On the role of atmospheric chemistry in the global CO₂ budget

G. Folberth¹
Canadian Center for Climate Modelling and Analysis, University of Victoria, Victoria, British Columbia, Canada

D. A. Hauglustaine, P. Ciais, and J. Lathière
Laboratoire des Sciences du Climat et de l’Environnement (LSCE), Gif-sur-Yvette, France

Received 21 October 2004; revised 8 March 2005; accepted 23 March 2005; published 16 April 2005.

[1] A global 3D-chemistry-transport model is applied to study the magnitude and geographical distribution of the in situ photochemical CO₂ production in the atmosphere. In the model 1823 TgC/y of reactive carbon compounds (RCC) are emitted at the surface on global and annual average. 46% of the RCC source is released by the vegetation, 27% from biomass burning, and 27% from fossil fuel incomplete combustion. Of these, 1213 TgC/y are oxidized to produce CO₂. Physical removal of the emitted species represents a loss of 154 TgC/y; wet and dry deposition of intermediate oxidation products account for approximately 360 TgC/y. The relative importance of different reaction pathways is assessed. Sensitivity experiments indicate that only 30% to 45% of the RCC emitted are oxidized to CO₂. Interhemispheric gradients of CO₂ at the Earth’s surface produced from RCC, including photochemistry and physical removal, are compared to CO₂ gradients from RCC assuming that 100% of the RCC are released as CO₂, common in CO₂ inverse models. A maximum difference of 0.3 ppmv in the CO₂ gradients is revealed, a result of potential significance for carbon cycle studies. Citation: Folberth, G., D. A. Hauglustaine, P. Ciais, and J. Lathière (2005), On the role of atmospheric chemistry in the global CO₂ budget, Geophys. Res. Lett., 32, L08801, doi:10.1029/2004GL021812.

2. Model Description

[4] Laboratoire de Météorologie Dynamique, zoom (LMDz) is a grid point General Circulation Model (GCM) developed initially for climate studies by Sadourny and Laval [1984]. Tracer transport is based on the finite volume transport scheme of Van Leer [1977] for large-scale advection, the mass flux scheme of Tiedke [1989] for the parametrization of deep convection, and a local second-order closure formalism representing turbulent mixing in the planetary boundary layer (PBL). LMDz (version 3.3) has a horizontal resolution of 3.8 times 2.5 degrees and 19 vertical levels up to 3 hPa. The Interactive Chemistry and Aerosols (INCA) model has been integrated into LMDz. INCA includes 85 chemical species and 303 chemical reactions simulating tropospheric chemistry, emissions, and deposition of primary trace species including nonmethane hydrocarbons. Anthropogenic emissions are based on EDGAR V3.0 [Olivier et al., 2001]. Biomass burning emissions are introduced according to the satellite based inventory developed by Van der Werf et al. [2003], averaged over the period 1997–2001. The Organizing Carbon and Hydrology in Dynamic Ecosystems (ORCHIDEE) dynamical vegetation model [Krinner et al., 2005] provided biogenic emissions of isoprene, terpenes, acetone, and methanol. A detailed description and evaluation of LMDz-INCA and the emission inventory is given by Hauglustaine et al. [2004] and G. Folberth et al. (Impact of biogenic hydrocarbons on tropospheric ozone: Results

¹Formerly at Laboratoire des Sciences du Climat et de l’Environnement (LSCE), Gif-sur-Yvette, France.
from a global chemistry-climate model, manuscript in preparation, 2005).

[5] A control run was initialized using restart files from previous model runs spanning more than 20 model years and has been continued for 30 additional model months. The last 12 months were used in the analysis. To quantify chemical CO₂ production due to individual biogenic VOC emissions, sensitivity experiments have been performed. Four such experiments have been carried out assessing isoprene, terpenes, biogenic methanol, and acetone oxidation, respectively. In these experiments the respective emissions were turned off separately and the CO₂ production was compared to the reference case. We note that non-linearities in photochemistry can somewhat bias the results of these sensitivity studies, presumably towards lower CO₂ production rates due to the prevailing increase in atmospheric reactivity (measured by the OH concentration) when turning off the emissions. However, changes in OH in general are well below 10% in the entire troposphere and only exceed 20% in the isoprene experiment at certain locations (northern midlatitude PBL, lower tropical free troposphere).

