

Interactive comment on “Influence of urban pollution on the production of organic particulate matter from isoprene epoxydiols in central Amazonia” by Suzane S. de Sá

Anonymous Referee #1

Received and published: 11 February 2017

In this work, de Sa et al. presented measurements of isoprene-derived secondary organic aerosol in central Amazonia. Specifically, using positive matrix factorization of aerosol mass spectrometry data, they isolated SOA from isoprene epoxydiol (IEPOX-SOA) and showed the complex dependence of this factor on anthropogenic emissions from nearby urban area (sulfate, nitrogen oxides). This work uses field measurements to highlight some aspects of isoprene chemistry that has been shown first in laboratory and then in other field studies. I believe this work is important and should be published in ACP. I have minor comments only:

1. It is a little puzzling that total PM does not trend with IEPOX SOA. Given the location, I would imagine that in this area the SOA chemistry is dominated by IEPOX SOA. I

C1

understand that there will be another manuscript addressing the full PMF work, but it seems like if there is any location in the world where IEPOX SOA is most dominant, it would be in the Amazon. It seems like the remaining OA dampens some of the variations in IEPOX-SOA, leading to the rather constant total OA. Perhaps the authors can consider just briefly address why in the manuscript?

2. How is the observed sulfate produced? Are they direct emissions from Manaus, or SO₂ emitted from Manaus and converted to sulfate in the few hours of transit to the field site? In the conclusions (Ln 534-542) the discussion seems to assume that SO₂ and sulfate are equivalent. They might not be if the sulfate is coming from SO₂ oxidation in transit.

3. Just another thought about sulfate: could sulfate just be an indicator of degree of oxidation? Since sulfate is a secondary product, it is possible that the variation in sulfate is driven by degree of processing, rather than variation in source strength. Have the authors looked at other indicators of oxidation (e.g. odd oxygen, NO_y/NO_x ratio, hydrocarbon clocks) to isolate this effect?

4. As the author stated, this environment is different from SE US, in that sulfate levels are generally lower and reduced sulfur can contribute to total sulfate. Are there any indications that reduced sulfur species would be measured as SO₄ in the AMS?

5. Are there any estimates of HO₂ concentrations? The switch from IEPOX production (under HO₂ dominated chemistry) to high NO_x chemistry happens at around HO₂/NO = 1 (since RO₂+NO and RO₂+HO₂ rate constants are quite close). From the data, it appears that the switch happens at around 0.5 ppb NO, which would suggest that HO₂ levels are also around 0.5 ppb. That seems reasonable, but perhaps the authors can explain that in the manuscript to solidify this point.

6. The authors have largely focused on R₂ when looking at regressions and demonstrated that, for example, IEPOX-SOA and SO₄ are correlated. It would be interesting to also look at the slopes, and compare the sensitivity of IEPOX-SOA to SO₄ across the

C2

different field studies (and maybe even lab studies). There are, of course, many other factors that would affect this sensitivity (pH, NO_x, aerosol liquid water content etc.). But maybe some simple relationships will emerge that would help construct simplified models to represent these complex chemical systems.

7. In Section 3.1, the authors compared the IEPOX-SOA factor to that observed in other studies. Listing the fractions is useful, but it would be even better to compare the mass spectra (like the authors did with the factor from previous study in the same location). That way it would be more convincing to argue IEPOX-SOA factor is ubiquitous.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1020, 2016.