Simulation of carbon isotope discrimination of the terrestrial biosphere

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[1] We introduce a multistage model of carbon isotope discrimination during C3 photosynthesis and global maps of C3/C4 plant ratios to an ecophysiological model of the terrestrial biosphere (SiB2) in order to predict the carbon isotope ratios of terrestrial plant carbon globally at a 1° resolution. The model is driven by observed meteorology from the European Centre for Medium-Range Weather Forecasts (ECMWF), constrained by satellite-derived Normalized Difference Vegetation Index (NDVI) and run for the years 1983–1993. Modeled mean annual C3 discrimination during this period is 19.2%; total mean annual discrimination by the terrestrial biosphere (C3 and C4 plants) is 15.9%. We test simulation results in three ways. First, we compare the modeled response of C3 discrimination to changes in physiological stress, including daily variations in vapor pressure deficit (vpd) and monthly variations in precipitation, to observed changes in discrimination inferred from Keeling plot intercepts. Second, we compare mean δ13C ratios from selected biomes (Broadleaf, Temperate Broadleaf, Temperate Conifer, and Boreal) to the observed values from Keeling plots at these biomes. Third, we compare simulated zonal δ13C ratios in the Northern Hemisphere (20°N to 60°N) to values predicted from high-frequency variations in measured atmospheric CO2 and δ13C from terrestrially dominated sites within the NOAA-Globalview flask network. The modeled response to changes in vapor pressure deficit compares favorably to observations. Simulated discrimination in tropical forests of the Amazon basin is less sensitive to changes in monthly precipitation than is suggested by some observations. Mean model δ13C ratios for Broadleaf, Temperate Broadleaf, Temperate Conifer, and Boreal biomes compare well with the few measurements available; however, there is more variability in observations than in the simulation, and modeled δ13C values for tropical forests are heavy relative to observations. Simulated zonal δ13C ratios in the Northern Hemisphere capture patterns of zonal δ13C inferred from atmospheric measurements better than previous investigations. Finally, there is still a need for additional constraints to verify that carbon isotope models behave as expected.


1. Introduction

[2] Atmospheric CO2 concentrations have been increasing for the past 150 years due to combustion of fossil fuels, manufacture of cement, and biomass burning. In the 1980s, this anthropogenic CO2 was added to the atmosphere at a rate of approximately 5.4 ± 0.3 Pg-C/year; in the 1990s the rate was 6.3 ± 0.4 Pg-C/year [Intergovernmental Panel on Climate Change (IPCC), 2001]. However, over these same periods, atmospheric CO2 only increased at rates of 3.3 ± 0.1 and 3.2 ± 0.1 Pg-C/year, respectively. Consequently, during this time, there were natural sinks for nearly half of the anthropogenically added CO2. However, in spite of this knowledge of bulk changes in atmospheric CO2, the spatial and temporal distribution of the sinks, partitioning of the fluxes into land and ocean components, and the processes involved are still uncertain.
Carbon isotopes can be helpful in investigations of the sink because they give information about both sources and processes of CO2 exchange. At the local level, carbon isotopes are helpful in understanding (1) plant water use efficiency and the response of plants to changes in precipitation and relative humidity [Farquhar and Richards, 1984; Farquhar et al., 1988; Condon et al., 1993; Hall et al., 1993; Schulze et al., 1996, 1998; Ekblad and Högberg, 2001; Bowling et al., 2002; Ometto et al., 2002], (2) variation in light distribution and stand structure [Berry et al., 1997; Buchmann et al., 1997a, 1997b; Le Roux et al., 2001], (3) recycling of respired CO2 [Keeling, 1961; Schleser and Jayasekera, 1985; Sternberg, 1989; Lloyd et al., 1996; Sternberg et al., 1997], and (4) determining the relative contributions of photosynthesis and respiration to total net ecosystem exchange [Yakir and Wang, 1996; Bowling et al., 2001]. At the global scale, carbon isotopes have been used to (1) determine spatial and temporal distribution of sources and sinks and, in some cases, determine partitioning of oceanic and terrestrial fluxes [Francey, 1985; Keeling et al., 1989, 1995; Francey et al., 1995; Tans et al., 1993; Ciais et al., 1995a, 1995b; Enting et al., 1995; Fung et al., 1997; Rayner et al., 1999; Bousquet et al., 1999a, 1999b] and (2) to examine relative contributions of C3 and C4 plants to total primary productivity [Lloyd and Farquhar, 1994; Ehleringer et al., 1997; Sage et al., 1999]. Many of these studies show that plant discrimination can change rapidly and that it is very sensitive to environmental changes; however, most of the global models must make simplifying assumptions concerning carbon isotope discrimination of the terrestrial biosphere, and few models function on multiple spatial and temporal scales, so that the results can be directly compared to observations at both flux towers and flask stations.

Previous studies that modeled carbon isotope discrimination of the terrestrial biosphere used monthly mean values of temperature, precipitation, and humidity, were driven by meteorology produced in a GCM, or were produced using modeled vegetation [Lloyd and Farquhar, 1994; Fung et al., 1997; Kaplan et al., 2002], and none operate within the framework of GCM which is simultaneously calculating turbulent exchange of heat, water, and carbon fluxes between the biosphere and atmosphere. We wanted to construct a model that was capable of being driven by observed meteorology and vegetation so that results could be compared to historical records. We also wanted a model that could function online with a GCM so that we could examine systematic relationships between...
The intent of this paper is to (1) present the mechanics of a model and simulation of terrestrial carbon isotope discrimination, (2) present the results of a global simulation at \( \frac{1}{176} \) resolution that is driven by observed meteorology and satellite-derived vegetation characteristics, and (3) evaluate simulation results by comparing them to observations taken at different temporal and spatial scales. Specifically, we compare (1) the simulated relationship between \( \delta^{13}C \) of assimilated carbon and mean daily vapor pressure deficit (vpd) to field data from Bowling et al. [2002]; (2) the simulated relationship between \( \delta^{13}C \) of assimilated carbon and monthly precipitation to field data from Ometto et al. [2002]; (3) mean \( \delta^{13}C \) ratios for four biomes (Broadleaf, Temperate Broadleaf, Temperate Conifer, and Boreal) to observed \( \delta^{13}C \) of ecosystem respiration from those biomes [Pataki et al., 2003]; and (4) zonal mean assimilation-weighted \( \delta^{13}C \) ratios of terrestrial biomass for 20\(^\circ\)N to 60\(^\circ\)N to \( \delta^{13}C \) ratios of \( CO_2 \) fluxes inferred for terrestrially dominated stations of the NOAA Globalview Flask Network in the same latitude band [Miller et al., 2003].

