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

2. Mapping the atmospheric signal

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[1] We have modeled the distribution of $\delta^{18}O$ in atmospheric CO$_2$ with a new comprehensive global three-dimensional model. We have focused in this study on the seasonal cycle and the meridional gradient in the atmosphere. The model has been compared with a data set of $\delta^{18}O$-CO$_2$, which merges measurements made by different laboratories, with allowance for recently elucidated calibration biases. The model compares well with the seasonal cycle of CO$_2$, but advances the measured $\delta^{18}O$-CO$_2$ seasonal cycle by two months. The calculated seasonal amplitude is typically 2/3 of the measured value, but the sensitivity to uncertainties in the input parameter set is such that a range of amplitudes over a factor of 3 is accommodated. Unlike the case for the amplitude, the sensitivity analyses demonstrate that the modeled phase of the seasonal cycle and the north-south gradient are practically unaffected by uncertainty in the parameter set. The north-south gradient comes, on the one hand, from the disequilibrium of the $\delta^{18}O$-CO$_2$ isofluxes at every grid point and, on the other hand, from rectification gradients, a covariance of the varying $\delta^{18}O$-CO$_2$ source with the atmospheric transport. The model exhibits a very strong rectification gradient that can lead to a misinterpretation of the measurements compared to the model. We therefore restrict comparison to the latitudinal means of only ocean grid cells with measurements from stations sampling the marine boundary layer. Assimilation and respiration are the determining factors of the seasonal cycle and the north-south gradient of $\delta^{18}O$-CO$_2$. In a number of sensitivity studies we have explored the range of possible processes affecting the simulated seasonal cycle and hemispheric gradient. None of these processes contributed significantly to improve the model-observation mismatch. The contribution of assimilation and respiration to the total signal does change significantly in the sensitivity studies, but, because of feedback processes, they change in such a way that the overall response of the model is only marginally altered. In particular, prescribing $\delta^{18}O$-H$_2$O soil values to monthly means of rain does not significantly change the modeled signal, either in the seasonal cycle or in the meridional gradient. This highlights the need to accurately model assimilation and respiration in order to understand $\delta^{18}O$ in atmospheric CO$_2$. INDEX TERMS: 1615 Global Change: Biogeochemical processes (4805); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 3210 Mathematical Geophysics: Modeling; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 1610 Global Change: Atmosphere (0315, 0325); KEYWORDS: isotope model, $\delta^{18}O$ in CO$_2$, isotope feedback mechanism, rectifier effect, global model

1. Introduction

The emission of human induced CO\(_2\), mostly in the northern hemisphere, causes the atmospheric CO\(_2\) mixing ratio to increase with time and imprints a strong north-south gradient on the CO\(_2\) mixing ratio. Regionally, Anthropogenic emissions of CO\(_2\) are typically of the same order of magnitude as natural net CO\(_2\) fluxes of the biosphere. This is different for the \(\delta^{18}O\) isotopic composition of atmospheric CO\(_2\). The fluxes for the isotopic CO\(_2\) signal are called isofluxes and are a convolution of CO\(_2\) fluxes and the difference between the isotopic ratio of these fluxes and the atmospheric isotope ratio. The latter difference is the apparent discrimination and the isoflux is the CO\(_2\) flux multiplied by the apparent discrimination. This means that for the isotopic composition of atmospheric CO\(_2\), the importance of each CO\(_2\) flux can be attenuated or amplified by the apparent discrimination. Peylin [1999] showed that the global \(\delta^{18}O\)-CO\(_2\) isoflux of anthropogenic emissions can be smaller by more than an order of magnitude in certain regions, compared to the global net (or total) \(\delta^{18}O\)-CO\(_2\) isoflux of the biosphere. It is hence mainly the biosphere which defines the spatial distribution of \(\delta^{18}O\)-CO\(_2\). (The gradient reflects in part the underlying gradient of the isotopic value of the soil water which is communicated, with modification, to the atmosphere only in the presence of fluxes with the terrestrial biosphere.) Because of the small seasonal variance of fossil fuel emissions, the seasonal cycle of \(\delta^{18}O\)-CO\(_2\) is also mostly determined by the biospheric CO\(_2\) fluxes, i.e., assimilation and respiration, which in contrast to fossil fuel combustion show big seasonal variations. To understand the atmospheric signal of \(\delta^{18}O\)-CO\(_2\), it is therefore essential to understand the biospheric CO\(_2\) fluxes and their associated apparent discriminations. On the other hand, one can learn about the biospheric CO\(_2\) fluxes by examining the atmospheric \(\delta^{18}O\)-CO\(_2\) signal.

We have developed a comprehensive global three-dimensional (3-D) model of \(\delta^{18}O\) in atmospheric CO\(_2\), which is described in detail in a companion paper [Cuntz et al., 2003] (hereinafter referred to as part 1). In the present paper, we focus on the modeled spatiotemporal distribution of atmospheric \(\delta^{18}O\)-CO\(_2\). We examine the mean seasonal cycle of CO\(_2\) and \(\delta^{18}O\)-CO\(_2\) at atmospheric stations and the gradient of \(\delta^{18}O\)-CO\(_2\) between the Arctic and Antarctica. Subsequently, we investigate the sensitivity of the model to different parameters, processes, and parameterizations.

2. Data and Model

2.1. Data Sets Used

The GLOBALVIEW-CO\(_2\) database presently consist of 165 stations at 118 locations with measurements of 22 different institutions [GLOBALVIEW-CO\(_2\), 2002] (also available on Internet via anonymous FTP to ftp.cmdl.noaa.gov, Path: ccg/co2/GLOBALVIEW). The stations are distributed world-wide with a strong bias toward coastal or marine environments. Some stations are still influenced by close-by terrestrial sources and sinks but the majority select air measurements from the marine boundary layer (MBL) and are referred to as marine background stations. The stations that are considered to be MBL sites can be found in the GLOBALVIEW-CO\(_2\) documentation. We added five non-GBL stations to GLOBALVIEW-CO\(_2\) comprising four new aircraft sites in Eurasia [Levin et al., 2002] plus one discrete sampling record at Schauinsland, Germany (SCH) [Schmidt et al., 2001]. A characteristic of MBL stations is that discrete and (quasi-)continuous measurements are very close in the monthly or annual mean. Non-MBL stations show quite large deviations between means of continuous and discrete samples even if one applies filter methods to catch continental air representing large regions. Figure 1 shows the distribution of 59 stations that we used here for the comparison because we have \(\delta^{18}O\)-CO\(_2\) data at these stations as well. Figure 2 presents seasonal cycles at 45 measurement sites (out of 59 stations in Figure 1) for which we have sufficient data to calculate seasonal cycles of \(\delta^{18}O\)-CO\(_2\) (continuous measurements are open and discrete measurements are closed symbols; the lines are model results and are explained in the result section). We take the model values at the latitude, longitude and altitude of the stations as plain monthly means. We do not sample the model at different times to emulate special sampling strategies at individual stations but we shift sometimes the sampled latitude and/or longitude by one or two grid cells in order to take into account different sampling and filtering methods applied to the measurements [cf. Ramonet and Monfray, 1996]. One number after the station abbreviation represents the number of model grid cells or vertical layers by which we shifted the model. For example MHD1 means that we took one grid cell further to the west than the actual Mace Head coordinate to sample our model. The 4 aircraft sites have the designation ‘030’ that is the GLOBALVIEW-CO\(_2\) affix for aircraft measurements made at 3000 m height, e.g., SYK030 for aircraft measurements over Syktyvkar, Russia in 3000 m a.s.l. One can see the difference between MBL and non-MBL stations at, e.g., the two stations Point Barrow (BRW), MBL, and Schauinsland (SCH), non-MBL, where continuous and discrete sampling procedures are installed. Whereas Point Barrow shows almost no difference between continuous and discrete sampling, Schauinsland shows a peak-to-peak amplitude in the discrete record 1/3 of that in the continuous record. The continuous record at Schauinsland is filtered to exclude night-time values and low wind speeds [Schmidt et al., 1996] whereas the flask is filled during morning and may to some extent be influenced by local sources and sinks. Schauinsland is a mountain station situated 1205 m above the Rhine valley. We do not take the ground level on Schauinsland, in our model at about 360 m, but the fourth vertical layer at about 1300 m. Our model box is therefore far from local sources and sinks so that it is more comparable with the continuous measurements there. This is important to keep in mind when comparing \(\delta^{18}O\)-CO\(_2\) monthly means of non-MBL flask records with model monthly means when the model was not sampled or filtered in the same way as the measurements.

We merged further \(\delta^{18}O\)-CO\(_2\) data at the 59 stations of Figure 1 where \(\delta^{18}O\)-CO\(_2\) is measured on atmospheric flask samples. This includes 50 sites, named CMDL/INSTAAR, where the flasks were collected from the NOAA Carbon Cycle Group at the Climate Monitoring and Diagnostics Laboratory (CMDL) and measured afterward from the Stable Isotope Laboratory of the Institute for Artic and Alpine Research (INSTAAR) at the University of Colorado. At most stations, air was not dried in the NOAA Global Air Sampling Network before 1998/1999. Trollet et al. [1996]
found out that $\delta^{18}$O-CO$_2$ measured at flasks collected at more humid sampling sites are most likely contaminated by exchange with water condensed on the flask wall [Gemery et al., 1996]. CMDL/INSTAAR records from higher-latitude sites appear credible for $\delta^{18}$O in atmospheric CO$_2$. Therefore we discarded all nondried flasks between 35°S and 35°N but kept the nondried flasks on all other latitudes.

