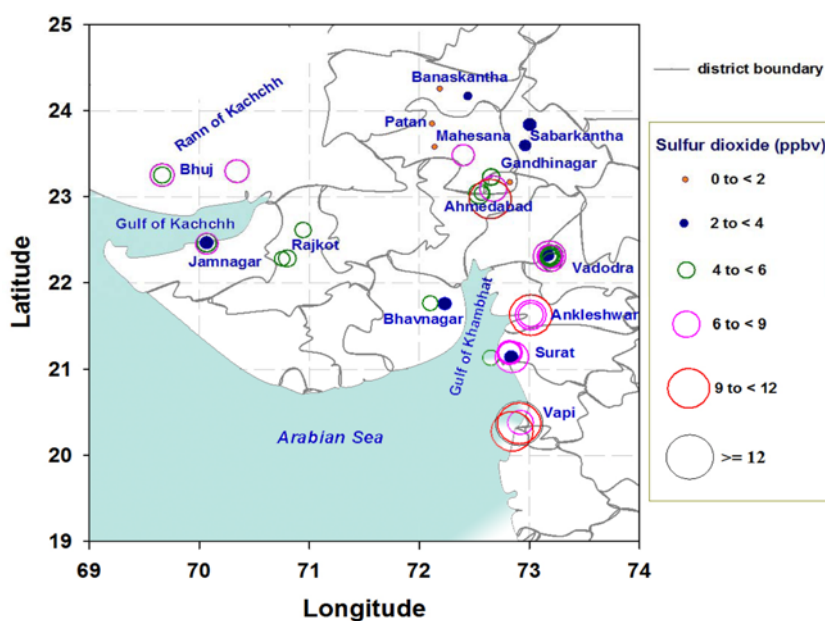


Fig. 2. SO₂ levels for 2009-2010 at various places in Gujarat based on data from Gujarat Pollution Control Board. The sizes of the circles are proportional to the SO₂ concentrations and the colors represent different concentration ranges.

are emitted from both fuel combustion as well as biomass burning; ethane (C_2H_6) and propane (C_3H_8) have emission sources in natural gas, vegetation and biomass burning. Formaldehyde (HCHO) is formed as a result of photochemical oxidation of reactive organic gases in polluted atmospheres containing O_3 and NO_x .

The air quality of Ahmedabad is controlled by complex processes because of its proximity to the Thar Desert in the north, the Arabian Sea in the south-west, and the changing wind patterns during different seasons, which carry pollution from neighboring industrial areas. In terms of SO_2 and NO_x emissions, this region is among the top 10 emitting districts in India (Garg *et al.*, 2001). The Ahmedabad-Mumbai corridor contains the maximum number of large point sources (LPS) for SO_2 emissions (mainly from power sector and sulphuric acid manufacturing). LPS account for about 32% of total SO_2 emissions in India (Garg *et al.*, 2002). In order to develop a general idea about the possible SO_2 sources in and around the study region, average SO_2 concentrations for 2009-10 in different regions of Gujarat are shown in Fig. 2 (<http://gpcb.gov.in/projects-ambient-air-quality-monitoring-programmes.htm>). The sizes of the circles are proportional to the SO_2 concentrations i.e. greater the radius of the circle, greater is the SO_2 concentration. Large sources of SO_2 (> 9 ppbv) are located in the Vapi - Ankleshwar belt. This region has numerous small to big industries, dominated by chemical industries. Jamangar in the south-west direction has significant concentrations of SO_2 in the range of 2-9 ppbv due to a major oil refinery (Fig. 2). There are also major sources of SO_2 in and around Ahmedabad (Fig. 2, also shown in right panel of Fig. 1).

c. Experimental details

Continuous in-situ measurements of surface SO_2 , O_3 and NO_2 during May, 2010 were made using online analyzers. SO_2 was monitored using a trace level analyzer from Thermo Scientific (43i-TLE). The analyzer is based on the principle of 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. The minimum detection limit of this analyzer is 50 pptv. Nitrogen dioxide (NO_2) was measured by an Environment SA (France) make analyzer (AC32M). It is based on chemi-luminescence corresponding to the oxidation of nitric oxide (NO) with O_3 in a reaction chamber and the chemical luminance is measured at $\lambda > 610$ nm. NO_2 is measured by converting it into NO using a molybdenum catalyst heated at 340°C. However, this converter also reduces other oxides of nitrogen such as PAN, HNO_3 etc. Hence, the actual concentrations of NO_2 may be lower than those measured and reported here (Lal *et al.*, 2008). The detection limit of this analyzer is 400 pptv. Ozone was monitored using a UV photometry analyzer (41 M) from Environment SA (France) with a detection limit of 1 ppbv. It is based on absorption of ~ 254 nm radiation from a low-pressure mercury vapor lamp by ozone molecules. SO_2 and NO_x analyzers were calibrated

using calibration mixtures from Linde (UK). Ozone was calibrated using a Sonimix calibrator.

