Isotopic and Concentration Analyses of CO₂ and CH₄ in Association With the Eddy-Covariance Based Measurements in a Tropical Forest of Northeast India

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Abstract Among the natural ecosystems, forests and wetlands emit a sizable amount of carbon dioxide (CO₂) and methane (CH₄) through autotrophic and heterotrophic respiration and bacterial activities. Interestingly, some evidence suggests that a significant amount of CH₄ is generated by the trees in forested ecosystems. The net ecosystem exchange (NEE), measured by the eddy covariance (EC) method, typically represents the net CO₂ flux arising from the photosynthetic and respiration processes in the biosphere. This flux is subsequently partitioned into two components, the respired carbon and the assimilated carbon. However, the usual method of partitioning introduces significant errors in each of these fluxes. The present study was undertaken to address this issue where the NEE partitioning was constrained by using the carbon isotopic ratios of CO₂. We used a real-time in situ analyzer in a tropical forest in northeast India, the Kaziranga National Park. The greenhouse gas analyzer provided CO₂ and CH₄ concentrations, as well as their carbon isotopic ratios. The isotopic data were used to partition the EC-derived NEE values and derive the isoflux values. Additionally, the isotopic data provided evidence of plant-generated CH₄ in conformity with some recent studies, which requires further investigation.

Plain Language Summary The terrestrial vegetation absorbs a vast amount of carbon in the photosynthetic process. They also emit a sizeable amount of carbon through respiration. Eddy-covariance-based technique is often employed to quantify these two opposing fluxes. An eddy-covariance-based system measures carbon dioxide (CO₂) concentrations along with wind speed, and covariance of their fluctuations is used to calculate the net ecosystem exchange (NEE). The NEE is then partitioned into the photosynthetic and respiration components through a series of numerical operations and environmental constraints. Flux measurements in association with carbon isotopic ratios can provide a unique way to partition NEE. We have measured the concentration and isotopic ratio of CO₂ and the eddy covariance-based measurements to obtain the respiratory and photosynthetic fluxes of CO₂ in a tropical forest in India. In addition, methane (CH₄) concentration and its isotopic ratio have been measured to identify if trees can be considered a CH₄ source in this ecosystem.

1. Introduction

Carbon dioxide (CO₂) and methane (CH₄), the two most important greenhouse gases (GHGs) are increasing since the dawn of the industrial era. After years of growth, atmospheric CH₄ achieved a steady state in the late 1990s and early 2000s but then grew rapidly in the 2010s at a rate of 7.18 ppb/yr (E. G. Nisbet et al., 2019). It was also observed that, along with the increase, the CH₄ carbon isotope ratio (denoted as δ¹³CH₄) shifted toward more negative values. This change in δ¹³CH₄, in association with the increased concentration, is a matter of intense study because it can elucidate the causative factors like, increase in biogenic emissions (wetlands, ruminants, waste) or a reduction in the atmospheric sink of CH₄ through OH oxidation. If such growth rate continues in the coming decades, it could negate or even reverse the effect of climate mitigation by reduced CO₂ emission (E. G. Nisbet et al., 2019). In this context, some investigators
have observed moderate-to-large emission of CH$_4$ (62–236 Tg yr$^{-1}$) from the terrestrial plants. For example, studies in Venezuela identified tropical savannah as a significant source of CH$_4$ (Crutzen et al., 2006). A recent study by Pangala et al. (2017) reported that trees from the Amazonian floodplain could emit 200 times more CH$_4$ than temperate wet forests. A contrary view was presented by Dueck et al. (2007), who carried out a laboratory experiment using several plant species and concluded that the contribution of terrestrial plants to global CH$_4$ emission is small. However, later studies on plant emission (R. E. R. Nisbet et al., 2009) and atmospheric CH$_4$ analysis (Houweling et al., 2008) strongly suggested that plant-derived CH$_4$ has been underestimated in the global budget. In fact, a growing number of studies report that trees can emit CH$_4$ from their stems, which should be considered in the budget (Angle et al., 2017; Kirschke et al., 2013; Saunois et al., 2016). In the Indian context, only a few studies exist on the CH$_4$ fluxes (Ganesan et al., 2013; Guha et al., 2018; Jha et al., 2014; Purvaja & Ramesh, 2000), and specifically, emission by trees and plants have not been addressed as yet. In particular, there has been no attempt to identify the source and sink of CH$_4$ in any Indian floodplain forest.

