Influence of Meteorology and interrelationship with greenhouse gases (CO$_2$ and CH$_4$) at a suburban site of India


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Abstract

Atmospheric greenhouse gases (GHGs), such as carbon dioxide (CO\textsubscript{2}) and methane (CH\textsubscript{4}), are important climate forcing agents due to their significant impacts on the climate system. The present study brings out first continuous measurements of atmospheric GHGs using high precision LGR-GGA over Shadnagar, a suburban site of Central India during the period 2014. The annual mean CO\textsubscript{2} and CH\textsubscript{4} over the study region are found to be 394±2.92 ppm and 1.92±0.07 ppm (μ±1σ) respectively. CO\textsubscript{2} and CH\textsubscript{4} show a significant seasonal variation during the study period with maximum (minimum) CO\textsubscript{2} observed during Pre-monsoon (Monsoon), while CH\textsubscript{4} recorded maximum during post-monsoon and minimum in monsoon. Irrespective of the seasons, consistent diurnal variations of these gases are observed. Influences of prevailing meteorology (air temperature, wind speed, wind direction and relative humidity) on GHGs have also been investigated. CO\textsubscript{2} and CH\textsubscript{4} show a strong positive correlation during winter, pre-monsoon, monsoon, and post-monsoon with correlation coefficients (Rs) equal to 0.80, 0.80, 0.61, and 0.72 respectively; indicating common anthropogenic source for these gases. Analysis of this study reveals the major sources for CO\textsubscript{2} are soil respiration and anthropogenic emissions while vegetation act as a main sink. Whereas the major source and sink for CH\textsubscript{4} are vegetation and presence of hydroxyl (OH) radicals.

Keywords: Carbon dioxide, Methane, OH radical.
1. Introduction

The Intergovernmental Panel on Climate Change (IPCC, 2013) reported that humankind is causing global warming through the emission of greenhouse gases (GHGs), particularly carbon dioxide (CO₂) and methane (CH₄). CO₂ and CH₄ concentrations have increased by 40% and 150% respectively since pre-industrial times, mainly from fossil fuel emissions and secondarily from net land use change emissions (IPCC, 2013; Huang et al., 2015). CO₂ measurements at MaunaLoa, Hawaii (Monastersky, 2013) have exceeded the 400 ppm mark several times in May 2013. CH₄ is also receiving increasing attention due to high uncertainty in its sources and sinks (Keppler et al., 2006; Miller et al., 2007; Frankenberg et al., 2008). Stefanie Kirschke et al., (2013) reported that in India, agriculture and waste constitute the single largest regional source of CH₄. Although many sources and sinks have been identified for CH₄, their relative contribution to atmospheric CH₄ is still uncertain (A. Garg et al., 2001; Stefanie Kirschke et al., 2013). In India, electric power generation contributes to half of India’s total CO₂ equivalent emissions (A. Garg et al., 2001).

Arid and semi-arid areas comprise about 30% of the Earth’s land surface. Climate change and climate variability will likely have a significant impact on these regions (Huang et al., 2008; Huang et al., 2015). The variability of environmental factors may result in significant effects on regional climate and global climate (Wang et al., 2010), especially the radiative forcing; via the biogeochemical pathways affecting the terrestrial carbon cycle. Global climate change has serious impact on humans and ecosystems. Due to this, many factors have been identified that may reflect or cause variations in environmental change (Pielke et al., 2002). Out of these, the Normalized Difference Vegetation Index (NDVI) has become one of the most widely used indices to represent the biosphere influence on global change (Liu et al., 2011). Greenhouse and other trace gases have great importance in atmospheric chemistry and for radiation budget of the atmosphere-biosphere system (Crutzen et al., 1991). Hydroxyl radicals (OH) are very reactive oxidizing agents, which are responsible for the oxidation of almost all gases that are emitted by natural and anthropogenic activities in the atmosphere. Atmospheric CO₂ measurements are very important for understanding the carbon cycle because CO₂ mixing ratios in the atmosphere are strongly affected by photosynthesis, respiration, oxidation of organic matter, biomass and fossil fuel burning, and air–sea exchange process (Machida et al., 2003).
The present study brings out first continuous measurements of atmospheric GHGs using high precision LGR-GGA over Shadnagar, a suburban site of Central India during the period 2014. In addition to GHGs observations, we have also made use of an automatic weather station (AWS) data along with model/satellite retrieved observation during the study period. Details about study area and data sets are described in the following sections.

2. Study Area

Shadnagar is situated in Mahabubnagar district of newly formed Indian state of Telangana. It is a suburban location situated ~70km away from urban site of Hyderabad (Northern side) with a population of ~0.16 million (Patil et al., 2013). A schematic map of study area is shown in Fig. 1a. Major sources of pollutants over Shadnagar can be from small and medium scale industries, biomass burning and bio-fuel as well as from domestic cooking. In the present study sampling of GHGs and related meteorological parameters are carried out in the premises of National Remote Sensing Center (NRSC), Shadnagar Campus (17°02’N, 78°11’E). Sampling site is near (aerial distance ~ 2.25 km) to National highway 7 (NH7) and a railway track (non-electrified) is in the East (E) direction.