In addition to these online measurements, air samples were collected from the terrace of the main building (~ 30 m altitude above ground level) every Monday, Wednesday and Friday at 1830 IST during May, 2010. IST is 5 hours and 30 minutes ahead of Greenwich Mean Time (GMT). These samples were filled into evacuated glass sample tubes of volume about 800 ml using a metal bellow air compressor to a pressure of ~ 2.5 bar. These glass bottles with teflon cocks were evacuated using a turbo-molecular pump (Balzers) down to 10^{-5} mbar before sampling. Each bottle was flushed several times with the ambient air before finally filling the sample air in it. The air samples were analyzed for CH_4 , CO, NMHCs and CO_2 . NMHCs (C_2 to C_3) were detected using a Hewlett Packard (HP) 5890 series II gas chromatograph (GC) coupled with a flame ionization detector (FID) operated at 250°C. These samples were pre-concentrated using cryo-trapping by liquid nitrogen before the injection into the GC-FID system. Separation was achieved with a porous layer open tubular (PLOT) column of KCl/Al_2O_3 stationary phase and of size $50\text{ m} \times 0.53\text{ mm}$ using high purity helium at a flow rate of 8 ml min^{-1} (Sahu and Lal, 2006). Methane and CO were analyzed using another GC-FID system (Varian Vista) which uses a methanizer (Ni catalyst at 325°C) for the detection of CO. Air samples were directly injected into the molecular sieve 13X packed column of about 5 m length, which was kept at an isothermal temperature of 80°C, for the analysis (Sahu and Lal, 2006). CO_2 was analyzed in the same GC but with a porapak-Q column (80/100 mesh, 2 m length) maintained at 50°C.

d. Satellite data

The ozone monitoring instrument (OMI) onboard the Aura satellite has been used to retrieve total SO_2 , HCHO and aerosol absorption optical depth in atmospheric columns (Lee *et al.*, 2011). Since most of the atmospheric burden of HCHO is contributed due to emissions from the surface, measurements of columnar HCHO can also provide constraints on the emission sources and photochemical processing of VOCs (Curci *et al.*, 2010). The OMI products (version 3, level 2) are averaged for the spatial grid of 16N-28N and 69E-78E. Since these data are not available on a daily basis for the Ahmedabad region, a larger grid was chosen to avoid missing values and to average out small scale variability. This OMI grid also contains the Mumbai-Ahmedabad belt which has the maximum number of large point sources for SO_2 in India (Garg *et al.*, 2002).

Precipitable water vapor (surface to 920 mb, 700 to 300 mb and total column) and aerosol optical depth (AOD) at 550 nm were obtained from MODIS Aqua (version 5.1) (http://gdata1.sci.gsfc.nasa.gov/daac-bin/G3/gui.cgi?instance_id=MODIS_DAILY_L3). The water vapor products are based on infra-red retrievals. These MODIS products used in this study are level 3 products averaged over a grid of 22N-23N and 72E-73E.

3. Results and discussion

Figure 3 (top panel) shows the day to day variability of SO_2 during 14-26 May, 2010. Its average value during this period was 0.95 ppbv with a spread of ± 0.88 ppbv. The average mixing ratios were higher between 1800 IST to 0200 IST with values of 1.44 ± 1.43 ppbv. The SO_2 data pattern during May revealed a night-time maximum (top panel in Fig. 3). The peak occurred between 2100-2200 IST with an average of around 1.61 ppbv. Correlation of hourly values of SO_2 with NO_2 during the study period shows a maximum of ~ 0.86 during late evening hours, indicating evening traffic as a potential source during this period.

a. High SO_2 event

A gradual rise in the peak levels of surface SO_2 was observed since the night of 17 May and the concentrations were conspicuously elevated in the night of 20 May, 2010 with values exceeding 17 ppbv (top panel in Fig. 3). The values again returned to normal after 22 May. On the same day, tropospheric columnar SO_2 from OMI showed almost 350% increase corroborating the surface observations over an extended height regime (top panel in Fig. 3). The columnar value of SO_2 was found to be 0.16 DU on 20 May while the average value during

14-26 May, 2010 was around 0.026 DU only. It is important to note that this was also the highest columnar value of SO_2 during the summer (March to May) of 2010 (bottom panel in Fig. 3).

b. Measurement of other trace gases

For further investigation, the variations in other trace gases like O_3 and NO_2 are looked into (top panel in Fig. 4). For most of May, night-time O_3 was below 25 ppbv. However, it increased to above 30 ppbv on the nights of 20 and 21 May. In fact, a gradual rise in the daily peaks of O_3 and NO_2 had begun since 17 May and culminated on 20 May after which these peak values started to subside (top panel in Fig. 4). The average maximum O_3 concentration was 20.7 ppbv during 11-30 May and occurred mostly during afternoon hours. For NO_2 , the average maximum concentration was 17.9 ppbv during 1-30 May and occurred mostly around 20-21 hours IST. However, on 20 May, these concentrations were around 32 ppbv for O_3 and 46 ppbv for NO_2 . Overall, NO_2 values were around 7.4 ± 5.2 ppbv for 1-30 May and O_3 values were around 11.2 ± 6.4 ppbv for 11-30 May.

