The relationship between $^{18}$O/$^{16}$O and $^{13}$C/$^{12}$C ratios of ambient CO$_2$ in two Amazonian tropical forests

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ABSTRACT

Oxygen and carbon isotopic compositions of ambient carbon dioxide in two tropical forests in the Amazonian basin were determined at the beginning and the end of the dry season. One site, Fazenda Vitoria, is typical of a seasonal forest with a pronounced dry season from May to November whereas the other site, Reserva Ducke, has a milder dry season. Samples collected at night revealed that in the beginning of the dry season, when the forest is still relatively wet, isotopic exchange between carbon dioxide and wet surfaces or fog is possible. Oxygen isotope ratios of ambient carbon dioxide collected during the day were correlated with the carbon isotope ratios. These correlations are representative of the mixing line between tropospheric and respired CO$_2$. The mixing lines were used to extrapolate the $\delta^{18}$O values of soil-respired CO$_2$. These values were compared with those derived from the isotopic composition of bulk soil water (as reflected by plant stem water) and a diffusion isotope effect of 8.8/$_{2}\%$. It was observed that $\delta^{18}$O values of respired CO$_2$ derived by extrapolation were greater than those calculated by using $\delta^{18}$O values of bulk soil water and the associated diffusion isotope effect. The results show that in tropical forests, assumptions used in previous studies of temperate regions to derive the oxygen isotopic composition of respired CO$_2$ do not hold.

1. Introduction

The increase in atmospheric CO$_2$ over the last century has precipitated interest in the carbon budget of the biosphere. It has been particularly important to identify the location of terrestrial sinks, since recent studies have concluded that terrestrial photosynthesis is a substantial CO$_2$ sink (Dixon et al., 1994; Tans, 1993). There is evidence that the land masses of the southern hemisphere comprise one of the most important CO$_2$ global sinks (Dixon et al., 1994). This assessment has been supported recently by eddy correlation tower based measurements in an Amazonian forest which indicate a net carbon uptake (Grace et al., 1995).

Isotopic analysis of atmospheric CO$_2$ is an important tool for the determination of global CO$_2$ sources and sinks. Pioneering work by Keeling et al. (1979) utilizing carbon isotope ratios of atmospheric CO$_2$ revealed that the increase in atmospheric CO$_2$ is due to fossil fuel burning. Other studies by Tans et al. (1990) led to the conclusion that there is a large terrestrial carbon sink. More recently the oxygen isotopic signature...
of atmospheric CO$_2$ has emerged as a means for assessing the global carbon budget (Francey and Tans, 1987; Farquhar et al., 1993; Friedli et al., 1997). This method takes advantage of the rapid equilibration between ambient CO$_2$ and leaf water during photosynthesis. The CO$_2$ absorbed by the leaf equilibrates with leaf water and “leaks” back out. Photosynthesis, therefore, will leave an isotopic signature on ambient CO$_2$.

The relationship between the $\delta^{18}O$ of leaf water, atmospheric CO$_2$, and the internal CO$_2$ concentration in the chloroplast versus the discrimination against $^{18}O$ of CO$_2$ during photosynthesis has been established by the following equation (Farquhar and Lloyd, 1993):

$$\Delta = \bar{a} + [(C_v/(C_a-C_v))\delta_c - \delta_a].$$

(1)

where $\bar{a}$ is the average fractionation during diffusion of CO$_2$ through the stomatal pores (~7.4/$\delta$); $C_v$ and $C_a$ are the CO$_2$ concentrations in the chloroplast and atmosphere respectively, $\delta_c$ and $\delta_a$ are the oxygen isotopic composition of CO$_2$ in chloroplast and atmosphere respectively. The discrimination factor ($\Delta$) is highly variable and depends on the biome (Farquhar et al., 1993). Discrimination values may range from ~20/$\delta$ in arctic tundra to $+32/\delta$ in the dry steppes of Kazakhstan and the Ukraine (Farquhar et al., 1993). In conjunction with $\delta^{13}C$ analysis, $\delta^{18}O$ analysis of tropospheric CO$_2$ may provide an accurate map of terrestrial CO$_2$ sinks (Farquhar et al., 1993).