Atmospheric CO$_2$ concentrations were about 260–280 ppm before the industrial emissions began and had been increasing continuously ever since. In recent years, the increase has been alarming. For example, the mean monthly CO$_2$ concentration was 414.6 ppm at Mauna Loa in May 2019 compared to the value of 402.5 ppm in 2016 (https://www.esrl.noaa.gov/gmd/ccgg/trends). Anthropogenic practices like fossil fuel burning are considered as one of the primary reasons for this increase. The terrestrial biosphere and ocean act as major sinks of CO$_2$, but their capacity is likely to change as a result of increased warming. To characterize the biospheric sink processes, long-term measurement of the atmospheric CO$_2$ is carried out at various sites across the globe (Aubinet et al., 1999; Baldocchi et al., 2001; Verma et al., 1986, 1989). Eddy covariance (EC) based technique measures the turbulent behavior of the boundary layer and is widely used to quantify the biosphere-atmosphere exchange of GHGs (Baldocchi et al., 1988). EC-based measurement of CO$_2$ flux is known as the net ecosystem exchange (NEE) which is a sum of two large oppositely directed fluxes, photosynthesis ($F_A$) and ecosystem respiration ($F_R$). Partitioning of NEE into its two components ($F_A$ and $F_R$) is necessary to understand how these fluxes respond to environmental and climatic changes (Bowling et al., 2001). Such information provides useful inputs for calibration and validation of various ecosystem models (Falge et al., 2002; Hanan et al., 2002; Reichstein et al., 2002, 2003). However, the NEE value is about an order of magnitude (Bowling et al., 2001) lower than its component fluxes which gives rise to considerable uncertainty during the partitioning. In this partitioning process, one term is normally parameterized and the other one is calculated by subtracting it from the measured NEE. Therefore, large variability in the parameters translates to considerable uncertainties in the fluxes.

Conventionally, static chambers are used to determine the $F_R$ component coming from the leaf, stem, and soil. This estimate is then scaled up to obtain respiration at the ecosystem level (Goulden et al., 1996; Gravenier et al., 2000). However, maintaining the complex experimental setup on a large scale poses a significant challenge and limits its feasibility (Ogée et al., 2003). Another widely used approach is to fit a regression line between the nocturnal NEE and soil/air temperature (Goulden et al., 1996; Lloyd & Taylor, 1994; Reichstein et al., 2005). However, a drawback in this approach is the reliability of the nighttime NEE values because the development of a stratified atmosphere at night enhances the role of advection rather than turbulence leading to an improper estimate of the NEE by the EC system. Also, the daytime and nighttime respiration could differ significantly due to light-induced inhibition of leaf respiration (Brooks & Farquhar, 1985; Villar et al., 1995). These complications introduce significant uncertainty in the partitioning of fluxes. Hence, an alternative method is needed to evaluate $F_R$ and $F_A$ from the NEE signal.

Bowling et al. (2001) provided an alternative means to partition measured NEE into $F_A$ and $F_R$, using measurements of fluxes of CO$_2$ along with estimates of the isotopic composition of ambient as well as respired CO$_2$. They used isotope data (from 61 flask samples) along with the EC results to determine $F_A$ and $F_R$ from a complex canopy structure. Yakir and Wang (1996) used micrometeorological flux and stable isotope measurements to calculate $F_R$ and $F_A$ from NEE in several croplands, with a simple canopy structure. In the present study, we have followed a similar isotopic technique in a forest of northeast India to partition the EC-derived NEE values in its two component fluxes. Besides, we also tried to delineate the sources and sinks of CO$_2$ and CH$_4$ in this ambience.
2. Source Identification by Miller-Tans Plot

An inverse relationship between the CO$_2$ concentration [CO$_2$] and its isotopic composition (denoted as $\delta^{13}$CO$_2$ or $\delta^{13}$CO$_2$) was established by Keeling (1961). This plot (Keeling plot) has been used subsequently by numerous researchers to identify the source or sink of CO$_2$ for a given region. An extension of the method has also been used to characterize the source/sink of other atmospheric gases by a large number of investigators (Bowing et al., 2001; Buchmann et al., 1997; Pataki et al., 2003). Application of the Keeling plot method requires the isotopic ratios of the two end-members (background atmosphere and the source) to remain constant during the investigation period over the region involved in the gas exchanges. To circumvent this limitation, Miller and Tans (2003) introduced a slightly modified method in identifying source CO$_2$ (denoted as $\delta^{13}$CO$_2$) by using a negative relation between the product of ambient/observed $\delta^{13}$CO$_2$ and [CO$_2$]. In this case, the slope of the fitted regression line is identified as $\delta^{13}$CO$_2$. However, this numerical method is valid only when the sources and sinks do not appear simultaneously (Vardag et al., 2016). For example, if photosynthesis (sink) and respiration (source) occur at the same time, the method gives the wrong source information (Miller & Tans, 2003). Therefore, NEE is the small difference between two major fluxes and is directly measured by the eddy-co

A regression line between [CO$_2$] and $\delta^{13}$CO$_2$ averaged over a suitable time interval can be called a moving Miller-Tans plot. For example, to find the mean source signature at 16:00 h, we regress $\delta^{13}$CO$_2$ against the hourly [CO$_2$] data for the period of 14:00 to 18:00 h (a total of five values). The same process is continued for the subsequent hours by shifting one hour each time. The approach essentially establishes a numerical link among the variable source signature values. In the case of CH$_4$, 11 hourly averaged measurements were used for both concentration and isotopic composition to regress (Röckmann et al., 2016). For example, to find $\delta^{13}$CH$_4$ at 16:00 h, we used hourly averaged [CH$_4$] and $\delta^{13}$CH$_4$ from 11:00 to 21:00 h. Application of the moving Miller-Tans plot method requires the presence of certain characteristics in the data set. Röckmann et al. (2016) and Vardag et al. (2016) suggested the following three criteria for application in case of CO$_2$ data: Criteria 1: square of the correlation coefficient R is higher than 0.99 ($R^2 > 0.99$); Criteria 2: monotrous increase in concentration during the 5 h of averaging; Criteria 3: [CO$_2$] increase must be greater than 5 ppm during the 5 h interval.

