

Interactive comment on “Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA” by D. Kubistin et al.

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We thank the referee #3 for the very helpful comments on our paper. The comments and our replies are listed below.

1. reference to other GABRIEL papers, previous studies of OH and HO₂ measurements in isoprene rich regions:

The GABRIEL campaign was performed to study the influence of the tropical rainforest to the atmospheric chemistry. Several aspects were analysed in the articles of this special issue. Each of the GABRIEL articles had different scopes, e.g. Martinez et al. (2008) focussed on the HO_x measurements, whereas Stickler et al. (2007) described the measurements and box model simulations for formaldehyde and the peroxides. Butler et al. (2008) analysed the data in respect to the simulations of a global model and our article concentrates on the simulation with a box model, constrained by measurements, with the focus on the OH and HO₂ budget over the tropical rainforest. This different analysis technique was used to show another aspect of the data and our article was not meant to be an overview article of the GABRIEL campaign.

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While it is true, that previous studies were performed in isoprene rich regions, no measurements of OH and HO₂ have been performed, to our knowledge, over a tropical rainforest. The Tropics are a major source region of OH and VOCs and control the oxidation capacity on a global scale. The GABRIEL measurements showed unexpectedly high concentrations of HO_x, in contrast to the simulations of global models, which predict a significant reduction of the oxidation capacity over the rainforest due to the emissions of VOCs. Therefore modifications in our knowledge of the tropospheric chemistry over the rainforest have a large impact on global scale and measurements in the tropical regions help us to understand the processes.

In our conclusions we will explicitly include the comparison with previous HO_x observations over different forests to strengthen our results that possible reactions schemes in isoprene chemistry have been not described by the common chemical mechanism yet.

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2. (a) mean values of important variables for OH and HO₂:

An overview of the measured species during the GABRIEL campaign and their mean values separated in boundary layer and free troposphere as well as for the tropical Atlantic and the tropical rainforest are shown in Lelieveld et al. (2008). More specific results for formaldehyde and the peroxides can be found in Stickler et al. (2007), the measurements for isoprene, methacrolein and methyl vinyl ketone, methanol and acetone are described in Eerdeken

et al. (2008) and the HO_x measurements are shown in Martinez et al. (2008) and in our article.

For a better explanation of our model results, the mean values of the measured species will be included in our article. Hereby we concentrate on the four cases discussed in section 4.3 and provide the values in an additional table.

(b) box model simulations with modelled formaldehyde and peroxide concentrations:

Performing simulations with modelled formaldehyde and peroxide concentrations was also mentioned by referee 1. Our box model simulations for OH and HO_2 were performed by constraining the box model with measured species, including formaldehyde and when available, the peroxides measurements. By constraining the model, the simulations are expected to describe the situation which was present during our measurements.

We also did simulations with unconstrained HCHO to model the HO_x concentrations. The OH concentration of simulation with "free" HCHO lead to 1 % more OH on average for the boundary layer over the rainforest in the afternoon. 4 % more HO_2 radicals were produced on average compared to the basic run. Therefore we do not see a large effect in relation with the HCHO concentrations.

Regarding the peroxides the simulations were already performed by modelling the peroxides concentrations when no measurements were available. Thereby we used a heterogenous loss rate, which was derived by the hydrogen peroxides measurements (described in section 3) and is consistent with the results of Stickler et al. (2007). Fig. 6 shows the comparison between observed and simulated peroxides concentrations and their 1σ uncertainty, caused by using the derived heterogenous loss rate. In our sensitivity studies we modified the peroxides concentrations inside these uncertainties, which only changes the OH concentration by a factor of 1.2 for $3 \cdot c(\text{H}_2\text{O}_2)$ and

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0.97 for $0.3 \cdot c(\text{H}_2\text{O}_2)$ and the HO_2 concentration by 1.04 and 0.99, respectively, on average for the boundary layer over the rainforest in the afternoon. Stickler et al.(2007) focussed on HCHO and the peroxides and performed simulations with the same box model, constrained to the observed OH and HO_2 concentrations. They found an overestimation of the HCHO mixing ratio by the model, which they attribute to an underestimation of the entrainment and perhaps of the dry deposition velocity. The organic peroxides were significantly overestimated, pointing at "either larger heterogeneous loss of organic peroxides and/or their radical precursors, underestimated photodissociation or missing reaction paths of peroxy radicals not forming peroxides in isoprene chemistry" (Stickler et al., 2007).

