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Atmospheric
Chemistry
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Discussions

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.

L. Ganzeveld et al.

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Dear reviewer,

First of all thanks for the constructive (and fast) review. We are quite pleased that you find that the manuscript in terms of the topic as well as the scope is well suited for publication in ACP.

Here is our response to the specific comments you have given including the modifications that we have implemented in the revised version to address these comments.

The first point being raised is about the uncertainties involved in inferred BVOC emission fluxes from the observed mixing ratios referred to as "observed" emissions to stress that these are not directly measured emission fluxes. We have modified the statement simply using the term inferred emission fluxes instead of "observed" emissions. In order to stress more our, by the reviewer appreciated, awareness of the sources of uncertainty in the inferred emission fluxes we have also modified the text of pp11917; lines 12-15 to: "The inferred emission fluxes include an uncertainty range that reflects, in addition to the uncertainty associated with chemistry and entrainment (Eerdekens et al., 2008), the difference between the BL depth and a deeper volume in which the actual tracer mixing occurs referred to as the mixed layer (ML) depth." We agree with the reviewer that the discussed sources of uncertainty related to BL structure and mixing should be addressed in more detail when comparing emission models with emission estimates. It is actually one of key features of this analysis that we want to convey to the AC community.

The next specific point being raised is the issue of canopy turbulence in tropical forests exchange of NOx. The importance of canopy turbulence in determining the efficiency of exchange with the distinct differences between nighttime and daytime is actually being raised regurarly in the various analyses that have been conducted with the implementation of the multi-layer exchanges model in the SCM. It was explicitly discussed in the Ganzeveld et al. (2002a) paper where we showed that, despite the highly parameterized representation of turbulence (K-theory using in-canopy wind speed profile) the model captured some of the key features of observed atmosphere-biosphere NOx and ozone exchange fluxes. In a follow-up study of peroxide exchanges with the SCM (Ganzeveld et al., Atmospheric Environment, 2006) this issue has been further discussed also because of the fact that H2O2 exchanges over a German forest site appeared to be controlled by turbulent transport to and into the canopy. One particular modification introduced that time was the definition of minimum nocturnal exchange efficiency to overcome the misrepresentation of the noctural inversion. Preferentially, such misrepresentations should be resolved by introducing much more advanced representations of turbulent exchanges, i.e. in the stable boundary layer (GABLS, Steeneveld et al., 2008). However, the multi-layer exchanges model representation in the

SCM is also applied in global scale model applications which requires a compromise in terms of process detail limited by available input parameters and relative coarse spatial and temporal resolution of the calculations. Nevertheless, the analyses presented here shows once more again how such subtle features of the exchange regime, i.e. the early morning transition from the nocturnal to early morning mixing regime, affect simulated reactive trace gas exchanges relevant to large scale AC studies.

The specific comment about how the various uncertainties actually add up in explaining in the discrepancy between the observed and simulated OH has been partly addressed in the conducted analysis conducting a selection of sensitivity runs but has not been discussed in detail in the current version of the ms. The only particular feature of these sensitivity analyses that is described in more detail in the ms is the potential role of terpene ozonolysis in OH production. This is done because this particular issue addresses the significance of chemical versus turbulent transport processes. However, other simulations were done to assess the impact on the simulated OH and HO2 concentrations including enhanced ozone mixing ratios above the BL and an increase in photolysis rates associated with the location of the clouds. Some of those simulations showed that these could explain to some extent some of the discrepancies between the observed and simulated OH and HO2 concentrations, especially above the BL. However, also to limit the amount of information provided in this ms and complementing the information provided in the other Gabriel ms's we have decided to mostly restrict the description of analysis to sources, sinks and transport of BVOC's, NOx and ozone. We showed the HOx concentrations as simulated by the SCM using a gas-phase chemistry scheme commonly applied in large scale AC models, for these precursor concentrations in reasonable agreement with the observations. As such it shows the expected discrepancies in simulated tropical BL HOx concentrations in any large-scale AC model (with similar isoprene emission fluxes; as mentioned in the ms quite often those models apply substantially lower emissions). In order to indicate that indeed more sensitivity analyses have been conducted and also to address the impact of the vertical precursor profiles on the HOx concentrations, we have included at pp11935, ˜line 15 the following

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text;

"This is confirmed by a simulation with a much higher vertical resolution, discussed in the next section, resulting in more efficient upward transport and, consequently, smaller vertical BL gradients in isoprene but which does not result in a substantial increase in OH and HO2 concentrations. We have conducted a number of sensitivity analyses including one with enhanced ozone mixing ratios above the BL, in better agreement with observations, and one in which we applied higher photolysis rates also to consider the impact of the SCM's misrepresentation of clouds. Those analyses showed indeed an increase in OH and HO2 concentrations and improved agreement between the observation and the SCM but mostly restricted to the lower free troposphere. One particular sensitivity analysis aimed to assess the role of potential missing OH formation through terpene ozonolysis."

