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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Speciation of OH reactivity above the canopy of an isoprene-dominated forest” *by* J. Kaiser et al.

Anonymous Referee #1

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Measurements of OH reactivity are made during the SOAS study in SE USA, at an isoprene dominated site, and compared with a model. The model is constrained with measured OH radicals, and also an impressive range of OH sinks, including those VOCs directly emitted by plants, and importantly for this environment, oxidation products, particularly oxidation products of isoprene, which is the dominant emitted species in this environment. The model uses a very detailed chemical mechanism (MCM v3.2) also includes updates in the chemistry from RO2 equilibration and RO2 H-atom shift isomerisations, as well as updated kinetics and photolysis rates of isoprene oxidation products. There is generally good agreement between the model and measured OH reactivity (average slope of 0.8 model to measured, 16 (+/- 20%) missing OH reactivity). So when measurement uncertainty is also factored in (20%) the model-measurement difference is not significant and it is not necessary to invoke that there is a significant

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amount of missing OH reactivity, and hence associated uncertainties in identifying what the missing OH reactivity is. These uncertainties can have important implications for calculating overall rates of VOC oxidation, and hence the production of ozone, SOA and other policy-related parameters. The difference between modelled and measured OH reactivity during an average diurnal profile is also discussed, with largest discrepancies observed in the early morning (30%). In fact the largest contribution towards the OH reactivity is calculated to be the primary biogenic emissions rather than oxygenated products.

An important conclusion from this study is that if these oxygenated products had not been measured, the model would have overpredicted the OH reactivity, leading to difficult conclusions, as the model used in this study significantly overpredicts the concentration of OVOCs (by large factors). The good agreement is achieved by being able to constrain the model with measured concentrations of isoprene oxidation products, which have been absent from many other studies, and this is a real strength of this paper. Measurements of ISOPOOH, ISOPN and isoprene HPALDS are novel and greatly aid the interpretation of OH reactivity in this environment. The fact that these OVOCs are actually measured is shown to be crucial, not because they are a major measured OH sink at this site, but because the model used in this study is not able to calculate the concentration of these oxygenated products with any degree of accuracy, e.g. the model overestimates by a factor of 6 for HPALD, and a factor of 4 for ISOPOOH. If the model had used the modelled OVOCs to calculate OH reactivity (rather than constrained to them), the overprediction of OH reactivity would have led to different conclusions. Reasons for the model overprediction of the OVOCs may be uncertainties in dilution rates following emission, which are discussed in the supplement. As the model overpredicts the OVOCs, the model underprediction of OH reactivity (when model is constrained to measured OVOCs) suggests that this is due to unmeasured primary emissions, and not missing OVOCs. A plot of measured OH reactivity versus that specifically for reaction with isoprene itself shows a slope of 1.43 showing that isoprene rather than its oxidation products dominates OH reactivity at this site.

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Significant here is that the paper notes that the rates of deposition of these OVOC species to the canopy, which is often a model parameter for which there is considerable uncertainty, have been measured by other groups in the SOAS study, and therefore does not have to be estimated in the model. A sensitivity study is presented on the impact of changes in the dilution factor on the OH reactivity.

The paper has some very interesting findings and the measurements are of good quality. The conclusions of the paper are significant for this type of environment, and are different to some earlier campaigns in a similar type of environment. However, some statements do not appear consistent with the data presented, and some further detail is missing in places. The authors should respond to the following points.

Abstract

(1) The abstract does not contain any quantitative information about the level of agreement between model and measured OH reactivity, which is the main result. There is a long introduction to the abstract and it is not until line 18 that any points specifically relevant to the results of this study are presented. Lines 10-17 need to be moved to the introductory material in the main paper, and some of the main results from the study (overall level of agreement (i.e. that the model underpredicts), slopes of main correlation plots, OH reactivity versus isoprene calculated reactivity, diurnal behaviour, statement that there are large model overprediction of OVOCs with values etc.) need to be stated. The abstract needs to be extended considerably in terms of summarising the main results.