In the present study, the $\delta^{13}$CH$_4$ was determined only when the first criterion was satisfied. Additionally, we discarded $\delta^{13}$CH$_4$ when the standard deviation of slope of the plot was more than 4. This latter requirement ensures that the background and source gases do not change significantly so that a meaningful source composition can be estimated.

3. Flux Partitioning Into Two Components

As mentioned before, NEE is the net result of photosynthetic uptake and respiratory release, and we can write:

$$ NEE = F_R + F_A $$ (1)

where $F_A$ is the photosynthetic flux (considered negative), $F_R$ is the respiratory flux (considered positive). Therefore, NEE is the small difference between two major fluxes and is directly measured by the eddy-covariance technique (see Supporting Information). However, $F_A$ and $F_R$ cannot be obtained individually from these measurements.

Bowling et al. (2001) introduced the term “isoflux” which takes into account the isotopic values of the respective fluxes. When the turbulence-driven eddy fluxes and the storage fluxes are multiplied by their respective isotopic values, total isoflux can be estimated. That is,

$$ \text{Isoflux} = \text{eddy isoflux} + \text{storage isoflux} $$ (2)
Isoflux can also be obtained if $F_R$ and $F_A$ (Equation 1) are multiplied by their corresponding isotopic values. Numerical derivation of Equation 2 is given in the Supporting Information (SI).

4. Photosynthetic Discrimination

Plant biomass has a lower $\delta^{13}C$ value relative to atmospheric CO$_2$. Discrimination of heavier isotopes by the C$_3$ plants is given as a parametric equation (Farquhar et al., 1982),

$$\Delta_{C_3} = a + \left( b - a \right) \frac{C_i}{C_a}$$

(3)

where $a$ is the fractionation that occurs due to diffusion in the air (4.4‰), $b$ is the net fractionation caused by carboxylation (mainly discrimination by Rubisco and is roughly 27.5‰), $C_i$ and $C_a$ are the [CO$_2$] concentrations in the intercellular leaf air space and ambient air respectively. Please refer to Table A1 for description of the parameters.

C$_4$ plants are enriched in isotopic ratios than the C$_3$ plants, and their $\delta^{13}C$ value ranges between $-19\%$ and $-9\%$ (Koch, 2007). The discrimination $\Delta$ for the C$_4$ plants is expressed as follows (Farquhar et al., 1989)

$$\Delta_{C_4} = a + \left( b_i + b_\phi - a \right) \frac{C_i}{C_a}$$

(4)

where $b_i$ is the effective discrimination by PEP carboxylase ($\sim-5.7\%$), and $\phi$ is the proportion of the carbon fixed by PEP carboxylation that subsequently leaks out of the bundle sheath and is < 1. Experimental evidence suggests that the factor $\left( b_i + b_\phi - a \right)$ is often close to zero and hence $\Delta_{C_4}$ is much smaller than $\Delta_{C_3}$. This makes C$_4$ plants enriched compared to the C$_3$ plants (O’Leary, 1988). Isotopic discrimination in photosynthesis follows a relation proposed by Buchmann et al. (1997):

$$\Delta_e = \left( \delta^{13}C_{\text{trop}} - \delta^{13}C_R \right) / \left( 1 + \delta^{13}C_R \right)$$

(5)

where $\delta^{13}C_{\text{trop}}$ and $\delta^{13}C_R$ are the carbon isotopic values of the tropospheric CO$_2$ and the respired CO$_2$, assuming no fractionation occurs during the respiration process. $\delta^{13}CO_2$ over Mauna Loa, Hawaii, is taken as the representative of the clean-air tropospheric value ($\delta^{13}C_{\text{trop}}$) for our site, and its value was $-8.6\%$ on February 12, 2019 (our sampling date) taken from the Scripps compilation (Keeling et al., 2001; https://scrippsc02.ucsd.edu/data/atmospheric_co2/mlo.html). Using these parameters, the computed values of $\Delta_e$ are for the 11th night 13.4‰ and for the 12th night 19.7‰. The $\Delta_e$ for the second night is within the range of that determined by Buchmann et al. (1997) for an Amazonian rainforest.

Bowling et al. (2001) argued that $\Delta_e$ describes the isotopic influence of ecosystem respiration on the free troposphere, while $\Delta_{C_3}$ denotes carbon isotope discrimination associated with net photosynthesis, integrated over an entire plant canopy. To solve Equations 1 and 2, we require $\Delta_{C_3}$ which can be computed using meteorological and plant physiological parameters. A detailed calculation is given in the Supplementary Information (SI).

