Environ Sci Pollut Res (2015) 22:1877–1890
DOI 10.1007/s11356-014-3530-3

RESEARCH ARTICLE

Diurnal and seasonal variation of mixing ratio and $\delta^{13}C$ of air CO_2 observed at an urban station Bangalore, India

Tania Guha · Prosenjit Ghosh

Received: 27 December 2013 / Accepted: 28 August 2014 / Published online: 9 October 2014

Abstract We present here observations on diurnal and seasonal variation of mixing ratio and $\delta^{13}C$ of air CO_2, from an urban station—Bangalore (BLR), India, monitored between October 2008 and December 2011. On a diurnal scale, higher mixing ratio with depleted $\delta^{13}C$ of air CO_2 was found for the samples collected during early morning compared to the samples collected during late afternoon. On a seasonal scale, mixing ratio was found to be higher for dry summer months (April–May) and lower for southwest monsoon months (June–July). The maximum enrichment in $\delta^{13}C$ of air CO_2 (−8.04±0.02‰) was seen in October, then $\delta^{13}C$ started depleting and maximum depletion (−9.31±0.07‰) was observed during dry summer months. Immediately after that an increasing trend in $\delta^{13}C$ was monitored coincidental with the advancement of southwest monsoon months and maximum enrichment was seen again in October. Although a similar pattern in seasonal variation was observed for the three consecutive years, the dry summer months of 2011 captured distinctly lower amplitude in both the mixing ratio and $\delta^{13}C$ of air CO_2 compared to the dry summer months of 2009 and 2010. This was explained with reduced biomass burning and increased productivity associated with prominent La Nina condition. While compared with the observations from the nearest coastal and open ocean stations—Cabo de Rama (CRI) and Seychelles (SEY), BLR being located within an urban region captured higher amplitude of seasonal variation. The average $\delta^{13}C$ value of the end member source CO_2 was identified based on both diurnal and seasonal scale variation. The $\delta^{13}C$ value of source CO_2 (−24.9±3‰) determined based on diurnal variation was found to differ drastically from the source value (−14.6±0.7‰) identified based on seasonal scale variation. The source CO_2 identified based on diurnal variation incorporated both early morning and late afternoon sample; whereas, the source CO_2 identified based on seasonal variation included only afternoon samples. Thus, it is evident from the study that sampling timing is one of the important factors while characterizing the composition of end member source CO_2 for a particular station. The difference in $\delta^{13}C$ value of source CO_2 obtained based on both diurnal and seasonal variation might be due to possible contribution from cement industry along with fossil fuel / biomass burning as predominant sources for the station along with differential meteorological conditions prevailed.

Keywords Air CO_2 · Mixing ratio · $\delta^{13}C$ of CO_2 · Diurnal variation · Seasonal variation · Source identification · Urban station

Responsible editor: Gerhard Lammel

Electronic supplementary material The online version of this article (doi:10.1007/s11356-014-3530-3) contains supplementary material, which is available to authorized users.

T. Guha (✉) · P. Ghosh
Centre for Earth Sciences, Indian Institute of Science, Bangalore 560 012, India
e-mail: taniaguha@gate.sinica.edu.tw

T. Guha
e-mail: guha.tania@gmail.com

T. Guha
Research Centre for Environmental Changes, Academia Sinica, Taipei, Taiwan

Introduction

Increase in atmospheric CO_2 level due to human activities, like fossil fuel combustion, biomass burning, deforestation etc. (Team et al. 2007), is the primary factor responsible for global warming. The observed variability of atmospheric CO_2 is largely interpreted as net effect of CO_2 exchange among the terrestrial biosphere, ocean, and the atmosphere (Keeling et al. 1989a; Tans et al. 1993; Ciais et al. 1995a, 1995b; Fung et al. 1997); but in the industrial era, this balance in CO_2 is disrupted due to the participation of emission from

anthropogenic activities (Keeling et al. 1995). Moreover, the increase in atmospheric CO_2 mixing ratio (i.e., concentration) is found to be half of that produced by anthropogenic emission, with the remaining half being taken up either by the biosphere or the ocean (Ciais et al. 1995a; Pearman and Hyson 1986). Understanding the distribution of CO_2 among different reservoirs and their exchange is a current challenge in carbon cycle research (Schimel et al. 1994, 2001; Zobitz et al. 2006). The contribution of CO_2 fluxes from these reservoirs can be used in global carbon cycle models for predicting the future CO_2 emission (Heimann and Maier-Reimer 1996; Keeling et al. 1989a, 1989b, 1995; Tans et al. 1989, 1996) and developing strategies for reduction in CO_2 emissions (Nakazawa et al. 1993). To have better understanding on CO_2 fluxes from different reservoirs, it is necessary to identify the sources of CO_2 (Ciasis et al. 1995a, b; Keeling et al. 1995; Francey et al. 1995). Combined measurement of CO_2 mixing ratio and $\delta^{13}C$ of atmospheric CO_2 is used to identify the isotopic composition of source CO_2 responsible for the observed variability of atmospheric CO_2 (Keeling 1958, 1961; Keeling et al. 1989a, 1989b, 1995; Mook et al. 1983; Francey et al. 1995; Tans et al. 1990; Ciais et al. 1995a, 1995b; Fung et al. 1997). Thus, monitoring of atmospheric CO_2 is crucial as it carries information on CO_2 fluxes from/to the respective reservoirs. The routine measurement of atmospheric CO_2 was first started in 1957/58 by Keeling (Keeling 1958, 1961), and slowly the global network of CO_2 monitoring stations has been expanded and covered many continents (Tans et al. 1990). Observations on atmospheric CO_2 from these stations captured both spatial and temporal scale variations of CO_2 mixing ratio and isotopic ratio of atmospheric CO_2 (Tans et al. 1990; Ciais et al. 1995b). The observations on temporal scale variation provide information on the local sources and sinks of CO_2. The temporal variation of atmospheric CO_2 can either be short-term covering daily, seasonal, inter-annual time scales, or it can be long-term covering several years (Keeling et al. 1989a, 1989b). The short-term variations, i.e., diurnal and seasonal scale variations, capture the effect of processes like photosynthesis, respiration, and anthropogenic emission on the observed variability of atmospheric CO_2. Thus, it is interesting to identify the sources of CO_2 based on both diurnal and seasonal scale variations as it can provide information on the temporal variability in the contribution of sources along with CO_2 exchange between different reservoirs (Pataki et al. 2003a). Moreover, the isotopic composition of anthropogenic sources especially fossil fuel varies geographically (Andres et al. 2000); thus, the knowledge of isotopic ratios at regional and local scales is required to better understand the source contribution. To precisely estimate the source CO_2 composition at a local scale, it is important to monitor the composition of atmospheric CO_2 over an urban station. Urban stations are the immediate sources of anthropogenic emissions (Grimmond et al. 2002; Grimmond 2007) and can provide information on the temporal variability of anthropogenic emissions as well as the biospheric uptake affecting air CO_2 (Pataki et al. 2003a). Furthermore, being immediate hot spots of anthropogenic emission, urban station captures higher amplitude of variation in both CO_2 mixing ratio and $\delta^{13}C$ of atmospheric CO_2 compared to remote station and this allows precise identification of possible sources of CO_2. Observations of diurnal and seasonal variations in the contribution of anthropogenic and biogenic sources of CO_2 is well documented from many urban stations in Europe and the USA, but only a few cases are documented from Asia (Clark-Thorne and Yapp 2003; Demeny and Haszpra 2002; Kuc 1986, 1989, 1991; Kuc and Zimnoch 1998; Kuc et al. 2007; Pataki et al. 2003a, 2003b, 2006, 2007; Bush et al. 2007; Affek et al. 2007; Widory and Javoy 2003; Newman et al. 2008). Unfortunately, information about air CO_2 variation from Indian region is restricted only to the observations from the west coast of India (Bhattacharya et al. 2009).

The importance of India's contribution towards CO_2 emission is described by the International Energy Agency (www.iea.gov.in). CO_2 is emitted from the energy sector especially coal-based power plants in India [http://www.moef.nic.in/downloads/public-information/Report_INCCA.pdf], other sources include fossil fuel combustion in automobiles, biomass burning, forest fires (Crutzen and Andreae 1990; Heald et al. 2003), emission from cement industries, etc. (Anand et al. 2006). Biomass burning is very frequently recorded from India especially during dry seasons (Venkataraman et al. 2006). Apart from different sources contribution, the Indian region experiences seasonal reversals of the wind direction (Gadgil et al. 1984) associated with monsoon circulations, which lead to transport and mixing of trace gases like CO_2 (Bhattacharya et al. 2009). The existing knowledge of the long term variability in air CO_2 composition is available from the coastal station, Cabo De Rama (15° 05′N, 73° 50′E, masl=60 m), monitored for a decade. The effect of wind-driven transport of both northern and southern hemispheric air influencing the concentration of trace gases and their isotopic ratios was reported for the Cabo De Rama station (CRI; Bhattacharya et al. 2009; Tiwari et al. 2011). In addition, observations on air CO_2 composition from an island station (Seychelles; SEY) in Indian Ocean supports the transport processes, but lack of data on air CO_2 from urban regions prevented quantitative investigation on the transport of source air to the location. Together with this, the monsoon rainfall also enhances biological productivity which leads to the uptake of CO_2. Thus monitoring air CO_2 mixing ratios and $\delta^{13}C$ of air CO_2 from an urban station in India can provide important understanding on the net effect of all these processes in controlling the temporal variability of atmospheric CO_2 composition and end member source CO_2 contribution. The aim of this paper is to characterize the anthropogenic sources

of CO_2 in regional atmosphere and to further understand the diurnal and seasonal variability from the region.