For a greater understanding of terrestrial processes affecting the $\delta^{18}O$ values of global CO$_2$, studies on the interaction of respiration, photosynthesis, and atmospheric mixing on the isotopic signatures of ambient CO$_2$ in regional ecosystems will be necessary (Farquhar et al., 1993). The authors of this study are aware of three prior studies related to the above mentioned research direction (Flanagan and Varney, 1995; Yakir and Wang, 1996; Buchmann et al., 1997). The first two studies were conducted in temperate ecosystems. Both made 4 assumptions: (1) the $\delta^{18}O$ values of plant stem water reflects the $\delta^{18}O$ values of bulk soil water; (2) respired CO$_2$ equilibrates with bulk soil water before being released to the atmosphere; (3) there is a diffusion isotope discrimination factor of 8.8/$\delta$ as equilibrated CO$_2$ diffuses from the soil to the atmosphere, (therefore the $\delta^{18}O$ value of respired CO$_2$ was calculated by subtracting a diffusion isotope discrimination factor from the isotopic value of the CO$_2$ equilibrated with plant stem water); (4) the exchange between CO$_2$ and wet surfaces or clouds and/or fog is negligible. The first three assumptions were based in part on the observations of Hesterberg and Siegenthaler (1991). The validity of their equations, however, have recently been questioned (Tans, 1998).

To date, there are no studies of tropical ecosystems in which the $\delta^{18}O$ values of ambient CO$_2$ were related to soil water, photosynthetic discrimination, and tropospheric CO$_2$. Tropical regions may present conditions in which the aforementioned assumptions will not hold. First, the large amount of CO$_2$ produced by shallow roots and litter on the soil surface may not be subjected to the full expression of the diffusion isotope fractionation factor of 8.8/$\delta$ (Hesterberg and Siegenthaler, 1991) and may contribute a disproportionate amount of respired CO$_2$ equilibrated with surface water. This surface water would certainly be more isotopically enriched than bulk soil water. Second, high relative humidity and temperature changes may result in a considerable amount of condensation and wet surfaces where ambient CO$_2$ can exchange.

The purpose of this study was: (1) to compare measured $\Delta$ values in the Amazon basin with those calculated using the Farquhar et al. model (1993) and (2) to test whether the assumptions put forth in the studies cited (Flanagan and Varney, 1995; Yakir and Wang, 1996) hold for tropical ecosystems.

2. Approach

Values for $\Delta$ were determined by measuring the oxygen isotope ratios of leaf water and ambient CO$_2$. Some assumptions about the relationship between chloroplast water and leaf water and about the CO$_2$ concentration in the chloroplast were necessary in order to calculate the approximate $\Delta$ for the two locations in the Amazon basin. These assumptions will be discussed in the results.

To test the assumption that CO$_2$ will not equilibrate with wet surfaces or water droplets, and that the $\delta^{18}O$ of respired CO$_2$ can be determined by subtracting a diffusion isotopic fractionation factor from the $\delta^{18}O$ values of CO$_2$ equilibrated...
with bulk soil water, a graphical approach similar to
their interpretation of δ18O values of marine
CO2 was used. There are two major sources of
CO2 in a forest: respired and tropospheric (Fig. 1).
These sources will have different carbon and
oxygen isotopic composition, with tropospheric
CO2 having higher δ13C and δ18O values than those of respired CO2. Estimation of the δ18O
value of respired CO2 in other studies was based
on the previously mentioned assumptions.

If the effect of photosynthesis or ambient CO2
equilibration with water droplets or wet surfaces
is negligible, then a plot of δ18O versus δ13C values of ambient CO2 should fall along the mixing line
shown in Fig. 1. Photosynthesis has the potential
of causing a change in isotopic ratios of ambient
CO2. Given a high enough photosynthetic rate, a
plot of δ18O versus δ13C values of ambient CO2
can deviate from this mixing line (Fig. 1). The
extent of the deviation depends on two factors.
First, if the ratio of the oxygen (Δα) and carbon
(Δ) isotope discrimination factors (Δα/Δ) is signif-
cantly different from the slope of the mixing line,
then photosynthesis can cause a significant devi-
ation from the mixing line. Second, photosynthetic
signals are greater if the amount of turbulent
mixing between ambient forest CO2 and the tropo-
sphere is low (Sternberg et al., 1997). Thus lower
turbulence will cause a greater potential for devi-
ation from the mixing line.

Another factor which causes a deviation from
this mixing line is the equilibration of ambient
CO2 with wet surfaces or water droplets from
condensation. This deviation is controlled by two
factors: (1) the difference between the δ18O of the
CO2 equilibrated with the water surfaces or drop-
plets relative to expected values from the mixing
line and (2) the rate of turbulent mixing relative
to the equilibration rate.