The levels of other trace gases like CO and NMHCs were also found to be high on 21 May compared to their average values (Fig. 5). It is to be noted that the measurements of these

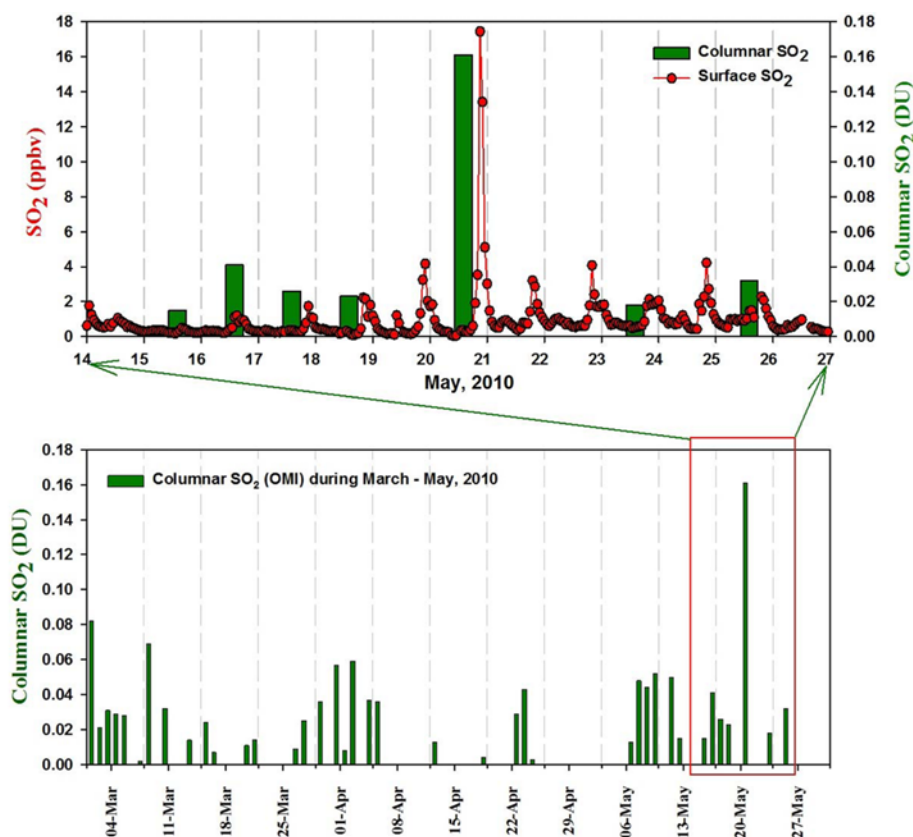


Fig. 3. Top panel: SO_2 variations during 14-26 May, 2010 based on in-situ surface measurements over Ahmedabad and satellite based columnar values from OMI. Bottom panel: OMI values during the summer (March-May) of 2010.

