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# A comprehensive global three-dimensional model of $\delta^{18}\text{O}$ in atmospheric $\text{CO}_2$ :

## 1. Validation of surface processes

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[1] We have built the first comprehensive global three-dimensional model of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$ . The constructed model goes beyond all other approaches made until now, by simulating the diurnal variations and transport of  $\text{CO}_2$ ,  $\delta^{18}\text{O}$  of water, and  $\delta^{18}\text{O}$  of  $\text{CO}_2$ . The  $\text{CO}^{18}\text{O}$  fluxes are thereby dependent on the atmospheric  $\text{CO}^{18}\text{O}$  composition. We have validated the model surface processes, showing that it compares well to other estimates and measurements of NPP, NEE, and stomata-internal  $\text{CO}_2$  mixing ratio ( $c_i$ ), except for high northern latitudes. Here, the model is considerably lower in NPP and higher in  $c_i$  than other model estimates. However, estimates derived indirectly from observations tend to support our model findings. The water isotopes of rain are reproduced very well at all latitudes. The soil bucket model used in the model integrates incoming rain in one single value. The bucket approach overattenuates the isotopic variations of rain, and hence our isotopic source signature of respiration shows almost no seasonal cycle and is thus isotopically too depleted during summer. *INDEX TERMS*: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 1610 Global Change: Atmosphere (0315, 0325); 1615 Global Change: Biogeochemical processes (4805); 3210 Mathematical Geophysics: Modeling; *KEYWORDS*: isotope model,  $^{18}\text{O}$  in  $\text{CO}_2$ ,  $^{18}\text{O}$  in  $\text{H}_2\text{O}$ , ecosystem model, biosphere-atmosphere exchange, isotope discrimination

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## 1. Introduction

[2] The atmospheric signal of  $\text{CO}_2$  is an integrated measure of all processes adding  $\text{CO}_2$  to and removing  $\text{CO}_2$  from the atmosphere. Consequently, one can deduce only the net  $\text{CO}_2$  flux from atmospheric measurements. Inversion studies of atmospheric  $\text{CO}_2$  measurements make therefore only predictions of net  $\text{CO}_2$  fluxes over different regions [e.g., Gurney *et al.*, 2002]. To separate the different components of the net flux, several tracers are used, depending on the component. For example,  $^{13}\text{C}$  is used to differentiate between ocean and terrestrial biosphere fluxes, or  $^{14}\text{C}$  is used to separate the fossil fuel combustion component.  $^{18}\text{O}$  offers the possibility to separate the different terrestrial biospheric gross fluxes, namely assimilation and respiration. This is because  $\text{CO}_2$  can exchange  $^{18}\text{O}$  atoms with two isotopically distinct water pools, either with leaf

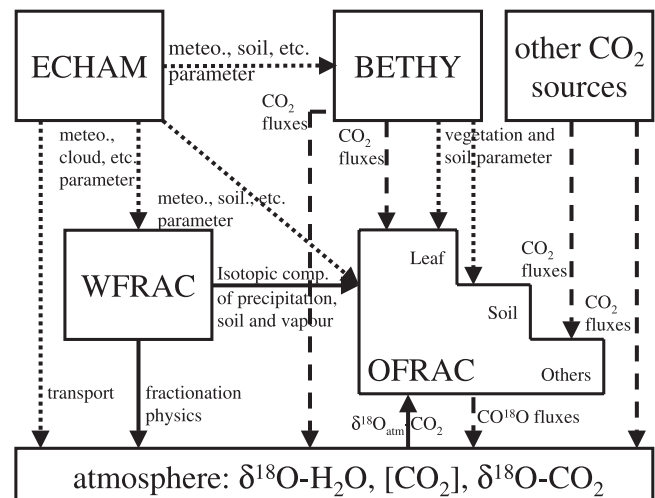
water or with soil water. Statistically, a  $\text{CO}_2$  molecule going into plant leaves is fixed by photosynthesis with a probability of 1/3 whereas it diffuses back to the atmosphere with a probability of 2/3. Nevertheless, the isotopic exchange between  $\text{CO}_2$  and water within leaves in the presence of the enzyme carbonic anhydrase is so fast that back-diffused  $\text{CO}_2$  re-entering the atmosphere is isotopically "tagged" by evaporating leaf water. Leaf water at the evaporating site is generally significantly enriched with respect to soil moisture and so is leaf  $\text{CO}_2$  with respect to soil respired  $\text{CO}_2$ . However, unlike the case of  $^{13}\text{C}$ , where the ocean,  $\text{C}_4$  plants, and  $\text{C}_3$  plants have distinct, narrowly defined signatures that are similar all over the globe, the  $^{18}\text{O}$  isotopic labeling of  $\text{CO}_2$  by photosynthesis and respiration varies in space and time, reflecting hydrological processes and climate-dependent fractionation factors. This means that in order to understand the integrated atmospheric signal of  $^{18}\text{O}$  in  $\text{CO}_2$ , one must use a spatially explicit model of surface fluxes bound to a three-dimensional model of the atmospheric transport including water isotopic composition.

[3] Few studies have attempted so far to model the distribution of  $^{18}\text{O}$  in atmospheric  $\text{CO}_2$ . The major conceptual difficulty lies in the requirement of a triad of models describing (1) the gross carbon fluxes, (2) the water isotope variability, and (3) the atmospheric transport. *Ciais et al.* [1997a, 1997b] have put together those three components using output from different published models that were sampled as monthly averages. This approach gave a reasonably good comparison with atmospheric observations and provided useful a priori estimates to inverse modeling of the gross fluxes [Peylin, 1999], but it remains unsatisfactory for three reasons: First, there were inconsistencies among the different models that were used to construct  $\text{CO}^{18}\text{O}$  fluxes inducing systematic errors that are impossible to estimate. Second, working with monthly mean fluxes does not permit proper up-scaling of biogeochemical processes from the ecosystem level up to the quasi global atmospheric signal. Third, working with monthly fluxes neglects the existence of a strong daily cycle in the fluxes of photosynthesis and respiration that unfortunately covary with atmospheric transport in the boundary layer to generate mean gradients in  $\text{CO}_2$  and in  $\delta^{18}\text{O}\text{-CO}_2$ .

[4] In this paper, we present a new, comprehensive model of  $^{18}\text{O}$  in atmospheric  $\text{CO}_2$  where leaf and soil processes that determine the isotopic fluxes are encapsulated into a land surface carbon flux model, interfaced to a global atmospheric circulation model. The  $\text{CO}_2$  and  $\text{CO}^{18}\text{O}$  flux model is described in section 2, and its results are compared against ground based, pointwise  $\text{CO}_2$  flux measurements and isotopic data in section 3. A companion paper is devoted to the comparison between background measurements of  $\text{CO}_2$  and  $\delta^{18}\text{O}\text{-CO}_2$  in flask samples and the modeled  $\delta^{18}\text{O}\text{-CO}_2$  values obtained by atmospheric transport acting on surface sources [Cuntz et al., 2003] (hereinafter referred to as part 2).

## 2. Model Description

[5] The model, named ECHAM/BETHY or BETHY online, includes four parts, which are shown in Figure 1. ECHAM is the Atmospheric General Circulation Model (AGCM) within which are embedded the calculations for the isotopic composition of different water reservoirs (WFRAC), as well as the atmospheric tracer transport. BETHY is a biosphere model which is driven with variables from ECHAM; it releases its calculated  $\text{CO}_2$  surface fluxes into the ECHAM atmosphere. OFRAC is the  $\text{CO}^{18}\text{O}$  flux module which takes ECHAM and BETHY variables and the  $\delta^{18}\text{O}$  value of  $\text{CO}_2$  in the ECHAM atmosphere to calculate  $\text{CO}^{18}\text{O}$  fluxes which are emitted in the atmosphere of ECHAM. Later, we will describe the different parts of the model. We introduce ECHAM and WFRAC only briefly because they are described in detail elsewhere [Modellbetreuungsguppe, 1994; Hoffmann et al., 1998]. Extensive descriptions of BETHY are given by Knorr [1997, 2000] and Knorr and Heimann [2001a, 2001b] but we describe the main aspects that influence the calculations of  $\text{CO}^{18}\text{O}$  fluxes. OFRAC is based on the equations of *Ciais et al.* [1997a], which were adapted to calculate the  $\text{CO}^{18}\text{O}$  fluxes online in an AGCM. We explain them in detail to elaborate on the differences between ECHAM/BETHY and earlier  $\delta^{18}\text{O}\text{-CO}_2$  models.



**Figure 1.** Interactions between the different parts of the model. ECHAM is the AGCM in which the water isotopes (WFRAC) and the tracer transport are included. BETHY is interfaced and the  $\text{CO}^{18}\text{O}$  isotope module (OFRAC) is ‘coupled’ to ECHAM. Solid lines stand for isotopic processes, dashed lines stand for  $\text{CO}_2$  and  $\text{CO}^{18}\text{O}$  fluxes and dotted lines stand for physical and meteorological parameters, and for transport.

[6] ECHAM is a state-of-the-art AGCM that has been used in several studies [e.g., Arpe et al., 1994; Roeckner et al., 1992]. In this study, we used the T21 spectral truncation scheme, which corresponds to a physical grid of  $5.6^\circ \times 5.6^\circ$  (time step of 40 minutes). The model has 19 vertical layers from surface pressure up to a pressure level of 30 hPa and includes a tracer transport scheme. WFRAC is implemented in ECHAM, and calculates for each phase of ‘‘normal’’ water,  $\text{H}_2\text{O}$ , two isotopic counterparts,  $\text{H}_2^{18}\text{O}$  and  $\text{HDO}$ . It has shown its excellent capability to simulate recent, paleo water and snow isotope distributions in a variety of studies [e.g., Hoffmann et al., 1998, 2000; Werner et al., 2001].

### 2.1. The $\text{CO}_2$ Flux Model BETHY

[7] We interfaced a process-based model of terrestrial vegetation activity, the Biosphere Energy—Transfer Hydrology scheme (BETHY) to the AGCM ECHAM. BETHY calculates  $\text{CO}_2$  fluxes of the terrestrial biosphere, together with additional diagnostic variables for the biosphere, e.g., stomatal conductance and vegetation temperature. For BETHY offline model descriptions please refer to Knorr [1997, 2000] and Knorr and Heimann [2001a, 2001b]. We interfaced BETHY rather than coupling it to ECHAM; this will be done in a future step. That means that BETHY online does not interfere in the AGCM ECHAM. BETHY online is forced by meteorological variables of ECHAM but ECHAM is not influenced by BETHY. In addition, BETHY uses its own land-surface scheme. Therefore in order to obtain realistic evapotranspiration rates, vegetation temperatures and, hence, realistic stomatal conductances from the ECHAM energy and water budgets, we recompute the latent and sensible heat fluxes from the canopy of BETHY (even if they are already computed by ECHAM with its internal land surface scheme). Since plants lose water through their sto-

**Table 1.** List of Plant Functional Types Used in the BETHY Online Model With Assigned Parameters<sup>a</sup>

	Plant Functional Types <sup>b</sup>	$V_m$	$J_m/k$	$h_V$	$C_4$
1	Trop. BL E trees	60	118	30.0	
2	Trop. BL D trees	90	179	15.0	
3	Temp. BL E trees	41	82	15.0	
4	Temp. BL D trees	35	70	15.0	
5	E coniferous trees	29	52	15.0	
6	D coniferous trees	53	95	15.0	
7	E shrubs	52	102	1.0	
8	D shrubs	160	266	1.0	
9	C <sub>3</sub> short grass	42	80	0.3	
10	C <sub>3</sub> long grass	42	80	2.0	
11	C <sub>4</sub> short grass	8	140	0.3	x
12	C <sub>4</sub> long grass	8	140	2.0	x
13	Tundra vegetation	20	37	0.3	
14	Swamp vegetation	20	37	0.3	
15	Arable crops	117	220	0.6	
16	Irrigated crops	123	227	0.6	
17	Tropical tree crops	60	106	2.0	
18	Citrus crops	60	106	2.0	
19	Temp. D tree crops	123	227	2.0	
20	Sugar cane	39	700	2.0	x
21	Maize	39	700	2.0	x
22	Rice	98	190	0.3	
23	Cotton	123	227	1.0	

<sup>a</sup> $V_m$ , maximum carboxylation rate at 25°C in  $\text{mol}(\text{CO}_2) \text{ m}^{-2} \text{ s}^{-1}$ ;  $J_m$ , maximum electron transport rate at 25°C in  $\text{mol}(\text{CO}_2) \text{ m}^{-2} \text{ s}^{-1}$  (C<sub>3</sub>), or  $k$ , PEPcase rate constant for CO<sub>2</sub> at 25°C (and standard pressure) in  $\text{mol}(\text{CO}_2) \text{ m}^{-2} \text{ s}^{-1}$  (C<sub>4</sub>);  $h_V$ , height in m; C<sub>4</sub>, using C<sub>4</sub> photosynthetic pathway instead of C<sub>3</sub>.

<sup>b</sup>Abbreviations: Trop., tropical; Temp., temperate; BL, broad-leaved; E, evergreen; D, deciduous.

matal pores while photosynthesizing, water availability is related closely to carbon uptake.

[8] The relationship between canopy net assimilation rate  $F_A$  (gross assimilation rate, “GPP”, minus leaf respiration,  $F_{Rleaf}$ ), canopy conductance  $g_c$  (integral over stomatal conductances  $g_s$ ), and stomata-internal CO<sub>2</sub> mixing ratio  $c_i$  is:

$$F_A = g_c(c_a - c_i) \quad (1)$$

where  $c_a$  is the mixing ratio of atmospheric CO<sub>2</sub> in ppm =  $\text{mol}(\text{CO}_2)/\text{mol}(\text{air})$  and  $g_c$  is expressed in  $\text{mol}(\text{CO}_2) \text{ m}^{-2} \text{ s}^{-1}$ . The photosynthesis part of the model computes absorption of photosynthetically active radiation (PAR) through the canopy with a two-flux scheme [Sellers, 1985] for three vertical layers of equal LAI, gross carbon uptake, and leaf respiration. Carbon uptake and leaf respiration are described with the so-called Farquhar model for C<sub>3</sub> [Farquhar et al., 1980] and a similar model for C<sub>4</sub> plants [Collatz et al., 1992]. These are process-oriented models which require a rather large number of kinetic and structural parameters. Plant functional types used, together with the assigned parameters are shown in Table 1. To describe the stomatal response to environmental factors a semi-empirical approach is used, with only one free parameter. Observations suggest that in the absence of water limitation, canopy conductance is determined by photosynthetic demand for CO<sub>2</sub> [Schulze et al., 1994]. So a non-water-stressed canopy conductance,  $g_{c0}$ , is first computed at a standard non-water-stressed stomata-internal CO<sub>2</sub> mixing ratio,  $c_{i0}$  [Jones, 1983; Knorr, 1997]:

$$g_{c0} = \frac{F_{A0}}{c_a - c_{i0}} \quad (2)$$

where  $F_{A0}$  is the non-water-limited net leaf CO<sub>2</sub> uptake in  $\text{mol}(\text{CO}_2) \text{ m}^{-2} \text{ s}^{-1}$  and  $g_{c0}$  is given in  $\text{mol}(\text{CO}_2) \text{ m}^{-2} \text{ s}^{-1}$ . If

photosynthesis is limited by availability of soil water, stomata are assured to close, in response to air vapor pressure deficit,  $\Delta e$  [Schulze et al., 1987; Schulze, 1986; Turner, 1986; Fischer and Turner, 1978]. We use the empirical formula [Lindroth and Halldin, 1986]:

$$g_c = g_{c0} \frac{1}{1 + b_e \Delta e}. \quad (3)$$

The factor  $b_e$  is assumed to change such that transpiration through the stomata does not exceed the root supply rate,  $S$  [Federer, 1982]:

$$S = c_w \frac{W_s}{W_{s,max}} \quad (4)$$

where  $W_s$  is the soil water content adjusted to take soil freezing into account,  $W_{s,max}$  the maximal root available soil water content and  $c_w$  an empirical parameter representing root density. We adopted a value of  $c_w = 0.5$  mm/hour from a comparison with measured values of  $F_A$  and  $g_c$  for single days [Knorr, 1997] and a global sensitivity study on this parameter [Knorr and Heimann, 2001a].

[9] The computational and logical steps are as follows: the BETHY online model first calculates  $F_A$  as  $F_{A0}$  from the Farquhar model using  $c_{i0}$ . The non-water-stressed canopy conductance,  $g_{c0}$ , is then computed from equation (2) (at  $c_i = c_{i0}$ ). After determining  $g_c$  from equation (3), the Farquhar model is resolved with unknown  $c_i$  but with the additional constraint that equation (1) must be satisfied.

[10] There are several descriptions of heterotrophic or soil respiration [Raich and Potter, 1995; Lloyd and Taylor, 1994; Raich and Schlesinger, 1992; Meentemeyer, 1978] that have in common that soil respiration approximately follows temperature, and that micro-organisms need water to produce CO<sub>2</sub>. We use the formulation of Raich and Potter [1995] with  $Q_{10} = 1.5$  and 2 m air temperature,  $T_a$ , because this smaller value is more consistent with the observed seasonal cycle of atmospheric CO<sub>2</sub> [Knorr and Heimann, 1995] compared to the more ‘traditional’ value of  $Q_{10} = 2.0$  [Raich and Schlesinger, 1992]. Furthermore, we include a proportional dependence on actual over potential evapotranspiration,  $f_e$  [Meentemeyer, 1978]:

$$F_{Rhet} = c_1 f_e Q_{10}^{T_a/10} \quad (5)$$

where

$$f_e = \frac{E_v}{E_{vmax}}. \quad (6)$$

$E_v$  is the actual and  $E_{vmax}$  the maximum possible transpiration rate from soil and vegetation. The rate  $c_1$  is renormalized such that the mean of  $F_{Rhet}$  over 10 years equals the mean of NPP at every grid point; i.e., the terrestrial biosphere is supposed to be in equilibrium.

