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¹⁸O in Atmospheric CO₂ Simulated by a 3-D Transport Model: A Sensitivity Study to Vegetation and Soil Fractionation Factors

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Abstract. The ${}^{18}O/{}^{16}O$ ratio in atmospheric CO₂ is a signal dominated by the processes by which the global land biosphere absorbs and respires CO_2 . Potentially it makes it possible to separate the photosynthesis from the total ecosystem respiration provided that leaf CO_2 and soil CO_2 have different isotopic signatures, that the air-sea exchange is correctly treated and that the isotopic value of anthropogenic emissions is well characterized. In this paper we simulate the δ^{18} O of atmospheric CO₂, using the 3-D tracer model TM2. We perform a specific sensitivity study of δ^{18} O to the fractionation factors for the diffusion of CO_2 out of the soils (ϵ_{soil}) and into/out of the leaves (ϵ_{leaf}) . The control run is similar to Ciais et al. (1996a). The latitudinal gradient, the seasonal amplitude in the northern hemisphere and the mean long term trend appear to be fairly sensitive to these two factors. The trend is nevertheless the most sensitive but it also highly depend on the atmospheric δ^{18} O mean value and on the stratospheric enrichment of ¹⁸O in CO_2 pertaining to the photolysis of O_3 .

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1 Introduction

An increasing attention has been given to the isotopes of CO_2 ($^{13}CO_2$ and more recently $C^{18}O^{16}O$), as they bring additional constrains to the global carbon cycle. The oxygen isotopic content of atmospheric CO_2 is primarily driven by interactions between CO_2 and the reservoirs of liquid water (see Eq. 2 in Table 1 for isotopic equilibrium between CO_2 and H_2O). Francey and Tans (1987) showed indeed that direct O atom exchange between CO_2 and H_2O vapor does not occur in the gas phase. On the other hand, when CO_2 dissolves in water, an isotopic equilibrium for oxygen atoms takes place. Because the amount of CO_2 , the ${}^{18}O/{}^{16}O$ ratio in CO_2 is de-

termined by the one of water at a given temperature. Francey and Tans (1987) and Farquhar et al. (1993) pointed out the major influence of CO₂ exchanges with leaf water (photosynthesis) and soil water (soil respiration). Ciais et al. (1996a,b) further tested these parameterizations in a global 3-D transport model, and obtained reasonable agreement between simulated and observed ¹⁸O/¹⁶O ratio in atmospheric CO₂. Following their work, we present here a sensitivity study of this ratio to the fractionation factors involved during the diffusion of CO₂ out of the soil and into/out of the leaves.

2 The observations

¹⁸O in CO₂ is routinely measured at specific locations around the world from three independent air sampling networks: the NOAA-CU network of 17 sites (Trolier et al., 1996), the SCRIPPS-CIO network of 10 sites (*Meijer et al.*, in preparation), and the CSIRO network of 5-6 sites (Francey et al., 1990). The ¹⁸O/¹⁶O isotopic ratios are reported in the δ scale (Eq. 1, Table 1), and δ ¹⁸O values are expressed in per mil (‰). At a global scale, three major features can be retrieved from the atmospheric observations.

- A north minus south difference of roughly -1.5‰: the northern hemisphere is permanently depleted in ¹⁸O, as first observed by Francey and Tans (1987).
- A strong seasonal cycle at high northern latitudes (Keeling, 1961): there is a maximum in early summer and a minimum in early winter. The observed peak-to-peak amplitude is 1.44‰ at Point Barrow (71°N, 156°W) while Cape Grim in the southern hemisphere (40°S, 140°E) has a lower peak-to-peak amplitude of 0.4‰.
- 3. The long time series of the SCRIPPS-CIO network (5 sites since 1977) shows no long term trend in the

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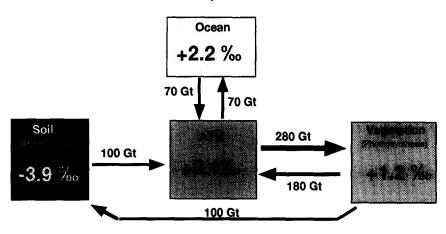


