

# ***Interactive comment on “Chemistry, transport and dry deposition of trace gases in the boundary layer over the tropical Atlantic Ocean and the Guyanas during the GABRIEL field campaign” by A. Stickler et al.***

**A. Stickler et al.**

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First we would like to thank the referee for his helpful comments on how to improve the quality of our paper.

Concerning the Anonymous Referee#1 Review we have applied the following changes to the paper:

1. We have significantly shortened the paper as suggested by the referee by leaving out the measurement section and referring to a joint overview paper by Lelieveld et al. (2007), to be written soon. Only Table 1 has been kept in the paper and moved to

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## Section 2.

2. We do not consider the section on the CO sensitivity to be much too extensive. It was our intent to discuss and explain in more detail the sensitivity of the photochemical CO production towards different other species. The discussion is in line with the topic of the paper, which encompasses chemistry. Furthermore, as we mention in the introduction, box model studies are particularly appropriate to address the question of sensitivity. We also regard it as reasonable to give the references chosen for the magnitude of the parameter variations, especially for readers not familiar with typical trace gas mixing ratios above the rainforest.

3. Similarly, we do not feel that the section on biomass burning and surface sources does contain any information unnecessary for the context of the discussion. The first part of the section includes information on local biomass burning that could have influenced the measurements, the second part contains information on the layer with enhanced CO mixing ratios frequently observed above the BL, which is used in the next section to derive an average entrainment rate, including its probable origin. Finally, the third part discusses results of previous studies on CO fluxes from different soil types in the light of our box model results. Considering all these different aspects is essential to understand the whole BL CO budget.

4. CI chemistry has been put into one single section for ease of reading, as suggested by the referee. We have decided to put the information from sections 4.3.1, 4.3.2 and 4.4.2 into section 3.6.

5. We have left out the statistical equations (Eq. 5).

6. Concerning your suggestion to stick to the use of one set of units, we have deleted the parts explicitly referring to the conversion of different units in the section on surface sources of CO.

7. It is true that the section about net ozone production is only loosely connected to

the rest of the analysis. Nevertheless we regard the finding that significant parts of the tropical rainforest seem to be a (weak) ozone source rather than a sink during the long dry season as important and relevant to the topic of the paper.

8. We have included a discussion of our results regarding entrainment/dilution in comparison with the Dillon et al. (2002) and Price et al. (2004) studies and references therein at the end of section 4.3.3.

9. Moving the entire discussion of unknown heterogeneous chemistry to the conclusions does not seem practicable, as this would make the conclusions section too long. Furthermore, we think that there is some support for our speculations from the Thornton et al. (2002) and Hasson et al. (2004) studies as well as from lab studies performed at the Max Planck Institute. Also the model simulations show that a respective change in the mechanism removes a significant part of the discrepancy. This is of course no proof for the suggested possible origin of the discrepancy of the model and the measurements, but it shows that the magnitude of the change in the result is of the same order than the discrepancy.

10. Unfortunately no aerosol measurements were performed during GABRIEL, so that we are not able to correlate the aerosol surface with the model-observation bias of the organic peroxide data. Thus we have to be a bit speculative on this side.

11. Probably mineral aerosol is not a major contributor to the total aerosol in the measurement region. We would expect biogenic organic and sea salt aerosol (over the ocean) to dominate. Nevertheless, we referred to de Reus et al. (2005), since to our best knowledge there is only a small number of studies on the influence of solid phase aerosol particles on peroxides.

12. By “inlet efficiency” we mean the percentage of a trace gas passing through the inlet, consisting of Teflon tubing and valves as well as a membrane pump, and reaching the fluorescence instruments before the stripping process. This inlet efficiency was on average 80% for H<sub>2</sub>O<sub>2</sub> and for the whole campaign (determined by gas calibration

with the permeation source). The length of the tubing before the instrument and the stripping was ca. 1 m (1/4") with a relatively small volume in the pump, so that the average gas residence time in the whole inlet was less than a few seconds at the mass flow of about 2 slm that we used. We have now left out the detailed description of the measurements as mentioned at the beginning. As you indicated, we have no exact information about the stickiness of the organic peroxide to the walls of the tubing. So the estimate of the total organic peroxide is an estimate rather than an upper estimate. If only 10% of the organic peroxide had reached the stripping region, our estimate would be too low by a factor of 10. However, we consider it unlikely that the organic peroxide exhibits a greater tendency to stick on surfaces than H<sub>2</sub>O<sub>2</sub>, based on the greater polarity of the latter compound.