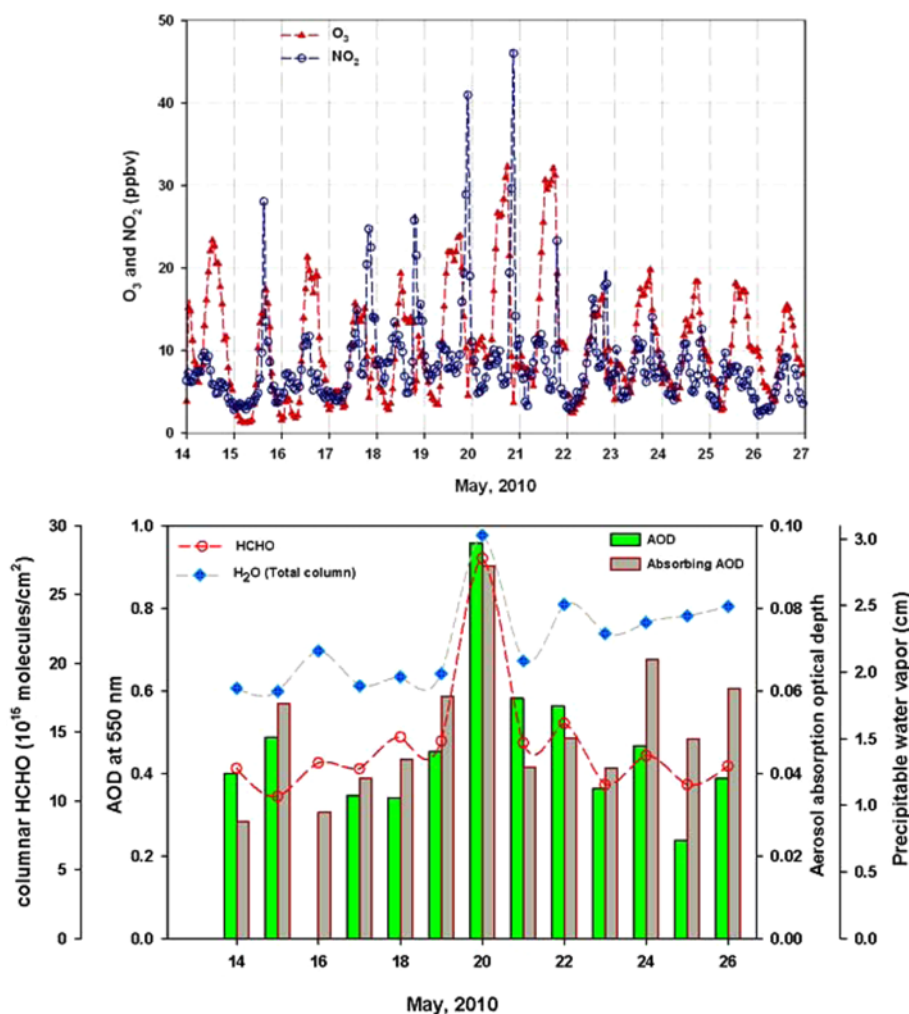


Fig. 4. Top panel: Variations of ozone and nitrogen dioxide for surface measurements over Ahmedabad during 14–26 May, 2010. Bottom panel: AOD (550 nm) and precipitable water vapor (total column) obtained from MODIS during 14–26 May, 2010 over Ahmedabad. HCHO column and AOD (absorption) is taken from OMI.

gases were not available for 20 May as it was not a sampling day. However, samples were collected at 1830 IST on 21 May, and the measurement data may be roughly estimated to have some remnant effect of the episodic high of 20 May. Mixing ratio of CO was higher by 78% from its average value of 314 ± 138 ppbv during the sampling days between 14–26 May at 1830 IST.

The distributions of the NMHCs measured in this study are influenced by local emissions. C₂H₄, C₂H₂ and C₃H₆ are mainly emitted from vehicles (Scheff and Wadden, 1993). However, there are large differences in their reactivities; C₂H₂ is less reactive while C₂H₄ and C₃H₆ are highly reactive species. The combined effects of reactivities and emission sources could result in higher increment for C₂H₂ (125% from its average value of 1.9 ppbv) compared to C₂H₄ (97% from its average value of 1.9 ppbv) and C₃H₆ (82% from its average value of 0.98 ppbv). Enhanced concentrations were also found to occur for C₂H₆ (102% from its average value of 3.7 ppbv), C₃H₈ (112% from its average value of 2.23 ppbv) and i-C₄H₁₀ (90% from

its average value of 1.24 ppbv) (Fig. 5). If total budget of C₂–C₄ NMHCS is accounted for, the maximum was contributed by C₂H₆ (~27%), followed by C₃H₈ (~16%), n-C₄H₁₀, C₂H₂ and C₂H₄ (~13–14% each) with minor contributions from i-C₄H₁₀ (~9%) and C₃H₆ (~7%) respectively.

c. Satellite based observations of aerosols, water vapor and formaldehyde

The total AOD is a measure of radiation extinction due to aerosol scattering and absorption. AOD value at 550 nm obtained from MODIS increased to 0.96 on 20 May for the Ahmedabad grid. In general, the values were below 0.6 on other days of May over the same spatial region (bottom panel in Fig. 4). Among aerosol species, when looked over the larger grid, contribution of absorbing aerosols to AOD was higher on 20 May (~79% increase from their average value of 0.05). Since elevated level in AOD is observed concomitantly with high concentrations of trace gases, both may have a common source.