[11] The BETHY online version does not include a phenology scheme but rather it is taken as monthly input from the offline version of BETHY optimized with satellite-derived fraction of photosynthetically active radiation absorbed by vegetation (FPAR) [Knorr and Heimann, 2001b].

## 2.2. Nonbiospheric CO<sub>2</sub> Fluxes

[12] Ciais et al. [1997b] stated that one needs biomass burning and fossil fuel emissions to model a more realistic



north-south gradient of  $\delta^{18}\text{O}\text{-CO}_2$ . Hence we introduce into the atmosphere nonbiospheric  $\text{CO}_2$  fluxes from linear interpolation between monthly mean input fields. First, we take the formulation of *Wanninkhof* [1992] to compute the air-sea gas exchange coefficient and the instantaneous ECHAM wind fields to calculate  $\text{CO}_2$  ocean fluxes from the ocean  $\Delta p\text{CO}_2$  compilation of *Takahashi et al.* [1999]. Second, we include fossil fuel  $\text{CO}_2$  emissions via the annual compilation of *Andres et al.* [1996] which we distributed on a monthly basis with coefficients given by *Marland et al.* [1998]. Further, we introduce biomass burning emissions into the atmosphere. These include forest and savannah burning (seasonal) and agricultural wastes and fuel wood burning (annually constant) [*Hao and Liu*, 1994]. All fluxes are scaled to values representative of the year 1990. However, regrowth after burning is not included in the online version of BETHY, and we have no closed carbon cycle, though, respiration is supposed to be in equilibrium with assimilation. One can see below in equation (23) that the  $\delta^{18}\text{O}\text{-CO}_2$  cycle depends on gross biospheric fluxes which are at least one order of magnitude higher than the net biospheric fluxes and especially the missing fluxes required to close the carbon cycle in the model.

### 2.3. The $\text{CO}^{18}\text{O}$ Flux Module OFRAC

[13] The  $\delta^{18}\text{O}$  isotopic signature of  $\text{CO}_2$  is determined mainly by the isotopic equilibrium reaction:



If this reaction occurs in nature, in most cases there are several orders of magnitude more water associated than  $\text{CO}_2$ . That means that the isotopic signature of  $\text{CO}_2$  is fully determined by the isotopic signature of the equilibrating water which is barely changing itself. This equilibration process is temperature dependent, and the fractionation follows the relationship [*Brenninkmeijer et al.*, 1983]:

$$\epsilon_{eq}(T) = \left( \frac{17604}{T} - 17.93 \right) / 1000, \quad (8)$$

where

$$\alpha_{eq}(T) = 1 + \epsilon_{eq}(T) \quad (9)$$

is the fractionation factor. For example, the fractionation at  $25^\circ\text{C}$  is:  $\epsilon_{eq} = +41.1\text{‰}$  and  $d\epsilon_{eq}/dT = -0.2\text{‰ } ^\circ\text{C}^{-1}$ . This implies that higher temperatures lead to more depleted  $\delta^{18}\text{O}\text{-CO}_2$  values with constant  $\delta^{18}\text{O}\text{-H}_2\text{O}$ . The isotope ratio of  $\text{CO}_2$ ,  $R$ , equilibrated with water of composition  $R^W$  is hence:  $R = \alpha_{eq}(T) R^W$ . The rate of isotopic equilibration,  $^{18}k_H$ , is thereby one third as fast as the rate of hydration of  $\text{CO}_2$  in water,  $k_H$ , because there are three oxygen atoms involved in reaction 7 and only one oxygen atom comes from  $\text{H}_2\text{O}$ .  $k_H$  is  $0.0062 \text{ s}^{-1}$  at  $20^\circ\text{C}$  [*Stern et al.*, 1999] and  $^{18}k_H$  is therefore  $0.0021 \text{ s}^{-1}$ . This means that the e-folding time of hydration is lower than 3 min (with the Bunsen solubility close to 1, which is true for  $\text{CO}_2$  and if the entry of  $\text{CO}_2$  into water is not rate limiting) and the e-folding time of isotopic equilibration is about 8 min.  $\text{CO}_2$  is thus equilibrated isotopically with ocean water, and with soil water in a certain depth (on the order of 10 cm). The

enzyme carbonic anhydrase present in leaf water speeds up the reaction rate by a factor of  $10^7$  [*Stryer*, 1981] so that  $\text{CO}_2$  is also equilibrated isotopically with leaf water. However, the e-folding time is too long for  $\text{CO}_2$  to hydrate in cloud droplets and more than ever too long to equilibrate isotopically with cloud water [*Francey and Tans*, 1987].

[14] A flux of  $\text{CO}_2$  from one contributing process,  $F$ , is accompanied by a flux of  $\text{CO}^{18}\text{O}$ ,  $^{18}F$ . If there are exchanges of  $\text{CO}_2$  between two compartments, pools or reservoirs, or if there is a phase transition, a fractionation occurs because of differing diffusivities ( $\alpha$  can be higher, lower or equal to 1). For example, the complex phenomenon of diffusion out of the soil is accompanied by just one fractionation factor in our model. The  $\text{CO}^{18}\text{O}$  flux is calculated therefore as:

$$^{18}F = \alpha \alpha_{eq}(T) R^W F \quad (10)$$

where  $\alpha$  represents the fractionation occurring at the transition from one compartment or phase into another.

[15] Our  $\text{CO}_2$  fluxes are supposed to be  $\text{C}^{16}\text{O}^{16}\text{O}$  fluxes alone and not the sum of  $\text{C}^{16}\text{O}^{16}\text{O}$  and  $\text{C}^{16}\text{O}^{18}\text{O}$  flux. This overestimates  $F$  by about 0.4% (the natural abundance of  $^{18}\text{O}$  is approximately 0.2% [*Firestone et al.*, 1999]) which is negligible. Treating  $F$  as  $\text{C}^{16}\text{O}^{16}\text{O}$  and  $\text{C}^{16}\text{O}^{18}\text{O}$  flux would require to recompute  $\alpha$ 's and  $R$ 's which are measured quantities and therefore the ratios of  $^{18}\text{O}$  to  $^{16}\text{O}$  concentrations (and not  $^{18}\text{O}$  to  $^{18}\text{O}$  plus  $^{16}\text{O}$ ). For example, this would change the soil fractionation  $\epsilon_s$  (see below), which is taken here as  $-7.20\text{‰}$ , to  $-7.19\text{‰}$ . The recomputation would change our  $^{18}F$  fluxes by approximately 0.2%, which leads to a change in  $\delta$  of 0.02‰. Recomputation would not lead to perceptible changes in the results so that we discard recomputation for simplicity. We would also like to point out that all tracers are calculated as  $\text{CO}_2$  and  $\text{CO}^{18}\text{O}$  concentrations in the model. The  $\delta$  notation, leading to isofluxes, discriminations etc. and used to display the results, is only introduced through post-processing. This guarantees mass conservation in our calculations.

#### 2.3.1. Respiration

[16] From the above it follows directly the soil  $\text{CO}^{18}\text{O}$  flux,  $^{18}F_R$ :

$$^{18}F_R = \alpha_s R_s F_R = \alpha_s \alpha_{eq}(T_s) R_s^W F_R \quad (11)$$

where  $R_s^W$  is the isotopic ratio of the soil water reservoir that exchanges with  $\text{CO}_2$  and is taken directly from the water isotope module, and  $F_R$  is the  $\text{CO}_2$  flux from the soil to the atmosphere which comes from BETHY (see below). Soil fractionation,  $\epsilon_s = \alpha_s - 1$ , is due to the different diffusivities of  $\text{CO}_2$  and  $\text{CO}^{18}\text{O}$  in air. The maximum theoretical value is  $-8.7\text{‰}$  is for a pure molecular diffusive process. The diffusion through the laminar-viscose boundary layer at the soil-atmosphere interface fractionates differently (approximately  $-5.8\text{‰}$ ) and the effective diffusion fractionation depends on the relative influence of molecular and 'laminar-viscose' diffusion. Former studies of  $\delta^{18}\text{O}\text{-CO}_2$  [*Ciais et al.*, 1997a, 1997b; *Peylin et al.*, 1997, 1999] claimed that model outcome is sensitive to this parameter. *Ciais et al.* used a value of  $-5.0\text{‰}$  in order to prevent a secular trend in  $\delta^{18}\text{O}\text{-CO}_2$  of the atmosphere. *Peylin et al.* [1997] studied the sensitivity of this fractionation factor together with the

fractionation associated with assimilation, and found possible values also around  $-5.0\%$ , matching the seasonal amplitude at Point Barrow and the inter-hemispheric difference. However, in their model  $\delta^{18}\text{O}$  of atmospheric  $\text{CO}_2$ ,  $\delta_a$ , was forced to  $0\%$  versus VPDB- $\text{CO}_2$  and they used the fractionation factors of soil and above-ground vegetation as free parameters to obtain zero trend in their recalculated  $\delta_a$  values. The ECHAM/BETHY isotope module calculates  $\delta_a$  ( $R_a$ ) and  $\text{CO}^{18}\text{O}$  fluxes depending on  $\delta_a$  ( $R_a$ ) at every time step, and therefore  $\delta_a$  stabilizes globally (see equation (23)). That means that the fractionation factors can theoretically have any possible value and  $\delta_a$  will have no trend after the asymptotic equilibrium value is reached. For  $\epsilon_s$ , we take the recent value of *Miller et al.* [1999]:  $\epsilon_s = -7.2\%$ . *Miller et al.* give this value for the fractionation of  $\text{CO}_2$  diffusion from soils when one takes the soil water isotopic composition at 15 cm depth. They included in this global estimate the “invasion” effect that is explained below. We include the portion of the autotrophic respiration,  $F_{R_{\text{auto}}}$ , which is not emitted via leaves,  $F_{R_{\text{root}}} = F_{R_{\text{auto}}} - F_{R_{\text{leaf}}}$ , into  $F_R$ . Most of the  $\text{CO}_2$  of the autotrophic respiration  $F_{R_{\text{auto}}}$  is emitted by roots belowground (root respiration) and is thus subject to the same fractionation as the heterotrophic respiration. There is a small part of  $F_{R_{\text{root}}}$  which is emitted aboveground by stems and twigs. *Bariac et al.* [1994a, 1994b] showed that there is almost no difference between the isotopic value of soil and plant organic water (except for leaves). Also,  $\text{CO}_2$  in stems and twigs is expected to be in isotopic equilibrium with water. Thence we include this flux in  $F_{R_{\text{auto}}}$  so that  $F_R$  is the heterotrophic plus autotrophic (without leaf) respiration:  $F_R = F_{R_{\text{het}}} + F_{R_{\text{auto}}} - F_{R_{\text{leaf}}}$ , which we call bio-respiration.

[17] There is another flux at the air-soil interface which exists for  $\text{CO}^{18}\text{O}$  and not for  $\text{CO}_2$ . The transport of  $\text{CO}_2$  is a diffusional process, and therefore the sum of two gross fluxes in and out of the soil. The flux into the soil is small because of the large mixing ratio difference of  $\text{CO}_2$  in the soil and in the atmosphere. *Tans* [1998] wrote the net flux for  $\text{CO}^{18}\text{O}$  as the sum of one flux leaving the soil, the above  $F_R$ , and a second flux of  $\text{CO}_2$ -molecules entering the soil with the atmospheric isotope signature, equilibrating with soil water and leaving the soil with the signature of soil water. This second flux is called the “abiotic flux” [*Stern et al.*, 2001] or “invasion flux” and the effect is called “invasion” [*Tans*, 1998]. This means,  $\text{CO}_2$  with the isotopic composition  $R_a$  entering the soil equilibrates with soil water,  $R_s^W$ , and leaves the soil with the isotopic signature  $R_s$ . The invasion flux,  $^{18}F_{\text{inv}}$ , is then:

$$\begin{aligned} ^{18}F_{\text{inv}} &= \sqrt{\Theta_a \kappa \Theta_w^{18} k_H D_{18} B c_a (R_s - R_a)} \\ &= F_{\text{inv}} (R_s - R_a) \end{aligned} \quad (12)$$

with

- $\Theta_a$  air-filled pore fraction of soil;
- $\kappa$  tortuosity;
- $\Theta_w$  water-filled pore fraction;
- $^{18}k_H$   $\text{CO}^{18}\text{O}$  equilibration rate with  $\text{H}_2^{18}\text{O}$ , equal to  $k_H/3$ ;
- $D_{18}$  free-air molecular diffusivity of  $\text{CO}^{18}\text{O}$ ;
- $B$  Bunsen solubility coefficient.

$F_{\text{inv}}$  may be seen as a virtual  $\text{CO}_2$  flux, which is convenient for further calculations.

### 2.3.2. Assimilation

[18]  $\text{CO}_2$  needs approximately 3 min at  $10^\circ\text{C}$  for hydration in water. The average residence time of a  $\text{CO}_2$  molecule in the stomata is about 0.02 s [*Ciais et al.*, 1997a]. However, there is the enzyme carbonic anhydrase in leaves which catalyzes and speeds up the reaction by a factor of  $10^7$  [*Stryer*, 1981]. This implies that every  $\text{CO}_2$  molecule entering the stomata is hydrated. Then, the isotopic equilibrium reaction (equation (7)) can take place and  $\text{CO}_2$  is in isotopic equilibrium with the water between the mesophyll cell wall and the chloroplast. There is a gradient between the  $\text{CO}_2$  concentration in the stomata,  $c_i$ , and in the chloroplast,  $c_c$ , during photosynthesis. There is no gradient if there is no photosynthetic activity. Leaf-scale measurements indicate that the average drawdown is of the order  $(c_i - c_c)/c_a \approx 0.1 - 0.2$  [*Yakir and Sternberg*, 2000; *Lloyd and Farquhar*, 1994]. However, the equilibration process occurs mainly at the chloroplast or cellular membrane (plasmalemma) where the average drawdown is approximately 0.1 [*Gillon and Yakir*, 2000a]. We denote the mixing ratio where the equilibrium reaction occurs as  $c_{cs}$  because it is likely to be at the surface of the chloroplast [*Yakir*, 1998]. We take for  $c_{cs}$  the stomata-internal  $\text{CO}_2$  mixing ratio  $c_i$  as a first guess and try to quantify the consequences of different equilibration places afterward (see the companion paper [*Cuntz et al.*, 2003]). Using  $c_{cs}$ , equation (1) becomes:

$$F_A = g_s(c_a - c_i) = g'_s(c_a - c_{cs}) \quad (13)$$

where  $g'_s$  is the (harmonic) sum of the stomatal conductance and the conductance between the stomata and the plasmalemma (precisely the inverse of the sum of the resistances). Assuming that the conductance is very similar for  $\text{CO}_2$  and for  $\text{CO}^{18}\text{O}$ , the diffusion equation (13) for  $\text{CO}^{18}\text{O}$  is:

$$^{18}F_A = \alpha_l g'_s (R_a c_a - R_l c_{cs}) = \alpha_l g'_s (R_a c_a - \alpha_{eq}(T_v) R_l^W c_{cs}) \quad (14)$$

where  $^{18}F_A$  is the flux of  $\text{CO}^{18}\text{O}$  molecules into the leaves,  $\alpha_l$  the kinetic fractionation factor for diffusion into the stomata ( $\epsilon_l = -7.4\%$  [*Farquhar et al.*, 1993]), and  $R_l^W$  the isotopic composition of leaf water at the site of equilibration. Equation (13) shows that net assimilation is the sum of two opposing fluxes, in and out of the stomata. Rewriting the equation gives that the gross flux into the stomata is  $F_A c_a / (c_a - c_{cs})$  and the flux out of the stomata is  $F_A c_{cs} / (c_a - c_{cs})$ . This means that only about 1/2 to 1/3  $[(c_a - c_{cs})/c_a]$  of all  $\text{CO}_2$  molecules entering the leaf will finally be assimilated. The isotopic composition of leaf water at the site of equilibration,  $R_l^W$ , is calculated with the *Craig and Gordon* [1965] steady state approximation:

$$R_{l-cg}^W = \alpha_{l-vap}^W \left( \frac{(1-h)R_i^W}{\alpha_k^W} + hR_{vap}^W \right) \quad (15)$$

with

- $h$  relative humidity adjusted to leaf temperature;
- $\alpha_{l-vap}^W$  fractionation factor for  $\text{H}_2^{18}\text{O}$  at the water-vapor phase transition;

$\alpha_k^W$  combined kinetic fractionation factor for  $\text{H}_2^{18}\text{O}$  for diffusion through the stomata and the leaf boundary layer;  
 $R_{vap}^W$   $^{18}\text{O}/^{16}\text{O}$  ratio of water vapor in canopy air;  
 $R_i^W$   $^{18}\text{O}/^{16}\text{O}$  ratio of xylem water, supplied to the leaf, approximately equal to  $^{18}\text{O}/^{16}\text{O}$  ratio of soil water.

The isotope ratios of vapor and soil water are calculated from the water isotope module at every time step. Relative humidity is an ECHAM diagnostic variable (adjusted to leaf temperature), and the canopy is approximated by the first ECHAM model layer. The fractionation of the water-vapor phase transition is calculated from *Majoube* [1971]. The kinetic fractionation,  $\epsilon_k^W$ , is higher for molecular than for turbulent diffusion [*Merlivat and Jouzel*, 1979]. It depends also on plant physiology [*White*, 1983] and on wind speed [*Förstel et al.*, 1975]. We take a global value of  $\epsilon_k^W = -26.0\%$  [*Farquhar et al.*, 1993] which itself results in an error. This error is diminished by the fact that  $\alpha_k^W$  is weighted with the factor  $(1-h)$  which is often close to 0. This is not true for dry areas but these are normally associated with low photosynthetic activity. The Craig and Gordon steady state approximation is probably not 'reached' by leaf water at every time step. Measurements indicate a time lag between measured values and values calculated with the Craig and Gordon model [e.g., *Roche*, 1999]. To overcome this problem, one can use a transitory model whereby the leaf water value is a mixture of the Craig and Gordon calculation and the value one time step before [*Dongmann et al.*, 1974; *Förstel et al.*, 1975; *Bariac et al.*, 1994a, 1994b]:

$$R_l^{W(t)} = R_{l-cg}^{W(t)} - \left( R_{l-cg}^{W(t)} - R_l^{W(t-1)} \right) \exp \left\{ -\frac{1}{\tau \zeta} \Delta t \right\} \quad (16)$$

with

$R_l^{W(t)}$  leaf water isotopic composition at the site of evaporation at time  $t$ ;  
 $R_l^{W(t-1)}$  leaf water isotopic composition at time step  $t-1$ ;  
 $R_{l-cg}^{W(t)}$  Craig and Gordon steady state solution at time  $t$ ;  
 $\tau$  turnover time of leaf water, equal to  $V_l/E_v$ , where  $E_v$  is the transpiration rate and  $V_l$  is the leaf water volume;  
 $\zeta = (1-h)(\epsilon_{l-vap}^W + 1)(\epsilon_k^W + 1)$ .