Mean monthly variations of temperature (°C) and relative humidity (RH %) observed at Shadnagar during 2014 are shown in Figure 1e and 1d respectively. The Indian Meteorological Department (IMD) defined monsoon as June-July-August-September (JJAS), post-monsoon (October-November-December-OND), winter (January-February-JF) and pre-monsoon (March-April-May-MAM) in India. Temperature over Shadnagar varies from ~20°C to ~29°C. Relative humidity (RH) in Shadnagar reached a maximum of ~82 % in monsoon from a minimum of ~48 % recorded during pre-monsoon. Surface wind speed (Fig. 1c) varies between 1.3 to 1.6 m s⁻¹ with a maximum observed during monsoon and minimum in pre-monsoon. The air mass advecting (Fig. 1b) towards study site is either easterly or westerly. The easterly wind prevails during winter and gradually shifts to south-westerlies in pre-monsoon, and dominates during monsoon.

3. Data set and Methodology

Details about the instrument and data utilized are discussed in this section. The availability and frequency of the observations all data used in present study are tabulated in Table 1.
3.1 *In-situ observations*

3.1.1 Greenhouse Gas Analyser (GGA)

The Los Gatos Research’s - Greenhouse Gas Analyser (model: LGR-GGA-24EP) is an advanced instrument capable of simultaneous measurements of CO₂, CH₄ and H₂O. This instrument is well known for high precision and accuracy which are crucial towards understanding background concentrations of atmospheric GHGs, with specifications meeting WMO standards of measurement (Berman et al., 2012; Shea et al., 2013; Mahesh et al., 2015). It is based on enhanced Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) technology (Paul et al. 2001, Baer et al., 2002), which utilizes true wavelength scanning to record fully resolved absorption line shapes. Considering the nature of the site, flow rate is fixed to be 7 liters per minute (lpm). Ambient air entering the GGA is analysed using two near infrared (NIR) distributed feedback tunable diode lasers (TDL), one for a CO₂ absorption line near 1.60 µm (ν₀ = 6250 cm⁻¹) and the other to probe CH₄ and H₂O absorption lines near 1.65 µm (ν₀ = 6060.60 cm⁻¹). The concentration of the gases is determined by the absorption of their respective characteristic absorption lines with a high sampling time of 1 sec. A detailed explanation regarding the configuration, working and calibration procedure performed for GGA in NRSC can be found elsewhere in Mahesh et al., (2015). In the present study we used GGA retrieve CO₂ and CH₄ data. High resolution data sets are diurnally averaged and used in further analysis. Due to failure of internal central processing unit (CPU) of the analyzer, data are not recorded from pre-monsoon month of 1st May to 18th June during the study period.

3.1.2 O₃ and NOₓ analyzer

Surface concentrations of O₃ and NOₓ have been measured continuously using on-line analyzers (Model No.s: 49i and 42i for O₃ and NOₓ respectively), procured from Thermo Scientific, USA since July 2014. The trace gases (O₃ and NOx) sampling inlet is installed on the top of a 2 m mast fixed on the roof of an 8 m high building, and ambient air flow is supplied to the instruments. The inlet prevents the ingress of rain water, and is equipped with 0.5 µm filter to prevent accumulation of dust within the instrument. The ozone analyzer is based on Beer-Lambert-Baugher law which relates absorption of light to the concentration of species as its operating principle and has an in-built calibration unit for conducting periodical span and zero checks. The NOₓ analyzer utilizes a molybdenum converter to convert NO₂ into NO and estimates the NOₓ
concentration by the intensity of light emitted during the chemiluminescent reaction of NO with \( \text{O}_3 \) present in the ambient air. The analyzer is integrated with zero and span calibrations which are performed twice monthly.

Simultaneous observations of meteorological parameters are obtained from an automatic weather station (AWS) installed in NRSC, Shadnagar campus as a part of Calibration and Validation (CAL/VAL) project in March 2012 is equipped with nine sensors to measure fifteen weather parameters. Weather parameters measured are at surface level and height of the AWS mast is \(~10\) meters. Wind speed and direction measurements are collected at the maximum height (3m) and all others are at 1-1.5m height.

### 3.2 Satellite and Model observations

#### 3.2.1 MODIS

Moderate-resolution Imaging Spectrometer (MODIS) is launched in December 1999 on the polar-orbiting NASA-EOS Terra platform (Salomonson et al. 1989; King et al. 1992). It has 36 spectral channels and acquires data in 3 spatial resolutions of 250 m, 500 m, and 1 km (channels 8–36), covering the visible, near-infrared, shortwave infrared, and thermal-infrared bands. In the present study we used monthly Normalised Difference Vegetation Index (NDVI) data obtained from Terra/MODIS at 5 km spatial resolution. The NDVI value is defined as following ratio of albedos \((\alpha)\) at different wavelengths:

\[
\text{NDVI} = \frac{\alpha_{0.86\mu m} + \alpha_{0.67\mu m}}{\alpha_{0.86\mu m} - \alpha_{0.67\mu m}}
\]

NDVI values can range from -1.0 to 1.0 but typical ranges are from 0.1 to 0.7, with higher values associated with greater density and greenness of plant canopies. More details of the processing methods used in generating the data set can be found in James and Kalluri (1994).