5. Methods

A 50 m tall micrometeorological tower was installed in Kaziranga National Park (26°34’N, 93°6’E) in 2014 as part of the MetFlux India project (Chakraborty et al., 2020). Being a reserve forest, the environment in the park is free of carbon-emitting interfering anthropogenic activities. The forest area is approximately 864 km$^2$, of which 60% is covered by wild grasses, 20% by semi-deciduous and semi-evergreen trees, and the remaining area represents swampy land. The average canopy height surrounding the tower is 20 m. Detail site information is provided in Sarma et al. (2018). The local climate is humid subtropical (CWa type). Figure S1 (see SI) shows the tower and the vegetation pattern in the neighboring areas.
5.1. Concentration and Stable Isotope Measurement

Concentrations of CO$_2$, CH$_4$, and their carbon isotopic ratios were measured in a special campaign during February 2019 using a state-of-the-art Greenhouse Gas Analyzer (Model: G2201-I, Picarro Inc.; henceforth termed as Analyzer). It works on the principle of cavity ring-down spectrometry (Lopez et al., 2017; Rella et al., 2015). Precisions obtained by high frequency (1 Hz) measurements are the following: for isotopic ratios 0.16‰ ($\delta^{13}$CO$_2$) and 0.55‰ ($\delta^{13}$CH$_4$) when averaged over 5 min; for concentrations 200 ppb (for [CO$_2$]) and 50 ppb (for [CH$_4$]) when averaged over 30 s. Before the campaign, the Analyzer was calibrated using the NOAA calibration cylinders. Since this analyzer was not ideal for open-air field measurements during rains, we planned for a few days of observation during the dry winter season. Unfortunately, an unexpected heavy shower during the campaign disturbed the plan and allowed us to get data only for two days (February 10–12). However, the unseasonal shower provided us a unique opportunity to study the GHGs characteristics during a moist regime, as will be discussed later.

The air inlet of the Analyzer was placed at a height of 37 m, next to the Infra-Red Gas Analyzer (IRGA). Details of the IRGA are provided in the next section. The Analyzer was kept in a makeshift enclosure adjacent to the tower.

5.2. Eddy Covariance System

A detailed description of the EC measurements and data analysis is beyond the scope of this study and we only provide a brief description here (see also SI). The existing tower was equipped with an EC system (the IRGA sensor and a 3D sonic anemometer). A few other weather and radiation sensors installed there provided quasi-continuous data for the period 2016 to present. These sensors are described in Sarma et al. (2018) and Deb Burman et al. (2019). In the present study, we used an enclosed-path CO$_2$/H$_2$O Infra-Red Gas Analyzer (IRGA) (Model: Li 7200, LiCOR Biosciences) to measure the CO$_2$ concentration at 10 Hz frequency at 37 m level. The sonic anemometer (Windmaster Pro by Gill Instruments) was used for measuring the wind components. The raw data were subjected to rigorous quality control (Debburman et al., 2017; Sarma et al., 2018), after which the 30-min fluxes (NEE) were computed using an open access EddyPro software (version 6.2.1) by LI-COR (https://www.licor.com).

6. Results and Discussion

6.1. Time Series of CO$_2$ Concentration and δ$^{13}$CO$_2$

10-minute averaged CO$_2$ concentration and corresponding δ$^{13}$CO$_2$ values are shown in Figure 1a. The average value of [CO$_2$] during the entire campaign was 451.5 ± 36.0 ppm ($\mu$ ± $\sigma$). An early morning (04:00–06:00 h) peak and a minimum during the afternoon (14:00 h) are the two main features of [CO$_2$]. Two distinct night-time peaks were observed on February 12, 2019. The smaller peak occurred around (00:00–01:30 h), followed by a sudden drop of ∼20 ppm. A second major peak occurred in the morning at 06:00 h. The daytime is characterized by photosynthetic activity resulting in low [CO$_2$] due to drawdown. Interestingly, post 10:00 h, [CO$_2$] minimum remains almost constant at ∼400 ppm until 16:00 h. It is important to note that [CO$_2$] decreases sharply (∼100 ppm) from early morning high to afternoon low within a short interval of about 4 h.

Associated with the concentration variation, there is a strong change in the δ$^{13}$CO$_2$. The mean observed value is −10.1 ± 2.6‰ ($\mu$ ± $\sigma$). The δ$^{13}$CO$_2$ attains a maximum during the afternoon (∼14:00 h) and a minimum around 06:00 h. The isotopic values maintain in general an inverse relation with [CO$_2$] but, interestingly, it steadily increases during the period of 12:00–15:00 h when [CO$_2$] remains nearly invariant. The δ$^{13}$CO$_2$ remains high during the day-time, occasionally registering a value as high as −4‰. During the night-time, the value reduces to around −12‰ to −14‰.

During the night, respiratory fluxes are high, and lower turbulent mixing leads accumulation of CO$_2$ within the canopy with a peak in early morning hours ∼6:00 a.m. (Figure 1a). However, after the sunrise, increasing solar radiation and air temperature cause turbulent mixing and stronger vertical wind that dilute the
CO₂ concentration; this is aided by photosynthetic sink that further decreases the CO₂ level. Therefore, we observe a sharp decline of [CO₂] from the morning peak within a few hours (Figure 1a).

6.2. Time Series of CH₄ Concentration and δ¹³CH₄

Figure 1b shows 10-min averaged [CH₄] and corresponding isotopic values. Methane concentration and its isotopic value δ¹³CH₄ appear to follow a similar pattern as those of CO₂. The mean concentration is 2.3 ± 0.4 ppm (μ ± σ) and the mean carbon isotopic value is −48.0 ± 5.3 ‰. Both of them show distinct diurnal variation. Like CO₂, the concentration is characterized by early morning maxima and afternoon minima, and the opposite pattern occurs for the isotope ratio.

