

Interactive comment on “Anthropogenic influence on biogenic secondary organic aerosol” by C. R. Hoyle et al.

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I read the Hoyle et al. paper with interest as it addresses an important topic, and I have listed below a few comments about various points which I hope will be useful in revising the paper. (However I am not a referee and I have not attempted to provide a comprehensive evaluation, or to address all the issues I noticed).

- I concur with previous comments from Jason Surratt about the potential importance of the NO₂/NO ratio for isoprene SOA and of organosulfates, and with Referee 2 about the fact that the paper seems to be really a review and it should be presented as such.
- The abstract states that “However, until now, the possible anthropogenic enhancement of secondary organic aerosol formation from naturally emitted precursors has not

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been explicitly accounted for.” This is incorrect. This topic has been addressed directly and explicitly by a recent paper by Carlton et al. (“To what extent can biogenic SOA be controlled?”, ES&T 2010), and which is cited in the current paper. Even before the Carlton paper, the topic had been addressed multiple times before in experimental (e.g. Weber et al. 2007, cited in the manuscript) and modeling papers (e.g. Tsigaridis et al., 2006, cited in the manuscript). E.g. the latter paper states in the abstract “The presence of anthropogenically emitted primary particles in the atmosphere facilitates the condensation of the semi-volatile species that form SOA onto the aerosol phase, particularly in the boundary layer” which seems to precisely do what the abstract of the present paper says it hasn’t been done.

- Page 19519 Line 13: the study of An et al. (2007) is mentioned as reporting the volatility of SOA from oxidation of BVOCs. First, the An et al. paper only reports results for α -pinene, not all important BVOCs or even the few most important ones. Second, the very high volatility of α -pinene SOA reported by An et al. (2007) has not been confirmed by other studies. While An et al. report that only 2% of the SOA mass remains at 75C, Huffman et al. (2009) report that 50% of the mass remains at that temperature, using a thermal denuder with 2/3 of the residence time of that of An et al. An almost identical curve to that of Huffman et al. is reported by Poulain et al. (2010), using a thermal denuder of the same design and residence time as that of Huffman et al. A thermogram with ~70% of the mass remaining at 75C was reported by Meyer et al. (2009). These authors do not report a residence time, which may be shorter than in the other studies. At the recent International Aerosol Conference I saw a thermogram in a poster from a different group using a similar thermal denuder to those of Huffman and Poulain, and with very similar results to those studies. Thus, and until these discrepancies have been understood, it is inappropriate to make conclusions based solely in the results of An et al. and ignore multiple other reports which contradict those results.

- Page 19521, Line 16: the authors state here that “The presence of a well-mixed

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organic phase with little or no water present is likely in controlled chamber experiments, and is generally observed far from point sources (Murphy et al., 2006).” I can’t see any mention to the number of phases of the organic aerosol or its / their water content in that Murphy et al. paper, which rather addresses the presence of organics on individual atmospheric particles. To my knowledge the PALMS instrument doesn’t have the ability to discriminate the phase state of the organic species or the water content specifically associated with the organic phase(s).

- Page 19521 line 27: the effect of acidity is mentioned here without any reference. I expected to find a whole section on the effect of acidity on biogenic SOA, as acidity is mainly due to anthropogenic sources, but other than this brief mention and the mostly unrelated review of nucleation by SO₂, it is not discussed in the paper. The recent body of work on organosulfates deserves mention. A large body of laboratory literature on possible acid-catalysis effects on SOA yields should also be mentioned, even if the initial large yield enhancements have been tempered by later results. In addition, several studies tried to assess whether there was an effect of acidity on SOA formation under ambient conditions and found the evidence unconvincing (Takahama et al., Zhang et al., 2007), and this could be discussed here.

- Page 19524 and Figure 1: a broader compilation and re-parameterization of the isoprene SOA yield data has been published recently by Carlton et al. (2009). This paper is not cited, but the authors need to address whether their brief discussion and figure on SOA yields from isoprene really goes beyond what Carlton et al. had already published.

- Page 19526 lines 20-25: on the topic of OA in the Amazon, the recent reports from Chen et al. (2009) and Martin et al. (2010), as well as Poschl et al. (2010 – published after Hoyle et al.) report that the submicron mode (during periods without outside source contribution) is dominated by biogenic SOA while primary biological particles are mostly confined to the supermicron mode.