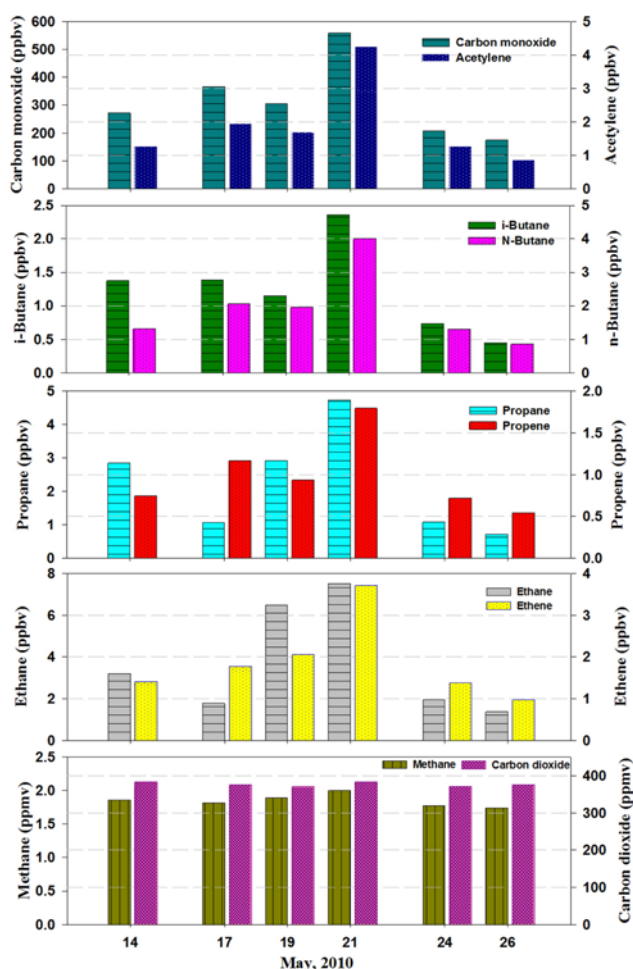


Fig. 5. GC based measurements over Ahmedabad from air samples collected on alternate days during 14-26 May, 2010 at 1830 IST.

Water vapor is one of the most important greenhouse gases of the atmosphere. More than fifty percent of all of the atmospheric water vapor is found below 2 km altitude. Precipitable water vapor is the amount of water (depth of vertical column of unit-cross sectional area) which would be obtained if all the water vapor in a specified column of the atmosphere were condensed to liquid. Satellite data revealed that the precipitable water vapor content within the boundary layer, the surface - 920 mb product from MODIS, was very high on 20 May. The value was 0.94 cm when compared to the average value of 0.72 cm during 14-26 May, 2010 for the Ahmedabad grid. This high amount was also seen for total precipitable water vapor content (~36% increase from its average value of 2.2 cm) (bottom panel in Fig. 4) but not observed for the 700-300 mb retrievals. This indicates that the effect could be more confined to the lower troposphere. However, long-lived gases like CH_4 and CO_2 did not show much variation (Fig. 5). The increase in CO_2 was around 1.8% only on 21 May when compared to its average value of 377 ± 5.65 ppmv only during the study period. Similarly, the increase for CH_4 was only around 8% for 21 May when compared to its average value of 1.85 ± 0.09

ppmv during the study period. These gases are very well mixed in the atmosphere and their concentrations generally do not change very rapidly.

While methane oxidation is the largest HCHO source to the global troposphere, its variability over land is dominated by its production from non-methane VOCs (Stavrakou *et al.*, 2009). Photochemical oxidation can contribute as much as 90% of annual HCHO concentrations in the outdoor ambient air. The HCHO column value was 27.6×10^{15} molecules cm^{-2} on 20 May, the highest during the study period. This was around 114% higher when compared to its average columnar value of 12.9×10^{15} molecules cm^{-2} for other days between 14-26 May (bottom panel in Fig. 4). The dominant atmospheric removal mechanism for HCHO is by photolysis and oxidation by hydroxyl radicals (OH) during daylight hours. This results in the overall tropospheric lifetime of approximately 0.3 days. Normally, combustion of fuels from mobile sources and process emissions from oil refineries are the largest sources of directly emitted HCHO. The increase in absorbing aerosol column and HCHO column on 20 May connote to a less oxidizing atmosphere on 20 May (Li *et al.*, 2011).

d. Meteorological conditions

Meteorological data on an hourly average basis for all days of May, 2010 were obtained from an automatic weather station installed at a nearby place. During 20-21 May, 2010, Gujarat was under the grip of severe heat wave. In fact, on 21 May, Ahmedabad temperature was 46.8°C , the highest recorded since 1916 for May. There was no conspicuous variation in temperature and humidity during 20-21 May (Fig. 6). However, higher temperatures may also cause higher emissions from emitting sources. A positive association between the evaporative emissions from motor vehicles and ambient air temperature (6.5% increase in vapor pressure-driven per degree Celsius increase in maximum temperature) has been found to occur for afternoon hours (Rubin *et al.*, 2006). The study period was also the transition period from summer to monsoon in that year. There were high winds with dust during 24-27 May, 2010. While the wind speed was in general above 1.5 m s^{-1} for all other days, it stayed below 1 m s^{-1} since the evening of 20 May till early hours of 21 May (Fig. 6). Thus, extremely low wind speed could have caused stagnant/very stable conditions resulting in the inability of pollutants already present to get dispersed quickly. Wind rose diagram showed that the local wind-direction was mainly westerly (sometimes from north-west or from south-west also) for 1-31 May, 2010 (right panel in Fig. 7). However, wind direction was distinctly different (mostly north-westerly to northerly since the evening of 20 May till early hours of 21 May) from most other days (Figs. 6 and 7).

