

Interactive comment on “OH and HO₂ radical chemistry during PROPHET 2008 and CABINEX 2009 – Part 1: Measurements and model comparison” by S. M. Griffith et al.

Anonymous Referee #3

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The manuscript “OH and HO₂ Radical Chemistry during PROPHET 2008 and CABINEX 2009 – Part 1: Measurements and Model Comparison” by S. M. Griffith et al. describes results of two large field campaigns from 2008 and 2009 with focus on radical chemistry in the forested environment of Northern Michigan, the same field site as has been used in previous PROPHET studies. The Indiana University FAGE instrument is used to measure OH and HO₂ above the canopy height. Due to the experimental set-up (long optical fibre), very low laser power was available and resulted in bad detection limits of 1.5 and $1 \times 10^6 \text{ cm}^{-3}$ (2-h averaging) in 2008 and 2009, respectively, compared to OH peak concentrations of some $2\text{--}4 \times 10^6 \text{ cm}^{-3}$ at noon. HO₂ detected by the IU-FAGE is compared to modelled HO₂+ISOP (isoprene-based hydroxy peroxy radicals)

with fairly good agreement. Radical budgets are analysed and discussed for the two campaigns and in relation to PROPHET 1998. Main difference to PROPHET 98 is the lower OH, especially at night. For PROPHET 2008 and CABINEX, measurements and model are roughly (within the uncertainties) in line. Differences in biogenic reactive compounds at ground and above the canopy are discussed as potential explanations for the discrepancies between the PROPHET 98 and the current studies, but this issue remains unresolved.

Studies to improve our understanding of radical chemistry in forested environments are needed as discrepancies between measured and modelled values in past studies have caused questions about missing chemistry. Recently, however, artefacts of FAGE type instruments in measuring OH radicals (Mao et al., 2012) and HO₂ radicals (Fuchs et al., 2011) in environments with high levels of biogenic VOC were reported. For example, Mao et al. (2012) demonstrated that their FAGE type instrument needed a modulation technique to periodically scavenge ambient OH and thus measure internally produced OH in order to correct their OH measurement for this internally produced OH. The corrected OH was inline with model predictions during day and night, whereas the uncorrected signal was higher by factors of 2-3. Thus, the question came up whether previously observed discrepancies were due to measurement artefacts. This question is also addressed in the current manuscript but not really solved for the used technique. Overall, the paper is well written and figures and tables are clear and informative. The paper is in the scope of ACP. However, the following comments should be considered:

1. The authors cite and discuss recent findings on potential artefacts in LIF measurements of OH and HO₂ by Fuchs et al. (2011), Mao et al. (2012) and others. They mention own results of characterisation experiments they performed with respect to OH artefacts (page 11 and supplement) which indicated potential interferences in CABINEX 2009 which were not confirmed in later experiments. However, these experiments were mostly performed under different conditions, e.g. at the ground or different

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locations or different times, such that it is not really clear weather artefacts have occurred during PROPHET 2008 and CABINEX 2009. With respect to HO₂, the authors mention interference experiments with respect to a few organic compounds (p. 12 and supplement), but again the amount of artificially measured RO_x in HO₂* mode is not clear. Given the uncertainty in the scientific community concerning photochemistry in forested environments, the potential artefacts of the Indiana University FAGE measurements should be better presented and discussed more thoroughly.

2. There exist some discrepancies in the measured atmospheric compositions between PROPHET 2008 and CABINEX 2009 which need some further discussion. NO₂ differs by factor 2 between 2008 and 2009 though the NO, O₃ and J(NO₂) are apparently very similar. In the supplement it is mentioned that different inlet lines have been used. Has the titration of NO by ozone in the inlet line been taken into account, or what else could have caused this difference? Formaldehyde in 2008 was not measured during the campaign but only subsequently and a correlation with ozone was used to construct the levels of HCHO in 2008 (see Supplement). What is the uncertainty contribution of this assumption? Isoprene and VOC were measured by different methods in both years – how has the comparability of the results been achieved? Finally, the photolysis rates are given with 50 and 30% 1-sigma uncertainties in 2008 and 2009, respectively. Also, diurnal cycles of J(O₁D) on clear sky days differ by up to 20%. Given the high sensitivity of the model with respect to photolysis frequencies, NO, and VOC, the different model results in 2008 and 2009 are questionable because these may be due to errors or artefacts in ancillary parameters. This should be further discussed.

