A study of CO$_2$ and related trace gases using a laser-based technique at an urban site in western India

S. Lal$^{1*}$, N. Chandra$^{1,2}$ and S. Venkataramani$^1$

$^1$Physical Research Laboratory, Ahmedabad 380 009, India
$^2$Indian Institute of Technology, Gandhinagar 382 424, India

Continuous measurements of surface-level carbon dioxide (CO$_2$) along with its co-emitted carbon monoxide (CO) and methane (CH$_4$) are being made at Ahmedabad using a laser-based cavity ring down spectrometer, which offers much longer path length for accurate and fast measurements of these species simultaneously. The average data during November 2013 show large variability in all the three species. These measurements also show significant diurnal variations with maximum in CO being relatively the shortest-lived species in this set of gases. The correlations and slopes among them have been used to identify potential emission sources.

**Keywords:** Cavity ring down spectroscopy, fossil fuel, greenhouse gases, India, vehicular emissions.

Carbon dioxide (CO$_2$) is the most important greenhouse gas (GHG) of anthropogenic origin. It is found to increase with time due to increasing use of fossil fuel combustion and biomass burning. The present level of background CO$_2$ has crossed 400 ppm and it is currently increasing at an average rate of 2.13 ppmv per year (in 2014) based on the Mauna Loa data (www.esrl.noaa.gov/gmd/ccgg/trends). Recent measurements show that the amplitude of seasonal variation of atmospheric CO$_2$ in the northern hemisphere has increased since 1950s (ref. 1). Effects of rising levels of this gas as well as other GHGs like CH$_4$ and N$_2$O are clearly evident in rising air temperature and associated effects all over the globe$^2$, as well as in the Indian region$^3$–$^5$. The Asian countries, including India and China are growing fast, which leads to increase in the emissions of these gases. Since the lifetimes of these species are high, the effects are going to be felt all over the globe irrespective of the emission locations.

Sources and sinks of these GHGs need to be identified and estimated accurately to understand their variability and future trends. The budgets of these gases can be estimated using top-down and bottom-up approaches. However, both approaches show larger uncertainties (100–150%) in the biospheric flux of CO$_2$ over South Asia than other continents, as shown by Patra et al.$^6,7$. One of the major sources for these larger uncertainties is the lack of measurements with required temporal and spatial resolutions. There are several groups in the developed countries making such measurements, but these are lacking in India. Hence, there is a need for an observational network covering different ecosystems in India to make precise measurements of these gases in order to understand their variability, trends and improved understanding of their emission budgets in the Indian region. Since CO$_2$ is also related to the biosphere (photosynthesis and respiration), its measurements in different ecosystems are necessary. Several groups are now involved in the measurement of surface-level CO$_2$ in India$^8$–$^{12}$. Some of them are also making measurements of CO$_2$ flux using tower measurements$^{13,15}$. However, there are limited measurements of CO$_2$ with other co-emitted gases like carbon monoxide (CO), methane (CH$_4$), etc. Simultaneous measurements of CO$_2$ with CO and CH$_4$ have their importance in terms of constraining emission sources and their nature. CO$_2$ measurements alone can give information on basic features in terms of diurnal variation, seasonal variation and their amplitudes, but cannot give information related to source types. Interrelations among these gases can yield important information on the type of emission sources. This communication presents some initial results from a recently initiated project as a part of the ISRO-GBP to study the levels, variability and trends in CO$_2$ and related trace gases at Ahmedabad.

There are many techniques to measure CO$_2$ in air. The collected air samples can be analysed using a gas chromatograph equipped with a flame ionization detector and a Ni-catalyst to convert CO$_2$ to methane, which is finally detected. Though the system is rugged, it has limitation related to portability, precision and accuracy. Infrared absorption-based (using non-dispersive infrared NDIR technique) analysers are highly portable with better sensitivity and accuracy. These systems have been extensively used for field studies, including aircraft-based measurements$^6,17$. However, these have the problem of drift (zero and temperature drift) in the system and need frequent calibration. This problem is overcome in the systems based on cavity ring down spectroscopy (CRDS) technique. This technique is based on the measurement of the rate of absorption rather than the magnitude of absorption of a laser pulse confined in a closed optical cavity filled with the sample air. Since many atmospheric gases have absorption bands in the near-infrared region, it is possible to tune the laser wavelength for a specific gas molecule. Since the effective path length inside the cavity becomes very large (many kilometres), the sensitivity of this system becomes extremely good. It can measure gases in parts per billion level with high accuracy and with very fast response in seconds or less$^{18,19}$. We have used an analyser based on this technique for the simultaneous measurements of CO$_2$, CO, CH$_4$ and water vapour (Picarro, G2401). The precisions for a 5 min average are ∼50, ∼2 and ∼0.7 ppb for CO$_2$, CO and CH$_4$ respectively. It uses a pump to suck the inlet air through the analyser. Since we are not interested in measuring water vapour and to avoid

---

*For correspondence. (e-mail: shyam@prl.res.in)
its calibration and correction to calculate dry mole fractions, we remove water in the sample air before it enters into the system using a Nafion dryer (100 tubes, 24 inch length). It brings down the water level to about 0.03% from 2% to 3%. This analyser is frequently calibrated using three CO₂ mixtures from NOAA, USA at 350, 400 and 425 ppmv. The analyser is also calibrated for CO and CH₄ using gas mixtures from Linde, UK.

