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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.

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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 1 to 17 raised by reviewer #4 are provided here. The remaining comments are dealt with in part 2 of this response.

Anonymous Referee #4

1. Criticisms of measurement methods, instrumental techniques, and laboratory and

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field measurements have been made in good taste. Recommendations found throughout the text tend to be reasonable. The only case where I believe some repetition is valuable is in assembling all recommendations found throughout the text into Section 4, Future Research Direction.

Response:

We have done our best to ensure that the major recommendations featured throughout the text are also included in the Future Research Directions section.

2. While this is meant to be a comprehensive review, some of the sections are particularly long and the section would be more readable by editing to shorten the presentation. E.g., the discussion of the upper and lower limits for the global budget on pp. 3561-3565; Sections 2.2.1 and 2.2.2 on atmospheric degradation mechanisms on pp. 3570-3576; the discussion of particle formation from emissions of boreal forests on 3652-3653.)

Response:

The discussion on the upper and lower limits for the global budget is a key feature of this paper. A series of careful deductions and calculations are performed in this section and, as indicated in our response to point 8 raised by this reviewer, we believe that it is written as concisely as possible. However we have followed the suggestions of the reviewer and edited Sections 2.2.1 and 2.2.2 on atmospheric degradation mechanisms and Section 3.5, the discussion of aerosol formation from real plant emissions.

We have also significantly shortened the text in Section 2.7.2 in response to point 25 raised by this reviewer.

3. By contrast, some subjects are treated insufficiently such as, FTIR analysis of aerosol (page 3586 lines 12-16); the use of PILS (page 2590 line 9-15).

Response:

We have added further detail on the use of FTIR spectroscopy and PILS for the analysis of atmospheric aerosol.

The extended version of the text on FTIR spectroscopy now reads:

"A final type of off-line analysis is based on collection of aerosol on impactors or filters followed by analysis by FTIR spectroscopy, to determine the concentration of different organic functional groups such as saturated aliphatic (C-C-H), unsaturated aliphatic (C=C-H), aromatic (C=C-H), organosulfur (C-O-S), carbonyl (C=O), organic hydroxyl (C-OH), etc. (Blando et al., 1998; Havers et al., 1998; Maria et al., 2003; Sax et al., 2005; Polidori et al., 2008). A particular strength of this technique may be the ability to measure the total concentrations of certain functional groups, such as amines or organosulfur species, which are difficult to quantify with other field methods. FTIR spectroscopic analysis has been applied to field samples (e.g. Maria et al., 2003; Polidori et al., 2008; Coury and Dillner, 2008, 2009; Russell et al., 2009). Maria et al. (2003) used aerosol concentrators to obtain sub 1 hr time resolution with this technique from aircraft platforms. The OA concentration determined by FTIR spectroscopy showed good agreement with AMS measurements in several studies (Gilardoni et al., 2007; Russell et al., 2009). Sequential solvent rinsing can be used to further separate the organic compounds by polarity (Maria et al., 2002, 2003; Polidori et al., 2008). The OM:OC ratio can also be estimated from these measurements (Gilardoni et al., 2009)."

The expanded part of the text on PILS now reads as follows:

"Particle into liquid samplers (PILS) collect particles into water for subsequent analysis (e.g., IC) (Weber et al., 2001; Orsini et al., 2003; Sullivan et al, 2004; Sorooshian et al., 2006a). A continuous measurement of WSOC (as well as inorganic and organic ions by IC) with a time resolution of minutes has been coupled to a PILS instrument and deployed in several aircraft campaigns (e.g., Sorooshian et al., 2006a, b; Peltier et al., 2007a; Sorooshian et al., 2007a, b; Weber et al., 2007). The main sources of WSOC are SOA and biomass burning OA (Sullivan et al., 2006). Miyazaki et al. (2006)

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showed that WSOC in Tokyo correlated well with SOC estimated with the EC-tracer method, while water-insoluble organic carbon (WIOC) correlated well with EC and CO in that study. Kondo et al. (2007) and Docherty et al. (2008) have shown that the WSOC measurement is very similar to the total AMS OOA in Tokyo and Riverside, respectively. Based on measurements made in Cairo, Favez et al. (2008) suggested that anthropogenically-dominated SOA may have a higher insoluble fraction. Recently, a measurement of total carbon following PILS collection has also been demonstrated in the field, yielding a slope similar to 1:1 within the uncertainties of both measurements. However, a non-zero intercept was also determined, which is possibly related to the inability of the TOC analyzer to digest larger insoluble particles (Peltier et al., 2007b). Another very promising recent development is the simultaneous measurement of particle and gas-phase WSOC by Hennigan et al. (2008, 2009). During the summer in Atlanta at elevated RH levels ($>$70%), a significant increase in WSOC partitioning to the particle phase was observed and followed the predicted water uptake by fine particles. These results suggest that SOA formation involving partitioning to liquid water may be a significant pathway that is often not considered. Sorooshian et al. (2007a,b) have pioneered the analysis of organic acids by IC analysis following PILS collection. These authors report that organic acids averaged 3.4% of the water-soluble PM mass during an airborne study in the Houston area. Organic acids were most abundant above clouds, presumably as a result of aqueous phase chemistry in cloud droplets, followed by subsequent droplet evaporation above cloud tops with the main product of this chemistry being oxalic acid. Suppressed organic acid formation was observed in clouds with relatively acidic droplets and lower liquid water content."