13. The referee is correct that Williams et al. (2001) suggested that the isoprenic hydroperoxides were a possible candidate for mass 101 during the 1998 campaign over Suriname. This seemed likely since the isoprenic hydroxy hydroperoxides (C<sub>5</sub>H<sub>10</sub>O<sub>3</sub>, MW 118) (Jenkin et al., 1998) are known to result from the reaction of isoprene peroxy radicals and HO<sub>2</sub>, in particular in conditions of low NO<sub>x</sub>. They were assumed to be found at mass-to-charge ratio (m/z) 101 because isoprenic hydroxy hydroperoxides were predicted to lose H<sub>2</sub>O upon protonation, analogous to other long chain molecules containing an OH group (Warneke et al., 2001, J. Atmos. Chem.; Williams et al., 2001). Furthermore the relationship of this mass to isoprene and its photo-oxidation products MACR+MVK fitted with this designation, and box model studies predicted similar levels of these species. In 1998 the measurements indicated mixing ratios up to 2 nmol/mol at this mass, but these large mixing ratios were not confirmed during the GABRIEL 2005 data set above the same rainforest. m/z 101 was measured on all flights at dwell times similar to those used for the measurement of MACR+MVK, namely between 0.9 to 1.3 seconds and the instrument used in 2005 was more sensitive than that used in 1995. There are no available standards for the hydroxy hydroperoxides. Therefore, their direct response factor (in normalised counts per second per nmol/mol) could not be determined. However, based on the transmission curve, determined for

a set of known compounds for which standards were available, the interpolation for intervening protonated masses and a reaction rate constant for  $\text{H}_3\text{O}^+$  and  $\text{H}_3\text{O}^+\text{H}_2\text{O}$  of both  $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , the signal of mass 101 has been converted into mixing ratios. For data above a signal-to-noise ratio of 3, mixing ratios varied from  $\sim 0.1$  to  $\sim 0.4 \text{ nmol/mol}$  in the mixed layer ( $< 1400 \text{ m}$ ). This is a factor of 5-6 lower as has been stated in the study by Warneke et al. (2001). It should be noted that mass 69 (which was attributed to isoprene in 1998) was similar in concentration in 1998 and 2005. During the GABRIEL 2005 campaign, we found by comparison with GC-MS data that mass 69 was not entirely isoprene. This is explained in detail by Eerdekens et al. (2007, manuscript in preparation).

14. Since this paper is the first paper of a Special Issue on the GABRIEL measurement campaign, we have included a description of the flights to give a brief overview of the campaign. To none the less shorten the mission description (which we have arranged into an own short section now), we have put the detailed flight pattern information into a separate table, as suggested by referee #2. Additionally we have added a part giving a short introduction to entrainment and deposition, as suggested by the referee. We think however that an appropriate introduction to isoprene oxidation mechanisms under low  $\text{NO}_x$  is beyond the scope of this paper, because the focus of the paper is not on isoprene chemistry.

15. One should expect the calculated entrainment rate not to be a function of the trace gas used to calculate it. That is why we have chosen  $\text{CO}$ , with a generally long lifetime compared to the timescale of entrainment, to determine the average entrainment rate. We did not calculate dilution coefficients in the sense of an e-folding time for the trace gas concentrations while being transported along the trajectories. The longitudinal dependency of the vertical gradient of the median mixing ratio is included in this calculation.  $\text{HCHO}$  was only used to calculate an estimated lower limit of the maximum daytime entrainment rate from the FT to the BL assuming that the dynamical timescale must be of the order of the chemical lifetime to significantly influence the mixing ratio,

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again using longitude-dependent vertical gradients. Thus the estimate of the mean entrainment rate is essentially based on one trace gas which has been assumed not to undergo significant dry deposition compared with the chemical sink. It is therefore not possible to derive an optimum pair of entrainment rate and deposition velocity from our dataset. The results of the studies presented in the section on soil or vegetation emissions indicate that the order of magnitude of the emissions or of deposition is likely to be small compared to the flux of entrained CO. We consider it very difficult to draw further conclusions with respect to the entrainment without having detailed meteorological information from the BL.

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