2. Method

[6] SiB2 is a model of the terrestrial biosphere that calculates surface fluxes of sensible and latent heat, radiation, moisture, \( CO_2 \), and momentum for vegetated land points [Sellers et al., 1986, 1996a; Denning et al., 1996a; Schaefer et al., 2002]. SiB2 functions at local, regional, and global spatial scales, and can be driven by observed meteorology or coupled to a global climate model. In the present simulation, SiB2 is driven by assimilated meteorology for 1983–1993 provided by the European Centre for Medium-Range Weather Forecasting (ECMWF) with a \( \frac{1}{176} \) spatial resolution and a 6-hour time step (Figure 1) (see Schaefer et al. [2002] for more results from this particular simulation). ECMWF provides (1) wind speed at 10 m height, (2) temperature at 2 m, (3) relative humidity at 2 m, (4) total incident solar radiation, and (5) precipitation [Gibson et al., 1999]. Time-varying phenological properties such as leaf area index (LAI), the fraction of photosynthetically active radiation absorbed by the green canopy...
(FPAR), and canopy greenness fraction are linearly interpolated each day from monthly maps of processed normalized difference vegetation index (NDVI) calculated from AVHRR red and near-infrared reflectance [Los, 1998; Los et al., 2000]. Vegetation type is from Defries and Townshend [1994]. Other constant parameters, including canopy height and soil properties, are from look-up tables [Zobler, 1986; Sellers et al., 1996b]. The distribution of C3 and C4 plants (Figure 2) [Still et al., 2003] is determined using remote sensing products [Defries and Townshend, 1994; DeFries et al., 1998, 1999a, 1999b, 2000], physiological modeling [Collatz et al., 1998], crop fraction maps [Ramankutty and Foley, 1998], and areal coverage data on crop types [Food and Agriculture Organization (FAO), 1998]. Spatial resolution in the simulation is $1^\circ \times 1^\circ$. Recent improvements to SiB2 include the introduction of a six-layer soil temperature submodel based on the work of Bonan [1996, 1998] and a revised surface energy budget that includes prognostic temperature and moisture of the canopy air space reservoir [Baker et al., 2003]. The calculations are implicit and allow for canopy storage, i.e., memory. Model results have been evaluated at local scales [Baker et al., 2003], regional scales [Denning et al., 2003; Nicholls et al., 2004] and global scales [Denning et al., 1996b].

Another major change to SiB2 is the introduction of a scheme for calculating carbon isotope ratios of terrestrial CO$_2$ fluxes. Discrimination against $^{13}$C during C3 photosynthesis is the result of a multistage process (Figure 3) involving relatively small isotope effects during transport of CO$_2$ from the canopy to the chloroplast and a large isotope effect associated with fixation by ribulose biphosphate carboxylase/oxygenase (rubisco). Similar to equation (A6) in the Appendix of Farquhar and Richards [1984], we model this with three transport steps: (1) molecular diffusion across a laminar boundary layer at the leaf surface, (2) molecular diffusion through a stomatal pore into the stomatal cavity, and (3) dissolution into mesophyll water and aqueous transport to the chloroplast. This is followed by fixation with rubisco or other enzymes. Unlike Farquhar and Richards [1984], we do not include isotope effects associated with either dark respiration or photorespiration. This is because these effects are poorly characterized and probably quite small [Farquhar et al., 1989; O'Leary, 1993; Brugnoli and Farquhar, 2000]. During photosynthesis, a CO$_2$ concentration gradient from the atmosphere to the chloroplast produces a flux into the plant. At each step, there is a slightly different CO$_2$ concentration which we designate as follows: $C_a$ is CO$_2$ in the canopy air, $C_s$ is CO$_2$ in the leaf boundary layer, $C_i$ is CO$_2$ in the stomatal cavity, and $C_c$ is CO$_2$ at the chloroplast. A resistance modulates transport from one step to the next: $r_b$ for transport from the canopy air into the leaf boundary layer, $r_s$ for transport through the stomatal pore, and $r_m$ for transport to the chloroplast. These steps are also associated with isotope effects discriminating against $^{13}$C: $\Delta_{b}$, $\Delta_{s}$, $\Delta_{diss}$, and $\Delta_{aq}$, respectively. Finally, there is an isotope effect during enzymatic fixation with rubisco, $\Delta_f$. The $\Delta$ values that we use are $\Delta_{b} = 2.9\%o$, $\Delta_{s} = 4.4\%o$, $\Delta_{diss} = 1.1\%o$, $\Delta_{aq} = 0.7\%o$, $\Delta_f = 28.2\%o$.
and $\Delta_f = 28.2\%$, where $\Delta$ is defined as follows. For the reaction $A \rightarrow B$,

$$\Delta_{AB} = 1000 \cdot (\alpha_{AB} - 1)$$  \hspace{1cm} (1)