To estimate the exponential weighting factor, one needs the leaf water volume contributing to evapotranspiration,  $V_l$ , for which, to our knowledge, there are no estimates in the literature for different plant functional types. So we compared the steady state Craig and Gordon model and the transitional nonsteady state model to laboratory measurements on Rajmah red kidney beans (*Phaseolus vulgaris*) [*Roche*, 1999] and field measurements made during the EUROSIBERIAN CARBONFLUX (compare Appendix A) campaign in a 150 year old *Picea abies* (Norway Spruce) forest in Russia [*Langendörfer et al.*, 2002]. Both data showed a time lag of about two hours between Craig and Gordon and the transitory model and the transitory model compared much better with the measurements (results not shown here). Therefore we assigned  $\tau$  a fixed value of about three hours ( $2/\ln 2$ ) to account for nonsteady state dynamic evolution of leaf water. This leads to a delayed development

of leaf water isotopic composition compared to Craig and Gordon. This implicates that the maximum leaf water enrichment is later in the day and also that night-time values of leaf water are much higher than calculated with Craig and Gordon. The transitional nonsteady state model imitates therefore the numerical solution of the isotopic diffusion equation in leaves [see *Cernusak et al.*, 2002].

[19] The enzyme carbonic anhydrase is distributed uniformly in the mesophyll cells and speeds up hydration of  $\text{CO}_2$  in leaf water by a factor of  $10^7$  [*Stryer*, 1981]. This leads to the assumption that every  $\text{CO}_2$  molecule once entered the stomatal cavity is almost instantaneously hydrated and soon isotopically equilibrated with leaf water.  $\text{CO}_2$  molecules which cannot be carboxylated in plants because of limitations like electron transport, diffuse back in the atmosphere carrying the leaf water isotopic composition. Recent findings suggest that the carbonic anhydrase activity could be reduced so that not every  $\text{CO}_2$  molecule which diffuses in the stomate becomes hydrated immediately but that a fraction of the  $\text{CO}_2$  molecules could diffuse back in the atmosphere without being "tagged" by leaf water [*Gillon and Yakir*, 2000b, 2001]. This translates in equation (14) to a modified  $R_l$ . Let  $\theta$  be the degree of equilibration expressed as a fraction, i.e., if 80% of all  $\text{CO}_2$  molecules entering the leaf become hydrated immediately,  $\theta = 0.8$ . The fraction  $\theta$  of the  $\text{CO}_2$  molecules will still get the isotopic signature of leaf water where the remaining  $(1-\theta)$  will only be affected by diffusion fractionation,  $\alpha_l$ . The modified  $R_l$ , named  $R_{l-ca}$ , will then be [*Gillon and Yakir*, 2000b]:

$$R_{l-ca} = \theta R_l + (1-\theta) \left\{ 1 + \left( 1 - \frac{c_{cs}}{c_a} \right) \alpha_l \right\} R_a. \quad (17)$$

The  $\text{CO}^{18}\text{O}$  flux is therefore equation (14) with  $R_l$  replaced by  $R_{l-ca}$ :

$$\begin{aligned} {}^{18}F_{A-ca} &= \alpha_l g_s' (R_a c_a - R_{l-ca} c_{cs}) \\ &= \alpha_l g_s' \left\{ R_a c_a - c_{cs} [\theta R_l + (1-\theta) \left\{ 1 + \left( 1 - \frac{c_{cs}}{c_a} \right) \alpha_l \right\} R_a] \right\} \\ &= \alpha_l g_s' (R_a c_a - R_l c_{cs}) \\ &\quad - \alpha_l g_s' \left\{ (1-\theta) c_{cs} \left[ \left\{ 1 + \left( 1 - \frac{c_{cs}}{c_a} \right) \alpha_l \right\} R_a - R_l \right] \right\}. \end{aligned} \quad (18)$$

One can see that the second term in the difference is always positive (because the ratio of  $R_a$  will be only a few per mil lower than  $R_l$ , but  $R_a$  is multiplied by a factor between 1 and 2). The first term in the summation is the  $\text{CO}^{18}\text{O}$  flux with full carbonic anhydrase activity and it is normally positive. So the reduced carbonic anhydrase activity results in a reduced  $\text{CO}^{18}\text{O}$  flux from the atmosphere into the leaf. Measurements of *Gillon and Yakir* [2001] indicate that carbonic anhydrase activity is more reduced in  $\text{C}_4$  plants than in  $\text{C}_3$  plants.  $\text{C}_4$  grasses for example can have a reduced carbonic anhydrase activity of down to  $\theta = 0.4$  whereas  $\text{C}_3$  plants lie around  $\theta = 0.9$  or higher. *Gillon and Yakir* estimate a global mean  $\theta$  of 0.78 with their vegetation distribution, and quite similar to our



global mean value of 0.8 with BETHY's vegetation distribution.

### 2.3.3. Ocean and Anthropogenic Emissions

[20] The  $\text{CO}^{18}\text{O}$  flux of the ocean is calculated as:

$$\begin{aligned} {}^{18}F_o &= -\alpha_w R_a F_{ao} + \alpha_w R_o F_{oa} \\ &= \alpha_w R_a F_o + \alpha_w (R_o - R_a) F_{oa} \end{aligned} \quad (19)$$

with

- $\alpha_w$  fractionation factor of  $\text{CO}_2$  crossing the air-sea interface, including hydration;
- $R_a$   $^{18}\text{O}/^{16}\text{O}$  ratio of  $\text{CO}_2$  in air;
- $R_o$   $^{18}\text{O}/^{16}\text{O}$  ratio of  $\text{CO}_2$  equilibrated with ocean surface water;
- $F_{ao}$  and  $F_{oa}$   $\text{CO}_2$  one way fluxes between atmosphere and ocean and vice versa;
- $F_o$  net air-sea flux of  $\text{CO}_2$  between atmosphere and ocean, equal to  $F_{oa} - F_{ao}$ .

The fractionation is taken as  $\epsilon_w = +0.8\text{‰}$  [Vogel *et al.*, 1970]. The equilibration process is calculated via equation (8) with ECHAM driving climatological sea surface temperatures, and the  $^{18}\text{O}/^{16}\text{O}$  of ocean surface water is fitted to the empirical relationship:

$$\delta_o^w = a_1 + a_2 \cdot SAL \quad (20)$$

where  $SAL$  is the salinity in gram salt per kilogram water, and  $a_1 = -16.75\text{‰}$  versus VSMOW and  $a_2 = 0.5\text{‰}$  versus VSMOW are taken from *Ciais et al.* [1997a].

[21] Fossil fuel emissions and biomass burning are assumed to be without fractionation, i.e., that the  $\text{CO}_2$  emitted carries the signature of atmospheric oxygen,  $R_f$ :

$${}^{18}F_{fos} = R_f F_{fos} \quad (21)$$

$${}^{18}F_{bur} = R_f F_{bur} \quad (22)$$

with  $\delta_f = (R_f/R_{VPDB} - 1) \cdot 1000 = -17\text{‰}$  versus VPDB- $\text{CO}_2$ ;  $F_{fos}$  and  $F_{bur}$  are described in section 2.2.

### 2.3.4. Global Budget of $\delta^{18}\text{O}\text{-CO}_2$

[22] One can write down the global budget equation for the temporal evolution of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$  (taking only the processes of *Ciais et al.* [1997a, 1997b] for the moment):

$$\begin{aligned} \frac{d\delta_a}{dt} &= \frac{1}{C_a M_a} [F_R \Delta_R + F_A \Delta_A + F_{ao} \Delta_o^{des} \\ &\quad + F_o \Delta_o^{equ} + (F_{fos} + F_{bur}) \Delta_f] \end{aligned} \quad (23)$$

with

$$\begin{aligned} \Delta_R &= \delta_s - \delta_a + \epsilon_s; \\ \Delta_A &= -\epsilon_l + \frac{c_{cs}}{c_a - c_{cs}} (\delta_l - \delta_a); \\ \Delta_o^{equ} &= \epsilon_w; \\ \Delta_o^{des} &= \delta_o - \delta_a; \\ \Delta_f &= \delta_f - \delta_a. \end{aligned}$$

$M_a$  is the conversion factor between fluxes in GtC and mixing ratios in ppm ( $M_a = 2.122 \text{ GtC ppm}^{-1}$ , i. e., about 2 GtC are required to change the atmospheric  $\text{CO}_2$  mixing

ratio by 1 ppm),  $\Delta_A$  the discrimination of photosynthesis, and  $\Delta_o^{equ}$  the equilibrium discrimination between ocean and atmosphere. The others are not real discriminations in a proper physical sense but follow the same mathematical description [Farquhar *et al.*, 1982]. These  $\Delta$ s are simply the difference between the  $\delta$ -value of the  $\text{CO}_2$  flux and the atmospheric  $\delta$ -value,  $\delta_a$ . We use the same symbol,  $\Delta$ , for simplicity and denote them in this paper generically "apparent discriminations".  $\Delta_R$  is therefore the apparent discrimination associated with soil-respired  $\text{CO}_2$ ,  $\Delta_o^{des}$  the ocean disequilibrium or the tendency to equilibrate the difference between atmospheric and ocean dissolved  $\text{CO}_2$ , and  $\Delta_f$  the difference between the isotopic signature of  $\text{O}_2$  (involved in combustion) and  $\text{CO}_2$ . Analogous to plain  $\text{CO}_2$ , one calls the product of  $\text{CO}_2$  flux and apparent discrimination an isoflux. Just as the change of  $\text{CO}_2$  in the atmosphere is the sum of all  $\text{CO}_2$  fluxes, the change of  $\delta^{18}\text{O}$  is the sum of all isofluxes. One can rewrite equation (23) as a differential equation:

$$\frac{d\delta_a}{dt} = k_1 - k_2 \delta_a \quad (24)$$

whose solution is an exponential evolution of atmospheric  $\delta^{18}\text{O}\text{-CO}_2$  with time:

$$\delta_a(t) = \frac{k_1}{k_2} + \left( \delta_{a0} - \frac{k_1}{k_2} \right) \exp\{-k_2 t\}. \quad (25)$$

The factor  $k_1$  is a combination of  $\text{CO}_2$  fluxes and  $\delta$ -values in the compartments, and  $k_2$  consists only of positive  $\text{CO}_2$  fluxes, by definition.  $\delta_{a0}$  is the (arbitrary) value of the atmosphere at time  $t = 0$ . Therefore this is a stable differential equation, and the global  $\delta^{18}\text{O}$  value stabilizes at  $k_1/k_2$  when  $t$  becomes infinite:

$$\begin{aligned} k_1 &= \frac{1}{C_a M_a} [F_R (\delta_s + \epsilon_s) + F_A \left( \epsilon_l + \frac{c_{cs}}{c_a - c_{cs}} \delta_l \right) + F_{ao} \delta_o \\ &\quad + F_o \epsilon_w + (F_{fos} + F_{bur}) \delta_f] \end{aligned} \quad (26)$$

$$k_2 = \frac{1}{C_a M_a} \left[ F_R + \frac{c_{cs}}{c_a - c_{cs}} F_A + F_{ao} + F_{fos} + F_{bur} \right]. \quad (27)$$

In contrast to earlier simulations of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$ , we do not have to adjust the fractionation factors to obtain a stable solution. We rather calculate  $\delta_a$  at every time step and couple it to the  $\text{CO}^{18}\text{O}$  surface fluxes, and hence  $\delta_a$  will always stabilize if there is no trend in the  $\text{CO}_2$  fluxes or the  $\delta$ -values in the compartments, e.g., the water isotopic composition.

[23] Including other processes in the calculation of  $\delta^{18}\text{O}$  just adds fluxes and/or isofluxes in the global budget equation. Invasion for example adds the isoflux  $F_{inv} \Delta_{inv}$  to equation (23) with  $\Delta_{inv} = \delta_s - \delta_a$ , the apparent discrimination of invasion. This in turn adds terms within the parentheses of equations 26 and 27, which adds  $F_{inv} \delta_s$  to the parenthesis of  $k_1$ , and  $F_{inv}$  to the parenthesis of  $k_2$ , for the invasion effect. This changes the global mean value that  $\delta_a$  approaches with time,  $k_1/k_2$ . The effect of invasion now



reduces the global mean  $\delta_a$ . The proposed reduced activity of carbonic anhydrase changes leaf discrimination to:

$$\begin{aligned} \Delta_{A-ca} &= -\epsilon_l + \frac{c_{cs}}{c_a - c_{cs}} \left\{ \theta(\delta_l - \delta_a) + (1 - \theta) \left( 1 - \frac{c_{cs}}{c_a} \right) \epsilon_l \right\} \\ &= -\epsilon_l + \frac{c_{cs}}{c_a - c_{cs}} (\delta_l - \delta_a) \\ &\quad - \frac{c_{cs}}{c_a - c_{cs}} (1 - \theta) \left\{ \delta_l - \delta_a - \left( 1 - \frac{c_{cs}}{c_a} \right) \epsilon_l \right\}. \end{aligned} \quad (28)$$

The first two terms are leaf discrimination with full carbonic anhydrase activity,  $\Delta_A$ , so that a reduced carbonic anhydrase activity normally reduces leaf discrimination and the global mean  $\delta_a$  value will also stabilize at a lower value.

### 3. Results

[24] In order to validate our model, we have to validate first the different modules: the biosphere model and associated  $\text{CO}_2$  fluxes, the  $\text{CO}^{18}\text{O}$  fluxes, the water isotope ratios, and the atmospheric transport. We focus in this paper on the surface processes and compare the outcome of our model with other estimates and observations. We will validate only the terrestrial biosphere component and exclude ocean fluxes, fossil fuel and biomass burning. We show in part 2 that in order to simulate the seasonal cycle at almost all stations and to simulate the north-south gradient, ocean fluxes, fossil fuel, and biomass burning are not essential; contrary to the results of *Ciais et al.* [1997a, 1997b]. For the north-south gradient, this comes mainly from the fact that in our model, the atmospheric  $\delta^{18}\text{O-CO}_2$  mixing ratios influence the  $\delta^{18}\text{O}$  fluxes. This was not implemented in prior  $\delta^{18}\text{O-CO}_2$  models. BETHY offline was validated extensively by *Knorr* [1997, 2000] and *Knorr and Heimann* [2001a, 2001b] but the implementation of BETHY in ECHAM can lead to very different results. ECHAM/BETHY computes for example on a much coarser grid than BETHY offline and the meteorological parameters are taken from ECHAM which is of course different than the climatologies of *Leemans and Cramer* [1991] used in BETHY offline. One example of differing results is the global annual NPP which amounts to 70.0  $\text{GtC yr}^{-1}$  in BETHY offline and 55.7  $\text{GtC yr}^{-1}$  in BETHY online.