[6] In situ CO₂ production by oxidation of VOC essentially occurs through three distinct channels. The major channel corresponds to oxidation of RCC into CO and then into CO₂. This channel includes in our study both direct anthropogenic and biomass burning CO emissions as well as secondary CO from methane and NMVOC oxidation in the atmosphere. The second channel includes carboxyperoxy radical (RCO₃) self- and cross-reactions, e.g., CH₃CO₃ + CH₃CO₃ → 2 CH₃O₂ + 2 CO₂ as well as RCO₃ + NO and RCO₃ + RCO₂ reactions. The third, and minor, channel is associated with alkenoid ozonolysis, e.g., reaction of ethene with ozone (C₂H₄ + O₃), which produces fractional amounts of CO₂. In this study channel 1 is referred to as the “CO channel” and channels 2 and 3 are merged into the “radical + ozonolysis” (R+O) channel. For each channel a tagged CO₂ tracer has been included to analyze also the role of transport.

[7] Table 1 summarizes the RCC surface flux in the model. RCC includes all carbon containing compounds that are chemically broken down in the atmosphere, excluding CO₂ which is chemically inert. Table 1 shows that the terrestrial vegetation decisively contributes to the RCC surface flux. In our inventory 46% of RCC originates from biogenic emissions. 88% of NMVOC are of biogenic origin. Note that estimates of surface emissions still vary widely between inventories. In the GEIA inventory [Guenther et al., 1995], for instance, biogenic isoprene and terpene emissions are estimated to amount to 501 TgC/y and 127 TgC/y, respectively. Furthermore, we assert best estimates but uncertainties in current emission inventories for biogenic NMVOC are large, reaching factors of 2 to 3.

### Table 1. Summary of the Total Reactive Carbon (Non-CO₂) Surface Emissions in LMDz-INCA (TgC/y)

| Source        | Fossil Fuel | Biomass Burning | Biogenic | Total |
|---------------|-------------|-----------------|----------|-------|
| Methane       | 227.4       | 27.3            | 150.8    | 405.5 |
| CO            | 209.3       | 426.2           | 21.4     | 656.9 |
| Isoprene      | 0.0         | 0.0             | 411.5    | 411.5 |
| Methanol      | 0.0         | 4.3             | 99.9     | 104.2 |
| Acetone       | 0.6         | 2.0             | 96.1     | 99.7  |
| Terpenes      | 0.0         | 0.0             | 411.5    | 411.5 |
| Other VOCs    | 49.0        | 38.8            | 11.5     | 99.3  |
| Total         | 486.3       | 496.8           | 838.3    | 1823.2|

### 3. Results

[8] Figure 1 shows the horizontal distribution of CO₂ production, P(CO₂), for both channels. Column integrated P(CO₂) generally is strongest at tropical latitudes yielding up to 6.0 × 10⁻⁹ TgC km⁻² yr⁻¹ in case of CO oxidation and ranges between 0.8 and 2.5 × 10⁻⁹ TgC km⁻² yr⁻¹ in the tropical latitude belt for the R+O channel. Biomass burning is the dominant component in the CO surface flux and is plainly discernible in the CO channel (e.g., equatorial Africa). The biogenic VOC sources produce a clear signal in the R+O channel (tropical forests of equatorial Africa and tropical South America, southeast Asia and Indonesia).

[9] Table 2 gives the global annual mean in situ P(CO₂) for both channels. The model calculates a total chemical CO₂ production of 1213 TgC/y, which is higher by 30−70% than previously published estimates [Enting and Mansbridge, 1991; Tans et al., 1995; Erickson et al., 1996]. This difference is due mainly to the updated emission set and chemical scheme used in this study and, to a lesser extent, due to the contribution of the previously unaccounted R+O channel which contributes 6% to the total production. The CO channel dominates the tropospheric CO₂ production globally. But near the surface at locations strongly affected by biogenic VOC fluxes (e.g., tropical South America and Africa, southeast Asia, Eastern United States) the R+O channel is comparable in magnitude to the CO channel ranging between 25% and 50% of the total in situ CO₂ production (Figure 1 (bottom)). The R+O channel rapidly falls off with altitude.
Table 2. Breakdown of in Situ CO₂ Production, P(CO₂), by Tropospheric Subdomains (TgC/y)\(^a\)

| Subdomain | PBL | FT | UT | TOT |
|-----------|-----|----|----|-----|
| NET       | 140 | 98 | 38 | 276 |
| TRO       | 433 | 294| 95 | 822 |
| SET       | 45  | 47 | 23 | 115 |
| TOT       | 618 | 439| 156| 1213|

\(^a\)Horizontal: northern extratropics (NET, 90°–30°N), tropics (TRO, 30°N–30°S), southern extratropics (SET, 30°–90°S); vertical: planetary boundary layer (PBL, below 750 hPa), free troposphere (FT, 750–500 hPa), upper troposphere and tropopause region (UT, 500–250 hPa), respectively.