In this paper, we will show that in the tropics
the observed relationships between δ18O and 13C
values of ambient CO2 can deviate from theoret-
ical mixing lines constructed on the basis of the
forementioned assumptions. Further, we will
show that this deviation is caused by CO2 equilib-
rating with wet surfaces. We will also demonstrate
that the assumptions used to estimate the δ18O
values of respired CO2 in temperate studies do
not hold for tropical forests.

3. Methods

3.1. Sites of study

Air samples were collected in two sites: Fazenda
Vitoria in the state of Pará (2° 59'S, 47° 31'W) and
Reserva Ducke in the state of Amazonas (3° 8'S,
60° 1'W). These two sites have contrasting climates.
The Fazenda Vitoria site is typical of the dryer
and more seasonal climate found in the eastern
Amazon basin and the Reserva Ducke site is
typical of the wetter and more aseasonal climate of
the central and western Amazon.

The forest structure at these two sites differ in
part because of climatic differences and anthro-
pogenic effects. The Fazenda Vitoria site is located
in an area of extensive deforestation; thus, it is a
somewhat smaller forest parcel than that of the
Reserva Ducke. Higher wind speeds at the
Fazenda Vitoria site coupled with a smaller forest
parcel cause erasure of any isotopic signals associ-
ated with photosynthesis (Sternberg et al., 1997).
Other characteristics of these sites are described
in Moreira et al. (1997) and Sternberg et al. (1997).

3.2. Collection of samples

3.2.1. Air samples. Air samples were collected
on two dates at each site: at the beginning of the

![Fig. 1. Hypothetical relationships between δ18O and δ13C values of ambient CO2 in forests. The mixing line is a simple straight line intersecting the values of the two sources of the ambient CO2 mixture: respired and tropospheric CO2. Deviations from this mixing line can be caused by photosynthesis and by equilibration between ambient CO2 and moist surfaces or water droplets.](image)
dry season on 1 and 7 July at the Reserva Ducke and Fazenda Vitoria site, respectively, and at the end of the dry season on 7 and 15 December at the Reserva Ducke and Fazenda Vitoria respectively. Samples were collected at approximately 0 and 6 hours (night samples) and at 10, 14, and 17 hours (day samples). Ambient air samples were collected in 500 cm³ pre-heated and pre-evacuated flasks similar to previous studies (Moreira et al., 1999; Sternberg et al., 1997).

In order to desiccate the sample before collection, a magnesium perchlorate trap (2 cm diameter by 20 cm length) was placed between the collection flask and the manifold (Flanagan and Varney, 1995; Buchmann et al., 1997). This trap was evacuated before sample collection. Although the trap did not completely eliminate moisture, it was sufficient to prevent any condensation on the vessel walls during transport from the field to the laboratory. Samples were collected at 0.5, 18, 45 and ~900 m elevation at the Reserva Ducke site and collected at 0.5, 18 and ~300 m elevations at the Fazenda Vitoria site in the manner described in Sternberg et al. (1997).

3.2.2. Stem, leaf and soil samples. Within one to two days of air sample collection, stem, leaf and soil samples were also collected. Soil samples were collected only at the Fazenda Vitoria site. Stem and leaf samples were collected at the approximate height of 18 m after 10:00 AM when plants are actively transpiring. Soil samples were collected at the surface and at 20 cm intervals below the surface down to 2 m. Sections of stems (approximately 1 cm diameter and 15 cm length), leaves and soil samples were placed in glass tubes and sealed with parafilm. Water was distilled from these samples as described in Moreira et al. (1997).

3.2.3. Isotopic analysis of samples. Oxygen isotopic composition of water extracted from leaves and stems was analyzed by the CO₂ equilibration method as described by Epstein and Mayeda (1953).

Air samples were taken to the University of Miami. CO₂ from air samples was then cryogenically distilled and sealed in 6 mm by 15 cm Vycor ampoules containing 0.3 g of copper and baked at 450°C for 1 h to remove nitrous oxides. Vycor ampoules were used because oxygen from CO₂ can exchange with Pyrex at high temperatures, but does not exchange with Vycor (Burk, 1979).

All extracted gas samples were analyzed in a PRISM mass spectrometer with a precision of ±0.1/‰. δ²H values are expressed either on the SMOW scale for isotopic composition of plant water and soil water or on the PDB–CO₂ scale for ambient CO₂.

