

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.

Anonymous Referee #1

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Review of Stickler, et al “Chemistry, transport, and dry deposition of trace gases during GABRIEL”

This paper describes efforts to model observations of CO, HCHO, H₂O₂, and organic peroxides made over the tropical Atlantic ocean and rainforests of the Guyanas in South America. The scientific focus is to determine the physical and chemical factors that control the mixing ratios of these species both over the ocean and the rainforest ecosystem. A Lagrangian chemical model and a steady-state box model are used to assess the importance of exchange between the boundary layer and free troposphere,

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dry deposition, and of the accuracy of the chemical mechanisms. The paper represents a significant contribution and will be appreciated by readers of ACP. I feel the paper should be published in ACP but only after significant revisions are made as detailed below.

Comments

1. I think the paper contains important findings regarding the validity of current isoprene oxidation mechanisms, and the importance/uncertainty of entrainment and dry deposition. However, the findings are not as apparent because the paper is a bit difficult to read. I find redundancy and often the level of detail is too much. While I appreciate the great amount of thought and work that went into diagnosing various issues, some of the detail is probably not necessary for the general ACP reader to have to sift through.

Suggestions on how to streamline the paper: 1. Reduce the use of qualifiers, such as “rather lower”, and transitional phrases such as “on the one hand”, “at first glance”, etc. 2. Condense much of the discussion on CO sensitivity study (section 4.2.1), simply summarize in a few sentences where the greatest sensitivity was. 3. The biomass burning and surface sources section could also be shortened significantly. 4. Condense all issues relating to Cl chemistry into one section. 5. Delete the statistical test equations (equations 5 on pg 13). 6. Choose one set of units to work with, let the readers do the conversions. 7. Possibly remove the section on ozone production, while important, I’m not finding anything particularly revealing. I leave this decision up to the authors but as it is now, the section is only loosely related to the rest of the effort.

2. The authors do a good job putting their deposition velocities into a context of previous determinations. However, they do little comparison of their derived entrainment rates. Several studies of North American pollution have derived estimates of BL - FT entrainment rates or plume dilution rates in a manner similar to that which is described in this paper. The authors should examine their entrainment rates in the context of other studies (e.g. Dillon, et al JGR and Price, et al JGR 2004).

3. Perhaps the discussion of unknown heterogeneous chemistry affecting the conclusions should be moved to the conclusion section. There is no support either way, and it seems to interrupt the flow. I agree it could explain some of the discrepancies, but the reaction probabilities of HO₂ (or RO₂) would have to be quite high to significantly impact organic peroxide formation rates. It is possible that the peroxides are lost to aerosol, but again, it would be nice to examine the model-observation bias as a function of aerosol surface area or volume to see if there is at least support from the data. The reference to de Reus et al is a bit misleading in this regard, because it is my recollection that they were directly assessing the impact of a dust storm. Is mineral dust a significant contribution to the aerosol in this region?

4. On page 3, “An upper limit estimate to the organic peroxide mixing ratio was obtained by assuming that the stripping efficiency has a constant value of 80%, and that the inlet efficiency, i.e. the fraction passing through the inlet without loss, is 100%.” I must not understand what is meant by “inlet efficiency”. Is this after stripping? What length of tubing did the gas travel through before being stripped?

If the isoprene peroxides stuck to or reacted on the inlet walls, such that only 10% were transferred to the stripping region, how would that alter the inferred concentrations? I doubt inlet transmission was tested with isoprene derived peroxides. This issue should be clarified.

5. Williams, et al in the J. Atm Chem 2002(?) published interpretations of PTR-MS spectra that indicated organic peroxides derived from isoprene could be detected by PTR-MS. Was this dataset analyzed for these species?

6. The introduction could use some rearranging and additions. It is too heavy on the description of the flight experiment. The flight experiment description should have its own separate section and the introduction should be expanded to give a better overview of the problems associated with entrainment and deposition over land and oceans, and with isoprene chemical mechanisms under low NO_x.

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7. Is it possible to be more consistent with the entrainment rate constants? That is, should one expect the entrainment rate constant be the same for all species? I tend to think of this value as an air exchange time scale. The rate of dilution or enhancement in the concentration of a species by entrainment will of course be different due to different gradients for each species. Is there one set of deposition velocities and entrainment rates that minimize the measurement-model differences? It was hard to glean from the manuscript whether recommended values could be derived from this work.

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

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