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On the role of atmospheric chemistry in the global CO₂ budget

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[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.

1. Introduction

[2] The atmospheric CO₂ gradients are not only associated with transport acting on regional surface sources and sinks but also depend on in situ photochemical production from hydrocarbon and carbon monoxide (CO) oxidation [Tans *et al.*, 1995]. Using budget models, the CO₂ production from CO oxidation has been estimated to be 860 and 920 TgC/y by Enting and Mansbridge [1991] and Tans *et al.* [1995], respectively, owing to different emission inventories and photochemical schemes. Using an early, unreleased version of the 3D-MOZART model, Erickson *et al.* [1996] have calculated a source of 700 TgC/y. Biogenic volatile organic compounds (VOC) represent a substantial carbon source from the ecosystems to the atmosphere and VOC oxidation has been shown to represent a significant loss of photosynthetically fixed carbon [Kesselmeier *et al.*,

2002]. Anthropogenic and biogenic VOC are introduced in carbon cycle models as direct surface emissions of CO₂. However, the oxidation of VOC in the atmosphere is rather complex and the role played by these short-lived compounds in the CO₂ production requires particular attention.

[3] In this study we apply a state of the art global 3D-chemistry-transport model with a fairly detailed hydrocarbon chemical scheme including biogenic VOC to provide an updated estimate of the magnitude and distribution of CO₂ photochemical production in the atmosphere. We also investigate the importance of secondary channels, arising from radical self- and cross-reactions or ozonolysis of alkenoid compounds, for the atmospheric carbon budget and global CO₂ distribution. We also assess carbon sinks due to physical removal of RCC by dry and wet deposition. Finally, we illustrate the impact of an explicit calculation of the CO₂ production on the CO₂ gradient versus a simplified approach assuming a direct release of RCC as CO₂ at the surface.

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

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

	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
Terpenes	0.0	0.0	96.1	96.1
Acetone	0.6	2.0	47.1	49.7
Other VOCs	49.0	38.8	11.5	99.3
Total	486.3	498.6	838.3	1823.2

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 nonlinearities 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 peroxy 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.

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 in situ 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.

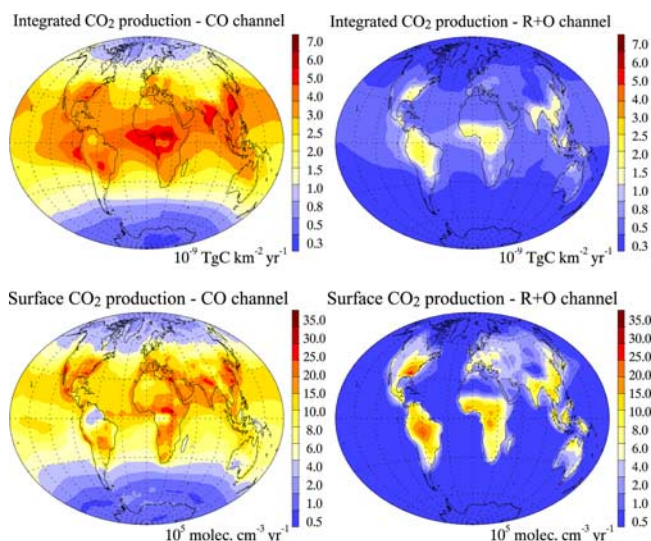


Figure 1. Horizontal distribution of the annual mean in situ CO₂ production rate for (left) the CO channel and (right) the R+O channel. (top) Column integrated production rates (10^{-9} TgC km⁻² yr⁻¹); (bottom) annual mean production rates at the surface (10^5 molecules cm⁻³ yr⁻¹). Results are taken from the lowermost model level representing a layer height of approximately 140 meters.