Methods

Sampling site

During the period of our study, we have sampled air from the campus of Indian Institute of Science (IISc), Bangalore (mentioned here after as "BLR"), Karnataka State (13° 02′ N, 77° 35′ E, masl=920 m), India. Bangalore is one of the rapidly developing urban areas in India. The city is undergoing large urbanization associated with industrial and economic development. During 1973–2009, the Bangalore urban area has experienced a rapid growth of 632 % and the average atmospheric temperature of the city recorded an increase of 2 to 2.5 °C in the last decade (Ramachandra and Kumar 2010). Topographically, it is ideally located at an elevation within the Plateau region of the Southern Indian peninsula and equidistant (~300 km) from both the west and east coast (Sudhira et al. 2007); Arabian Sea is in the west and Bay of Bengal is in the east. The coastal plain of the Arabian Sea surrounded by the hills of the Western Ghats lies towards the west, while the Plateau region, the Nilgiri Mountain is in the southwest and the Eastern Ghats mountain lie in the east (Fig. 1a). The Indian Institute of Science campus is located in the Bangalore urban district which occupies the south-eastern boundary of the Karnataka state as shown in the map (Fig. 1a). The district is a flat terrain with slightly increasing steepness as one approach from southwest to the northeast direction (Fig. 1b). Due to its topographic location, the site receives air packet from both the west and the east during different seasons. The green area marked in Fig. 1b is the IISc campus designated here as BLR station, from where air samples were collected and is further zoomed in Fig. 1c where the exact sampling location is marked with a red dot. The BLR station experiences four distinct seasons: dry summer (March–May), southwest monsoon (SWM; June–September), post monsoon (October–November), and winter (December–February). Amongst the four different seasons observed at BLR, during the dry summer the relative humidity approaches minima (~30 %) with maximum temperature reaching ~29 °C. Such conditions sometimes promote biomass burning through natural or manmade forest fires. Amongst Southeast Asian countries, biomass burning frequency is high in India (Crutzen and Andreae 1990; Heald et al. 2003). Biomass burning includes agricultural and crop waste burning and burning of forest and grassland (Streets et al. 2003). An increase in burning events was observed during February to May when dry conditions prevails (Venkataraman et al. 2006). Two major forest regions in proximity to the BLR region are Bandipura National Park, Nagarhole National Park, and Mudumalai Tiger Reserve. Regular events of forest fires were reported at these sites during February till May (Narendran 2001). Although the major source of CO_2 for Indian region is the coal-based thermal power plants [http://www.moef.nic.in/downloads/public-information/Report_INCCA.pdf], events of enhanced biomass burning and cement production also serve as other important sources of CO_2 (Anand et al. 2006). The region receives heavy rainfall during the southwest monsoon months which promotes high natural and agricultural productivity. Thus, the monsoon rainfall increases green cover and also likely has an impact on atmospheric CO_2 due to enhanced CO_2 uptake through productivity. All these features make the BLR station interesting to study both the diurnal and seasonal scale variation of atmospheric CO_2 and identify the possible sources of CO_2 responsible for the observed variability. Routine air samples were collected from the roof top of a one-storey building (5 m above the ground level) within the campus of IISc. In order to negate the influence of factors like local sources, a separate set of experiment was conducted where air sample were collected simultaneously at different heights (5 and 10 m above the ground level) from two location placed at an aerial distance of less than 10 m between them. The experiments were conducted on three different days during the month of June 2011. The results are given in a table in the Supplementary material (Supplementary Table A), where average differences in $\delta^{13}C$ of air CO_2 at two different heights were well within the analytical uncertainty. This suggests that our sampling station is well presentative station for understanding the temporal variability.

Air sampling details

Sampling timing

The study was conducted during 2008 till 2011 covering different months representing all the four seasons. The purpose of the study was to determine the source air CO_2 composition based on both diurnal and seasonal scale variation. To collect the diurnal air samples, 4–5 days were selected in every month. The data set obtained during a month was considered for calculating the average representative value for that month. On individual days air samples were collected twice in a day one in the early morning (~0530–0730 hours, Indian Standard Time, mentioned hereafter as IST) and another in the late afternoon (~1430–1730 hours, IST). The timing of sampling was decided based on experimental observation where air CO_2 composition was monitored throughout the day at 3 h time interval (see, Supplementary Figure A). Maximum variation in both mixing ratio and $\delta^{13}C$ of air CO_2 was recorded in the samples collected between early morning and late afternoon hours. In order to capture this maximum variability (Pataki et al. 2003b) in daily air CO_2 composition, we have chosen sampling time coinciding with early morning and late afternoon for studying the diurnal variation.

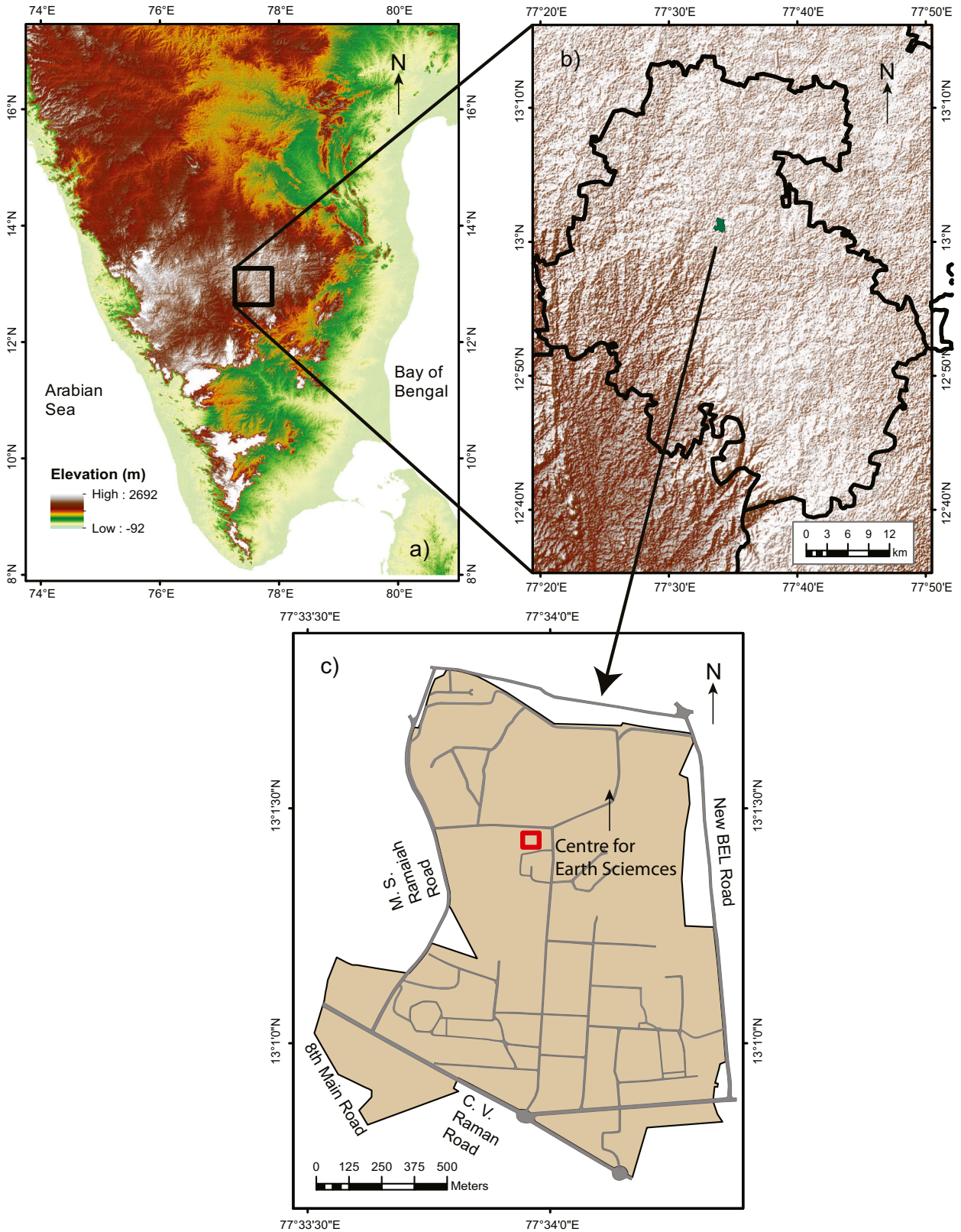

Fig. 1 **a** Air sampling station located in the Plateau region of Southern India peninsula. The *black box* in the figure indicates the Bangalore district within which the sampling station exists. **b** The *enlarged view of the black box*, the Bangalore district. The *green mark* indicates the Indian Institute of Science. **c** The campus map of Indian Institute of Science with the sampling site, Centre for Earth Sciences building, indicated with *red rectangle*

To understand the seasonal variation, air samples were collected routinely (in alternate days) during the afternoon time (1430 hours, IST) when influence of boundary layer processes on local air composition was found to be minimal (Guha and Ghosh 2010).