Fig. 1. The global "pre-anthropogenic" exchange fluxes of CO₂ (in GTC (10^{15} g) yr⁻¹) between the atmosphere and the terrestrial biosphere and the ocean, as well as the isotopic composition of CO₂ (expressed in \mathcal{H}_o PDB-CO₂), in equilibrium with the exchangeable water. The δ^{18} O value of these three reservoirs is weighted in space and time with the exchange fluxes.

mean atmospheric δ^{18} O (e.g., record at Mauna-Loa, Meijer et al., private communication).

Exchange with leaves and soils is strongly seasonal over temperate and boreal ecosystems which likely account for most of the observed δ^{18} O annual cycle. Moreover the combined effects of photosynthesis and respiration tend to decrease the local δ^{18} O in atmospheric CO₂ at high northern latitudes. This pattern follows the composition of precipitation which is depleted in ¹⁸O relative to sea-water towards high latitudes and towards the interior of continents.

3 Biospheric fluxes

We coupled the surface exchange fluxes of CO_2 and C¹⁸O¹⁶O for each reservoir to an atmospheric 3-D tracer model (TM2) in order to simulate the global distribution of δ^{18} O in atmospheric CO₂. The TM2 model (Heimann, 1995) uses atmospheric forcing from ECMWF in Reading (UK) and it is run at a resolution of 7.5° by 7.5° in the horizontal, with 9 vertical levels (σ coordinates). We will focus on the global "pre-anthropogenic" steady state budget of δ^{18} O in atmospheric CO₂ and more specifically on the terrestrial biospheric fluxes. Figure 1 presents the CO_2 gross exchange fluxes between the atmosphere and the vegetation, the soils and the ocean, as well as the δ^{18} O of CO₂ in isotopic equilibrium with chloroplast water, soil water or sea surface water. The main equations used to describe these processes are reported in Table 1.

- Leaf exchange : During photosynthesis, all of the atmospheric CO_2 that enters the chloroplasts, isotopically equilibrates with the evaporating water, in presence of enzyme Carbonic Anhydrase. Some of the CO_2 is then assimilated by photosynthesis

(net Assimilation, A) but more than half of it diffuses back to the atmosphere. Chloroplast water is enriched in ¹⁸O compared to soil water because heavier water molecules evaporate less efficiently than the lighter ones. The degree of enrichment of leaf water is sensitive to the relative humidity, the canopy temperature and to ¹⁸O/¹⁶O ratio in water vapor (Craig and Gordon, 1965). It can be thus highly variable in space and time: the Assimilation weighted mean value in our simulation is $\pm 1.2\%_{o}$ (Fig. 1). Moreover C¹⁸O¹⁶O diffuses more slowly than C¹⁶O₂ into/out of the leaves (coefficient α_l in equation 3, Table 1). The overall effect of photosynthesis is to increase the δ^{18} O in atmospheric CO₂.

- Soil exchange : The decomposition of dead organic matter by soil microorganisms and root respiration in the soil produce CO₂ which diffuses up to the atmosphere. This net flux augmented by the stem and twigs respiration, balances on annual mean the net uptake of CO₂ during photosynthesis. We thus neglect any net carbon storage or loss by ecosystems on an annual mean basis. Diffusion in the soil is likely slow enough for CO₂ to fully exchange ¹⁸O with the water at the soil surface, even without Carbonic Anhydrase (Ciais et al., 1996a). The ¹⁸O/¹⁶O ratio of soil water tends to follow the variations in surface soil moisture, and thereof the precipitation. This leads in our simulation to a respiration weighted mean value of -3.9% for CO2 isotopically equilibrated with soil water (Fig. 1). As for leaf exchange, a diffusive fractionation occurs during diffusion of CO_2 out of the soil (coefficient α_s in equation 4, Table 1), and the effect of soil respiration is to decrease the δ^{18} O in atmospheric CO_2 .