#### 3.1. Fluxes and Apparent Discriminations

[25] The sum of all  $\text{CO}_2$  fluxes determines the temporal change of the  $\text{CO}_2$  mixing ratio in the atmosphere; the sum of the isofluxes of  $\delta^{18}\text{O-CO}_2$  determines the change of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$ , accordingly. We calculate  $\text{CO}_2$  fluxes and isofluxes directly in our model, so the apparent discriminations are a combination of both, namely, the ratio of isoflux and  $\text{CO}_2$  flux. Our back-calculated apparent discriminations are consequently flux-weighted discriminations. Earlier  $\delta^{18}\text{O-CO}_2$  models calculated  $\text{CO}_2$  fluxes and discriminations separately and multiplied them to get isofluxes. These apparent discriminations were thus not flux-weighted. They tried to get around this problem using flux-weighted variables to calculate their discriminations, thereby neglecting nonlinearities in the calculations, mainly in the discrimination associated with assimilation. Inconsistencies among the different models, used to calculate isofluxes in the end,

**Table 2.** Global Annual  $\text{CO}_2$  Fluxes, Assimilation Weighted Annual Mean  $\text{CO}_2$  Mixing Ratios, Assimilation Weighted Annual Mean  $\delta$  Values, and  $\epsilon$  Constants Calculated and Used in ECHAM/BETHY<sup>a</sup>

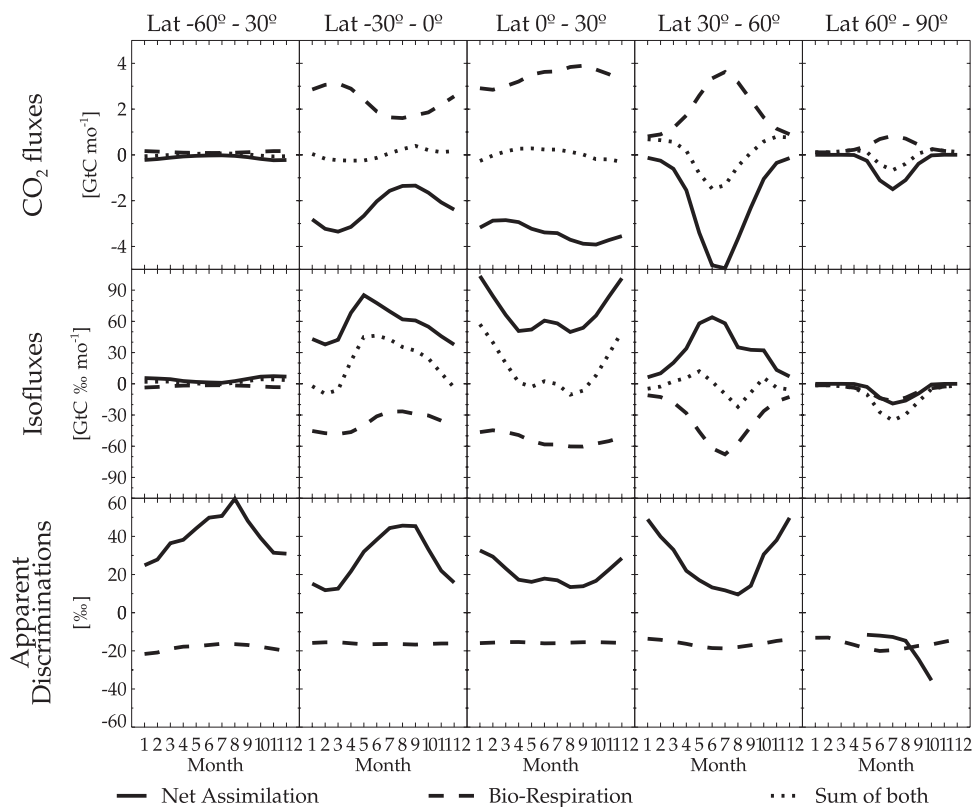
Flux, Mixing Ratio, $\delta$ , $\epsilon$ /	Value in ECHAM/BETHY
$F_A$	97.3
$F_R$	98.0
$F_{ao}$	99.4
$F_o$	2.6
$F_{fos}$	5.8
$F_{bur}$	3.1
$c_a$	353
$c_{cs}$	264
$\delta_l$	6.3
$\delta_s$	-6.9
$\delta_o$	1.2
$\delta_f$	-17.0
$\epsilon_l$	-7.4
$\epsilon_s$	-7.2
$\epsilon_w$	0.8

<sup>a</sup>Global annual  $\text{CO}_2$  fluxes are given in  $\text{GtC yr}^{-1}$ , assimilation weighted annual mean  $\text{CO}_2$  mixing ratios are given in ppm, assimilation weighted annual mean  $\delta$  values are given in ‰ versus VPDB- $\text{CO}_2$ , and  $\epsilon$  constants are given in ‰.

added errors which were neither commensurable nor estimable. This problem is not present in our model, in which  $\text{CO}_2$  fluxes and isofluxes are consistently calculated, leading to apparent discriminations that can be compared to measurements. Unfortunately, measurements of discriminations of  $\delta^{18}\text{O-CO}_2$  are difficult to achieve and therefore very sparse in the literature.

[26] Table 2 gives an overview of the main variables calculated and used in ECHAM/BETHY. The table includes all necessary values to calculate the global budget and/or the asymptotic global  $\delta_a$  value.  $F_A$  is thereby not GPP but net assimilation that is GPP minus leaf respiration.  $F_R$  is therefore what we call biorespiration that is heterotrophic plus autotrophic minus leaf respiration. The  $\delta$  values are consequently flux-weighted means, weighted with the fluxes on every time step of 40 minutes. It is noteworthy that  $\delta_b$ , the isotopic composition of  $\text{CO}_2$  equilibrated with leaf water at the evaporating site, is about 2‰ higher than former estimates, like, e.g., *Ciais et al.* [1997a]:  $\delta_l = 3.9\%$  versus VPDB- $\text{CO}_2$ .

[27] Figure 2 shows seasonal cycles of the sum of  $\text{CO}_2$  fluxes and isofluxes in  $30^\circ$  latitude bands, and resulting apparent discriminations as  $30^\circ$  zonal means.  $\text{CO}_2$  fluxes are given in  $\text{GtC month}^{-1}$  so one can see that the northern boreal zone ( $30^\circ$  to  $60^\circ\text{N}$ ) is even more productive during the northern summer than the tropical zone during austral summer. Poleward of  $60^\circ\text{N}$ , net assimilation (and biorespiration) decreases visibly. The seasonal cycle of leaf discrimination seems to contradict intuition but one can see in the apparent soil discrimination that soil water isotopes do not change significantly during the course of a year (we examine this further in the section about the nighttime terrestrial source signature). It is therefore increasing leaf temperature during summer together with decreasing  $c_i$  values which dominate the leaf discrimination signal and lead to lower discrimination during summer compared to winter. Contrary to assimilation, the northern boreal zone does not show the same maximum value in leaf isoflux as

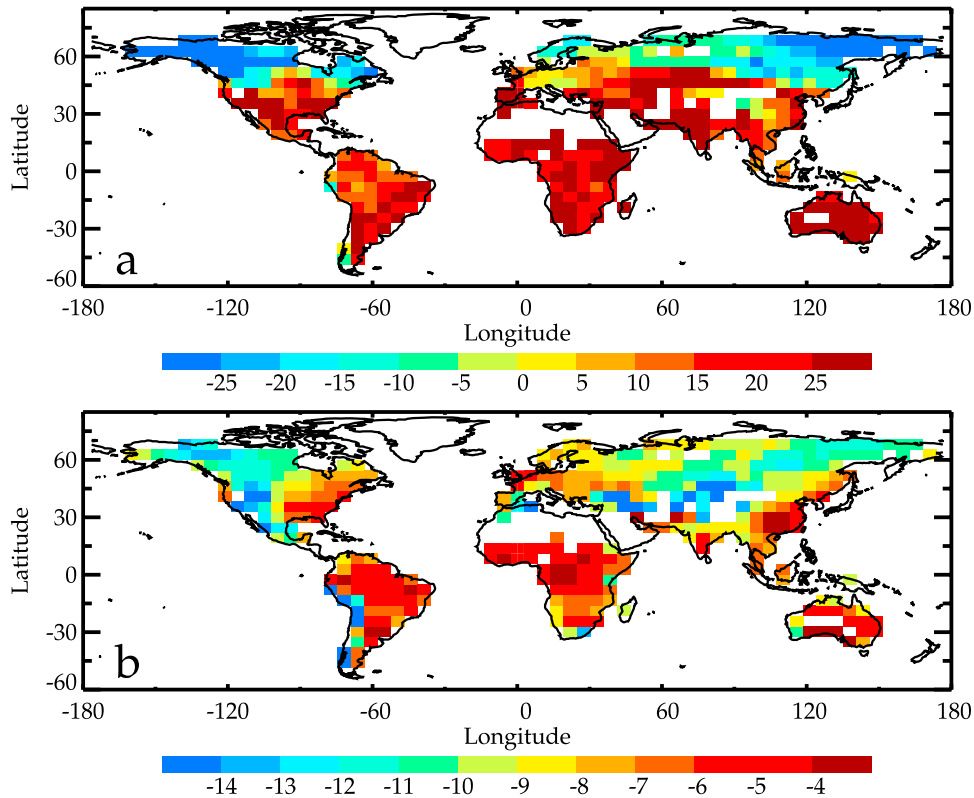


**Figure 2.** Seasonal cycle of the sum of  $\text{CO}_2$  fluxes and isofluxes, and resulting apparent discriminations (isoflux/ $\text{CO}_2$  flux) in  $30^\circ$  latitude bands calculated by ECHAM/BETHY. Here, mo, month.

the tropical zone does. Comparing  $30^\circ$  to  $60^\circ\text{N}$  with  $0^\circ$  to  $30^\circ\text{S}$  shows that leaf discrimination diminishes similarly during the respective summer with about  $40\text{‰}$  in winter and  $20\text{‰}$  in summer. However, winter  $\text{CO}_2$  assimilation is much higher in the southern latitude band, which, along with high discriminations, leads to the peak in leaf isoflux in the southern winter. Leaf discrimination becomes negative in high northern latitudes (missing values come from numerical instabilities at very low net assimilation when post-processing). In Eurasia, 25% of the cause of negative leaf discrimination can be attributed to the depletion of rain in the interior of the continent and 75% can be attributed to the increase of relative humidity from West to East Siberia which biases leaf water at the evaporating site to the isotopic composition of water vapor rather than to soil water [Cuntz *et al.*, 2002]. ECHAM temperatures are about  $2^\circ\text{C}$  lower than those from ECMWF re-analysis in East-Siberia but very similar to ECMWF in Canada and Alaska [Roeckner *et al.*, 1996]. Lower temperature translates into higher relative humidities which in turn gives lower leaf water values and consequently lower leaf discriminations ( $2^\circ\text{C}$  lower temperature translates to about  $10\text{‰}$  lower leaf discrimination in our model). The ECMWF re-analysis in Eastern-Siberia is very questionable because it is not well constrained, because of sparse measurement coverage. We think that it is realistic that leaf discrimination should become negative in Eastern-Siberia, and it should be measurable, as argued by Cuntz *et al.* [2002]. Negative photosynthetic discrimination is in fact directly implied by some concurrent vertical profiles of  $\text{CO}_2$  and  $\delta^{18}\text{O}\text{-CO}_2$  in and

above the convective boundary layer for central Siberia, even in mid-summer [Lloyd *et al.*, 2002a; Styles *et al.*, 2002a]. We show in Figure 3a the assimilation-weighted annual mean leaf discrimination (in  $\text{‰}$ ), which can be compared to other estimates (e.g., to Farquhar *et al.* [1993]). One can see that leaf discrimination becomes negative already at around  $45^\circ\text{N}$  in certain regions. On the other hand, Australia, Africa, and South America are very uniform in their mean discrimination (except for the Andes). The distribution pattern of leaf discrimination is similar to the one estimated by Farquhar *et al.* [1993] but differs in magnitude by approximately a factor of 2. Farquhar *et al.* calculate a global mean leaf water isotopic composition of  $4.4\text{‰}$  versus VSMOW, weighted by assimilation on a monthly basis, whereas our leaf water isotopic composition is  $6.3\text{‰}$  versus VSMOW, weighted by assimilation on every time step of 40 minutes. Farquhar *et al.* have a global mean stomata-internal  $\text{CO}_2$  mixing ratio,  $c_i$ , of 235 ppm while we calculate a mean of 264 ppm. They do not take  $c_i$  but the  $\text{CO}_2$  mixing ratio at the chloroplast,  $c_c$ , which further reduces their enhancement factor  $c_{cs}/(c_a - c_{cs})$  (where  $c_{cs}$  is either  $c_i$  or  $c_c$ ) to about 1.3 in the global mean, compared to about 3 in our model. Taking assimilation-weighted leaf water isotopic composition on a sub-daily basis is certainly more realistic but whether  $c_{cs}$  is closer to  $c_i$  or  $c_c$  is still a matter of debate (see below).

[28] Unlike leaf discrimination, the apparent soil discrimination is not real discrimination. What we call apparent discrimination is the difference between the isotopic signature of the  $\text{CO}_2$  flux of one process and the  $\delta^{18}\text{O}\text{-CO}_2$  in the



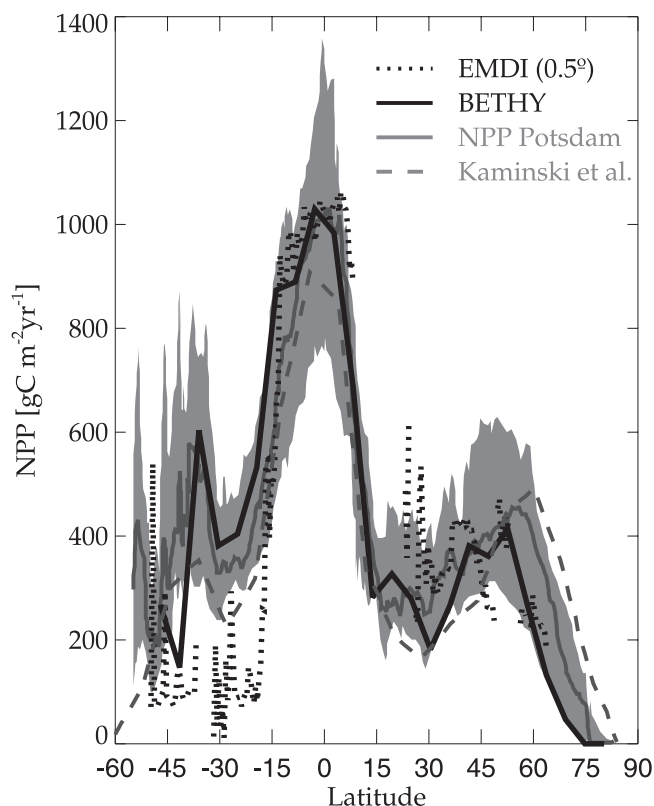
**Figure 3.** (a) Annual mean leaf discrimination in ‰ and (b) annual mean isotopic composition of  $\text{CO}_2$  in equilibrium with soil water in ‰ versus VPDB- $\text{CO}_2$ , calculated by ECHAM/BETHY.

atmosphere. While the isotopic signature of the  $\text{CO}_2$  soil flux does not depend on the atmospheric  $\delta^{18}\text{O}$  level, apparent soil discrimination does. One can see in equation (11) and equation (14) that the  $\text{CO}^{18}\text{O}$  flux of respiration is independent of the isotope ratio in the atmosphere,  $R_a$ , whereas the  $\text{CO}^{18}\text{O}$  flux of assimilation depends on it. If we include a new process in our calculation (e.g., computing with or without fossil fuel fluxes), the atmospheric  $\delta^{18}\text{O}$  level will change, according to equations 23–27. This will change the apparent soil discrimination but the soil  $\text{CO}^{18}\text{O}$  flux will stay the same. The leaf  $\text{CO}^{18}\text{O}$  flux instead will adapt to the new  $\delta^{18}\text{O}$  level in the atmosphere so that leaf discrimination and apparent soil discrimination will change differently. (In contrast to  $^{13}\text{C}$ ,  $\delta_a$  does not cancel out in leaf discrimination of  $^{18}\text{O}$ .) We show in Figure 3b the isotopic composition of  $\text{CO}_2$  equilibrated with soil water in ‰ versus VPDB- $\text{CO}_2$  (and not the apparent soil discrimination in ‰). To derive the apparent soil discrimination from Figure 3b, one has to add soil fractionation during diffusion,  $\epsilon_s$ , taken as  $-7.2\text{‰}$  [Miller *et al.*, 1999] in the model, and subtract the atmospheric  $\delta^{18}\text{O}\text{-CO}_2$ .  $^{18}\text{O}$  isotopes in soil  $\text{CO}_2$  are quite uniform inside continents and result in about  $-11\text{‰}$  versus VPDB- $\text{CO}_2$  in the northern hemisphere and about  $-5\text{‰}$  versus VPDB- $\text{CO}_2$  in the southern hemisphere. This result is very similar to Ciais *et al.* [1997a], which is surprising, because Ciais *et al.* used rain isotopic composition and we use soil isotopic composition, and the large seasonal cycle of isotopes in rain is very much attenuated. In addition, our annual values are all flux-weighted. We will show below that  $\text{CO}_2$  leaving the soil in our model is isotopically almost constant during the year. Our respiration weighted

annual mean is therefore very similar to our unweighted annual mean. Because soil integrates the rain signal over long time periods, the annual mean of isotopes in rainwater and soil water are very similar. Thus we end up with an annual mean isotopic composition of  $\text{CO}_2$  in equilibrium with soil water very similar to the estimate of Ciais *et al.* [1997a].

### 3.2. Net Primary Productivity

[29] The Potsdam NPP Model Intercomparison Project [Kicklighter *et al.*, 1999] compared 15 net primary productivity models. The shadowed area in Figure 4 shows the range between the 10th and 90th percentiles of the 15 models together with the median (grey solid line). Note that y axis units are in  $\text{gC m}^{-2} \text{s}^{-1}$ . The BETHY online model (black solid line) is very similar to the median of the 15 models and lies well in between the 10th to 90th percentile range. The most noteworthy difference is the lower productivity of ECHAM/BETHY at high latitudes. In the northern hemisphere poleward of  $60^\circ\text{N}$ , ECHAM/BETHY is at the 10th percentile level of the intercomparison and in the southern hemisphere between  $40^\circ$  and  $45^\circ\text{S}$ , it falls even below the 10th percentile level. We included in Figure 4 (black dotted line) the gridded data set compiled by the Ecosystem Model-Data Intercomparison (EMDI) project [Olson *et al.*, 2001] (details in Appendix A). In the southern extra-tropics, the NPP measurements of EMDI are primarily from grassland. Grassland NPP measurements are often pointwise above-ground NPP measurements, converted to total NPP with a constant factor. EMDI used a conversion factor of 2 to calculate total NPP from pointwise measured



**Figure 4.** Comparison of Net Primary Productivity (NPP) of the EMDI measurement compilation (black dotted line), the Potsdam NPP model intercomparison [Kicklighter *et al.*, 1999] (grey solid line, plus area between 10th and 90th percentiles, grey), BETHY online (black solid line), and result of a data assimilation study [Kaminski *et al.*, 2002] (grey dashed line) as latitudinal average.

above-ground NPP. This factor seems to be too low for grasslands because grasses may lose carbon to processes which are hidden from single above-ground NPP measurements. For instance, the above-ground part of grasses can be eaten by herbivores, destroyed by fires or die because of environmental conditions and can regrow afterward, while the belowground part of the grasses can lose carbon because of exudates or secretions of roots, or transfer of carbon to mycorrhizae [Long *et al.*, 1989]. At any rate, the EMDI estimates are a factor of 4 lower than the model results. Scurlock *et al.* [2002] compared different methods of estimating NPP of grasslands and found differences of up to a factor of 3 in the NPP estimates of different methods. So it is not certain that our model values are too high, but they should be taken with care. On the rest of the globe, the median of the 15 models and BETHY online compare well with the NPP estimations. Poleward of  $50^\circ\text{N}$ , the NPP data seems to agree more closely with the lower range of the Potsdam NPP models, and especially ECHAM/BETHY. However, there are only few measurements in the data compilation poleward of  $50^\circ\text{N}$ , ending around  $60^\circ\text{N}$ , so that tundra vegetation is not represented whereby tundra vegetation has potentially the same conversion problems as grasslands. Also included in the Figure 4 is the result of a data assimilation study (grey dashed line) [Kaminski *et al.*, 2002] that will be discussed in section 4. It is noteworthy

that all estimates of global annual NPP, including the data compilation, lie all very close together around  $55 \text{ GtC yr}^{-1}$  (see Table 3) whereby the models of the Potsdam NPP Model Intercomparison show a range of about 40 to  $80 \text{ GtC yr}^{-1}$ . Knorr and Heimann [2001b] optimized the BETHY offline model with satellite data and found that a global annual NPP of  $70 \pm 35 \text{ GtC yr}^{-1}$  is consistent with measurements of the  $\text{CO}_2$  atmospheric seasonal cycle and with reflectance measurements from satellite. Sensitivity runs of BETHY offline showed a range of  $48.3 - 77.1 \text{ GtC yr}^{-1}$  [Knorr, 2000] with the bulk of sensitivity runs yielding approximately  $62 \text{ GtC yr}^{-1}$ . The largest uncertainty comes thereby from the formulation of respiration and the second largest uncertainty from the used assimilation description. For example, using a light-use efficiency formulation [Monteith, 1977], NPP changes by about 13%. However, BETHY online simulates reasonable NPP with a conservative estimate of NPP over almost the whole latitude range except for the high northern latitudes where it predicts comparably low NPP values.