#### 3.2.2 COSMIS-RO

COSMIC (Constellation Observation System for Meteorology, Ionosphere and Climate) is a GPS (Global Positioning System) radio occultation (RO) observation system (Wang et al., 2013). It consists of six identical microsatellites, and was launched successfully on 14 April 2006. GPS radio occultation observation has the advantage of near-global coverage, all-weather capability, high vertical resolution, high accuracy and self-calibration (Yunck et al., 2000). Geophysical
parameters (such as, temperature and humidity profiles) have been simultaneously obtained from refractivity data using one-dimensional variational (1DVAR) analysis. Further COSMIC-RO profiles are used to estimate planetary boundary layer height (BLH). BLH is defined to be the height at which the vertical gradient of the refractivity or water vapor partial pressure is minimum (Ao et al., 2012), explained detail methodology for calculating the BLH from refractivity (N). The planetary boundary layer (PBL) is part of the atmosphere closest to the Earth’s surface where turbulent processes often dominate the vertical redistribution of sensible heat, moisture, momentum, and aerosols/pollution (AO et al., 2012).

3.2.3 Hysplit model

The general air mass pathway reaching over Shadnagar is analysed using HYSPLIT model (Draxler and Rolph, 2003) [http://ww.arl.noaa.gov/ready/hysplit4.html]. We computed 5 day isentropic model backward air mass trajectory for all study days with each trajectory starting at 00:60 UTC and reaching study site, (Shadnagar) at different altitudes(1 km,2 km,3km and 4 km). Even though the trajectory analysis have inherent uncertainties (Stohl, 1998), they are quite useful in determining long range circulation.

4. Results and Discussion

4.1 Seasonal variations of CO₂ and CH₄

Temporal variations of CO₂ and CH₄ during the study period are shown in Figure. 2a and 2b. The circles indicate the daily mean, while triangular markers represent weakly averages and monthly mean by square markers. Annual mean of CO₂ over study region is found to be 394±2.92 (mean (μ) ± standard deviation (1σ)) ppm with an observed minimum in monsoon and maximum in pre-monsoon. Seasonal mean values of CO₂ observed during different seasons are 393±5.60, 398±7.60, 392±7.0, and 393±7.0 ppm in winter, pre-monsoon, monsoon, and post-monsoon respectively. Minimum CO₂ during winter (dry season) can be due to respiratory loss of carbon (Gilmanov et al., 2004; Aurela et al. 2004) as decreased temperature and solar radiation during this period inhibit increases in local CO₂ assimilation (Thum et al., 2009). A steady increase in CO₂ concentration is observed as season changes from winter to pre-monsoon months. Enhancement in Pre-monsoon is due to higher temperature and solar radiation prevailing during these months which stimulate the assimilation of CO₂ in the daytime and respiration in the night (Fang et al., 2014). The enhanced soil respiration during these months also compliments the
increase in CO₂ concentration during this period. In addition to these natural causes, biomass burning over Indian region can also have a significant effect on pre-monsoon CO₂ concentration. More detailed explanation of biomass burning influence on pre-monsoon GHGs concentration is discussed in section 4.6. Surface CO₂ concentration recorded a minimum during monsoon months can be mainly because of enhanced photosynthesis processes with the availability of greater soil moisture. A decrease in CO₂ concentration is also observed as the monsoon progress. The decreases in temperature (due to cloudy and overcast conditions prevailing during these months) reduce leaf and soil respiration which contributes to the enhancement of carbon uptake (Patil et al., 2013; Jing et al., 2010). Further increase during post-monsoon CO₂ is associated with high ecosystem productivity (Sharma et al., 2014) also an enhancement in soil microbial activity (Stefanie Kirschke et al., 2013).

CH₄ concentration in the troposphere is principally determined by a balance between surface emission and destruction by hydroxyl radicals (OH). The major sources for CH₄ in the Indian region are rice, paddies, wetlands and ruminants (Schneising et al., 2009). Annual CH₄ concentration over study area is observed to be 1.92 ± 0.07 ppm, with a maximum (2.02±0.01 ppm) observed in post-monsoon and minimum (1.85±0.03 ppm) in monsoon. Seasonal mean (average) values of CH₄ observed during different seasons are 1.93±0.05, 1.89±0.05, 1.85±0.03, and 2.02±7 ppm with respectively winter, pre-monsoon, monsoon, and post-monsoon. The highest concentration appears during post-monsoon and may be associated with the Kharif season (Goroshiet al., 2011). Hayashida et al. (2013) reported that the seasonality of CH₄ concentration over monsoon Asia is characterized by higher values in the wet season and lower values in the dry season; possibly because of the effects of strong emissions from rice paddies and wetlands during the wet season. Low mixing ratios of CH₄ observed during monsoon season were mainly due to the reduction in atmospheric hydrocarbons because of the reduced photochemical reactions and the substantial reduction in solar intensity (Abhishek Gaur et al 2014). The rate of change of CH₄ was found to be high during post-monsoon. Both biological and physical processes control the exchange of CH₄ between rice paddy fields and the atmosphere (Nishanth et al., 2014; Goroshiet al., 2011). Due to this, enhanced CH₄ observed during post-monsoon at present study area.

