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Atmospheric Chemistry and Physics Discussions

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#2 Review we have changed the paper as described below:

1. As mentioned in the discussion of the Referee#1 review, we have significantly shortened the paper as suggested also by Referee#2 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 Section 2. To shorten the introduction we have put the information about the single flight patterns into a table, as recommended by the referee.

2. Concerning the suggestion to use the units pptv and ppbv in the paper, as was indeed done in a previous paper by the lead author, we refer to a IUPAC recommendation (Schwartz and Warneck: Units for use in atmospheric chemistry, Pure & Appl. Chem., 67(8/9), 1377-1406) that discourages the use of these units for several reasons and instead recommends pmol/mol and nmol/mol for gas phase mixing ratios.

3. As recommended by the referee we have taken the mission description out of the introduction and put into a separate section.

4. The introduction already contains the information about the time of the dry seasons, namely February-March in case of the short dry season and August-November in case of the long dry season. As suggested we have included the following additional information into the introduction: a) Time of the local biomass burning season (there is no pronounced local biomass burning season, and fresh ($<$ 2 d) biomass burning pollution is rarely encountered), b) Impact of long range transport on the region (long range transport of biomass burning pollution predominantly from Africa but also from South America as well as of anthropogenic pollution from the NH into the FT above the Guyanas has been reported to occur on a frequent basis (both Peters et al., 2004)). Brief information on the scientific goals of the previous LBA-CLAIRE campaign and on how the GABRIEL campaign goes beyond these, in particular by an extended payload that allows for new studies e.g. of the HOx chemistry, is already included in the now separately organised mission description section. We have added a little bit of information on this point.

5. Concerning the suggestion to leave out a too detailed description of the flight patterns in the mission part we have put this information in a table as mentioned above.

6. In Fig. 1., we prefer not to expand the view too much on the rest of South America,

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since the exemplary flight pattern would become too small.

7. As denoted under point 1, we have significantly shortened the paper by leaving out the measurement section.

8. Referring to the comment on the Stickler (2006) citation there is one Stickler (2006) and one Stickler et al. (2006) reference, so the references should be correct following the EGU bibliography style used. The PhD thesis is freely available online and a link has been introduced into the reference.

9. As recommended by the referee, a table containing the mixing ratio data of the fixed species for the box model runs including references has been included, leaving out the explicit description in the text.

10. We have added a sentence to the first part ("Model description") of the box model section stating that "Here we use different model runs to calculate CO, HCHO, H2O2 and organic peroxide mixing ratios. The remainder of the measured species is constrained by the measurements as described below. All other species are held constant (see next section)." We have left out the respective explicit listing of the values in the section on the "Specific settings in the Lagrangian mode" and instead introduced a table, as suggested by the referee.

11. We have left out the "seconds after midnight" and just use LT now.

12. We have added an explanation of why we are using the "equivalent longitude" in the respective paragraph stating that we thereby try to account for "non-linear effects of photochemistry associated with the variance of the sampling time." 13. We have included a vertical line at 52°W in Figs. 2-5 separating the longitudinal regions dominated by BL measurements over the ocean in the east from BL measurements taken predominantly over land in the west, adding some explanatory text to the caption.

14. With respect to the referee's suggestion to insert a second longitude x axis into Figs. 6-16, this is unfortunately not easy to do as there is no unique relationship be-

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tween LT and longitude, since the use of the "equivalent longitude" implies varying starting times of the trajectories at the same longitude. I.e., all 57 trajectories plotted in the figures start at 51.5°W and end at 57.5°W, but with a time shift in the range +-140 min. We have followed the referee's recommendation to combine the figures of each species belonging together (expected and modelled). We prefer to keep different y axes though, as e.g. in the case of CO there is quite a large difference between the span of the expected results from the measurements and that from the model prediction so that one would not be able to see details of the diurnal cycle in the modeled mixing ratios anymore.

15. Regarding remark 14, Williams et al. (2001a) report that "Fire activity in Surinam was not widespread during the LBA-CLAIRE campaign and did not generally impact the measurements" except during single local burning events. The observed horizontal CO gradient was used at that time to estimate the overall strength of the rainforest CO source. On the other hand, the paper did not discuss explicitly the influence of biomass burning plumes advected into the region by long range transport. What we can say without speculating too much is that during both campaigns the local biomass burning influence was comparably low. What exactly is the cause for the different CO gradients remains unclear and cannot be easily attributed to one origin or another. Nevertheless the present study indicates that advection of polluted air from the FT into the BL in the region rather than photochemical production is the most likely explanation for the relatively strong gradient found during GABRIEL in October 2005.

16. When removing ozone data from the morning and noon hours from our analysis we would expect to see an even higher gradient, since over land surfaces we have higher dry deposition velocities than over the ocean.

