**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Modelling atmospheric OH-reactivity in a boreal forest ecosystem" *by* D. Mogensen et al.

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Ref #2: The authors describe the modelling of the OH radical reactivity for 2008 in the boreal forest station in Hyytiälä, Finland, and compare the output with the measured OH reactivity from August in 2008 at this site. Modelling has been performed using organic emissions from the MEGAN model and chemical transformation was described mainly by MCM. PTR-MS measurements revealed a good agreement between measured and modelled monoterpene concentrations. OH reactivity measurements have been performed in an indirect way by following pyrrole disappearance in competition to the OH reaction with the ambient air constituents. Modelled OH reactivity was found to be significantly lower than the measured data. The authors are discussing possible reasons. The paper is well structured and well written and within the scope of this

journal. Before publishing, some revisions could improve this manuscript.

RE (2.1): We thank the reviewer for helpful comments. Below we provide point to point response to each comment.

Ref #2: 1) Emissions of organics were taken from MEGAN. It would be nice to see a comparison measurement vs. model e.g. for isoprene concentrations and monoterpenes in total at ground allowing an impression how accurate concentrations of organics are described. Degradation pathways for alpha- and beta-pinene were explicitly taken into account by modelling. What was done with other monoterpenes, especially limonene? Nothing was said regarding sequiterpenes!

RE (2.2): In Figure 8, daily averaged modelled and measured monoterpene concentration for the 3 lowest measured heights (4, 14, and 22 m) are presented, and good agreement between model and measurements is found. As also mentioned in the paper, isoprene is not a good measure for the models accuracy, due to the large difference in emitted isoprene at the station, and ambient isoprene concentration, due to the isoprene footprint (the trees at the station are mainly low isoprene emitting pine, while a large fraction of the surrounding area is covered by higher isoprene emitting spruce). When this study was carried out, no explicit chemistry for limonene was available. Also the concentration of limonene is small compared to other monoterpenes in Hyytiälä. First order reactions between OH, O3, NO3 and all 10 monoterpenes were also included in the chemistry. The same is the case for beta-caryophyllene, farnesene, and a term we call 'other sesqueterpenes' (which have the same rate coefficients for reactions with OH, O3, NO3 as beta-caryophyllene). This information will now be provided in Section 2.3.

Ref #2: 2) NMHC account for 21% of total OH reactivity, cf. Fig.3. A couple (or the majority) of organic concentrations are directly available by PTR-MS measurements. What is the resulting OH reactivity using theses measured organics with respect to the usage of modelled organics in a more comprehensive way. Is the OH reactivity using

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modelled organics definitely higher than the OH reactivity with the measured organics according to eq.(R1)? What is the improvement using the complex modelling by MCM?

RE (2.3): In the paper by Sinha et al., 2010 the OH-reactivity was calculated based on measured gas concentrations, why we do not include these calculations in this paper. In the calculations are included NO, NO2, CO, CH4, O3, and the following VOCs: methanol, acetone, propanal, acetaldehyde, formic acid, acetic acid, isoprene, methacrolein and methyl vinyl ketone, methyl ethyl ketone, methyl butenol, toluene, cis-3 hexenol and hexanal, monoterpenes, and pinonaldehyde. Sinha et al., 2010 find the calculated OH-reactivity to be approximately the same as the modelled OH-reactivity in this paper. However, it must be thought to be a more uncertain calculation than what the modelling approach provide, since only little information was given about e.g. the distribution of the different monoterpenes; measured GC-MS data of individual hydrocarbons, including the monoterpenes speciation, were only available during two 1.5-days periods during the BFORM campaign (Sinha et al., 2010). Therefore an average of the most know monoterpene reaction rate with OH is used for the calculation of the OH-reactivity in the paper by Sinha et al., 2010. In this paper we are able to e.g. separate the different monoterpenes, and calculate there individual contribution. Furthermore, some of the advantages of this complex modelling with explicit chemistry is that 1) we gain information about the OH-reactivity with any wanted time resolution and 2) at any height 3) and at periods were the OH-reactivity (or the gas concentrations of the compounds OH react with) are not measured.

Ref #2: 3) The authors should discus more in detail the other OH reactivity measurements given in literature, the comparison with model predictions and the resulting discrepancies.

RE (2.4): We thank the referee for this suggestion. This will partly be included in the introduction, and partly in the results and discussion section while comparing to our results.

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Ref #2: 4) A hot topic in gas-phase chemistry at the moment is the point that obviously the HOx chemistry especially under low-NOx conditions is not well understood. A series of field measurements for OH and HO2 cannot be explained by the current understanding of atmospheric degradation mechanisms especially for isoprene. Measured OH radical concentrations are significantly higher than data from modelling runs. Very efficient OH recycling is proposed, i.e. OH + isoprene -> n OH + products, n>1 (Stone et al., Atmos. Chem. Phys. Discuss., 11, 10343–10401, 2011). The authors of this paper here should point to this topic. However, a possible underestimation of OH radical concentrations by models (also by MCM) does not help to explain the discrepancy of modeled OH reactivity vs. measured OH reactivity, it would strengthen the difference.

RE (2.5): Another paper that discuss the OH budget in Hyytiälä is currently under preparation, and model calculations using recycling mechanisms to regenerate OH will be used, and we will therefore not include any recycling calculations of OH in this paper. Also, OH concentrations were not measured in 2008, which will make this discussion as the referee suggests, hard. However, as the referee points out, it would definitely be worth mentioning.

References: Sinha et al., OH Reactivity Measurements within a Boreal Forest: Evidence for Unknown Reactive Emissions. Environ. Sci. Technol. 2010, 44, 6614–6620.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 9133, 2011.

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