4.2 Influence of vegetation on GHGs.
In India cropping season is classified into (i) Kharif and (ii) Rabi based on the onset of monsoon. The Kharif season is from July to October during the south-west (SW) monsoon and Rabi season is from October to March (Koshal Avadhesh, 2013). NDVI being one of the indicators of vegetation change, monthly variations of CO₂ and CH₄ against NDVI is studied to understand the impact of land use land cover on mixing ratios of CO₂ and CH₄. Monthly mean changes in NDVI, CO₂ and CH₄ are shown in Figure 2c and 2d.Monthly mean of GHGs represented in this analysis is calculated from daily mean in day time (10-16 LT). Analysis of the figure reveals that an inverse relationship exists between NDVI and CO₂; while a positive relation is observed w.r.t CH₄. Generally over this part of the country vegetation starts during the month of June with the onset of SW monsoon and as vegetation increases a decrease in CO₂ concentration is observed, due to enhancement in photosynthesis. Further a decline in NDVI is observed as the season advances from post monsoon to winter and then to pre-monsoon, and it is associated with an increase in CO₂ concentration. Similarly, the main source for CH₄ emissions are soil microbial (Stefanie Kirschke et al., 2013) activity which are more active during monsoon and post monsoon seasons.

Biomass burning (forest fire and crop residue burning) is one of the major sources of gaseous pollutants such as carbon monoxide (CO₂), methane (CH₄), nitrous oxides (NOx) and hydrocarbons in the troposphere (Crutzen et al., 1990, 1985; Sharma et al., 2010). In order to study the role of biomass burning on GHGs a case study is discussed. Figure 3c shows the spatial distribution of MODIS derived fire counts over Indian region during 14-21 April 2014 with air mass trajectories ending over study area overlaid on it at different altitudes viz. 1000 m, 2000 m and 4000 m respectively. Analysis of the figure shows a number of potential fire locations on the north-western and south-eastern side of study location and trajectories indicate its possible transport to study area. Daily mean variation of GHGs during the month of Aril 2014 (Figure 3b) indicates an enhancement in GHGs during the same period (14-21 April 2014). Analysis reveals that CO₂ and CH₄ have increased by ~2% and ~0.06% respectively during event days with respect to monthly mean. This analysis reveals that long range / regional transported biomass burning have a role in enhancement of GHGs over study site. Further to understand the seasonal variation of biomass burning contribution to GHGs we analysed long term (2003-2013) Fire Energetics and Emissions Research version 1.0 (FEER v1) data over study
area. Emission coefficient ($C_e$) products during biomass burning is developed from coincident measurements of fire radiative power (FRP) and AOD from MODIS Aqua and Terra satellites (Ichoku and Ellison, 2014). Figure 3a shows seasonal variation of CO$_2$ emission due to biomass burning over the study site. Enhancement in CO$_2$ emission is seen during pre-monsoon months; which also supports earlier observation (Figure 2a). This analysis reveals that biomass burning has a role in pre-monsoon enhancement of CO$_2$ over study site. For a qualitative analysis of this long range transport, we have analysed air mass trajectories ending over study site during different seasons.

4.3 Correlation between CO$_2$ and CH$_4$

A correlation study is carried out between hourly averaged CO$_2$ and CH$_4$ during all season for the entire study period. The statistical analysis for different seasons is shown in Table 2. Fang et al., (2015) suggest the correlation coefficients (Rs) value higher than 0.50 indicates a similar source mechanism of CO$_2$ and CH$_4$. Also a positive correlation dominance of anthropogenic emission on carbon cycle. Our study also reveals a strong positive correlation observed between CO$_2$ and CH$_4$ during winter, pre-monsoon, monsoon, and post-monsoon with R equal to 0.80, 0.80, 0.61, and 0.72 respectively. Seasonal regression coefficients (slope) and their uncertainties ($\psi_{\text{slope}}$, $\psi_{\text{y-int}}$) are computed using Taylor (1997) which showed maximum during winter, pre-monsoon, and minimum in a monsoon that figure out the hourly stability of the mixing ratios between CO$_2$ and CH$_4$. This can be due to relatively simple source/sink process of CO$_2$ in comparison with CH$_4$. Figure 4 shows the seasonal variation of $\Delta$CH$_4$/$\Delta$CO$_2$. Dilution effects during transport of CH$_4$ and CO$_2$ can be minimized to some extent by dividing the increase of CH$_4$ over time by the respective increase in CO$_2$ (Worthy et al., 2009). In this study, background concentrations of respective GHGs are determined as mean values of the 1.25 percentile of data for monsoon, post-monsoon, pre-monsoon and winter (Pan et al., 2011; Worthy et al., 2009). Annual $\Delta$CH$_4$/$\Delta$CO$_2$ over the study region during the study period is found to be 7.1 (ppb/ppm). This low value clearly indicates the dominance of CO$_2$ over the study region. The reported $\Delta$CH$_4$/$\Delta$CO$_2$ values from some of the rural sites viz Canadian Arctic and Hateruma Island (China) are of the order 12.2 and ~10 ppb/ppm respectively (Worthy et al., 2009; Tohjima et al., 2014). Average $\Delta$CH$_4$/$\Delta$CO$_2$ ratio during winter, pre-monsoon, monsoon and post-monsoon are 9.40, 6.40, 4.40, and 8.20 ppb respectively. Monthly average, of $\Delta$CH$_4$/$\Delta$CO$_2$, is relatively high from late post-monsoon to
winter, when the biotic activity is relatively dormant (Tohjima et al., 2014). During pre-monsoon
decease in $\Delta CH_4/\Delta CO_2$ ratio indicates the enhancement of CO$_2$ relative to that of CH$_4$.