We added to the CMDL/INSTAAR stations seven stations with samples collected for and measured by the Division of Atmospheric Research at the Commonwealth Scientific and Industrial Research Organisation (CSIRO). The samples are all dried prior to filling so that the above problem does not apply to CSIRO data. CSIRO established a link to the VPD/B-CO$_2$ scale in 1987 [Francey and Goodman, 1988]; however, with a change of mass spectrometer in 1991, the calibration of $\delta^{18}$O-CO$_2$ was propagated under the assumption of similar instrument responses. A new assignment onto the VPD/B-CO$_2$ calibration scale was introduced in 1999 (CG99) that recognized much greater susceptibility of the new mass spectrometer to “cross contamination” and thus removed a relative bias of around 0.8‰ in data obtained using the new mass spectrometer. Full details, including a minor revision of the CG99 assignment, are in preparation for publication. CMDL/INSTAAR and CSIRO measurements at the same stations differ now by this offset [Masarie et al., 2001]. It is very likely that the CMDL/INSTAAR values are wrong by this offset because of erroneous standard material preparation. We shifted thus all CMDL/INSTAAR values by 0.8‰ to merge the two independent data sets. We focus in this paper on seasonal cycles and on the north-south gradient of $\delta^{18}$O in atmospheric CO$_2$. The mean seasonal cycle in the merged data is not altered by the offset but the absolute annual mean values are, determining the north-south gradient. However, both laboratories have a sampling site at South Pole, Antarctica, so that we can refer all annual means relative to the South Pole annual mean value of its sampling network and merge the respective north-south differences to give a consistent north-south gradient. Corrected for the 0.8‰ offset, the annual mean $\delta^{18}$O-CO$_2$ at SPO was in 2000: 1.14‰ versus VPDB-CO$_2$ for CSIRO and 1.06‰ versus VPD/B-CO$_2$ for CMDL/INSTAAR. Taking South Pole is somewhat arbitrary but South Pole station is far from sources and sinks of CO$_2$ and $\delta^{18}$O-CO$_2$ and therefore reasonable as a reference point.

As for CO$_2$, we added four $\delta^{18}$O-CO$_2$ flask aircraft sites in Eurasia [Levin et al., 2002] plus the $\delta^{18}$O-CO$_2$ flask record at Schauinsland [Schmidt et al., 2001]. Measurements of samples from these sites were made at the Institut für Umweltphysik, University of Heidelberg (IUP-HD), Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Max-Planck Institut für Biogeochemie (MPI-BGC), and CSIRO. Because all five stations are non-MBL stations, they are only used here for comparison of the seasonal cycles so that systematic offsets between different labs [Levin et al., 2003] play no role in this context. These stations were already used to analyze the East-West distribution of CO$_2$ and $\delta^{18}$O-CO$_2$ over Eurasia [Levin et al., 2002; Cuntz et al., 2002] whereby systematic offsets may modify the statements made in these publications.

The new combined data set of $\delta^{18}$O-CO$_2$ shows slightly reduced seasonal amplitudes only at equatorial stations compared to a former data compilation [Peypin et al., 1999] whereas it is rather similar over the rest of the globe. A north-south gradient of $\delta^{18}$O-CO$_2$ of about 1.7‰ was recognized in the first six-site CSIRO data compilation in 1987 [Francey and Tans, 1987] and confirmed later by CMDL/INSTAAR measurements [Ciais et al., 1997b; Peypin et al., 1999]. The new combined data set exhibits an Arctic-to-Antarctic difference of 2.0‰ with very little interannual variability. We are confident that this is a robust feature of $\delta^{18}$O-CO$_2$ and will not change in possible future data revisions.

2.2. Model Runs

The model ECHAM/BETHY is described in detail in part 1. It is possible to run the model with or without the diverse processes described in part 1. The CO$_2$ fluxes are calculated interactively with the $\delta^{18}$O value of the atmo-

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Figure 1. Global distribution of the 59 atmospheric measurement stations used in this study. Different symbols denote different laboratories that measure CO$_2$ (and $\delta^{18}$O-CO$_2$).
Figure 2. Mean seasonal cycle of CO₂ at atmosphere observatories. Measured monthly means are plotted with different symbols for each institution. Filled symbols are flask measurements of different laboratories, open symbols denote (quasi-) continuous measurements, the solid thick line is the ECHAM/BETHY standard run and thin lines show the contribution of each process. Individual processes are only plotted if their peak-to-peak amplitude exceeds 30% of the total model amplitude. Ass signifies assimilation (thin solid line), Resp respiration (thin dotted line), Oce the ocean contribution (thin dash dot line), and fossil fuel combustion and biomass burning are combined in FF & BB (thin dash triple dot line). Note that differences sometimes exist between laboratory CO₂ scales.
Mixing ratios in ppm,

\[ \text{part 1:} \]

\[ \text{e.g., around 3.0} \]

\[ \text{Tendency to equilibrate the difference between atmo-} \]

\[ \text{sphere. We explained in part 1 that we call the} \]

\[ \text{particular model run. This can be seen from the global} \]

\[ \text{budget equation for} \delta^{18}O-CO_2 \text{which we repeat here from} \]

\[ \text{part 1:} \]

\[ \frac{d\delta_o}{dt} = \frac{1}{C_o M_o} \left[ F_R \Delta_R + F_A \Delta_A + F_{as} \Delta_{as} + F_o \Delta_{so} + \left( F_{fas} + F_{bar} \right) \Delta_f \right] \]

\[ \text{with} \]

\[ \Delta_R = \delta_R - \delta_o + \epsilon; \]

\[ \Delta_A = -\epsilon_o + \frac{c_o}{c_A - c_o} (\delta_f - \delta_o); \]

\[ \Delta_{as} = \epsilon_{as}; \]

\[ \Delta_{so} = \delta_o - \delta_i; \]

\[ \Delta_f = \delta_f - \delta_o. \]

\( M_o \) is the conversion factor between fluxes in GtC and mixing ratios in ppm, \( \Delta_A \) the discrimination of photosynthesis, \( \Delta_{as} \) the equilibrium discrimination between ocean and atmosphere. We explained in part 1 that we call the difference between the \( \delta \)-value of the CO\(_2\) flux and the atmospheric \( \delta \)-value “apparent discrimination”, for simplicity. \( \Delta_R \) is thus the apparent discrimination associated to soil respired CO\(_2\), \( \Delta_{so} \) the ocean disequilibrium or the ‘tendency’ to equilibrate the difference between atmospheric and ocean dissolved CO\(_2\), and \( \Delta_f \) the difference between the isotopic signatures of O\(_2\) and CO\(_2\). The product of CO\(_2\) flux and apparent discrimination is called isoflux. Writing the global budget equation in a short form gives:

\[ \frac{d\delta_o}{dt} = k_1 - k_2 \delta_o, \]

with

\[ k_1 = \frac{1}{C_o M_o} \left[ F_R \delta_R + \left( \delta_A + \frac{c_o}{c_A - c_o} \delta_f \right) + F_{as} \delta_A + F_o \delta_o \right] + \left( F_{fas} + F_{bar} \right) \delta_f \]

\[ k_2 = \frac{1}{C_o M_o} \left[ F_R + \frac{c_o}{c_A - c_o} F_A + F_{as} + F_{bar} \right]. \]

The solution of this differential equation is:

\[ \delta_o(t) = \frac{k_1}{k_2} + \left( \delta_o - \frac{k_1}{k_2} \right) \exp\left( -k_2 t \right). \]

\[ \text{So the global} \delta_o \text{will stabilize at} \frac{k_1}{k_2} \text{when} t \text{becomes much larger than} k_2^{-1}. \text{Including or excluding a process in a model run is like setting the} \]

\[ \text{apparent CO}_2 \text{flux to zero and} \frac{k_1}{k_2} \text{will change accordingly. Table 1 repeats from part 1 the annual totals resp. annual mean} \]

\[ \text{values of ECHAM/BETHY variables.} \]

\[ \text{Our model stabilizes around a global} \delta^{18}O-CO_2 \text{value of 2.3\%o versus VPDB-CO}_2 \text{including all processes and, e.g., around 3.0\%o versus VPDB-CO}_2 \text{taking only assimilation and respiration into account. The data, based on the} \]

\[ \text{CSIRO assignment onto the VPDB-CO}_2 \text{scale, indicate a global MBL surface mean of 0.5\%o versus VPDB-CO}_2 \text{(with a South Pole value of 1.1\%o versus VPDB-CO}_2). \text{In} \]

\[ \text{our model, the global mean value depends on} \]

\[ \text{what processes are included. For example, taking “invasion” into} \]

\[ \text{account (CO}_2 \text{ isotopically equilibrated with soil water because of diffusion in and out of the soil,} \]

\[ \text{Tans [1998] and explained in detail in part 1}, \text{there is the extra term} \]

