

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

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Received and published: 2 December 2010

We would like to thank Jose Jiminez for taking the time to provide such a detailed comment on our manuscript, which has lead to substantial improvements. The manuscript was intended as a review of published results and not a presentation of new work. The title and abstract have been slightly modified to clarify this.

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

You are correct, I have changed the reference, and also added Kanakidou et al. 2005.

Page 19519 Line 13: the study of An et al. (2007) is mentioned as reporting the
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Full Screen / Esc

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Interactive Discussion

Discussion Paper



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.

We fully agree with Dr. Jimenez assessment of the evidence about the volatility of first-generation BVOC oxidation products. We did not mean to evaluate similarities and differences in various volatility experiments, but simply to highlight that partitioning seems to control, at least in part, organic mass loading. The lead into this section was poorly worded and we rewrote it for the revised version of the manuscript: “In the atmosphere BVOC molecules react with OH, O₃ or NO₃ to form more functionalized molecules. These reaction products form a distribution in volatility space, with some being able to reversibly partition into the condensed phase. Observations of organic mass loading dependent aerosol yield are generally modelled using equilibrium gas/particle partitioning (Pankow, 1994; Odum et al., 1996; Donahue et al., 2006b), and observations show often lower yields under conditions with low organic aerosol loadings (0.1–1 $\mu\text{g m}^{-3}$). Any process that increases organic aerosol mass loading (e.g. anthropogenic SOA or POA) should then, in principle, result

in increased BVOC yields. This reasoning implicitly assumes that the aerosol forms a well-mixed liquid phase containing myriad mutually miscible organic compounds, and that dissolution of organic vapours in a pre-existing organic liquid will increase the equilibrium uptake of the reacted BVOC products (Seinfeld and Pankow, 2003; Kroll and Seinfeld, 2008)....”

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

This is a good point, the wording in our paper was not good. We did not intend to state that PALMS can resolve the phase state of the organic fraction in the aerosol. Instead we meant to argue the almost trivial point that aerosol are externally mixed near sources and become internally mixed as the aerosol ages and blends into the background. Single particle mass spectrometry does back up this claim. The conjectured corollary is that the organic compounds become more varied in composition and internally mixed. As was shown by Marcolli et al. (2004) a thermodynamically stable liquid or amorphous solid phase is expected when a large number of sufficiently miscible compounds is present. Combined this let us to argue that a well-mixed (liquid) organic phase might be expected far from, but not near of sources. We reworded the paragraph accordingly.

“The preceding discussion highlights the importance of both aerosol mixing state and single particle phase state of the organic compounds. The assumption of a well-mixed organic phase with little or no water present is likely correct in controlled chamber experiments, and may be correct far from point sources in the atmosphere. This is

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expected because single particle mass spectrometry suggests that far from sources organic and inorganic constituents are internally mixed (Murphy et al., 2006), and because under those conditions a thermodynamically stable liquid phase is likely to form (Marcolli et al., 2004). The aerosol in urban areas and near sources, however, is more complex and typically externally mixed (Moffet et al., 2008), further complicating the interaction of reacted BVOC products and pre-existing aerosol.”

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.

Dr. Jimenez raises an important issue about the role of acidity which has only been mentioned briefly in the manuscript. Indeed this is a point that strengthens the argument for anthropogenic effects on biogenic SOA yields. It also highlights the difficulty to apply equilibrium partitioning models under conditions when heterogeneous aerosol chemistry irreversibly ties up volatile compounds. We now include more detailed discussion on acid heterogeneous chemistry as suggested by the reviewers. The revised paragraph is as follows:

“Finally, reversible and irreversible condensed-phase accretion reactions (Barsanti and Pankow, 2004), may significantly increase condensed-phase products due to esterification, oligomerization, hemiacetal formation, aldol addition, or Criegee intermediate adduct reactions (Kroll and Seinfeld, 2008), though at least in chamber experiments condensation of biogenic SOA remains reversible upon dilution after many hours

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(Grieshop et al., 2007). Heterogeneous reactions that proceed at low pH (a subset of aforementioned reactions) may be particularly important since anthropogenic activities can provide acidic aerosol seed material in the form of sulfuric and nitric acid production from SO₂ and NO_x emissions (Jang et al., 2002).

Zhang et al. (2007) examined Aerosol mass spectrometer (AMS) data collected in Pittsburgh, and found a 25% increase in SOA mass during periods when the aerosol was more acidic. They did not, however, find evidence for any chemical difference in the SOA which would explain this increase, such as oligomer formation. Takahama et al. (2006) also observed a mild (0.61) correlation between aerosol acidity and OA burden in Pittsburgh, and were also unable to find any evidence for acid catalyzed heterogeneous chemistry which would lead to enhanced SOA. In both cases, the observed increase in OA with aerosol acidity could also be explained by processes which affect both acidity and SOA, such as air mass origin and history. On the other hand, several laboratory studies show dramatically increased aerosol yields under acidic conditions (e.g. Edney et al., 2005; Kleindienst et al., 2006; Surratt et al., 2007). Additionally, for SOA formed from isoprene oxidation products, Surratt et al. (2007) demonstrate the existence of particle phase acid catalysed reactions, leading to the formation of 2-methyltetrols, sulphate esters and high molecular weight SOA products. Isoprene derived SOA was also investigated by Edney et al. (2005), who found that concentrations of 2-methyltetrols and 2-methylglyceric acid increased significantly under acidic conditions. In regions where isoprene is present, sulfuric acid seeds may lead to the formation of epoxydiols (Paulot et al. 2009) and reactive uptake of these on acidic aerosols may lead to a 30-fold increase in OA mass yields from isoprene (Surratt et al., 2010). Similarly, sulfuric acid may pull in glyoxal into the particle phase due to esterification (Liggio et al., 2005).