Sampling procedure

Air samples were collected in the 1-l glass flasks after being entrained through Magnesium per chlorate ($MgClO_4$) moisture removal trap. During the period of 2008–2009, air samples were collected following evacuation method (Guha and Ghosh 2010), while from the end of 2009, flush fill method was used for air sampling (Guha and Ghosh 2013). Soon after air sampling, CO_2 was extracted and purified using a cryogenic separation method (Craig 1953), involving CO_2 extraction line designed to trap CO_2 and remove other gaseous components from the air sample. During 2008–2009, CO_2 was extracted using glass extraction line (Guha and Ghosh 2010); whereas from 2009, end sample was extracted using stainless steel extraction line (Guha and Ghosh 2013). The reproducibility of analytical results using both these methods is discussed later.

Measurement of mixing ratio and $\delta^{13}C$ of the extracted CO_2

The extracted and purified CO_2 was collected in a volumetrically calibrated sample ampoule and the mixing ratio of the extracted CO_2 was determined based on pressure reading obtained using the MKS Baratron gauge (Guha and Ghosh 2013). The precision for mixing ratio measurement is ±2 μmol.mol^{-1}, determined based on repeat measurements of CO_2 extracted from air samples using pressure reading from MKS Baratron gauge.

The extracted CO_2 is analyzed for isotope ratios ($\delta^{13}C$ and $\delta^{18}O$) using the dual inlet peripheral of isotope ratio mass spectrometer, IRMS MAT 253 (Thermo-Fisher, Bremen, Germany). The working (in reference below) gas used for analyses was high purity CO_2 calibrated to VPDB scale using primary carbonate standard NBS19 (Guha and Ghosh 2013). In this study, we have focused mainly on mixing ratio and $\delta^{13}C$ of atmospheric CO_2. The internal precision for $\delta^{13}C$ measurement was ±0.03‰ (Guha and Ghosh 2013) based on 10 repeated measurements of CO_2 from Linde high purity cylinder. The details of the standardization procedure was described elsewhere (Guha and Ghosh 2013). A correction factor of +0.2‰ for ~300 ppb of N_2O was used for correcting $\delta^{13}C$ value of air-CO_2 for N_2O contribution. JRAS reference air mixtures provided by MPI-BGC (Max Planck Institute for Bio-geochemistry; Wendeberg et al. 2012; http://www.bgc.mpg.de/service/iso_gas_lab/JRAS_web/) were analyzed to finally convert the isotopic values of air CO_2 samples in VPDB scale. The paired JRAS reference air, i.e., JRAS MAR-J1 and JRAS OMC-J1, were analyzed together with the extracted CO_2 from two calcite standards (NBS19 and MARJ1). The JRAS reference air was measured with a precision (standard deviation of the repeat measurements of JRAS for 3times) of ±2 μmol.mol^{-1} and ±0.02‰ for mixing ratio and $\delta^{13}C$ of CO_2, respectively. The analysis of JRAS reference air allowed determination of the offset of our local scale from the JRAS reference scale. We observed an offset of 0.005‰ for $\delta^{13}C$ based on these experiments, while for mixing ratio the offset value was 0.05 μmol.mol^{-1} (Guha and Ghosh 2013). These offset values were introduced into the final data evaluation for air CO_2 samples.

During 2008–2009, when sample was collected using the evacuation method and extracted using glass extraction line, the precision of mixing ratio and $\delta^{13}C$ measurement of air CO_2 was ±9.3 μmol.mol^{-1} and ±0.09‰, respectively. Whereas during 2009–2011, when sampling method was changed to flush fill and stainless steel line, extraction line was used for the extraction of CO_2 from air sample, the precision became ±7 μmol.mol^{-1}, and ± 0.05‰ for mixing ratio and $\delta^{13}C$ of atmospheric CO_2, respectively. During the entire period of 2008–2011, the primary carbonate standard NBS19 was measured intermittently with an accuracy of ~0.005‰ for $\delta^{13}C$ of CO_2 using both the experimental set up.

Both the diurnal and seasonal scale variation in CO_2 mixing ratio and $\delta^{13}C$ of air CO_2 allowed the identification of end member sources CO_2 using Keeling plot method (Keeling 1958). The observations on seasonal variation in CO_2 mixing ratio and $\delta^{13}C$ of air CO_2 over Bangalore station were also compared with observations from other air CO_2 monitoring stations, namely CRI located at the west coast of India and SEY in the Indian Ocean region.

Results

Diurnal variation of mixing ratio and $\delta^{13}C$ of CO_2 observed from Bangalore station in different seasons (months)

The observations on the diurnal variation of CO_2 mixing ratio and $\delta^{13}C$ of air CO_2 from the BLR station are plotted in Fig. 2a, b. The mixing ratio was found to be higher during the early morning (0530–0730 hours, IST) (showed with up-arrow in Fig. 2a) compared to the late afternoon (1600–1800 hours, IST); whereas, the $\delta^{13}C$ values were recorded to be highly depleted (lower compared to mean) during the early morning (showed with down-arrow in Fig. 2b) compared to the late afternoon. The diurnal variation in mixing ratio and $\delta^{13}C$ of CO_2 was first reported from the station during October–November, 2008, where the effect of the nocturnal boundary layer capturing the signature of CO_2 from pollution was

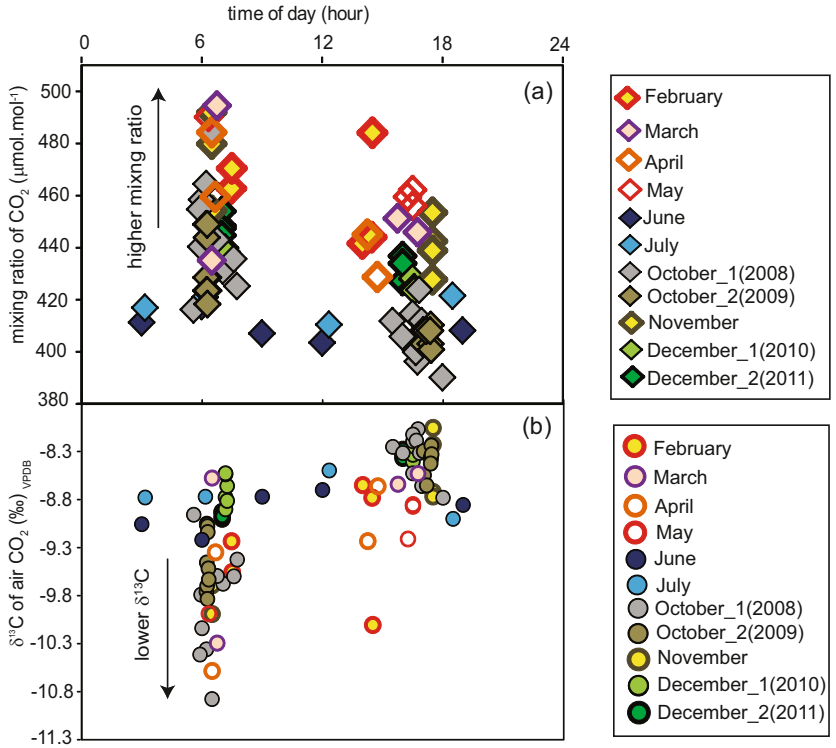

Fig. 2 Diurnal variation of mixing ratios and carbon isotopic ratios of atmospheric CO_2 observed over Bangalore during October 2008–December 2011

proposed (Guha and Ghosh 2010). The experiment on diurnal variation was repeated several times, over different months covering 3 years. Based on observations on diurnal variation of air CO_2 for successive days in a particular month, the $\delta^{13}C$ value of the end member local source CO_2 was identified using Keeling plot method (Keeling 1958). The large range in both mixing ratio and $\delta^{13}C$ of air CO_2 observed in a day allowed precise identification of the $\delta^{13}C$ value of the local source CO_2 (Pataki et al. 2003b) for individual months. The inverse relationship between the mixing ratio and $\delta^{13}C$ of air CO_2 in the Keeling plot was fitted with a geometric mean regression (GMR) line and the intercept of the regression line determined the carbon isotopic ratio of the end member source CO_2. The GMR fit to the data is a more appropriate approach adopted based on our observation, as neither the mixing ratio nor the $\delta^{13}C$ of CO_2 were independent variables and they were associated with analytical error (Pataki et al. 2003b; Miller and Tans 2003). The Keeling plots for the respective months were shown in Fig. 3 with the intercept values. The error estimates of $\delta^{13}C$ value of source CO_2 was derived using the LINEST function in Excel 2007. While estimating the error for the source CO_2, the analytical errors associated with the measurement of both the CO_2 mixing ratio and $\delta^{13}C$ of air CO_2 were also taken into account. The overall error was found to be well within the estimated error obtained by the LINEST function. The $\delta^{13}C$ values (along with the estimated error) of the local source CO_2 for different months are displayed in Table 1. The average $\delta^{13}C$ value of local source CO_2 for all the months was found be −24.9‰, with an error of ±3‰. To check whether the source CO_2 identified were representative for the respective months, the experiment on diurnal variation was repeated for different years. The identified source values were found to be consistent within ±0.5‰ from observations carried out in the other years. The source CO_2 composition identified for the individual month was associated with a large uncertainty (For example, during May and July, as marked with '#' in Table 1), and there were month to month variability as well (shown in Table 1). The potential factor responsible for this might be the variability in the height of atmospheric boundary. Simultaneous observations on both atmospheric boundary layer height and air CO_2 composition may allow us to understand the potential influence of atmospheric boundary layer condition on the in air CO_2 variability.