### 3.3. Net Ecosystem Exchange

[30] We now compare the  $\text{CO}_2$  flux component of our model with eddy flux measurements of Net Ecosystem Exchange (NEE). Although our model has a grid dimension of about 500 km, while eddy flux measurements represent an area of around  $1 \text{ km}^2$ , this is nevertheless a useful semi-quantitative indication of the ECHAM/BETHY model performance. In addition, most NEE measurement sites are located in young regrowing forests which gives a bias toward higher absolute NEE values. Also, the climate for our NEE calculations is simulated by ECHAM and is thus not the one observed at the stations. However, the phasing of NEE in our model should be comparable to that of the measurements, and the amplitude should be of the same order of magnitude. We used the compilation of eddy flux measurements of FLUXNET [Running *et al.*, 1999] (FLUXNET data are available from the ORNL DAAC at <http://www.daac.ornl.gov/>) and added two forest sites in western and central Russia [Milyukova *et al.*, 2002; Lloyd *et al.*, 2002b; Shibistova *et al.*, 2002] (details in Appendix A). We chose only those stations for which we have the same ecosystem in the corresponding grid cell of the model (or surrounding grid cells). If the model does not have the same ecosystem in the appropriate grid cell, we took an adjacent grid cell if possible, otherwise discarded the station. A list of all 20 stations used, including the associated BETHY plant functional type number, can be found in Table A1.

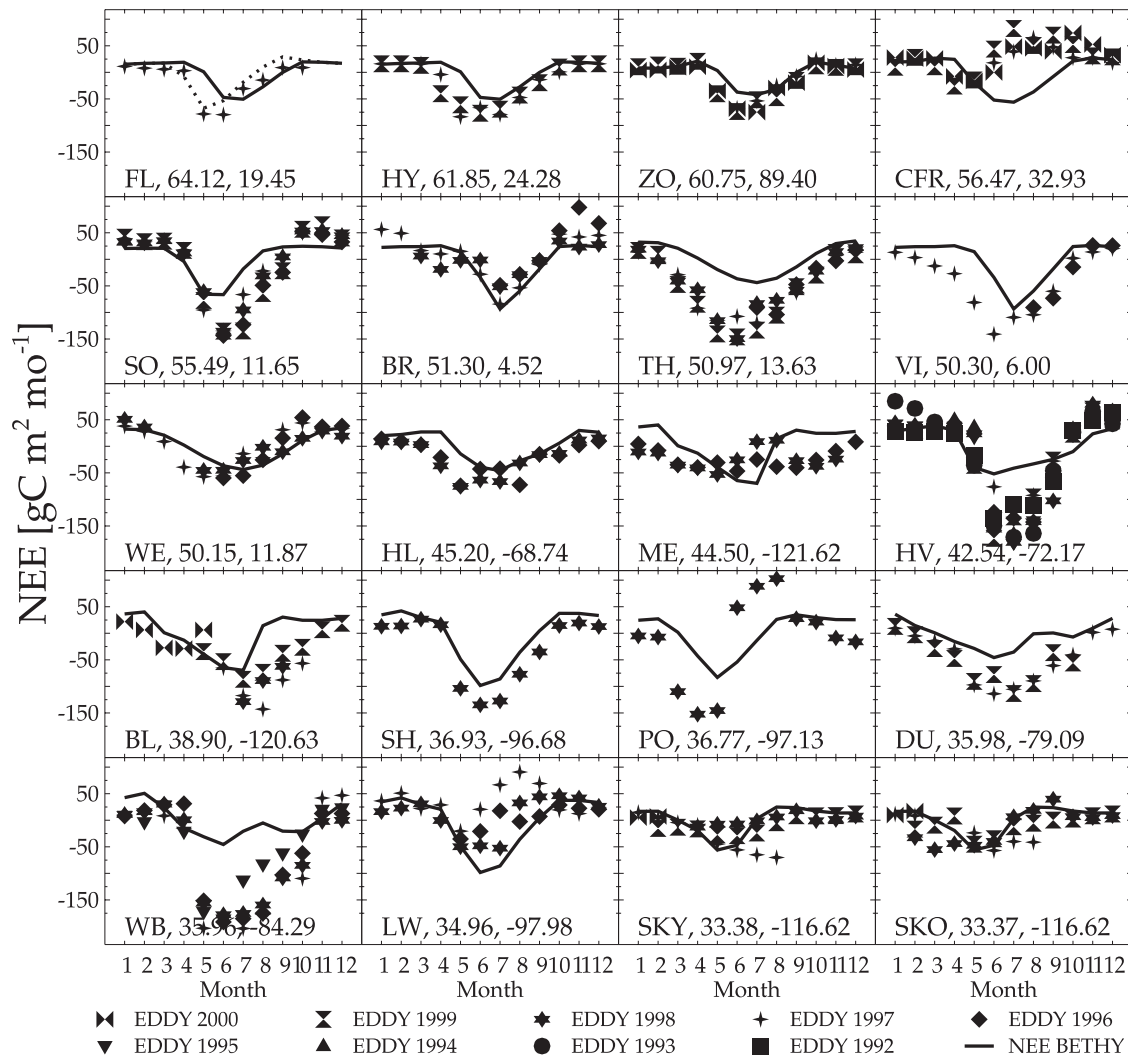
[31] Figure 5 shows the comparison between BETHY online monthly mean NEE fluxes and individual measure-

**Table 3.** Global Annual Net Primary Productivity<sup>a</sup>

Model/Data Estimate	Global NPP, $\text{GtC yr}^{-1}$
ECHAM/BETHY	55.7
Potsdam Range	39.9–80.5
Potsdam Mean	55.4
Kaminski <i>et al.</i> [2002]	54.9
EMDI Data (Estimate)	~55
BETHY offline	70.0

<sup>a</sup>The range and mean of the Potsdam NPP Intercomparison comes from Cramer *et al.* [1999], considering only the 15 models of Kicklighter *et al.* [1999]. The EMDI global estimate was calculated using a polynomial fit through the data of Figure 4.





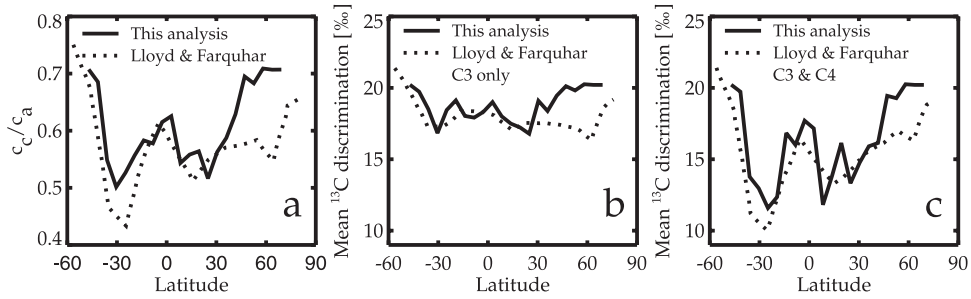
**Figure 5.** Net Ecosystem Exchange (NEE) at 20 different eddy flux sites (different symbols for each year) compared to mean ECHAM/BETHY (solid line). The values after the station abbreviation stand first for latitude and second for longitude of the site. The sites are in descending latitude order. The dotted line at Flakaliden is model NEE with assimilation shifted arbitrarily one month in advance.

ment years, the latter to demonstrate the large interannual variability of the measurements. ECHAM's monthly means variables, aggregated from 40 minute output, instead represent a climatological mean state, so there is no such interannual variability. We arranged the sites in latitudinal order so that one can easily see that all sites are poleward of  $30^\circ\text{N}$  and mainly in Europe and North America. ECHAM/BETHY seems to underestimate the NEE flux amplitude at half of the stations. Notably poleward of  $60^\circ\text{N}$ , ECHAM/BETHY is too low in amplitude which corresponds to the low NPP predictions of ECHAM/BETHY at high northern latitudes (compared to the 15 NPP models, not compared to the EMDI NPP data compilation). The model overpredicts minimum NEE only at Central Forest Reserve (CFR) and Little Washita (LW) which both show a source of  $\text{CO}_2$  in the measurements (this is not possible in the model because NEE is set to zero in the long term mean). The limit of the comparison can be seen at the stations Braschaat (BR), Tharandt (TH), Vielsalm (VI), and Weidenbrunnen (WE) which all lie in close proximity. They

occupy actually only two neighboring grid cells in the model, so Braschaat and Vielsalm as well as Tharandt and Weidenbrunnen are compared to the same NEE flux of the model. However, one can see that the compared stations show a different NEE amplitude, about a factor of 2 larger. So ECHAM/BETHY simulates much better the lower NEE amplitude stations. In the latitude range poleward of  $50^\circ\text{N}$ , ECHAM/BETHY is always slightly out of phase. Its minimum NEE arrives about one month too late. This behavior cannot be seen between  $30^\circ$  and  $40^\circ\text{N}$  and the comparison is equivocal in between.

### 3.4. Stomata $\text{CO}_2$ Mixing Ratio

[32] The  $\text{CO}_2$  mixing ratio inside stomates is an important variable for leaf discrimination (see equation (23)). The factor  $c_{cs}/(c_a - c_{cs})$  amplifies the difference between leaf water equilibrated  $\text{CO}_2$  and atmospheric  $\delta^{18}\text{O}\text{-CO}_2$ . At an ambient  $\text{CO}_2$  mixing ratio of 350 ppm and a stomatal  $\text{CO}_2$  mixing ratio of 230 ppm, this factor is about 2. With further drawdown of  $c_{cs}$ , the factor diminishes as well, reaching 1 at



**Figure 6.** Latitudinal distribution of the stomata-internal  $\text{CO}_2$  mixing ratio. The ratio of stomatal to atmospheric  $\text{CO}_2$  mixing ratio is compared with *Lloyd and Farquhar* [1994] via  $c_c/c_a$  for (a)  $\text{C}_3$  and  $\text{C}_4$  plants, (b)  $^{13}\text{C}$  photosynthetic discrimination of  $\text{C}_3$  assimilation and (c)  $\text{C}_3$  together with  $\text{C}_4$  assimilation.

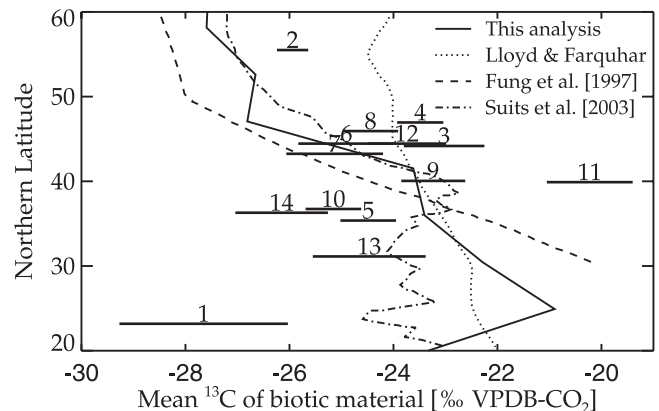
175 ppm. Even lower values of  $c_{cs}$ , e.g., at high assimilation rates, lead to a vanishing influence of leaf water on atmospheric  $\delta^{18}\text{O}\text{-CO}_2$ . We explained in section 2.3 that we take as a first guess the stomata-internal  $\text{CO}_2$  mixing ratio  $c_i$  as an estimate of  $c_{cs}$ . Our global assimilation weighted value of  $c_i$  is very high with 264 ppm. This leads to  $c_{cs}/(c_a - c_{cs}) = 3$ . This comes from the fact that we start from rather high non-water-limited  $c_i$  values, which come from *Schulze et al.* [1994]. This literature survey of field measurements gives a  $c_{i0}$  of  $0.87 c_a$  for  $\text{C}_3$  plants which is much higher than laboratory measurements suggest:  $\sim 0.7 c_a$  [*Farquhar et al.*, 1989b; *Boyer et al.*, 1997]. We try to validate our  $c_i$  estimates indirectly via  $^{13}\text{C}$  leaf discrimination. However,  $^{13}\text{C}$  fractionation by photosynthesis is determined by  $\text{CO}_2$  mixing ratio in the chloroplast,  $c_c$ , rather than in the stomata. *Lloyd and Farquhar* [1994] give a range of  $0.16 c_a$  to  $0.2 c_a$  for the difference between  $c_i$  and  $c_c$  at saturating photon irradiance. They use a value of  $0.1 c_a$  suggesting leaves operating on roughly 50% of their maximum (light-saturated) photosynthetic capacity. *Yakir and Sternberg* [2000] recommend a value of  $0.2 c_a$  for an average drawdown on the chloroplast level. We take a value midway between the different estimates and  $c_i - c_c = 0.16 c_a$ .

[33] In Figure 6a, the latitudinal distribution of  $c_c/c_a$  in ECHAM/BETHY is compared to the estimate of *Lloyd and Farquhar* [1994]. Both estimates are similar, but be aware that the global mean level of both curves depend on the above discussed drawdown from  $c_i$  to  $c_c$ . The difference in the southern hemisphere comes mainly from the different distribution of  $\text{C}_4$  plants in the two approaches. This can also be seen comparing Figures 6b and 6c. We calculated, along with  $c_c/c_a$ , the  $^{13}\text{C}$  leaf discrimination of  $\text{C}_3$  plants, using the simple formula [*Farquhar et al.*, 1989a]:

$$\Delta_A^{13}\text{C} = a + (b - a) \frac{c_c}{c_a}. \quad (29)$$

$a = 4.4\text{‰}$  is the kinetic fractionation of  $^{13}\text{C}$  diffusion in air and  $b$  is the fractionation associated with carboxylation. There is a considerable amount of uncertainty regarding the correct value of  $b$ . *Farquhar et al.* [1989a] found the best fit to measurements with  $b = 27\text{‰}$  but using  $c_i$  instead of  $c_c$ . *Lloyd and Farquhar* [1994] expanded the formula of *Farquhar et al.* by dividing the gradient between stomata and chloroplast into several components.  $b$  is therefore a mixture of carboxylation of RUBISCO (Ribulose BISpho-

sphate Carboxylase/Oxygenase) ( $b_3 = 29\text{‰}$ ) and 5 to 10% carboxylation of PEP (phospho enolpyrvate) carboxylase ( $b_4 = -5.6\text{‰}$  at  $25^\circ\text{C}$ ). They found a value of  $b = 27\text{‰}$  but using  $c_c$ . We follow their later conclusions and take  $b = 27\text{‰}$  together with  $c_c$  for  $\text{C}_3$  plants. We take a constant value of  $a = 4.4\text{‰}$  for  $\text{C}_4$  plants. Taking only the simple formula (equation (29)) for calculating  $\Delta_A^{13}\text{C}$  is of minor importance because the expansion of *Lloyd and Farquhar* results in only small changes in the latitudinal mean compared to the simple formula. Note that we follow the historical convention that fractionation and therefore discrimination in  $^{13}\text{C}$  and  $^{18}\text{O}$  have opposite signs. So the isoflux of  $\delta^{13}\text{C}$  is  $-\Delta_A^{13}\text{C}$  times assimilation and the isoflux for  $\delta^{18}\text{O}$  is  $+\Delta_A^{18}\text{O}$  times assimilation, i.e., a positive  $\Delta_A^{13}\text{C}$  is comparable in its effect on the atmosphere to a negative  $\Delta_A^{18}\text{O}$ . Plotted in Figure 6b is the latitudinal distribution of  $^{13}\text{C}$  discrimination of  $\text{C}_3$  plants only and in Figure 6c of  $\text{C}_3$  and  $\text{C}_4$  plants together. (Figures 6a and 6c are very similar and are different presentations of the same result. However, Figure 6a is the actual variable we are interested in, Figures 6b and 6c show the results detailed for  $\text{C}_3$  and  $\text{C}_4$  plants in a notation that is, via equation (30), closely related to Figure 7, the comparison with observations.) The  $\text{C}_3$  distributions are extremely similar except for the high northern latitudes. Poleward of  $30^\circ\text{N}$ , the two estimates diverge. ECHAM/BETHY reaches its base, non-water-



**Figure 7.** Latitudinal distribution of  $\delta^{13}\text{C}$  source signature,  $\delta_{bio}^{13}\text{C}$ . Both studies of Figure 6 are compared to measurements of mean biotic  $^{13}\text{C}$  of *Miller et al.* [2003]. The numbers correspond to continental sampling sites of NOAA/CMDL and are explained in Table A2.

limited level of  $c_c/c_a$  of about 0.71 (=0.87–0.16) (Figure 6a) whereas Lloyd and Farquhar do not reach such high values (they do in the southern extra-tropics). Lloyd and Farquhar remarked the same phenomena in comparison to earlier estimates of Farquhar *et al.* [1993] that also diverged at high northern latitudes. The differences between BETHY online and the earlier investigation below 30°N come mainly from the different distribution of  $C_4$  plants. With the vegetation distribution used, big parts of the African vegetation belt are covered by  $C_4$  long grasses, which give the modeled minimum  $\Delta_A^{13}\text{C}$  at 10°N.  $C_4$  plant assimilation contributes 21% of global GPP according to Lloyd and Farquhar [1994] whereas BETHY online calculates 18%;  $C_4$  long grasses alone (PFT 12, Table 1) contribute 12%. This gives a mean discrimination for the terrestrial biosphere of 16.1‰ versus VPDB- $\text{CO}_2$  in BETHY online compared to 14.8‰ versus VPDB- $\text{CO}_2$  of Lloyd and Farquhar. For  $C_3$  plants only, BETHY online gives 18.7‰ whereas Lloyd and Farquhar estimate 17.8‰ versus VPDB- $\text{CO}_2$ . However, the overall global mean discrimination deviates quite a lot from other investigations: 15.7‰ [Fung *et al.*, 1997], 18.0‰ [Tans *et al.*, 1993], 20.0‰ [Quay *et al.*, 1992], 17.6‰ [Keeling *et al.*, 1989]. However, most studies were made only with  $C_3$  plants except Fung *et al.*, and therefore they are not far from our  $C_3$  estimate.