The measurements are being made from the sixth floor of the main building of the Physical Research Laboratory (PRL), Ahmedabad (23°N, 72.5°E, 49 m asl). It is located in the western region of the city, dominated by various educational organizations and residential societies. A power house and some industries are located in the eastern parts of the city. The city has a population of about 50 lakhs and about 32 lakh registered vehicles, which are growing by about 10% per year. All these stationary and mobile fossil-fuel burning systems are a good source of gaseous and particulate pollutants. The city has a warm climate with high temperatures going up to 44°C in May and lowest temperature of about 8°C in January. The wind is mostly from the west except during the monsoon season, when it becomes southwest. Cool air during the winter comes from the northwest direction. The average annual rainfall is about 780 mm, which mostly occurs in July and August. Figure 1 shows air temperature, relative humidity, wind direction and wind speed, and solar radiation received at the ground in November 2013. These measurements are made using a weather station located in the PRL campus. There are some breaks in the data due to technical problems. The air temperature during this month was in the range 17–33°C. The relative humidity was in the range 25–75%. Wind speed varied from 1 to 4 m s⁻¹ and the direction changed from northeast to southwest. The relative humidity as well as the solar radiation showed slight decreasing trend during this month.

Continuous in situ surface-level observations of CO₂, CO and CH₄ using this system started at PRL in November 2013. Figure 2 shows the 30-min average mixing ratios of these species from 3 to 30 November. There is a large variability in the levels of these gases during this month. Relatively lower values of these gases were observed during 16–19 November, while higher levels were observed during 20–27 November. A plume of very high levels of these gases was observed on 21 November. However, CH₄ level was highest on 7 November when the other two gases did not show any abnormal increase. The minimum level of CO₂ observed during this month was about 390 ppmv and it went as high as 558.6 ppmv. The average level of CO₂ during this month was found to be 418.3 ± 17.6 ppmv. Similarly, minimum level of CO was found to be 0.2 ppmv and highest level (7.0 ppmv) was observed coinciding with the high level of CO₂. The average level of CO was found to be 0.73 ± 0.65 ppmv. Methane showed 1.95, 5.7 and 2.41 ± 0.42 ppmv respectively, for minimum, highest and mean levels. Maximum variability has been observed in the levels of CO as its lifetime (few weeks to two months) is the shortest among the three gases.

To illustrate the nature of average diurnal cycle of CO₂, CO and CH₄, we standardized it by averaging...
of every second data for respective hour of all the days of observations after removing the outer values beyond two sigma as outliers. Figure 3 shows the average diurnal patterns based on hourly average values for these gases during November 2013. Highest values of hourly average CO_2 (431 ppmv) are observed during the morning around 0800 h and in the late evening around 2200 h. These are also the periods of maximum variability. There is a slow increase in the levels of CO_2 after the midnight (~0200 h) low. This is mainly due to respiration by the plants. After the peak around 0800 h, the level of CO_2 starts decreasing as the planetary boundary layer (PBL) height increases and as the photosynthesis in plants increases. The minimum CO_2 (396 ppmv) during the day is observed around 1600 h, when the diurnal value of air temperature is highest and the PBL height is also high. This gives higher volume for mixing of the pollutants in the atmosphere. CO_2 levels again increase after this minimum due to lowering of the PBL, increase in the vehicular traffic as well as decrease in the photosynthesis activity. The variability in CO_2 is high from late night to morning (2–3%) and minimum (0.6%) during afternoon hours. The average diurnal amplitude during this month is about 35 ppmv. The only other measurements for diurnal variations in India are available for Dehradun and Gadanki\textsuperscript{10}, and for Sriharikota\textsuperscript{11}. Dehradun and Gadanki show diurnal amplitudes of 30 and 40 ppmv respectively, whereas Sriharikota shows an amplitude of only 17 ppmv. Though the diurnal amplitude observed at Ahmedabad is in the range of Dehradun and Gadanki, but their average CO_2 levels during 2010–2011 are much lower (~355–360 ppmv), than the average CO_2 level of 418.3 ppmv observed at Ahmedabad during November 2013. CO also shows a similar diurnal variation but with some differences. Its levels keep on decreasing after the evening maximum around 2000 h to a low value of about 0.370 ppmv around 0500 h. After this, there is a slight increase till about 0900 h after which its values start decreasing again.

