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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 #3: This work uses a 1D vertical transport model combined with a MEGAN emissions module to calculate the OH reactivity at a boreal forest site in Finland. The calculated OH reactivities are then compared to observations made over a period of 16 days during August 2008. The study highlights the impact of local meteorology on observed OH reactivity. The 50-70% underestimate of the observed OH reactivity is consistent with previous studies of OH reactivity, and with the box model comparison for the same data set reported in Sinha et al. (2010). I recommend that this work should be published subject to the following major changes being made.

RE (3.1): We thank the reviewer for helpful comments. Below we provide point to point response to each comment.

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Ref #3: Major issues

In general the paper should show more model validation through comparison with the available observations at the site. Other than for monoterpenes, model-measurement failures are only discussed qualitatively making interpretation less than solid. The Authors references Boy et al. (2011) for model to measurement comparisons of VOC concentrations, however this reference also uses only monoterpene observations.

RE (3.2): We will include a paragraph, discussing how good SOSA predicts different organic gas concentrations of e.g. methanol, acetaldehyde, formic acid, acetic acid, and pinonaldehyde. A paper on SOSA modelled and measured organic gas emissions and concentrations is currently under preparation, and we will therefore not include any figures.

Ref #3: The model description is also incomplete. PTR-MS observations are used as an ‘input’ but the nature of this input is not described. Are they used as an initial condition or are model concentrations constrained to the observations?

RE (3.3): Measured monoterpene concentrations were not used as an input but only used for comparison. We used the model MEGAN to calculate emissions from the canopy for all organic molecules used in the OH-reactivity study because measured concentrations would not give any information about the vertical distribution above the canopy.

Ref #3: The author needs to discuss the contribution of model generated secondary products to the calculated OH reactivity. It is not obvious from Figure 3 how much of the OH reactivity is coming from primary emitted species and how much from their secondary oxidation products. Are these species significant for OH loss or would the same outcome be obtained using only observations of the inorganic and key organic species, without the need for a large explicit chemistry scheme? Some detail on the relative composition of the “other organics” fraction in Figure 3 would assist in this.

RE (3.4): This is a good point, and we will include a separation in ’other organics’; ’other primary emitted organics’, and ’other secondary organics’ in Figure 3, followed by discussion of this topic.

Ref #3: The under prediction of reactivity discussed by the authors is hard to evaluate as the concentrations of modelled primary and secondary species are not described in sufficient detail.

RE (3.5): See RE 1.2, 1.4, 1.5, 1.9 (in response to referee #1), 2.2 (in response to referee #2) and 3.3.

Ref #3: The author mentions that the emissions used do not accurately represent observed isoprene concentrations. However, no indication of the scale of this discrepancy is provided. Although the authors believe isoprene is not a dominant component of the reactivity in this environment, they go on to admit that their model underestimates the isoprene concentration but don’t quantify this. A significant failure in the model’s simulation of isoprene could address some of the missing reactivity but this is not discussed in detail. How much higher would isoprene emissions have to be to match the isoprene observations? How much higher would the isoprene have to be to match the OH reactivity observations?

RE (3.6): Sinha et al. (2010) calculated the OH-reactivity due to contribution from isoprene, using measured ‘isoprene’ concentrations. The difference between Sinha et al. (2010) and our OH-reactivity due to isoprene reactions is ∼0.3 s-1. Isoprene is therefore not a possible candidate for the missing OH-reactivity, since it would only be able to explain ∼10-15% of the missing OH-reactivity.

Ref #3: There is a significant body of work addressing uncertainties in isoprene oxidation chemistry in low NOx environments((e.g. Lelieveld et al. (2008), Hofzumahaus et al. (2009), Paulot et al., (2009); Whalley et al., (2011); Stone et al., (2011)). The authors do not discuss these results nor the impact on their calculations. This should be addressed. A modelled under estimate in OH would suggest an even larger missing source of isoprene than is currently considered in the model.

RE (3.7): see RE 1.6, 1.7, (in response to referee #1) and 2.5 (in response to referee #2).

Ref #3: Insufficient detail is given about the chemistry scheme used within the model. Specifically MCM version number would help when referencing the scheme used. Changes to the MCM scheme used should be referenced. The author lists 10 monoterpenes that contribute to the calculated OH reactivity within the model. How does the chemistry scheme treat these species as, other than α- and β-pinene (+limonene in V3.2), the MCM does not contain explicit monoterpene degradation schemes. How does the model treat the deposition of species?

RE (3.8): See RE 1.4, 1.5, 1.9, (in response to referee #1) and 2.2 (in response to referee #2).

Ref #3: Is a factor of 2 uncertainty realistic for the rates of OH reaction with all the species chosen to be included in this sensitivity study? The quoted uncertainty on many of the reactions quoted is significantly less than this. The uncertainties that exist in the chemistry are generally not with the oxidation step by OH but in the subsequent degradation chemistry. This section of the paper should either be re-written with a more realistic definition of the uncertainties on these parameters or removed from the paper.

RE (3.9): The largest uncertainties on rate constants are surely to be found on secondary product reactions (and here the uncertainties are higher than a factor of 2). Likewise the chemistry of secondary product are in general more poorly understood than the chemistry of the primary compounds included here. Therefore it does not make much sense to tune the reaction coefficients for secondary (organic) product reactions with OH. A factor of 2 was used, not based on our experience, but others (Atkinson 1992).

Ref #3: Overall this paper offers an advance in our ability to understand OH reactivity in forested environments. However, as it stands the paper does not provide sufficient details or explanation to allow the reader to interpret the results provided. More work is needed to provide additional information, comparisons and evaluation of the data.

Specific comments

Ref #3: Pg 9135 line 1-3: The statement “Measuring total OH-reactivity using LIF is difficult since it requires the rapid measurement of OH at very low concentrations and requires complicated corrections due to atmospheric NO to be taken into account.” implies that the CRM instrument used does not suffer the same NO interference. This is not true as Sinha et al. (2008) show that the OH reactivity measured by the CRM instrument is indeed sensitive to the NO + HO2 interference. The low NOx conditions at SMEAR II mean that this interference should not be significant in either CRM or LIF instruments at this site (Sinha et al., 2010). The author should re-phase to avoid ambiguity.

RE (3.10): We thank the referee for this suggestion, and will reformulate the phrase.

Ref #3: Pg 9141 line 1 to 3 (and Table 1): It would be useful for comparison if the author attempted to quantify the observational and modelled variability. Stating if the average quoted is mean or median and quoting a standard deviation over the averaging period would help with this.

RE (3.11): The values are given as means, which we now will include in the paper. Further, also standard deviations will be included.

Ref #3: Pg 9144 line 15 and in other locations in the paper: Model calculations are exact and diagnosable. Thus the use of words such as “probably” is inappropriate as the model can be diagnosed to reveal why it has calculated such values. The model may be wrong but we should be able to understand why it has done what it has done.

RE (3.12): We appreciate that the referee brings this to our attention, and we intend to reformulate.

Ref #3: Fig 4: Light blue trace is difficult to see.

RE (3.13): It is difficult to see the overlying lines, and we have now changed the plot, so that there is a zoom of the bottom part of the figure.

Ref #3: Fig 6, 7, 9: Units on OH reactivity legend not labelled.

RE (3.14): This has now been added.

References

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.

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Sinha et al., The comparative reactivity method – A new tool to measure total OH reactivity in ambient air. Atmos. Chem. Phys., 8, 2213-2227, 2008.

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