$$\alpha_{AB} = \frac{R_d}{R_B} = \frac{(\delta_d + 1000)}{(\delta_B + 1000)}.$$  \hspace{1cm} (2)

where $R_d = [^{13}C/^{12}C]_d$ and $R_B = (R_d/R_{PDB}) - 1 \times 1000$ and $R_{PDB}$, the $^{13}C/^{12}C$ ratio of Pee Dee Belemnite, is equal to 0.0112372 [Craig, 1957]. Units for $\delta$ and $\Delta$ are per mil ($\%$). $\Delta = (\delta_d - \delta_B)/(\delta_B/1000 + 1) \approx (\delta_d - \delta_B)$. $\delta_d$ and $\Delta_d$ are from theoretical calculations of molecular diffusion of $CO_2$ through air and across a laminar boundary layer [Craig, 1953; Farquhar, 1983]. $\Delta_{dis}$ and $\Delta_{aq}$ are from laboratory measurements [Mook et al., 1974; O’Leary, 1984]. At the chloroplast, $CO_2$ can react with rubisco or other enzymes. The fraction reacting with other enzymes is not well known. Raven and Farquhar [1990] have suggested that the upper limit is about 10%. In our simulation, $\Delta_f$ is calculated by assuming that 92.5% of the assimilated $CO_2$ reacts with rubisco with an isotope effect of 30.0% [Brugnoli and Farquhar, 2000], while the remaining reacts with phospho-phenyl pyruvate carboxylase (PEPC), with an isotope effect of 5.7% [Farquhar, 1983], giving a net isotope effect ($\Delta_f$) of 28.2%. Total isotope fractionation during C3 photosynthesis ($\Delta_{PS(C3)}$) is given by the sum of the concentration gradient-weighted isotope effects for each stage,

$$\Delta_{PS(C3)} = \Delta_a \left( \frac{C_{s} - C_{a}}{C_{a}} \right) + \Delta_s \left( \frac{C_{s} - C_{i}}{C_{a}} \right) + \left( \Delta_{dis} + \Delta_{aq} \right) \left( \frac{C_{i} - C_{c}}{C_{a}} \right) + \left( \Delta_{f} \right) \frac{C_{c}}{C_{a}}$$  \hspace{1cm} (3)

Mesophyll conductance ($g_{m}$, where $g_{m} = 1/r_{m}$) is calculated using the following equation:

$$g_{m} = 4000 \times v_{m0} \times \Pi \times RSTFAC,$$  \hspace{1cm} (8)

where $v_{m0}$ is the maximum rate of photosynthesis of sunlit leaves at the top of the canopy and is derived from the literature. $\Pi$ is an integrating factor that expresses photosynthetic rate of the entire canopy as a function of the top leaf rate and the ability of the canopy to use photosynthetically active radiation (PAR). $\Pi$ is strongly influenced by changes in NDVI. RSTFAC is a soil water stress factor [Sellers et al., 1996a] (see also Evans and Loreto [2000] and references therein for a discussion of the effects of soil water stress on mesophyll conductance). Four thousand is a constant used to adjust mesophyll conductance to achieve a drop in $CO_2$ pressure between $C_i$ and $C_c$ of about 8 Pa at high rates of photosynthesis [Evans and Loretto, 2000].

[8] C4 photosynthesis also discriminates against $^{13}C$, but to a much lesser extent. In C4 plants, $CO_2$ is “captured” in the stomatal cavity and transported to the site of enzymatic fixation with PEPC. Since nearly all of the $CO_2$ that reaches the site of fixation in C4 plants is assimilated, the kinetic isotope effects that are expressed are largely those involved in transport. Consequently, in this model we assume that carbon isotopic discrimination in C4 plants is constant and equal to the isotope effect associated with diffusion through the stomatal pore, i.e., $\Delta_{PS(C4)} = 4.4\%$.

[9] There have been several previous studies modeling global terrestrial discrimination [Lloyd and Farquhar, 1994; Fung et al., 1997; Kaplan et al., 2002]. These studies differ from ours in the following ways (Table 1). Lloyd and Farquhar calculate monthly net assimilation as a simple function of climatologic monthly mean 0.5° × 0.5° temperature and precipitation [Friedlingstein et al., 1992; Leemans and Cranker, 1991] and monthly 2.5° × 2.5° wet and dry bulb temperatures from ECMWF. Landcover is from Wilson and Henderson-Sellers [1985]. Stomatal $CO_2$ concentrations are calculated using an analytic model of optimal stomatal behavior with respect to water use efficiency. Chloroplastic $CO_2$ concentrations are based on observed relationships between canopy $CO_2$, stomatal $CO_2$, and chloroplastic $CO_2$. C3 discrimination is calculated using an equation similar to (3), although they include effects of autotrophic respiration and photorespiration and neglect the effect of transport across the leaf boundary layer. The effect of both of these differences on net discrimination is small. C3/C4 distributions in the work of Lloyd and Farquhar are based on a combination of physiological modeling and landcover maps from Wilson and Henderson-Sellers [1985]. C4 plants account for 21% of global GPP. C4 discrimination is a function of internal $CO_2$ concentrations and the leakiness of the bundle sheath cells. Net global C4 discrimination in the work of Lloyd and Farquhar is 3.6%. Total discrimination (C3 and C4) in the work of Lloyd and Farquhar is 14.8%; C3 discrimination is 17.8%. 