4. Results

Average daytime oxygen isotope ratios of ambient CO₂ at 18 m elevation of CO₂ at equilibrium with chloroplast water, the ratio Cᵢ/Č₀, and the oxygen isotope discrimination factor (Δᵢ) for each site are shown in Table 1. δ²H values of the chloroplast water were derived by measuring δ²H values of leaf water and using a mass balance equation. The equation assumes that 20% of the water in the leaf has the isotopic identity of stem water and 80% (which includes the chloroplast water) has the identity of water undergoing evaporation (Leaney et al., 1985).

The issue of δ²H values of chloroplast water is controversial and still unresolved. On the one hand Farquhar et al. (1993) have evidence that chloroplast water has the isotopic identity of evaporative water; on the other hand Yakir (1992) has evidence that chloroplast water has the isotopic identity of a mixture of non-evaporated and evaporated water. For the purpose of our study, it was assumed that chloroplast water has the isotopic signature of water undergoing evaporation.

Table 1. δ²H values ± SEM (CO₂ – PDB scale) of ambient CO₂ (δ₀) and CO₂ equilibrated with chloroplast water (δᵢ), ratio of CO₂ concentration at the chloroplast relative to atmospheric concentration (Cᵢ/Č₀), and the oxygen isotopic discrimination against oxygen-18 in ambient carbon dioxide during photosynthesis (Δᵢ) at the two sites

<table>
<thead>
<tr>
<th>Site and date</th>
<th>δ₀</th>
<th>δᵢ</th>
<th>Cᵢ/Č₀</th>
<th>Δᵢ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ducke 7/96</td>
<td>−0.9 ± 0.2</td>
<td>−0.8 ± 0.3</td>
<td>0.53</td>
<td>7.5</td>
</tr>
<tr>
<td>Vitoria 7/96</td>
<td>−0.6 ± 0.4</td>
<td>+9.4 ± 1.0</td>
<td>0.53</td>
<td>18.7</td>
</tr>
<tr>
<td>Ducke 12/96</td>
<td>−2.7 ± 0.4</td>
<td>+1.8 ± 0.3</td>
<td>0.53</td>
<td>12.5</td>
</tr>
<tr>
<td>Vitoria 12/96</td>
<td>−2.0 ± 0.3</td>
<td>+11.9 ± 0.6</td>
<td>0.53</td>
<td>23.1</td>
</tr>
</tbody>
</table>
if our assumption were incorrect, \( \Delta_a \) values would be less than those shown in Table 1.

Values of \( C_a/C_w \) were calculated by first calculating the ratio of CO\(_2\) concentration in the sub stomatal cavity (\( C_w \)) to that of ambient (\( C_a \)) using the following equation (Farquhar et al., 1982):

\[
\delta_p = \delta_{amb} - a + (a - b) C_w/C_a,
\]

where \( \delta_p \) and \( \delta_{amb} \) are the \( \delta^{13}C \) values of leaf biomass and ambient CO\(_2\), respectively. The constants \( a \) and \( b \) are the values of discrimination associated with stomatal diffusion (4.4/°c) and the carboxylation reactions (29°/°c), respectively. The average \( \delta^{13}C \) values of \(-28°/°c\) and \(-8°/°c\) for leaf biomass and ambient CO\(_2\) at 18 m elevation, respectively, was used in the above equation (Merwe and Medina, 1989, Sternberg et al., 1997, Lloyd et al., 1996). The concentration of ambient CO\(_2\) at 18 m elevation during the day was measured to be approximately 340 ppm (Buchmann et al., 1997, Sternberg et al., 1997). \( C_a/C_w \) was then calculated by using the relationship \( (C_w - C_a)/C_a = 0.1 \) (Farquhar et al., 1993).

Photosynthetic discrimination against \( ^{18}O \) of ambient CO\(_2\) is lower at the beginning of the dry season (7.5 and 18.7°/°c) than at the end of the dry season (12.5 and 23.1°/°c) for both sites and dates of collection. The theoretical mixing line is also shown. This line was drawn by connecting points representing the hypothetical \( \delta^{18}O \) and \( \delta^{13}C \) values of respired CO\(_2\) with those representing the \( \delta^{18}O \) and \( \delta^{13}C \) values of tropospheric CO\(_2\) (as shown in Table 2). The \( \delta^{13}C \) value of respired CO\(_2\) of \(-27°/°c\) as measured by several investigators was used (Buchmann et al., 1997; Sternberg et al., 1997; Quay et al., 1989; Lloyd et al., 1996).