3. Measurement and model uncertainties

(a) interferences in the LIF instrument

The measurements of OH and HO_2 are described by Martinez et al. (2008) in detail. This also include the discussion of possible interferences of the LIF instrument. This reference will be included in our article.

(b) isoprene measurements in error, interferences in measurements of HCHO

A detailed discussion of the isoprene and HCHO measurements can be found in Eerdekens et al. (2008) and Stickler et al. (2007). The focus of our article was on the side of box model simulations. Hereby the measurement uncertainties were included in our simulations (s. Fig. 9), showing, that these are not sufficient to describe the observations. In our sensitivity studies we varied the concentration of isoprene and HCHO by factors of 0.5 and 2, which only changed the OH concentrations by a factor of 1.5 and 1.03. So far the addressed errors of the measurements of that species must be larger then a factor of $2^{\pm 1}$ to reproduce the HO_x observations.

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(c) cloud corrections

In situ measurements of $J(\text{NO}_2)$, using a filter radiometer, were performed on the aircraft to account for changes due to clouds, aerosols etc. Due to limited space in an aircraft, no other photolysis frequencies could be measured. The observations of $J(\text{NO}_2)$ were rather used to scale the modelled photolysis frequencies by the radiative transfer TUV model (Madronich et al., 1998). Hereby the ozone column was taken into account by determining it from satellite data for each flight (GOME, available at www.knmi.nl).

For small cloud fraction the scaling factor, obtained from $J(\text{NO}_2)$ is approximately independent on the wavelength spectrum (Crawford et al., 2003). As the GABRIEL campaign took place during the dry season, only sparse cloud cover occurred. Therefore this approach should be valid for our analyses. However, for overcast skies, the effect for the actinic flux at 420 nm differs only about 30% than for the actinic flux at 320 nm and cannot be the reason for the discrepancies of the HO_x measurements and simulations.

(d) errors of unmeasured species

In the degradation of hydrocarbons many intermediate species are produced which were not and could not be measured during the campaign. Therefore in the box simulations the uncertainty of these species are a function of their key species. By varying the concentrations of the key species in our sensitivity studies, the concentrations of the intermediates are also effected. The variation of the isoprene concentrations by a factor of 0.5 only led to an enhancement of the OH concentration by a factor of 1.5. Some of the species which were calculated by MECCA are hydroxy acetone, acetaldehyde, methylglyoxal, etc. The chemical reactions are provided in the accompanying supplement. For additional sources or sinks of these species, which are not described by the model, the uncertainties cannot be specified as no measurements are available.

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4. Monte Carlo simulations

In our Monte Carlo simulations we varied the rate coefficient constants within an uncertainty of 15 % and obtained an uncertainty for OH of $\approx 15\%$ and for HO_2 of $\approx 10\%$. The most impact on the OH concentrations had the reaction of $\text{H}_2\text{O} + \text{O}(^1\text{D})$ ($\approx 9\%$), $\text{N}_2 + \text{O}(^1\text{D})$ ($\approx 6\%$) and $\text{ISOP} + \text{OH}$ ($\approx 10\%$), depending on the different measurement situations. The rate coefficients for these reactions have changed from Sander et al. (2003) to Sander et al. (2006) of about 1 % to 20 %, their uncertainties were reported to be $< 20\%$ for our measurement conditions. For HO_2 , the reactions of $\text{HO}_2 + \text{HO}_2$ and $\text{ISO}_2 + \text{HO}_2$ influenced the simulated HO_2 concentration of about 6% and 8%, respectively.

Varying the photolysis of $J(\text{O}(^1\text{D}))$ by a factor of 2 lead to 1.6 times more OH and 1.05 times more HO_2 for the forest boundary layer afternoon case, showing their importance for OH production. But still the factor of 2 is not sufficient enough to explain the discrepancies between observations and model for HO_x .

We will include the variation of $J(\text{O}(^1\text{D}))$ in our sensitivity studies.