- Ocean exchange : The net CO_2 flux between the ocean and the atmosphere can be split in two gross (one way) fluxes (equation 5, Table 1). The CO_2 gross flux out of the ocean is assumed to be isotopically equilibrated with sea-water, according to reaction (2). The $\delta^{18}O$ of sea-surface water is computed from the sea-surface temperature and the salinity, as in Farquhar et al. (1993). The fractionation during CO_2 diffusion at the air-sea interface is very small (-0.8‰) and the global effect of air-sea exchange is to increase the atmospheric $\delta^{18}O$ value (Fig. 1).
- Stratospheric enrichment: Recent measurements of δ^{18} O of CO₂ reported by Gamo et al. (1989) showed a mass independent enrichment in ¹⁸O of 2% in the lower stratosphere (19 km) relative to the mean tropospheric value. This enrichment increases with altitude and pertains to the photolysis of O₃ in the stratosphere (Yung et al., 1991). We parameterized this effect by simply adding a source of C¹⁸O¹⁶O, constant in time and space in the upper two levels of the transport model in order to simulate a mean vertical profile of δ^{18} O of CO₂ close to that observed (Fig. 4).

The CO_2 gross fluxes between the atmosphere and the vegetation (F_{la} and F_{al} , Table 1) are derived from the SIB2 land-surface parameterization (Sellers et al., 1986, 1996; Randall et al., 1996) coupled to the CSU-GCM (Randall et al., 1992; Randall and Pan, 1993; Fowler et al., 1996). The total respiration $(F_{resp}, Table 1)$ equals the net assimilation of carbon over a year but it is distributed in time according to the ground moisture and soil temperature. The oceanic gross fluxes (F_{oa} and F_{ao} , Table 1) are calculated using ΔpCO_2 from the Hamburg Model of the oceanic carbon cycle (Maier-Reimer, 1993; Six and Maier-Reimer, 1996), and gas exchange coefficients derived from ECMWF 10 meter wind fields. These coefficients follow the Liss and Merlivat relationship (Liss and Merlivat, 1986) and they are scaled by a global factor of 1.9 in order to be consistent with the global inventory of ¹⁴C in the ocean. The monthly means δ^{18} O of precipitation are taken from the GISS simulations (Jouzel et al., 1987). We run the tracer model for each component described above and with the atmospheric wind fields corresponding to the period 1990-1994. The choice of this particular period has no importance regarding the mean budget of $\delta^{18}O$ in CO₂. The specific δ^{18} O field relative to one process can be then calculated. But as the δ fields are not additive we use the δ -anomalies (δ^* , defined in Eq. 1, Table 1) which are additive, in order to combine and compare several components (Fig. 2-3).

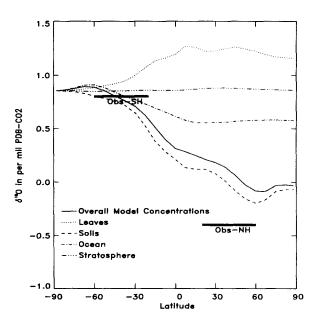


Fig. 2. Simulated δ^{18} O-anomalies (δ^* , see equation 1, Table 1) of atmospheric CO₂ at the surface using the 3-D transport model TM2 (zonal average). The different components correspond to the separate δ^{*18} O implied by leaf exchange, soil exchange, ocean exchange and stratospheric enrichment. The observations represent the mean value between 20° and 60° for the northern hemisphere and between 20° and 60° for the southern one (derived from a zonal fit to the observations made by the NOAA-CU network).

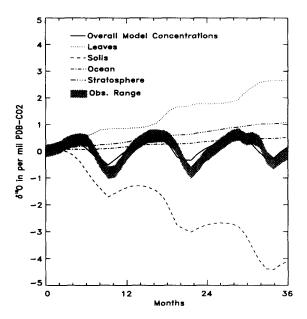


Fig. 3. Simulated δ^{18} O-anomalies (δ^*) in atmospheric CO₂ simulated at Point Barrow (71°N, 156°W) for the period 1990 to 1993. The different components are as in Fig. 2. The grey region represent the observations from the NOAA-CU network (the range is two times the standard deviation of the function used to fit the observations).