The CH₄ concentration is controlled by the boundary layer dynamics. For example, night-time [CH₄] maxima can be caused by accumulation in night-time shallow, stable boundary layer conditions.

6.3. Principal Component Analysis

We have carried out Principal Component Analysis (PCA) to estimate the quantitative control of the weather and other variables on the total variation of the two GHGs. Several environmental parameters are known to control GHG dynamics. Since these parameters are inter-related to some degree, an idea of their independent controlling effect can be obtained by PCA.

Figure 1. Time series of 10-min averaged (a) carbon dioxide (CO₂) concentration (yellow triangles) and its carbon isotopic ratios (black dots) (b) methane (CH₄) concentration (green) and its isotopic values (purple).
We considered the following weather parameters for the PCA: wind direction (Dir), vapor pressure deficit (VPD), air temperature (T), wind speed (Speed), Monin-Obukhov stability parameter (stability), obtained as primary or secondary parameters from the eddy flux measurement. Additionally, CO₂ concentration (co2) and its δ¹³C (dco2) as well as CH₄ concentration (ch4) and its δ¹³C (dch4) obtained from the Analyzer were used. Based on simultaneous observation of the variables, half-hourly averages were calculated for all of them. Eighty sets of consecutive observation points (n = 80) were available. PCA of these data points yields three main components by which 82% of the variance can be explained. PC1 captures ~57% (Table 1), PC2 captures 12.7% and PC3 represents 11.7% variance of the main data set. In the two-dimensional space of two leading principal components, we use the biplot technique (Gabriel, 1971) to describe the PCA result. This technique is often used for atmospheric applications (Ivanov & Evtimov, 2014; Lone et al., 2020) and GHG studies (Metya et al., 2021). The two axes in the biplot represent the first two principal components, and the arrow vectors describe the variables in this space. The length of an arrow represents the variance, and the cosine between two arrows represents the linear correlation between the two variables. All the variables are scaled to unit variance before performing PCA. Therefore, the unit circle represents the variance of each variable. The variables that are better explained by the two principal components will be longer and closer to the unit circle. Acute and obtuse angle represents positive and negative correlation, respectively, while a right angle implies a lack of correlation.

The analysis shows (Figure S2) that CO₂, CH₄, VPD, and T are characterized by high variabilities. A close association of CO₂ and CH₄ indicates that their concentrations are strongly correlated, but surprisingly their carbon isotopic values are only weakly correlated. The high correlation between the CO₂ and CH₄ concentration (i.e., co2 and ch4) may indicate contributions from the same source (Fang et al., 2015; Sreenivas et al., 2016). The correlation coefficient at night-time (18:00–07:00 h) is 0.94 (n = 52, p = 0.0) and at day-time (07:30–17:30 h) it is 0.89 (n = 28, p = 0.0). The obtuse angles between the pairs (co2–dco2) and (ch4–dch4) present negative correlations between concentration and isotope ratio, which reflects an inverse relation. As mentioned before, such inverse relation is quite well known (Keeling, 1961; Röckmann et al., 2016) and helps find the source signature of CO₂ and CH₄. We explain in Section 2 how to find the source signature and its significance. The angles (Figure S2) between wind speed-co2 and wind speed-ch4 (representing inverse correlation) are also obtuse and denote the presence of sources near the measurement site (Ramachandran & Rajesh, 2007).

### 6.4. Source Identification

Figure 2 illustrates the source signatures of CO₂ and CH₄ using the moving “Miller-Tans plot.” The isotopic values of the source CO₂, that is, δ¹³C (CO₂) were obtained using only night-time observations on two sampling dates. The data were fitted under two types of criteria (see Section 2 for definition) and are shown in Table 2.

For computing the δ¹³C (CO₂), we used the night-time observations of this pristine forest environment. Since no photosynthetic uptake takes place at night, we expect these values to be representative of the ecosystem respiration. Interestingly, the δ¹³C (R) value, the isotopic composition of the respiratory flux, was lower by ~6‰ on February 12 compared to February 11.

The question arises, what can be the source of high δ¹³C (R) (Figure 2) observed on the 11th night? Did it arise due to the presence of any C₄ plant respiration? It is known that the C₄ plants emit isotopically enriched carbon, such as pastures compared to forest ecosystems (Ometto et al., 2002) but our site is dominated by C₃ trees (see Figure S1). Hence, the observation of isotopically enriched CO₂ on the 11th night is most likely due to the respiration by C₃ plants but with altered fractionation. Several investigators have studied the effect of environmental condition on δ¹³C (R) on different temporal as well as spatial scales over the globe. Bowling et al. (2002) found depleted δ¹³C (R) in association with high annual precipitation in six coniferous forests in western Oregon, USA. They observed much-depleted δ¹³C (R) (~27.5‰ to