The local source CO_2 can be derived from several sources which include coal combustion (energy sector), respiration from vegetation, biomass burning, automobile exhaust and emission from cement industries etc. Available data for inventories of greenhouse gas (mentioned hereafter as GHG) emissions from India suggest that the contribution from energy sector is 40 % and is mainly from the coal based power plants and from biomass burning [http://www.moef.nic.in/downloads/public-information/Report_INCCA.pdf]. The average $\delta^{13}C$ value of the source CO_2 identified in the present study closely matches with the $\delta^{13}C$ value of Permian coal (−24.8‰; Osborne and Beerling 2006) which is the main fuel ingredient in the regional thermal power plant. The other possible CO_2 sources are biomass burning / fossil fuel combustion in automobile having $\delta^{13}C$ values similar to −

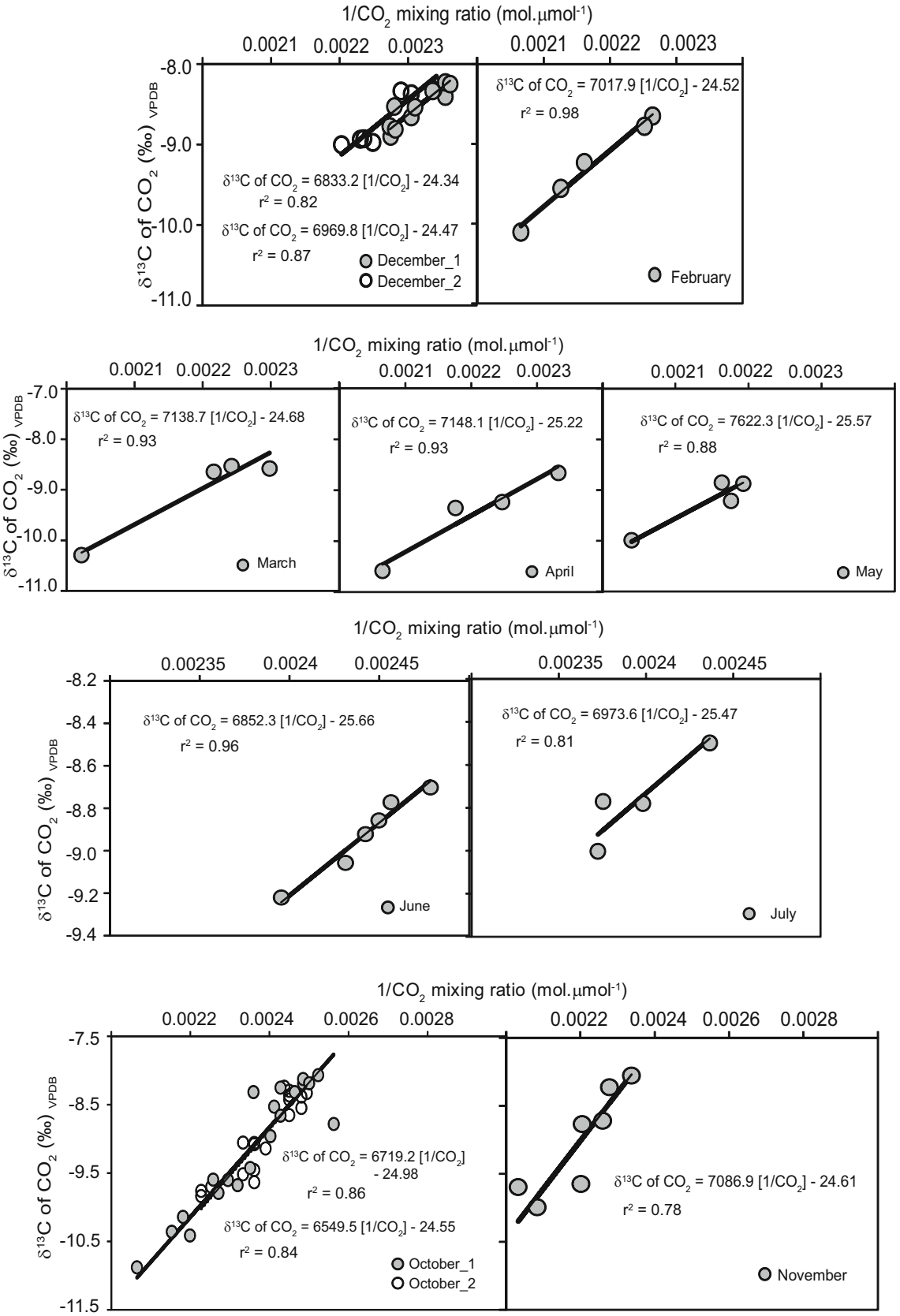

Fig. 3 Keeling plots of the two component mixing model approach for the diurnal variation data to identify the $\delta^{13}C$ value of the source CO_2 for the respective months

Table 1 $\delta^{13}C$ values of source CO_2 for respective months determined during 2008–2011

Months	
January	–
February	−24.5±1 (n=5, r^2=0.98, p=0.001)
March	−24.7±3 (n=4, r^2=0.93, p=0.04)
April	−25.2±3 (n=4, r^2=0.93, p=0.03)
May[#]	−25.6±4 (n=4, r^2=0.88, p=0.06)
June	−25.7±2 (n=5, r^2=0.96, p=0.01)
July[#]	−25.5±5 (n=4, r^2=0.81, p=0.09)
August	–
September	–
October 1 (Oct–Nov 2008)	−24.6±1 (n=20, r^2=0.86, p=4.7×10^{-9})
October 2 (2009)	−25.0±2 (n=18, r^2=0.84, p=1.2×10^{-7})
November	−24.6±3 (n=7, r^2=0.78, p=0.008)
December 1 (2010)	−24.3±2 (n=11, r^2=0.82, p=0.0001)
December 2 (2011)	−24.5±3 (n=7, r^2=0.87, p=0.002)

25‰. While compared with the carbon isotopic composition (a range of −23.9 to −25.9‰) in aerosol samples containing soot, produced from biomass burning near Chennai, India (Pavuluri et al. 2011), there were consistency found between their results and the source value identified based on our observation. These further supported that biomass burning might be one of the important processes of CO_2 emission for the station. Fossil fuel combustion from vehicle, i.e., automobile exhaust can also account for the GHG emission. The car exhaust air analyzed and reported in our previous paper suggested $\delta^{13}C$ value of −25.9±0.2‰ (Guha and Ghosh 2010), closely matching with the source CO_2 identified in this study. Thus the source CO_2 identified for BLR station based on diurnal variation is indicative of fossil fuel combustion/ biomass burning as possible sources. Our observations also showed no seasonal variation in local source CO_2 composition which is consistent with previous conclusions by Rotty 1987 who argued that the latitudinal position of India limits seasonal variation in fuel consumption for the region (Rotty 1987).

Seasonal variation of mixing ratio and $\delta^{13}C$ of CO_2 observed from Bangalore station

Seasonal variation of both CO_2 mixing ratio and $\delta^{13}C$ of air CO_2 is shown in Fig. 4. Here, we compare air CO_2 observations from the BLR station with other stations - the nearest coastal stations, i.e., Cabo de Rama (CRI) (~450 km from away from BLR) in India (monitored by CSIRO, Australia) and Seychelles (SEY; monitored by NOAA), an island station in the Indian Ocean (55.47°E and 4.67°S; ~3,000 km away from BLR). These stations were monitored for a much longer time period and have captured many similarities in seasonality as seen at Mauna Loa (Bhattacharya et al. 2009). The data for both CRI and SEY for the specific months and years used in the present study, were obtained from WMO World Data Centre for Greenhouse Gases, WDCGG (wdcgg@met.kishou.go.jp). The range in CO_2 mixing ratio observed at BLR for the year 2009–2010 was 390 to 493 μmol.mol^{-1}, and for the year 2010–2011, it was 393 to 463 μmol.mol^{-1}. The seasonal pattern recorded at the coastal station CRI showed seasonal maxima and minima values ranging between 386 and 400 μmol.mol^{-1} for the year 2009–2010 and 383 to 408 μmol.mol^{-1} for the year 2010–2011. Similarly, at the open ocean station SEY, the CO_2 mixing ratio varied between 383 and 391 μmol.mol^{-1} for the year 2009–2010 and 387 to 398 μmol.mol^{-1} for the year 2010–2011. Thus, the amplitudes of variation recorded at CRI and SEY are much smaller compared to the range observed at BLR. Similarly, the range in $\delta^{13}C$ recorded at BLR was −9.35 to −8.03‰ for the year 2009–2010 and −8.89 to −8.0‰ for year 2010–2011. Simultaneous observation at CRI registered the range of −8.91 to −8.21‰ during 2009–2010 and −8.99 to −8.03‰ during 2010–2011. Furthermore, for the coastal station SEY, the range was −8.69 to −7.99‰ for year 2009–2010 and −8.51 to −8.08‰ during 2010–2011. Comparison of observations from these three stations showed that being an urban station, BLR has captured higher amplitudes of seasonal variation in both mixing ratio and $\delta^{13}C$ of air CO_2 compared to CRI and SEY.