5. Combining all chemical hypotheses together

In our article we discussed possible pathways for additional OH production. We analysed the strength of OH loss via the formation of organic peroxides by neglecting these specific reaction. We also implemented additional reactions, eg. $\text{HO}_2 + \text{RO}_2 \rightarrow \text{OH} + \text{RO} + \text{O}_2$ and $\text{RO}_2 + h\nu \rightarrow \text{R}'\text{O} + \text{OH}$. We used upper limits showing that none of them could explain the measured OH concentrations. We also combined the last two hypotheses leading to an enhancement factor of 5.1 ± 1.1 for isoprene mixing ratios of (5.6 ± 0.4) ppbV for the simulated OH concentrations compared to the base run (see section 4.3). Here we did not include the study of neglecting the organic peroxides formation, as the sum of organic peroxides was measured during GABRIEL.

6. Chemical mechanism of MECCA

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The chemical mechanism of MECCA, which was used for the simulations for the GABRIEL data, can be found in the applied supplement. It is based on Sander et al.(2005) and Pöschl et al.(2000). Pöschl et al.(2000) developed a reduced isoprene reaction scheme which was crosschecked with the detailed Master Chemical Mechanism (Pinho et al., 2005). The two mechanisms showed an agreement of about 10 - 15 % for OH under low NO_x conditions (Pöschl et al., 2000). We also did simulations with the more detailed isoprene chemistry of the MCM and found no significant difference to the simulations done with MECCA (section 4.2).

The numerical solver, which was used for the simulations, was the third-order Rosenbrock solver with automatic time-step control (ros3). This solver is very robust and capable of integrating very stiff sets of equations (Sandu et al., 1997, Sandu and Sander, 2005, Sander and Kerkweg, 2006).

In our analyses we have shown that the complex isoprene chemistry might not be fully understood and additional OH recycling is a possible way to explain the observed OH concentrations over the tropical rainforest during GABRIEL. In general, the degradation of isoprene contains several reactions producing also several intermediates, which can produce or destroy OH. Reducing the whole isoprene chemistry to methane chemistry might lead to an underestimation of the OH reactivity, as the reactivity coming from the intermediates of isoprene are not considered. We will provide all production and loss rate terms of our simulations for a typical datapoint over the rainforest boundary layer in the afternoon, so that comparison with the simplified Excel model from referee 3 with the more comprehensive chemical mechanism of MECCA is possible.

For isoprene levels of 1 - 2 ppbV mean values of $(3.8 \pm 0.9) \cdot 10^6 \text{ molec cm}^{-3}$ for OH and $(7.0 \pm 1.7) \cdot 10^8 \text{ molec cm}^{-3}$ for HO_2 were observed. Simulation with our box model produces mean values of $(0.7 \pm 0.3) \cdot 10^6 \text{ molec cm}^{-3}$ for OH and $(2.3 \pm 0.8) \cdot 10^8 \text{ molec cm}^{-3}$ for HO_2 , leading to a deviation of 7 ± 3.6 and 3.2 ± 0.8 for OH and HO_2 , respectively. For isoprene levels > 5 ppbV the mean OH and

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HO_2 concentration is $(4.7 \pm 0.6) \cdot 10^6 \text{ molec cm}^{-3}$ and $(10.5 \pm 2) \cdot 10^8 \text{ molec cm}^{-3}$ and the calculated concentration $(0.35 \pm 0.07) \cdot 10^6 \text{ molec cm}^{-3}$ and $(2.9 \pm 0.6) \cdot 10^8 \text{ molec cm}^{-3}$, respectively. A deviation between observation and simulation of 13 ± 2 for OH and 3.7 ± 0.8 for HO_2 is obtained.

This discrepancies are not able to be explained by our performed sensitivity studies and measurements uncertainties.

7. Technical comments:

- Page 15241, line15-16. Should "irradiation intensity" be "radiation intensity":
Changed.
- Page 15243, line 3. "topical" should be "tropical":
Changed.
- Page 15243, line 11. It states that "all" species relevant for fast photochemistry were measured, but later some VOCs were inferred. Also, apparently NO_2 was not measured. Perhaps the statement should be that "many important species relevant for fast photochemistry were measured":
Changed.
- Page 15244, line 25. The reason for the selected ozone column should be discussed (i.e. average for the flight days, average for the month, or whatever):
For the calculations of the photolysis frequencies the selected ozone column was determined for every flight as an average value. Therefore we used the satellite data of GOME, available at the www.knmi.nl.
We will include a short comment on this in the paper.
- Page 15245, line 1. As stated above, I am concerned about scaling j-value changes from clouds and aerosols that are predominately in the UV-B region to $j(\text{NO}_2)$ that is weighted toward the UV-A:

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Please see comment above.