Fig. 4. Simulated δ^{18} O-anomalies (δ^*) in atmospheric CO₂ averaged over all grid points (vertical profile). The dot curve corresponds to a simulation where the "stratospheric enrichment" is double compared to the control run (solid line). Triangles are data by Gamo et al. (1989) over Japan and circles by Thiemens and Jackson (1991) over Palestine.

4 Sensitivity of δ^{18} O in CO₂ to fractionation factors

4.1 Control run

Ciais et al. (1996b) realized a simulation of δ^{18} O in atmospheric CO₂ over the course of a year. Their results fit reasonably well the observations in terms of north minus south difference and seasonal amplitudes at the Point Barrow, Mauna-Loa and Cape Grim stations. We use in this study a slightly different control run. The CO₂ exchange coefficient for the oceanic fluxes (*Kex* in equation 5, Table 1) is derived from Liss and Merlivat relationship instead of from the stability dependent theoretical formulation of Erickson (1993). We also included the stratospheric enrichment of ¹⁸O in CO₂, for the "pre-industrial" scenario.

Figure 2 plots the zonal average of the simulated δ^{18} Oanomalies (δ^*) at the surface. It shows the relative contribution of the terrestrial biosphere and of the ocean and the opposite effect of vegetation and soils. The simulated north-south gradient is compared to an estimate of the observed difference between the northern and the southern hemisphere (see caption, Fig. 2). This control run with only the "pre-industrial" fluxes explain a large part of the observed difference, although the additional depletion of the ¹⁸O/¹⁶O ratio in CO₂ due to fossil fuel burning is missing in this scenario.

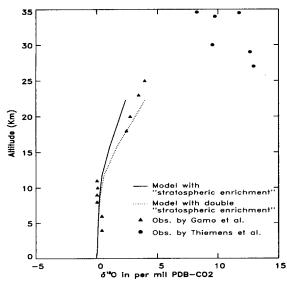
Figure 3 presents the simulated trend in δ^{18} O-anomalies (δ^*) at Point Barrow (71°N, 156°W) for each compo-

nents as well as the observations from the NOAA-CU network. The trend is primarily determined by the biospheric exchanges, while the ocean plays a weaker role. There is a competing effect between soils and vegetation for the net budget of ¹⁸O in atmospheric CO₂. While the ecosystem global respiration depletes the atmospheric CO₂ in ¹⁸O, the photosynthesis enriches it. Ciais et al. (1996b) used only a global formulation similar to equation 6 (Table 1). They solved this global equation for the parameter α_s to obtain a zero trend for δ^{18} O in atmospheric CO₂. In our simulation, we verified that with the TM2 model such an approach gives similar results if we compare the real trend simulated at many locations and the one calculated through the global budget.

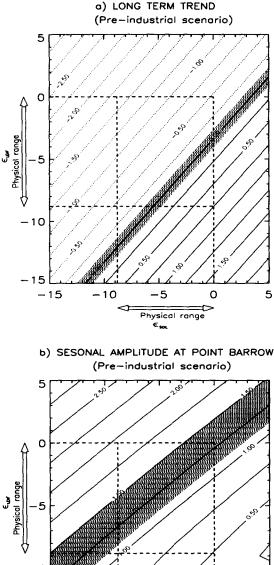
Concerning the "pre-anthropogenic" steady state budget for ${}^{18}O$ in CO₂ we would like to simulate a long term trend close to zero as well as realistic inter-hemispheric difference and seasonal amplitude at Point Barrow. Even if the exchange time for the oxygen atom in CO_2 with the biosphere was estimated by Farguhar et al. (1993) to be much smaller than with the ocean (2.2 and 8.3)years respectively), the two reservoirs are connected to each other by the mean atmospheric δ^{18} O level. At long time-scales both reservoirs will thus contribute to the mean δ^{18} O value. Concerning the biosphere, the δ^{18} O fluxes (Eqs. 3-4, Table 1) are driven mainly by the CO_2 gross exchanges fluxes $(F_{resp}, F_{al}, F_{la})$, the isotopic ratio of water in isotopic equilibrium with CO_2 and the fractionation during the diffusion of CO₂ (α_s and α_l). In the following, we specifically analyze the sensitivity of δ^{18} O in atmospheric CO₂ to the two fractionation factors.