Table 2. Breakdown of in Situ CO₂ Production, P(CO₂), by Tropospheric Subdomains (TgC/y)^a

Subdomain	PBL	FT	UT	TOT
<i>P(CO₂)_{tot}</i>				
NET	140	98	38	276
TRO	433	294	95	822
SET	45	47	23	115
TOT	618	439	156	1213
<i>P(CO₂)_{CO}</i>				
NET	126	95	37	258
TRO	392	285	91	768
SET	43	46	22	111
TOT	561	426	150	1137
<i>P(CO₂)_{R+O}</i>				
NET	14	3	1	18
TRO	41	9	4	54
SET	2	1	0	3
TOT	57	13	5	75

^aHorizontal: 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/y (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 (135 TgC/y via CO the channel, 40 TgC/y via the R+O channel). 21 TgC/y (5%) are removed via isoprene dry deposition, and the remaining 215 TgC/y (~52%) are lost through removal of intermediate compounds. In case of the 96 TgC/y emitted as terpenes 29 TgC (~30%) are converted to CO₂ (19 TgC/y CO channel, 10 TgC/y R+O channel), 3 TgC (~3%) are subject to dry deposition of terpenes, 27 TgC (~28%) are due to physical sinks of intermediates, and 37 TgC (~39%) are lost through the chemical mechanism representing implicitly the formation of organic aerosols. Note that the aerosol formation is not accounted for explicitly but is rather taken into account as a carbon imbalance in the scheme for specific reactions. These budgets indicate that 360 TgC/y are lost by dry and wet deposition of intermediates (aldehydes, peroxides, ketones, etc.). We conclude that the remaining 96 TgC/y are lost to the stratosphere, most likely as methane and CO. Defining the conversion efficiency as the ratio of RCC emitted to carbon eventually converted to CO₂ expressed in percent, the model calculates a global conversion efficiency for isoprene, terpenes, methanol, and acetone of 43%, 30%, 41%, and 36%, respectively.

[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). 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.

[13] Note, though, that in both cases the CO₂ signal from RCC sources is small compared to the first order accumulation of fossil fuel CO₂ in the Northern Hemisphere (e.g., 3 to 5 ppm pole to pole difference) [Gurney *et al.*, 2002]). Other sources of uncertainties as for instance variability in emission magnitude, atmospheric transport, or chemical processes appear more important for the CO₂ budget than the corrections introduced by the full photochemical calculation of CO₂ production presented here. However, not accounting for it could yet introduce a bias in inversion

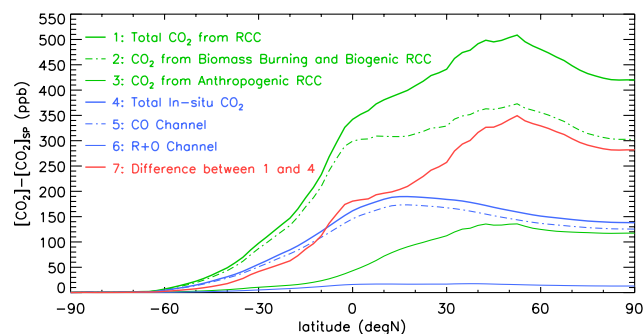


Figure 2. Normalized interhemispheric CO₂ gradients. 2: CO₂ from biomass burning and biogenic NMVOC assuming that 100% of the RCC emitted is released as CO₂; 3: CO₂ from fossil fuel consumption under the same assumption; 1: sum of 2 and 3; 4: total in situ CO₂ from RCC accounting for photochemistry and 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 CO₂ would be misallocated by an inversion without accounting for in situ CO₂ production, in particular sources over those regions strongly affected by RCC emissions. It is interesting to note that the CO₂ 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 CO₂ 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 CO₂ production. Out of these 1823 TgC/y emitted as RCC, 1213 TgC/y are oxidized to CO₂. Our model study has aimed to quantify CO oxidation as well as release of CO₂ by carboxy-peroxy radical self- and cross-reactions and alkenoid ozonolysis as sources of CO₂ 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 CO₂ production over areas with high biogenic VOC emissions. The spatial distribution of in situ CO₂ 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 CO₂. 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 CH₄.

[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 CO₂ 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 CO₂ 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 CO₂. 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-CO₂ oxidation and the nonunity conversion efficiency of RCC to CO₂ as caused by the physical removal of intermediates.

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