\[ F_{inv} \Delta_{inv} \text{in the global budget equation (equation (1)) with} \]

\[ \Delta_{inv} = (\delta_i - \delta_o), \text{the discrimination of invasion. This adds} \]

\[ F_{inv} \delta_i \text{to the parenthesis of} k_1 \text{and} F_{inv} \text{to the parenthesis of} k_2 \text{ (equations (2) and (3)). Our model calculates 18.6 GtC} \]

\[ \text{yr}^{-1} \text{CO}_2 \text{invasion flux that would reduce the global mean to 1.9\%o versus VPDB-CO}_2.} \]

\[ \text{[12] When we start the model from one particular global} \]

\[ \text{uniform value,} \delta_{q0} \text{in the atmosphere,} k_2^{-1} \text{denotes the e-folding time of the stabilization. The e-folding differs between 1.3 and 1.9 years depending on the processes included and it needs at least 3 e-folding times to establish a stable annual mean north-south gradient. So we initialize our model with 0\%o versus VPDB-CO}_2 \text{everywhere and let the model run for 15 years. We then take the mean of the} \]

\[ \text{last 5 years for our analyses. The model is not sensitive to} \delta_{q0} \text{but the stabilization process is always determined by} k_2. \text{Our sub-diurnal time step produces rather a seasonally cyclo-stationary result than a fixed asymptote, i.e., that the model shows seasonal variations around an asymptote, which is exactly} k_1/k_2. \text{An exponential fit to the global model} \delta^{18}O-CO_2 \text{value during spin-up gives also exactly} k_2^{-1} \text{as e-folding time. Our standard model run includes the same processes as included by Ciais et al. [1997a, 1997b], namely assimilation, respiration, ocean exchange, fossil fuel combustion, and biomass burning. Individual process contributions to the atmospheric} \delta^{18}O-CO_2 \text{signal are not just the} \delta-\text{values, which would occur if only the individual process were present,} \delta^*, \text{because} \delta \text{is not a conserved quantity.} \]

\[ \text{\delta^*} \text{in contrast is a mass conserving tracer with} \epsilon \text{as the contribution of process} i \text{to the overall} \]

\[ \text{CO}_2 \text{mixing ratio. The contribution of an individual process} \]

\[ \text{Table 1. Global Annual CO}_2 \text{Fluxes, Assimilation Weighted Annual Mean CO}_2 \text{Mixing Ratios, Assimilation Weighted Annual Mean} \delta \text{Values, and} \epsilon \text{Constants Calculated and Used in ECHAM/}

\[ \text{BETHY}^{\text{a}} \]

\[ \begin{array}{|c|c|}
\hline
\text{Flux, Mixing Ratio,} & \text{Value in ECHAM/BETHY} \\
\hline
F_t & 97.3 \\
F_R & 98.0 \\
F_{as} & 99.4 \\
F_o & 2.6 \\
F_{fas} & 5.8 \\
F_{bar} & 3.1 \\
c_o & 353 \\
c_{as} & 264 \\
\delta_i & 6.3 \\
\delta_o & -6.9 \\
\delta_f & 1.2 \\
\delta^* & -17.0 \\
\epsilon_l & -7.4 \\
\epsilon_{as} & -7.2 \\
\epsilon_\text{inv} & 0.8 \\
\hline
\end{array} \]

\[ ^a \text{Global annual CO}_2 \text{fluxes are given in GtC yr}^{-1}, \text{assimilation weighted annual mean CO}_2 \text{mixing ratios are given in ppm, assimilation weighted annual mean} \delta \text{values are given in \%o versus VPDB-CO}_2, \text{and} \epsilon \text{constants are given in \%o.} \]
is thus calculated as the normalized $c_{i}^{bg}$ relative to an atmospheric background value, $c_{i}^{bg}$, and is called $\delta$-anomaly, $\delta^{*}$ [Heimann and Keeling, 1989]:

$$\delta^{*} = \frac{c_{i}^{(\delta^{*} - \delta^{bg})}}{c_{a}} = \frac{c_{i}^{(\delta^{*} - \delta^{bg})}}{c_{a}}, \quad (5)$$

$\delta^{bg}$ is taken as $0\%$ versus VPDB-CO$_2$. The sum of all $\delta^{*}$ gives $\delta_{a} - \delta^{bg}$. They are hence additive whereas the individual $\delta^{*}$ are not (compare, e.g., the results of Peylin et al. [1997], who used $\delta^{*}$, with the results of Ciais et al. [1997b], who used $\delta$).

3. Results and Discussions

[13] The $^{18}$O value of atmospheric CO$_2$ depends on the CO$_2$ fluxes and the apparent discriminations of the involved processes. It is therefore essential to model properly atmospheric CO$_2$ values. We showed in part 1 that ECHAM/BETHY computes generally very realistic CO$_2$ fluxes. These are transported in ECHAM and the resulting signal is compared here to atmospheric observations. We focus then on the comparison between measured and modeled atmospheric $^{18}$O-CO$_2$.

3.1. CO$_2$ Seasonal Cycle

[14] We show in Figure 2 mean seasonal cycles of atmospheric CO$_2$ at the 45 selected stations, alphabetically sorted by their GLOBALVIEW-CO$_2$ abbreviation. The seasonal cycle is mostly determined by assimilation and respiration so that another process becomes important only at 11 out of 45 stations. ECHAM/BETHY performs very well at most stations with 10 evident exceptions, namely Baltic Sea (BAL), Black Sea (BSC), Mariana Islands, Guam (GMI), Halley Station, Antarctica (HBA), Mauna Loa, Hawaii (MLO), Palmer Station, Antarctica (PSA), Tutuila, American Samoa (SMO), Norwegian Shipboard (STM), Tierra Del Fuego, Argentina (TDF), and Wendover, Utah (UTA). The Baltic is a closed basin in the ECHAM T21 spectral truncation. Therefore the nearby continental signal is transported very quickly over the basin so that BAL is influenced excessively by adjacent terrestrial biosphere fluxes in the model. The Black Sea does not exist at all in the T21 truncation. However, BSC station is located at the west coast of the Black Sea so that BSC in the model will “see” a totally different micro-climate than the measurement station BSC. Tutuila (SMO) lies in the Pacific Ocean. The South Pacific Convergence Zone (SPCZ) passes over SMO only once per year in the model so that it misses the peculiar form of the seasonal cycle at SMO. A similar problem in simulating the passage of the Intertropical Convergence Zone (ITCZ) is present in ECHAM T21 truncation at Christmas Island (CHR, not shown here). This is likely a resolution-dependent problem with T21 being too coarse. However, it seems that the problem of ECHAM T21 exists only in the Pacific Ocean because ECHAM/BETHY captures the peculiar seasonal cycle of Mahe Island, Seychelles (SEY) in the Indian Ocean and at Ascension Island in the Atlantic Ocean (not shown here because we have no $^{18}$O-CO$_2$ measurements there), the seasonal cycles of both are also mainly determined by the ITCZ. The modeled amplitude is too low at Mariana Islands (GMI) and too high at Wendover (UTA) and both show a phase shift of about one month compared to the data. We showed in part 1 that it is possible that this behavior comes from a incorrect timing between assimilation and respiration. Shifting the respiration CO$_2$ contribution in the output of the model does indeed lead to a much better agreement between model and measurements at GMI and UTA. Halley Station (HBA), Palmer Station (PSA), and Tierra Del Fuego (TDF) lie all around the Antarctic circumpolar current and are strongly influenced by the ocean CO$_2$ net flux. ECHAM4 has up to 6 m s$^{-1}$ stronger winds in the southern ocean during summer compared to reanalyses of the European Centre of Medium-range Weather Forecast (ECMWF) [Roeckner et al., 1996] which results in a higher CO$_2$ ocean sink in the vicinity of Antarctica (oceanic CO$_2$ fluxes are parameterized with speed, see part 1). Comparing Cape Grim (CGO) and South Pole (SPO) with stations at the intervening latitudes (HBA, PSA, TDF) shows that the peak-to-peak amplitude of the mean seasonal cycle in the model is very similar at CGO and SPO but doubled in between. This suggests an ocean effect at the Antarctic coastal stations. Mauna Loa (MLO) and Cape Kumukahi (KUM) are two stations on Hawaii. MLO station is situated in 3397 m on the northern flank of the Mauna Loa volcano. KUM is a ground station on the eastern most projection of the island of Hawaii. The peak-to-peak amplitude at MLO is only about 60% of the KUM amplitude and its phase lags by about one month. ECHAM/BETHY catches well the seasonal cycle at KUM but is too weak at MLO. It is recognized that the vertical advection in ECHAM is too strong for tracers [Timmreck et al., 1999] but that convection is quite realistically reproduced [Mahowald et al., 1995]. So it depends on the relative strength of vertical advection and convection around sources to simulate high-altitude stations well and these could be poorly represented by ECHAM/BETHY. This could be the reason why the Norwegian Shipboard (STM) station is out of phase by one month with excess amplitude. We showed in part 1 that the maximum in Net Ecosystem Exchange (NEE) occurs in June/July in Europe but most northern hemispheric atmospheric stations show their minimum in August/September. This time-lag comes from the atmospheric transport which accounts for about one month [Ciais et al., 2001]. The model, however, shows an immediate response to NEE fluxes in atmospheric CO$_2$ at STM with an even earlier July minimum in the atmosphere.