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- Page 19531: the method which is being proposed here and billed as new seems to be the same as already implemented in several papers by Szidat and co-workers.

The difference between modern (as measured) and “non-fossil” or “contemporary” carbon that takes into account the enhancement in modern carbon due to atmospheric nuclear bomb tests should be mentioned, as it causes much confusion in the interpretation of ¹⁴C studies. E.g. Marley et al. (2009) reported modern carbon as if it was non-fossil carbon without any mention of this effect. Szidat et al. (2009) report that wood burning OA contains 116% modern carbon, and this effect needs to be corrected for before a quantitative interpretation is possible.

In addition the fact that a substantial fraction of urban emissions may be composed of modern carbon (e.g. ~20% in Los Angeles in an older study, Hildemann et al., 1994) is not accounted for explicitly in the method as proposed here. This fraction may in fact be higher for modern urban areas after the application of stringent emission controls to motor vehicles, e.g. several recent papers report contributions of cooking OA of the same magnitude as those from motor vehicles. E.g.:

+ Allan et al. (2010) reported 40% POA from vehicle emissions and 34% from cooking in London

+ Sun et al. (2010) report that cooking OA contributes 21% of the OA to 25% of HOA (~traffic POA) in New York City

+ Huang et al. (2010) report 18% for combustion HOA and 25% for cooking-related POA in Beijing.

These recent papers are consistent with some previous literature using molecular markers such as Zheng et al. (2007), who reported an average contribution of cooking of 36% of the OC in Atlanta. To first order one should assume that the emissions of SOA precursors are proportional to the POA emissions (following Robinson et al., 2007, cited in the manuscript), so the POA fractions reported there would also translate

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to the modern fraction of urban POA + SOA.

In any case this fraction may be more far important than the authors seem to acknowledge, and needs to be estimated directly in any study attempting to use ^{14}C data in urban areas for source apportionment. E.g. if in an urban area 50% of the carbon is non-fossil, many readers of this paper will assume that it is all biogenic SOA (a different crowd will assume it is all from biomass burning). However if 25% of the POA and a similar fraction of the SOA is due to cooking and another 10% of the POA and SOA to other urban sources of non-fossil carbon, a quick calculation shows that only $\sim 23\%$ of the non-fossil carbon would be due to non-urban sources, which points to quite a different interpretation. Again, these effects needs to be accounted for explicitly in methods such as the one proposed in this paper.

- Page 19533 line 16: a recent report by Lee et al. (2010) shows a remarkably constant ratio of the AMS biomass burning marker (m/z 60) to total BB POA. In addition the effect of atmospheric aging on BBOA markers such as levoglucosan and m/z 60 (they seem to be reduced but not eliminated, probably due to the solid nature of ambient OA, see Virtanen et al., Nature, this week) could be mentioned.

- Page 19357 lines 28-29: regarding the use of CO as a tracer in e.g. the Weber and de Gouw studies, my understanding is that enhancements of CO in the urban plumes were clear (few hundreds of ppbs in relatively narrow plumes), and are unlikely to be confused with the biogenic contribution which would be much more diffuse and not result in plumes.

- Page 19538 lines 6-7: production of CO within the plume is mentioned, but this would only reduce the estimates of SOA when using $\text{OA}/\Delta_{\text{CO}}$ as the metric and thus accounting for this effect would result in stronger, not weaker conclusions about the strength of SOA formation in urban plumes. It is unclear then why it is mentioned in this paragraph, where the authors list caveats to the conclusions of the previous studies. In addition, my understanding was that CO formation on the timescales of

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these plumes would be only a couple of percent, e.g. Griffin et al. (2007).

Minor comments

- Page 19517 line 15: I believe the reference should be to Zhang et al. 2007, not 2006 for this point.

- Page 19524 line 1: do the authors really mean OH + NO here?

- Page 19528 line 14: the Stolzenburg paper cited here reached conclusions about the contribution of sulphuric acid to nucleation events in Pittsburgh based on growth rate measurements. It seems that the direct composition measurements of growing particles at this same location from Zhang et al. 2004 could also be mentioned.

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