[34] BETHY online (as well as Lloyd and Farquhar [1994]) deviates from measurements of  $\delta^{13}\text{C}$  source signature,  $\delta_{\text{bio}}^{13}\text{C}$ , of Miller *et al.* [2003] (Figure 7), which are recalculated estimates of Bakwin *et al.* [1998]. (We plotted as well all model studies included in the comparison of Miller *et al.* [2003], namely Lloyd and Farquhar [1994], Fung *et al.* [1997], and N. S. Suits *et al.* (Seasonal and spatial variations in carbon isotopic ratios of plant biomass, terrestrial  $\text{CO}_2$  fluxes and atmospheric  $\text{CO}_2$ , submitted to *Global Biogeochemical Cycles*, 2003) (hereinafter referred to as Suits *et al.*, submitted manuscript, 2003).) Because of the lack of a full carbon cycle (but also transported fossil fuel emissions and other factors), the terrestrial isotopic signature,  $\delta_{\text{bio}}^{13}\text{C}$ , is calculated here as:

$$\delta_{\text{bio}}^{13}\text{C} = \frac{-7.9 - \Delta_A^{13}\text{C}}{1 + \Delta_A^{13}\text{C}/1000}, \quad (30)$$

i.e., with an atmospheric  $\delta^{13}\text{C}$  value of  $-7.9$ ‰ versus VPDB- $\text{CO}_2$  which is the annual northern hemispheric mean of Bakwin *et al.* [1998]. This formulation assumes that the respiration source has the same signature as assimilation which is not true because of the fossil fuel input (so called  $^{13}\text{C}$  Suess effect). Equation (30) and the lack of a closed carbon cycle in our model are shortcomings in the comparison but should not alter the qualitative results. However, we cannot stretch this comparison too much without including a full  $\delta^{13}\text{C}$ -cycle. ECHAM/BETHY shows slightly enriched values below 35°N and lighter values in the high latitudes than the measurements (for the description of the numbers see Appendix A). Miller *et al.* [2003] and Bakwin *et al.* [1998] attributed the heavier values of Lloyd and Farquhar [1994] to the  $C_4$  distribution used by Lloyd and Farquhar. (Bakwin *et al.* used the same argument for Fung *et al.* [1997].) We have a different  $C_4$  distribution than Lloyd and Farquhar, but one can see in

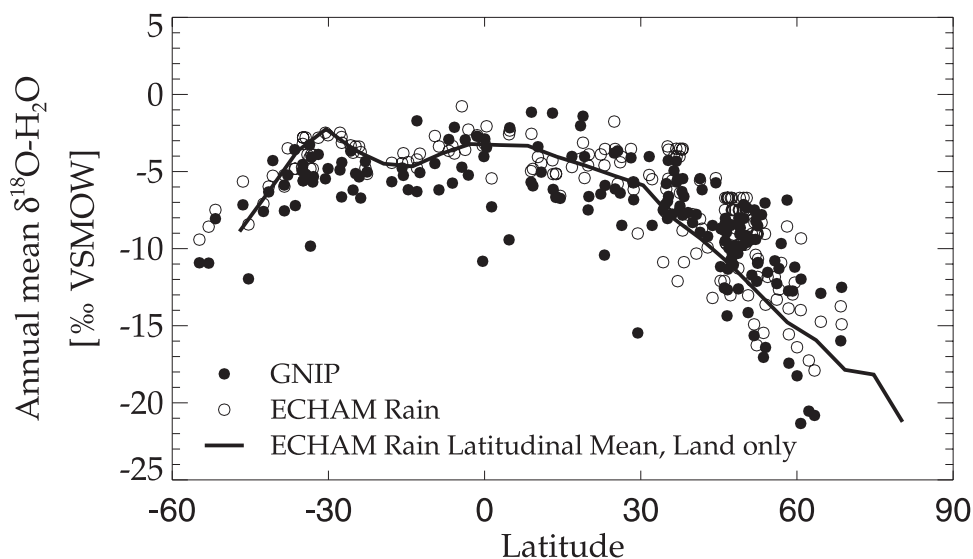
Figures 6b and 6c that the  $^{13}\text{C}$  discrimination of both models is very similar between 30° and 40°N for  $C_3$  and  $C_4$  plants together but very different for  $C_3$  plants only. So the difference need not come only from the difference in  $C_4$  distribution. At high latitudes, we already noted the small assimilation values of ECHAM/BETHY as well as the high  $c_c$  values.

### 3.5. Water Isotopes

[35] Apart from the  $\text{CO}_2$  fluxes and their interdependent variables,  $\delta^{18}\text{O}\text{-CO}_2$  is mainly determined by the isotopic composition of the water pools. The water isotope module (WFRAC) has been extensively tested, so we focus here on the north–south gradient, which will in turn determine the latitudinal distribution of  $\delta^{18}\text{O}\text{-CO}_2$ . We used stations of the Global Network of Isotopes in Precipitation (GNIP) of the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) (see Global Network of Isotopes in Precipitation: The GNIP database, available at <http://isohis.iaea.org>) (details in Appendix A) and calculated the mean precipitation weighted annual average. In Figure 8 are shown the GNIP values (filled circles) together with the ECHAM annual means at the same stations (open circles). A standard deviation of around 10‰ refers to the GNIP values. The solid line in Figure 8 is the latitudinal mean of ECHAM land grid points, because most GNIP stations are on land and we are interested in the  $\text{CO}^{18}\text{O}$  fluxes of the terrestrial biosphere. One can see that ECHAM works very well at most stations, not considering the outliers in the measurements. We showed in an earlier publication [Cuntz *et al.*, 2002] that ECHAM simulates equally well the east–west gradient in Eurasia. ECHAM follows nicely the dip at 15°S resulting from the Intertropical Convergence Zone (ITCZ). However, it has a slight tendency to weakly overestimate the annual values.

### 3.6. Nighttime Terrestrial Source Signature

[36] The  $\text{CO}^{18}\text{O}$  module (OFRAC) uses soil water isotopic composition, not the composition of rain, to calculate soil  $\text{CO}^{18}\text{O}$  fluxes. The soil acts as an integrator of rain, damping the sometimes large seasonal cycle of  $\delta^{18}\text{O}\text{-H}_2\text{O}$ . ECHAM uses a soil bucket model for water, which almost totally erases the seasonal cycle. The soil bucket model has only one soil layer for water. (ECHAM uses more than one soil layer for other variables like temperature.) This could already be seen in the apparent soil discrimination of Figure 2. We assess this damping effect further with  $\text{CO}_2$  and  $\delta^{18}\text{O}\text{-CO}_2$  measurements, made in or above canopies. With the method developed by Keeling [1961], known as “Keeling plot”, many studies have attempted to investigate the carbon isotope composition of  $\text{CO}_2$  fluxes. One of the major assumptions of the Keeling plot is that the single source does not change during the period of investigation (neither should the background mixing ratio). For  $\delta^{13}\text{C}$ , this can be assumed with confidence during night, but it is a priori not true for  $\delta^{18}\text{O}\text{-CO}_2$ , because temperature changes over the course of the night and therefore the equilibrium fractionation between water and  $\text{CO}_2$  changes as well (see equation (8)). There are other factors, such as the invasion effect which make a Keeling plot a priori unusable for  $\delta^{18}\text{O}$ . These factors often give a curved appearance to  $\delta^{18}\text{O}$  Keeling plots. In any case, one sometimes finds very ‘good’



**Figure 8.** Annual mean values of the isotopic composition of rain from GNIP (closed circles) compared to the water isotope module (WFRAC) of ECHAM (open circles). The latitudinal mean of all land points (line) is given as an integrated comparison measure.

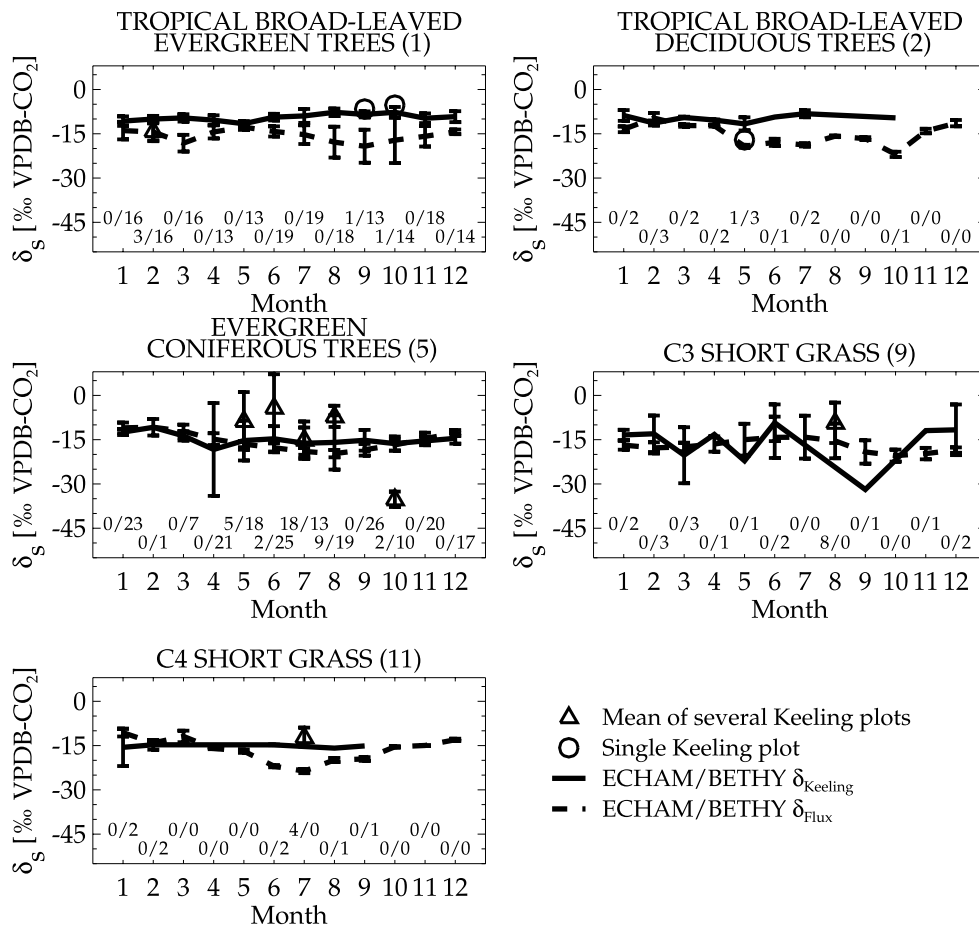
Keeling plots, i. e., with high correlation coefficient, and the measurements lying on a straight line. It is possible that this is due to compensating effects, because the equilibration fraction tends to heavier values over the course of the night (with decreasing temperatures, equation (8)) and the invasion effect tends to lighter values because of increasing influence (with increasing  $\text{CO}_2$  mixing ratios, equation (12)). However, it is unlikely that these effects exactly cancel. Rather, these effects should be negligible in situations with ‘good’ Keeling plots. We therefore queried the database of the Biosphere-Atmosphere Stable Isotope Network (BASIN) of the Global Change and Terrestrial Ecosystem core project (GCTE) Focus 1 [Pataki *et al.*, 2003] in which we found 2470 data points of ecosystem  $\text{CO}_2$  and  $\delta^{18}\text{O}\text{-CO}_2$  measurements. We updated the measurements of French Guiana (N. Buchmann, personal communication, 2001), added data of Australia, Brazil and Cameroon (J. Lloyd, personal communication, 2001), and incorporated measurements from Russia [Langendörfer *et al.*, 2002; Styles *et al.*, 2002b] (details in Appendix A). Table A3 lists all measurement sites, along with the associated BETHY plant functional type number. We found 54 ‘good’ ( $r^2 > 0.7$ ) nighttime Keeling plots (using reduced major axis regression, also known as geometric mean regression). We ran our model (without invasion) for three consecutive days each month acquiring  $\text{CO}_2$  and  $\delta^{18}\text{O}\text{-CO}_2$  values each 40 minutes in the lowest model layer (about 30 meter height). We then produced Keeling plots from all nights on each grid point, and selected only Keeling plots with ‘good’ correlations ( $r^2 > 0.9$ ). Taking the same coordinates as the measured Keeling plots (moving to adjacent grid cells if necessary) gave 503 individual source signature estimates in the model (out of 1110 for all stations, i. e., about half of the Keeling plots in our model were usable and the effect of source signature change negligible). We further grouped the stations according to BETHY plant functional types. The result is shown in Figure 9. If there is more than one Keeling plot, the standard deviation is plotted as an error bar at the error-weighted mean value. We take the lowest layer in ECHAM/

BETHY, which is not really a canopy air space, however. Except for  $\text{C}_3$  short grasses, stations which correspond to a given plant functional type are either single stations or all lie around the same latitude band. So ECHAM/BETHY looks quite uniform in each plant type with small error margins. The comparison is not very enlightening because of the lack of suitable measurements in which the discussed effects are not present. In summer, nighttime temperature drifts are important, and in winter, high  $\text{CO}_2$  mixing ratios amplify the invasion effect so that no ‘good’ Keeling plot can be found. Keeling plots assume entrainment of the trace gas only in the vertical, with constant signature. However, measurements are also influenced by horizontal entrainment; not constant signature should give a bend look to the Keeling plots and are discarded in the analysis. We plotted therefore in Figure 9 the signature of the source flux in ECHAM/BETHY as well (dashed line) to illustrate that the Keeling plots do not always give exactly the source signature (theoretically, they should be equal). That is why we constructed Keeling plots in our model to match as closely as possible the observational constraints. What can clearly be seen in Figure 9 is that BETHY online shows almost no seasonal cycle in the isotopic source composition. The small seasonal cycle of the water isotopes in soil is entirely cancelled out (or even overshoot) by the temperature difference between summer and winter. The sites of the BETHY plant functional types 5, 9 and 11 lie almost entirely in the northern hemisphere (except Wagga Wagga in Australia). Here BETHY online shows lower values for the source isotopic composition during the summer months. A bucket model seems to be too crude to simulate well the influence of respiration on  $\delta^{18}\text{O}\text{-CO}_2$  in canopies.

#### 4. Discussion

[37] There are two ominous results in the preceding section: the low assimilation values in high northern latitudes and the unchanging source signature of respired  $\text{CO}_2$ . We will further on summarize the above results and discuss these two points.





**Figure 9.** The isotopic signature of the nighttime respiration  $\delta^{18}\text{O}\text{-CO}_2$  source derived from “Keeling plots”. Triangles are the mean of several Keeling-plot-derived source signatures at the given BETHY plant functional type at one or several stations. The error bar is the standard deviation of the different source estimates. Circles instead signify a single Keeling plot. The errors of single Keeling plots are all on the order of the size of the circles, and therefore no error bars are plotted to single Keeling plot values. The solid line connects the mean of the Keeling-plot-derived values in BETHY online. Here as well, an error bar is associated if more than one Keeling plot estimate exists. The numbers in each plot are first the number of measurement Keeling plots which entered the plotted value and second the number of model Keeling plots. The dashed line is the  $\delta^{18}\text{O}$  signature of the soil  $\text{CO}_2$  source, calculated in BETHY online.