Observation from BLR station also showed a clear pattern in seasonal variation of both CO_2 mixing ratio and $\delta^{13}C$ of air CO_2 as shown in Fig. 4. The CO_2 mixing ratio was observed to be higher during the dry summer months (March–May) and lower during the southwest monsoon months (June–September). The maximum enrichment (higher compared to mean) in $\delta^{13}C$ of air CO_2 (−8.04±0.02‰) was found during October, then it slowly started decreasing and the maximum depletion (lower compared to mean) in $\delta^{13}C$ was seen in the dry summer months (−9.31±0.07‰). Subsequently, an increasing trend was recorded in the $\delta^{13}C$ of air CO_2, coinciding with the onset and advancement of the southwest monsoon prior to reaching the enriched value again in October. The balance between the CO_2 emissions from the anthropogenic activity and its uptake during biospheric productivity is playing an important role in controlling the seasonal variation. The possible anthropogenic sources identified for BLR station includes fossil fuel combustion/ biomass burning as described in the previous section. Differential contributing of these sources is expected to affect the observed seasonal variation in air CO_2. For example, there are enhanced events of forest fire and biomass burning (agricultural waste and crop waste) during the dry seasons reported for the station (Narendran 2001). Several events of forest fire have been reported for the nearest forest region (Bandipura and Nagarhole) to BLR station during the

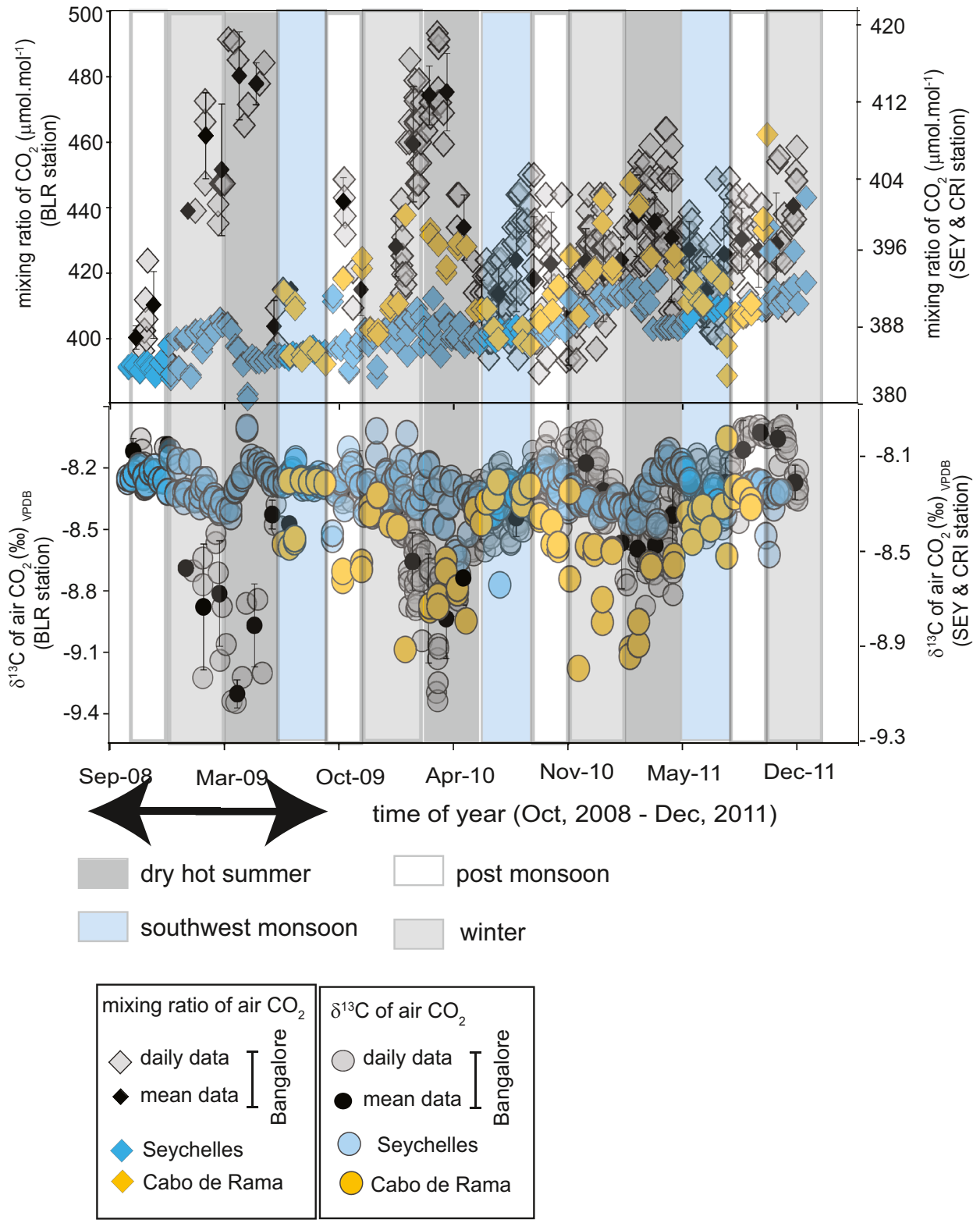

Fig. 4 Seasonal variation on mixing ratio and carbon isotopic ratio of atmospheric CO_2 observed over Bangalore during October 2008–December 2011. The daily data is represented with *gray symbols*; whereas, the monthly mean values are indicated with *black symbols*. The *black arrow* indicates the time frame when air samples were collected using evacuation method and extracted using glass extraction line. For the rest of the time, sampling was done using the flush fill method and extracted using stainless steel extraction line. The seasonal variation is compared with the seasonal variation observed in the data from both Cabo de Rama (data source: WDCGG) represented by *yellow symbols* and Seychelles, by *blue symbols*

period of our observation (http://www.hindu.com/2008/03/10/stories; http://www.hindu.com/2009/02/19/stories). This can enhance CO_2 mixing ratio and depletes $\delta^{13}C$ of air CO_2 during the dry summer months as seen in our observation. The hypothesis can be further supported by independent observations on aerosol optical depth (AOD) during the month of April from the BLR region (Vinoj et al. 2004). Subsequently the biomass burning subsides with the arrival of southwest monsoon (June, July, August, and September); contribution from the biomass burning decreases and the observed $\delta^{13}C$ values started showing an increasing trend as the southwest monsoon progresses. The rainfall during the southwest monsoon enhances the regional productivity (both as agriculture and natural vegetation) and led to the expansion of green cover. This increase in green cover results in preferential uptake of ^{12}C by the biosphere during photosynthesis and as a result enrichment in $\delta^{13}C$ values was observed in the air CO_2. The present observations indicate that the emission from fossil fuel combustion, forest fire, biomass burning, and increased green cover (i.e. biological productivity) during different seasons are all possible factors responsible for the observed seasonal variations in CO_2 mixing ratio and $\delta^{13}C$ of air CO_2. Although the differential emission from these sources are expected to cause the seasonal variability in air CO_2, their effect will largely be controlled by the meteorological conditions like atmospheric boundary layer height, mean wind speed, atmospheric circulation driven mixing etc., matters for further investigation.

Although the pattern of seasonal variation remained same for the three consecutive years of our observation, during the dry summer months of 2011, the CO_2 mixing ratio was found to be distinctly lower compared with the dry summer months of 2009 and 2010, and for the same season, the $\delta^{13}C$ of air CO_2 was also found to be less depleted in 2011 compared to 2009 and 2010. It is important to note that the year 2011 was characterized as a La Nina year by NOAA National Climatic Data Centre [http://www.ncdc.noaa.gov/sotc/global/2011/13]. During La Nina year, increased wetness over tropical region promotes higher land productivity as compared to an El Nino year (Jones et al. 2001) and the moist condition also reduces the chances of forest fires. It has also been reported for Bandipura and Nagarhole forest region, located close to BLR station, that in 2011 the enhanced pre-monsoon rainfall, i.e., the rainfall during dry summer months has drastically reduced the chances of forest fires over the forest region (http://www.hindu.com/2011/05/02/stories/2011050254850500.htm). This might supports the explanation that the events of forest fire at these nearby forest regions has an effect on air CO_2 variability observed at BLR station. The higher mixing ratio and the depleted $\delta^{13}C$ seen in dry summer months of 2009 and 2010 is largely due to biomass burning from forest fire events and similar effect is absent in dry summer months of 2011when forest fire intensity was reportedly reduced.