4.4 Diurnal variations of CO$_2$ and CH$_4$

Figure 5a to 5d shows the seasonally averaged diurnal cycle of CO$_2$ and CH$_4$ over Shadnagar
during study period. The vertically bar represents the standard deviation from respective mean.
Irrespective of seasonal variation GHGs showed a similar diurnal variation, with maximum mixing
ratios observed during early morning (06:00 hrs) as well as early night hours (20:00 hrs) and
minimum during afternoon hours. However the difference observed in the maximum diurnal
amplitudes can be attributed to seasonal changes. The observed diurnal cycle of GHGs is closely
associated with diurnal variation of planetary boundary layer height (PBLH). For better
understanding of the diurnal behavior of CO$_2$/CH$_4$, we used European Centre for Medium-range
Weather Forecasting (ECMWF) Interim Reanalysis (ERA) PBL data set which gives the data for
every three hours viz. 00:00, 03:00, 06:00, 09:00, 12:00, 15:00, 18:00, and 21:00 UTC with a
resolution of 0.25°x0.25° (http://data-portal.ecmwf.int). Figure 5a to 5d portrays the diurnal
evolution of CO$_2$/CH$_4$ during different season along with the evolution of Boundary Layer Height
(m) on secondary y axis. The morning peak arises due to combined influence of fumigation effect,
(Stull 1988) and morning build-up of local anthropogenic activities (household and vehicular
transport). Low value of GHGs as the day progress can be attributed to increased photosynthetic
activity during day time and destruction of stable boundary layer and residual layer due convective
activity. In the evening hours, surface inversion begins and form a shallow stable boundary layer
(Nair et al., 2007) causing the enhancement in GHGs concentration near the surface. Similar trend
in diurnal variation of GHGs is reported from other parts of the country (Patil et al., 2013; Mahesh
et al., 2014; Sharma et al., 2014; Nishanth et al., 2014).

4.5 Influence of prevailing meteorology

Redistribution (both horizontal and vertical) of GHGs also plays a role in their seasonal
variation, as it controls transport and diffusion of pollutants from one place to another (Hassan
2015). A good inverse correlation between wind speed and GHGs suggest the proximity of sources
near measurement site, while a not so significant correlation suggests the influence of regional
transport (Ramachandran and Rajesh, 2007). Figure 6a and 6b shows scatter plot between GHGs and wind speed during different seasons. Analysis of Figure 6 shows that there exists an inverse correlation between daily mean wind speed and GHGs. Correlation coefficients (Rs) between wind speed and CO$_2$ during pre-monsoon, monsoon, post-monsoon, and winter is 0.56, 0.32, 0.06, and 0.67 respectively. While for CH$_4$ it is found be 0.28, 0.71, 0.21, and 0.60 respectively. Negative correlation indicates that the influence of local sources on GHGs, however, poor correlation coefficients during different seasons suggest the role of regional/local transport (Mahesh et al 2014). Also an understanding of prevailing wind direction and its relationship with GHGs helps in determining their probable source regions. Table 3 shows the monthly mean variation of CO$_2$ and CH$_4$ with respect to different wind direction. Enhancement in CO$_2$ and CH$_4$ level over Shadnagar are observed to mainly come from NW and NE while the lowest is from the S and SW. This can be associated to some extend with industrial emissions located in western side of sampling site, and the influence of emission and transport from nearby urban center on the NW side of the study site.

The influence of meteorological parameters (temperature and relative humidity) on trace gases is also examined. Figure 7a and 7b (top panel corresponds to CO$_2$ and bottom panel represents CH$_4$) show the scatter plot of temperature versus relative humidity as a function of GHGs during different seasons. Daily mean data is used instead of hourly mean data, to avoid the influence of the diurnal variations on correlations. CO$_2$ showed a positive correlation with temperature during all season except during winter. This negative correlation can be attributed to different response of photosynthesis rate to different air temperature. IPCC (1990) reports that many mid-latitude plants shows an optimum gross photosynthesis rate when temperature varied from of 20 to 35 °C. The rate of plant respiration tends to be slow below 20°C. However, at higher temperatures, the respiration rate accelerates rapidly up to a temperature at which, it equals the rate of gross photosynthesis and there can be no net assimilation of carbon. While CH$_4$ showed a weak positive correlation with temperature during pre-monsoon and post-monsoon, while a weak negative correlation is observed during monsoon and winter. This could be due to the rate of chemical loss reaction with OH is faster in summer and minimum in other seasons. A case study on CH$_4$ sink mechanism has discussed in section 4.6. Seasonal variation of GHGs also showed an insignificantly negative correlation with relative humidity. One of the supporting argument can be in humid conditions, these stoma can fully open to increase the uptake of CO$_2$ without a net water
loss. Also, wetter soils can promote decomposition of dead plant materials, releasing natural
fertilizers that help plants grow (Abhishek et al., 2014).

Figure 8a and 8b illustrates the daily mean variation of GHGs with respect to soil moisture and
soil temperature (Top panel represent the seasonal variation of CO₂ w.r.t soil moisture and soil
temperature, while bottom panel represent the seasonal variation of CH₄ against the same
parameters). It’s quite interesting to observe that GHGs behave differently w.r.t soil moisture
during different seasons. CH₄ shows a positive relationship during monsoon and post-monsoon
and an inverse relationship exist during pre-monsoon and winter; while a reverse relationship exist
for CO₂. During wet season aeration is restricted (Smith et al. 2003) hence soil respiration is
limited, which decrease CO₂ flux. This can be one of the factors for low values of CO₂ during
monsoon months, during dry months soil may act as sink of CH.

