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Atmospheric
Chemistry
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Discussions

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

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Ref #1: 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 NOx 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 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.

RE (1.1): We thank the reviewer for helpful comments. Below we provide point to point response to each comment.

Ref #1: 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 NOx and O3) 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!).

RE (1.2): We agree that it would be beneficial to provide information about the inorganic gas concentrations, and we therefore intend to include some of the most important once as a rough concentration estimate at the height of 14 meters. The concentrations of selected inorganic gases are in the order of; O3: ∼2-11E11, NO: ∼3-4E9 (daytime), NO2: 1-6E10, NO3: 1-3E7, SO2: ∼1-5E9 , and CO: ∼3E12 all in the unit of molecules/cm3. The model runs without any continuous input beside the upper boundary met-conditions at 3 km and the long-range-influenced transported gases (NOx, SO2 and CO) which are given at every time-step (10 minutes) from measurements with a vertical gradient estimated on simulations with the global aerosol model ECHAM5-HAM. A detailed description of the model-setup and -description was published recently in the paper Boy et al., 2011.

Ref #1: Section 2.2 Emission. Is Scots pine a big monoterpene emitter in comparison

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with other needle-leaf trees? How would the model results change if a higher emitting species is used everywhere instead?

RE (1.3): The monoterpene emission of Scots pine is in the same range with other Eurasian coniferous trees (Rinne et al., 2009). However, the monoterpene species emitted vary between species and even within species. Individual Scots pine trees differ especially in there relative alpha-pinene and D3-carene emissions, while the atmospheric concentrations at SMEAR II are dominated by alpha-pinene. D3-carene reacts 64% faster with OH than alpha-pinene does. The diurnal cycle of monoterpene emission and resulting atmospheric concentration can be different between the coniferous trees and monoterpene emitting deciduous boreal trees, which do not have night-time emission from specialized monoterpene storage structures. Thus the diurnal cycle of OH-reactivity might be different were the vegetation is dominated by e.g. birches.

Ref #1: 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 NOx 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.

RE (1.4): As the referee points out, the study was carried out before the release of MCM version 3.2, and therefore we used MCM version 3.1. In this section we intend to include the following line: “Most chemical reaction equations were selected from the Master Chemical Mechanism v3.1 (Jenkin et al., 1997; Saunders et al., 2003) via website: http://mcm.leeds.ac.uk/MCM/.” as also instructed in MCM version 3.2 citation protocol (to our knowledge there exists no such protocol for version 3.1).

Ref #1: 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.

RE (1.5): We intend to add the reference to the publication by DeMore et al., 1997. (The rate constant in MCM version 3.1 is from Atkinson, 1994).

Ref #1: 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-RO2-HO2 system included in the definition of sinks? Could the modelled to measured reactivity be improved if the recycling reactions were included in the calculation?

RE (1.6): Our definition of ’sinks’ and ’sources’ are the same as what the referee mentions. For regeneration of OH through OH-RO2-HO2(-NOx), only what is available in MCM version 3.1 was used. But this e.g. includes NOx regeneration of OH from the oxidation of CO and hydrocarbons. The individual reactions are valued separately: e.g. NO can participate in several reactions with OH, and in these reactions NO will be a sink for OH. However, NO can at the same time also participate in several reactions that produce OH, and in these cases, NO is a source of OH. If NO in the end then is a source or sink of OH, depends on how much OH is reacting or produced by reactions involving NO. We will clarify this in the paper. If the referee thinks of recycling mechanisms through isoprene reactions, then these have not been taken into account. Another paper that discusses the OH budget in Hyytiälä is currently under preparation, and model calculations using recycling mechanisms to regenerate OH will be used.

Ref #1: 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

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is much debate about the ability of chemistry schemes to model OH (and HO2 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 HO2. 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.

RE (1.7): We agree strongly with the referee. Unfortunately OH concentrations were not measured in August 2008. However, in summer 2010 both OH-reactivity and OH concentration were measured, and we intend to discuss the points of the referee in the OH budget paper that is under preparation.

Ref #1: 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?

RE (1.8): We used the organics from the MEGAN code and because we do not have any standard emission potential for toluene it is not possible to include it, as we do not want to use measured data because of the missing vertical information.

Ref #1: 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 study then please cite your source.

RE (1.9): First order reactions between OH, O3, NO3 and all 10 monoterpenes are included in the chemistry. This information will now also be provided in Section 2.3.

Ref #1: Minor corrections

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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'

RE (1.10): we apologise for the typos, which all of course have been corrected.

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 HO2 over a South-East Asian tropical rainforest during the OP3 field campaign. Atmos. Chem. Phys. Discuss., 11, 10343-10401, 2011.

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

Rinne et al., Biogenic volatile organic compound emissions from the Eurasian taiga:

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current knowledge and future directions, Boreal Env. Res., 14, 807-826, 2009.

Demore et al., Chemical kinetics and photochemical data for use in stratospheric modeling, JPL Pub. No. 97-4, Jet Propulsion Laboratory, 1997.

Boy et al., SOSA – a new model to simulate the concentrations of organic vapours and sulphuric acid inside the ABL – Part 1: Model description and initial evaluation , Atmos. Chem. Phys., 11, 43–51, 2011.

Atkinson, Gas-phase tropospheric chemistry of organic compounds. Journal of Physical and Chemical Reference Data, Monograph 2, 1-216, 1994.

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

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