

Reviewer #1

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 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<sub>x</sub> 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 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 (CH<sub>2</sub>O<sup>+</sup>) 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 CH<sub>2</sub>O<sup>+</sup> 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 clogged 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 clogged 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 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 NH<sub>4</sub> in the particle phase (Mensah et al., 2011). Also recent discussions point towards a more complex role of NH<sub>4</sub> 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 NH<sub>4</sub> 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.**

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."

Reviewer #2

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<sub>x</sub> isoprene SOA; these do not only include the 2-methyltetrols but also the C<sub>5</sub>-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.**

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<sub>x</sub> 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<sub>x</sub> isoprene SOA markers, i.e., the 2-methyltetrols and the C<sub>5</sub>-alkene triols, were measured in PM<sub>2.5</sub> 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/m<sup>3</sup> during the dry period versus 157 ng/m<sup>3</sup> during the transition period and 52 ng/m<sup>3</sup> 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<sub>x</sub> below for another 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<sup>-3</sup>, 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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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) GOAMAZON campaign with much interest.

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

Reviewer #3

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 NO<sub>x</sub> dependence. These include Kroll et al. (2006, ES&T), 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, ES&T).**

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 RO<sub>2</sub> + 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 NO<sub>x</sub> discussion: "Furthermore, recent work by Jacobs et al. (2014) indicates that it is also possible to form IEPOX from isoprene hydroxynitrates in the 'high NO<sub>x</sub>' regime." This, combined with the Claeys et al. (2010) paper (see response to reviewer #2), leads us to believe that NO<sub>x</sub> is not the critical factor.

**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.**

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 ( $R^2 > 0.8$ ). 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.**

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.