Even though we have determined the possible sources of CO_2 for BLR station based on diurnal variation of air CO_2, we have further identified the $\delta^{13}C$ values of source CO_2 based on the seasonal scale variation of mixing ratio and $\delta^{13}C$ of air CO_2 (Fig. 5). The samples collected during monsoon (southwest) and non-monsoon periods were treated separately. During the monsoon time, it was difficult to identify the sources of CO_2 precisely. One of the possible factors must be the presence of strong monsoonal wind which might have diluted the effect of local sources on the air CO_2 variability. While during the non-monsoon period of a year, it was possible to identify the source CO_2 precisely, as shown in Fig. 5. The dataset are plotted for three different years, i.e., January till December for the year 2009, 2010, and 2011 and the time between October 2008 and December 2008 was considered separately. The source CO_2 was identified for each year using the Keeling plot method (Keeling 1958). In the Keeling's approach, the intercept of the geometric mean regression line provides the $\delta^{13}C$ values of the source CO_2. A similar approach is used to identify the isotopic composition of source CO_2 for both Cabo de Rama and Seychelles and the source value identified for non-monsoon months are highlighted in Fig. 5. The statistical significance for the r^2 for different plots was determined using Pearson product moment test (two-tailed t test). The intercept obtained for different years were mentioned here along with its statistics (no. of samples, r^2, p value).

The end member source CO_2 composition identified for BLR station varies between the years (Fig. 15.0±0.6 (n=99, r^2=0.09, p=0.003) 5). The intercept values were −12.2‰ (n=8, r^2=0.66, p<0.05) for air CO_2 samples collected between October 2008 and December 2008, −17.54‰ (n=21, r^2=0.47, p<0.05) for air CO_2 samples collected between January 2009 and December 2009, −13.74‰ (n=92, r^2=0.62, p<0.05) for air CO_2 samples collected between January 2010 and December 2010 and −15.02‰ (n=99, r^2=0.09, p<0.05) for air CO_2 samples collected between January 2011 and December 2011 as presented in the Table 2 along with their estimated error (determined using the LINEST function in Excel 2007). The uncertainties attributed from the analytical error in determination of both CO_2 mixing ratio and $\delta^{13}C$ of air CO_2 was taken into consideration while using the LINEST function. The average $\delta^{13}C$ value of source CO_2 determined based on the seasonal scale variation of air CO_2 covering different years of observations (2008–2011) from the BLR station was −14.6‰ with an uncertainty of ±0.7‰. The identified source value was found to match closely with the global model predicted value of plant carbon for Indian region which is indicating large contribution from biosphere especially from C_4 type vegetation (Suits et al. 2005). Please note here, the end member

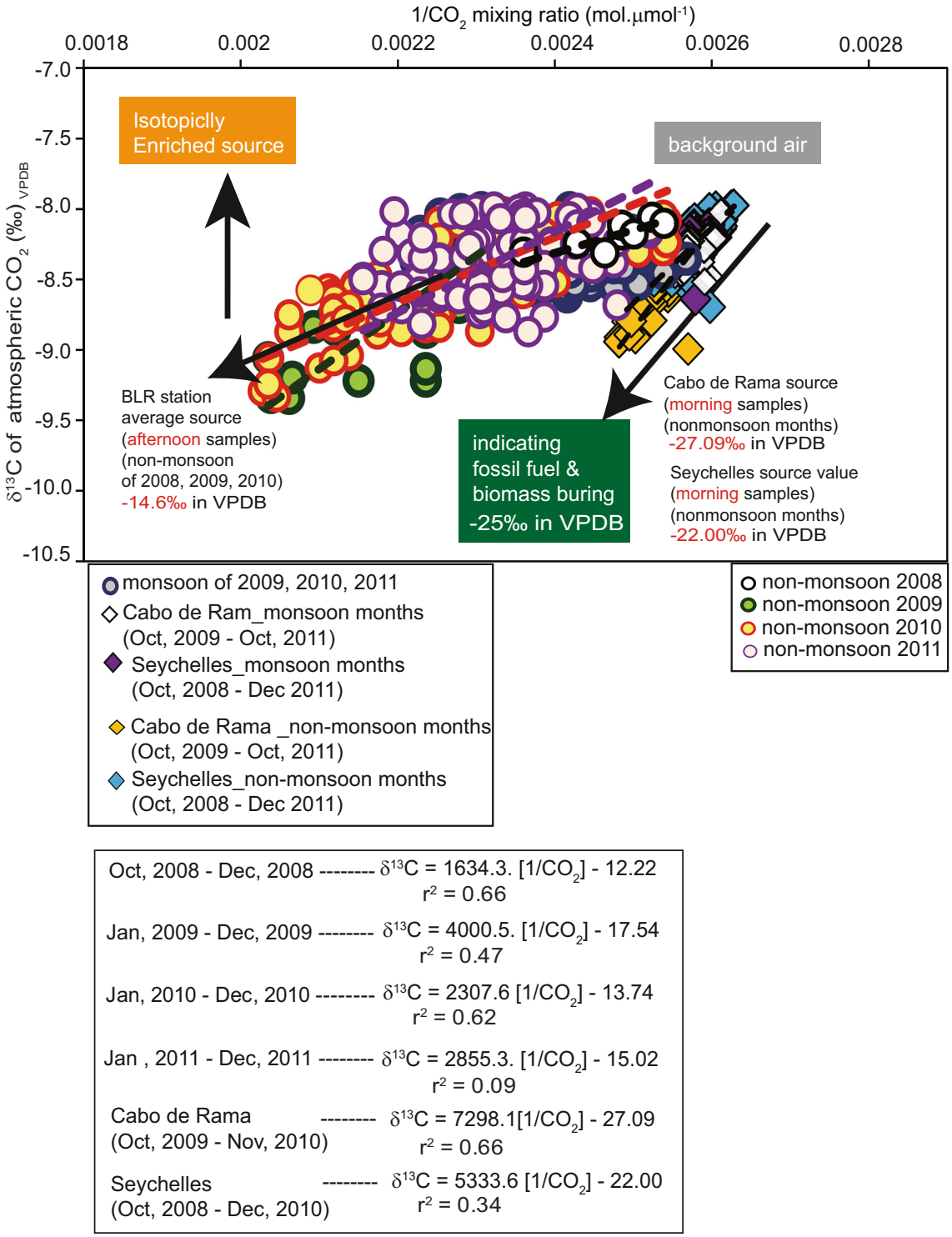

Fig. 5 Keeling plot of two component mixing model approach for the seasonal variation data to identify the $\delta^{13}C$ value of the source CO_2 for respective years. This approach is also applied to the seasonal variation observed at both Cabo de Rama and Seychelles, data source: WDCGG. The observations obtained during monsoon and non-moon period were plotted with different legends

source CO_2 identified for BLR station based on seasonal scale variation differs from the values determined based diurnal scale variation and this also differs from the source value obtained for CRI ($\delta^{13}C=-27.09\pm2‰$, $n=44$, $r^2=0.66$, $p<0.05$) and SEY($\delta^{13}C=-22\pm0.7‰$, $n=224$, $r^2=0.34$, $p<0.05$). Interestingly, the seasonal scale variation was monitored entirely based on afternoon samples; whereas, the diurnal scale variation was observed based on both early morning and late afternoon samples. Moreover it is also important to mention here that the

Table 2 $\delta^{13}C$ values of source CO2 for individual years based on the seasonal scale variation during 2008–2011

Years	$\delta^{13}C$ (‰ VPDB)
2008	−12.2±1 (n=8, r^2=0.66, p=0.01)
2009	−17.5±1 (n=21, r^2=0.47, p=0.0006)
2010	−13.7±0.3 (n=92, r^2=0.62, $p=1.3\times10^{-2}$)
2011	−15.0±0.6 (n=99, r^2=0.09, p=0.003)

seasonal variation of air CO_2 for both CRI and SEY station was also monitored based on mostly morning time samples. On the basis of these observations, it is implicit that the timing of sampling of air CO_2 is quite crucial while addressing the possible sources of CO_2 for a particular region.

There might be certain reasons behind the fact that different timing of sampling of air CO_2 of a particular region gives completely different source identification. In this case, source identified based on morning–afternoon samples differs drastically from the source identified explicitly based on afternoon samples. The most likely reason for this difference is that for the morning samples all fluxes contributing to the signal are positive and a simple keeling plot can be used, while for the afternoon sources and sinks act at the same time, which complicates the interpretation of CO_2 and $\delta^{13}C$ (Miller and Tans 2003). Alternatively, a plausible enriched source proposed here is active during the afternoon time while less prominent during other time in a day. One such reservoir of isotopically enriched carbon is CO_2 emitted from the cement industries which is never been discussed and found responsible component in the anthropogenic CO_2 emission. During the process of cement production CO_2 is produced from limestone (Deja et al. 2010). The limestone used in this process is isotopically enriched relative to the atmospheric CO_2 thus $\delta^{13}C$ of the emitted CO_2 will be isotopically enriched. India is one of the prime emitters of CO_2 from cement industries (Ali et al. 2011), and the Southern Indian region (Gulbarga) is known to be the largest emitter (Garg et al. 2001). Cement production in this region is steadily growing with economic development and enhanced demand of cement for construction work. Bhima limestone, which belongs to Proterozoic age, is commonly mined by the cement industry. The $\delta^{13}C$ value of the carbonate used in the cement industry is reported to be around 2.0‰ (Nagarajan et al. 2008). The mechanism of mixing of CO_2 emitted from the cement industry (with $\delta^{13}C$ value of 2.0‰) with CO_2 emitted from fossil fuel and biomass combustion (−25‰) can explain the enriched $\delta^{13}C$ value of source CO_2 (−14.6‰) determined based on seasonal scale variation of air CO_2. Further study is required to exactly identify why two different time scales of variation of air CO_2 is providing two different sources identification? The present study clearly demonstrates the need for continuous monitoring of mixing ratio and $\delta^{13}C$ of air CO_2 to indentify the contribution of each of these end members, whose contribution varies seasonally as seen in our observation.