Paper

(1) Page 7 (there are no page numbers, so pages here refer to pages with the cover page as page 1) lines 2-3. In the measurement of OH reactivity, how was the zero of the instrument determined, and what is the value? Also, presumably in this environment the level of NO is low enough that any corrections for recycling of OH from HO2+NO within the sampling airstream are not necessary? If this is the case it should be stated.

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It would also be worth stating how the accuracy of the instrument is checked using known OH sinks.

(2) Page 7, line 25, MCM (not MVM).

(3) Page 8, line 29. Would any process immediately regenerate OH? The timescale may be fast compared with the OH decay, but the actual values should be compared, and one shown to be much faster than the other, rather than just this statement.

(4) Page 9, line 1. Small is subjective, please give a % value here to evidence this.

(5) Although not the subject of this paper (and measured OH is used to constrain the model), it would be useful to state the level of agreement between the model and measured OH and other measured radicals (HO2 and maybe RO2). It would be useful just to confirm how the model performs for these species (given that the model comparison for OVOCs is discussed later).

(6) Page 10, line 1. The largest discrepancy is observed at 0700 LT (32%). Can the authors comment on the general shape of Figure 2?

(7) Page 10, line 16. It is stated that the slopes are not much larger than one. This is rather subjective as the observed slope of measured OH reactivity versus that from isoprene itself is 1.43, which although not a factor of 3, 5 etc., is significantly greater than 1 (by almost 50%). This statement ought to be qualified. It can be seen clearly from Fig 3 that at times the reactivity due to isoprene is considerably less than the total measured OH reactivity.

(8) Page 12, line 3. Not slope of fig 3? You mean slope of fig 4?

(9) It is difficult to compare the temperature dependence observed with that of Di Carlo et al., as the range of values of temperature only seem to have a limited range where they overlap. The parameterisation of Di Carlo seems to stop at 300 K, and in this region the current work's function does not change much. It is only above 300 K that the function for this work becomes significantly steeper than that of Di Carlo. Some further

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discussion of this is needed, and the parameterisation of Di Carlo needs extending to higher temperatures compare easily.

(10) Page 12. The paper states that "…the model is missing ∼ 1 s-1 that is temporally unrelated to the oxidation of ….. (Figure 3)". However, inspection of Figure 3 suggests that the difference between the measured OH reactivity (black points) and the cumulative modelled reactivity is more than 1 s-1? It looks more like between 2 and 5 s-1 (depending on time of day). Some modification of this statement is therefore needed.

(11) Page 12, line 12, missing "of"

(12) Page 13, line 2. Again 1s-1 seems to be a significant underestimate of the difference between measured and modelled shown in Figure 3. The amount of sesquiterpenes would therefore need to be more than ∼ 200 ppt.

(13) Page 13, line 22. The values quoted here are not consistent with the values quoted on page 10. The measured slope was quoted as 1.43 there, and modelled slope 1.22. Also, it says +/- 02 (should be 0.02).

(14) Table 1. Glyoxal row, space between 9% (1 s)

(15) Figure 1. Please plot this graph from the origin (0,0) as it will be more informative. At present it is rather misleading as it suggests the points go to the origin.

(16) Figure 1. The slope of the linear least squares fit weighted by uncertainty must be stated in the caption. This is one of the most important results of the paper.

(17) Caption for Fig 2, second line, "Points the in gray…" needs correction

(18) Figure 3. As commented above the difference is considerably more than 1s-1 quoted in the text (seems to be 2-5 s-1 depending on time of day). Suggest reversing the order of the legend. At present the measurement is at the bottom, with Inorganics at the top, whereas the figure is measurement at the top, and Inorganic at the bottom.

(19) Figure 4. Given the text gives the slopes at 1.43 and 1.22 (note inconsistency with

page 13), the equation given on the figure needs to reflect this quoted accuracy. What does “weighted by uncertainty” mean?

(20) Figure 6. See comments above about the degree of overlap in T for the solid and dashed lines. What is the value of Greek alpha for each?

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