[5]
Table 1. Comparison of the Most Important Features and Results From Three Previous Studies of Global Carbon Isotope Fractionation of the Terrestrial Biosphere to Those of the Present Studya

<table>
<thead>
<tr>
<th>Study</th>
<th>Net Assimilation</th>
<th>Internal CO₂ Concentrations</th>
<th>C₃ Discrimination Calculations</th>
<th>C₃/C₄ Ratios</th>
<th>C₄ Discrimination, %</th>
<th>C₃ Discrimination, %</th>
<th>Net Discrimination, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Lloyd and Farquhar</em> [1994]</td>
<td>calculated using climatologic monthly mean 0.5° x 0.5° temperature and precipitation and 2.5° x 2.5° wet and dry bulb temperatures from ECMWF</td>
<td>internal CO₂ calculated using observed relationships between canopy, stomatal, and chloroplast CO₂ concentrations</td>
<td>calculated similarly to equation (3) except that isotope effects of photorespiration and autotrophic respiration are included and leaf boundary layer effects are not</td>
<td>variable; averages 3.6%; calculated based on internal CO₂ concentrations and leakiness of bundle sheath cells</td>
<td>17.8%</td>
<td>14.8%</td>
<td></td>
</tr>
<tr>
<td><em>Fung et al.</em> [1997]</td>
<td>monthly mean 4° x 5° net assimilation from SiB2 coupled to global climate model</td>
<td>uses monthly assimilation-weighted Ci/Ca ratios calculated in SiB2, which simultaneously solves for Ci, stomatal conductance and net assimilation</td>
<td>C₃ discrimination is calculated in a two-step model that includes transport into stomatal cavity followed by fixation with rubisco</td>
<td>fixed at 4.4%</td>
<td>20.0%</td>
<td>15.7%</td>
<td></td>
</tr>
<tr>
<td><em>Kaplan et al.</em> [2002]</td>
<td>net assimilation modeled in BIOME4, driven by 0.5° x 0.5° climatology (Climate 2.2)</td>
<td>calculated water-limited Ci/Ca ratios in a process-based model of canopy conductance</td>
<td>C₃ discrimination is calculated in a similar fashion to Lloyd and Farquhar</td>
<td>calculated similarly to Lloyd and Farquhar</td>
<td>20.0 ± 1.0%</td>
<td>18.1% with the agricultural mask or 18.6% without it</td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>we determine net assimilation rates each 10 min using SiB2.5, which is driven by 6-hourly assimilated meteorology from ECMWF; vegetation parameters are constrained by satellite observations, i.e., FASIR-NDVI</td>
<td>each time step we simultaneously solve for Cc, stomatal conductance, and net assimilation; other internal CO₂ concentrations are functions of net assimilation and internal resistances</td>
<td>C₃ discrimination is calculated using a four-step model that includes transport across the leaf boundary layer, through the stomatal pore, aqueous phase transport, and fixation with rubisco</td>
<td>C₃/C₄ ratios are calculated using physiological modeling, satellite observations and agricultural maps; C₄ plants account for 24% of GPP</td>
<td>fixed at 4.4%</td>
<td>19.2%</td>
<td>15.9%</td>
</tr>
</tbody>
</table>

*Please see text for detailed references.
A. Mean Annual $\delta^{13}$C of Plant Carbon ($\%$ vs. PDB)

B. Standard Deviation in Annual $\delta^{13}$C of Plant Carbon ($\%$)

Figure 4
[11] Fung et al. [1997] calculate net assimilation at a 4° × 5° resolution using monthly mean output from an older version of SiB2 coupled to a global climate model [Sellers et al., 1996a, 1996b; Randall et al., 1996]. Fung et al. calculate net assimilation-weighted C3/C4 ratios by simultaneously solving for Cc, stomatal conductance, and net assimilation. Discrimination is based on a two-step model of photosynthesis that includes only transport of CO2 into the leaf, followed by enzymatic fixation. Fung et al. assume that savannas are 75% C4 and land areas covered by shrubs and groundcover are 50% C4. C4 plants make up 27% of GPP. C4 discrimination is fixed at 4.4‰. Total discrimination in the work of Fung et al. is 15.7‰; C3 discrimination is 20.0‰.

[12] Kaplan et al. [2002] calculate net assimilation using a model of the terrestrial biosphere (BIOME4) driven by 0.5° × 0.5° gridded climatology (Climate 2.2), which is an updated version of work by Leemans and Cramer [1991]. Vegetation, including C3/C4 distributions, is determined in a dynamic vegetation model with an agricultural mask. Kaplan et al. calculate water-limited C3/C4 ratios in a process-based model of canopy conductance. The discrimination model is similar to that of Lloyd and Farquhar. C4 plant distributions in BIOME4 are determined in a dynamic vegetation model with an agricultural mask. C4 plants constitute only about 15% of global GPP, significantly less than suggested by the models here (J. O. Kaplan, personal communication, 2004), which range from 21% to 27% or the 18% estimated by Ehleringer et al. [1997]. C4 discrimination in the work of Kaplan et al. is determined in a manner similar to that of Lloyd and Farquhar. Discrimination for C4 plants is not given. Total discrimination in the work of Kaplan et al. is 18.6‰ or 18.1‰ with the agricultural mask; C3 discrimination is 20.0 ± 1.0‰. The higher total discrimination in the work of Kaplan et al. relative to the other models, as well as observations [Balwin et al., 1998; Miller et al., 2003], is probably due largely to differences in global C3/C4 distributions.

[13] Our simulation calculates net assimilation each 10-min time step using an updated version of SiB2 coupled to assimilated 6-hourly 1° × 1° weather from ECMWF for 1983 through 1993. We calculate internal CO2 concentrations each time step in SiB2 as described earlier. One difference between our simulation and that of Fung et al. [1997] is that we calculate net assimilation solving for Cc instead of C4. Discrimination is determined using equation (3). As Fung et al. point out, all other things being equal, neglecting isotope effects during transport of CO2 from the stomatal cavity to the chloroplast can reduce total C3 discrimination by about 2–3‰. However, since we calculate net assimilation using Cc instead of C4, net assimilation rates are lower and consequently the change in discrimination is much less than 2–3‰. We use C4 maps based on physiological modeling, satellite observations, and agricultural maps [Still et al., 2003]. C4 plants constitute 25% of GPP. C4 discrimination is fixed at 4.4‰. Total discrimination in this study is 15.9‰; C3 discrimination is 19.2‰. A final feature of our discrimination module is that it can be coupled to a prognostic canopy air space and can thus be used to examine systematic variations between discrimination and transport on the time step of the simulation including recycling of respired CO2 and Rayleigh-type distillation of canopy CO2 during daytime photosynthesis.