The minimum (0.325 ppmv) is reached around 1500 h. Like CO_2, CO values also start increasing after this minimum, but peak around 2000 h in the evening. Timings are slightly different for CO compared to CO_2, which also has the effects of biosphere in addition to fossil-fuel combustion and biomass burning. The variability in CO is also high (30–65%) from late night to early morning, and minimum (16%) during afternoon hours. CH_4, on the other hand, has different diurnal variation. After the peak (2.81 ppmv) in the evening around 2200 h, its values keep on decreasing till the afternoon minimum (2.02 ppmv) around 15 h. This species also has high variability (12–16%) in the late night and early morning, and minimum (2%) during afternoon hours.

These three gases have some common emission sources and some specific different sources. As mentioned earlier, CO_2 has both biospheric and combustion of fossil fuel and biomass burning. CO has emission sources from fossil-fuel combustion and biomass burning as well as oxidation from hydrocarbons. However, CH_4 has different sources such as wetlands, rice agriculture, landfills, coal mines, biomass burning as well as losses of compressed natural gas (CNG). There are many buses and autos being run on CNG in this city. Hence, the diurnal variations of these gases are different. The only common features are minimum in the afternoon and maximum in late evening/night. These features are dominated by the change in the height of the PBL from highest in the afternoon to lowest in the night/early morning. Also, both CO and CH_4 have losses by OH radicals. Since mixing ratios of OH are maximum during noon hours, so is the loss of both these gases. However, the reaction rate of OH with CH_4 is very slow (6.3 × 10^{-15} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}), which is only 1/24th that of reaction with CO (1.5 × 10^{-13} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}). The lifetime of CH_4 is about 8–10 years. CO_2 does not have any chemical loss. Hence its lifetime is highest (~40–50 years) among these gases.

Meteorological factors also play an important role in the distribution of trace gases. We have already discussed

\textbf{Figure 3.} Average diurnal variations of CO_2, CO and CH_4 observed during November 2013 at Ahmedabad.
the role of PBL earlier. Air temperature and humidity also have an impact on some of the emission sources as well as chemistry. However, advection can change their concentrations significantly. Figure 4a shows variation of mixing ratios of these species with wind speed. It is clearly evident that higher wind speed lowers the levels of these gases. However, the correlations are not good as wind direction and other factors also contribute to their changes.

Figure 4b shows the wind polar diagrams, colour coded with the mixing ratios of CO₂, CO and CH₄, for November 2013. The diagrams show the variations of observed trace gases with wind speed and wind direction.

Figure 5. Correlations and slopes for CO–CO₂, CH₄–CO₂ and CO–CH₄ combinations during day and night. These are based on 15 min average data observed during November 2013 at Ahmedabad.
2013. The episodes of higher mixing ratios of CO₂ (>425 ppmv), CO (>1 ppmv) and CH₄ (>2.5 ppmv) are mostly found when wind direction is in between 30° and 150°. The main city, a power house and several industries lie in this direction range. Also, higher levels of these gases are observed when the wind speed is low.

These three gases have some common emission sources and losses. Correlations and slopes can give some hint on the dominant emission sources or losses. For example, fossil fuel and biomass burning both emit CO₂ and CO, but CO emission is more during biomass/biofuel burning compared to that from fossil-fuel combustion. Hence the correlation slopes of CO with CO₂ will vary with the efficiency of combustion and thus will provide a good proxy for evaluating the signature of source type and their combustion efficiencies. A good correlation between two gases will indicate if major emission sources or loss processes are common. In order to study the important common sources of CO₂, CO and CH₄, we calculated the correlations of CO–CO₂ and CH₄–CO₂ separately for day (07:00–18:45 h) and night (19:00–06:45 h). The ordinary least square regression method has been imposed to the 15-min average data of CO, CH₄ and CO₂ for estimating the correlation slopes and regression coefficients. Figure 5 shows correlations and slopes for different combinations.

Correlation of CO₂ with CO is not good, particularly during daytime as CO₂ has other biospheric sources and sinks and the lifetimes of the two gases are different. The slope (ΔCO/ΔCO₂) is found to be 8 and 37 ppbv/ppmv during day and night respectively, for this month at Ahmedabad. The average slope based on all the data is 16 ppbv/ppmv. The average ratio (ΔCO/ΔCO₂) is found around 13.4 ppbv/ppmv over Puducherry, India during April–May–June only based on weekly flask measurements during 2007–2011. Similar measurements for Hanle, India, a free tropospheric site, give this ratio in the range 35–55 ppbv/ppmv (ref. 12). Over China, the ΔCO/ΔCO₂ ratios are found in the range of 40–45 ppbv/ppmv (refs 23, 24), while southern California shows this ratio to be around 11 ppbv/ppmv (ref. 25). This shows the dominance of fossil fuel at Ahmedabad.