The most specific and critical comment is about how to reconcile the here presented results with those presented by Butler et al. (2008) and Lelieveld et al. (2008). We have considered to apply the modified scheme as suggested by Butler et al. (2008) and in a forthcoming paper by Taraborrelli et al. (2008) (MIM2) but such a modification through replacing the SCM's gas-phase chemistry scheme (CBM4) would require substantial recoding, something which will be considered for follow-up analysis. In addition, because of the detailed discussions on the gas-phase chemistry in the Lelieveld et al. (2008), Butler et al. (2008) and the forthcoming paper by Taraborrelli et al. (2008) we decided to mainly restrict ourselves to the evaluation of sources, sinks and BL transport of the main OH precursors. We wanted to focus in our paper on the importance of BL mixing for HOx precursor mixing ratios and profiles and as such stress that these features should also be critically analyzed in comparing large-scale chemistry models with observations. This has also been raised in the reviews of the Butler et al. (2008) manuscript. In order to indicate more specifically the applied chemical mechanism and the motivation to not apply the MIM2 scheme we have included at pp11915 the following text:

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"Note that he extra source of HOx in the isoprene oxidation mechanism according to Lelieveld et al. (2008) and Butler et al. (2008) has not been considered in the default setup of the SCM in this study but it will be considered in follow-up analyses through inclusion of a modified gas-phase chemistry scheme in the SCM. The here presented analysis is mainly limited to a detailed discussion of the sources, sinks and transport of HOx precursors and associated discrepancies in simulated tropical HOx concentrations in the SCM and any large-scale atmospheric chemistry model that uses comparable state-of-the art gas-phase chemistry implementations."

In addition, based on the specific comments by both reviewers we have conducted an additional sensitivity analysis in which we have modified the CBM4 implementation in the SCM through the inclusion of first-order estimate of the additional OH source such that the model simulates OH mixing ratios in the PBL in better agreement with observations. pp11937, after line 7

"Here we address the uncertainty in the HOx precursor concentrations associated with the demonstrated discrepancy between the simulated and observed HOx levels. This has been assessed through the introduction of a first-order estimate of the extra OH source involved in the isoprene oxidation mechanism. Since the lumping of hydrocarbon compounds in the CBM4 scheme of our model is different from that in the MIM chemistry scheme we have considered the recycling of OH associated with isoprene oxidation (Lelieveld et al., 2008; Butler et al., 2008) using the CBM4 reaction between HO2 and alkylperoxy radicals (XO2) mainly formed in the oxidation of organic compounds (see also Roelofs and Lelieveld, 2000). Scaling the amount of XO2 produced from the oxidation of isoprene and isoprene products (ISOPRD) with the total production of XO2 and taking an additional yield (on top of a yield of 0.4 in the CBM4 implementation) of 4.5 OH radicals for the XO2+HO2 reaction we simulate maximum BL OH and HO2 concentrations of about ˜5.5x10ˆ6 molecules OH cm-3 and 13x10ˆ8 molecules HO2 cm-3, respectively, for 17-20UT, in reasonable agreement with the observations. This substantial increase in HOx induces only a small relative increase

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(˜ 10%, relative to low HOx simulation) in the BL ozone mixing ratios. There is a decrease in isoprene mixing ratios $>$ 80%, resulting in simulated BL average mixing ratios of about 1 ppbv, being substantially lower than observed and consistent with the findings of Butler et al. (2008). The simulated enhanced HOx concentrations also result in an about 80% decrease in NOx mixing ratios (due to a simulated enhanced production of HNO3 and other reservoir species). These simulated decreases in both the isoprene and NOx mixing ratios due to the enhanced HOx concentrations would require a substantial increase ($>$ factor 2) in both the isoprene and NO emission fluxes to reconcile the simulated and observed isoprene and NO mixing ratio profiles as shown in Figure 12 and 5b, respectively. One possible explanation to reconcile the observed and simulated isoprene mixing ratios for the high HOx regime is a reduced efficiency of the isoprene-OH reaction associated with non-homogenous mixing conditions (the so-called intensity of segregation) proposed by Butler et al. (2008). Finally, the enhanced HOx concentrations result in decreases in MVK-METHAC mixing ratios of ˜50%, reflecting the combined effect of the enhanced production from isoprene oxidation and the substantial decrease in isoprene mixing ratios. Changes in the MVK-METHAC mixing ratio profile (Figure 14) are comparable to the changes induced by a different representation of turbulent tracer transport as discussed in the next section."

Concerning the last specific comment on the issues involved in OH observations by Faloona et al. (2001) and those collected during the Gabriel campaign, this addresses a more general comment to be discussed in the review process of the fortcoming articles on the OH observations by Martinez et al. (recently submitted to ACPD). The quality control of the data obtained by laser induced fluorescence and the possibility of interferences is discussed in detail there. It is beyond the scope of this paper to address this issue. To explain the discrepancies between the observed and simulated OH an iteration is needed involving the measurement as well as the modelling community to reconcile the overall uncertainty in tropical forest OH due to the uncertainties in gas-phase (and heterogeneous) chemistry, precursors emissions, deposition and turbulent convective transport.

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