The unreacted forms of the isoprene epoxydiols were detected at relatively low concentrations in ambient aerosol by Chan et al. (2010). Interestingly, many of the products of the acid catalysed particle phase reactions of these compounds, such as organosul-

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phates, 2-methyltetrols, 2-methylglyceric acid, 2,3-dihydroxymethacrylic acid and C5 alkene triols have also been observed in ambient aerosol (Claeys et al., 2004; Edney et al., 2005; Surratt et al., 2006), suggesting that these reactions do indeed lead to enhanced aerosol mass in the atmosphere under acidic conditions.

This body of work suggests that (1) equilibrium the equilibrium partitioning framework may not be sufficient to fully model OA aerosol formation unless heterogeneous chemistry is included, and (2) that anthropogenic activities may indeed influence biogenic SOA formation, perhaps explaining the correlation of modern carbon found in the condensed phase with concentrations of anthropogenic OA precursors. “

*Page 19524 line 1: do the authors really mean OH + NO here? **The text in brackets has been changed to:** “i.e., high-NO_x dominated by RO₂ + NO, low-NO_x by RO₂ + HO₂”*

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.

We have included the citation to Carlton et al. 2009. The discussion in our paper focuses on the NO_x/isoprene chemistry, and would be incomplete without the isoprene section.

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.

We added the following text: “Measurements made during the Amazonian Aerosol

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Characterization Experiment 2008 (AMAZE-08), under near pristine conditions, show that the submicrometer aerosol is mostly composed of BSOA, while supermicron particles consist mainly of primary organic matter (Pöschl et al. 2010). While the submicrometer fraction was found to account for more than 99% of the ca. 200 cm^{-3} particles observed, approximately 70% of the ca. $2 \mu\text{g m}^{-3}$ total particle mass was made up by the supermicron particles.”

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.

Actually, Stoltzenburg et al. was talking about Atlanta, we made a mistake there when we wrote Pittsburgh. We have corrected this. We added the Zhang paper anyway, with the following text:

“In Pittsburgh, USA, ultrafine mode particles (18-33nm diameter) were examined by (Zhang et al., 2004), who found that during nucleation events, sulphate was always the first aerosol component to increase, followed by ammonium, with organics contributing to the later growth.”

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.

We have changed the text to read: “We propose the following general methodology, in line with the recent work of Szidat et al. (2006,2009):”

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 ^{14}C 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

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wood burning OA contains 116% modern carbon, and this effect needs to be corrected for before a quantitative interpretation is possible.

We added: “In such calculations it is important to take into account that wood grown during the last 6 decades has elevated ^{14}C levels, due to atmospheric nuclear bomb tests. A ^{14}C isotopic ratio of 1.16 ± 0.05 is used for OA from wood combustion, by Szidat et al., (2009).”

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 to the modern fraction of urban POA + SOA. In any case the non-fossil fraction of urban OA 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 aerosol OC is non-fossil, many readers of this paper will assume that this 50% of OC is biogenic SOA (a different crowd will assume this 50% OC is from biomass burning) and the other 50% is urban OC. 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

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Interactive Discussion

Discussion Paper

urban sources of non-fossil carbon (which is not unrealistic, given the previously cited papers), a quick calculation shows that only 23% of the OC would be due to non-urban non-fossil sources, while 76% would be due to urban sources. Again, these effects need to be accounted for explicitly in methods such as the one proposed in this paper.

We have added the following text to address this issue: “Emissions from cooking have been found to contribute to 5-24% of OA at urban locations (Rogge et al., 1991; Zheng et al., 2002; Huang et al., 2010; Sun et al., 2010), and the influence of POA from cooking may now be comparable to POA from motor vehicle emissions (Allan et al., 2010; Sun et al., 2010). The OA contribution from cooking emissions should thus preferably be constrained in source apportionment studies by measurements of molecular marker compounds using off-line techniques (see e.g. Rogge et al., 1991; Zheng et al., 2002) or on-line gas chromatography (e.g. Williams et al., 2006), or by measurements of relevant mass fragments using an aerosol mass spectrometer (Sun et al., 2010; Allan et al., 2010; Huang et al., 2010).”

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.

We added the following text: “A recent Aerosol mass spectrometer (AMS) study by Lee et al. (2010) shows that in very fresh smoke (with an age of around 30 s), both for flaming and smoldering combustion conditions, molecular fragments with a mass-to-charge ratio (m/z) of 60.021 correlate very well with measurements of OA. The experiments were performed with several different fuels, suggesting that AMS measurements may be useful in estimating the contribution of POA from biomass burning to ambient OA.”

And later in the section: “One factor which needs to be addressed is the effect of

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atmospheric ageing on biomass burning markers, and their ratio to OA. This is currently not well quantified. However, recent experimental work strongly suggests that both levoglucosan (Hennigan et al GRL 2010) and the $m/z = 60$ biomass burning marker (Grieshop acp 2009) decay significantly during photochemical oxidation in chambers..”

The following text was added to section 4.1: “Pyrogenic carbon particles sampled in the Amazon, thought to be emitted by biomass or fossil fuel combustion, were examined by Pöschl et al. (2010) and found to have a partial organic coating. Chen et al. (2009) found that the organic loading in the Amazon basin increased by 50%, during periods with substantial influence of out of-Basin-air masses, although it is difficult to quantify what fraction of this organic aerosol was formed locally. Both of these observations qualitatively support an anthropogenic enhancement effect.”

Page 19357 lines 28-page 19538, line 7: 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. Production of CO within the plume is mentioned, but this would only reduce the estimates of SOA when using OA/Delta 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 these plumes would be only a couple of percent, e.g. Griffin et al. (2007).

We have removed the paragraph about CO.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 19515, 2010.

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