| PC1 | 5.19 | 57.7 | 57.7 |
|-----|------|------|------|
| PC2 | 1.15 | 12.7 | 70.4 |
| PC3 | 1.06 | 11.7 | 82.1 |
−28.5‰) in a tropical forest when annual mean precipitation ranged from 2,100 to 2,300 mm. Further, several studies found that the carbon isotope ratio of ecosystem respired CO\textsubscript{2} is likely dominated by the carbon that was primarily fixed by the leaves at the top of the dominant trees exposed to the sun during the previous few days (Bowling et al., 2002; Ekblad & Högberg, 2001). The isotopic value of C\textsubscript{3} plants is highly dependent on leaf level/iaCC/iaCC ratio as given by Equation 3. Several physiological parameters such as water-use efficiency (Farquhar et al., 1989), stomatal limitation of photosynthesis (Farquhar & Sharkey, 1982; Jones, 1992), optimal stomatal behavior (Cowan & Farquhar, 1977), and leaf nitrogen-use efficiency (Field et al., 1983) are directly associated with leaf/iaCC/iaCC ratio. Alteration in environmental conditions can affect changes in the ratio of photosynthesis to stomatal conductance leading to fluctuations in leaf δ\textsubscript{13}C values. As leaf δ\textsubscript{13}C changes, δ\textsubscript{13}C\textsubscript{R} will also change, assuming negligible fractionation during respiration. Ekblad and Högberg (2001) observed a strong lagged correlation between atmospheric humidity and the δ\textsubscript{13}C of CO\textsubscript{2} released from the soil surface in which δ\textsubscript{13}C lags by about 2–4 days in boreal coniferous forest. Further, Bowling et al. (2002) showed that the carbon isotope composition of δ\textsubscript{13}C\textsubscript{R} in coniferous forests in western Oregon was strongly correlated with the VPD of air. They found that depleted value of δ\textsubscript{13}C\textsubscript{R} lags the low VPD condition by a few days. Further, the lead-lag relationship is site dependent. There was a distinct change in the moisture regime in our site preceding the sampling days. Figure 4 shows sudden rain events on February 8 and 9 (squared yellow box) that lead to decrease in VPD. TRMM-3B42 rainfall data, averaged over box 26°N–27°N and 92.5°E–93.5°E, is used here. Hence, we argue that the enriched δ\textsubscript{13}C\textsubscript{R} of the February 11 night is due to high VPD observed on February 7. On the other hand, the depletion on February 12 is due to prevailing low VPD condition of the preceding days of February 8 and 9 (Figure 4).

For the carbon isotope ratio in CH\textsubscript{4}, an opposite scenario is seen. δ\textsubscript{13}C\textsubscript{CH\textsubscript{4}} is more depleted on the 11th (mean value = −84.9 ± 1.8‰) than the 12th (mean = −63.7 ± 3.7 ‰). Three main source pathways of atmospheric CH\textsubscript{4} are microbial- (includes wetlands, agriculture, ruminant, and waste) ~−60‰, thermogenic- (includes fossil fuels) ~−37‰, and pyrogenic- (includes biomass burning) ~−22‰ (Schaefer et al., 2016). δ\textsubscript{13}C\textsubscript{CH\textsubscript{4}} value on

![Figure 2. Moving Miller-Tans plot. Green solid circles denote source signatures when data satisfy the first criteria mentioned in the text. Solid red dots denote source signature satisfying all three criteria for carbon dioxide (CO\textsubscript{2}). Blue circles present the source signature of methane (CH\textsubscript{4}). The 1-standard deviation is also presented as error bars in both δ\textsubscript{13}C\textsubscript{CH\textsubscript{4}} and δ\textsubscript{13}C\textsubscript{CO\textsubscript{2}}. Error bars of δ\textsubscript{13}C\textsubscript{CO\textsubscript{2}} are very small and are within the diameters of green/red circles.](image-url)
the 12th night is within the range of tropical wetland emission. Wetlands are the largest source of atmospheric CH$_4$ (Kirschke et al., 2013). Tropical wetlands are potent sources of CH$_4$ due to substantial net primary productivity and high seasonal temperatures (Bloom et al., 2012). Tropical wetlands include a variety of ecosystems, including wet soils, swamps, bogs, peatlands, and rice fields. The isotopic signature of CH$_4$ from rice in India is $-57.2$‰ to $-54.3$‰ (Rao et al., 2008), which is much enriched than the value observed on the 12th night. Pangala et al. (2017) reported a large range, $-70.8$‰ to $-54.5$‰, in the carbon isotope composition of CH$_4$ in soil in Amazon floodplain. Devol et al. (1996) reported $\delta^4$CH$_4$ of $-63$‰ over open water areas of lakes. Kaziranga national park is situated in the floodplain of river Brahmaputra. There are various lakes (Figure is given in SI, Figures S4a and S4b) and small water bodies are present inside the park. Moreover, Pangala et al. (2017) found average $\delta^{13}$C value of tree-sourced CH$_4$ from Amazonian
floodplain is $-66.2 \pm 6.4\%$. Hence, we suspect that CH$_4$ emitted from the tree stems originated in the floodplain soil. Trees growing in areas under permanent or periodic inundation develop adaptive features such as enlarged lenticels and hollow aerenchyma tissue for the supply of more oxygen in their roots. The internal channel that provides downward movement of air also assists in the upward escape of soil CH$_4$ to the atmosphere. The Kaziranga encounters heavy inundation during monsoon (Figures S4c and S4d) season (June to September, Ghosh et al., 2016) possibly compels plants to develop such features, which can lead to CH$_4$ emission from plants. Another source of atmospheric CH$_4$ is enteric fermentation from ruminants. Kaziranga has a large population of ruminants like buffalo, deer, antelope, and so on. Chang et al. (2019) report country-specific $\delta^{13}$CH$_4$ from ruminants. They suggest that $\delta^{13}$CH$_4$ from ruminants from India is $\sim -64\%$ which is again in the range of our observed $\delta^4$CH$_4$ on 12th night. Hence, Kaziranga CH$_4$ emission on 12th night is from microbial source but the exact pathway, that is, whether it is from soil or water or from animals, is still unidentified.