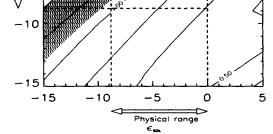
4.2 Sensitivity to the fractionation factors ϵ_s and ϵ_l

Figure 5 presents the results of three sensitivity tests where the two fractionation factors $\epsilon_s = (\alpha_s - 1) \cdot 10^3$ and $\epsilon_l = (\alpha_l - 1) \cdot 10^3$ vary over a given physical range (the other parameters were set as in the control run). These tests were performed with only one simulation. We multiplied the concentration fields produced by the transport model (TM2) with the desired ϵ_s and ϵ_l coefficients. This is possible because these coefficients only scale the ¹⁸O fluxes (Eqs. 3-4, Table 1) and because the concentration fields produced by TM2 for each component are additive. The first plot (Fig. 5a) presents the δ^{18} O trend in atmospheric CO₂ at Point Barrow. Because of the relatively short mixing time for CO_2 in the atmosphere, the trend at this station represents well the mean atmospheric trend, when sources and transport are at steady state. We realized the same sensitivity test for the seasonal amplitude at Point Barrow (Fig. 5b) and for the global difference between the northern hemisphere and the southern hemisphere (Fig. 5c: difference calculated as in Fig. 2). In grey we shade the region that corresponds to realistic "observed" values for the three quantities. We made the assumption that



a steady state was reached at "pre-industrial" time with a long term trend close to zero and that the amplitude of the seasonal cycles has not significantly changed compared to the actual observations.





Concerning the inter-hemispheric difference (Fig. 5c) the contribution of the burning of fossil fuel is to increase by 0.3 % this difference (e.g., Ciais et al. (1996b)). In this case we thus added this component to the "pre-



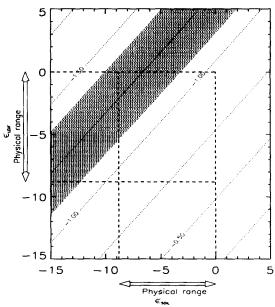


Fig. 5. Sensitivity test of δ^{18} O in atmospheric CO₂ simulated by TM2, to the fractionation factor involved during CO₂ diffusion out of soils (ϵ_{soil}) and CO₂ diffusion into/out of the leaves (ϵ_{leaf}). (a) correspond to the long term trend, (b) to the seasonal amplitude a Point Barrow (71°N, 156°W), and (c) to the inter-hemispheric difference (we took grid points between 20° and 60° for the northern hemisphere and between 20° and 60° for the southern one). (a) and (b) result only from the biospheric fluxes ("pre-industrial" scenario) while (c) includes also fossil fuel burning. The grey regions correspond to the observed range of values for each case.

industrial" budget in order to compare simulated differences in a realistic way to values given by the actual observations. We can also notice that fossil fuel should have induced a negative trend in the atmosphere of -0.14% per year. As this decrease is not observed in the measurements, other mechanisms must compensate for this effect in today's δ^{18} O budget as opposed to the "pre-industrial" simulation.

In each of these plots, we defined a physical range for the fractionation factors. The lower limit $(-8.8\%_o)$ corresponds to molecular diffusion with slower diffusion of $C^{18}O^{16}O$ compared to $C^{16}O_2$. On the other hand a value of zero would reflect no diffusive discrimination against ¹⁸O. For soils this extreme value seems unrealistic but the closer the CO₂ production to the soil surface is, the weaker the influence of the diffusive fractionation would be because of competition between the isotopic exchange of CO₂ with water and the diffusion of CO₂ out of the soil (Hesterberg and Siegenthaler, 1991).