3. There were substantial deviations in OH between model and measurements in the 1998 PROPHET study that were attributed to organic chemistry (Tan et al., 2001). In 2008 and 2009, such deviations are not observed. The authors do not appropriately analyse the differences between those studies and provide explanations. Especially, with respect to the known artefacts in FAGE radical measurements (see above), the authors should be able to separate experimental issues from atmospheric composition

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issues and model issues.

4. What can we learn from the studies at the PROPHET site? PROPHET 1998 was not in-line with models, whereas PROPHET 2008 and CABINEX 2009 agree (more or less) with model predictions. Given the current doubts in measurement technique of OH and HO₂ by LIF, the large experimental uncertainties especially for OH (laser power), and the model uncertainties mainly due to ancillary data, there is a fairly unclear situation of what the comparison between measurements and model can be useful for. Accordingly, the authors should further discuss the “agreement” with the model and the disagreement in 1998 in light of uncertainties and artefacts.

Specific comments:

p. 3, l.7: which other “long-lived greenhouse gases” are meant here?

p. 9, ll.7: please, specify the remaining laser power entering the cell and comment on the impact of all the mentioned effects (temperature and humidity) on the sensitivity of the instrument and how constant sensitivity/calibration was achieved.

p. 10, 1st §: as also the OH fluorescence signal depends on laser power, the argument that the interference is negligible due to the low laser power is not convincing. Please specify the typical and maximum OH artefact due to this ozone interference.

p. 10, last §: In ambient measurements during HO_xCOMP (Schlosser et al., 2009), two of the LIF instruments were higher by about 30% and one instrument was higher by about 60% than the CIMS instrument. At least with respect to the latter, this is not really well agreement.

p. 11: see also general comment 1 above. Obviously, contradicting results have been achieved in the interference tests. Since these interferences are a very important issue, it is recommended to present the results of these interference tests and discuss the potential uncertainty contribution due to this interference for the presented OH results.

p. 15, last §: Given the temperature variability of typically between 15 and 25°C, a

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difference of 1-2 degrees appears rather small. Thus, it appears harsh to speak of untypical conditions in 2009. Furthermore, isoprene emissions are mainly determined by light and the difference in isoprene mixing ratios can not be explained by temperature differences. Please specify that analytical problems can be ruled out as explanation of the difference.

p. 17, ll. 6-12: Please specify the percentage of data which are different from zero beyond their 2-sigma uncertainty.

p. 19 and Fig. 9: the main message of Figure 9 is that data are of insufficient quality to check for the corresponding dependencies. This should be mentioned in the text and the figure could be discarded.

p. 20, 1st §: There is a huge discrepancy with the results obtained in 1998, and the authors should discuss this further. Have any modifications to the instrument been made which might have affected the results? It is hard to follow the argument here, that in other studies interferences existed (Mao et al., 2012) but this remains vague for the Indiana university instruments. It is strongly recommended to include results of corresponding tests in this paper such that the interference problem can be quantified.

p. 24, section 4.3: Please, specify in the text how the budget is closed. Apparently, Figures 12 and 13 show balanced production and loss, however, the HO₂ and the RO₂ are not individually measured and the constrained model is partly not consistent with observations (Figures 5, 7 and 8).

p. 26, middle §: NO₂ was about a factor 2 higher in 2008 with similar NO and ozone as well as J(NO₂). Thus one would expect higher NO in 2008. The model, however, uses lower NO in 2008 with effects discussed in this §. It is recommended to discuss the uncertainty of the used constraints and assumptions and their effect on the model results.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 33165, 2012.

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