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Atmospheric
Chemistry
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Discussions

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

T. Karl et al.

tomkarl@ucar.edu

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We are thankful for a thorough review, which provides excellent suggestions for improvements. We address each comment below. As suggested we will expand the current discussion taking into account very recent literature:

Major concerns:

(1) The presentation of the vertical profiles and flux estimates (Sections 2.3 and 3.1) are tangential to the analysis and discussion and should be removed. These observations could form the basis of a separate paper.

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.

(2) The analysis approach considers a time trajectory in a box model with constant isoprene supply. While this approach addresses one aspect of the time dependence, it does not address the issue of mixing. The distribution function of oxidative age is not simply due to the continual addition of isoprene but also reflects the mixing of aged air from aloft. While it may not be possible to directly model how this impacts the conclusions of this work, the importance of this mixing should be addressed via a sensitivity study.

Response: The issue of mixing becomes important when investigating heterogeneous air masses where many different VOC sources within the concentration footprint can exist: Backtrajectories suggest that airmasses predominantly originated out of the NE during AMAZE; thus air masses were predominantly influenced by emissions from pristine forest. Based on regional scale aircraft flux measurements we have previously shown (Karl et al., JGR, 2007) that isoprene fluxes over pristine forest are fairly homogeneous in this part of the Amazon. As pointed out by the reviewer this leaves mostly vertical mixing. During a previous campaign we have investigated the impact of vertical down mixing based on aircraft flux measurements and obtained typical entrainment rates (see Karl et al., JGR, 2007). Entrainment rates for isoprene were estimated to fall between 10-30% of isoprene fluxes. Based on these findings we conclude that the time dependency of midday VOC evolution is mostly determined by photochemistry in the planetary boundary layer.

(3) The authors ascribe the rapid formation of hydroxyacetone to a first generation process involving the reaction of the isoprene peroxy radicals with NO. Paulot et al argued, however, that significant yields of hydroxyacetone arise quite promptly in the 2nd generation via the (very fast) reactions of the isoprene nitrates (ISOPN) and the hydroxycarbonyl (HC5) with OH. We suggest that the authors implement the Paulot et al. mechanism (Table 3, ACP, 9, 1479, 2009) to confirm that the hydroxyacetone

concentrations they measure are not consistent with the 2nd generation yields from the ISOPNs and HC5.

Response: The lumped mechanism by Paulot et al. has been implemented - the resulting analysis has been revised including the rapid secondary formation of hydroxyacetone from HC5 and isoprene nitrates. The hydroxyacetone yield (fast secondary production from HC5+isoprene nitrates (might play a minor role during AMAZE) + diboo) of the overall fast production route falls surprisingly close to our independent value inferred from the regression (e.g. 0.097 vs 0.083+/-0.022, both inferred for a MVK+MAC/isoprene ratio of 0.44). We will show the predicted OVOC reactivity along with previously lumped schemes in a revised figure.

(4) The authors should discuss the recent paper of Peeters, Nguyen and Vereecken (Phys. Chem. Chem. Phys., 2009, 11, 5935 - 5939, DOI: 10.1039/b908511d). Although Peeters et al did not comment on the implications of their study for environments such as AMAZE-08 where the peroxy radical chemistry is dominated by NO but where NO is less than 10 ppb, the thermochemical stability of the isoprene peroxy radicals calculated by Peeters et al implies that the distribution of isomers will be determined by thermodynamics rather than kinetics. This in turn suggests that the 1,4 and 4,1 isomers will react with NO much less frequently than estimated from the laboratory experiments. Indeed for NO mixing ratio of 100-300 pptv (pg. 13636), the yield of 1,4 and 4,1 products would be nearly zero, while the sum of the yields of MVK and MACR would be _90% with the remaining 10% being the 1,2 and 4,3 ISOPN. If true, this suggests that all the non-MACR routes to hydroxyacetone identified by Paulot et al would not occur in the AMAZE-08 environment.

