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Interactive comment on “Airborne observations of IEPOX-derived isoprene SOA in the Amazon during SAMBBA” by J. D. Allan et al.

J. D. Allan et al.

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We thank the reviewer for their constructive points and are happy to provide the following responses:

It would be relevant to mention here other major marker compounds for low-NO_x isoprene SOA; these do not only include the 2-methyltetrols but also the C₅-alkene triols and IEPOX-derived organosulfates. Suitable references would be Surratt et al. (2006) and (2010), of which the last one is already cited in the manuscript. The cited reference, Pye et al., 2013, is not so appropriate here. However, it could be cited in the context of acidity playing a major role in the formation of isoprene SOA through the IEPOX route.

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The purpose of the Pye et al. reference was not to introduce the markers, but to report that the modelled behaviour of the SOA generates the markers in the correct quantities in real-world scenarios. The text has been modified as follows: “One particular mechanism that has received much attention is through the formation of isoprene epoxydiols (IEPOX) under low-NO_x conditions and reactive uptake to the particle phase, which produces markers that have been observed in the atmosphere such as 2-methyltetrols (Paulot et al., 2009; Chan et al., 2010; Surratt et al., 2010; Surratt et al., 2006; Kroll et al., 2006). The work of Pye et al. (2013) indicates that model representation of these processes can produce the marker compounds in quantities comparable to observations.”

I would like to draw attention that an isoprene SOA marker data set is available for a field campaign conducted in the Amazon, namely the 2002 LBA-SMOCC campaign, which spanned part of the dry, the transition and part of the wet season (Claeys et al., 2010); hence, it would be worthwhile to evaluate whether the results obtained in the current study can be related to results obtained for the 2002 LBA-SMOCC campaign. The low-NO_x isoprene SOA markers, i.e., the 2-methyltetrols and the C₅-alkene triols, were measured in PM_{2.5} filter samples, and it could be shown that their levels were the highest in the dry season, where the aerosol was most acidic. More specifically, isoprene SOA marker compounds showed an average concentration of 250 ng/m³ during the dry period versus 157 ng/m³ during the transition period and 52 ng/m³ during the wet period. These data are consistent with acidity playing a major role in the formation of isoprene SOA.

We thank the reviewer for bringing this work to our attention. The following has been added to the discussion section regarding humidity: “The role of aerosol acidity has long been seen as necessary for uptake (Surratt et al., 2007b; Eddingsaas et al., 2010) and this conclusion was supported by observational data from this region presented by Claeys et al. (2010)...”. (see also response to the point regarding NO_x below for an-

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other use of this paper). In addition to this, another result from the SMOCC study (Karl et al., 2007) suggests that the enhanced photochemistry at the top of the boundary layer may arise from scattered light from cumulus clouds. A similar analysis from this dataset proved inconclusive and it may be that the clouds were too dispersed in this instance, however we have added this as a possibility to the actinic flux discussion as follows: “It should be noted that Karl et al. (2007) found evidence of enhanced isoprene photochemistry above the Amazon at cloud level that was attributed to scattered light from cumulous clouds. While this may be possible here, a similar analysis of MVK+MACR relative to isoprene did not show the pronounced enhancement at cloud level noted in that paper.”

The authors write: “none of the flights were completely free of influence of combustion sources, as evidenced by the presence of rBC”. Based on this observation one can thus expect that the organic aerosol will also contain organics originating from biomass burning, such as N-containing nitro-aromatic compounds, which are specific secondary organic marker compounds for biomass burning (Iinuma et al., 2010; Kitanovski et al., 2012). Nitroaromatic compounds such as methylnitrocatechols could contribute to the AMS m/z 30 signal, a proxy for organic nitrogen. It is thus well possible that the AMS m/z 30 signal is not only related to isoprene SOA nitrooxy organosulfates but also to nitro-aromatic compounds.

While this is hypothetically true, this is inconsistent with the vertical trends shown in Fig. 5. We have added the following text: “While the M30 may be due to nitro-aromatics which have been associated with biomass burning (Mohr et al., 2013), the vertical trends presented here do not match with the rBC, so it is not thought to be the case here.” We are reluctant to speculate too heavily on the precise chemical nature of any organic nitrates; see also response to reviewer 1.

Boundary layer profile: comment, no action necessary; a very relevant result is that there is a doubling of the m/z 82 AMS marker compound concentration from

20 to 40 ng m⁻³, although this concentration appears quite high considering that the precursors of this compound, 3-methyltetrahydrofuran-3,4-diols, are not major isoprene SOA marker compounds (Lin et al., 2012). The authors have done a considerable effort to come up with a reasonable explanation for this phenomenon. Among the different hypotheses the first one appears most likely but the last one, although somewhat speculative and impossible to test, also seems reasonable.

While the concentrations appear high, it is possible that they also represent MF from the thermal decomposition of other species. It is also possible that the 3-MeTHF-3,4-diol concentrations are higher in this environment than Lin et al., although this is all pure speculation.

Conclusions; lines 15-17: the authors mention that the rBC and NO_x concentrations were consistently low but exhibited some residual pollution, indicating that conditions do not have to be pristine for this mechanism to take place. I can concur with this conclusion; in fact, it is consistent with earlier field results from the 2002 LBA SMOCC campaign showing that the highest isoprene SOA marker concentrations were found during the dry period, where the impact of biomass burning pollution was the highest. It therefore would be worthwhile to conduct future airborne experiments in the Amazon and monitor the m/z 82 AMS signal during the dry season.

We have added the following to the NO_x discussion: “However, it is worth noting that Claeys et al. (2010) found that the isoprene SOA markers in Rondônia were highest during the dry season, corresponding to the highest NO_x concentrations, so in this context, it would seem unlikely.” We agree with the point about the need for further observations and on this note, we await the results of the (currently ongoing) GOAMA-ZON campaign with much interest.

I am aware of a paper reporting high isoprene SOA levels at the top of a Chinese

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mountain based on filter measurements and wonder whether these observations could be related to the observations of the current study (Fu et al., 2010).

We thank the reviewer for bringing this to our attention. A direct comparison is difficult because the geographic region is different and the sampling location is static, however we do note that they found that the isoprene tracer concentrations were greater at nighttime when temperatures were lower, so this may be relevant. We have added the following to the discussion, regarding repartitioning: “This would be consistent with the observations of Fu et al. (2010), who found an increase in isoprene SOA tracers at night-time at an elevated site in China, and the modelling work of Henze and Seinfeld (2006), who predict enhanced partitioning to the particle phase at higher altitudes.”

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