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Atmospheric Chemistry and Physics
Discussions

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

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We thank the reviewer for their comments. We are happy to respond as follows:

I would say it "mostly occurs" under the low-NO route, but recently Matt Elrod's group (Jacobs et al., 2014, ACPD) showed that OH radical-initiated oxidation of synthetic isoprene hydroxynitrates can yield IEPOX in lower yields (13%) compared to the OH radical-initiated oxidation of ISOPOOH (which is about 50-75% yield).

We thank the reviewer for bringing this to our attention, although we should point out that that this paper was unpublished at the time of the initial submission of our paper. Nevertheless, it is certainly a useful contribution to the discussion and we made the

modification as suggested.

Insert appropriate citations for the NOx dependence. These include Kroll et al. (2006, EST), Surratt et al. (2006, JPCA), and Surratt et al. (2010, PNAS).

These have been added as part of addressing reviewer 2's comments; see associated reply.

If you are going to be specific about sites, I would also say the ground-based Canadian observations by Slowik et al. (2011, ACP) and ground-based measurements in downtown Atlanta, GA by Budisulistiorini et al. (2013, EST).

Modified as follows: "This marker has now been reported in a number of environments using ground-based AMS and ACSM measurements, for example in Canada (Slowik et al., 2011) and downtown Atlanta, GA (Budisulistiorini et al., 2013)…"

Not necessarily true if hydroxynitrates are being formed from RO2 + NO. As recently shown by Elrod's group (Jacobs et al., 2014, ACPD), synthetic isoprene-derived hydroxynitrates will yield IEPOX once they are further oxidized by OH radicals.

See above. This line of discussion has been added as follows to the NOx discussion: "Furthermore, recent work by Jacobs et al. (2014) indicates that it is also possible to form IEPOX from isoprene hydroxynitrates in the 'high NOx' regime." This, combined with the Claeys et al. (2010) paper (see response to reviewer 2), leads us to believe that NOx is not the critical factor.

I think the arguements about IEPOX-OA factor (or m/z 82 ion) shifting from that factor to more LV-OOA is spectulative at this time and should be more stated as so. The reason for this is there is a lot more data from the recent SOAS 2013 study that shows from multiple sites that this IEPOX-OA factor is present, is incredibly low volatility, and likely has an atmospheric lifetime of 2 weeks. This data hasn't been published yet, but the authors should be aware of this and be

careful in making this conclusion with such a limited data set.

In the discussion, we very clearly state that this conclusion is dependent on the assumption that the organic matter aloft is from a common source as the boundary layer material, which may not be the case. While this result is far from conclusive, we feel it prudent to report the observation and it is not possible for us to take account of unpublished results that we have not yet seen. However, in light of this discussion, we have made the caveat clearer in the conclusions as follows: "While this could be due to mixing with a highly-processed free tropospheric background aerosol, it is also consistent with progressive oxidation and functionalization of the organic matter. If this is the case, it implies that the m/z=82 marker is not conserved and therefore may only be suitable as a marker in the near-field. More work in the laboratory and comparisons with other observations in the field are needed to investigate these hypotheses further."

The authors need to be careful here with this conclusion. Although the m/z 82 appears to not be conserved, PMF analyses which is typically used to evaluate AMS organic mass spectral data could still resolve a factor related to IEPOX chemistry. My group has consistently found this in the SE USA, especially from the recent SOAS 2013 field study. Comparison of off-line filter tracer data with this hypothesized IEPOX-OA PMF Factor (which typically has a m/z 82 characteristic ion for its associated mass spectrum) is highly correlated (R2 >0.8). These IEPOX-derived SOA tracers are only highly correlated with this PMF factor and NOT LV-OOA (or any other PMF factor). The question is would the IEPOX-OA factor be more fresh IEPOX-derived SOA at the ground? This seems to remain an unanswered question in the present study with this limited data set.

See response to previous comment regarding the caveat and our inability to take unpublished SOAS results into account. In the event that there is chemical degradation taking place, PMF will still succeed in quantitatively resolving the factor, providing that the degradation is not complete (i.e. the mass spectrum has not become indistinguishable from LV-OOA) and the amount of degradation experienced over a given dataset

does not vary. If the level of degradation is variable, a fraction would be misattributed as one of the other OOA factors, owing to limitations of the linear data model employed by PMF. Furthermore, given the factor seems to follow the signal at m/z=82 in Robinson et al. (2011), it is reasonable to expect that the underestimated IEPOX-SOA PMF factor would follow the chemical tracers responsible for this fragment, which in turn would follow the same hypothetical degradation. Therefore, a high degree of correlation between PMF and tracer analysis does not preclude any degradation between source and receptor taking place. The reviewer is correct in stating that the issue remains unresolved with this work, however we feel it is worth mentioning because the chemical lifetime of the tracers (which will not be infinite) is something that will need constraining. The need to investigate this further is already stated in the conclusions and I am sure that the SOAS data will make a significant contribution to our understanding when it is published.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 12635, 2014.