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

### **Anonymous Referee #1**

Received and published: 11 May 2011

This work is a modelled to measured comparison of OH reactivity during a month long campaign at Hyytiala in Finland. The measurements use a relatively new method for capturing the OH reactivity (the comparative reactivity instrument) that has been shown to be successful in low NO<sub>x</sub> environments such as forests. The model uses biogenic emissions from MEGAN, collocated measurements of other VOC species from Hyytiala and explicit chemistry from the Master Chemical Mechanism. The sink reactions for OH are identified and summed, to give the total OH reactivity.

The authors find that this modelling technique only accounts for between 30-50% of the measured OH sinks. The authors suggest that the gap can be filled by identifying other biogenic VOC species and reducing the uncertainties in rate constants and chemical schemes. The apparent low level of understanding is common amongst the current

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scientific literature, and we're discovering just how very little is known about OH.

I recommend the paper should be published in ACP subject to the following queries and corrections:

Section 2 Model simulations. A better description of how the model is run is needed. Is the model initialised and set to run for 1 month? Is a new simulation set off each day? How much model spin-up is needed before the results can be trusted? It would be useful to know what the concentrations of inorganic gases are (especially NO<sub>x</sub> and O<sub>3</sub>) as this gives an indication of the state of the atmosphere (eg clean, polluted etc). The authors state that measured data is used as input, but don't say whether this is just a one off initialisation or whether the model is constrained at regular intervals by the measurements. I don't think enough information is given to allow someone to repeat the experiment (if they so wished!).

Section 2.2 Emission. Is Scots pine a big monoterpene emitter in comparison with other needleleaf trees? How would the model results change if a higher emitting species is used everywhere instead?

Section 2.3 Chemistry. Considering one of the main conclusions is that the rate constants are uncertain, the mechanism used has not been well referenced. The version number of the Master Chemical Mechanism (MCM) must be given as a minimum. It would also be sporting to cite the major MCM papers (Jenkin et al., 1997; Saunders et al., 2003), as the authors have done so for KPP and the photodissociation constants.

I mention version number because MCM version 3.2 has been released. Version 3.2 contains new chemistry for limonene and beta-caryophyllene which would be of interest here, and also updates to the isoprene chemistry which now has a better treatment of nitrated species with regards to the amount of NO<sub>x</sub> returned. I suspect that this study was probably done before version 3.2 was released, but I think it provides food for a follow-on study.

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The authors mention on line 4 of page 9138 that a more recent acetone+OH rate constant is used but do not cite what this rate is.

Equation R1 – The authors need to define exactly what is meant by OH sources and sinks. From my reading of this, all reactions which use up OH are termed as ‘sinks’, and all those which produce OH are termed ‘sources’. Are the reactions which recycle OH through the OH-RO<sub>2</sub>-HO<sub>2</sub> system included in the definition of sinks? Could the modelled to measured reactivity be improved if the recycling reactions were included in the calculation?

It would be useful to assess how well the model has calculated [OH] in conjunction with the modelled reactivity. Were [OH] measurements made during the BFORM campaign? If the MCM is unable to explain the OH concentration then it follows that the identified reactions would not be sufficient to describe the measured reactivity. There is much debate about the ability of chemistry schemes to model OH (and HO<sub>2</sub> in tandem) in isoprene rich environments (e.g. Lelieveld et al 2008). Stone et al (2011) have attempted to force MCM chemistry to reproduce [OH] measurements made during the OP3 campaign in Borneo, but in doing so have made a worse job of modelling HO<sub>2</sub>. In other work, Whalley et al (2011) suggest there is a missing OH source (rather than a sink) in forest atmospheres. I think the paper warrants a better discussion of the biogenic chemistry debate in section 4.4 as this forms one of the paper’s major conclusions.

Section 3.2 VOC measurements. You mention toluene here as a measured (biogenic) compound, but do not include it as a primary VOC in the chemistry scheme? Are these VOC measurements the same as those measured at the SMEAR II site (P 9138 line 5) and used as input to the model?

Page 9143 line 4. The authors give an ordered list of monoterpene compounds contributing to modelled OH reactivity, but the chemistry for the majority of these compounds is not included in the model (Page 9137). If the list comes from a different

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study then please cite your source.

Minor corrections

P9135 line 23. 'Earths' should be 'Earth's'

P9135 line 29. 'Details' should be 'detail'

Page 9140 line 23. Change 'fluctuations' to 'fluctuation'.

Section 4.3 on page 9144. This whole section needs proof reading, particularly the first paragraph. The first word should be 'daily' I think. However, I lost count of the number of other missing words/mistakes.

Figures 2, 6, 7 and 9 are missing units next to the legends.

Figure 4. I think 'averaged over period A' should be included in the caption.

Figure 10 caption: change 'until the height of the boundary layer' to 'up to the top of the boundary layer'

References used:

Jenkin et al., The tropospheric degradation of volatile organic compounds: A protocol for mechanism development. *Atmos. Environ.*, 31, 81-104, 1997.

Lelieveld et al., Atmospheric oxidation capacity sustained by a tropical forest. *Nature*, 452. 737-740, 2008.

Saunders et al., Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of nonaromatic volatile organic compounds. *Atmos. Chem. Phys.*, 3, 161-180, 2003.

Stone et al., Isoprene oxidation mechanisms: measurements and modelling of OH and HO<sub>2</sub> over a South-East Asian tropical rainforest during the OP3 field campaign. *Atmos. Chem. Phys. Discuss.*, 11, 10343-10401, 2011.

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Whalley et al., Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest. *Atmos. Chem. Phys. Discuss.*, 11, 5785-5809, 2011.

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

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11, C3164–C3168, 2011

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