4.5.1 Influence of boundary layer height on GHGs mixing ratios

The planetary boundary layer is the lowest layer of the troposphere where wind speed as a
function of temperature plays major role in its thickness variation. It is an important parameter for
controlling the observed diurnal variations and potentially masking the emissions signal (Newman
et al., 2013). Since complete set of COSMIC RO data is not available during the study period, in
this analysis we have analysed RO data from July 2013 to June 2014, along with simultaneous
observations of GHGs. Monthly variations (Figure not show) of BLH computed from high vertical
resolution of COSMIC-RO data against CO₂ and CH₄ concentrations. Monthly BLH is observed
to be minimum (maximum) during winter and monsoon (pre monsoon) seasons and it closely
resembles with the air temperature pattern. The highest (lowest) BLH over study region was
identified 3.20 km (1.50 km). A monthly average air temperature is maximum (minimum) of 29°C
(20°C) during the summer (winter) months.

Seasonal BLH during winter, pre-monsoon, monsoon and post monsoon are 2.10 km, 3.15 km,
1.74 km and 2.30 km respectively. Its influence on CO₂ and CH₄ mixing ratios are shown in Figure
9a and 9b. X axis represents the seasonal transition i.e. monsoon to post monsoon (M-PM) etc and
y axis indicates seasonal difference of BLH and GHGs concentration respectively. As seasonal
BLH increase, mixing ratios of CO₂ (CH₄) decreased from 8.68 ppm to 5.86 ppm (110 ppb to 40
ppb). This effect clearly captured by seasonal diurnal averaged BLH data sets used from ECMWF-
ERA. The amount of biosphere emissions influence on CO$_2$ and CH$_4$ can be estimated through atmospheric boundary layer processes. Since the study region being a flat terrain, variations in CO$_2$ and CH$_4$ were mostly influenced by BLH through convection and biosphere activities.

### 4.6 Methane (CH$_4$) sink mechanism

Methane (CH$_4$) is the most powerful greenhouse gas after CO$_2$ in the atmosphere due to its strong positive radiative forcing (IPCC, AR5). Atmospheric CH$_4$ is mainly (70-80%) from biological origin produced in anoxic environments, by anaerobic digestion of organic matter (Crutzen and Zimmermann, 1991). The major CH$_4$ sink is oxidation by hydroxyl radicals (OH), which accounts for 90% of CH$_4$ sink (Vaghjiani and Ravishankara, 1991; Kim et al., 2015). OH radicals are very reactive and are responsible for the oxidation of almost all gases in the atmosphere. Primary source for OH radical formation in the atmosphere is photolysis of ozone (O$_3$) and water vapor (H$_2$O). Eisele et al., (1997) defined primary and secondary source of OH radicals in the atmosphere. Primary source of OH radical is as follows;

\[
O_3 + \text{hv} (\lambda \leq 310 \text{ nm}) \rightarrow O_2 + O(^{1}\text{D}) \quad (2)
\]

where $O(^{1}\text{D})$ is electronically excited atom

\[
O(^{1}\text{D}) + O_2 \rightarrow O + \text{M} \quad (3)
\]

\[
O(^{1}\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad (4) \text{ primary OH formation}
\]

Removal of CH$_4$ is constrained by the presence of OH radicals in the atmosphere. A 1 min time series analysis of CH$_4$, NO$_x$, O$_3$ and H$_2$O and associated wind vector for August 2014 to understand the CH$_4$ chemistry is shown in Figure 10a and Figure 10b. Low NO$_x$ (1-2 ppb) values are shown in horizontal elliptical region of Figure 10a and observed corresponding low CH$_4$ (1.80 ppm) concentrations. The low NO$_x$ in turn produces high OH radicals in the atmosphere due to conversion of HO$_2$ radical by NO, which removes CH$_4$ through oxidation process as shown below.

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad (5) \text{ when NO}_x \text{ levels } 1 - 2 \text{ ppb}
\]

\[
\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (6) \text{ main CH}_4 \text{ removal process}
\]
\[
\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad (7) \quad \text{if NO}_x > 2 \text{ ppb} \ (\text{OH} \downarrow, \text{CH}_4 \uparrow)
\]

Crutzen and Zimmermann, (1991) and Eisele et al., (1997) observed that at low NO\(_x\) (0.5-2.0 ppb) levels most HO\(_x\) family radicals such as HO\(_2\) and peroxo radicals (RO\(_2\)) react with NO to form OH radicals. Therefore OH radicals are much higher in the case of low NO\(_x\). When NO\(_x\) levels increase more than 2 ppb, most of the OH radicals react with NO\(_2\) to form nitric acid (HNO\(_3\)). In first order, the levels of CH\(_4\) in the atmosphere depend on the levels of NO\(_x\) though the production of OH radicals in the atmosphere is still uncertain. Figure 10a and 10b showed high CH\(_4\), H\(_2\)O, O\(_3\) and NO\(_x\) during a few days in August 2014. High concentrations of CH\(_4\), NO\(_x\) and other gases are observed in the eastern direction of study site. Very high NO\(_x\) levels above 10 ppb are observed and subsequently CH\(_4\) concentrations also increased to 2.40 ppm from 1.80 ppm. In the eastern direction of study site, a national highway and single line broad gauge railway network are present which act as possible sources of NO\(_x\), CH\(_4\) and CO\(_2\). Increase in emissions of NO\(_x\) causes decline in the levels of OH radicals and subsequently observed high CH\(_4\) over the study region.