There was a significant correlation between \( \delta^{18}O \) and \( \delta^{13}C \) values for samples collected during the day for both sites and dates of collection. The slope, intercept, \( r^2 \), and \( P \) values for the fitted relationships are shown in Table 3. We used a model I regression analysis since the parameters

![Image of Table 2](image-url)

**Table 2. Isotope ratios ± SEM of the two end points of the mixing line between respired CO\(_2\) and tropospheric CO\(_2\).** Table shows \( \delta^{18}O \) values of plant stem water, of CO\(_2\) at equilibrium with plant stem water at 25°C discriminated by a diffusion isotope fractionation factor of 8.8°/°c (theoretical value of respired CO\(_2\)).

<table>
<thead>
<tr>
<th>Site and date</th>
<th>( \delta^{18}O^* ) of plant water</th>
<th>( \delta^{18}O^# ) of resp. CO(_2) theoretical</th>
<th>( \delta^{18}O^# ) of CO(_2) high altitude</th>
<th>( \delta^{13}C^# ) of CO(_2) high altitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ducke 7/96</td>
<td>(-3.6 ± 0.3)</td>
<td>(-12.2 ± 0.3)</td>
<td>(-0.3 ± 0.4)</td>
<td>(-8.1 ± 0.2)</td>
</tr>
<tr>
<td>Vitoria 7/96</td>
<td>(-3.7 ± 0.7)</td>
<td>(-12.3 ± 0.3)</td>
<td>(-1.2 ± 0.3)</td>
<td>(-8.0 ± 0.2)</td>
</tr>
<tr>
<td>Ducke 12/96</td>
<td>(-4.4 ± 0.2)</td>
<td>(-13.0 ± 0.2)</td>
<td>(-3.4 ± 0.2)</td>
<td>(-9.0 ± 0.1)</td>
</tr>
<tr>
<td>Vitoria 12/96</td>
<td>(-3.9 ± 0.3)</td>
<td>(-12.5 ± 0.3)</td>
<td>(-2.2 ± 0.9)</td>
<td>(-8.8 ± 0.4)</td>
</tr>
</tbody>
</table>

* \( \delta^{18}O \) values given relative to SMOW.

\# \( \delta^{13}C \) and \( \delta^{13}C \) values given relative to PDB-CO\(_2\).
Fig. 2. Observed relationship between $\delta^{18}O$ and $\delta^{13}C$ of ambient $\text{CO}_2$ for samples collected at Reserva Ducke and Fazenda Vitoria at the beginning (July, 1996) and end (December, 1996) of the dry season. Full circles represent samples collected during the day and empty circles represent samples collected during the night. The figure also shows the mixing lines given the theoretical isotopic values of respired and observed isotopic values of tropospheric $\text{CO}_2$.

Table 3. Regression equations expressing the relationship between $\delta^{18}O$ and $\delta^{13}C$ values of ambient forest $\text{CO}_2$ sampled during the day; table shows the slope, intercept, correlation coefficient, and the probability for the regression equations for the two sites sampled in this study; also shown are the estimated $\delta^{18}O$ values of respired and tropospheric $\text{CO}_2$ from the regression equation assuming the $\delta^{13}C$ value of respired and tropospheric $\text{CO}_2$ is $-27^\circ/_{oo}$ and $-7.8^\circ/_{oo}$, respectively; all $\delta^{18}O$ values are given relative to PDB-$\text{CO}_2$.

<table>
<thead>
<tr>
<th>Site and date</th>
<th>Sl.</th>
<th>Int.</th>
<th>$r^2$</th>
<th>$P$</th>
<th>$\delta^{18}O$ of resp. $\text{CO}_2$</th>
<th>$\delta^{18}O$ of trop. $\text{CO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ducke 7/96</td>
<td>0.48</td>
<td>3.7</td>
<td>0.64</td>
<td>&lt;0.01</td>
<td>-9.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Vitoria 7/96</td>
<td>0.33</td>
<td>2.2</td>
<td>0.71</td>
<td>&lt;0.01</td>
<td>-6.7</td>
<td>-0.4</td>
</tr>
<tr>
<td>Ducke 12/96</td>
<td>0.37</td>
<td>0.7</td>
<td>0.38</td>
<td>&lt;0.05</td>
<td>-9.3</td>
<td>-2.2</td>
</tr>
<tr>
<td>Vitoria 12/96</td>
<td>0.56</td>
<td>3.0</td>
<td>0.72</td>
<td>&lt;0.01</td>
<td>-12.1</td>
<td>-1.4</td>
</tr>
</tbody>
</table>