3.2. The $^{18}$O-CO$_2$ Seasonal Cycle

[15] ECHAM/BETHY provides good simulations of the seasonal cycle of CO$_2$ at most stations. The seasonal cycle of $^{18}$O in atmospheric CO$_2$ at the same 45 stations is shown in Figure 3. As for CO$_2$, we plot all processes with amplitude at least 30% of the total model amplitude. The seasonal cycle in $^{18}$O-CO$_2$ is almost completely determined by assimilation and respiration. There are only two stations where another process has a noticeable influence. There is an oceanic influence at Halley Station, Antarctica (HBA) and a contribution of fossil fuel combustion at Mahe Island, Seychelles (SEY). SEY receives northern hemispheric air during northern spring, summer, and autumn.
and southern hemispheric air during winter. This leads to a
different contribution of fossil fuel combustion in winter
against the rest of the year and leads to a transport
contribution at SEY. Our model shows the correct amplitude
at high northern hemispheric stations but with a two months
phase shift, e.g., at Alert (ALT), Barrow (BRW), or Mace
Head (MHD). There \( \delta^{18}O-CO_2 \) has its minimum in October
whereas our model shows its minimum in August as for
\( CO_2 \). This time lag is present at almost all stations. It was
also present in earlier \( \delta^{18}O-CO_2 \) models [e.g., Peylin et al.,
1999], not as pronounced in the high northern and southern
latitudes but with the same strength elsewhere. The model
fails to catch the amplitude of the seasonal cycle outside the
high northern latitudes where it calculates about 2/3 of the
measured amplitude. Peylin et al. concluded that respiration
is the dominant process controlling the seasonal cycle and

Figure 3. Mean seasonal cycle of \( \delta^{18}O-CO_2 \) at atmosphere observatories. Symbol and line definitions are the same as in Figure 2. Note that differences sometimes exist between laboratory \( \delta^{18}O-CO_2 \) scales.
that assimilation acts like a correction to the respiration dominated seasonal cycle. As explained in part 1, we calculate \( CO_2 \) fluxes and isofluxes directly in our model so the apparent discriminations are the ratio of isoflux to \( CO_2 \) flux. Our leaf discrimination is therefore assimilation weighted on a sub-daily basis, making it bigger and strengthening its influence. Assimilation has the same influence on \( ^{18}O-CO_2 \) as respiration in our model in contrast to offline models like those of Ciais et al. [1997a, 1997b] and Peylin et al. [1997, 1999], so that the assimilation processes parameterizations become more important in our model. For example, as explained in part 1, changing only the non-water-limited stomatal \( CO_2 \) assimilation processes parameterizations become more importance in the model, whereas ECHAM/BETHY reproduces the time lag for \( CO_2 \) at MLO for \( ^{18}O-CO_2 \) as well.

Part 2: Well known example of the difference between ground and altitude stations is the station pair Kumukahi (KUM) and Mauna Loa (MLO), both situated on Hawaii, KUM at ground and MLO more than 3 km above sea level. MLO exhibits therefore a one month time lag in the \( CO_2 \) seasonal cycle compared to KUM. It is interesting to recognize that MLO and KUM show their minimum in \( CO_2 \) and \( ^{18}O-CO_2 \) at the same time in the observations whereas ECHAM/BETHY reproduces the time lag for \( CO_2 \) at MLO for \( ^{18}O-CO_2 \) as well.

At some continental stations, \( ^{18}O-CO_2 \) lags even further behind \( CO_2 \); e.g., 3 months at SCH, 4 months at BSC, and 5 months at KZM. ECHAM/BETHY does not reproduce these features but is very uniform in its response at the atmospheric stations, i.e., it shows the \( ^{18}O-CO_2 \) minimum the same time as \( CO_2 \) at ground stations and 1 month lagged at high-altitude stations.

In the southern hemisphere shows very small seasonal cycles with peak-to-peak amplitudes of about 0.2‰. A ‘good’ pair-to-pair difference between flasks filled simultaneously is about 0.05‰. If flasks are stored for a long time (e.g., at South Pole), \( CO_2 \) has time to exchange isotopically with residual water. However, this depends on the origin of tracer-water in the flasks and the temperatures during storage and transport. \( ^{18}O-CO_2 \) in the southern extratropics is very similar at all stations (CGO, HBA, PSA, SPO, and SYO) and we have been able to locate systematic measurement or data treatment biases that would contribute a significant seasonal artefact. In the southern hemisphere, the measurements and ECHAM/BETHY predictions are thus both uniform; the model precedes the data by one to two months, and shows only 2/3 of the measured amplitude.

We examine the seasonal cycle of ECHAM/BETHY further in section 3.4 where we explore the behavior of ECHAM/BETHY due to modified parameters, changed parameterizations, and the inclusion or exclusion of different processes.

### 3.3. North-South Gradient and Rectifier Effect

#### 3.3.1. Imbalance of Isofluxes in Latitude

By construction, the biospheric fluxes are equilibrated, i.e., we have locally no annual mean net \( CO_2 \) flux to or from the biosphere. However, the corresponding \( ^{18}O \) gross fluxes, or isofluxes, being the convolution of \( CO_2 \) fluxes and apparent discriminations, may not be equilibrated. Indeed, if the annual mean leaf discrimination does not equal the apparent soil discrimination, the total biospheric isoflux can be nonzero. Consequently, in our coupled model, the atmospheric \( \delta \) value will change according to equation (1). Since \( \delta_0 \) feedbacks on leaf and apparent soil discrimination, its global value will finally stabilize at \( k_1/k_2 \) (see equations (1)–(3)) and the annual mean leaf and apparent soil discriminations will adjust to cancel each other. Making a run with only biospheric fluxes, \( \delta_0 \) stabilizes at about 3‰ versus VPDB-CO\(_2\) with isofluxes of + and −1650 GtC %/yr\(^{-1}\), for assimilation and respiration respectively, which is equivalent to global apparent discriminations of about ±16.8‰. However, leaf and soil isofluxes are not equal in every grid.
cell unlike for CO₂ assimilation and respiration fluxes (see part 1) because equation (1) is only valid for the globe, but in one atmospheric grid box, there is also transport from adjacent grid boxes that change the atmospheric δ¹⁸O-CO₂. Leaf isoflux is about the same in the northern and southern hemispheres, adding up to 825 GtC % yr⁻¹ per hemisphere in the biosphere-only run. This is because northern hemisphere net assimilation accounts for 57.3 GtC yr⁻¹ and southern hemisphere net assimilation for 40.0 GtC yr⁻¹ leading to leaf discrimination of 14.4% and 20.6%, respectively in both hemispheres. In contrast, soil isoflux does not apportion equally between the two hemispheres: −985 GtC %₁₀₀ yr⁻¹ in the northern hemisphere and −665 GtC %₁₀₀ yr⁻¹ in the southern hemisphere, yielding apparent soil discriminations of −17.1% and −16.4%, respectively. There is therefore an imbalance in the isofluxes between northern and southern hemisphere. The southern hemisphere emits an isoflux of +160 GtC %₁₀₀ yr⁻¹ which is balanced in the northern hemisphere by a total isoflux of −160 GtC %₁₀₀ yr⁻¹. This is mirrored, through atmospheric transport, in a north-south gradient in the atmospheric δ¹⁸O-CO₂ values.

3.3.2. Modeled and Observed Latitudinal Gradient in δ¹⁸O-CO₂

[23] We show in Figure 4 the north-south gradient of δ¹⁸O-CO₂. We added to the 45 stations of the seasonal cycle analysis 11 ship “stations” between 35°S and 35°N (POCS35 to POCN35), Christmas Island (CHR), Ragged Point, Barbados (RPB), and Gobabeb, Namibia (NMB) where either the record length or the data density were not sufficient to calculate a seasonal cycle; but the absolute atmospheric level should not be corrupted. Only CSIRO and CMDL/INSTAAR data were considered. We then excluded all non-MBL stations, which are under more regional continental influences, including rectification effects (see below). We included in Figure 4c ECHAM/BETHY predictions at the actual stations together with the zonal mean of the lowest model layer over ocean grid cells, which we consider as being more closely comparable to the data. To demonstrate this, we did two least squares fits of a polynomial function, one to the measurements and one to the model values at the stations. The χ² of the least squares fits does not change significantly if we used more than 4 polynomials. One can see for the model values that the fit deviates only in the tropics from the latitudinal mean of ocean grid cells and is otherwise nearly identical to it. A cubic fit, often used to represent measurements of CO₂ [e.g., Denning et al., 1995], had much higher χ² values and did not represent the measurements as accurately. We can compare in Figure 4d the latitudinal means of all grid cells, of only ocean grid cells, and of land grid cells only. The conventionally used latitudinal mean of all grid cells to represent the north-south gradient is very similar for δ¹⁸O-CO₂ to the only ocean only latitudinal mean but shows a local minimum at around 60°N. This is the combined effect of continental isofluxes and of their covariance with atmospheric transport patterns, which is analyzed next.

