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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Secondary Organic Aerosol from biogenic VOCs over West Africa during AMMA" *by* G. Capes et al.

Anonymous Referee #2

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This manuscript describes measurements of organic aerosol and VOCs measured from an aircraft platform during the AMMA campaign, and an analysis of the magnitude of secondary organic aerosol (SOA) sources. The analysis suggests that the oxidation of isoprene and monoterpenes forms a sufficient amount of SOA to account for all the aerosol measured, rendering the SOA budget essentially "closed". This is in contrast to other measurements taken at higher latitudes, which find much more aerosol than models predict, implying that purely biogenic SOA (formed under pristine conditions) is well-understood whereas anthropogenically-influenced SOA is not. The topic of the paper is of great interest; the data and the writing are of high quality; and the analysis is for the most part carefully done. However there is one major error in the analysis, related to the choice of SOA yields used (discussed below). This error unfortunately

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is large enough that correcting it will dramatically affect (and possibly reverse) the conclusions of the work. Thus this manuscript cannot be published until this is corrected (or at least addressed in detail) and the conclusions are rewritten accordingly.

The SOA yields chosen were 3% for isoprene, 15% for a-pinene, 3.2% for b-pinene, and 8.7% for limonene. These are stated to be constrained by chamber studies, specifically Griffin et al., 1999, Kroll et al., 2006, and Ng et al., 2007. Several yields were measured in each of those chamber studies; the yields chosen for this work were often (but not always) those measured at the lowest levels of aerosol loading. However, in all cases but isoprene, those lowest loadings were still much higher than what was measured in AMMA: 7-40 ug/m3 vs 1 ug/m3. Because SOA yields are loading-dependent (due to semivolatile partitioning) the yields in those chamber experiments therefore will be higher than those in the atmosphere. Taking the yield fits from Griffin et al. [1999], extrapolating down to 1 ug/m3 of aerosol, and correcting the partitioning coefficients to 298K (assuming dHvap=42 kJmol/mol), gives SOA yields from monoterpene oxidation of 1-3%, 3-10 times lower than the values used in this manuscript. Similarly, SOA yields from isoprene have been measured at such low loadings, and were found to be about 1% [Kroll et al., 2006], 3 times lower than the yield used here.

Use of these yields would lead to significantly lower calculated amounts of SOA (by a factor of 3 or more). Loading-dependent yields were used in most of the "higher-latitude" studies, [e.g., Volkamer et al., 2006] and so using the same approach would seem to be necessary before any sort of direct comparison between studies can be made. I think the authors should redo their analysis using the same yields used in one of those studies before making any conclusions about biogenic vs. anthropogenically-influenced SOA. Based on the above numbers, however, it would seem that SOA is underpredicted in this case as well, by an amount roughly consistent with the numbers in Figure 2 of Volkamer et al., 2006. This is an important conclusion, as the dataset (SOA and VOC measurements in a low-latitude, pristine environment) is unique, but it's the reverse of what is concluded in the current form of the manuscript.

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There are several factors which might explain the underprediction, such as effects of NOx level and errors from extrapolating chamber data to low loadings [Presto and Donahue, 2006], but these are general issues and not specific to the current measurements/analysis. In other words they point to problems with chamber studies [Griffin et al., 1999; Kroll et al., 2006; Ng et al., 2007] and/or the inclusion of chamber yield data in atmospheric models [Heald et al., 2005; Volkamer et al., 2006]; they do not necessarily imply fundamental differences between SOA formation in clean vs. polluted environments.

Other comments:

- I agree that the neglect of sesquiterpenes will contribute to an underestimation of SOA loadings; however this general issue - neglect of lower-volatility, high-yield SOA precursors - is not unique to biogenically-influenced areas. For example the oxidation of large (C15+) alkanes is not included in most models but forms SOA extremely efficiently [Lim and Ziemann, 2005; Robinson et al., 2007].

- p.2534, line 26: the discussion of SOA underestimation should probably reference more papers to show it's a common model result. One of the papers that is cited [Jang et al., 2002] does not directly deal with model-measurement comparisons.

- p. 2535, line 18: only 17 of 24 flights were included; it's never stated why 7 were omitted (I assume it's to remove the effects of biomass burning, etc., but this should be stated explicitly).

- Equation 1: a short derivation might be helpful here. The key assumption is that the measured MVK and MACR gives the total amount of isoprene oxidized; but this only works for the first several (8) hours, before MVK and MACR begin reacting away also. If the air masses measured have spent a lot of time (many hours to days) over vegetated areas, this approach may underestimate integrated isoprene (and therefore monoterpene) emissions. On the other hand, if this air is relatively "young" (coming from the ocean), or the lifetimes of the particles (vs. vertical transport, for example) are short,

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then this method should be an accurate estimate of total isoprene (and monoterpenes) emitted and oxidized. A discussion of meteorology may help distinguish these.

- p. 2543, line 9: I'm unaware of any chamber studies that show continuous growth after 24 hours (or even last that long!). In batch reactor studies of SOA formation from isoprene, aerosol growth appears to be over after 6-10 hours [Kroll et al., 2006; Dommen et al., 2006].

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