Tellus 50B (1998), 4
for the regression equation were used for the purposes of prediction (Sokal and Rohlf, 1981). Using the respective regression equations and the assumption that respired and tropospheric CO$_2$ have $\delta^{13}C$ values of $-27/_{\infty}$ and $-7.8/_{\infty}$, respectively, we extrapolated the regression equations to $\delta^{18}O$ values of respired and tropospheric CO$_2$. These values are shown in the sixth and seventh column on Table 3.

$\delta^{18}O$ values of the water in the soil profile at the Fazenda Vitoria site for both sampling dates are shown in Fig. 3. $\delta^{18}O$ values of water from surface soil samples differed by only $0.5/_{\infty}$ between the two sampling dates ($-0.9/_{\infty}$ for July and $-1.4/_{\infty}$ for December). $\delta^{18}O$ values of water from the soil profile between surface and 1.2m depth ranged from $-10.0/_{\infty}$ to $-5.1/_{\infty}$ for the July samples and between $-9.6/_{\infty}$ and $-5.2/_{\infty}$ for the December samples. Therefore, differences in isotopic composition of soil water between the two sampling dates were small for soil samples collected on the above depth interval. There were greater differences between the $\delta^{18}O$ values of soil water collected at the two dates at depths below 1 m, with the July samples having an average $\delta^{18}O$ value of $-9.9 \pm 1.7$ (SDEV) and the December samples having an average $\delta^{18}O$ value of $-6.9 \pm 0.95$.

5. Discussion

5.1. Calculation of the photosynthetic discrimination factor

The discrimination factors ($D_a$) for the Reserva Ducke site (7.5 and 12.5$/_{\infty}$, Table 1) are low compared to the one estimated by Farquhar et al. (1993) for the Amazon region (18–20$/_{\infty}$). Note that Figs. 2 and 3 are reversed in the paper published by Farquhar et al. (1993). The discrimination factor for Fazenda Vitoria during the beginning of the dry season (18.7$/_{\infty}$) is similar to that estimated by Farquhar et al. (1993) but is higher at the end of the dry season (23.1$/_{\infty}$).

Although we were not able to calculate all parameters for the model reported in Farquhar et al. (1993), we note that the equation used to calculate soil water (equation 3 in their paper) gave $\delta^{18}O$ values of soil water in the Amazon region of $+12.3/_{\infty}$ (we used the following parameters for this region: temperature $T(\degree C)=25\degree C$; precipitation $P_a(m)=2.0$m; and elevation $E_v(m)=30$m). This value is highly enriched compared with our measurements of $-4$ to $-3/_{\infty}$ for plant water and $-5.0/_{\infty}$ for water from soil samples below the surface. We suspect, however, that another error in the model lies in the estimates of leaf water. Leaf water had low enrichment in the Reserva Ducke site whereas at the Fazenda Vitoria site, leaf water may have been more enriched than predicted by the model. Furthermore, the circulation model used to predict $\delta^{18}O$ values of ambient vapor (Jouzel et al., 1987) underestimates $\delta^{18}O$ values of ambient vapor. Our measurements (Moreira, M. Z., personal communication) at the end of October and beginning of November gave

![Fig. 3. $\delta^{18}O$ values of water extracted from soil samples throughout the soil profile at Fazenda Vitoria in 7 July and 15 December 1996.](image-url)
\( \delta^{18}O \) values of ambient vapor averaging \(-10\) to \(-9^{\circ}/\text{o} \). The Jouzel et al. model predicts values ranging from about \(-19\) to \(-14^{\circ}/\text{o} \).

5.2. Deviation between \( \delta^{18}O \) versus \( \delta^{13}C \) values of ambient \( \text{CO}_2 \) and the theoretical mixing lines

A plot of \( \delta^{18}O \) versus \( \delta^{13}C \) values of daytime ambient \( \text{CO}_2 \) deviates considerably from the theoretical mixing lines for the Reserva Ducke samples (Fig. 2). Values for the Fazenda Vitoria site samples fall above the theoretical mixing line at the beginning of the dry season and along the theoretical mixing line at the end of the dry season.