[14] The δ13C values reported here are weighted by assimilation. 12C and 13C fluxes are calculated separately for C3 and C4 plants and then summed to get grid values for each time step. At the end of the year, we divide by total net assimilation to retrieve the δ13C of plant carbon assimilated within that grid cell during the preceding year. At the end of the 11-year run, we calculate mean and standard deviation of annual assimilation weighted δ13C ratios for each 1° × 1° grid cell. Since we want to focus here on the response of the terrestrial discrimination to climate variations, we hold the concentration and carbon isotope ratio of canopy CO2 constant. This necessarily neglects the influence of variations in δ13C of canopy CO2 on δ13C of assimilated carbon due to (1) recycling of respired CO2, (2) enrichment of canopy CO2 in 13C due to preferential removal of 12C during photosynthesis, (3) turbulent mixing with the atmospheric boundary layer, and (4) seasonal variations in δ13C of atmospheric CO2. A subsequent analysis will evaluate the influence of a dynamic canopy on δ13C of terrestrial fluxes.

3. Results and Discussion

3.1. Spatial Variations in δ13C of Plant Carbon

[15] Spatial variations in δ13C of plant carbon are complex and reflect climate, water availability, biome type and C3/C4 distributions (Figure 4a). In general, the lightest δ13C values for are found at high northern latitudes and reflect both the absence of C4 plants and increased discrimination in C3 plants due to zonal variations in the modeled Cc/C4 ratio. The starkest contrasts globally are those produced by variations in C3/C4 distributions. There is a zonal trend to this discrimination and its influence on δ13C; that is, the heaviest δ13C values are found approximately 10° to 20° north and south of the equator, mirroring the distribution of C4 grasslands.

Figure 4. (a) Mean annual assimilation-weighted δ13C of terrestrial plant carbon from an 11-year simulation (1983–1993) and (b) standard deviation in annual δ13C values. During each time step, net assimilation is multiplied by the δ13C of assimilated plant carbon. At the end of the year, the sum of net assimilation times δ13C is divided by total annual net assimilation to give the δ13C value of carbon assimilated in each grid cell during that calendar year. The mean is the average of the 11 annual values. The standard deviation is also for those 11 values. Please note the higher resolution used in reporting more negative mean values (Figure 4a). This is done in order to highlight spatial variations in C3 discrimination. There is tremendous spatial variability in δ13C values of terrestrial carbon. The sharpest spatial contrasts are the result of differences in C3/C4 ratios. Variation in δ13C values of C3 plants is largely driven by differences in relative humidity during the growing season. Larger than average standard deviations are found in areas where ECMWF predicts significant variations in annual precipitation. See color version of this figure at back of this issue.


Table 2. Simulated δ13C of Total Plant Carbon and δ13C of C3 Plant Carbon

<table>
<thead>
<tr>
<th>Biome</th>
<th>n</th>
<th>δ13C(C3) mean (%)</th>
<th>δ13C(C3) 1σ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Broadleaf Evergreen</td>
<td>1098</td>
<td>−25.0 ± 2.8</td>
<td>−26.6 ± 0.34</td>
</tr>
<tr>
<td>Broadleaf Deciduous</td>
<td>320</td>
<td>−21.9 ± 4.9</td>
<td>−25.9 ± 1.2</td>
</tr>
<tr>
<td>Broadleaf and Needleleaf</td>
<td>769</td>
<td>−25.4 ± 1.9</td>
<td>−26.3 ± 0.42</td>
</tr>
<tr>
<td>Needleleaf</td>
<td>2018</td>
<td>−27.1 ± 0.6</td>
<td>−27.1 ± 0.41</td>
</tr>
<tr>
<td>Needleleaf Deciduous</td>
<td>952</td>
<td>−26.6 ± 0.4</td>
<td>−26.6 ± 0.38</td>
</tr>
<tr>
<td>Broadleaf With Groundcover</td>
<td>1457</td>
<td>−18.3 ± 4.6</td>
<td>−26.5 ± 0.89</td>
</tr>
<tr>
<td>Groundcover (maize optical)</td>
<td>779</td>
<td>−15.4 ± 4.4</td>
<td>−25.8 ± 1.6</td>
</tr>
<tr>
<td>Broadleaf Shrubs and Bare Soil</td>
<td>1035</td>
<td>−21.3 ± 6.0</td>
<td>−25.4 ± 1.1</td>
</tr>
<tr>
<td>Tundra and Dwarf Trees</td>
<td>1528</td>
<td>−27.0 ± 0.5</td>
<td>−26.9 ± 0.50</td>
</tr>
<tr>
<td>Low-Latitude Deserts</td>
<td>1602</td>
<td>−25.7 ± 2.2</td>
<td>−26.0 ± 0.87</td>
</tr>
<tr>
<td>Broadleaf Deciduous Over Wheat</td>
<td>3079</td>
<td>−24.3 ± 3.3</td>
<td>−25.8 ± 0.73</td>
</tr>
</tbody>
</table>

*Values are means and standard deviations for all grid cells within the biome from the map of 11-year mean values. The δ13C values of plant carbon are based on a δ13C value for atmospheric CO2 of −7.9‰ versus PDB.