- 15245, line 20. The symbolism for the deposition rate isn't really described. As I understand it, $1.35 \times 10^{-5} \dots 10^{-4} \text{ s}^{-1}$ means ranging 1.35×10^{-5} to $1.35 \times 10^{-4} \text{ s}^{-1}$. I would suggest just spelling this out in the text. Do these small deposition rates have any impact on the radical levels?

We will change the notation to $1.35 \times 10^{-5} \text{ s}^{-1}$ up to $1.35 \times 10^{-4} \text{ s}^{-1}$.

The heterogeneous loss rate for H_2O_2 was determined using the measured concentrations (section 3). The deviation between simulated and observed peroxides was taken for an estimation of the uncertainty. In our sensitivity studies we modified the peroxides concentrations inside these uncertainties, which only changes the OH concentration by a factor of 1.2 for $3 \cdot c(\text{H}_2\text{O}_2)$ and 0.97 for $0.3 \cdot c(\text{H}_2\text{O}_2)$ and the HO_2 concentration by 1.04 and 0.99, respectively, on average for the boundary layer over the rainforest in the afternoon.

- Page 15246, line 17. It is stated that the underestimation of OH is an indication of the inadequacy of the hydrocarbon chemistry scheme. Couldn't this also be indication of problems with the measurements or both?

The inadequacy of the hydrocarbon chemistry scheme is a likely way to explain the discrepancies between observations and simulations. But measurements always have uncertainties concerning their measurement technique and therefore the additional uncertainty can never be excluded. We will include a comment on that in our article.

- Page 15247, line 5. "ranging from 0 and 3" should be "ranging from 0 to 3": Changed.
- Page 15253, line 21. The statement that "OH recycling via reaction of HO_2 is weak compared to primary production" is worrisome. Even in low NO environments, the recycling of OH is important. I calculate (for $\text{NO}=13 \text{ pptv}$) recycling rates that are about twice the primary production:

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We discussed the OH budget for four different cases (section 4.4). The results are shown in table 7. For case 2, 3 and 4 50-60 % of total OH formation comes from the primary production and only $\approx 10\%$ from the reaction $\text{NO} + \text{HO}_2$. We concluded therefore that "OH recycling via reaction of HO_2 is weak compared to primary production" for these three cases with NO mixing ratios below 20 pptV. This sentence must be read completely and in its own context: "For all other cases the OH recycling via reaction of HO_2 is weak compared to the primary production", to be clear that this is not a general statement for low NO_x conditions.

Also the simulation for OH with constrained HO_2 concentrations still led to underestimation of OH compared to the measurements (section 4.3), which reflects the weak coupling between these two radicals in the common mechanism.

As mentioned above we provide all production and loss rate terms for better comparison for the referee 3.

- Page 15254, line 23. My little model for the forest afternoon case gives $[\text{HO}_2]/[\text{OH}] = 241$, close to the observed value of 234, if I use an equivalent isoprene of 2 ppb. For the forest morning case, it gives a ratio of 132, using equivalent isoprene of 0.5 ppb, compared to the observed value of 127. I don't think lack of understanding in OH- HO_2 cycling is a serious problem. It may be that isoprene measurements are the problem.

As referee 3 already mentioned the two box models (the simplified Excel box model and the more detailed model MECCA) seems to show a different behaviour. For isoprene mixing ratios between 1 - 2 ppbV the observed HO_2/OH ratio is 190 ± 46 , whereas the calculated HO_2/OH ratio is still higher (404 ± 172). Even with the same isoprene levels the two box models give different results. Concerning the isoprene measurements and their uncertainties they are described in detail by Eerdekens et al. (2008). Concerning the different behaviour of the two box model, the production and loss terms

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are provided for one typical point for the afternoon (see table below).