e. Back-trajectories and PSCF analysis

The mixing ratio of a trace gas at a given point in time and

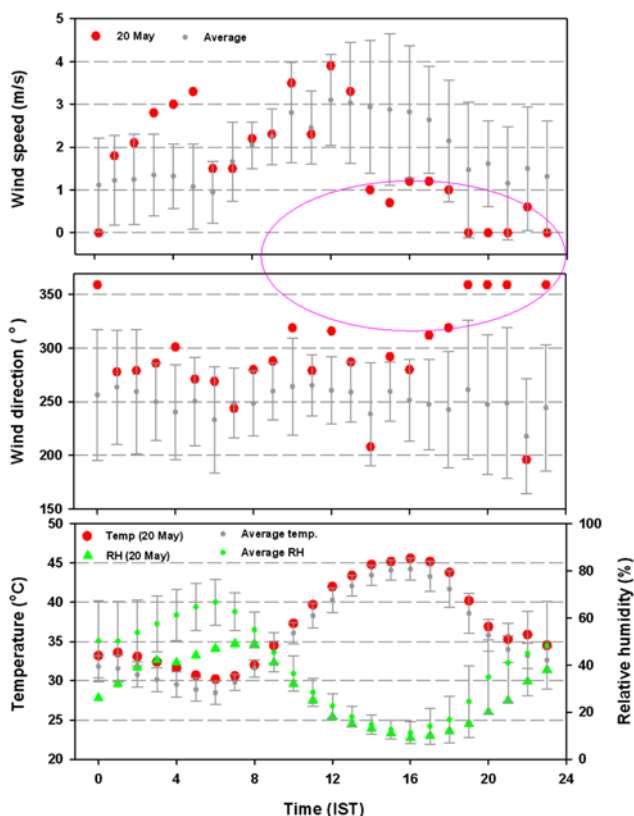


Fig. 6. Variations of meteorological parameters over Ahmedabad during 14-26 May, 2010.

space has concurrent effects of emission sources, photochemical processing, dynamical mixing and removal processes that have influence on an air mass as it is transported. Three day back-trajectories (obtained using National Centers for Environmental Prediction; NCEP reanalysis datasets) revealed that synoptic wind direction on a larger scale was not very different on 20 or even on 21 May i.e. prevailing wind direction was mainly from western side (not shown). The trajectory to trajec-

tory variation during 14-26 May, 2010 was very small in terms of their origin and path. These back-trajectories, calculated for 500 m altitude level using Hybrid Single particle Lagrangian Integrated Trajectory (HYSPLIT) model indicate effect of transport from the west.

Potential source contribution function (PSCF) analysis is widely used to identify the important geographic source areas contributing to measured concentration (Ashbaugh *et al.*, 1985; Begum *et al.*, 2005; Asatar and Nair, 2010). PSCF is defined as:

$$PSCF = m_{ij}/n_{ij}$$

where n_{ij} denotes the total number of trajectory segment endpoints falling in the grid cell (i, j) and m_{ij} is the number of times that the source concentration exceeded the arbitrary threshold, when the trajectories passed through the cell (i, j). Thus, the PSCF value can be interpreted as the conditional probability that the concentrations of a given pollutant sample greater than the threshold level are related to the passage of air parcels through the ij^{th} cell during transport to the receptor site.

In the present study, PSCF analysis was carried out for the grid region covering 69E-74 E and 21N-24 N, using TrajStat software (<http://ready.arl.noaa.gov/HYSPLIT.php>) (Wang *et al.*, 2009). The cell size was taken as $1^\circ \times 1^\circ$. The receptor site was 23N, 72.5E which represents Ahmedabad. SO₂ concentrations measured at PRL during 16 to 26 May, along with a backward run time of 48 hours with wind data from NOAA (<ftp://arlftp.arlhq.noaa.gov/pub/archives/reanalysis>) were used in the calculation of PSCF. SO₂ values above 3 ppbv were considered polluted. The cluster having SO₂ concentration > 3 ppbv is shown in a different color (left panel in Fig. 7). Since sample concentrations on the event day were drastically higher than the criterion, all the potential source grids show the same PSCF value, making it difficult to distinguish moderate sources from strong ones. This is also a limitation of the PSCF method. Figure 7 shows the contribution from 69E -72E and 22N -23N (also, see Fig. 2).