However, there are also important longitudinal patterns in δ13C values that are produced not only by C3/C4 distributions, but also by variations in climate and biome type. Examples of this include the influence of high C4 ratios in the North American Plains and African Sahel on δ13C of terrestrial biomass of the Western and Eastern Hemispheres. Table 2 presents δ13C ratios of all plants (δ13CTot) and C3 plants only (δ13C(C3)) broken down by biome.

[16] The standard deviations in annual δ13C values for individual grid cells for the 11 years are generally less than 0.3‰ (Figure 4b). The largest standard deviations are generally found in areas where ECMWF predicts large variations in annual precipitation and occasional drought. The most prominent example is the western and southern edges of the Amazon basin, which in ECMWF reanalysis experienced significantly drier conditions in 1983–1986, relative to the rest of the 11-year simulation.

3.2. Evaluation of Model Results

3.2.1. C3 Discrimination and Vapor Pressure Deficit

[17] Laboratory and field studies show that discrimination in C3 plants is largely controlled by the influence of vapor pressure deficit (vpd) on stomatal conductance and C3/C4 ratios [Farquhar and Richards, 1984; Farquhar et al., 1982, 1989; Berry, 1988; Condon et al., 1993; Hall et al., 1993]. Since vpd of canopy air changes over the course of the day and from one day to the next, carbon isotope discrimination should change as quickly. Until recently, however, it has been difficult to quantify changes in discrimination in natural ecosystems on these short timescales.

[18] Nighttime Keeling plot intercepts record δ13C of respired CO2 fluxes (δ13CvR) from aboveground (bole, stem, leaf, and heterotrophic) and belowground (root and decomposing soil organic matter) sources [Keeling, 1958]. Högborg et al. [2001] have shown that tree girdling reduced soil respiration by up to 37% after only 5 days, indicating that roots are responsible for approximately 40% of the total soil CO2 flux. Using the fact that δ13C of root respiration reflects the carbon isotope ratio of recent photosynthate [Andrews et al., 1999; Lin et al., 1999], Ekblad and Högborg [2001] and Bowling et al. [2002] then demonstrated that variations in δ13C of ecosystem respiration are strongly correlated with changes in relative humidity and/or vapor pressure deficit that have occurred within the previous 2 to 10 days. Consequently, changes in nighttime Keeling plot intercepts reflect humidity-induced changes in discrimination through the release of recently fixed carbon during autotrophic respiration.

[19] In order to evaluate the ability of our model to accurately represent the relationship between C3 discrimination and relative humidity, we compare simulated mean daily vapor pressure deficits and assimilation-weighted δ13C values for C3 plants to the observed relationships (Figure 5). We have chosen sites similar to those presented by Ekblad and Högborg [2001] and Bowling et al. [2002], as well as others spanning a range of vapor pressure deficits and biomes. In general, the model successfully captures the relationship between vpd and δ13C and is bracketed by the observations. However, there are differences between model results and observations that are worth noting. The δ13C values in the simulation are similar to those observed by Ekblad and Högborg, but slightly less negative than those of Bowling et al. There are a couple of reasons that it is difficult to assess the importance of these absolute differences in δ13C values. First, both sets of observations include undetermined offsets due to the fact that the δ13C of decomposing soil organic matter (SOM) is unknown. In general, CO2 from decomposing SOM is thought to be enriched in δ13C relative to recently fixed photosynthate as a consequence of a terrestrial “Suess Effect” [e.g., Ciais et al., 1999]. On the basis of flux-weighted ages of decomposing SOM [Fung et al., 1997] and a long-term record of δ13C of atmospheric CO2 [Francey et al., 1999], we might expect δ13C of SOM in northern Sweden to be enriched relative to recent photosynthate by about 0.7‰, whereas the sites of Bowling et al. would be slightly less enriched and more variable (0.2‰ to 0.7‰). However, these are only rough estimates, and more would have to be known about the age and turnover rate of the SOM at specific sites to be more precise. If decomposing soil organic matter produced 60% of the soil CO2 flux, a 0.7‰ offset would mean that δ13C of recently fixed carbon was approximately 0.4‰ more negative than observations indicate. Another problem with comparing the two studies is that they use slightly different methodologies. The differences include: (1) different methods were used for collecting and analyzing gas samples, (2) Ekblad and Högborg looked at a single site, whereas Bowling et al. used four sites, (3) Ekblad and Högborg used a 2- to 3-day lag time, whereas Bowling et al. used lag times ranging from 5 to 10 days, and (4) Ekblad and Högborg took climate data from a weather station at the site, whereas Bowling et al. had to infer climatic conditions from stations located farther afield. Finally, Ekblad and Högborg fit the data to a linear equation, while Bowling et al. were more successful with a logarithmic fit. Nevertheless, the simulated results are consistent with both studies, and both the model and observations show that stomatal response to changes in vapor pressure...
deficit in the canopy air is a dominant control on discrimination on diurnal timescales.

3.2.2. C3 Discrimination and Monthly Precipitation

Ometto et al. [2002] examine the relationship between C3 discrimination and monthly precipitation in tropical forest sites of the Amazon basin. In data collected near Santarém, Brazil, there is an inverse relationship between δ13C of ecosystem respiration (δ13CR) and monthly precipitation that persists at rain rates up to 300 mm/month. At much higher rates of precipitation, i.e., greater than 400 mm/month, the relationship appears to reverse. They argue that at the lower rain rates, changes in δ13CR are controlled by stomatal-induced variations in C3 discrimination caused by a combination of soil water stress and relative humidity. It is unclear why discrimination decreases at precipitation rates greater than 400 mm/month. Ometto et al. also collected data from a second tropical forest site near Manaus, Brazil. At Manaus, the relationship between δ13CR and monthly precipitation is less clear, even though the site is similar in many respects to that of Santarém.

