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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Rapid formation of isoprene photo-oxidation products observed in Amazonia" *by* T. Karl et al.

Anonymous Referee #1

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This study by Karl et al. presents field data which indicates that the production of certain isoprene oxidation products (notably hydroxyacetone) is underestimated and fails to occur sufficiently quickly in current chemistry schemes. This could help explain the 'missing' OH sinks found in many studies in highly vegetated regions. Given the importance of isoprene to the chemistry of the atmosphere and composition / climate feedback I think that this is an important paper. The paper makes a very useful and interesting point and advances the field. It feels that this paper has been written in a rush and hasn't been read through appropriately. It is often difficult to understand that the authors are trying to convey. However, I would recommend publication with the following changes.

Major comments

1) Section 2.3 does not contribute towards the scientific conclusions of the paper. It is not referred to in abstract or in the rest of the paper. This section should be removed. 2) There is in sufficient referencing throughout the paper. Facts are stated without references to back them up. Examples of this problem are given below. The authors should ensure there is the appropriate reference for all previous literature. 3) I find many of the figure captions difficult to understand as they are too short. Examples are given below. The authors should ensure that the figure captions and meaningful, useful and comprehendible.

Minor comments

âĂć P13635, L16. A more detailed description of the causes for the shape of the profiles in Fig.1, why is there the dip in the C5H8 concentrations. The authors refer to deposition but could this not also be interpreted as mixing out of the canopy or chemical removal? In general I don't think this section adds anything to the conclusions of the paper and should be removed âĂć P13636, L10. The C5H8 + OH branching ratios are given without reference or uncertainty. There is no comment on the fate of the remaining 45% that does not go to MVK or MAC. âĂć P13636, L18. Reference for rate constants. âĂć P13636, L20. Stating the estimated lifetime of MVK and MAC compared with isoprene would be useful. âĂć P13636, L21. As well as quoting the mean (MVK+MAC)/isoprene ratio of 0.44 the standard deviation would be useful. âĂć P13637, L10-13. A reference for mentioned other possible sources of hydroxyacetone should be included. âĂć P13637, L17-18. A reference for biomass burning as large source of hydroxyacetone should be included. âĂć P13637, L22. Maximum acetonitrile mixing ratio enhancement of 0.6 ppbv should be quoted with the background level upon which it is elevated from. âĂć P13638, L6. Would state 'chemical trajectory' to avoid any unnecessary confusion with a meteorological / dynamical trajectory. âĂć P13638, L18. Authors should reference non-linear least square regression procedure used. âĂć P13639, L28. Reference should be given to back up the importance of formaldehyde in total VOC reactivity used. âĂć Conclusions and summary. This sec-

tion doesn't summarize the work. It has some conclusions but there should be a little more thought about the global implications of this work. âĂć Table 1. Presumably this is the rate of reaction with OH? It is not specified. Are these numbers missing the minus signs in the power? The rate constant for isoprene + OH is ∼1e-10 cm3 s-1 not 1e10. âĂć Table 2. Where does this scheme come from? There are no references or explanation of this. âĂć Figure 1. This figure and the section should be removed. âĂć Figure 2. More description of data plotted and where each plot comes from in figure caption would be useful. The axis labels should be in the same colour as the dots used. A reference should be given to the 'robust fitting procedure.' The sections of the paper where the steady state concentrations and the predicted ratio (this should also be described more in the figure caption) are deried should be given in the figure caption. âĂć Figure 3a caption. 'Triangular correlation plot ...' explain what normalised to 1 means in this case. It could be that the mean value is normalized to one but it appears that the maximum value is normalized to 1 or is the maximum total carbon normalized to 1. This is confused. âĂć Figure 3a caption. 'Circles show case that includes fast production' of what? âĂć Figure 3b caption. This is a non-linear regression of what, on to what? Presumably this is a fitting of the model output onto the observations but this not specified. What technique has been used for this regression? What are the units of the graph or has this been normalized. Again this should all be specified in the figure caption. âĂć Figure 4. It is again unclear what is being described here. Do the colour regions represent a simulation without the inclusion of fast photochemistry? Does the blue dashed line represent the same simulation but for all species (does the white space between the blue line and the coloured areas represent unspecified compounds?). Should there be a blue continuous line to represent the simulation without the fast photochemical production? I don't think the inclusion of the RACM mechanism adds anything to the discussion and should be removed.

General English comments

âĂć P13631, L3-5. 'Isoprene is also highly reactive and its photochemical evolution

of isoprene therefore plays a central role in atmospheric chemistry.' What do authors mean by this statement? Should sentence read, 'Isoprene is also highly reactive and its photochemical evolution of its photo-oxidation products therefore plays a central role in atmospheric chemistry.' âĂć P13635, L8. Is this the same model described in previous section? âĂć P13637, L27. 'In order to check . . ...' should be start of new paragraph. âĂć P13638, L21. Branching ratio quoted here is a percentage, in contrast to branching ratios quoted earlier as fractions.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13629, 2009.