3.3.3. Covariance Between CO₂ Biospheric Fluxes and Atmospheric Transport

[24] In the case of CO₂, even with locally, annually balanced fluxes, covariance between horizontal and vertical
transport and the diurnal, seasonal fluctuations in NEE generates annual mean CO₂ gradients, which are referred to generically as rectification gradients. In our model that includes diurnal and seasonal variations in NEE, rectification gradients show off as a north minus south difference of 2.5 ppm (Figure 5) which is even bigger than the estimate of Denning et al. [1995]. Taking a plain latitudinal mean over all grid points shows two broad maxima, one around the equator, and one around 55°–60°N, reaching values of 5 ppm (Figure 5). The same behavior can be seen in the TRANSCOM project phase 1 [Law et al., 1996] where models with a high rectifier effect show all maxima around 60°N and a drop in mixing ratio afterward. Such latitudinal signal is not sampled in the actual station network of GLOBALVIEW-CO₂, where most of the sites are MBL stations, and we thus decided to use only ocean grid points to safely compare measurements with model latitudinal means. Tans et al. [1990] and Denning et al. [1995] bypassed this problem by using a fit through modeled station values. Figure 4c shows that both approaches are very similar whereas considering the latitudinal mean over ocean grid cells is easier to calculate, more robust to the fit procedure used, and less sensitive to a wrong station representation in the model (e.g., data selection, smoothed model orography, etc.) [cf. Ramonet and Monfray, 1996].

[25] We show in Figure 6 the spatial distribution of CO₂ related to the biospheric fluxes. We subtracted from all atmospheric values the trend at South Pole as a reference to make Figure 6 directly comparable with Figures 4 and 5. Vertical transport during daytime in the growing season is vigorous when the Net Ecosystem Exchange (NEE) is negative, giving a sink. This results into only a small negative gradient in CO₂ mixing ratio between the surface and the Planetary Boundary Layer (PBL). Vertical transport is almost suppressed during nighttime when NEE is positive, giving a source. This yields a strong positive gradient in mixing ratio between the surface and the PBL. Taking the daily (monthly) mean in one height leads to a shift in CO₂ mixing ratio that is positive near the ground and negative in the higher PBL, i.e., the average values are higher at the ground than in mid-PBL. The magnitude of the vertical gradient due to diurnal flux-transport covariance, sometimes called Diurnal Rectifier Effect, obviously varies throughout the season [Stephens et al., 1999], as can be seen in tall tower CO₂ measurements [e.g., Bakwin et al., 1998]. Beyond daily timescales, transport patterns in summer and winter are on average different, e.g., higher wind speeds inside the continents during winter lead to a faster dilution of concentration differences, and they covary as well with the seasonal pattern of negative NEE during summer and positive NEE during autumn/winter [Ciais et al., 2000; Taylor, 1998]. This seasonal covariance controlling the spatial patterns of CO₂ shows up in models even without diurnal cycles, and it is often called Seasonal Rectifier Effect. Both rectifier effects are superimposed in nature and in our model, whereby the diurnal rectifier effect contributes about 80% of the amplitude over land and only 25% of the amplitude over ocean [Denning et al., 1996b]. In Figure 6g over the ocean, one can hardly detect the CO₂ interhemispheric gradient of Figure 5 because it is lower than the steps of the color scale but one can easily spot the local maximum of CO₂ in the northern boreal zone which leads to the characteristic maximum at 60°N in Figure 5, and is entirely implied by rectification processes. The third model level lies in the middle of the PBL (approximately 800 m) in summer but outside of the PBL in winter and during night (most times). ECHAM/BETHY shows a very strong accumulation of CO₂ at the ground level with respect to the third level (third column in Figures 6a–6i) over the continents most of the time. The difference between ground and mid-PBL gets negative only in eastern Siberia and in Alaska in July (Figure 6f). The very low daily amplitude of NEE in those two Arctic regions covaries there with a zonal transport which is stronger than the vertical transport, i.e., that the seasonal rectification processes outweighs diurnal rectification processes in those regions. The Amazon and Equatorial Africa regions show generally the biggest CO₂ rectification gradients yielding accumulations near the ground of up to 20 ppm in the annual mean compared to surrounding ocean grid boxes (Figure 6i). Daytime convection is very strong and repetitive over the Amazon and together with high NEE amplitudes [Araujo et al., 2002], this leads to a strong diurnal rectifier signal. For the same reasons, East-Europe, West-Siberia, and South-East-Asia show as well very large vertical rectification gradients between ground and 800 m in July which attain values of up to 30 ppm (Figure 6f) comparable with rectification gradients in the Amazon (Figure 6c). It is nevertheless surprising that the average ground level CO₂ over Eurasia shows lower values than over the ocean almost everywhere in July (Figure 6d). The rectification effects get revealed there only in the difference to the 800 m level (Figure 6f).

3.3.4. Covariance Between δ¹⁸O-CO₂ Biospheric Fluxes and Atmospheric Transport

[26] In the case of δ¹⁸O, we also expect rectification effects to be strong, as for CO₂ discussed above. In addition, since the δ¹⁸O-CO₂ budget is not closed on every grid cell, rectification gradients are everywhere convoluted with gradients induced by nonzero annual mean isofluxes. We show in Figure 6 the spatial distribution of δ¹⁸O in CO₂ related to biospheric fluxes. Conceptually, the picture is similar to the one of CO₂, with accumulation over the continents and a more uniform meridional distribution over the oceans.
Figure 6. (a–r) Rectifier effect of the biospheric fluxes in ECHAM/BETHY for CO$_2$ and $\delta^{18}$O-CO$_2$.

The first column is the ground level (around 30 m), the second column the third model level (around 800 m), and the third column is the difference between ground and third level. Note that the color bar in the third column differs from the combined color bar for column one and two. We subtracted the trend at South Pole from each grid point as a reference.
Accumulations of CO$_2$ near the ground over active vegetation are generally mirrored by more negative $\delta^{18}$O-CO$_2$ values. An exception to this is the Amazon where the isotopic enrichment effect of leaves dominates almost all year-round the isotopic depletion induced by respiration. However, the ground minus mid-PBL vertical difference in $\delta^{18}$O is still negative over the Amazon (Figure 6r), because the negative iso-flux signal of respiration accumulates in shallow nocturnal boundary layers. The negative difference of CO$_2$ between ground and mid-PBL over Eastern Siberia and Alaska in July (Figures 6d–6f) is mirrored by very negative differences in $\delta^{18}$O-CO$_2$ (Figures 6m–6o). This comes from negative leaf discrimination in this region in the model, which superimpose on rectification effects similar to those of CO$_2$ (see part 1 and Cuntz et al. [2002]). This affects the annual mean vertical distribution of $\delta^{18}$O-CO$_2$ in such a way that, overall, $\delta^{18}$O-CO$_2$ at the ground is more negative than at 800 m over the whole Eurasian and the North-American continents (Figure 6r) whereas CO$_2$ shows an accumulation over land only in Eastern Europe, Western Siberia, and over the North American East Coast (Figure 6i). One can see over the ocean the north-south gradient of Figure 4d in Figure 6p, with values about $-2.0\%$ versus VPDB-CO$_2$ lower than at South Pole between 45°N and 60°S. Over land however, in the same mid-northern latitude band, $\delta^{18}$O-CO$_2$ is reduced to $-2.5\%$. This is the minimum in the $\delta^{18}$O-CO$_2$ north-south gradient of all grid points in Figure 4d and present in earlier $\delta^{18}$O-CO$_2$ modeling studies [Ciais et al., 1997b; Peylin et al., 1999].

In summary, both $\delta^{18}$O and CO$_2$ are subject to the same rectification processes, affecting the annual mean spatial distribution of both species, in particular their ocean-land contrast near the ground. Rectification processes are present in the world of models and likely in the real world as well, superimposed with the signal of mean sources and sinks. Uncertainties in modeled rectifications translate therefore in huge errors when applying inverse modeling techniques to the present set of stations. Noting the importance of gross fluxes for $\delta^{18}$O-CO$_2$ and of net fluxes for CO$_2$, the small imbalance of CO$_2$ sources and sinks plays a role essentially for CO$_2$ but very minor for $\delta^{18}$O-CO$_2$. Therefore (with optimism), if we knew the iso-fluxes very well, including their diurnal and seasonal patterns (for instance from systematic studies at eddy covariance towers [e.g., Bowling et al., 1998]), then $\delta^{18}$O-CO$_2$ could be used in the future to validate independently from CO$_2$ rectification effects in atmospheric transport models.

3.4. Sensitivity Studies

Our standard run includes assimilation, respiration, ocean fluxes, fossil fuel combustion and biomass burning. These are the same processes that Ciais et al. [1997a, 1997b] included in their model study. First, they claim that assimilation and respiration are responsible for the seasonal cycle of $\delta^{18}$O-CO$_2$ but that one needs fossil fuel combustion input and the biomass burning process to simulate a realistic north-south gradient. We performed several sensitivity runs that are summarized in this section, notably we included or excluded a variety of processes, and added new processes that were explained in part 1. Specifically, we changed further the globally fixed fractionations, and changed the formulation of some processes. We show in the plots only a selection of these sensitivity runs because $\delta^{18}$O-CO$_2$ in ECHAM/BETHY is almost exclusively determined by assimilation and respiration.