We examined the relationship between monthly precipitation and C3 discrimination in the simulation for the grid cell containing Santarém, Brazil, as well as a temperate forest grid cell containing the WLEF tall tower site in Wisconsin (Figure 6). In the simulation, C3 discrimination increases with increasing monthly precipitation. The relationship is slightly nonlinear, with a steeper slope at very low rates of precipitation. In other words, changes in
precipitation rates have a greater impact on carbon isotope discrimination under very dry conditions than they do when the environment is already wet. Discrimination at WLEF is about 1% less than that predicted for Santarém, largely because of the greater relative humidity of the tropical forested site. Model results agree with the observations to the extent that we predict a positive correlation between monthly precipitation and discrimination; however, there are several important differences between the model and observations. First, observed \( \delta^{13}C_{\text{R}} \) for both Santarém and Manaus is depleted in \(^{13}\text{C} \) by up to 2% relative to modeled discrimination. Second, the slope of the relationship in the observations at Santarém is about 3 times greater than the slope predicted for the grid cell containing Santarém. In the observations, \(^{13}\text{C} \) of ecosystem respiration decreases by approximately 3% for changes in precipitation from 50 to 300 mm/month; in the simulation, the change is closer to 1%. Third, at Santarém, \(^{13}\text{C} \) of ecosystem respiration returns to heavier values at precipitation rates greater than 400 mm/month, whereas modeled discrimination continues to increase with increasing precipitation rates.

Figure 6. Relationship between monthly precipitation and C3 discrimination. Discrimination has been converted from del values using the formula: Discrimination = \((\delta^{13}\text{C}_{\text{air}} - \delta^{13}\text{C}_{\text{R}})/(1000)\); where \(\delta^{13}\text{C}_{\text{air}} = -7.9\%o\) and \(\delta^{13}\text{C}_{\text{R}} \) is the carbon isotope ratio of ecosystem respiration. Triangles and asterisks are from measurements in primary evergreen tropical forests: triangles (Santarém, Brazil), asterisks (Manaus, Brazil) [see Ometto et al., 2002, Figure 7]. The error bars represent the standard error of the isotope measurement. The curve is a second-order polynomial fit to the data from Santarém. The open circles are simulated discrimination for the grid box containing Santarém. Simulated data from Manaus are nearly identical. The solid squares are simulated discrimination for summer months for the grid box containing WLEF tower in Wisconsin. The lines through the simulated data are logarithmic fits to the data.

[22] Reasons for the enrichment in modeled values relative to observations at both Santarém and Manaus will be addressed later in the paper. With respect to the relationship between discrimination and monthly precipitation, we think that there may be several reasons for the differences between the model and observations at Santarém. First, while we have no reason to doubt the results of Ometto et al. [2002], the question must be asked: Is this site representative of tropical forest behavior in general? Data collected at Manaus do not refute the relationship observed at Santarém; however, neither do they confirm it. In part, this is because of the narrow range of monthly precipitation rates observed at Manaus; however, more data will have to be collected before we can say that the behavior at Santarém is characteristic of tropical forests in general. A second possibility is that there are important natural variations accompanying changes in monthly precipitation that are not captured in the model. The two most probable candidates are relative humidity and/or soil water. Since SiB2 seems to do a good job simulating the relationship between discrimination and vapor pressure deficit, the problem may be with the way that we model soil water stress. Throughout the 11 years of the simulation, there is no significant soil water stress on plant growth in the grid cell containing Santarém, even during the driest months. Unfortunately, we have no observations to directly compare to the simulation. Terrestrial ecosystem models sometimes predict decreases in photosynthetic rates during the tropical forest dry season due to drought stress; however, this decline in assimilation rates is not always supported by the observations [Tian et al., 1998; Saleska et al., 2003]. Finally, there is a similar
pattern between observed mean carbon isotope composition of ecosystem respiration and mean annual precipitation; that is, discrimination increases with increasing precipitation up to a point, where it then returns to lower values at very high rain rates. In the simulation, annually integrated $\delta^{13}C$ values are generally more negative in wet climates, and they do not return to less negative values in extremely wet climates.

3.2.3. C3 Discrimination by Biome

The number of measurements of $\delta^{13}C_R$ that have been collected is constantly increasing and can serve as an additional method for evaluating simulation results. Data for Figure 7 are taken from Pataki et al. [2003] and show mean $\delta^{13}C_R$ values and standard deviations for four different biomes: Broadleaf, Temperate Broadleaf, Temperate Conifer, and Boreal. We have plotted mean $\delta^{13}C_R$ values and standard deviations for comparable biomes from our simulation against the observed values. In general, simulated mean values are relatively close to the observed means, and the standard deviations encompass the range of observed values. However, there are a couple of important differences between the simulation and the observations. First, the mean model $\delta^{13}C_R$ for the tropical forests is 1% less negative than the mean of the observations. If simulated discrimination in the tropical forests is incorrect, it could be the result of a couple of factors. First, our estimate for maximum C3 discrimination (28.2%) may be too small. This could be because the isotope effect that we use for CO$_2$ fixation with Rubisco (30%) is not large enough, or because of our assumption that 7.5% of the carbon fixed by C3 plants occurs through reactions with PEPC is too great. Either one is a possibility. Measurements of isotope effects associated with rubisco are precise, but the values range from approximately 26% to 38% [O’Leary, 1981; Brugnoli and Farquhar, 2000]. With respect to the amount of CO$_2$ in C3 plants that reacts with PEPC, very little is known. A maximum of 10% has been suggested [Raven and Farquhar, 1990] and Lloyd and Farquhar [1994] assumed that it was 5%, so perhaps our estimate of 7.5% is too high. Changing from 7.5% to 5% reduces discrimination by about 0.6%. Of course, while the change improves the match to observed $\delta^{13}C_R$ for tropical forests, it hurts the fit with Boreal and Temperate Broadleaf biomes. Another possibility is that there are biome-specific differences in this fraction of which we are unaware. A second reason why our $\delta^{13}C$ values for tropical forests are enriched in $^{13}C$ relative to observations could be due to the fact that we do not include the effects of recycling of isotopically depleted respired CO$_2$. In this study we hold $\delta^{13}C$ of canopy CO$_2$ constant at $-7.9\%$. Estimates of the amount of respired CO$_2$ that is recycled are as high as 30 to 40% [Sternberg et al., 1997], although others have argued that it is actually quite negligible [Lloyd et al., 1996, 1997]. In sensitivity tests in which we coupled the biosphere to a dynamic canopy, recycling was greatest in tropical forests, which is consistent with observations, and caused $\delta^{13}C$ of assimilated carbon to be depleted in $^{13}C$ by 1–4%. Working against this effect, however, is an offset due to the terrestrial “Suess Effect.” On the basis of flux-weighted ages of decomposing SOM [Fung et al., 1997] and a long-term record of $\delta^{13}C$ of atmospheric CO$_2$ [Francey et al., 1999], the terrestrial Suess Effect in tropics is estimated to be about $+0.6\%$, which would counter some of the effects of recycling. A second
and perhaps more important difference between the observations and the model is that there appears to be a wider range of values in the observations than in the model. Unfortunately, there are still so few observations that it is difficult to know how representative they are. Nonetheless, it is entirely possible that the wider range of values in the observations is due to heterogeneity within biomes that is not captured by the model.