The main feature that comes out of these graphs is a large sensitivity of the three quantities to the fractionation factors. Nevertheless the long term trend presents the largest sensitivity within the physical range defined for ϵ_s and ϵ_l , compared to the seasonal amplitude and the north minus south difference. We also notice that for the trend and the north minus south difference, the iso-lines follow the diagonal which indicates a linear response to both fractionation factors. On the other hand, the seasonal amplitude is more sensitive to ϵ_l than to ϵ_s (the slope of the iso-lines is smaller).

4.3 Discussion

By changing the two fractionation factors we can find a set of values that would give a reasonable agreement with the observations for both the amplitude and the inter-hemispheric difference. Concerning the long term trend, a different set of values would be required. Nevertheless this latter constraint also highly depends on other parameters. It is first sensitive to the mean $\delta^{18}O$ value of atmospheric CO₂ (δ_a in equations in Table 1). A change of +1% in δ_a for the calculation of the C¹⁸O¹⁶O flux associated with the photosynthesis $({}^{18}F_{leaves}$ in Eq. 3, Table 1) would induce a change of +0.4% per year in the mean long term trend. Globally the measurements of δ_a remain relatively sparse in term of spatial coverage and associated uncertainties are large, particularly over the tropics due to possible reaction between CO_2 and water in the flask samples. The trend also depends on the "stratospheric enrichment" of ¹⁸O in CO_2 through isotopic exchange between CO_2 and O_3 (e.g., Yung et al. (1991)). Figure 4 plots the simulated vertical profile for the control run defined with a given "stratospheric enrichment" (solid line). In this case the isotopic exchange between CO2 and O3 induces a mean long term trend for δ^{18} O in atmospheric CO₂ of +0.36% yr^{-1} (see Fig. 3). The dot curve in figure 4 shows the same vertical profile for a simulation where we double the "stratospheric enrichment". The resulting profile is still in agreement with the observations of Gamo et al. (1989) and Thiemens and Jackson (1991), and in this case the contribution of the "stratospheric enrichment" to the mean long term trend is twice that in the control run: +0.72% yr⁻¹. It is still difficult to select one profile from the other because (i) the measurements of δ^{18} O in stratospheric CO₂ are lacking, (ii) the isotopic exchange between CO2 and O3 is still poorly understood and (iii) we know that the transport model TM2 overestimates vertical mixing between the troposphere and the stratosphere (the tropopause is located at too high altitudes). The range of uncertainty for δ_a and for the "stratospheric enrichment" are thus large enough to fulfill the trend constraint with different sets of values within the physical range for the fractionation factors ϵ_* and ϵ_l . The two other constraints (amplitude and interhemispheric difference) could be fulfilled with only one set of values for ϵ_s and ϵ_l , but this would lead to a fairly low discrimination of ¹⁸O during CO₂ diffusion through leaves.

Table 1. Equations for exchanges of oxygen isotope of CO_2 with terrestrial ecosystems.

	(1)
Isotopic equilibrium with water : $COO + H_2^{18}O \longrightarrow CO^{18}O + H_2O$ with $\alpha_{equ} = \frac{(1^8O/1^6O)_{co2}}{(1^8O/1^5O)_{H_2O}} = f(T)$	(2)

LEAF exchange of "O:	
${}^{18}F_{leaves} = -\alpha_l R_a F_{al} + \alpha_l R_l F_{la}$	
with $A = -F_{al} + F_{la}$	(3)

SOIL exchange of ¹⁸ O :	
$^{18}F_{soils} = -\alpha_s R_s F_{resp}$	(4)

