

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

Anonymous Referee #3

Received and published: 8 August 2014

Overall Comment and Recommendation:

This study presents novel aircraft AMS measurements of a marker ion at m/z 82 that is ascribed to isoprene epoxydiol (IEPOX)-derived SOA over the Amazon during the transition to the wet season. The m/z 82 ion signals observed in AMS/ACSM data sets have been clearly shown in prior work to be associated with IEPOX-derived SOA products (such as the isomeric 3-methyltetrahydrofuran-3,4-diols) (Robinson et al., 2011, ACP; Lin et al., 2012, ES&T; Budisulistiorini et al., 2013, ES&T); I disagree with one of the other reviewers about their concerns with this ion, especially when PMF is involved. This work seems to support prior lab (Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T; Nguyen et al., 2014, ACP), field (Froyd et al., 2010, PNAS; Lin et al., 2012, ES&T; Lin et al., 2013, ACP; Budisulistiorini et al., 2013, ES&T) and modeling

C5705

(Pye et al., 2013, ES&T; Karambelas et al., 2014, ES&T Letters) studies that indicate the importance of acidic sulfate aerosol in promoting IEPOX-derived SOA formation. The measurements presented here are very unique and lacking in the literature and will likely provide a lot of future discussions on how to think about IEPOX-derived SOA formation throughout the boundary layer and free troposphere. I highly recommend this manuscript for publication in ACP, but I kindly request that the authors seriously consider my specific comments/suggestions below before publication as well as the other two reviewer's comments.

Specific Comments/Suggestions:

1.) Page 12636, Abstract, Lines 6-7:

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 ISOPPOOH (which is about 50-75% yield).

2.) Page 12637, Introduction, Lines 4-7:

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

3.) Page 12638, Introduction, Lines 9-13:

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, ES&T).

4.) Page 12647, Results, Lines 26-29:

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.

C5706

5.) Page 12653, Discussions, Lines 1-4:

I think the arguments about IEPOX-OA factor (or m/z 82 ion) shifting from that factor to more LV-OOA is speculative 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.

6.) Page 12653, Conclusions, Lines 18-27:

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 ($R^2 > 0.8$). 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.

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

C5707