

Interactive comment on “The formation, properties and impact of secondary organic aerosol: current and emerging issues” by M. Hallquist et al.

M. Hallquist et al.

Received and published: 9 June 2009

We would like to thank the reviewer for the comments and helpful suggestions. We have made changes to the manuscript in order to address these issues and also performed editing and updates to the document. Most of these changes are minor and the overall content and conclusions of the work remain the same. Nevertheless, the comments of the reviewer have helped us to improve the quality of the manuscript and are very much appreciated. Our responses to comments numbered 18 to 33 raised by reviewer #4 are provided here. The other comments are dealt with in part 1 of this response.

Anonymous Referee #4

18. In my opinion, the issues addressed starting on page 3579 have been very well

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stated. I would suggest that they should also be better incorporated into Section 4. It may already be there and I simply do not see it.

Response:

The following sub-section has been inserted into the future research directions (section 4.2 in ACPD version):

"Gas-particle partitioning - The link between the fundamental understanding of gas-particle partitioning and its application to atmospheric or laboratory generated SOA is complex. Several factors complicate the interpretation of data such as the nature of the condensed phase, effect of temperature and the validity of thermodynamics and solution theory for non-ideal partitioning. In addition, the application of fundamental data, such as vapor pressures, molar activity coefficients and the mean MW of the condensing phase has proven to be difficult. Further improvements in the use of gas-particle partitioning theory to interpret experimental data, obtained in both laboratory and field studies, are required."

19. On p. 3579 under point 3, the reference of Hideto Takekawa, Hiroaki Minoura, Satoshi Yamazaki Temperature dependence of secondary organic aerosol formation by photooxidation of hydrocarbons Atmospheric Environment 37 (2003) 3413-3424, should be included.

Response:

We have added the reference as requested. In addition two sentences about the temperature dependence of SOA yields has been added at the end of the second paragraph in the section on laboratory studies.

20. On page 3582 line 3, the author might discuss in a bit more detail the meaning and implications of Figure 4. It is not self evident.

Response:

Some of the text needed to understand the figure was given before, from p. 3581, line 20 to p 3582 line 3. To further clarify the interpretation of the figure, we have rewritten its description as follows:

"Figure 4 highlights how some of the most important current field-deployable techniques compare for three important characteristics: completeness, chemical resolution, and time/size resolution. As described above, techniques that provide molecular speciation, represented by GC-MS in the figure, can only do so for a small mass fraction of the OA (of the order of 10%) present in ambient aerosol. Time resolutions are typically of many hours although recently a 1 hr GC-MS instrument has been demonstrated (Williams et al., 2006, 2007), but without any size resolution. Improvements in this type of speciated techniques are highly desirable and are being actively pursued by several groups (e.g. Goldstein et al., 2008) but it is very unlikely that in the foreseeable future a technique or combination of techniques can provide the fully speciated and quantitative composition of all the OA with time resolution of minutes or better and some size resolution. Thermal-optical EC/OC analyzers can quantify total OC with 1 hr time-resolution but without size-resolution. The PILS-WSOC technique can quantify water-soluble OC with a time-resolution of minutes and without size-resolution (and also water-insoluble OC by difference from e.g. a thermal-optical instrument, but then limited to 1 hr time-resolution). A family of complementary techniques (AMS, FTIR and NMR spectroscopy) attempts to analyze most of the OA mass while providing resolution of some chemical classes or functional groups. Of these techniques AMS has much higher time and size-resolution (e.g. DeCarlo et al., 2008) and can provide elemental composition (Aiken et al., 2008), but the chemical characterization provided by FTIR and NMR spectroscopy is more directly related to functional groups (e.g. Maria et al., 2003; Decesari et al., 2007). Thus a perfect field instrument with all the ideal characteristics does not exist, and at present a combination of techniques is required for a more complete characterization of OA and SOA."

21. Page 3595 line 5, An alternative approach to yield determination given in 2001

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should be included in the references - Michael D. Hurley , Oleg Sokolov, Timothy J . Wallington, Hideto Takekawa, Masa Yoshikarasawa, Bjorn Klotz, Ian Barnes, Karl H . Becker Organic Aerosol Formation during the Atmospheric Degradation of Toluene Environ. Sci. Technol. 2001, 35, 1358-1366

Response:

This reference has been added.

22. Page 3601 line 9-11, include recommendations in Section 4.

Response:

The following sentence has been added to the section on Measurements of Aerosol Composition (section 4.3 in ACPD version) under the heading; Characterization of SOA formation and aging processes:

"Measurements of organic aerosol density could be used to provide information on atmospheric processing and aging of particles."

23. Page 3602 line 2-6, there is no need for a section outline since it is not used elsewhere. As noted above, an overall of the entire paper could be valuable if included in the introduction.

Response:

With the new format, each of the sections on laboratory, field and modeling studies contain a small introductory paragraph. As a consequence, we would prefer to retain this paragraph. However, we agree with the reviewer that it reads like a section outline and consequently have altered the last few lines to make it more consistent with the other parts of the manuscript.

24. Page 3611 line 14-29, the following references should be incorporated; Manish K. Shrivastava, Timothy E. Lane, Neil M. Donahue, Spyros N. Pandis, Allen L. Robinson. Effects of gas particle partitioning and aging of primary emissions on urban and

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regional organic aerosol concentrations, JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 113, D18301, doi:10.1029/2007JD009735, 2008. Timothy E. Lane, Neil M. Donahue, Spyros N. Pandis Simulating secondary organic aerosol formation using the volatility basis-set approach in a chemical transport model Atmospheric Environment 42 (2008) 7439-7451

Response:

This has been done.

