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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.

T. Karl et al.

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We are thankful for the reviewer's comments which are addressed in detail below:

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.

Response: The rational for including and keeping Figure 1 is to show that m/z 75 observed by PTRMS is not compromised by a primary emission from the forest, as it is deposited to the canopy. The source sink distribution strongly suggests photochemical origin. We will expand discussion and rational in a revised manuscript.

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

Response: These are actually cumulative fluxes and not concentrations. There could be many reasons why isoprene is lost in the canopy (dry deposition mediated by biological activity or chemical removal via NO3 etc.), for this study we want to show the total cumulative flux (at the top of the canopy) that exits the forest or is deposited to the forest (for OVOCs). Rational for keeping this figure is that it clearly shows that m/z 75 is not a primary emission from the forest. We will expand the discussion on this section to clarify some confusion that might have been caused.

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.

Response: Ok we will add the uncertainty and will comment on table 1, which includes most of the remaining 45%. It is noted that due to the complexity of isoprene oxidation mechanism there will always be some remaining uncertainty in closing the reactivity budget.

Reference for rate constants: Response: We have documented all rate constants in Table 1, but will include additions as suggested by reviewer 2.

Stating the estimated lifetime of MVK and MAC compared with isoprene would be useful. Response: This will be included in a revised manuscript.

As well as quoting the mean (MVK+MAC)/isoprene ratio of 0.44 the standard deviation would be useful: Response: OK we will include the std.

A reference for mentioned other possible sources of hydroxyacetone should be included. A reference for biomass burning as large source of hydroxyacetone should be included. Response: We will add added Yokelson et al, ACP, Atmos. Chem. Phys., 8, 3509-3527, 2008

Maximum acetonitrile mixing ratio enhancement of 0.6 ppbv should be quoted with the background level upon which it is elevated from. Response: Typical background levels of acetonitrile are 0.1-0.2 ppbv.

Would state 'chemical trajectory' to avoid any unnecessary confusion with a meteorological / dynamical trajectory. Reponse: ok we will incorporate this suggestion.

Authors should reference non-linear least square regression procedure used. Response: Seber, G. A. F., and C. J. Wild, Nonlinear Regression, John Wiley & Sons Inc., 1989.

Reference should be given to back up the importance of formaldehyde in total VOC reactivity used. Response: The importance originates from atmospheric chemistry schemes such as Carter, W. P. L. and Atkinson, R.: Development and evaluation of a detailed mechanism 377 for atmospheric reactions of isoprene and NOx, Int. J. Chem. Kinetics, 28, 497–530, 378 1996.

It has some conclusions but there should be a little more thought about the global implications of this work. Response: In a revised version of the manuscript we will address the impact of our observations on recent literature (Peeters et al., Paulot et al.), in particular uncertainties of modeling isoprene chemistry, which has a global impact. The influence on proposed HOx cycling mechanisms will also be addressed.

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. Response: yes this is the reaction with respect to OH, unfortunately the minus sign of the exponents got dropped during typesetting. We will fix this error.

Where does this scheme come from? There are no references or explanation of this. Response: this scheme is based on Table 1 (which includes all necessary references). The Yiso yields are based on this work, but have been extrapolated to other OVOCS which should exhibit fast production. We will update this table to accommodate sug-

gestions concerning yields for methylfuran by reviewer 2.

Figure 1. This figure and the section should be removed: Response: see our comment earlier. We believe there is valuable information in keeping this figure as it shows the photochemical origin of m/z 75.

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 derived should be given in the figure caption. Response: We will divide this figure in 2 panels, which will avoid the cluttering that the reviewer refers to. Reference for robust fitting: Holland, P.W., and R.E. Welsch. "Robust Regression Using Iteratively Reweighted Least-Squares." Communications in StatisticsâĂŤTheory and Methods. Vol. A6, 1977, pp. 813–827.

'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. Response: Normalized to 1 means that the sum of isoprene, MVK,MAC and hydroxyacetone on a molar basis adds to 1.

'Circles show case that includes fast production' of what? Response: of Hydroxyacetone

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. Regression: Same data as in figure 3a are used (normalized units). We performed a non-linear regression that minimizes the cost-function (= the system of differential equations outlined in equation 2 extended by a direct/fast hyac formation route) to obtain an optimal yield for the

production of hydroxyacetone that would explain the observed VOC ratios shown in figure 3a. We used a non linear least squares regression: Seber, G. A. F., and C. J. Wild, Nonlinear Regression, John Wiley & Sons Inc., 1989.

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. Response: We will add more information. The colored regions represent the reaction scheme outlined in table 2 without fast production of OVOCs. The dashed blue line represents the same scheme with fast production. Thus, the white space between the blue line and colored area presents the additional contribution of OVOCs if fast production as outlined in table 2 is included. We will extend this figure by including a mechanism proposed by Paulot et al. (as recommended by reviewer 2) and also leave the RACM mechanism as it shows the effect of lumping on the distribution of OVOCs. More discussion will be added in a revised manuscript.

General English comments: Response we will correct typos as suggested.

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