We label in Table 2 only the sensitivity studies which are discussed in the text in detail and show which processes are included in the runs. For example, AR stands then for the run which includes only assimilation and respiration and STD denotes our standard run. We added in the sensitivity runs each time one process extra to the AR run to examine the influence of each process individually. For example, we added ocean CO$_2$ exchange fluxes to the AR run, named AROCE. ARMM denotes a model run where the online calculated water isotopic composition was replaced by monthly mean input fields of $\delta^{18}$O-H$_2$O of rain and vapor. STD is our standard run including the processes of Ciais et al. [1997a, 1997b] and the water isotopic composition is calculated online at each time step in the model. STDMM replaces therein the online calculated water isotopes again with monthly means of $\delta^{18}$O-H$_2$O of rain and vapor.

3.4.1. Sensitivity of $\delta^{18}$O-CO$_2$ North-South Gradient

3.4.1.1. Feedback of $\delta_{\text{H}_2\text{O}}$

Previous models of $\delta^{18}$O in atmospheric CO$_2$ described the influence of different processes on the north-south gradient as well. We show in Figure 7a the contribution of each individual process to the latitudinal mean of $\delta^{18}$O-CO$_2$ of the standard run. Respiration and assimilation show by far the strongest influence on the total signal, making each about $-0.6$ to $-0.7\%$ of the total signal of approximately $-1.5\%$. The oceanic and burning contributions are small, contributing only slightly less than $+0.1$ and $-0.2\%$ respectively to the overall north-south gradient. The Figure seems to suggests that if one removes one process, the total signal is also reduced by this process. However, this is not true in the online model because adding or removing a process feedbacks on the global $\delta^{18}$O-CO$_2$ level in the atmosphere, therefore changes apparent discriminations and thus the contributions of all other processes to the atmospheric signal. This can be studied in Figures 7b and 8, where we plotted the results of several sensitivity runs. For example, adding up assimilation and respiration in Figure 7a gives a $\delta^{18}$O-CO$_2$ value at the North Pole of $-1.2\%$ (relative to South Pole). The total $\delta^{18}$O-CO$_2$ value at the North Pole of the standard run is in-between $-1.3$ and $-1.4\%$ but the Arctic-to-Antarctic difference goes down to $-1.5\%$ in the AR run. One can see in Figure 7b that all three extra processes of the standard run together reduce the north-south gradient by only about 0.1 to 0.2%. The strongest influence is demonstrated by the ARMM and CA runs.

3.4.1.2. Monthly Mean Water Isotope Input

ECHAM uses a soil bucket model for water as explained in part 1. So there is only one soil water content and one soil water $\delta^{18}$O-H$_2$O. This simplification yields soil $\delta^{18}$O-H$_2$O seasonal amplitudes that appear much too small (see part 1). $\delta^{18}$O in CO$_2$ leaving the soil has therefore the same value all yearlong in the model even if there is a major change in $\delta^{18}$O-H$_2$O of incoming rain. In reality, $\delta^{18}$O-H$_2$O at the soil surface changes considerably when it rains but this is attenuated in deeper soil so that $\delta^{18}$O-H$_2$O of very deep soil does not change markedly [e.g., Melayah et al., 1996]. The prevailing opinion is that $\delta^{18}$O of CO$_2$...
leaving the soil is in isotopic equilibrium with soil water at about 15 cm depth [Riley et al., 2002; Miller et al., 1999]. \( \delta^{18}O \) at 15 cm depth does not track the whole range of \( \delta^{18}O \) of incoming rain but the variation is notably attenuated. Previous models of \( \delta^{18}O-CO_2 \) used monthly rain and its isotope values as an approximation for the “correct” \( \delta \)-value of equilibrating soil water [e.g., Peylin et al., 1999]. \( \delta^{18}O \) in 15 cm depth will lie between the two extremes, rain and soil bucket respectively, most of the time but can reach much higher values during longer drought periods. However, these periods are also marked by reduced \( CO_2 \) production in soil and by roots due to the limitation of water. We conducted thus a sensitivity experiment where \( \delta^{18}O \) fluxes of the standard run (STD) do not depend on the online calculated \( \delta^{18}O-H_2O \) values but are rather prescribed to monthly means of \( \delta^{18}O-H_2O \) rain of the standard model run (STDMM). We treat this sensitivity run in detail because it shows one of the largest influences on the north-south gradient of all sensitivity runs (see Figure 7). Figure 9 shows results of the STD and STDMM runs, displayed as difference between model and measurements at the stations and as north-south gradient. Monthly mean water isotope input does not change greatly the north-south gradient in \( \delta^{18}O-CO_2 \). The spread in the differences between model and measurements is not reduced and the latitudinal mean over ocean grid cells changes only marginally. The north-south gradient exhibits only the annual

![Figure 7. Contribution of different processes to the north-south gradient in \( \delta^{18}O-CO_2 \).](image-url)

(a) The total north-south gradient of the standard run (STD) split up in the contributions of individual processes. The \( \delta \)-anomalies are additive and sum up to the total signal so that adding up the different contributions at every latitude gives the total signal (solid line). Ass = contribution of assimilation, Resp = respiration, Oce = ocean, FF & and BB = fossil fuel and biomass burning. (b) The total north-south gradient signal of different runs, including a specific extra process, minus the north-south gradient of a run with only assimilation and respiration included (AR). The names of the runs are explained in Table 2, together with run descriptions.

### Table 2. Names and Contents of Sensitivity Runs

| Name   | Ass | Resp | Oce | FF | BB | Inv | Carb. | Anhy. | Vari. | Rain 
|--------|-----|------|-----|----|----|-----|-------|-------|-------|-----
| AR     | X   | X    | X   |    |    | X   |       |       |       |     
| AROCE  | X   | X    | X   |    |    | X   |       |       |       |     
| ARBB   | X   | X    | X   |    |    | X   |       |       |       |     
| ARINV  | X   | X    | X   |    |    | X   |       |       |       |     
| ARCA   | X   | X    | X   |    |    | X   |       |       |       |     
| ARCaVar| X   | X    | X   |    |    | X   |       |       |       |     
| ARMM   | X   | X    | X   |    |    | X   |       |       |       |     
| STD    | X   | X    | X   |    |    | X   |       |       |       |     
| STDMM  | X   | X    | X   |    |    | X   |       |       |       |     

*Ass stands for assimilation (A in name), Resp for respiration (R), Oce for the ocean exchange (OCE), FF for fossil fuel combustion (FF), BB for biomass burning (BB), Inv for the invasion effect (INV), Carb. Anhy. for reduced carbonic anhydrase activity (CA), \( c_w \) Vari. for variable atmospheric \( CO_2 \) mixing ratios in assimilation calculation (CaVar), and \( \delta^{18}O \) Rain for monthly mean rain and vapor isotope input instead of \( \delta^{18}O-H_2O \) online calculation (MM). The names are then composed of the letters in the parentheses.
mean, also from the underlying source functions. The respiration-weighted annual mean of soil water isotopes did change but influenced both, assimilation and respiration. Together with the feedback of the atmospheric δ value on apparent discriminations, the influence of monthly mean water isotope input is cancelled almost completely.

3.4.1.3. Reduced Carbonic Anhydrase Activity

As explained in part 1, the enzyme carbonic anhydrase, distributed in the mesophyll cells, speeds up the hydration of CO₂ by a factor 10⁷ [Stryer, 1981]. CO₂ molecules entering the stomata are hence immediately hydrated even if they cannot be taken up by RUBISCO because of limitations of, e.g., electron transport (cf. part 1). If CO₂ molecules are not assimilated by the plant, they diffuse back into the stomata and subsequently into the canopy. However, once CO₂ molecules were hydrated in leaf water, they have most probably isotopically equilibrated with it and the back-diffused CO₂ molecules carry the leaf water isotopic signature in the atmosphere. If the activity of carbonic anhydrase is reduced, not all CO₂ molecules entering the stomata are hydrated before they diffuse back into the canopy [Gillon and Yakir, 2001]. This reduces leaf discrimination by only 1% in the global mean in our model and reduces hence the influence of assimilation on δ¹⁸O of atmospheric CO₂. Lower stomata-internal CO₂ mixing ratios increase the effect of reduced carbonic anhydrase activity. We have high stomata-internal CO₂ mixing ratios (at least at high northern latitudes, see part 1) so that Gillon and Yakir [2001] estimate a greater global reduction of leaf discrimination of 2–3%. However, this effect is of the same order of magnitude as the ARMM run and likewise its influence on the meridional gradient is negligible.

3.4.1.4. Other Processes

To demonstrate the change of leaf discrimination and apparent soil discrimination due to different processes in more detail, we plot in Figure 8a the meridional gradient of δ¹⁸O-CO₂ in the atmosphere. If the activity of carbonic anhydrase is reduced, not all CO₂ molecules entering the stomata are hydrated before they diffuse back into the canopy [Gillon and Yakir, 2001]. This reduces leaf discrimination by only 1% in the global mean in our model and reduces hence the influence of assimilation on δ¹⁸O of atmospheric CO₂. Lower stomata-internal CO₂ mixing ratios increase the effect of reduced carbonic anhydrase activity. We have high stomata-internal CO₂ mixing ratios (at least at high northern latitudes, see part 1) so that Gillon and Yakir [2001] estimate a greater global reduction of leaf discrimination of 2–3%. However, this effect is of the same order of magnitude as the ARMM run and likewise its influence on the meridional gradient is negligible.