[10] Table 2 also shows P(CO₂) broken down by tropospheric subdomains. In situ CO₂ production via CO oxidation is strongest in the tropical troposphere with 392 TgC/y (tropical PBL) and 285 TgC/yr (tropical FT). The R+O channel is distinctly limited to the PBL with the tropical PBL yielding 41 TgC/y. Tables 1 and 2 show that the RCC surface sources globally exceed the in situ CO₂ production, indicating a significant carbon sink due to dry and wet deposition and organic aerosol formation in the case of terpenes. The magnitude of that sink as calculated in our model totals 610 TgC/y. Dry and wet deposition of primary emitted RCC account for 154 TgC/y. In case of isoprene, the sensitivity experiments indicate that 176 TgC/y (43% of the total 412 TgC/y emitted) are transformed chemically into CO₂. To illustrate the effects of this approximation, we compare in Figure 2 the interhemispheric gradients of CO₂ at the surface originating from RCC, assuming that 100% of the RCC are released as CO₂, versus accounting for chemistry and physical removal. The biggest difference occurs at northern midlatitudes (40°–60°N). In this latitude range, chemistry and physical removal reduce the total CO₂ gradient at the surface by up to two thirds compared with the case where it was assumed that 100% of RCC are released as CO₂.

[11] We note that biogenic sources are subject to large uncertainties and interannual variations. A detailed discussion of these uncertainties and their implications for in situ CO₂ production would exceed the scope of this study. In order to illustrate the impact of these uncertainties, we have repeated the calculations with the same model, using the GEIA database as the basis for the biogenic emissions of isoprene and terpenes [Guenther et al., 1995]. These calculations show a difference of less than 20% in the total primary NMVOC emission flux, though individual species can show much higher variations. These differences seem to propagate fairly linearly into the CO₂ production rates due to the predominance of methane and CO oxidation as the major chemical CO₂ source and their long photochemical lifetimes, generally resulting in variations of under 10% in P(CO₂).

[12] These results have implications for carbon cycle related studies. In atmospheric CO₂ modelling studies, for instance, it is assumed that 100% of the carbon flux from RCC surface sources is directly released as CO₂ [e.g., Tans et al., 1995], thus not accounting for photochemistry and physical removal of the emitted RCC before a certain fraction is converted to CO₂. To illustrate the effects of this approximation, we compare in Figure 2 the interhemispheric gradients of CO₂ at the surface originating from RCC, assuming that 100% of the RCC are released as CO₂, versus accounting for chemistry and physical removal. The biggest difference occurs at northern midlatitudes (40°–60°N).

Figure 2. Normalized interhemispheric CO₂ gradients. 2: CO₂ from biomass burning and biogenic NMVOC assuming that 100% of the RCC emitted is released as CO₂; 3: CO₂ from fossil fuel consumption under the same assumption; 1: sum of 2 and 3; 4: total in situ CO₂ from RCC accounting for photochemistry and physical removal; 5 and 6: CO channel and R+O channel fractions; 7: difference between 1 and 4. All quantities refer to annual mean zonal averages, normalized by subtracting their individual South Pole concentration.
results. These inversion studies are beyond the scope of this paper, but it is anticipated that regional surface sources and sinks of CO$_2$ would be misallocated by an inversion without accounting for in situ CO$_2$ production, in particular sources over those regions strongly affected by RCC emissions. It is interesting to note that the CO$_2$ photochemical production and dry deposition are maximum in summer and correlated to mixing in the PBL. Hence, we would expect that the seasonal rectifier effect, proposed by [Denning et al., 1996] to account for such a correlation, will apply to some extent to the differences illustrated in Figure 2. A more detailed analysis is required to quantify the implication of the rectifier effect in our results.

4. Conclusion

[14] Based on the state of the art surface emission inventory and photochemical scheme used in this model study, 1823 TgC/y are emitted as RCC into the atmosphere and are then oxidized in situ to CO$_2$ with efficiencies ranging between 30% and 45%. About 50% of the RCC originate from the terrestrial vegetation. Dry and wet deposition of emitted species and oxidation products compete with the chemical CO$_2$ production. Out of these 1823 TgC/y emitted as RCC, 1213 TgC/y are oxidized to CO$_2$. Our model study has aimed to quantify CO oxidation as well as release of CO$_2$ by carboxy-peroxy radical self- and cross-reactions and alkenoid ozonolysis as sources of CO$_2$ in the atmosphere. To our knowledge, the latter processes have been assessed for the first time in relation to the global carbon budget. The R+O channel globally seems to be of minor importance as it is mostly limited to the PBL, but on a regional scale, near the surface its contribution can become significant, ranging between 25% and 50% of the total in situ CO$_2$ production over areas with high biogenic VOC emissions. The spatial distribution of in situ CO$_2$ production basically reflects the different lifetimes of the chemical compounds, the CO lifetime being on the order of 2 months. Contrariwise, the R+O channel is dominated by VOCs with lifetimes between several hours and a few weeks. The confinement of significant R+O channel contributions to the tropical PBL is an immediate consequence of these short photochemical lifetimes.