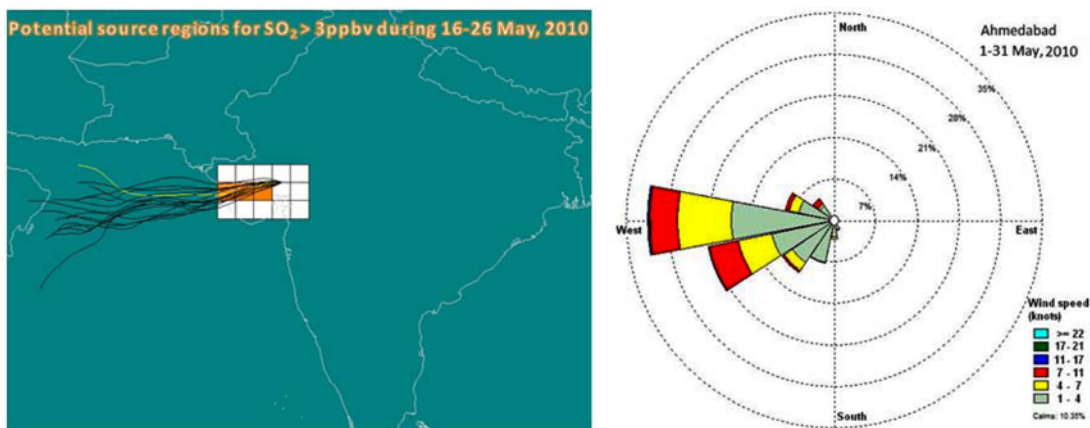


Fig. 7. Left panel: Potential source regions for SO₂ > 3 ppbv at Ahmedabad and air mass back-trajectories. Right panel: Wind rose for 1-31 May, 2010.

f. Profiles and inversion

While wind speed and direction play a crucial role in transport of pollutants, the role of boundary layer/inversion is also substantial in the build-up/removal of pollutant gases (Krishnan and Kunhikrishnan, 2004). Occasionally, a combination of meteorology and dynamics including wind parameters and inversion can cause pollutants to shoot up (Wang *et al.*, 2003; Xie *et al.*, 2004; Angelo and Black, 2008). To get an insight into the stability conditions, 0000 GMT (0530 IST) upper air data for Ahmedabad (obtained from University of Wyoming's website: <http://weather.uwyo.edu/upperair/>) were analyzed for profiles of thermodynamic variables like temperature, relative humidity and equivalent potential temperature (θ_e). A minimum in θ_e was used to identify characteristic features of inversions (Kumar *et al.*, 2010). θ_e is more advantageous than normal temperature because it is normalized with respect to pressure and moisture content also. A mixing ratio of $\sim 25 \text{ g kg}^{-1}$ at $\sim 970 \text{ hPa}$ suggested a higher evaporative potential of the atmosphere during the heat wave in comparison with standard weather conditions. However, a very strong inversion is seen between 970-900 mb (0.3-0.9 km) at 0000 GMT (0530 IST) on 21 May, when the θ_e value dropped from 380 K to 305 K (Fig. 8). The time corresponded to early morning (around pre-sunrise time) of 21 May and the values are representative of the nocturnal boundary layer of 20 May. This shows that conditions were calm and stable and the inversion acted as a lid by preventing locally emitted as well as transported pollutants from escaping into the free troposphere.

g. Emission characteristics

Hydrocarbons may also be used as tracer of anthropogenic pollution. For instance, CO and C_2H_2 are both derived from combustion and biomass burning, thus air masses containing

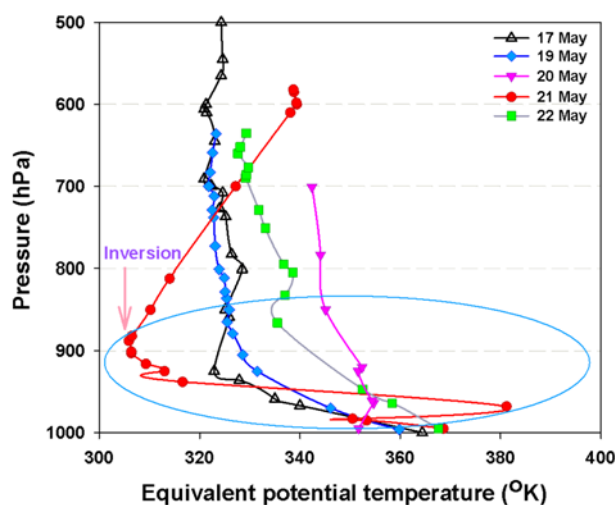


Fig. 8. Variations in equivalent potential temperature at 0000 GMT (0530 IST) during 17-22 May, 2010 over Ahmedabad. Data are not available for 18 May; hence the profile for that day is not shown.

