Atmos. Chem. Phys. Discuss., 8, S4988–S4991, 2008
www.atmos-chem-phys-discuss.net/8/S4988/2008/

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.

Received and published: 17 July 2008

Dear reviewer,

First of all thanks for the constructive (and fast) review. We are very pleased to read your positive judgement on the topic, the way the ms is written, and selected approach and that you deem the conclusions to be important for further progress on atmosphere-biosphere exchange research.

Here is our response to your specific comments/questions including modifications of the revised version to properly adress these comments/question.

The first point being raised is an interesting one; How does the misrepresentation

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of HOx concentrations for the presented HOx precursor regime in turn affect those precursor concentrations? We have not checked this in detail also since from previous tropical forest analyses it became clear that some of the precursor mixing ratios, in particular that of ozone, are mainly controlled by turbulent and convective transport and surface deposition and with a minor role for chemistry. The chemical tendency, including the HO2+NO reaction is substantially smaller compared to the dry deposition and turbulent transport tendencies indicating that this misrepresentation of HOx is not expected to explain a substantial discrepancy in ozone. However, appreciating this particular issue, as well as the issue about the consequences of the HOx discrepancy for the oxidation products (MVK and METHAC) and because of some of the comments raised by the other reviewer, we have conducted an extra sensitivity analysis in which we have introduced a first-order estimate of the OH recycling as discussed by Lelieveld et al. (2008), Butler et al. (2008) and Taraborrelli et al. (2008, fortcoming paper). 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 HOx mixing ratios in the PBL in better agreement with the observations. The text that has been included in the revised version of the ms adresses the comments/issue raised on the consequences of the HOx disrepancy for the precursor concentrations, the MVK and METHAC concentrations as well as the comment made on constraining the model with the HO2 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

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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 (˜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."

The underestimation of the photolysis rates over the ocean affects the partioning of NOx over the ocean but not so much the total amount of NOx with relative slow transport between the marine boundary layer and the free troposphere and no deposition to the ocean. Consequently, the NOx concentrations over the continental boundary reflect to a large extent the selected initial concentrations which is default taken from

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the output of the chemistry and transport model TM3. However, since these concentrations resulted in simulated NOx concentrations quite different from the observations these profiles have been adjusted to simulate oceanic NOx conditions in reasonable agreement with the observations.

We have removed the C23+NO contribution to the chemical tendency since it is indeed a minor source term with C22 representing the peroxyacyl radical in the CBM4 chemistry scheme. We have modified the text to clarify the role of the "XO2+NO" reaction which refers to the reaction between NO and alkylperoxy radicals produced in the oxidation of the organic compounds like isoprene, olefines, higher aldehydes, etc. pp11928, line 14: "..due to the NO-HO2 and NO-XO2 (XO2 represents the alkylperoxy radicals in the SCM's chemistry scheme) reactions". The caption of Figure 14 has also been modified.

With respect to the comment about a short discussion on the relevant measurement techniques; We feel that this is beyond the scope of this paper. We recognize that especially the quality of the observations must be considered with respect to the demonstrated uncertainty in the model simulations. However, other papers of the Gabriel special issue (Eerdekens et al., 2008, BVOC measurements, Martinez et al., soon to be published in ACPD, HOx measurements, Stickler et al., NOx, O3, CO and peroxide measurements) address in more detail the various aspects of the measurement techniques as well as the various issues on data quality. We have added a sentence to indicate that in these papers more details about the measurement technology and quality can be found. Pp11913; after line 1: More details about the measurements that have been used in the here presented evaluation, including the concentration measurements of VOC's, NOx, O3 and HOx, are provided by Eerdekens et al. (2008), Stickler et al. (2007) and Martinez et al. (in press).

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