Response: Peeters estimate that 70% goes through the 1,6-H-shift isomerization channel and that ~30% of the carbon flux is still channeled through conventional NOx paths. While it is true that the reported 1,6-H-shift would be so fast that it would always outcompete the traditional NO route, some fast production of hydroxyacetone could still occur through other channels (HC5 and ISOPN) assuming the mechanism by Paulot

et al. is representative for this environment. If the isomerization reaction postulated by Peeters is indeed as important, most of the fast (Z-1,4 and Z4,1) chemistry outlined by Paulot et al. would be almost irrelevant for the real atmosphere, as NO mixing ratios of >50 ppbv are needed to compete with the 1,6-H-shift. To our knowledge such high NO mixing ratios have never been observed in environments where isoprene plays an important role. Our observations and analysis on relative VOC ratios suggest that the 1,6 shift does not happen as fast as proposed. Whether these isomerization channels are as fast as proposed should be determined by future experiments. For example the energy barriers are already quite high (e.g. ~18-20 kcal/mol) and if they were only a little bit higher it could make these reactions so slow that they would not play a significant role anymore. Putting this in context of our findings suggests that the isomerization reactions proposed by Peeters et al. occur at a slower rate; this would obviously also have implications for the efficiency of HOx cycling through the 1,6-H isomerization channels. Various isomerization reactions reported by Peeters et al. (e.g. 1,5-H-shift vs 1,6-H-shift) span 3 orders of magnitude (>0.004 to >8 s-1). As suggested we have implemented the lumped reaction mechanism proposed by Paulot et al. (which also includes the formation route proposed by Dibble et al.) Assuming it can be used for conditions encountered during AMAZE, it could explain most of the fast production of hydroxyacetone observed in this and similar environments. Furthermore the MVK/MAC ratios inferred from GC-MS analysis suggest ratios on the order of 1.3-2.4. According to Peeters mechanism these would be expected to be significantly (e.g. >10) higher (see attached figure). We will include a detailed discussion and new data in a revised manuscript to clarify this point. We will also add discussion on a very recent paper by Paulot et al. (Science, 2009), who report observations of ISOPOOH under low NOx conditions. Their observations independently point towards a slower 1,6 shift. In a revised manuscript we will discuss consequences originating from the Peeters et al. mechanism with respect to two complementary approaches: for a given (MVK+MAC)/Isoprene ratio of 0.44 (figure 2) we have calculated corresponding MVK/MAC and HYAC/(MVK+MAC) ratios. From observations (including AMAZE) these are 1.3-2 and 0.2-0.3 respectively. From Peeters et al. we calculate 9.7 and 0.04 (thus both ratios are more than an order of magnitude off). These OVOC observations could be reconciled if the 1,6 shifts were lower and the thermodynamic stability of the trans 1,4 and 4,1 isomers was higher (significantly lower k's) as calculated by Peeters et al.

(5) The presentation of the material is not kind to the reader. It would be very helpful to have the prose divided into more PP each with topic sentences to guide us through your data and analysis. Many PP go on for pages while containing many ideas and pointing to numerous figures. The section headings are misleading.

Response: We will address this issue in a revised manuscript.

Technical corrections:

*p13633 line 7: Correlation btw glycolaldehyde+acetic acid and isoprene. Response: Here we can not exclude a significant presence of acetic acid which can have biomass burning, biogenic and other photochemical sources. This will influence the correlation.

p13638 line 24-29 The discussion of the chemical mechanism should be expanded along the following lines: The authors do not refer to the proper work of Dibble (2004 a,b) to support the discussion of double hydrogen shift mechanism (these papers, contrary to the statements in the manuscript, did not suggest hydroxyacetone formation). We suggest the authors reproduce the double H transfer hypothesized by Dibble et al. to help the reader understand the proposed source of hydroxyacetone (4% yield) as described by Paulot et al.

Response : Dibble et al., 2004, J. Phys. Chem. A, 2004, 108 (12), 2208-2215 âĂć DOI: 10.1021/jp0312161, suggested a scheme (scheme 2; page 2214) where Hydroxyacetone can be produced from IX'OH. Further on page 2214 it is mentioned that: 'Glyoxal, methylglyoxal, glycolaldehyde, and hydroxyacetone have been observed previously as products of the OH-initiated degradation of isoprene in smog chamber experiments,

but their formation was attributed to the secondary chemistry of the major products of isoprene. The present results do not falsify that suggestion, but do suggest an alternative or additional path for their formation.' We expanded discussion on this 'alternative or additional' (=fast) path for hydroxyacetone formation proposed by Dibble et al. 2004.

Finally there is no mention of a double H transfer in the work of Paulot et al. with respect to the organic acids or organic nitrates. (line 28).