17. With respect to the derived entrainment rate of section 4.2.3, we do not deny its uncertainty. Nevertheless, the sensitivity test mentioned in section 4.4.1 indicates the order of magnitude of our number to be correct (with 0.01 h-1 being too small and 0.7 h-1 being too large). Additionally we have added some supporting citations referring to

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other studies (Dillon et al., 2002; Price et al., 2004) that find comparable numbers for US urban plumes and smaller numbers for long-range intercontinental transport in the FT (see answers to first referee). The estimated rate is valid for the environment found during GABRIEL and is an upper limit of the 24 h average. It would be expected to differ along the trajectories from the ocean to the land, generally being weaker (at least during daytime) over the ocean than over the land, due to differences in the stability of the atmosphere in both regions.

18. Since the purely photochemical model result does not at all fit to the observed CO gradient, it is difficult to infer something about the CO yield of different VOCs compared with previous assumptions. We can just say that the CO gradient can be fully explained by assuming entrainment with the estimated rate, which is also supported in tendency by the HCHO data. A higher than previously thought yield of CO from VOCs would probably imply a higher HCHO yield which is in contradiction to our model result, being already too high compared to the measurements. The only possibility to solve this dilemma would be a higher CO yield that is simultaneously less efficient in producing HCHO.

19. The uncertainty of the HCHO dry deposition calculated with the 1-D SCM is probably quite high. There are only a few measurements of the HCHO dry deposition over forested areas available in the literature. In our study we already cite the PhD thesis of Krinke (1999), who has made measurements of the HCHO dry deposition velocity over a forest in southern Germany, and compare his results to the values calculated with our 1-D SCM. This comparison reveals significantly higher values from the measurements compared to the model, as mentioned in our paper. We have now added two other papers: that of Rottenberger et al. (2004) reporting dry deposition velocities of 0.16 cm/s in the wet-to-dry season above two different canopy species typical for South American lowland rainforests (in this case, the measurements indicate less efficient deposition than in our model); and that of Sumner et al. (2001) reporting an estimated nighttime dry deposition velocity of (0.65+-0.36) cm/s above a forest canopy

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in Michigan. These studies show that there is an uncertainty of probably one order of magnitude with the model results standing within the range covered by the measurements. With regard to heterogeneous removal processes of HCHO, de Reus et al. (2005) found no removal in a dense Saharan dust plume, as stated in section 4.3.1. To our best knowledge there is no further literature available which demonstrates the existence of significant heterogeneous removal processes for HCHO.

20. Regarding the possible heterogeneous removal of organic peroxides, the paper by de Reus et al. (2005) pointed towards its existence (by means of loss of RO2, which was clearly seen), but it is difficult to adopt their results to our study and to try to infer the magnitude of such an effect, since no aerosol measurements are available for GABRIEL. A further critical point brought up already by the first referee in the context of this discussion is the comparability of the type of aerosol particles encountered during GABRIEL (presumably organic with some sea salt close to the ocean) and during MINATROC (dust particles). There is a relatively new study by Docherty et al. (2005, Environ. Sci. Technol.) indicating that organic peroxides constitute a major fraction of the secondary organic aerosol (SOA) mass formed in the alpha- and beta-pinene plus ozone reactions, respectively. Our model results seem to lack a sink and not a source of organic peroxide, though. This implies that if a significant amount of organic peroxide containing SOA had influenced our measurements (which seems not very likely but cannot be excluded, as no filter was used in the inlet to minimise surface losses), the missing sink would even be larger. To our best knowledge no further literature is available on this topic.

21. The difference in the overall ozone budget with a slight increase over the rainforest found during GABRIEL and a significant decrease found for LBA-CLAIRE can probably not be explained by differences in the occurrence of biomass burning, since there are no large differences in fire activity between the two campaigns. As mentioned above, in both cases local fires were only sporadically encountered. One could speculate about the dry deposition having been stronger during LBA-CLAIRE, e.g.

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due to lower soil or vegetation surface wetting during LBA-CLAIRE (although the "wet" season just before GABRIEL was extremely dry in the whole Amazon region), or the entrainment of ozone-rich air from above having been stronger during GABRIEL due to slightly differing meteorological situations. Different soil moisture conditions could also have affected vegetative trace gas emissions (by means of drought stress) and therewith NOP. Anyway, we did not find a clear indication for the difference in our data. What our data analysis highlights is that the BL rainforest environment in this part of South America appears to be in a chemically critical range relative to the "compensation point" between production and destruction. Unfortunately no NOy was measured during GABRIEL so that we cannot check if NOy was possibly transported down into the BL from aloft. At least the NO median mixing ratios show a clear tendency to be higher in the free troposphere just above the BL. If our conclusions about the relatively effective entrainment are correct, this would probably indicate a significant contribution of the NOx (and certainly also NOy) advection from above to the ozone budget in the BL. Whether PAN plays a dominant role at the altitude of the observed enhanced CO layers is not obvious since the temperature is still quite high there (above 10°C, tau(PAN) $<$ 10 h).

22. Thanks to the referee for calling attention to the mistake made in the conclusions. We exchanged the entrainment rate there to 0.12 h-1, consistent with the value stated in the abstract.

23. We changed the description of TUV as an "external module" to a "radiative transfer model" on p. 4789.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 4781, 2007.