these species are known to have a continental source. Hydrocarbon ratios can also qualitatively indicate the age of an air mass when they have similar sources but different lifetimes (Smyth *et al.*, 1996). For example, a common indicator that is used for this purpose is the C_2H_2 to CO ratio. C_2H_2 has a much shorter lifetime (~ 2 weeks) than CO (~ 2 months). Therefore, as an air mass ages, the C_2H_2 mixing ratio decreases faster, lowering the $\text{C}_2\text{H}_2/\text{CO}$ ratio rapidly. A lower ratio (less than 0.0005) indicates a photochemically aged air mass that has undergone extensive atmospheric processing (i.e., oxidation and dilution) and a higher ratio (greater than 0.001) means that the air mass is younger and has been influenced by fresh emissions (McKeen and Liu, 1993; Gregory *et al.*, 1996; Smyth *et al.*, 1996). The $\text{C}_2\text{H}_2/\text{CO}$ value on 21 May was 0.0076, about 42% higher than its average value of 0.0053 for other days of analysis. This ratio on 21 May indicates that the ambient air was influenced fresh emissions or it could be possible that dilution effect by more aged air mass was less because of stagnant conditions. The average $\text{C}_3\text{H}_8/\text{C}_2\text{H}_6$ ratio of 0.6 during the study period also points at local urban sources (Wang *et al.*, 2003). The average $\text{C}_3\text{H}_8/\text{CO}$ value was 0.0068 indicating influence from fossil fuel combustion (Baker *et al.*, 2011). The CO/NO_2 value during the evening of 21 May (~ 1830 IST) was 55.1, while the average value was 41.1 during the study period for the same time of the day. A study involving criteria pollutant measurements over New Delhi found CO/NO_x to be ~ 50 indicating mobile sources as predominant contributors to air pollution over Delhi (Aneja *et al.*, 2001). The same study also found the SO_2/NO_x value to be ~ 0.6 over New Delhi indicating point sources as the major contributors to SO_2 . The average SO_2/NO_2 value was 0.12 during the evening hours (1830 IST) of the study period indicating contributions from mobile sources rather than point sources. However, during the event period (2000 IST on 20 May to 0100 IST on 21 May), this ratio was ~ 0.36 indicating other influences like transport of polluted air apart from local effects of mobile sources. These values are also close to the SO_2/NO_x value of 0.41 for Western US (Aneja *et al.*, 2001).

4. Conclusions

Simultaneous measurements of various trace gases carried out during 14-26 May, 2010 enabled detection of a pollution event that occurred during this period. In this paper, this occurrence is explored in detail and documented in terms of trace gas variations and dynamics. The mean concentration of SO_2 during the study period was 0.95 ppbv. However, the concentrations were highly elevated (~ 17 ppbv) in the night of 20 May. High values were also observed in the tropospheric columnar SO_2 from OMI which showed almost 350% increase confirming the impacts at higher heights also. This was also the highest columnar value of SO_2 during the summer of 2010. Satellite data for aerosols, columnar water vapor and HCHO indicate that this effect was not only confined to the surface but could have extended to higher altitudes. Increased concen-

trations were also found to occur for trace gases like CO, C₂H₂, C₂H₄, C₃H₆, C₂H₆, C₃H₈ and i-C₄H₁₀ to the extent of 78, 125, 97, 82, 102, 112 and 90 percentages above their average values during the study period. However, long-lived trace gases like CH₄ and CO₂ did not show much variation. The CO/NO₂ and SO₂/NO₂ values indicated contributions from mobile sources in general. However, non-local processes were in play during the event period on 20 May as revealed by a higher SO₂/NO₂ ratio of 0.36. Analysis of meteorological parameters suggested combined impacts of transport and inversion causing higher levels of SO₂ and other pollutants during 20 May. However, the ratio of C₂H₂/CO on 21 May suggested the impact of relatively fresh emissions. θ_e profile at 0530 IST on 21 May revealed the presence of an inversion layer near 900 mb. The analysis suggests the role of meteorological factors viz. wind and inversion leading to higher levels of SO₂ and other pollutants during 20-21 May. Episodes of such high pollutant levels need to be investigated carefully. Also, monitoring of trace gases like SO₂ are important for atmospheric and climate research and ameliorating air pollution.

Acknowledgements. We acknowledge PRL and ISRO - Geosphere Biosphere Programme - ATCTM project for funding. The Giovanni online data system (NASA GES DISC) provided an easy and user-friendly platform to look into satellite data. Upper air data were obtained from University of Wyoming's web-site. Wind data from National Centers for Environmental Prediction (NCEP) reanalysis were used. Region representative SO₂ data were obtained from Gujarat Pollution Control Board's website. We thank Mr. T.K. Sunil Kumar for his contributions in the laboratory. Various software like TrajStat, WR-View, Sigmaplot were used for plotting. The authors acknowledge the Korean Meteorological Society for supporting the publication fee.

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