- Page 15255. In order to under recycling in the forested troposphere, don't you want to run the model so it agrees well with the radical observations? The calculations in section 4.5 were run with the model base case. Wouldn't it be better to run them with the OH and HO₂ constrained?

In section 4.5 the missing OH production term is discussed. Hereby the production and loss terms of OH were calculated by MECCA in the base simulation. As steady state was required, the production term equals the loss term $L = G = 5.06 \cdot 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$.

In a second simulation the measured OH and HO₂ concentrations additionally constrained the box model. This led to a production term of $G = 6.65 \cdot 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$ and a total loss term of $L = 56.64 \cdot 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$, showing the missing source strength of $S^* = 5 \cdot 10^7 \text{ molec cm}^{-3} \text{ s}^{-1}$.

To make the information of the second simulation clearer, we have changed the sentence.

- Page 15256, line 7. Suggest changing "independently" to "independent". Changed.
- Page 15258, line 1. Change "combing" to "combining": Changed.
- Page 15268. The results for the reference run just don't seem to make sense. To obtain such low OH values, I suggest there is a mistake in one or more rate coefficients, or species concentrations, or parameter (i.e. j-values, deposition velocities). I can only get my little model OH to go below $1 \times 10^6 \text{ cm}^{-3}$ if I increase the equivalent isoprene to 30 ppbv or more:

The chemical mechanism used for our simulations was provided in the electronic supplement. For the simulations the differential equations, containing the chemical reactions, are generated automatically, so that the used mechanism is identical with the mechanism of the electronic supplement.

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The difference between the simplified model of referee 3 and the comprehensive MECCA model might again lie in the neglect of the intermediates of the isoprene degradation scheme. As mentioned before all production and loss rate terms for one specific point will be provided for better comparison between these two models.

- Figures 10,12,14,16, and 17. I suggest a logarithmic scale on the ratio plots, so the values at ratios less than unity are clearer.
The scope of our paper was to show that box model simulations underestimate the OH and HO₂ concentrations over the tropical boundary layer significantly. Therefore a detailed description of the observed-to-model ratios around unity were neglected. For our analysis and conclusions the non-logarithmic scale is sufficient.
- Figure 15 caption. Suggest "Comparison" rather than "Deviation". Changed.

References

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Characteristic Datapoint

We provide the production and loss rates of our simulations for a typical datapoint over the rainforest boundary layer in the afternoon:

Production rate terms for point =134 at 551 m, 15:35 LT, p=0.946 hPa, T = 28.5° C