The correlation between CH₄ and CO₂ is found to be higher, 0.67 and 0.55 during day and night respectively, even though they are not emitted from common major sources. The atmospheric lifetimes of both gases are much longer than the timescale for mesoscale transport. Even if emitted from different sources, the dynamics in the boundary layer will cause mixing on very short timescales. The slope (ΔCH₄/ΔCO₂) is observed to be 11.1 and 23.8 ppbv/ppmv during day and night respectively, and the slope based on all the data is found to be 18 ppbv/ppmv in November at Ahmedabad. Puducherry, a southeast coastal station shows this ratio in the range of 6–9 ppbv/ppmv (ref. 12). Several studies have reported strong correlation between CH₄ and CO₂ over different urban regions and observed slopes in the range of 5–8 ppbv/ppmv (refs 25, 26). Higher ratio at Ahmedabad indicates relatively stronger source for methane.

Further, we have also derived the slope for CO–CH₄ (ΔCO/ΔCH₄), which is observed to be 0.71 and 0.95 ppmv/ppmv during day and night respectively. These are not very different from the average slope of 0.96 ppm/ppmv based on all the data. However, correlations are poor (−0.35). Puducherry and Port-Blair show this ratio in the range of 0.4–1.4 ppb/ppmv (ref. 12). The difference in the slopes is due to different types of emission sources.

Continuous measurements of CO₂ together with CO and CH₄ have been initiated at Ahmedabad. The average values of CO₂, CO and CH₄ for November 2013 are 418.3 ± 17.6, 0.73 ± 0.65 and 2.41 ± 0.42 ppmv respectively. Higher variabilities have been observed during the day and from day-to-day. Higher variability in CO is due to its relatively shorter lifetime. The observed ΔCO/ΔCO₂ slope indicates emissions in Ahmedabad are dominated by fossil fuel. The ΔCH₄/ΔCO₂ slope is higher than other sites, which suggests that there is significant source for CH₄ also in this city.

This analysis shows the importance of such simultaneous measurements to find the major emission sources.

Observations of snow–meteorological parameters in Gangotri glacier region

H. S. Gusain*, Manish Kala, Ashwagosha Ganju, V. D. Mishra and Snehmani

Snow and Avalanche Study Establishment, Research and Development Centre, Chandigarh 160 036, India

In this communication analysis of the snow–meteorological parameters recorded in the Gangotri glacier region has been presented. Maximum temperature, minimum temperature, snowfall, snow cover thickness, incoming shortwave radiation flux, reflected shortwave radiation flux and albedo have been recorded at ‘Bhojbasa’ observation station. Meteorological data of 13 years from 2000 to 2012 have been presented for annual and seasonal variations in temperature, snowfall and snow cover thickness. Winter, pre-monsoon, monsoon and post-monsoon data have been considered for analysis. Annual mean maximum and minimum temperature are 11.1 ± 0.7°C and −2.3 ± 0.4°C respectively. Mean values of these parameters obtained for winter season are 3.0 ± 1.0°C and −10.4 ± 1.3°C respectively. Mean annual snowfall amount is 257.5 ± 81.6 cm and maximum snow cover thickness varies from 42 to 205 cm for different years. Incoming shortwave radiation flux and reflected shortwave radiation flux have been recorded using pyranometer sensor mounted on automatic weather station, and data for 2012 and 2013 are presented. Incoming shortwave radiation flux and total atmospheric transmissivity have been estimated. Mean annual atmospheric transmissivity is 0.37 at the observation location. Mean seasonal albedo for winter season is observed to be quite high compared to other seasons. Maximum and minimum temperature reveal an increase of 0.9°C and 0.05°C respectively, during the decade. Annual snowfall amount reveals a decrease of 37 cm in the decade. The observed temperature and snowfall patterns during the past 13 years, at the present study location, indicate that trends in Central Himalaya may be in accordance with the observed trends in the Western Himalaya.

Keywords: Albedo, glacier, snowfall, snow cover, temperature.

The Himalaya Mountains are the abode of the largest number of glaciers outside the polar regions. These glaciers are the major source of many perennial river systems, including the Ganga, Indus and Brahmaputra. These rivers play a critical role in meeting the demands of water, irrigation and hydropower. Gangotri glacier is one of the most well-studied glaciers in India and is the largest glacier in the Garhwal Himalaya. Studies of the Gangotri glacier have been conducted for analyses of glacier

*For correspondence. (e-mail: gusain_hs@yahoo.co.in)