Figure 8. North-south gradient of all runs in Figure 7b split up in their individual processes. Figure 8a is the run with only assimilation and respiration, whose total δ¹⁸O-CO₂ signal was subtracted in Figure 7b from the δ¹⁸O-CO₂ north-south gradient of the different runs. Figures 8b–8h show runs identical to Figure 8a, but with one further process added in the calculation (names in Table 2). In Figure 8b, ocean CO₂ fluxes were added to assimilation and respiration fluxes, AROCE. In Figure 8c, fossil fuel combustion was added, ARFF; in Figure 8d, biomass burning fluxes were added, ARBB; in Figure 8e, δ¹⁸O of water was prescribed to monthly means of δ¹⁸O-H₂O rain of the standard run, ARMM; in Figure 8f, invasion was present in the model, ARINV; in Figure 8g, the activity of carbonic anhydrase were reduced, ARCA; and in Figure 8h, assimilation fluxes were calculated with instantaneous CO₂ mixing ratios of the lowest model layer, ARCaVar.
\(\delta^{18}O-CO_2\) of the AR run together with the individual contributions of assimilation and respiration. Figures 8b–8h show then the results of sensitivity runs where other processes are added to assimilation and respiration, namely the ocean fluxes, fossil fuel combustion, biomass burning, the isotopic water source as monthly mean input fields of rainwater isotopes, the invasion effect, the reduced carbonic anhydrase activity, and varying \(CO_2\) concentrations in air, \(c_a\). (Normally, \(c_a\) is fixed to 353 ppm in the calculation of assimilation in ECHAM/BETHY but not in the \(CO_2\) flux calculations.). Comparing Figure 8a with Figure 8c shows the change in the model behavior due to fossil fuel combustion input. One can see in Figure 7b that the total meridional mean changes only little but Figures 8a and 8c show that the contributions of assimilation and respiration change considerably. Fossil fuel combustion adds about \(-0.2\%\) to the total signal, assimilation changed also about \(-0.2\%\) compared to the AR run but this is almost totally compensated for by the change in the respiration contribution of around +0.3 to 0.4\%. Monthly mean rain isotope input strengthens the influence of assimilation and weakens the respiration contribution (Figure 8e) whereas reduced carbonic anhydrase acts the other way round (Figure 8g), weakening assimilation influence and consequently strengthening respiration (\(\delta_8\) is reduced because of reduced leaf discrimination that in turn reinforces the apparent soil discrimination). Figures 7b and 8f show that the “invasion effect” (explained in part 1) does not change markedly the meridional gradient. In further runs, we changed the fractionations, \(\epsilon\), applied to the different processes (as explained in part 1) but the interactively calculated apparent discriminations changed accordingly as demonstrated in Figure 8 so that we ended up always with a very similar picture (results not shown here). We also exchanged the global fractionations with parameterizations depending on climate and/or biospheric variables [e.g., Ball, 1987; Farquhar and Lloyd, 1993; Roden and Ehleringer, 1999; White, 1983] but the effect on the meridional gradient were again negligible (results not shown here).

[34] In summary, assimilation and respiration are the determining factors of the meridional gradient and because of interactively calculated apparent discriminations, none of the proposed processes helps to improve our modeling of the north-south gradient.

3.4.2. Sensitivity of \(\delta^{18}O-CO_2\) Seasonal Cycle

[35] The seasonal variations of the isofluxes alter the influence of individual processes with time. The seasonal cycle can be influenced by changes to model formulations even if the meridional gradient is not. We explain in this section the influence of different sensitivity tests on the seasonal cycle but do not plot the results because all of the performed sensitivity studies changed mainly the amplitude of the seasonal cycle and not significantly the phase. We diagnose the seasonal amplitude of \(\delta^{18}O-CO_2\) as somewhat adjustable and must resolve the phase mismatch between model and measurements first before we can find a feasible set of parameters for the amplitude.

[36] The ARMM and STDMM runs were explained in detail in the previous section. The water isotopic composition distribution is reflected in the north-south gradient mainly as a respiration weighted annual mean. However, the ARMM and STDMM runs differ from their ‘parent’ runs, with \(\delta^{18}O-H_2O\) calculated online, stronger in the seasonal cycle than in the annual mean of \(\delta^{18}O-H_2O\). The phasing of the rainwater isotopes coincides with the phase of the \(CO_2\) fluxes in our model so that the ARMM and STDMM runs did not significantly change the seasonal cycle of \(\delta^{18}O-CO_2\) (results not shown here). The evidence of reduced carbonic anhydrase activity leads to a different pattern in atmospheric \(\delta^{18}O-CO_2\). Carbonic anhydrase activity in \(C_3\) plants is significantly less reduced than in \(C_4\) plants, and we tested that this effect can substantially change the seasonal cycle at some stations because of a modified influence of assimilation on the total signal but it does not improve the phase mismatch between model and measurements. Predictably, other processes with no great seasonal variation, like fossil fuel combustion, had almost
no influence on the seasonal cycle of $\delta^{18}$O-CO$_2$. Assimilation and respiration isofluxes changed when introducing these processes because of modified apparent discriminations caused by the feedback. These changes were very small, though. However, some seasonal processes missing in our model might influence $\delta^{18}$O-CO$_2$. We confirmed that the “invasion effect” cannot be a significant influence (results not shown here; one can see the influence of invasion on the north-south gradient in Figure 8f, and it is very small there, the same is true for the seasonal cycle).

[37] It is very possible that the parameterizations used, comparable to Ciais et al. [1997a, 1997b], are not sufficient to describe the seasonal cycle of $\delta^{18}$O-CO$_2$. Exchanging for example the global fractionations, $\epsilon$, with parameterizations that depend on climate and/or biospheric variables (see previous section for citations) did change the amplitude and therefore the phase of the seasonal cycle of $\delta^{18}$O-CO$_2$. The modified parameters sometimes changed the amplitude significantly, but not very much the phase. Sensitivity studies with different sets of global fractionation values showed the same behavior. Reducing for example the kinetic fractionation of $\delta^{18}$O-CO$_2$ leaving the soil, thereby diminishes the influence of respiration on $\delta^{18}$O-CO$_2$. Changing the fractionation in a reasonable range can amplify or divide the amplitude of the seasonal cycle by almost a factor of 1.5. However, the phase is not changed greatly.

[38] None of the tested processes and parameterizations resolved the mismatch between our model and the observations in either the north-south gradient or in the seasonal cycle. Although, we have changed biosphere apparent discriminations considerably, this did not greatly change the phasing of the seasonal cycle. Therefore either an important process is missing in the model, an included process is wrongly parameterized or the biosphere CO$_2$ gross fluxes are erroneous. The very good CO$_2$ seasonal cycle comparison argues against erroneous gross fluxes, even though a good comparison in CO$_2$ can be found with quite different flux patterns [Kaminski et al., 2001]. From a mechanistic point of view, the weakest parameterization in our model is the formulation of the heterotrophic respiration because it is described with only a very simple formulation (see part 1). We use air temperature to parameterize heterotrophic respiration [Raich and Potter, 1995]. Using soil temperature instead [Lloyd and Taylor, 1994] changes the shape of heterotrophic respiration so that it peaks later in year. This test resulted in a convergence of model and observations in $\delta^{18}$O-CO$_2$ but the model deviated from the observations in CO$_2$. This effect can be seen in the simulation of Ciais et al. [1997a, 1997b] and Peylin et al. [1999] who used monthly biosphere fluxes from the SIB2 biosphere model [Denning et al., 1996a, 1996b] to compute $\delta^{18}$O-CO$_2$. SIB2 shows the same phase in assimilation as BETHY but respiration has its maximum 1 to 2 month later in the extratropics (SIB2 uses soil temperature for heterotrophic respiration [Denning et al., 1996a]). Therefore the simulations of Ciais et al. and Peylin et al. show $\delta^{18}$O-CO$_2$ seasonal cycles closer to the measurements than ours in high latitudes but their simulated CO$_2$ seasonal cycle shows a phase shift compared to the observations. SIB2 and BETHY are very similar in the phase of respiration in the tropical region so that consequently the simulations of Ciais et al. and Peylin et al. show the same phase lag as ECHAM/BETHY in $\delta^{18}$O-CO$_2$ at mid-latitudes whereas the CO$_2$ seasonal cycles match the phase of the observed cycles in both models.