4. I find the organization to be ad hoc; The heart of the manuscript is in Sections 2 and 3. I find the titles "Overview" and "Current and Emerging Issues in Secondary Organic Aerosol Research" to be non-descriptive and arbitrary. The review gives little rationale for decisions made for which topics appear in which sections. Perhaps better titles could be adopted. Alternatively, the end of the Introduction could have a paragraph giving some guidance in the placement of topics in sections 2 and 3.

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Response:

This is a good point. It is of course quite difficult to bring together a large number of topics into a coherent form. We have made some changes to help improve the structure and readability of the document. The original Section 2 ("Overview") has been split into three parts; Global SOA Budget, Formation and Properties of SOA and Recent Developments in Laboratory, Field and Modeling Studies. The titles of these sections are self-explanatory and the topics provide a description of the fundamental aspects and background material required for the section on "Current and Emerging Issues in Secondary Organic Aerosol Research". This latter section retains the same title and content as it groups together a number of selected "hot" topics for detailed discussion. The last few lines of the Introduction have been rewritten so as to guide the reviewer through the topics covered in the paper.

5. In many place throughout the review there is unneeded duplication, e.g., in the definition of the term oligomer in page 3591 line 29 and page 3627 line 11. While this is unavoidable with multiple authors, the lead author should make an effort to eliminate obvious duplications.

Response:

The additional definition of oligomers on p. 3627 has been deleted. The manuscript has also been proof-read to avoid unwanted duplication.

6. Page 3560, line 5-10, I would include a broader range of review articles, for example, Daniel J. Jacob Heterogeneous chemistry and tropospheric ozone Atmospheric Environment 34 (2000) 2131-2159.

Response:

The review by Jacob has been included. We have also incorporated the recent reviews by Sun and Ariya (2006) and Rudich et al (2007). It should be noted that a number of other review articles are cited later in the manuscript where relevant.

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7. Page 3560 line 25, I would recommend using more formal terminology than "bottom-up" and "top-down" (e.g., inductive/deductive approach?).

Response:

In this case we believe that the terminology we have used is clear, and that "more formal" terminology would, if anything, make the text less clear. The chosen terminology is identical to that used in Goldstein and Galbally (2007), so retaining it will help readers of both articles to avoid confusion.

8. The determination of the upper and lower bounds of globally produced SOA appears to be an original calculation and perhaps somewhat outside the scope of this article. While I believe the authors will ultimately decide to retain this calculation in the revised version, it could be edited to be more concise. For example, the comments included in line 24 (p.3563) to line 4 (p.3564) could easily be removed without detracting from the argument.

Response:

We hope that this paper will be useful to scientists beginning their careers in secondary organic aerosol research or perhaps approaching this field from another. This section represents an extension of the flux calculations performed by Goldstein and Galbally (2007), and it is indeed "new". However, we believe that this paper is a good place for the calculation, because it places Biogenic SOA (BSOA) in context. The flux calculation is not suitable for a stand-alone paper because it is simply a refinement of the work of Goldstein and Galbally (2007), but with the ultimate conclusion that there are quite enormous uncertainties in BSOA production (and most of the other terms in the global flux balance) that are not yet significantly constrained. For young researchers, this should be very good news - there is a lot of work to be done - and we believe that starting the present work with this discussion is appropriate. However, because we cannot simply cite other work, and because uncertainty is the subject, a certain amount of detail and a certain pedantic tone is very difficult to avoid. We believe that there is not much to be gained by reducing the length of this section and that the clarity of the discussion would be put at risk. The manuscript has been shortened in other places, but not here.

9. Page 3565 line 24, the sentence starting on this line should have a reference.

Response:

This is a scenario, and the reader is referred to the flux estimates shown in Table 1. We are not referring directly to any published work and have amended the text to make this clear.

10. Page 3568 line 15, what time scale is being referred to. If a VOC process produces SOA which is then removed by wet or dry deposition, can the carbon lost be converted to CO2? If one were to take seriously the VOC conversion to 910 TgC y-1 SOA, very little of the degraded carbon would be left in the atmosphere to be converted to CO2.