### 4.7 Long range circulations

To understand the role of long range circulation, we separated the trajectory into 4 clusters based on their pathway, namely North-East (N-E), North-West (N-W), South-East (S-E), South-West (S-W). The main criterion of trajectory clustering is to minimize the variability among trajectories and maximize variability among clusters. Cluster mean trajectories of air mass and their percentage contribution to the total calculated for each season over the study period at 3 Km altitude are depicted in Figure 11. Majority of air mass trajectories during winter (~44%), pre-monsoon (~64%), monsoon (~80%) and post-monsoon (~41%) are originating from NW parts of the study site. For a comprehensive analysis, percentage occurrences of cluster mean trajectories of air mass over study area during different season at different altitudes are also tabulated in Table 4. During post-monsoon to early pre-monsoon periods which are generally the post-harvest period for some of the crops agriculture residue burning which are quite common in the NW and NE regions part of India (Sharma et al, 2010). Our analysis reveals that during this period majority of air mass reaching the study site at different altitudes come from this part of the country.
5. Conclusions

The present study analysed the seasonal variations of atmospheric GHGs (CO$_2$ and CH$_4$) and associated prevailing meteorology over Shadnagar, a suburban site of Central India during the period 2014. The salient findings of the study are the following:

- Irrespective of seasons, major sources for CO$_2$ are soil respiration and anthropogenic emissions while vegetation acts as a main sink. Whereas the major source and sink for CH$_4$ are vegetation and presence of hydroxyl (OH) radicals. In addition, boundary layer dynamics and long range transport also plays a vital role on GHGs mixing ratios.

- The annual mean of CO$_2$ and CH$_4$ over the study region are found to be 394±2.92 ppm and 1.92±0.07 ppm (μ±1σ) respectively. CO$_2$ and CH$_4$ show a significant seasonal variation during the study period. Maximum (Minimum) CO$_2$ is observed during Pre-monsoon (Monsoon), while CH$_4$ recorded maximum during post-monsoon and minimum in monsoon. Seasonal analysis of FEER data also showed maximum emission of CO$_2$ due to biomass burning during pre-monsoon months which indicates the influence of biomass burning on local emissions.

- CO$_2$ and CH$_4$ showed consistent diurnal behavior in spite of their significant seasonal variations, with an observed morning (06:00 IST) maxima, followed by afternoon minima (14:00 IST) and enhancing in the late evening (~22:00 IST).

- Correlation coefficient (Rs) between wind speed and CO$_2$ during pre-monsoon, monsoon, post-monsoon and winter is 0.56, 0.32, 0.06 and 0.67 respectively. While for CH$_4$ it is found be 0.28, 0.71, 0.21, and 0.60 respectively. Negative correlation indicates that the influence of local sources on GHGs, however, poor correlation coefficients during different seasons suggest the role of regional/local transport.

- CO$_2$ showed a positive correlation with temperature during all seasons except during winter. Whereas CH$_4$ showed a weak positive correlation with temperature during pre-monsoon and post-monsoon, while showing a weak negative correlation during monsoon and winter.

- CO$_2$ and CH$_4$ showed a strong positive correlation during winter, pre-monsoon, monsoon and post-monsoon with Rs equal to 0.80, 0.80, 0.61 and 0.72 respectively. This clearly indicates common anthropogenic sources for these gases.
Acknowledgment

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Table 1 Data used

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Period</th>
<th>Parameter</th>
<th>resolution</th>
<th>Source</th>
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<tr>
<td>GGA-24EP</td>
<td>Jan-2014 to Dec 2014</td>
<td>CO₂, CH₄ and H₂O</td>
<td>1 Hz time</td>
<td>ASL, NRSC</td>
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<tr>
<td>42i-NO-NO₂-NOₓ</td>
<td>Jul-2014 to Sep-2014</td>
<td>NOₓ(=NO+N O₂)</td>
<td>1 min time</td>
<td>ASL, NRSC</td>
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<tr>
<td>49i-O₃</td>
<td>Jul-2014 to Sep-2014</td>
<td>O₃</td>
<td>1 min time</td>
<td>ASL, NRSC</td>
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<td>AWS</td>
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<td>WS, WD, AT, RH</td>
<td>60 min time</td>
<td>NRSC</td>
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<td>Terra/MODIS</td>
<td>Jan-2014 to Dec-2014</td>
<td>NDVI</td>
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<td>HYSPLIT</td>
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<td>Backward trajectory</td>
<td>5 day isentropic model (1km to 4 km)</td>
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<td>FEER v1</td>
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<td></td>
<td><a href="http://ladsweb.nasa.gov/data/search.html">http://ladsweb.nasa.gov/data/search.html</a></td>
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Table 2 Statistical correlation between CO₂ and CH₄