Much depleted value of $\delta^4$CH$_4$ was observed for bacterial carbonate reduction (Whiticar, 1999) in saline sediment. Moreover, plant methoxyl groups are also associated with exceptionally depleted isotopic values. Plant methoxyl pool is the predominant source of biospheric methanol, chloromethane, and bromomethane and works as an important substrate for methanogenesis (Keppeler et al., 2004). $\delta^4$CH$_4$ originated from plant methoxyl pool (lignin and pectin) can have much lower value as observed for CH$_4$ produced by bacterial carbonate reduction. We hypothesize that the heavily depleted $\delta^4$CH$_4$ value on the 11th night is most likely due to aerobic CH$_4$ production from plant (the plant methoxyl groups). However, this is to be noted that $\delta^4$CH$_4$ is a derived parameter. It is computed using the regression line between 1/ [CH$_4$] ([CH$_4$] is ambient methane concentration) versus $\delta^4$CH$_4$ (ambient or observed isotopic signature) known as Keeling Plot technique (Keeling, 1961) or product of ambient/observed $\delta^4$CH$_4$ and [CH$_4$] versus [CH$_4$]. As mentioned before, this method requires the criteria that the source and background remain constant. This was ensured by using the filters: 1. $R^2 > 0.99$, and 2. Standard deviation of slope of the regression should be less than 4. Choosing the threshold value for error or standard deviation of slope is subjective. If we use more stringent threshold, that is, error in slope <2.5‰, then the depleted $\delta^4$CH$_4$ value on 11th simply disappears. Hence, the depleted $\delta^4$CH$_4$ arises during more relaxed filter criteria. This leads to the fact that depleted $\delta^4$CH$_4$ on 11th night is evident skeptically and further investigation is necessary to confirm the hypothesis.

6.5. Environmental Parameters and NEE

Figure 3a shows the diurnal variations of mean air temperature (MAT) and VPD during the two sampling days (February 10–12). The MAT ranged from 20°C to 27°C. Correspondingly, a very high evaporative demand occurred in the afternoon (15:00 h) when the mean VPD approached 2.5 kPa.

6.5.1. NEE and Isoflux

In this section, we present the results of the isoflux calculation, the details of which are provided in the Section SI.1. By definition, the isoflux is the NEE multiplied by its isotopic composition. During the noon hours, when photosynthetic uptake is high, NEE is highly negative. Since this uptake implies enhanced abstraction of isotopically lighter CO$_2$, the ambient leftover CO$_2$ becomes isotopically enriched, which is manifested in corresponding variations in the isoflux shown in Figure 3b. The negative NEE peaks occur in the morning 11:00 h (ca. $-9.3 \mu$mol m$^{-2}$s$^{-1}$‰) and, in parallel, the isoflux attains a maximum value of 585.6 $\mu$mol m$^{-2}$s$^{-1}$‰. It is instructive to see that both NEE and isoflux are closely linked with the VPD (Figure 3a). The VPD attains a maximum value at around 14:30 h when NEE is reduced. This is because a higher VPD leads to the partial closure of the stomata as a biological response of the tree to water loss, which results in lower drawdown or less-negative CO$_2$ flux. This reduction is reflected in the NEE value (Sarma et al., 2018).
Isotope Based Partitioning of NEE

As mentioned above, the diurnal variation of NEE (Figure 3b) shows high negative values around morning (11:00 h) as expected from intense photosynthesis. In contrast, the night-time values derived mainly from respiration yield positive quantities (Debburman et al., 2017; Sarma et al., 2018). This pattern is reflected in the isotope-based partitioning of NEE, which shows that $F_A$ reaches a high negative value of $-13.0 \mu$mol m$^{-2}$s$^{-1}$ at about 11.00 h and then decreases gradually. Interestingly, the respiration flux $F_R$ also has a high positive value of 3.7 $\mu$mol m$^{-2}$s$^{-1}$ at the same time. Two anomalously high positive values of NEE are noted during the night, which lead to erroneous values of $F_A$ and $F_R$. We consider these as outliers and reject them from consideration.

Conclusions

This study reports a set of measurements of concentrations and carbon isotopic ratios of CO$_2$ and CH$_4$ from an Indian forest ecosystem. In association with the EC data, CO$_2$ concentration and its isotopic composition are used to partition the NEE fluxes into their various contributing components. Such high-frequency isotopic data obtained using an in situ isotopic analyzer, provide a unique way to partition the NEE. Specifically, a two-day campaign was carried out to measure the above parameters in a tropical forest environment. The well-known moving "Miller-Tans" plot was used to identify the sources of CO$_2$ and CH$_4$. As an example, a mean $\delta^{13}C_{\text{O2}}$ of one night was $-21.8 \pm 0.5\%o$ while the following night registered a value of $-27.8 \pm 0.3\%o$. A large change of $\sim 6\%$ of $\delta^{13}C_{\text{O2}}$ between the consecutive nights is attributed to the change in VPD as a result of sudden rain preceding the sampling days. A large variation was also observed in the case of $\delta^{4}CH_{4}$. Mean $\delta^{4}CH_{4}$ for the successive nights were $-84.9 \pm 1.8\%o$ and $-63.7 \pm 3.7\%o$, respectively. The large depletion (ca 16%) in $\delta^{4}CH_{4}$ on the first observation night was most likely linked to aerobic CH$_4$ production from the plant methoxyl groups.