4. Summary and Concluding Remarks

[39] We have built a detailed global 3-D model of $\delta^{18}$O in atmospheric CO$_2$. The model simulates very well the seasonal cycle of CO$_2$ at atmosphere observatories, even though at 25% of the stations, ECHAM/BETHY fails to follow closely the seasonal cycle of CO$_2$ because of model deficiencies. This is mainly due to deficiencies in the AGCM ECHAM rather than in the biospheric part BETHY. ECHAM/BETHY shows a seasonal cycle of $\delta^{18}$O in atmospheric CO$_2$ very similar to the cycle in CO$_2$, i.e., that CO$_2$ and $\delta^{18}$O-CO$_2$ show their minimum and maximum at the same time. The modeled seasonal cycle of $\delta^{18}$O-CO$_2$ precedes the measurements by two months at almost all stations. None of the sensitivity studies performed with ECHAM/BETHY did resolve this model shortcoming but did impact on the amplitude. Whereas the seasonal amplitude of $\delta^{18}$O-CO$_2$ changes with different parameters or parameterizations up to a factor of 3, there is no significant effect on the phase. We think that it is always possible to find a reasonable set of parameters that fits the seasonal amplitude at most stations but consider it a futile exercise while the question of the phase mismatch is unresolved.

[40] The biosphere is set to equilibrium in our model, i.e., there is no annual mean net biosphere flux from any land point in the model. The annual mean net $\delta^{18}$O-CO$_2$ isoflux is zero only in the global mean but imbalanced on every grid point. This yields a northern hemispheric isoflux of $-160$ GtC $\% yr^{-1}$ which is balanced in the southern hemisphere by $+160$ GtC $\% yr^{-1}$. A first-order two box model such as that used in TRANSCOM Phase 1 [Law et al., 1996] relates concentration differences, $c$, with source strength differences, $S$:

$$c = \frac{\tau}{2} S .$$

where $\tau$ is the interhemispheric exchange time. The range in $\tau$ in the models of TRANSCOM Phase 1 was roughly between 1 and 2 years (we did no experiment to determine $\tau$ in ECHAM). The source strength difference between northern and southern hemispheric $\delta^{18}$O-CO$_2$ isofluxes yields therefore a concentration difference of $-0.3$ to $-0.5\%$ whereas the model shows a difference of about $-0.6\%$ in the lowest model layer over the ocean. The excess in the model comes from the rectifier effect, i.e., the covariance between the diurnal and seasonal cycle of $\delta^{18}$O-CO$_2$ with transport. It has a much stronger impact on the north-south gradient than any other process in our model apart from assimilation and respiration.

[41] None of the sensitivity studies changed the gradient of $\delta^{18}$O-CO$_2$ between Arctic and Antarctica by more than 10% neither did they change the phase of the modeled seasonal cycle of $\delta^{18}$O-CO$_2$ significantly. We speculate five mechanisms which could be responsible for the mismatch:

[42] The first possible mechanism is the interfacing of BETHY and ECHAM. BETHY is interfaced to ECHAM rather than coupled. This means that BETHY is driven by ECHAM meteorological parameters but ECHAM itself is not influenced by BETHY. A real coupling of a biosphere
model with an AGCM would imply that the AGCM is influenced by the biosphere model, e.g., through albedo and evapotranspiration. Coupling BETHY with ECHAM could lead to quite different or only subtle CO$_2$ flux changes. It would also change the calculation of the water isotopic composition. This would influence CO$_2$ as well as $\delta^{18}$O-CO$_2$ and it is not foreseeable if it would make the comparison better or worse.

[41] Second, the imbalance in the net $\delta^{18}$O-CO$_2$ isoflux could be responsible for the mismatch. A mean $\tau$ of 1.5 years (assuming that the rectifier effect is correctly represented) implies that the imbalance should be greater by a factor of approximately 1.5, means $S_{\text{d}} = 480$ GtC $\%$ yr$^{-1}$. This can be achieved in several ways and Figure 8e shows that a more varying rain isotope source points in the right direction. However, also a change in CO$_2$ fluxes can lead to another imbalance in the net $\delta^{18}$O-CO$_2$ isoflux. We discussed in part 1 that ECHAM/BETHY feature low-CO$_2$ fluxes at high northern latitudes. Increasing assimilation and therefore the respiration in high northern latitudes yields a greater imbalance in $\delta^{18}$O-CO$_2$ net isoflux. We discussed as well in part 1 that the accompanying stomata-internal CO$_2$ mixing ratios, $c_i$, of ECHAM/BETHY are higher than other estimates. However, reduced $c_i$ (at high northern latitudes) would lead to a reduced imbalance between northern and southern hemisphere in the $\delta^{18}$O-CO$_2$ net isoflux which causes our model to depart further from the observations.

[42] Third, the rectifier effect could be modeled erroneously. The covariance between the diurnal and seasonal cycle of $\delta^{18}$O-CO$_2$ transport is already very strong in our model and achieves a meridional gradient in CO$_2$ which is higher than all models in TRANSCOM Phase 1 except for the CSIRO model which is comparable to ECHAM/BETHY [Law et al., 1996]. To bring modeled and observed north-south gradient in $\delta^{18}$O-CO$_2$ closer together, the rectifier effect has to be even stronger as it already is in our model.

[43] The soil water isotopes are the fourth possibility that could lead to the described mismatch. The soil bucket model of ECHAM attenuates too much the seasonal cycle of $\delta^{18}$O-H$_2$O of water in the unsaturated soil zone. Soil CO$_2$ efflux exhibits therefore almost the same $\delta^{18}$O-CO$_2$ value all yearlong. The performed sensitivity analysis used monthly mean rain isotope input that coincided in its seasonal phasing with the seasonal phasing of assimilation in the model, so that no strong sensitivity could be observed. This could be an artefact due to the synchronous seasonal cycles. A more realistic formulation of the soil water profile like the one of Riley et al. [2002] leads to an integration of rainwater isotopes with higher seasonal variations than the soil bucket model. The integrated signal shows then a seasonal amplitude lagging the rain water isotope input, which would translate in a greater amplitude of the apparent soil discrimination and also in a different seasonal phasing of the apparent soil discrimination respectively soil isoflux.

[44] Fifth, the missing stratosphere-troposphere exchange (STE) of enriched $\delta^{18}$O-CO$_2$ could ameliorate the comparison. Gamo et al. [1989] reported for the first time $\delta^{18}$O-CO$_2$ values in the stratosphere that were enriched by 2 to 3$\%$ compared to tropospheric values. This is probably due to the isotopic exchange of CO$_2$ with ozone in the stratosphere [Thiemens, 1999] that is known to be highly enriched in $^{18}$O [e.g., Mauersberger, 1981]. The exchange between troposphere and stratosphere has a strong seasonal cycle, is much bigger in the northern hemisphere than in the southern hemisphere, and has a maximum exchange in spring [Zahn et al., 1999, 2000, and references therein]. Intrusion into the stratosphere passes mainly in the tropics whereas stratospheric air penetrates the troposphere in the extra-tropics contributing to a north-south gradient in $\delta^{18}$O-CO$_2$ [Peylein et al., 1997] and possibly to the seasonal cycle at tropospheric stations. Having 19 model levels, the representation of the stratosphere is very coarse in ECHAM so that STE exchange is not realistic [Timmreck et al., 1999; Kjellström et al., 2000]. We could therefore not include this process in our model and it is possible that the seasonal exchange of the STE changes the $\delta^{18}$O-CO$_2$. However, the isotopic enrichment of CO$_2$ in the lower stratosphere compared to the upper troposphere is only around 2$\%$. The box model of Hessheimer [1997] estimates a gross STE CO$_2$ flux of 200 GtC yr$^{-1}$ that yields an isoflux of about 400 GtC $\%$ yr$^{-1}$ which is of the order of magnitude of other processes like, e.g., fossil fuel combustion. However, the only $\delta^{18}$O-CO$_2$ modeling study that includes the stratospheric enrichment [Peylein et al., 1997] adapted a CO$^{18}$O flux in the upper troposphere in order to match the measured profiles in $\delta^{18}$O-CO$_2$ of Gamo et al. [1989] returning an isoflux of 200 GtC $\%$ yr$^{-1}$. It is possible that the stratospheric enrichment plays its role in the $\delta^{18}$O-CO$_2$ cycle but it is likely that the Arctic-to-Antarctic difference does not change significantly but behaves similar to the other sensitivity runs because of the interactive nature of the calculations. However, the STE is highest in spring and more pronounced in the extra-tropics. This could transport enriched $\delta^{18}$O-CO$_2$ to tropospheric stations mainly in spring which could shift the maximum of the seasonal cycle and consequently the minimum, too.

[45] The atmospheric transport and the biospheric $\delta^{18}$O-CO$_2$ fluxes determine almost completely the seasonal cycle and the north-south gradient of $\delta^{18}$O in atmospheric CO$_2$. This underlines the high potential of $\delta^{18}$O in atmospheric CO$_2$ to quantify the biospheric CO$_2$ gross fluxes, when $\delta^{18}$O-CO$_2$ is eventually fully understood. If one controls the atmospheric transport, the atmospheric signal of $\delta^{18}$O-CO$_2$ can thus be used to deduce CO$_2$ gross fluxes. Inversion techniques with global atmospheric transport models attempt this on a global scale [Peylein, 1999]. On a local scale, investigators handle the atmospheric transports either with transport tracers like $^{222}$Radin [Langendörfer et al., 2002] or with theoretical calculations [Yakir and Wang, 1996]. However, until now, no global study has been able to resolve the discrepancy between modeled and measured seasonal cycles of $\delta^{18}$O-CO$_2$.

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