3.2.4. Zonal Trends in δ13C of Plant Carbon Compared to Atmospheric Data

[24] Results of the simulation can also be compared to atmospheric data. Miller et al. [2003] have analyzed high-frequency deviations from a seasonal spline fit to time series of CO2 and δ13C measurements from continental stations from the NOAA Globalview Flask Network in order to deduce the carbon isotopic ratios of growing season CO2 fluxes in the Northern Hemisphere. They argue that these deviations from the seasonal signal are produced by fluxes to and from the local vegetation and are therefore a record of the isotopic ratio of that vegetation. Miller et al. have plotted the δ13C values from these sites as a function of latitude, as well as zonal mean δ13C values from Fung et al. [1997] and Lloyd and Farquhar [1994]. Their figure is recreated here with the addition of our zonal mean assimilation-weighted δ13C values for the Northern Hemisphere growing season (Figure 8). While it is difficult to make a direct comparison, because the observations largely represent regional values of terrestrial discrimination, it appears that our zonal mean is an improvement over previous simulations in that it captures some of the flatness of the signal between 20°N and 40°N, as well as the rapid descent to more negative values north of 40°N. Furthermore, although we are still limited by a paucity of data, both observations and simulated results indicate that spatial distribution of δ13C values of the terrestrial biosphere are more complex than previously thought.

4. Conclusion

[25] A multistage model of carbon isotope discrimination during photosynthesis and global maps of C3/C4 plant ratios coupled to an ecophysiological model of the terrestrial biosphere driven by observed meteorology and constrained by satellite-derived NDVI has been used to predict the carbon isotope ratios of terrestrial plant carbon. Simulated mean annual C3 discrimination for 1983–1993 is 19.2%; total mean annual discrimination by the terrestrial biosphere (C3 and C4 plants) is 15.9%.

[26] It is very difficult to constrain the details of the simulated results because we are still sorely lacking in observations. However, within these limitations we find the following. The modeled response to changes in vapor pressure deficit compares favorably to observations. Simulated monthly discrimination in tropical forests is less sensitive to changes in precipitation than is suggested by some observation. Mean model δ13C ratios for Broadleaf, Temperate Broadleaf, Temperate Conifer, and Boreal biomes compare well with the few measurements available; however, there is more variability in observations than in the simulation, and modeled δ13C values for tropical forests appear heavy relative to observations. Finally, simulated zonal δ13C ratios in the Northern Hemisphere capture the complexity of the zonal δ13C inferred from atmospheric measurements better than previous investigations.

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Figure 2. Distribution of C3 and C4 plants [Still et al., 2003] is determined using remote sensing products [Defries and Townshend, 1994; DeFries et al., 1998, 1999a, 1999b, 2000], physiological modeling [Collatz et al., 1998], crop fraction maps [Ramankutty and Foley, 1998], and areal coverage data on crop types [FIO, 1998].
Figure 4

A. Mean Annual $\delta^{13}$C of Plant Carbon (%o vs. PDB)

B. Standard Deviation in Annual $\delta^{13}$C of Plant Carbon (%o)
Figure 4. (a) Mean annual assimilation-weighted $\delta^{13}C$ of terrestrial plant carbon from an 11-year simulation (1983–1993) and (b) standard deviation in annual $\delta^{13}C$ values. During each time step, net assimilation is multiplied by the $\delta^{13}C$ of assimilated plant carbon. At the end of the year, the sum of net assimilation times $\delta^{13}C$ is divided by total annual net assimilation to give the $\delta^{13}C$ value of carbon assimilated in each grid cell during that calendar year. The mean is the average of the 11 annual values. The standard deviation is also for those 11 values. Please note the higher resolution used in reporting more negative mean values (Figure 4a). This is done in order to highlight spatial variations in C3 discrimination. There is tremendous spatial variability in $\delta^{13}C$ values of terrestrial carbon. The sharpest spatial contrasts are the result of differences in C3/C4 ratios. Variation in $\delta^{13}C$ values of C3 plants is largely driven by differences in relative humidity during the growing season. Larger than average standard deviations are found in areas where ECMWF predicts significant variations in annual precipitation.
Figure 8. Zonal $\delta^{13}$C ratios of terrestrial biosphere from Miller et al. [2003] (data points with error bars), Lloyd and Farquhar [1994] (red line), Fung et al. [1997] (green line), and this study (blue line).