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Loss rate terms (molec/cm ³ /s)	Reaction no (see supplement)	Loss rate terms (molec/cm ³ /s)	Reaction no (see supplement)	Loss rate terms (molec/cm ³ /s)	Reaction no (see supplement)	Loss rate terms (molec/cm ³ /s)	Reaction no (see supplement)
0.1287986E+09	G1001	0.7528085E+05	G4108	0.7598085E+04	G2109	0.7569595E+02	J4305
0.1176685E+09	J1001b	0.7473338E+05	G4505	0.7493967E+04	J3103a	0.7048825E+02	G4417
0.7255695E+07	J1001a	0.7253489E+05	G4405	0.7064335E+04	J4100	0.6310959E+02	G3204
0.4958920E+07	J3101	0.7215937E+05	G4101	0.5683063E+04	G4502	0.5806624E+02	J4200
0.4343106E+07	G3101	0.6480019E+05	J4500	0.4492847E+04	G4107	0.4395863E+02	J4304
0.3119885E+07	G4501	0.5918959E+05	G2112	0.4078392E+04	G4215b	0.3692956E+02	G4207
0.2760671E+07	G3103	0.5168903E+05	J4202	0.2515025E+04	G3202	0.2795726E+02	G4315
0.1820525E+07	G1000	0.4288950E+05	J4302	0.2166374E+04	G4106b	0.1684559E+02	J4300
0.1563379E+07	G4503	0.3726197E+05	G4412	0.2127861E+04	G4210	0.1484985E+02	G4206
0.1092064E+07	G2111	0.3670552E+05	G4215a	0.1682600E+04	G4318	0.1475497E+02	J4400
0.9300798E+06	G4504	0.3287372E+05	G4218	0.1570235E+04	G4311	0.1213130E+02	G4413
0.8054807E+06	G2100	0.3261245E+05	G4202	0.1338653E+04	G4106a	0.1094277E+02	G4214
0.7148903E+06	G4500	0.3007836E+05	G4508	0.1268766E+04	G4200	0.1071163E+02	G4307
0.6098159E+06	G3201	0.2772185E+05	J4401	0.1259359E+04	G4204	0.9384018E+01	G4404
0.5819782E+06	J4101b	0.2656511E+05	G4316	0.9596596E+03	J3103b	0.9266929E+01	G4105
0.5587449E+06	G4507	0.2582924E+05	G4211b	0.9396644E+03	G4203	0.7006090E+01	G4414
0.5149493E+06	J2101	0.2516690E+05	G2105	0.7444388E+03	G4313	0.6553862E+01	J3202
0.3803659E+06	G4406	0.2383984E+05	G4208	0.7083934E+03	G4312	0.5176798E+01	G4415
0.3600700E+06	G4213	0.2268561E+05	G4309	0.5973155E+03	G4310	0.3986544E+01	J4306
0.3595960E+06	G4221	0.1956473E+05	G4217	0.5758076E+03	G4300	0.3094419E+01	G3208
0.3592115E+06	G2110	0.1844506E+05	G4102	0.5640580E+03	G3200	0.2996656E+01	G4306
0.3086249E+06	G3203	0.1518507E+05	G4410	0.5634372E+03	J3200	0.2624772E+01	G4401
0.3086151E+06	G3207	0.1485382E+05	G4302	0.5580300E+03	G3108	0.2554890E+01	G4220
0.2758602E+06	G4506	0.1477990E+05	G3106	0.4149747E+03	G4400	0.1448031E+01	G4109
0.2604263E+06	G4407	0.1440480E+05	J4402	0.2787057E+03	J4403	0.1350584E+01	G4303
0.2288015E+06	G4212	0.1420921E+05	G4308	0.2716579E+03	G4304	0.1166070E+01	G4209
0.2276467E+06	G4104	0.1340899E+05	G4219	0.2379452E+03	G4402	0.6465398E+00	G3205
0.2232176E+06	G2107	0.1287463E+05	G4201	0.2208570E+03	J4406	0.4233388E+00	J4404
0.1983357E+06	G4110	0.1232407E+05	J4501	0.2007279E+03	G4305	0.2692393E+00	G4416
0.1889829E+06	G4408	0.1216328E+05	J4203	0.1840414E+03	G4216	0.2164267E+00	G4320
0.1799006E+06	G4317	0.1197747E+05	G4111	0.1839009E+03	J4204	0.7873785E-01	G4205
0.1497647E+06	G4409	0.1138921E+05	G4411	0.1758177E+03	G4403	0.3134781E-01	J3104
0.1480143E+06	G4319	0.1085887E+05	G4103b	0.1258267E+03	G4314		
0.1153935E+06	G4103a	0.1014240E+05	G4301	0.7647722E+02	G3109		
0.1071065E+06	G4211a	0.9102424E+04	G2104	0.7644574E+02	G3110		

BudgetOH: 0.4943630E+07 molec/cm³/s BudgetHO2: 0.3967121E+07 molec/cm³/s

fixed concentrations:

O3	20 ppbV	ROOH	1.2 ppbV	methanol	3.2 ppbV	C4H10	28 pptV
NO	13 pptV	HCHO	1.4 ppbV	C2H4	0.7 ppbV	CO2	377 ppmV
CO	135 ppbV	isoprene	5.1 ppbV	C2H6	0.8 ppbV	H2	563 ppbV
H2O	23 mmol/mol	MVK+MACR	2.4 ppbV	C3H6	83 pptV	HNO3	0
H2O2	5.6 ppbV	acetone	1.4 ppbV	C3H8	83 pptV	J(O1D)	2.24 * 10 ⁻⁵ s ⁻¹

measured OH 3.84 * 10⁶ molec/cm³ measured HO2 1.21 * 10⁹ molec/cm³
modelled OH 2.71 * 10⁹ molec/cm³ modelled HO2 2.55 * 10⁸ molec/cm³

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