Conclusion

The observation on CO_2 mixing ratio and $\delta^{13}C$ of air CO_2 for the urban station BLR was found to vary both diurnally and seasonally. This variation allowed identification of $\delta^{13}C$ of source CO_2 for the station. The average monthly source value (−24.9‰) identified based on diurnal scale variation drastically differ from the source value (−14.6‰) identified based on seasonal scale variation. This discrepancy in source identification using two different time scales of variation clearly depicts the importance of reporting the timing of sampling while addressing the source CO_2 for a particular region. Moreover, the combined effect of fossil fuel combustion, biomass burning, photosynthetic uptake of CO_2 and emissions from the cement manufacturing industry have found to control the air CO_2 variability. The dry environmental condition during dry summer months (February–May) causes enhanced biomass burning which produces higher CO_2 mixing ratio and depleted $\delta^{13}C$ (−9‰) of air CO_2 as seen in 2009 and 2010 summer months; whereas, this feature is not prominent during the dry summer of 2011 as it was a La Nina year. Every year, the wet conditions of the southwest monsoon enhances biosphere uptake and gives rise to lowers CO_2 mixing ratio with enriched $\delta^{13}C$ (−8‰) of air CO_2. In spite of the contribution of source CO_2, there is a presence of large sink of CO_2 during the southwest monsoon. Thus it will be interesting to further study the direct effect of Indian monsoon and its break phases on the air CO_2 variability and the corresponding source and sink contribution. To get an overall picture on the air CO_2 variability for Indian region, we need similar efforts to be carried out in different parts of India. The comparison of observations and validation of the interpretation from other stations can help in understanding both the transport and partitioning of CO_2 between different reservoirs. Long term monitoring of such kind from a tropical urban city can lead to a better understanding on the global carbon budget especially the contribution from urban CO_2 emission.

Acknowledgments This project was possible with the funding received from the Indian Institute of Science, Department of Science and Technology, India, Ministry of Earth Science, Government of India and Divecha Centre for Climate Change. We would like to thank Dr. Willi Brand for the JRAS references. A special thank to both CSIRO Marine and Atmospheric Research—GASLAB, Aspendale, Victoria, Australia

for permitting us to use the monthly flask data of air-CO_2 measurement for the Cabo de Rama station and Global Monitoring Division of NOAA's Earth System Research Laboratory for providing air-CO_2 data for the Seychelles station and we further thank the Institute for Arctic and Alpine Research at University of Colorado for the isotopic ratio data of air-CO_2 for the Seychelles station. We thank Ishwar Kumar C for help in drafting Fig. 1.

References

Affek HP, Xiaomei X, Eiler JM (2007) Seasonal and diurnal variations of $^{13}C^{18}O^{16}O$ in air: initial observations from Pasadena. CA Geochim Cosmochim Acta 71:5033–5043. doi:10.1016/j.gca.2007.08.014

Ali MB, Saidura R, Hossain MS (2011) A review on emission analysis in cement industries. Renew Sust Energ Rev 15:2252–2261

Anand S, Vrat P, Dahiya RP (2006) Application of a system dynamics approach for assessment and mitigation of CO_2 emissions from the cement industry. J Environ Manag 79:383–398

Andres RJ, Marland G, Boden T, Bischof S (2000) Carbon dioxide emissions from fossil fuel consumption and cement manufacture, 1751 – 1991, and an estimate of their isotopic composition and latitudinal distribution. In: Wigley TML, Schimel DS (eds) The carbon cycle. Cambridge University Press, New York, pp 53–62

Bhattacharya SK, Borole DV, Francy RJ, Allison CE, Steele LP, Krummel P, Langenfelds R, Masarie KA, Tiwari YK, Patra PK (2009) Trace gases and CO_2 isotope records from Cabo de Rama, India. Curr Sci 97(9):1336–1344

Bush SE, Pataki DE, Ehleringer JR (2007) Sources of variation in delta C-13 of fossil fuel emissions in Salt Lake City, USA. Appl Geochem 22(4):715–723. doi:10.1016/j.apgeochem.2006.11.001

Ciais P, Tans PP, White JMC, Trolier M, Francey RJ, Berry JA, Randall DR, Sellers PJ, Collatz JG, Schimel DS (1995a) Partitioning of ocean and land uptake of CO_2 as inferred by $\delta^{13}C$ measurements from the NOAA climate monitoring and diagnostics laboratory global air sampling network. J Geophys Res 100:5051–5070

Ciais P, Tans PP, Trolier M, White JWC, Francey RJ (1995b) A large northern-hemisphere terrestrial CO_2 sink indicated by the $^{13}C/^{12}C$ ratio of atmospheric CO_2. Science 269(5227): 1098–1102

Clark-Thorne ST, Yapp CJ (2003) Stable isotope constraints on mixing and mass balance of CO_2 in an urban atmosphere: Dallas metropolitan area, TX, USA. Appl Geochem 18(1):75–95. doi:10.1016/S0883-2927(02)00054-9

Craig H (1953) The geochemistry of the stable carbon isotopes. Geochim Cosmochim Acta 3:53

Crutzen PJ, Andreae MO (1990) Biomass burning in the tropics—impact on atmospheric chemistry and biogeochemical cycles. Science 250: 1669–1678

Deja J, Uliasz-Bochenczyk A, Mokrzycki E (2010) CO_2 emissions from polish cement industry. Int J Greenh Gas Control 4(4):583–8

Demeny A, Haszpra L (2002) Stable isotope compositions of CO_2 in background air and at polluted sites in Hungary. Rapid Commun Mass Spectrom 16:797–804. doi:10.1002/rcm.640

Francey RJ, Tans PP, Allison CE, Enting IG, White JWC, Trolier M (1995) Changes in oceanic and terrestrial carbon uptake since 1982. Nature 373(6512):326–330

Fung I, Field CB, Berry JA, Thompson MV, Randerson JT, Malmström CM, Vitousek PM, Collatz GJ, Sellers PJ, Randall DA, Denning AS, Badeck F, John J (1997) Carbon-13 exchanges between the atmosphere and the biosphere. Glob Biogeochem Cycles 11:507–533

Gadgil S, Joseph PV, Joshi NV (1984) Ocean–atmosphere coupling over monsoon regions. Nature 312:141

Garg A, Bhattacharya S, Shukla PR, Dadhwal VK (2001) Regional and sectoral assessment of greenhouse gas emissions in India. Atmos Environ 35:2679–2695

Grimmnod S (2007) Urbanization and global environmental change: local effects of urban warming. Cities and global environmental change. R Geogr Soc 83–88

Grimmond CSB, King TS, Cropley FD, Nowak DJ, Souch C (2002) Local-scale fluxes of carbon dioxide in urban environments: methodological challenges and results from Chicago. Environ Pollut 116: S243–S254

Guha T, Ghosh P (2010) Diurnal variation of atmospheric CO_2 concentration and $\delta^{13}C$ in an urban atmosphere during winter—role of the Nocturnal Boundary Layer. J Atmos Chem 65:1–12. doi:10.1007/s10874-010-9178-6

Guha T, Ghosh P (2013) An experimental set up for carbon isotopic analyses of atmospheric CO_2 and an example of ecosystem response during solar eclipse 2010. J Earth Syst Sci 122(3):623–638

Heald CL, Jacob DJ, Palmer PI, Evans MJ, Sachse GW, Singh HB, Blake DR (2003) Biomass burning emission inventory with daily resolution: application to aircraft observations of Asian outflow. J Geophys Res 108(D21):8811. doi:10.1029/ 2002JD003082

Heimann M, Maier-Reimer E (1996) On the relations between the oceanic uptake of CO_2 and its carbon isotopes. Glob Biogeochem Cycles 10:89–110

Jones CD, Collins M, Cox PM, Spall SA (2001) The carbon cycle response to ENSO: a coupled climate-carbon cycle model study. J Clim 14:4113–4129

Keeling CD (1958) The concentration and isotopic abundances of carbon dioxide in rural areas. Geochim Cosmochim Acta 13:322–334. doi: 10.1016/0016-7037(58)90033-4

Keeling CD (1961) The concentration and isotopic abundances of carbon dioxide in rural and marine air. Geochim Cosmochim Acta 24:277–298. doi:10.1016/0016-7037(61)90023-0