[15] The sensitivity experiments have shown that between 30% and 45% of the RCC emitted as biogenic VOC are oxidized to CO$_2$. This implies that physical loss processes, such as dry and wet deposition, are important sinks for atmospheric carbon. The experiments indicate that approximately 154 TgC/y are lost via dry and wet deposition of the primary species, whereas physical removal of intermediate products account for ~360 TgC/y; approximately 96 TgC/y are lost to the stratosphere, most likely as CO and CH$_4$.

[16] This study also points to a potential significance of photochemistry and physical removal of RCC in carbon cycle studies. From our results we conclude that neglecting these processes would result in a nonnegligible difference when analyzing the interhemispheric CO$_2$ gradients originating from RCC sources, at least northward of 60°S and at the surface, where most of the in situ stations are located.

The CO$_2$ gradient exhibits a significantly lower increase with increasing latitude when RCC photochemistry and physical removal is taken into account, versus the case when it is assumed that 100% of the RCC are released as CO$_2$. Since the same emission inventory was used in both cases, the calculated difference must be attributed to photochemistry and physical removal due to a time delay in RCC-to-CO$_2$ oxidation and the nonunity conversion efficiency of RCC to CO$_2$ as caused by the physical removal of intermediates.

[17] Acknowledgments. This work was partly funded by the European Commission under contracts EVK2-CT-1999-0030 and EVK2-CT-1999-0002. Additional funding has been received from the GCC project and support by NSERC and CFCA is acknowledged. Computer resources were provided by the Commissariat à l’Energie Atomique under project p24.

References

Denning, A. S., et al. (1996), Simulations of terrestrial carbon metabolism and atmospheric CO$_2$ in a general circulation model. 2. Simulated CO$_2$ concentrations, Tellus, Ser. B, 48, 543–567.

Enting, I., and J. Mansbridge (1991), Latitudinal distribution of sources and sinks of CO$_2$. Results of an inversion study, Tellus, Ser. B, 43, 156–170.

Erickson, D. J., et al. (1996), The seasonal cycle of atmospheric CO$_2$: A study based on the NCAR Community Climate Model (CCM), J. Geophys. Res., 101, 15,079–15,097.

Guenther, A., et al. (1995), A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892.

Gurney, K. R., et al. (2002), Towards robust regional estimates of CO$_2$ sources and sinks using atmospheric transport models, Nature, 415, 626–630.

Hauglustaine, D. A., F. Hourdin, L. Jourdain, M.-A. Filiberti, S. Walters, J.-F. Lamarque, and E. A. Holland (2004), Interactive chemistry in the Laboratoire de Météorologie Dynamique general circulation model: Description and background tropospheric chemistry evaluation, J. Geophys. Res., 109, D04314, doi:10.1029/2003JD003957.

Kesselmeier, J., et al. (2002), Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget, Global Biogeochem. Cycles, 16(4), 1126, doi:10.1029/2001GB001813.

Krinner, G., N. Viovy, N. de Noblet-Ducoudr, J. Ogge, J. Polcher, P. Friedlingstein, P. Ciais, S. Stich, and I. C. Prentice (2005), A dynamic global vegetation model for studies of the coupled atmosphere-biosphere system, Global Biogeochem. Cycles, 19, GB1015, doi:10.1029/2003GB002199.

Olivier, G. J. J., et al. (2001), Applications of EDGAR including a description of EDGAR 3.0: Reference database with trend data for 1970–1995, RIVM Rep. 773301 001, Rijksinstituut voor Volksgezondheid en Milieu, Bilthoven, Netherlands.

Sadourny, R., and K. Laval (1984), January and July performance of the LMD general circulation model, in New Perspectives in Climate Modelling, edited by A. Berger and C. Nicolis, pp. 173–197, Elsevier, New York.

Tans, P., I. Fung, and I. Enting (1995), Storage versus flux budgets: the terrestrial uptake of CO$_2$ during the 1980s, in Biotic Feedbacks in the Global Climatic System, pp. 351–361, Oxford Univ. Press, New York.

Tiedke, M. (1989), A comprehensive mass-flux scheme for cumulus parameterization in large scale models, Mon. Weather Rev., 117, 1779–1800.

Van der Werf, G., et al. (2003), Carbon emissions from fires in tropical and subtropical ecosystems, Global Change Biol., 9, 547–562.

Van Leer, B. (1977), Towards the ultimate conservative difference scheme, part IV: A new approach to numerical convection, J. Comput. Phys., 23, 276–299.