[38] The results of the NPP comparison are somewhat contradictory (Figure 4). The BETHY online model lies only at the 10th percentile of the 15 NPP models poleward of  $60^\circ\text{N}$ . On the other hand, the EMDI NPP compilation shows qualitatively the same behavior as BETHY. NPP is defined as the total photosynthetic gain minus (respiratory) losses of vegetation (per unit ground area). Many earlier estimates of NPP ignored the turnover and belowground processes, taking only above-ground NPP into account. Total NPP measurements are hard to make because below-ground processes, e.g., fine root growth and death, are not easily accessible [Long *et al.*, 1989]. Different methods are thus used to estimate total NPP from measurements of above-ground NPP, but most methods still neglect quite a number of processes. The EMDI project uses conversion factors from above-ground NPP to make its estimates. Scurlock *et al.* [2002] showed, at least for grasslands, that this method can lead to substantial errors. They state that current NPP estimates are clearly an underestimate of the

magnitude of NPP. So the NPP compilation values are likely to be too small, to a different degree for different biomes. A recent atmospheric  $\text{CO}_2$  data assimilation study points in the same direction, stating that a much higher NPP in high northern latitudes is needed to match the seasonal cycle of  $\text{CO}_2$  [Kaminski *et al.*, 2002]. NPP derived by Kaminski *et al.* is even higher than the 90th percentile of the Potsdam intercomparison. However, the results are very sensitive to, e. g., the transport model used, or the parameterization of respiration. However, the seasonal cycle of atmospheric  $\text{CO}_2$  is derived from the net  $\text{CO}_2$  fluxes and not from gross fluxes. We showed in Figure 5 that BETHY online underestimates NEE amplitudes at about half of the stations compared, notably poleward of  $60^\circ\text{N}$ . However, the two most northern stations, Flakaliden in Sweden and Hyytiälä in Finland, are both located in young, regrowing forests so that we cannot expect BETHY online to reproduce these rather high amplitudes. It is more vexing that ECHAM/BETHY is not able to reproduce the right phase poleward of

50°N. NEE is the difference between respiration and assimilation, and these show maxima at different times of the year (normally, respiration peaks later in the year than assimilation). Different NEE phasing can be due to overestimation or underestimation of one process (or both) or the different phasing of just one process. Taking Flakaliden as an example: shifting assimilation arbitrarily so that its minimum occurs one month earlier, results in the right phase and even the right amplitude in our model compared to the eddy measurements (dotted line in Figure 5). It is therefore not clear if the results of *Kaminski et al.* [2002] are transferable to our model, i.e., that we should increase the overall productivity beyond 60°N.

[39] Another item suggesting that ECHAM/BETHY underestimates carbon fluxes in high northern latitudes is the high stomata-internal  $\text{CO}_2$  mixing ratio modeled by BETHY. The estimates of *Lloyd and Farquhar* [1994] and the measurements of *Miller et al.* [2003] suggest lower  $c_i$  values poleward of 45°N. Lower  $c_i$  normally means higher assimilation. This is also true in models, but only if the model has no thresholds in the computation. BETHY calculates first a non-water-limited assimilation rate at a given  $c_i$ . This means that it takes carboxylation and electron transport limitation into account in this step. Then, it incorporates the water limitation of assimilation in the empirical formulation expressed in equation (3). The last step is to recalculate assimilation, this time with fixed stomatal conductance from the water limitation step before, adjusting  $c_i$  compatibly. Therefore  $c_i$  cannot be higher than the non-water-limited  $c_i$ , which is  $0.87 c_a$  for  $\text{C}_3$  plants and  $0.67 c_a$  for  $\text{C}_4$  plants in our model. This is much higher than laboratory measurements suggest (around  $0.7 c_a$  for  $\text{C}_3$  and  $0.4 c_a$  for  $\text{C}_4$  plants [*Boyer et al.*, 1997; *Farquhar et al.*, 1989b]) but comes from a literature survey of field measurements [*Schulze et al.*, 1994]. However, this plays a role mostly in non-water-limited cases. Reducing the non-water-limited  $c_i$  to laboratory values would bring Lloyd and Farquhar and ECHAM/BETHY very close together. However, using the non-water-limited  $c_i$  of *Schulze et al.* [1994] or of *Farquhar et al.* [1989b] does not produce large changes in assimilation. It reduces assimilation only by about 5% in our model. We point out in part 2 that we use this  $c_i$  value in order to better model the seasonal cycle of atmospheric  $\delta^{18}\text{O}\text{-CO}_2$ . We show as well in part 2 that the seasonal cycle of  $\text{CO}_2$  is rather large in the model at northern hemispheric stations, which contradicts the evidence of small assimilation at high latitudes. In this regard, the mean  $\delta^{13}_{\text{bio}}\text{C}$  of the only station poleward of 50°N, Baltic Sea (2), points more in the direction of ECHAM/BETHY than in the direction of Lloyd and Farquhar, and BETHY online is very similar in this region to a recent modeling study of *Suits et al.* (submitted manuscript, 2003).

[40] The above points support that BETHY online calculates too little assimilation in the northern hemisphere, but it also might be the case that it is the phasing of assimilation and/or respiration which is not well represented. We exclude in the discussion the possibility that ECHAM state variables are poorly represented, like temperature or relative humidity. ECHAM takes part of the Atmospheric Model Inter-comparison Project (AMIP) and is tested extensively in the framework of AMIP [e.g., *Gates et al.*, 1998]. We summarize here only the key features of ECHAM for temperature

and precipitation. *Roeckner et al.* [1996] compared ECHAM temperatures with ECWMF (European Centre for Medium-Range Weather Forecasts) re-analysis climatology and precipitation to observational estimate produced by *Legates and Wilmott* [1990]. The most apparent model error is in the upper troposphere and lower stratosphere that are both not very important for our ECHAM/BETHY simulations. Over land, model errors of more than 2° occur mainly over high mountain ranges, the Sahara and during winter in Scandinavia; all these errors only minor influence our simulations. There is a small but persistent bias to higher temperatures in the Amazon region and over the United States that could lead to higher assimilation. ECHAM/BETHY predicts moderate assimilation over these regions neglecting this bias. The leaf water isotopic composition should be influenced by this bias due to lower humidity (increased leaf water) and increased equilibration (reduced leaf water). Both effects oppose each other so that the small temperature bias should be less than the error that is e.g., introduced by taking our current leaf water formulation. *Roeckner et al.* [1996] could not find any systematic differences in precipitation northward of 10°N over land but suspect a small underestimate of precipitation over Eurasia. In the southern hemisphere, the largest errors are over the oceans and over Antarctica, regions of little interest to biosphere simulations. Precipitation over the Amazon is too large during austral summer (DJF) and too small during austral winter (JJA). Assimilation depends strongly on available soil water in BETHY, overestimating assimilation in the Amazon region during austral summer. Again, ECHAM/BETHY seems not to overestimate assimilation in the Amazon region. A definite weakness is the poor representation of the monsoon in South-East Asia leading to reduced assimilation. This can be guessed in Figure 4 by the local minima at around 30°–35°N.

[41] A second point warrants discussion in the validation of ECHAM/BETHY is the invariant signal of  $\delta^{18}\text{O}\text{-CO}_2$  of respiration over the course of the year. This comes from the attenuation of the  $\delta^{18}\text{O}\text{-H}_2\text{O}$  signal with the soil bucket model used in ECHAM. This behavior is probably true for deep soil but not for the upper soil layers. *Miller et al.* [1999] proposed to take the water isotope value at around 15 cm depth to equilibrate with  $\text{CO}_2$  and apply afterward an effective kinetic fractionation of  $-7.2\text{‰}$ . *Riley et al.* [2002] showed that the approach of *Miller et al.* gives similar values as the analytical solution of *Tans* [1998] for moderate soil moisture conditions. During longer drought periods or after rain fall, *Riley et al.* calculate deviations from the simple approach of up to about 5‰, with tendency to higher values. They did not include the invasion effect in the *Miller et al.* approach, which would converge the two calculations [*Stern et al.*, 2001]. The *Miller et al.* approach seems therefore very robust, especially in a global model, if one includes the invasion effect. However, *Miller et al.* take the water isotope value at around 15 cm depth to equilibrate with  $\text{CO}_2$  whereas we have a bucket model, i.e., an integrated value over the total root zone. *Melayah et al.* [1996] measured (and modeled) the gradient in  $\delta^{18}\text{O}\text{-H}_2\text{O}$  in the unsaturated soil layer of a clay loam (bare soil) over the course of three weeks. Surface water  $\delta^{18}\text{O}$  changed during that time by about 10‰ (because of evaporation and rain) whereas soil water at 10 cm depth changed only by about

2‰ and there was almost no change at all at 50 cm depth, even during and after the rain event. So water isotopic composition varies more in reality (at the place where  $\text{CO}_2$  equilibrates with water) than the bucket model indicates, but the variation is still much attenuated, compared to rainwater. Still, our nighttime source signature comparison (Figure 9) suggests that BETHY online calculates  $\text{CO}_2$  source signatures a few ‰ too low, leading to lower apparent soil discrimination, especially during summer with lower soil moisture.

[42] As mentioned before, we take the high non-water-limited  $c_i$  values to better model the seasonal cycle of atmospheric  $\delta^{18}\text{O}\text{-CO}_2$ . However, the seasonal cycle of  $\delta^{18}\text{O}$  depends strongly on the phasing of the isofluxes, just as  $\text{CO}_2$  depends on the phasing of the  $\text{CO}_2$  fluxes. So taking high  $c_i$  values could be an overcompensation effect of the wrong apparent soil discrimination. Thus the model approach of *Riley et al.* [2002] seems a promising way to better include soil processes in  $\delta^{18}\text{O}\text{-CO}_2$  models.

## 5. Conclusions

[43] ECHAM/BETHY showed its capability in simulating the different components necessary to properly estimate  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$ . It is very similar in NPP to the median of 15 NPP models of all different kinds. In the northern hemisphere, it departs from the median and ends more at the lower estimates of the 15 models. An NPP data compilation agrees better with the lower BETHY online NPP in these latitudes, but the compilation is potentially biased toward lower values. Maximum NEE appears too low as well at latitudes poleward of  $50^\circ\text{N}$  but data and model can easily be brought into agreement if one shifts assimilation or respiration by about one month. The high  $c_i$  values at high northern latitudes suggest as well that assimilation could be too low at high northern latitudes but this argument does not hold if one introduces thresholds into its computation so that two interdependent variables decouple at the introduced threshold (here assimilation and  $c_i$ ). It is therefore not deducible, using the current surface data, whether the northern hemispheric  $\text{CO}_2$  fluxes are as low as BETHY online predicts or, on the other extreme, much higher as indicated by inversion techniques. The modeled total rain isotopic composition is very similar to the observed values. ECHAM uses the simplest formulation for soil water, namely a bucket; so there is only one soil water value and hence only one soil water isotope signature. Mixing new rain into the bucket does not substantially change the bucket isotopic value. The large seasonal change in the isotopic composition of rain is almost totally damped out in the soil. Together with the seasonal cycle of temperature, this leads to almost no variation in the isotopic composition of soil-respired  $\text{CO}_2$ .  $\text{CO}_2$  fluxes, the stomata-internal  $\text{CO}_2$  mixing ratio and the isotopic composition of soil water are thus the main determinant of atmospheric  $\delta^{18}\text{O}\text{-CO}_2$ . In the companion paper by *Cuntz et al.* [2003] (part 2), we show that we need high  $c_i$  values to simulate the seasonal cycle of  $\delta^{18}\text{O}\text{-CO}_2$ . However, our  $c_i$  estimates are most likely too high in the northern hemisphere. Diminishing  $c_i$  in the high northern latitudes would be very counterproductive for  $\delta^{18}\text{O}\text{-CO}_2$  and would not produce large changes in  $\text{CO}_2$  fluxes.

However, the wrong signal of respired  $\text{CO}_2$  could act as a compensation to the  $c_i$  effect.

[44] The presented interfacing of ECHAM and BETHY offers the possibility to study some relevant  $\delta^{18}\text{O}\text{-CO}_2$  interactive processes in a global context much more realistic than any approach up-to-date. Simulating a daily cycle provides the capacity to study the complex timing of the different processes involved, in order to obtain  $\text{CO}_2^{18}\text{O}$  fluxes. We have demonstrated this capability in sampling the model to obtain nighttime “Keeling plots” on the 40 minute time step; a mandatory time resolution to compare the model with on site measurements. The interactive nature of ECHAM/BETHY along with its short calculation time step results in an altogether much more realistic analysis for  $\delta^{18}\text{O}\text{-CO}_2$ . We further explore the potential of ECHAM/BETHY in part 2, in which we focus on the atmospheric signal.

## Appendix A: Data Sets

### A1. EMDI

[45] The Ecosystem Model-Data Intercomparison project [*Olson et al.*, 2001] aims to compare model estimates of terrestrial carbon fluxes (NPP) to estimates from ground-based measurements and to improve the understanding of environmental controls on carbon allocation. It extended the work of the Global Primary Production Data Initiative (GPPDI) and compiled NPP estimates for 2523 sites. We used the 3855 so-called Class C cells that represent NPP estimates for  $0.5^\circ$  grid cells for which inventory, modeling, or remote-sensing tools were used to scale up the point measurements. 17 grid cells were associated with two

**Table A1.** Stations Used for NEE Comparison With Station Abbreviations Utilized in Figure 5<sup>a</sup>

ABB Site	Latitude	Longitude	Type	Reference <sup>b</sup>
BL Blodgett For., CA, US	38.90	-120.63	5	a
BR Braschaat, BE	51.30	4.52	4	b
DU Duke For., NC, US	35.98	-79.09	5	c
FL Flakaliden, SE	64.12	19.45	5	d
HL Howland For., ME, US	45.20	-68.74	5	e
HV Harvard For., MA, US	42.54	-72.17	4	f
HY Hyytiälä, FI	61.85	24.28	5	g
LW Little Washita, OK, US	34.96	-97.98	11	h
ME Metolius, OR, US	44.50	-121.62	5	i
PO Ponca City, OK, US	36.77	-97.13	15	j
SH Shidler, OK, US	36.93	-96.68	11	j
SKO Sky Oaks, Old, CA, US	33.37	-116.62	7	k
SKY Sky Oaks, Yng, CA, US	33.38	-116.62	7	k
SO Soroe, DK	55.49	11.65	9	l
TH Tharandt, DE	50.97	13.63	5	m
CFR Centr. For. Res., RU	56.47	32.93	5	n
VI Vielsalm, BE	50.30	6.00	4	o
WB Walker Branch, TN, US	35.96	-84.29	4	p
WE Weidenbrunnen, DE	50.15	11.87	5	q
ZO Zotino, RU	60.75	89.40	5	r

<sup>a</sup>The second-to-last column is the number of BETHY’s plant functional type (compare Table 1).

<sup>b</sup>References: a, *Goldstein et al.* [2000]; b, *Janssens et al.* [2001]; c, *Lai et al.* [2002]; d, *Lindroth et al.* [1998]; e, *Hollinger et al.* [1999]; f, *Barford et al.* [2001]; g, *Markkanen et al.* [2001]; h, *Meyers* [2001]; i, *Law et al.* [2001] and *Anthoni et al.* [1999]; j, *Burba and Verma* [2001]; k, *Oechel et al.* [1998]; l, *Pilegaard et al.* [2001]; m, *Bernhofer et al.* [2003] and *Grünwald and Bernhofer* [2000]; n, *Milyukova et al.* [2002]; o, *Aubinet et al.* [2001]; p, *Baldocchi et al.* [2001]; q, *Bernhofer et al.* [2003]; r, *Lloyd et al.* [2002b] and *Shibistova et al.* [2002].



estimates for different biomes where we took the biome consistent with adjacent cells. We ended up with 3838  $0.5^\circ$  grid cells mainly in Australia, China, the United States, Scandinavia, Senegal and South America.

## A2. FLUXNET

[46] FLUXNET is a global network of micrometeorological tower sites that use eddy covariance methods to measure the exchanges of  $\text{CO}_2$ , water vapor, and energy between terrestrial ecosystems and the atmosphere [Running *et al.*, 1999]. It builds on regional networks of tower sites: Ameriflux (South and North America), CarboEurope/Euroflux (Europe), AsiaFlux (mainly East Asia), OzFlux (Australia and New Zealand), KoFlux (Korea and Thailand), and some independent tower sites. Only Ameriflux and Euroflux data is available through the Oak Ridge National Laboratory Distributed Active Archive Center (ORNL DAAC). The data is available in half-hourly, daily, weekly, monthly, and annual time intervals for each site and year. Selected gap-filling methods were used on both  $u^*$  corrected data and data that had not been corrected for  $u^*$  ( $u^*$  correction = correction for underestimation of carbon fluxes due to stable atmospheric stratification;  $u^*$ : friction velocity). The original eddy data were processed using four methods developed by Falge *et al.* [2001a, 2001b]. The “Look-up table” method with  $u^*$  corrected NEE algorithm is recommended to be the most robust method for most sites. The data for Hyytiälä in Finland was updated by T. Suni (personal communication, 2001) because of problems in winter fluxes.

## A3. EUROSIBERIAN CARBONFLUX

[47] We added two eddy flux measurement forest sites in Russia from the EUROSIBERIAN CARBONFLUX project [Milyukova *et al.*, 2002; Lloyd *et al.*, 2002b; Shibistova *et al.*, 2002]. The EUROSIBERIAN CARBONFLUX project includes a combination of surface flux measurements by means of the eddy covariance technique at selected stations together with atmospheric observations from aircraft of the  $\text{CO}_2$  mixing ratio, and other atmospheric tracers linked to the carbon cycle (carbon isotopes,  $\text{N}_2\text{O}$ ,  $\text{SF}_6$ ,  $\text{O}_2/\text{N}_2$ ,  $\text{CH}_4$ ) [Schulze *et al.*, 2002]. The eddy measurements are provided as half-hourly,  $u^*$  corrected NEE estimates from which we calculated the monthly means.

[48] Table A1 provides the coordinates of all 20 FLUXNET and EUROSIBERIAN CARBONFLUX stations together with the number of BETHY’s plant functional type (compare Table 1) and the abbreviations used in Figure 5.

## A4. NOAA/CMDL

[49] The numbers in Figure 7 correspond to continental sampling sites of the NOAA/CMDL Cooperative Air Sampling Network. We took the same numbers for each stations as Miller *et al.* [2003], and the corresponding station names are given in Table A2.