At the beginning of the dry season, when humidity is usually high, large deviations on the \( \delta^{18}O \) values ambient night time \( \text{CO}_2 \) are noticeable without a concomitant variation on the \( \delta^{13}C \) values (Fig. 2). This pattern is typical of \( \text{CO}_2 \) exchange with moist surfaces or water droplets (Fig. 1). Since this occurred at both sites only at night, it may represent exchange which occurs with water droplets during the condensation and formation of fog, often seen over tropical forests. It is interesting to note that the 1 July sampling occurred as a cold front ("friagem") moved in, bringing unusually low temperatures for the tropics (Minimum temperature on 1 July at the Reserva Ducke was \( 17^\circ \text{C} \)). This could have led to condensation resulting in the equilibration of the ambient \( \text{CO}_2 \) with water droplets or wet surfaces.

Although evidence of equilibration between \( \text{CO}_2 \) and water droplets cannot account for global and tropospheric patterns of \( \delta^{18}O \) values (Francey and Tans, 1987; Friedli et al., 1987), it may explain local and regional patterns. The assumption that there is no equilibration between ambient \( \text{CO}_2 \) and water droplets or wet surfaces cannot be applied to the tropics. Under certain conditions (particularly during the wet season) equilibration between \( \text{CO}_2 \) and water droplets or wet surfaces may be an important factor modulating \( \delta^{18}O \) values of ambient \( \text{CO}_2 \).

There is a significant relationship between \( \delta^{18}O \) and \( \delta^{13}C \) of ambient \( \text{CO}_2 \) for gas collected during the day at both sites on the two sampling dates (Table 2). By extrapolating with the regression equations fitted to data collected at each site and time of sampling to \( \delta^{13}C \) values of respired \( \text{CO}_2 \), the \( \delta^{18}O \) values of respired \( \text{CO}_2 \) can be estimated (Table 2). \( \delta^{18}O \) values of respired \( \text{CO}_2 \) were \(-9.3^{\circ}/\text{o} \) for the Reserva Ducke site both at the beginning and end of the dry season (Table 3). These values are greater than the values of \(-12.2\) to \(-13.0^{\circ}/\text{o} \), which were derived with the assumptions: (1) that isotope ratios of plant water reflect that of the bulk soil; (2) respired \( \text{CO}_2 \) equilibrates with bulk soil water; (3) that the diffusion isotope fractionation factor of \( 8.8^{\circ}/\text{o} \) is fully expressed. It would appear that in wet tropical forests at least one of these assumptions do not hold.

For the seasonal site, the \( \delta^{18}O \) values of respired \( \text{CO}_2 \) varied. At the beginning of the dry season, the \( \delta^{18}O \) value of respired \( \text{CO}_2 \) was extrapolated to be \(-6.7^{\circ}/\text{o} \). At the end of the dry season, the \( \delta^{18}O \) value of respired \( \text{CO}_2 \) was calculated to be \(-12.1^{\circ}/\text{o} \), nearly the same as that expected in which the following conditions exist: plant water reflects bulk soil water, respired \( \text{CO}_2 \) equilibrates with bulk soil water, and the diffusion isotope fractionation factor is fully expressed (Table 2).

Given the discrepancy between our observed \( \delta^{18}O \) values of respired \( \text{CO}_2 \) and those calculated using the previously mentioned assumptions, we can think of four possible explanations which could cause these discrepancies.

First, photosynthesis alters the oxygen and carbon isotopic composition of ambient \( \text{CO}_2 \) in such a way that its \( \delta^{18}O \) and \( \delta^{13}C \) values deviate from the theoretical mixing line. This possibility is highly unlikely. At the Reserva Ducke site the average ratio of oxygen to carbon isotopic discrimination is approximately 0.5. Thus any effect of photosynthesis on the relationship between \( \delta^{18}O \) and \( \delta^{13}C \) values of ambient \( \text{CO}_2 \) would hardly deviate from the theoretical mixing line which as an average slope of 0.57. For the Vitoria site, previous measurements indicate that turbulence at this site erases any photosynthetic signal (Sternberg et al., 1997).