Response: Ok we corrected this statement.

p13639 Section 3.3 The discussion of OH lifetime in the literature is very clouded and this manuscript could help clarify things by showing how sensitive the calculated OH lifetime is to assumptions about the general mechanism when many/most of the short-lived intermediates are not quanitified. A case in point: If the major 'fast' source of hydroxyactone is from the oxidation of ISOPN and HC5 (rather than the double-H transfer), this chemistry converts more reactive OVOC (HC5 and ISOPN) to less reactive OVOC (hydroxyacetone), in contrast to the claims made.

Response Here we discuss OH reactivity measurements mainly in the context of previous field experiments that were done close to isoprene emission sources. The photochemical age with respect to isoprene oxidation in these experiments is therefore low. It is beyond the scope of this manuscript to investigate every potential issue of previous OH lifetime measurements. We focus primarily on measurements that were conducted close to the isoprene emission source and that were used to infer large primary biogenic emissions. In order to explain these measurements in the context of photooxidation of isoprene, fast production of reactive OVOCs is needed. Indeed the production of ISOPN, which was previously not considered, could add additional reactivity. The overall impact of photochemical conversion from short – to longer lived species is depicted in Figure 4 and should answer the concern which is raised here. We will discuss this issue in more depth in the revised version by including results from the lumped mechanism proposed by Paulot et al.

The use of Yiso for 3-MF is perhaps not sound.

Resonse: ok we will change the analysis to reflect the recommended yields

*p13633 line 7: sentence will be clarified and changed accordingly

*p13634: ok more details on gradient flux method will be presented

p13637 Section 3.2 line 18 Evidence for the formation of hydroxyacetone from biomass burning requires a reference line 19 the use of acetonitrile as a biomass marker needs a reference

Response: We will add added Yokelson et al, ACP, Atmos. Chem. Phys., 8, 3509-3527, 2008

p13633 line 7 It is somewhat unclear whether the authors actually took into account the photooxidation of hydroxyacetone as suggested by Table 1 and 2 or neglected it as suggested by equation (2). This should be clarified.

Response: Photooxidation of hydroxyacetone was considered. This is now stated more clearly.

Fig 2 Fig 2 would be easier to understand if separated into two panels: a) MVK/MACR vs isoprene b) hydroxyacetone vs MVK/MACR

Response: Ok will be separated in two panels.

Fig 3a caption Booth ? Both: will be corrected.

Table 1: all the 10ËĘa should read 10ËĘ-a. Response: We corrected this typo which occurred during typesetting.

HC5 IUPAC name should be given what was assumed for HC5 fate? Response We used (2Z) 4-Hydroxy-2-methylbut-2-enal as a surrogate.

The authors should mention that the rate constant measured by Dillon et al (2006) is larger than the one commonly used (IUPAC states 3x10-12 a factor of two slower). This recent measurement was found to be consistent with the hydroxyacetone signal measured in chamber experiments (Paulot et al.)

Response: Ok this statement will be included.

Table 2: We now state. For sufficiently high NOx conditions. . .

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

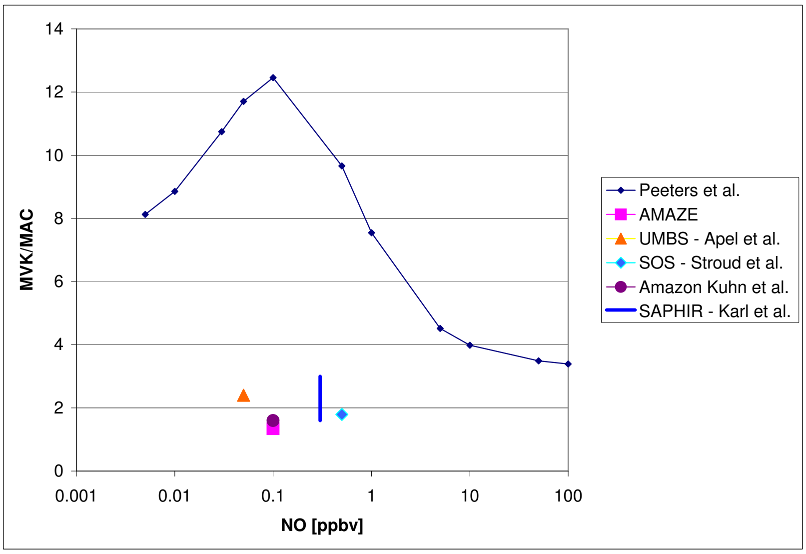

Fig. 1. MVK/MAC ratios