Response:

It is not at all clear that there are significant experimental constraints on this. However, one should note that this review doest NOT conclude that 910 Tg C yr-1 is a likely SOA number. In Table 1 one can see that the best estimate of OA flux is 150 Tg C yr-1 with a range from 60 to 240. The estimate shown in Figure 1 (with the 150 Tg C yr-1 OA deposition) is 800 Tg C yr-1 vapor deposition, but this is simply a difference of other numbers. The point is merely that the thermodynamic endpoint of any gas-phase organic mechanism must be VOC + oxidants –> nCO2 + mH2O. We make no claim that most of the carbon gets to that endpoint – in fact the mass balance in Figure 1 amounts to a deduction that about 1/3 of the carbon makes it to CO2.

11. Page 3570 line 6, any precursor compounds that can generate high yields of dicarbonyl compounds, particularly, glyoxal are potential SOA producers regardless of how large or small the precursor is. This is basically the same reason that laboratory experiments show the formation of SOA from benzene.

Response:

In agreement with part of the referee's statement, the point being made is that large and small precursors can make SOA, and the formation of glyoxal from acetylene is used as an example of a small precursor. However, it is over-simplistic to equate the SOA-forming abilities of all precursors to their abilities to make alpha-dicarbonyl products. Whereas compounds such as glyoxal play an important (and fully acknowledged) role, many other compound classes are also important. In the case of benzene, raised by the referee, it is very clear that the formation of SOA, and its dependence on conditions, cannot be attributed only to its ability to make glyoxal.

12. In the top paragraph on p. 3567, I would suggest including the reference of M.J. Molina, A. V. Ivanov, S. Trakhtenberg, and L. T. Molina et al. Atmospheric evolution of organic aerosol GEOPHYSICAL RESEARCH LETTERS, VOL. 31, L22104, doi:10.1029/2004GL020910, 2004

Response:

We thank the reviewer for pointing out this inadvertent omission. We have added a citation to the work of Molina et al. at this point.

13. In Section 2.2.1, many of the sentences are poorly constructed (e.g., Page 3570 line 17). The whole paragraph needs considerable editing. The last sentence in the section is incomprehensible.

Response:

This section aims to provide an overview of a large amount of background material in a relatively small space. It may therefore have suffered to some extent from previous editing and reduction. The need to refer to many publications within the text stream also inevitably disrupts the flow in places, and makes those sentences more difficult to read. On the whole, we felt we had done a reasonably good job. In view of the referee's comment, several of the sentences have been deconstructed and reconstructed to yield a (hopefully) clearer end product.

The final sentence, which was particularly highlighted by the referee, has been clarified, by separation into two sentences:

"As a result of this complex chemistry, the product distribution (and therefore SOA-formation propensity) is sensitive not only to the presence of NOx (Donahue et al., 2005) and water (Bonn et al., 2002; Jonsson et al., 2006), but has also been shown to be influenced in chamber experiments by addition of different scavengers for both OH and Criegee biradicals. The use of different scavengers for OH can influence the [RO2]/[HO2] ratio in the system (e.g., Docherty et al., 2003; Keywood et al., 2004; Jenkin, 2004; Jonsson et al.,2008a), whereas addition of Criegee biradical scavengers such as carbonyls and acids have been shown to generate various high MW secondary ozonides and acyloxyalkyl hydroperoxides, respectively (e.g., Neeb et al., 1998; Tobias and Ziemann, 2000; Bonn et al., 2002)."

14. The use of the word, respectively on page 3573 line 12, is unclear.

Response:

The rearrangement of the final sentence (as described in the response to comment 13), should clarify the use of the word "respectively"

15. Page 3570 line 27, use significantly.

Response:

In this sentence, both "significant" and "emitted" are adjectives, used to describe the noun "VOCs". Therefore "significant emitted VOCs" is analogous to saying something like "large atmospheric particles". Significantly (adverb) would be applied to a verb, and would be incorrect in this instance.

16. Page 3574 line 27-29, the sentence needs a reference.

Response:

The referee is correct. A reference to Pinho et al. (2007) has been added, which discusses the role of O(3P) atoms in chamber experiments on alpha- and beta-pinene. The sentence now reads:

"Under the conditions typically employed in chamber hydrocarbon/NOx photooxidation experiments, the initial reaction with O(3P) atoms can also be significant (Pinho et al., 2007)."

17. Page 3575, the paragraph starting on line 9 lacks a level of precision needed to understand what the author is actually trying to say (e.g., "Such methods invariably identify exotic reaction pathways which are not predicted by extrapolation methods....").

Response:

The sentence has been revised to read:

"Such methods invariably identify reaction pathways which are not predicted by the relatively simple structure-reactivity relationships derived from the understanding of the chemistry of simpler compounds, as outlined in the previous section."

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