The NEE components, $F_A$ and $F_R$, were estimated using the Isotope-EC combination method proposed by Bowling et al. (2001). To our knowledge, the results presented in this study are the first work that combined the eddy-covariance-based flux observations and the stable carbon-isotope measurements of CO$_2$ for a better understanding of the carbon sequestration processes in a complex forest environment of India where multiple but highly diverse sources are present.

The study gains importance because there are no methods for source characterization when the concentration changes rapidly. As demonstrated in this work, the technique works well for CO$_2$; but it may not perform satisfactorily for highly variable source contributions in the case of CH$_4$. Unfortunately, there is no other method in practice; and despite its limitation, two possible sources could be identified. Further
study is required to clarify the matter. In a nutshell, the research shows that a moving Miller-Tans method works well for partitioning the NEE, and the sources are different in the two consecutive days, especially for CH$_4$.

**Appendix:**

| Table A1 | Symbols Used in the Text |
|----------|--------------------------|
| Parameter | Description | Value | Units |
| a | Fractionation occurring due to diffusion | 4.4 | ‰ |
| b | Net fractionation caused by carboxylation (mainly discrimination by Rubisco) | 27.5 | ‰ |
| b$_4$ | Effective discrimination by PEP carboxylase | ~5.7 | ‰ |
| $\phi$ | Proportion of the carbon fixed by PEP carboxylation that subsequently leaks out of the bundle sheath | <1 | |
| $\delta_e$ | Isotopic signature of source-mix | | ‰ |
| $\delta^{13}$CO$_2$ | Carbon isotope composition of CO$_2$ | | ‰ |
| $\delta^{13}$C$_{soil}$ | Source $\delta^{13}$CO$_2$ | | ‰ |
| $\delta^{13}$CO$_2$, dco2$_s$ | Carbon isotope composition of CO$_2$ in ambient air as measured by Picarro G2201-i | | ‰ |
| $\delta^{13}$C$_R$ | Carbon isotopic composition of ecosystem respiration | | ‰ |
| $\delta^{13}$C$_{trop}$ | Carbon isotopic composition of CO$_2$ in free tropospheric air | | ‰ |
| $\Delta$ | Carbon isotope discrimination of net photosynthesis, integrated over the canopy | | ‰ |
| $\Delta_e$ | Net ecosystem discrimination (free troposphere vs. ecosystem respiration – (Buchmann et al., 1997)) | | ‰ |
| $\Delta_C_3$ | Carbon isotope discrimination of net photosynthesis in C$_3$ plants | | ‰ |
| $\Delta_C_4$ | Carbon isotope discrimination of net photosynthesis in C$_4$ plants | | ‰ |
| $\delta^{13}$CH$_4$ | Carbon isotope composition of CH$_4$ | | ‰ |
| $\delta^{13}$CH$_4$, dch4$_a$ | Ambient $\delta^{13}$CH$_4$ observed by the GHG Analyzer | | ‰ |
| $\delta^{13}$CH$_4$, dch4$_s$ | Source $\delta^{13}$CH$_4$ | | ‰ |
| [CO$_2$], [CH$_4$], CO2, ch4 | CO$_2$ and CH$_4$ concentration (mixing ratio) observed by the GHG Analyzer | | Ppm |
| $C_a$, $C_c$ | CO$_2$ mixing ratio in the intercellular air space and ambient air | | Ppm |
| IRGA | Infra-red Gas Analyzer. It measures high frequency (10 Hz) CO$_2$ concentration | | |
| VPD | Vapor pressure deficit obtained by IRGA | | kPa |
| $F_A$ | Total ecosystem net photosynthetic assimilation flux | | μmol CO$_2$ m$^{-2}$ s$^{-1}$ |
| $F_R$ | Total ecosystem respiration flux | | μmol CO$_2$ m$^{-2}$ s$^{-1}$ |
| NEE | Net ecosystem exchange of CO$_2$ | | μmol CO$_2$ m$^{-2}$ s$^{-1}$ |
| Speed | Wind speed observed by sonic anemometer | | ms$^{-1}$ |
| T | Air temperature obtained from IRGA | | ºC |
| Dir | Wind direction observed by sonic anemometer | | º |
| Stability | Monin-Obukhov stability parameter | | |
Acknowledgments
The Indian Institute of Tropical Meteorology, Pune (IITM), is fully supported by the Earth System Science Organization of Ministry of Earth Sciences, Govt. of India. The authors thank the Director, IITM and R. Krishnan, Executive Director, Center for Climate Change Research, IITM for their support and encouragement. S. K. Bhattacharya thanks IIT Kharagpur for a Visiting Professorship. The logistical support provided by the forest officials at the Kaziranga forest division is gratefully acknowledged.

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