Keeling CD, Bacastow RB, Carter AF, Piper SC, Whorf TP, Heimann M, Mook WG, Roeloffzen H (1989a) A three-dimensional model of atmospheric CO_2 transport based on observed winds: 1. Analysis of observational data. In: Peterson DH (ed) Aspects of climate variability in the Pacific and the Western Americas, 55th edn. Geophys. Monogr. Ser, Washington D.C., pp 165–236

Keeling CD, Piper SC, Heimann M (1989b) A three-dimensional model of atmospheric CO_2 transport based on observed winds: 4. Mean annual gradients and interannual variations. In: Peterson DH (ed) Aspects of climate variability in the Pacific and the Western Americas, 55th edn. Geophys. Monogr. Ser, Washington, D. C, pp 305–363

Keeling CD, Whorf TP, Wahlen M, Van der Plicht J (1995) Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980. Nature 375:666–670

Kuc T (1986) Carbon isotopes in atmospheric CO_2 of the Krakow region: a two-year record. Radiocarbon 28(2A):649–654

Kuc T (1989) Changes of carbon isotopes in atmospheric CO_2 of the Krakow region in the last five years. Radiocarbon 31(3):441–447

Kuc T (1991) Concentration and carbon isotopic composition of atmospheric CO_2 in southern Poland. Tellus Ser B 43:373–378

Kuc T, Zimnoch M (1998) Changes of the CO_2 sources and sinks in a polluted urban area (southern Poland) over the last decade, derived from the carbon isotope composition. Radiocarbon 40(1):417–423

Kuc T, Rozanski K, Zimnoch M, Necki J, Chmura L, Jelen D (2007) Two decades of regular observations of (CO_2)-C-14 and (CO_2)-C-13 content in atmospheric carbon dioxide in central Europe: long-term changes of regional anthropogenic fossil CO_2 emissions. Radiocarbon 49(2):807–816

Miller JB, Tans PP (2003) Calculating isotopic fractionation from atmospheric measurement at various scales. Tellus 55B:207–214

Mook WG, Koopmans M, Carter AF, Keeling CD (1983) Seasonal, latitudinal and secular variations in the abundance and isotopic ratios

of atmospheric carbon dioxide. 1. Results from land stations. J Geophys Res 88(10):915–10,933

Nagarajan R, Sial AN, Armstrong-Altrin JS, Madhavaraju J, Nagendra R (2008) Carbon and oxygen isotope geochemistry of Neoproterozoic limestones of the Shahabad Formation, Bhima basin, Karnataka, southern India. Revista Mexicana de Ciencias Geológicas. 25, núm. 2, 225–235.

Nakazawa T, Moromoto S, Aoki S, Tanaka M (1993) Time and space variations of the carbon isotopic ratio of tropospheric carbon dioxide over Japan. Tellus 45B:258–274

Narendran K (2001) Forest fires: Origin and ecological paradoxes, general article, Resonance.

42) Newman S, Xu X, Affek HP, Stopler E, Epstein S (2008) Changes in mixing ratio and isotopic composition of CO_2 in urban air from the Los Angeles basin, California, between 1972 and 2003. J. Geophys. Res. 113(D23304), doi: 10.1029/2008JD009999.

Osborne CP, Beerling DJ (2006) Nature's green revolution: the remarkable evolutionary rise of C4 plants. Phil Trans R Soc B 361:173–194. doi:10.1098/rstb.2005.1737

Pataki DE, Bowling DR, Ehleringer JR (2003a) Seasonal cycle of carbon dioxide and its isotopic composition in an urban atmosphere: anthropogenic and biogenic effects. J Geophys Res 108(D23):4735. doi:10.1029/2003JD003865

Pataki DE, Ehleringer JR, Flanagan LB, Yakir D, Bowling DR, Still CJ, Buchmann N, Kaplan JO, Berry JA (2003b) The application and interpretation of Keeling plots in terrestrial carbon cycle research. Glob Biogeochem Cycles 17(1):1022

Pataki D, Bowling DR, Ehleringer JR, Zobitz JM (2006) High resolution atmospheric monitoring of carbon dioxide sources. Geophys Res Lett 33, L03813. doi:10.1029/2005GL024822

Pataki DE, Xu T, Luo YQ, Ehleringer JR (2007) Inferring biogenic and anthropogenic carbon dioxide sources across an urban to rural gradient. Oecologia 152:307–322. doi:10.1007/s00442-006-0656-0

48) Pavuluri CM, Kawamura K, Swaminathan T, Tachibana E (2011) Stable carbon isotopic compositions of total carbon, dicarboxylic acids and glyoxylic acid in the tropical Indian aerosols: Implications for sources and photochemical processing of organic aerosols. J. Geophys. Res. 116(D18307), doi: 10.1029/2011JD015617.

Pearman GI, Hyson P (1986) Global transport and inter-reservior exchange of carbon dioxide with particular reference to stable isotope distribution. J Atmos Chem 4:81–124

Ramachandra TV, Kumar U (2010) Greater Bangalore: Emerging urban heat island. Geospatial application paper. Urban planning. 2010.

Rotty RM (1987) Estimates of seasonal variation in fossil fuel CO_2 emissions. Tellus 39B:184–202

Schimel DS, Brawell BH, Holland EA, McKeown R, Ojima DS, Painter TH, Parton W, Townsend AR (1994) Climatic, edaphic, and biotic controls over storage and turnover of carbon in soils. Glob Biogeochem Cycles 8:279–293

Schimel DS, House JI, Hibbard KA, Bousquet P, Ciais P, Peylin P, Braswell BH, Apps MJ, Baker D, Bondeau A, Canadell J, Churkina G, Cramer W, Denning AS, Field CB, Friedlingstein P, Goodale C, Heimann M, Houghton RA, Melillo JM, Moore IIIB, Murdiyarso D, Noble I, Pacala SW, Prentice IC, Raupach MR, Rayner PJ, Scholes RJ, Steffen WL, Wirth C (2001) Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems. Nature 414:169–172

Streets DG, Yarber KF, Woo JH, Carmichael GR (2003) Biomass burning in Asia: annual and seasonal estimates and atmospheric emissions. Glob Biogeochem Cycles 17(4):1099. doi:10.1029/2003GB002040

Sudhira HS, Ramachandra TV, Bala Subrahmanya MH (2007) City profile Bangalore. Cities 24(5):379–390. doi:10.1016/j.cities.2007.04.003

Suits NS, Denning AS, Berry JA, Still CJ, Kaduk J, Miller JB (2005) Simulation of carbon isotope discrimination of the terrestrial biosphere. Glob Biogeochem Cycles 19, GB1017. doi:10.1029/2003GB002141

Tans PP, Conway TJ, Nakazawa T (1989) Latitudinal distribution of the sources and sinks of atmospheric carbon dioxide from surface observations and an atmospheric transport model. J Geophys Res 94:5151–5172

Tans PP, Fung IY, Takahashi T (1990) Observational constraints on the global atmospheric CO_2 budget. Science 247:1431–1438

Tans PP, Berry JA, Keeling RF (1993) Oceanic $^{13}C/^{12}C$ observations: a new window on ocean CO_2 uptake. Glob Biogeochem Cycles 7:353–368

Tans PP, Bakwin PS, Guenther DW (1996) A feasible global carbon cycle observing system: a plan to decipher today's carbon cycle based on observations. Glob Chang Biol 2:309–318

Team CW, Pachauri RK, Reisinger A (2007) Climate Change 2007, IPCC Fourth Assessment Report, ISBN 92-9169-122-4

Tiwari YK, Patra PK, Chevallier F, Francey RJ, Krummel PB, Allison CE, Revadekar JV, Chakraborty S, Langenfelds RL, Bhattacharya SK, Borole DV, Kumar KR, Steele LP (2011) Carbon dioxide observations at Cape Rama, India for the period 1993–2002: implications for constraining Indian emissions. Curr Sci 101(12):1562–1568

Venkataraman C, Habib G, Kadamba D, Shrivastava M, Leon JF, Crouzille B, Boucher O, Streets DG (2006) Emissions from open biomass burning in India: Integrating the inventory approach with high-resolution Moderate resolution imaging spectroradiometer (MODIS) active-fire and land cover data. Glob Biogeochem Cycles 20(GB2013):1–12. doi:10.1029/2005GB002547

Vinoj V, Satheesh SK, Suresh Babu S, Krishna Moorthy K (2004) Large aerosol optical depths observed at an urban location in southern India associated with rain-deficit summer monsoon season. Ann Geophys 22:3073–3077

Wendeberg M, Richter JM, Rothe M, Brand WA (2012) Jena Reference Air Set (JRAS): a multi-point scale anchor for isotope measurements of CO_2 in air. Atmos Meas Tech Discuss 5:6627–6642

Widory D, Javoy M (2003) The carbon isotope composition of atmospheric CO_2 in Paris. Earth Planet Sci Lett 215(1–2):289–298. doi:10.1016/S0012-821X (03)00397-2

Zobitz JM, Keener JP, Schnyder H, Bowling DR (2006) Sensitivity analysis and quantification of uncertainty for isotopic mixing relationships in carbon cycle research. Agric For Meteorol 136:56–75