Second, the \( \delta^{18}O \) value of plant water does not reflect the \( \delta^{18}O \) values of water with which \( \text{CO}_2 \) equilibrates during its residence time in the soil profile. According to our results, \( \text{CO}_2 \) equilibrates with water which is isotopically more enriched than that reflected by plant water. In a study of the global \( \text{CO}_2 \) budget (Farquhar et al., 1993) observed that on a global basis the average \( \delta^{18}O \) value of the respired \( \text{CO}_2 \) pool was \( 1.2^{\circ}/\text{o} \) higher than the value expected if the discrimination factor of \( 8.8^{\circ}/\text{o} \) was fully expressed on the \( \text{CO}_2 \) equilibrated with bulk soil water. One of the factors to
which this discrepancy was attributed was similar to this explanation, i.e., the soil water at the evaporation front is slightly more enriched than that of bulk soil water.

Third, the diffusion isotope fractionation factor is not fully expressed as CO₂ from respiration is liberated from the surface layer of the soil. This explanation follows from the observation that respiration in tropical forest soils can come from very shallow litter and root layers.

Fourth, there are other above ground sources of respired CO₂ in the forest liberating CO₂ which equilibrates with water having a higher δ¹⁸O value then soil water.

Observations on the δ¹⁸O values of water from the soil profile collected at the Fazenda Vitoria site during the sampling dates (Fig. 3) may help us determine which of the latter three explanations is more plausible. Recall that δ¹⁸O values of respired CO₂ (−6.7/‰) during the July sampling at the Fazenda Vitoria sites were higher than those predicted by previously used assumptions (−12.3/‰, Table 3). To test the second explanation, we consider the extreme case in which all the respired CO₂ is equilibrated with soil surface water. This water is the most enriched water available in the soil profile for equilibration. CO₂ equilibrated with surface water and subjected to the diffusion isotopic fractionation factor of 8.8/‰ would have a δ¹³C value of −9.5/‰. The value is still considerably lower than the observed δ¹⁸O value of respired CO₂ (−6.7/‰). If the discrimination factor is not expressed, then the δ¹⁸O value of the equilibrated CO₂ would be −0.7/‰ and substantially greater than that observed. This explanation cannot fully explain the discrepancy between observed and calculated δ¹⁸O values of respired CO₂, since only small differences in the isotopic composition of water in the Fazenda Vitoria soil profile to 1m depth were observed between July and December, yet there are large differences between δ¹⁸O values of respired CO₂ sample at these two dates (Table 3).

The fourth explanation can be eliminated by the observation that there are no differences in δ¹⁸O values of rainfall between July and December (Victoria et al., 1991). Since December is the end of the dry season one would expect that any above ground water source available for CO₂ equilibration would have a higher δ¹⁸O value in December compared to July. Using the above reasoning the δ¹⁸O values of the respired CO₂ from a hypothetical above ground respired source would be higher in December compared to July. Yet the opposite is observed: δ¹⁸O value of respired CO₂ in July is higher than that collected during December.

By the process of elimination we must conclude that a lower than 8.8/‰ diffusion isotopic fractionation factor contributes to the discrepancy between calculated and observed δ¹⁸O values of respired CO₂. This explanation is consistent with the phenomenon of litter decay and surface root respiration during periods when the soil surface is relatively wet (July samples). Because this source of CO₂ is so close to the surface the diffusion isotope fractionation factor may not be fully expressed. Therefore the δ¹⁸O values of respired CO₂ in July are higher than expected. Whereas at the end of the dry season (December samples), litter decay and surface root respiration decreases, the source of respired CO₂ is from lower depths of the soil profile, and the diffusion isotopic fractionation factor is fully expressed. Therefore δ¹⁸O values of respired CO₂ in December are as expected. This variation in the δ¹⁸O values of respired CO₂ is not seen in the Ducke reserve since this site does not have a pronounced seasonality as the Fazenda Vitoria site.

6. Conclusion

Our observations indicate an agreement between measured discrimination against ¹⁸O of CO₂ during photosynthesis in an eastern Amazonian site to that previously modeled in the Amazon basin. However, large discrepancies between measured and modeled ¹⁸O discrimination was observed in a central Amazonian site. The reasons for these discrepancies could be miscalculation of δ¹⁸O values of leaf water and/or vapor by the previous model. The determination of the various factors responsible for tropical ecosystem’s isotopic signature on the oxygen of CO₂ will be more complicated than temperate systems. Ambient CO₂ can equilibrate with wet surfaces and fog during nighttime condensation. Further, the isotopic identity of respired CO₂ cannot be calculated based on bulk soil water and a constant isotopic fractionation factor.
REFERENCES