## A5. GNIP

[50] The Global Network of Isotopes in Precipitation (GNIP) of the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) (see Global Network of Isotopes in Precipitation: The GNIP

**Table A2.** Continental Station Sites With Correspondent Numbers Used in Figure 7 to Compare With ECHAM/BETHY’s  $\delta_{\text{bio}}^{13}\text{C}$

	Code	Site	Latitude	Longitude
1	ASK	Assekrem, DZ	23.18	5.42
2	BAL	Baltic Sea, PL	55.50	16.67
3	BSC	Black Sea, RO	44.17	28.68
4	HUN	Hegyhsal, HU	46.95	16.65
5	ITN	North Carolina, US	35.37	-77.39
6	KZD	Plateau Assy, KZ	44.45	77.57
7	KZM	Sary Taukam, KZ	43.25	77.88
8	LEF	Wisconsin, US	45.93	-90.27
9	NWR	Colorado, US	40.05	-105.58
10	TAP	Tae-anh Penin., KR	36.73	126.13
11	UTA	Utah, US	39.90	-113.72
12	UUM	Ulaan Uum, MN	44.45	111.10
13	WIS	Negev Desert, IL	31.13	34.88
14	WLG	Mt. Waliguan, CN	36.29	100.90

database, available at <http://isohis.iaea.org>) has been surveying the content of hydrogen and oxygen isotopes in precipitation since 1961. More than 550 meteorological stations in 93 countries have been collecting monthly precipitation samples for GNIP, i.e., they have been collecting monthly composite total rainfall, for tritium, deuterium and  $^{18}\text{O}$  analysis. We filtered out 186 station records with sufficient data and calculated the precipitation weighted annual mean  $\delta^{18}\text{O}\text{-H}_2\text{O}$ .

## A6. BASIN and Further Ecosystem Resources

[51] The Biosphere-Atmosphere Stable Isotope Network (BASIN) is an activity of the Global Change and Terrestrial Ecosystem core project (GCTE) Focus 1, which aims to improve the understanding of carbon cycle processes at the ecosystem, regional, and global scales [Pataki *et al.*, 2003].

**Table A3.** Stations Used for Source Signature Comparison of Respired  $\text{CO}_2$  in Figure 9<sup>a</sup>

	Site	Latitude	Longitude	Type
	Boreas, Pine, CA	55.93	-98.62	5
	Boreas, Spruce, CA	55.91	-98.51	5
	Cascade, WA, US	47.32	-121.58	5
	Cascade Head, OR, US	44.48	-124.10	5
	Brasilia, BR	-10.57	-47.58	2
	Corvallis, OR, US	44.62	-123.20	5
	Konza Prairie, KS, US	39.08	-96.58	11
	Lethbridge, CA	49.90	-112.60	9
	Logan, UT, US	41.90	-111.82	15
	Manaus, For., BR	-2.59	-60.11	1
	Manaus, Pasture, BR	-2.59	-60.11	12
	Mbalmayo, CM	3.51	11.50	1
	Metolius, OR, US	44.48	-121.62	5
	Ottawa, CA	45.32	-75.67	5
	Paracou, GF	5.03	-53.00	1
	Red Butte Canyon, UT, US	40.78	-111.77	4
	Rondonia, For., BR	-10.08	-61.93	1
	Rondonia, Pasture, BR	-10.76	-61.36	1
	Santarem, For. km 64, BR	-2.86	-54.96	1
	Santarem, For. km 83, BR	-3.02	-54.97	1
	Santarem, Pasture, BR	-3.02	-54.96	12
	Sisters, OR, US	44.25	-121.23	5
	Central For. Reserve, RU	56.47	32.93	5
	Wagga Wagga, AU	-35.12	147.37	9
	Wind River, 500 yr, WA, US	45.82	-121.95	5
	Wind River, 40 yr, WA, US	45.82	-121.95	5
	Wind River, 20 yr, WA, US	45.82	-121.95	5
	Zotino, RU	60.75	89.40	5

<sup>a</sup>The last column is the number of BETHY’s plant functional type (compare Table 1).



It assembles a collection of  $\text{CO}_2$  and stable isotope measurements mainly in Europe and North and South America.  $\text{CO}_2$  and  $\delta^{13}\text{C}$  are measured at all sites of the BASIN database but  $\delta^{18}\text{O}\text{-CO}_2$  measurements are rather sparse. We identified 25 sites in the database with valid  $\delta^{18}\text{O}$  measurements, but for two of these sites, we did not find the appropriate ecosystem in our model. This gave 2470 data points with  $\text{CO}_2$  and  $\delta^{18}\text{O}\text{-CO}_2$  out of the BASIN database. We updated the record of Paracou in French Guiana with 42 measurements made by N. Buchmann (personal communication, 2001). In addition, we included 93  $\text{CO}_2$  and  $\delta^{18}\text{O}\text{-CO}_2$  measurements made by J. Lloyd and colleagues (personal communication, 2001) in Wagga Wagga, Australia, Brasilia, Brazil [Miranda *et al.*, 1996] and Mbalmayo, Cameroon. We added as well 192 data points in Russia from the EUROSIBERIAN CARBONFLUX project described above [Langendörfer *et al.*, 2002; Styles *et al.*, 2002b]. Table A3 lists the stations, their coordinates, and the numbers of the corresponding BETHY plant functional types. Together, this gives 2797 single measurements of  $\text{CO}_2$  and  $\delta^{18}\text{O}\text{-CO}_2$ , in which we found 54 nighttime events with data appropriate for Keeling plots.

## Notation

- $a$  kinetic fractionation of  $^{13}\text{C}$  diffusion in air, equal to 4.4‰.
- $a_1$  intercept of regression between salinity and  $\delta^{18}\text{O}\text{-H}_2\text{O}$  of ocean surface water, equal to  $-16.75\text{‰}$  versus VSMOW.
- $a_2$  slope of regression between salinity and  $\delta^{18}\text{O}\text{-H}_2\text{O}$  of ocean surface water, equal to  $0.5\text{‰}$  versus VSMOW.
- $\alpha$  fractionation factor.
- $\alpha_d$  kinetic fractionation factor of  $\text{CO}_2$  in (free) air, equal to 0.9913.
- $\alpha_k^W$  effective kinetic fractionation factor of water vapor, equal to 0.974.
- $\alpha_l$  effective fractionation factor for  $\text{CO}_2$  diffusion in and out of stomata, equal to 0.9926.
- $\alpha_{l\text{-vap}}^W$  fractionation factor for  $\text{H}_2^{18}\text{O}$  at the water-vapor phase transition.
- $\alpha_s$  effective fractionation factor for  $\text{CO}_2$  diffusion out of soil, equal to 0.9928.
- $\alpha_w$  effective fractionation factor of  $\text{CO}_2$  crossing the air-sea interface, including hydration, equal to 1.0008.
- $b$   $^{13}\text{C}$  fractionation associated with carboxylation, equal to 27‰.
- $b_3$   $^{13}\text{C}$  fractionation associated RUBISCO carboxylation, equal to 29‰.
- $b_4$   $^{13}\text{C}$  fractionation associated PEP carboxylation, equal to  $-5.6\text{‰}$  (at  $25^\circ\text{C}$ ).
- $b_e$  factor linking water pressure deficit and stomatal conductance without water limitation to actual stomatal conductance.
- $B$  Bunsen solubility coefficient.
- $c_a$   $\text{CO}_2$  mixing ratio in (free) air, ppm.
- $c_1$  renormalization constant to get biosphere in equilibrium,  $\text{mol}(\text{H}_2\text{O}) \text{m}^2 \text{s}^{-1}$ .
- $c_c$   $\text{CO}_2$  mixing ratio in chloroplast, ppm.

- $c_{cs}$   $\text{CO}_2$  mixing ratio at the site of isotopic  $\text{CO}_2$  equilibration with water, ppm.
- $c_i$   $\text{CO}_2$  mixing ratio in stomata, ppm.
- $c_{i0}$   $\text{CO}_2$  mixing ratio in stomata without water limitation, ppm.
- $c_w$  empirical parameter representing root density, equal to  $0.5 \text{ mm/hr}$ .
- $D$  molecular diffusivity of  $\text{CO}_2$  in (free) air,  $\text{m}^2 \text{s}^{-1}$ .
- $D_{18}$  molecular diffusivity of  $\text{CO}^{18}\text{O}$  in (free) air, equal to  $\alpha_d D$ .
- $\delta_a$   $\delta^{18}\text{O}\text{-CO}_2$  value of (free) air, ‰ versus VPDB- $\text{CO}_2$ .
- $\delta_{a0}$  global initial  $\delta^{18}\text{O}\text{-CO}_2$  value of (free) air in the model, ‰ versus VPDB- $\text{CO}_2$ .
- $\delta_f$   $\delta^{18}\text{O}\text{-CO}_2$  value of  $\text{CO}_2$  produced by burning processes, equal to  $-17.0\text{‰}$  versus VPDB- $\text{CO}_2$ .
- $\delta_o$   $\delta^{18}\text{O}\text{-CO}_2$  value of  $\text{CO}_2$  equilibrated with ocean surface water, ‰ versus VPDB- $\text{CO}_2$ .
- $\delta_{bio}^{13}\text{C}$   $\delta^{13}\text{C}$  source signature of terrestrial biosphere, ‰ versus VPDB- $\text{CO}_2$ .
- $\Delta e$  air vapor pressure deficit, Pa.
- $\Delta p\text{CO}_2$  air-sea partial pressure difference of  $\text{CO}_2$ .
- $\Delta_A$  discrimination of assimilation for  $^{18}\text{O}$ .
- $\Delta_A^{13}\text{C}$  discrimination of assimilation for  $^{13}\text{C}$ .
- $\Delta_A^{18}\text{O}$  discrimination of assimilation for  $^{18}\text{O}$ , equal to  $\Delta_A$ .
- $\Delta_f$  difference between the isotopic signature of  $\text{O}_2$  (involved in combustion) and  $\text{CO}_2$ .
- $\Delta_{inv}$  apparent discrimination of invasion.
- $\Delta_o^{des}$  ocean disequilibrium or the tendency to equilibrate the difference between atmospheric and ocean dissolved  $\text{CO}_2$ .
- $\Delta_o^{equ}$  equilibrium discrimination between ocean and atmosphere.
- $\Delta_R$  apparent discrimination of soil respiration.
- $\epsilon$  fractionation.
- $\epsilon_{eq}$  equilibrium fractionation of  $\text{CO}_2$  with water, equal to  $+41.1\text{‰}$  (at  $25^\circ\text{C}$ ).
- $\epsilon_k^W$  effective kinetic fractionation of water vapor, equal to  $-26.0\text{‰}$ .
- $\epsilon_l$   $-7.4\text{‰}$ , effective fractionation factor for  $\text{CO}_2$  diffusion in and out of stomata.
- $\epsilon_{l\text{-vap}}^W$  fractionation for  $\text{H}_2^{18}\text{O}$  at the water-vapor phase transition.
- $\epsilon_s$   $-7.2\text{‰}$ , effective fractionation factor for  $\text{CO}_2$  diffusion out of soil.
- $\epsilon_w$   $+0.8\text{‰}$ , effective fractionation factor for  $\text{CO}_2$  diffusion in and out of ocean water.
- $E_v$  actual transpiration rate,  $\text{mol}(\text{H}_2\text{O}) \text{m}^2 \text{s}^{-1}$ .
- $E_{vmax}$  potential transpiration rate,  $\text{mol}(\text{H}_2\text{O}) \text{m}^2 \text{s}^{-1}$ .
- $f_e$  actual/potential evapotranspiration.
- $F$   $\text{CO}_2$  flux,  $\text{mol}(\text{CO}_2) \text{m}^2 \text{s}^{-1}$ .
- $^{18}F$   $\text{CO}^{18}\text{O}$  flux,  $\text{mol}(\text{CO}^{18}\text{O}) \text{m}^2 \text{s}^{-1}$ .
- $F_A$  net assimilation rate, equal to  $\text{GPP} - F_{Rleaf}$ ,  $\text{mol}(\text{CO}_2) \text{m}^2 \text{s}^{-1}$ .
- $F_{A0}$  net assimilation rate without water limitation,  $\text{mol}(\text{CO}_2) \text{m}^2 \text{s}^{-1}$ .
- $^{18}F_A$   $\text{CO}^{18}\text{O}$  net assimilation rate,  $\text{mol}(\text{CO}^{18}\text{O}) \text{m}^2 \text{s}^{-1}$ .

$F_{bur}$	biomass burning $\text{CO}_2$ flux, equal to $3.1 \text{ GtC yr}^{-1}$ , $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$R_{l-ca}$	effective $[\text{O}^{18}]/[\text{O}^{16}]$ of $\text{CO}_2$ equilibrated with leaf water, taking reduced carbonic anhydrase activity into account and using the same formulation as with full carbonic anhydrase activity.
$F_{fos}$	fossil fuel consumption $\text{CO}_2$ flux, equal to $5.8 \text{ GtC yr}^{-1}$ , $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$R_{l-cg}^{W(t)}$	Craig and Gordon steady state solution of $[\text{O}^{18}]/[\text{O}^{16}]$ of water at the site of evaporation at time $t$ .
$F_{inv}$	invasion flux; virtual $\text{CO}_2$ in and out of soil, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$R_s^W$	$[\text{O}^{18}]/[\text{O}^{16}]$ of soil water.
${}^{18}F_{inv}$	$\text{CO}^{18}\text{O}$ invasion flux out of soil, $\text{mol}(\text{CO}^{18}\text{O}) \text{ m}^2 \text{ s}^{-1}$ .	$R_o$	$[\text{O}^{18}]/[\text{O}^{16}]$ of $\text{CO}_2$ equilibrated with ocean surface water.
$F_R$	biorepiration flux, equal to $F_{Rhet} + F_{Rauto} - F_{Rleaf}$ , $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$R_{vap}^W$	$[\text{O}^{18}]/[\text{O}^{16}]$ of water vapor.
${}^{18}F_R$	$\text{CO}^{18}\text{O}$ biorepiration flux, $\text{mol}(\text{CO}^{18}\text{O}) \text{ m}^2 \text{ s}^{-1}$ .	$R_{VPDB}$	standard isotope ratio of Vienna Pee Dee Belemnite (VPDB)- $\text{CO}_2$ [Allison et al., 1995], equal to $2088.349077 \times 10^{-6}$ .
$F_{Rauto}$	$\text{CO}_2$ autotrophic respiration flux, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$R_{VSMOW}$	standard isotope ratio of Vienna Standard Mean Ocean Water (VSMOW) [Baertschi, 1976], equal to $2005.2 \times 10^{-6}$ .
$F_{Rhet}$	$\text{CO}_2$ heterotrophic respiration flux, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$S$	root supply rate.
$F_{Rleaf}$	$\text{CO}_2$ leaf (dark) respiration flux, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$SAL$	salinity, $\text{g}(\text{salt}) \text{ kg}(\text{water})^{-1}$ .
$F_{Rroot}$	$\text{CO}_2$ autotrophic respiration flux that leaves plants by roots, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$t$	time step.
$F_{ao}$	$\text{CO}_2$ gross air-ocean flux, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$T_a$	air temperature, $^\circ\text{C}$ .
$F_{oa}$	$\text{CO}_2$ gross ocean-air flux, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$\tau$	turnover time of leaf water, equal to $V_l/E_v$ ( $\approx 3$ ), hr.
$F_o$	$\text{CO}_2$ net flux between ocean and atmosphere, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$\Theta_a$	air-filled pore fraction of soil.
$g_c$	canopy conductance, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$\Theta_w$	water-filled pore fraction.
$g_{c0}$	canopy conductance without water limitation, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$u^*$	friction velocity, $\text{m s}^{-1}$ .
$g_s$	stomatal conductance, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$V_l$	leaf water volume.
$g_s'$	combined stomatal plus mesophyll conductance, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$V_m$	maximum carboxylation rate at $25^\circ\text{C}$ , $\text{mol}(\text{CO}_2) \text{ m}^{-2} \text{ s}^{-1}$ .
$GPP$	Gross Primary Productivity, $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .	$W_s$	actual soil water content, m.
$h$	relative humidity adjusted to leaf temperature.	$W_{s,max}$	maximal root available soil water content, m.
$h_V$	vegetation height, m.	$\zeta$	$=(1-h)(\epsilon_{l-vap}^W + 1)(\epsilon_k^W + 1)$ .
$J_m$	maximum electron transport rate at $25^\circ\text{C}$ , $\text{mol}(\text{CO}_2) \text{ m}^{-2} \text{ s}^{-1}$ .		
$k$	PEPcase rate constant for $\text{CO}_2$ at $25^\circ\text{C}$ (and standard pressure), $\text{mol}(\text{CO}_2) \text{ m}^{-2} \text{ s}^{-1}$ .		
$k_1$	constant of global balance equation, $\% \text{ yr}^{-1}$ .		
$k_2$	inverse of e-folding time of model equilibration, $\text{yr}^{-1}$ .		
$k_H$	$\text{CO}_2$ hydration rate, $\text{s}^{-1}$ .		
${}^{18}k_H$	$\text{CO}_2$ isotope equilibration rate with water, equal to $k_H/3$ , $\text{s}^{-1}$ .		
$\kappa$	soil tortuosity.		
$M_a$	conversion factor between fluxes in GtC and mixing ratios in ppm, equal to $2.122 \text{ GtC ppm}^{-1}$ .		
$NPP$	Net Primary Productivity, equal to $GPP - F_{Rauto}$ , $\text{mol}(\text{CO}_2) \text{ m}^2 \text{ s}^{-1}$ .		
$Q_{10}$	relative change in $F_{Rhet}$ per $10^\circ$ change in (air) temperature, equal to 1.5.		
$r^2$	coefficient of determination.		
$R$	isotope ratio.		
$R_a$	$[\text{O}^{18}]/[\text{O}^{16}]$ of (free) air.		
$R_f$	$[\text{O}^{18}]/[\text{O}^{16}]$ of combusted fossil fuel.		
$R^W$	isotope ratio of water.		
$R_i^W$	$[\text{O}^{18}]/[\text{O}^{16}]$ of xylem water, approximately equal to soil water.		
$R_l$	$[\text{O}^{18}]/[\text{O}^{16}]$ of $\text{CO}_2$ equilibrated with leaf water at the site of evaporation.		
$R_l^W$	$[\text{O}^{18}]/[\text{O}^{16}]$ of leaf water at the site of evaporation.		
$R_l^{W(t)}$	$[\text{O}^{18}]/[\text{O}^{16}]$ of leaf water at time step $t$ .		
$R_l^{W(t-1)}$	$[\text{O}^{18}]/[\text{O}^{16}]$ of leaf water one time step before $t$ .		

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