OCEAN exchange of ¹⁸O: ¹⁸ $F_{ocean} = -\alpha_w R_a F_{ao} + \alpha_w R_o F_{oa}$ with $F_{oa} - F_{ao} = Kex \Delta pCO_2$ (5)

(6)

Global mass balance (with the δ -notation): $C_a d\delta_a/dt = A \Delta_A + R_{soils}(\delta_s - \delta_a + \epsilon_s)$ $+ \epsilon_w(F_{ao} - F_{oa}) + F_{oa}(\delta_o - \delta_a)$

	SYMBOLS
A	Net rate of CO_2 assimilation
F_{resp}	CO_2 released by soil and plant respiration
$18F_{soils}$	Flux of $C^{18}O^{16}O$ from soils
$18 F_{leaves}$	Flux of $C^{18}O^{16}O$ from leaves
$^{18}F_{ocean}$	Flux of $C^{18}O^{16}O$ from ocean
Fal	Gross flux of CO_2 into the leaves
F_{la}	Gross flux of CO_2 out of the leaves
F_{ao}	Gross flux of CO_2 into the ocean
F_{oa}	Gross flux of CO_2 out of the ocean
Kex	exchange coefficient for CO_2 between the
	atmosphere and sea-surface water
ΔpCO_2	Difference in partial pressure of CO_2
	between the air and sea water
α_{equ}	Isotopic equilibration factor between CO_2
	and H ₂ O
α_s	CO_2 fractionation factor for diffusion out of soil
α_l	CO_2 fractionation factor for diffusion
	into/out of the leaves
α_w	Fractionation factor for CO_2 during dissolution
	and diffusion in water
$\epsilon_s, \epsilon_l, \epsilon_w$	$(\alpha_i - 1) \cdot 10^3$ (for i = s,l,w)
R_s	$^{18}O/^{16}O$ ratio of CO_2 in isotopic equilibrium
	with soil moisture
R_l	18 O/ 16 O ratio of CO ₂ in isotopic equilibrium
•	with chloroplast water
R_{o}	$^{18}O/^{16}O$ ratio of CO_2 in isotopic equilibrium
Ť	with sea-water
R_a	¹⁸ O/ ¹⁶ O ratio of atmospheric CO ₂ : zonal fit
	(Loess curve) to the monthly mean δ^{18} O values
	derived from the NOAA-CU observations
$\delta_a, \delta_s, \delta_o$	isotopic ratio in δ units for atmosphere, soil, ocean
δ _{ba}	"background" atmospheric δ (set up to 0.0%)
δ_i	simulated δ field corresponding to process i
Δ_A	Discrimination against ^{18}O (compared to ^{16}O)
	during net CO_2 assimilation by photosynthesis
	(Farguhar et al., 1993)
Ca	Number of moles of CO_2 in the atmosphere
C_i	Concentration field corresponding to process i
PDB-CO ₂	CO_2 derived from Pee Dee Belemnite calcite
100-002	ooy derived nom i ce Dee Detennite calcite

5 Conclusion

This short study discusses the sensitivity of the seasonal amplitude, the north minus south difference and the long term trend of δ^{18} O in atmospheric CO₂ to the fractionation factors for diffusion of CO₂ out of the soil and into/out of the leaves. Variation of these factors within the physical range induce large variations of the atmospheric δ^{18} O signal. The long term trend is nevertheless the most sensitive. But the simulation of this quantity highly depends on others processes such as the "stratospheric enrichment" of ¹⁸O in CO₂ (discussed above) and on the isotopic composition of the water in the leaves. The δ^{18} O of the water inside the chloroplast is fairly sensitive to the δ^{18} O of the water vapor inside the canopy. As a first test we changed the $\delta^{18} {\rm O}$ of water vapor to the extreme case where it is set to the ${}^{18}O/{}^{16}O$ ratio of precipitation (i.e., assuming that vapor in the canopy is constituted by $100^{\circ}/_{\circ}$ of plant transpiration). In this case we obtain a positive long term trend with only little changes of the seasonal amplitude and the latitudinal gradient.

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