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Interactive comment on “Surface and boundary layer exchanges of volatile organic compounds, nitrogen oxides and ozone during the GABRIEL Campaign” by L. Ganzeveld et al.

Anonymous Referee #2

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General comments:

The authors present a study of chemical exchange between surface and boundary layers over the Amazon using a single-column chemistry and climate model. The study focuses on nitrogen oxides, ozone, and volatile organic compounds, including methanol, acetone, and isoprene and its oxidation products. The goal of the study is to evaluate the simulated transport of chemicals with a variety of sources and lifetimes by comparing observed and predicted mixing ratios as a function of altitude. Observations were made by aircraft during the October 2005 GABRIEL campaign. The major findings of the study are: (1) the model accurately predicts the NO_x and O₃

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atmosphere-biosphere exchange processes, chemical evolution, and boundary layer transport over the continent, (2) OH and HO₂ concentrations are underestimated, suggesting a missing HO_x source related to isoprene chemistry in low NO_x regions, consistent with recently published results from the GABRIEL campaign and elsewhere, (3) the compensation point / bi-directional approach for treating methanol and acetone fluxes at the surface suggests that their tropical forest source strengths are commonly over-predicted, (4) a more vertically resolved model treats turbulent transport throughout the boundary layer more accurately, and significantly improves predictions of biogenic VOCs, and (5) nocturnal production and removal of isoprene and its oxidation products are not well-understood and can have a significant effect on simulating daytime chemistry, even using improved vertical resolution in transport model. The authors suggest that future campaigns focus on nocturnal boundary layer measurements to provide a basis for evaluating transport during the nighttime and boundary layer break-up dynamics in the early morning.

The article addresses important issues regarding the exchange of gases between the atmosphere and biosphere and reaches some important conclusions. It has been well documented that there are significant gaps in our understanding of the atmospheric chemistry of low-NO_x / high-BVOC regions. This paper does a nice job of identifying the important issues with the way that transport is typically modeled in biogenically impacted regions and the implications for accurately predicting the chemistry of these regions.

The topics addressed here are well within the scope of ACP, the paper is well written, the scientific approach appears sound, and the conclusions, I believe, are important for understanding atmosphere-biosphere exchange. Aside from a few issues that are outlined below, I find this paper suitable for publication in ACP.

Specific comments/questions:

HO_x radicals are central in controlling the chemical composition of the atmosphere.

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The substantial under-prediction of the OH and HO₂ concentrations, which is a common occurrence in modeling of low-NO_x high isoprene environments, should have some very significant repercussions on the other model outputs. Yet, the discussion of HO_x is treated as though it were an isolated problem with the model with no bearing on the rest of the authors' conclusions.

For example, the effect of under prediction of OH and HO₂ has implications for the NO_x cycle and ozone production. From figures 9 and 10, it is apparent that the 'HO₂+NO' chemical tendency is a significant driver of O₃ concentrations in the model. If HO₂ is under-predicted by a factor of 2, does that imply that there is some other deficiency in the model acting in the opposite direction on O₃ concentrations such that predicted concentrations coincidentally match observations?

What are the implications of over predicting HO_x for treating isoprene chemistry? Clearly, one would expect to see the predicted isoprene concentrations decrease in a HO_x-constrained model, but it is not completely intuitive to understand whether MVK+METHAC will increase or decrease in the model if OH concentrations increase. A discussion of this should be included.

The authors claim that because the predictions of O₃, H₂O, and NO are accurate, and because the dominant sources of OH are ozone photolysis and HO₂+NO, there must be some other mechanism leading to significant OH production (page 11935, lines 1-8). However, HO₂ concentrations are also under-predicted, in some cases by over a factor of 2. This would also increase the contribution from HO₂+NO by a factor of 2. If the model is constrained by HO₂ observations, how does this affect the OH predictions?

How does the underestimate of photolysis rates over the ocean affect the initialization of NO_x at the continental boundary?

What is the relevance of the 'C₂₃+NO' O₃ chemical tendency, which is included in figure 10, but not discussed? It seems minor; perhaps it should be left out of the figure

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if it doesn't merit a discussion.

I would request that 'XO₂+NO', the 'NO-to-NO₂' operator, be clarified. Is this the remaining NO plus peroxy radical (RO₂) chemistry? The way it is described leads the reader to assume that it is the total NO to NO₂ chemistry, but C₂₃+NO and HO₂+NO add up to be greater than XO₂+NO in figure 10.

There should be, at minimum, a short discussion of the relevant measurement techniques with citations to a more detailed description of the techniques and measurements (if available). While I understand that evaluation of the SCM is the important component to this article, the observations are critical to the authors' conclusions, and some discussion should be included.

Minor comment:

Page 11916, line 21: Should read: 'twice as large as the resistance'.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 11909, 2008.

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