

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.

james.allan@manchester.ac.uk

Received and published: 9 September 2014

We thank the reviewer for their helpful and stimulating comments. We would like to provide the following responses:

The analysis of the contribution of isoprene as SOA precursor is based on a single m/z peak (m/z 82). As the authors correctly state this mass peak is observed from organic aerosol in a variety of laboratory and field measurements and not by itself specific. In particular it is also found in SOA from biogenic monoterpene emissions (e.g. Kiendler-Scharr et al., EST 2009). An unambiguous identification of isoprene SOA is thus not provided by the presence of m/z 82 alone, even with the fractional contribution of m/z 82 exceeding typical values of 4%. Although

C6698

the authors state that factor analysis of the in flight data did not lead to conclusive isoprene-SOA factors, they should attempt to strengthen their analysis by including other mass peaks found in SOA from isoprene. Experiments using fully deuterated isoprene as precursor have identified a number of more prominent ions in the SOA from isoprene (Kiendler- Scharr et al., 2012). Surely there is more information on AMS spectra in the literature from laboratory experiments producing SOA from isoprene at low NO_x conditions that can be used in this context. This could also support the interpretation of the mass spectral differences between “fresh” and “aged” organic aerosol (Figure 6).

See comments from reviewer 3, who feels that the use of the marker is appropriate. While we recognise that using only a single peak has limitations, the reason this approach is chosen is because this is the mass spectral feature that most clearly distinguishes this from other SOA types. Regarding Kiendler-Scharr (2009), the signals at m/z=82 do not appear to be as high as 8% and furthermore they are not higher than the mean of m/z=81 and 83 which is another defining feature described by Robinson et al. (2011). The fact that there are other, higher-intensity peaks present in the isoprene SOA spectrum is clearly recognised in Robinson et al. (2011), however these other peaks are also very prevalent in monoterpene SOA and would therefore give inconclusive results if used in a tracer analysis such as this. In absence of a successful PMF factorisation, the only way of using the complete mass spectra would be to assume a mass spectral response to IEPOX SOA and apply an algorithm such as ME-2, however there is insufficient consistency within the literature to make such an a priori assumption and we would therefore not be able to make such an analysis with any confidence. To address this point, we have added the following to the introduction: “While the majority of the mass is contained within other peaks (Kiendler-Scharr et al., 2012; Robinson et al., 2011), these are common to many other forms of SOA and are therefore unsuitable for marker-based analysis.”

I am concerned with the interpretation that a higher contribution of m/z 30 in

C6699

some flights can be taken as evidence that organic nitrates play a role during these flights. If I understand correctly, the C-TOF instrument used here does not provide the mass resolution required to distinguish individual peaks on nominal mass m/z 30? How can a contribution from organic ions (CH₂O⁺) be excluded?

We are not strictly concluding that there are organic nitrates present, but that there could be organic nitrogen, as amines could also be responsible. While the reviewer is correct in saying CH₂O⁺ could also be responsible for a signal at m/z 30, this is generally a minor fragment in organic mass spectra but we recognise that we should include this as a caveat. However, it is also important to point out that even if this is the case, it is still unlikely that inorganic nitrate is responsible, so the main point of discussion regarding acidity still stands. The following text has been added: "While this generally tends to be a very minor organic fragment under most ambient conditions, the dominance of organics over inorganics in this instance means that it cannot be ruled out. However, this being the case, this would not detract from the argument that it is not as a result of inorganic nitrate."

Refer to table 1 when first mentioning the different flights discussed.

Modified as suggested.

Using data from a flight where the orifice was partially clocked needs more caveats to be mentioned. How can one be sure that ratios are unchanged by this? Is there evidence that ratios discussed are independent of particle size and losses through the clocked orifice are independent of size?

While the results from this flight are compromised, we believe them to be worth including because they are still consistent with the overall picture. While the losses are likely to be size-dependent, this will not impact the ratios if the composition is independent of size, which given that we consider the composition to be dominated by SOA, is an assumption we believe to be reasonable. We have added the following caveat: "This is assuming that the losses apply to all chemical constituents equally; while the

C6700

losses may be size-dependent, the composition is likely to be equal for all sizes if it is dominated by secondary material."

The exclusion of the possibility to observe "excess ammonium" is too strong in my opinion. It was shown previously that at least oxalic acid is readily partially neutralized by NH₄ in the particle phase (Mensah et al., 2011). Also recent discussions point towards a more complex role of NH₄ in particle chemistry (e.g. Nguyen et al., 2013). In a forested region ammonia and amines may be crucial.

While we don't believe this to be true in this instance (oxalic acid gives a strong signal at m/z=44, which is not observed here), this is besides the point; the NH₄ balance using only sulphate is purely hypothetical and the important detail here is that there is more ammonium present than can be explained by sulphuric acid alone (as opposed to the Amazonas flights). Regardless of the nature of the additional acid (be it nitric or oxalic), this strongly suggests that the particles are pH neutral. We already state that we have not accounted for organic acids and we go on to discuss the role of ammonia in SOA formation later in the manuscript.

The discussion that inorganic matter during B749 and B750 may have been present as solids seems unlikely in the context of a CE of 1 for all flights.

This is a fair point. While we speculate that the CE of 1 is due to the particles being liquid, we believe this to be a property of the organic matter that dominates the composition and given the apparently low oxygen content of the organic matter, it is likely that this is in the form of an organic liquid rather than an aqueous solution, which is what is required to promote the Nguyen et al. mechanism. This point is clarified in the revised text as follows: "As such, it is possible that the inorganic matter during B749 and B750 existed as a solid or as a non-aqueous organic liquid..."

The discussion on the role of nitrogen and sulphur in organic aerosol is purely speculative and should be skipped.

C6701

Given the amount of discussion devoted to this topic in the literature (See response to reviewer 2), we felt that we should comment on how this work contributes to this, or rather doesn't; the intended purpose of this paragraph was to state that this avenue of investigation would require additional instrumentation. The paragraph has been reworded as follows: "While there is considerable interest in the literature concerning the role of sulphur and nitrogen in the formation mechanisms (Nguyen et al., 2014; Gomez-Gonzalez et al., 2008; Surratt et al., 2007a), it should be noted that only very limited conclusions can be drawn here. In addition to the M30/M46 data possibly indicating some role of organic nitrogen, the sulphate to rBC ratio shows a positive gradient with altitude within the boundary layer in B749 (albeit a weaker gradient than the equivalent organic ratio). This may point to the measurement being influenced by organosulphates, although the fact that the sulphate ratio continues to increase at a similar rate above 1 km (unlike the organic ratio) would detract from this argument. Ultimately, while these data give some intriguing results, given the difficulties in discriminating and quantifying organic sulphur and nitrogen species with the AMS (in particular with the C-TOF), it is difficult to see that any strong conclusions can be drawn here. Further investigation will require the use of additional measurement techniques."

In the discussion on vertical boundary layer profiles of Org82 gas-phase photochemistry is excluded as potential reason for the strong gradient based on the observation of constant actinic flux. Yet the temperature did change in the discussed region. Can T-dependent lifetimes of intermediate species play a role here?

Hypothetically, this is a possibility, but answering this would require modelling work that currently lacks constraint. This is added as a speculative possibility: "Hypothetically, it is possible that the reduced temperature at altitude may also be affecting the chemical reactions, but this is difficult to test here without detailed modelling that is difficult to constrain."

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

C6702