25. Page 3613-3614, much of this is repetitive from Section 2.3, and should be reduced to cover only the essential ideas required for modeling.

Response:

We agree. There is also some overlap here with the recent review of Kroll and Seinfeld (2008), which is in many ways, complementary to the present paper. As a result we have made a significant reduction in this part of the manuscript. Specifically, the section from p.3612, line 8; "Possible reasons for..." To p. 3615, line 13; "...SOA precursors", has been replaced with the following text:

"The recent review from Kroll and Seinfeld (2008) discusses potential reasons for model-measurement discrepancies in detail. Potential factors include actual differences in chemistry between chamber experiments and the atmosphere, incomplete treatment of SOA chemistry in models, and omission of important (unrecognized) precursors in models. Even for those compounds which are known (or suspected) to be important in SOA formation, critical information is missing. Indeed, for many, if not most, of the identified SOA compounds, measured vapor pressures are unavailable, and one must employ a semi-empirical model to estimate vapor pressures. Several such methodologies exist (e.g., Asher et al., 2002; Asher and Pankow, 2006; Camredon and Aumont, 2006), but uncertainties for specific compounds can cover several orders of magnitude (Clegg et al., 2008a). The importance of these uncertainties was

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demonstrated by the Simpson et al. (2007) study which made use of two sets of vapor pressure estimates for BSOA formation, both sets derived from a combination of theory and smog chamber experiments. These two simulations gave dramatic differences in modelled BSOA and OC estimates. Difficulties with other thermodynamic quantities are discussed further in section 3.8. Among the potentially important precursors, much attention has been devoted recently to "intermediate volatility" and semivolatile organics, such as those in diesel exhaust and biomass burning (Robinson et al., 2007; Weitkamp et al., 2007, Grieshop et al., 2008). Indeed, Chan et al. (2009) recently demonstrated that polycyclic aromatic hydrocarbons found in diesel exhaust can produce SOA upon photooxidation under low- and high-NO_x conditions. Aqueous pathways are also possible (Warneck, 2003; Carlton et al., 2006, Ervens et al., 2008,) but very uncertain. There is also strong evidence for the presence of an ambient pool of hydrocarbons that is largely unaccounted for in models (Lewis et al., 2000; Di Carlo et al., 2004; Holzinger et al., 2005)."

26. Page 3627 line 20-22, The sentence needs a reference.

Response:

Reference now included (Muller et al, 2009).

27. Page 3629 line 20, It is unclear how writers are using the term reference compounds; while oligomers do not have reference compounds neither do a wide variety of individual multifunctional organic compounds. Where standards are considered, it should also be emphasized that many of the calibration standards are frequently synthesized in-house at low, uncertain synthetic yields thus mitigating their value as reference compounds. Verification of the reference compounds by NMR and assays for their concentrations are also essential. I recognize that the use of laboratory generated standards may be sufficient for the types of studies being considered in this review but not in the classical sense of reference compounds such as those generated by NIST.

Response:

The reviewer is correct. The unambiguous identification of a chemical species requires a sample of the compound in question and in many cases, synthesis and verification is required. However, a reference compound is not to be confused with a standard reference material, such as that provided by NIST, which is usually a substance (e.g. fly ash) containing a combination of different species present in known amounts. Here, we use the term reference compound to mean a chemical substance with the same molecular structure as the target species, which has been characterized by one or more analytical measurement techniques (e.g. NMR spectroscopy or mass spectrometry). This meaning is very familiar to those researchers working in the area of chemical identification. We have deliberately used the word unambiguous in the opening sentence of this paragraph to emphasize this. In addition, the following few lines of the paragraph describe an example from the literature where specific reference compounds were synthesized, characterized and used to identify higher-MW reaction products within SOA produced in a laboratory study.

28. Page 3643 line 1-5, It is not clear as to what exactly needs further investigation. Perhaps the paragraph should be expanded somewhat.

Response:

The final sentence of this paragraph has been replaced with the following text:

"This highlights the need for further experimental work that employs a variety of different techniques to identify oligomer identification and their formation mechanisms."

29. Page 3630 line 24, It would be of great benefit if additional comments can be made to critically evaluate the quantification of oligomers in laboratory experiments.

Response:

The following sentence has been added to the text to emphasize that these measurements are subject to a high degree of uncertainty.

"However, many of these estimates were made indirectly, e.g. based on a change of

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the volatility (increase of the remaining volume fraction after a thermal treatment), and are therefore subject to a high level of uncertainty."

The last sentence in this paragraph states that "...there is insufficient data for an extrapolation of laboratory data to the ambient atmosphere to be made."

We consider the combination of the last two sentences to be a critical evaluation.

30. Page 3650 lines 20-29, one or more references are needed for the final 5 sentences in the paragraph.

Response:

One reference has been added, Mentel et al. (2009).

31. Page 3652 lines 5-28, The detail for these measurements are far in excess of other sections in the review. I would suggest reducing this paragraph.

Response:

This section has been reduced accordingly.

32. Page 3676 line 9, The introduction should also point out that a section on abbreviations is included immediately before the references

Response:

A footnote has been added to this effect.

33. In the reference list, manually reorder Pöschl to precede Poulain.

Response:

This has been done

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 3555, 2009.

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