<table>
<thead>
<tr>
<th>S.No</th>
<th>Seasons</th>
<th>Correlation coefficient (R)</th>
<th>Slope (\frac{Y_{CH₄}(ppm)}{X_{CO₂}(ppm)})</th>
<th>(\Psi_{Slope}) (ppm)</th>
<th>(\Psi_{Y-int}) (ppm)</th>
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<tr>
<td>1</td>
<td>Monsoon (JJAS)</td>
<td>0.61</td>
<td>0.005</td>
<td>0.00015</td>
<td>1.91</td>
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<td>2</td>
<td>Post-monsoon (OND)</td>
<td>0.72</td>
<td>0.0065</td>
<td>0.00014</td>
<td>1.52</td>
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<tr>
<td>3</td>
<td>Winter (JF)</td>
<td>0.80</td>
<td>0.0085</td>
<td>0.00018</td>
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<td>4</td>
<td>Pre-monsoon (MAM)</td>
<td>0.80</td>
<td>0.0059</td>
<td>0.00021</td>
<td>2.73</td>
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</table>
Table 3 Seasonal amplitudes of CO₂ and CH₄ over study region arriving from different directions

<table>
<thead>
<tr>
<th>Wind Direction</th>
<th>Winter CO₂/CH₄ (ppm)</th>
<th>Pre-monsoon CO₂/CH₄ (ppm)</th>
<th>Monsoon CO₂/CH₄ (ppm)</th>
<th>Post-monsoon CO₂/CH₄ (ppm)</th>
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<td>0-45</td>
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<td>45-90</td>
<td>391.66/1.94</td>
<td>399.59/1.89</td>
<td>388.82/1.91</td>
<td>390.23/1.98</td>
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<td>90-135</td>
<td>391.57/1.93</td>
<td>397.79/1.87</td>
<td>388.99/1.87</td>
<td>389.06/1.97</td>
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<td>135-180</td>
<td>389.34/1.89</td>
<td>393.87/1.85</td>
<td>391.81/1.86</td>
<td>387.69/1.97</td>
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<td>180-225</td>
<td>391.14/1.89</td>
<td>396.75/1.85</td>
<td>390.28/1.82</td>
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<td>225-270</td>
<td>389.13/1.88</td>
<td>394.81/1.86</td>
<td>390.26/1.82</td>
<td>384.40/1.94</td>
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<tr>
<td>270-315</td>
<td>388.68/1.87</td>
<td>398.68/1.89</td>
<td>389.58/1.82</td>
<td>384.99/1.93</td>
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<tr>
<td>315-360</td>
<td>390.87/1.91</td>
<td>401.17/1.89</td>
<td>387.58/1.83</td>
<td>389.32/1.98</td>
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Table 4 Cluster analysis of air mass trajectories reaching Shadnagar at various heights during different seasons

<table>
<thead>
<tr>
<th>Seasonal Backward trajectory (%)</th>
<th>NW 1 km</th>
<th>NW 2 km</th>
<th>NW 3 km</th>
<th>NW 4 km</th>
<th>SE 1 km</th>
<th>SE 2 km</th>
<th>SE 3 km</th>
<th>SE 4 km</th>
<th>SW 1 km</th>
<th>SW 2 km</th>
<th>SW 3 km</th>
<th>SW 4 km</th>
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<tr>
<td>Winter</td>
<td>54</td>
<td>32</td>
<td>2</td>
<td>0</td>
<td>32</td>
<td>24</td>
<td>44</td>
<td>52</td>
<td>10</td>
<td>25</td>
<td>11</td>
<td>7</td>
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<tr>
<td>Pre-monsoon</td>
<td>24</td>
<td>9</td>
<td>8</td>
<td>1</td>
<td>26</td>
<td>31</td>
<td>64</td>
<td>78</td>
<td>36</td>
<td>46</td>
<td>2</td>
<td>10</td>
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<tr>
<td>Monsoon</td>
<td>0</td>
<td>1</td>
<td>7</td>
<td>19</td>
<td>12</td>
<td>34</td>
<td>80</td>
<td>70</td>
<td>4</td>
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<tr>
<td>Post-monsoon</td>
<td>42</td>
<td>15</td>
<td>11</td>
<td>14</td>
<td>47</td>
<td>53</td>
<td>41</td>
<td>49</td>
<td>8</td>
<td>30</td>
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Figure 1  a) Schematic representation of study area; b-e) Seasonal variation of prevailing meteorological conditions during 2014
Figure 2  a-b) Temporal variations of CO$_2$ and CH$_4$; c-d) Seasonal variations of CO$_2$ and CH$_4$ in conjunction with NDVI (Normalized Difference Vegetation Index) during 2014
Figure 3  a) Long term analysis of CO$_2$ biomass burning emissions over study region b) Biomass signatures on CO$_2$/CH$_4$ during 14-21 April 2014, a case study c) Spatial distribution of MODIS derived fire counts over Indian region during 14-21 April 2014.
Figure 4 Monthly variation of $\Delta$CH$_4$/$\Delta$CO$_2$ during study period

Figure 5 a-d) Seasonal variations of diurnal averaged CO$_2$/CH$_4$ against boundary layer height during 2014

Figure 6 a-b) Daily mean scatterplot between wind speed and GHGs (CO$_2$ and CH$_4$).
Figure 7 a-b) Daily mean seasonal variation of CO₂ and CH₄ as function of humidity and air temperature during 2014
Figure 8 a-b) Daily mean seasonal variation of CO$_2$ and CH$_4$ as function of soil temperature and soil moisture during 2014

Figure 9 Seasonal difference in BLH against respective change in a) CO$_2$ and b) CH$_4$
Figure 10 Time series analysis of a) CH$_4$ vs. NO$_x$, b) H$_2$O vs. O$_3$

Figure 11 a-d) Long range circulation of air mass trajectories ending over Shadnagar at 3 km during winter, pre-monsoon, monsoon and post-monsoon