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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aerosol mass spectrometer constraint on the global secondary organic aerosol budget" *by* D. V. Spracklen et al.

Anonymous Referee #1

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1 Overview

This work uses measurements from AMS instruments, IMPROVE and ^{14}C datasets, along with a global aerosol model, to constrain the total SOA budget as well as attribute the observed SOA to precursors from biogenic vs anthropogenically controlled sources. The paper is very clear and well written, and presents detailed sensitivity and uncertainty analysis of the model calculations. The authors argue that there is a substantial amount of SOA, 100 Tg / yr, which is governed by anthropogenic processes, and from ^{14}C analysis estimate that a bulk of this is biogenic VOCs whose SOA yields are anthropogenically induced. As well, the implications of the SOA budget are extrapolated to impacts on aerosol radiative forcing, which, while an interesting estimate,

feels a bit superfluous to the main objectives of SOA source attribution. Overall, the approach presented is new and timely, and a good fit for ACP. There have been a few other recent works which have attempted to place bounds on SOA budgets, and this work compliments these efforts and takes a step in a new and valuable direction. Still, I have several concerns about the methods, which seem a bit ad hoc, and the interpretation of the results, particularly in the context of other works, which I hope can be addressed prior to publication. These are outlined below.

2 Major comments

1. It seems that the broader objective of this work is to reduce uncertainty in our understanding of global SOA budgets. If the authors wish to do the best possible job of addressing the SOA budget conundrum, then they could also bring in observations from other sources (e.g., EMEP, WSOC, etc). Indeed, use of measurement from IMPROVE and from ^{14}C dataset prove critical to this work's analysis. So if the real goal is to constrain the SOA budget, then perhaps additional data could be used, and the title of the paper adjusted. Otherwise, if the goal is rather to further understand what AMS alone can constrain, then more explanation / motivation along these lines might be beneficial.

2. The assumption that SOA forms direct and irreversibly from the all precursors could use more consideration. Would this assumption give an upper bound for local sources and an underestimate of any slower, longer scale formation processes? How would such a model account for observations of SOA aloft (e.g., Heald 2006), or for biogenically influenced background concentrations observed at the surface (e.g., Hodzic 2010)? It it perhaps by construction that the source attribution ascribes a bulk of the SOA to the sector with the largest overall influence in the northern hemisphere? So I wonder if the impacts of secondary (or

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higher) oxidation pathways, fragmentation and volatility could be brought more into the discussion.

3. One of the main conclusions of the paper is that there is a large source of SOA that is biogenic in nature yet anthropogenically driven. And yet, the model simulations (24-32) including such properties did little to improve the model fit to the observations. This at first seems like a bit of a contradiction, despite the authors stressing that these simple schemes are not mechanistically representing SOA formation. Wouldn't it also be fair to say that none of the simulations, 1-32, mechanistically represent SOA formation, as all schemes considered are simplified empirical descriptions? Yet we are asked to believe that such simplifications are permissible for describing the SOA formation in simulations 1 - 23, so I found this a bit inconsistent. Are the authors suggesting that the anthropogenic mechanism for controlling the SOA is one that is entirely different than those presently considered, and fundamentally more complicated to represent than the direct formation pathways?

4. While the authors clearly strive to place their results in context with prior works, I feel that the sentiment of previous modeling studies investigating anthropogenic SOA is not always well represented. I don't think there are any (or at least not many) modeling studies of SOA post 2005 which unequivocally claim that anthropogenic SOA is negligible relative to biogenic SOA. As chamber studies and field measurements have lead to new insights, modeling work has checked individual processes for their contribution to SOA on global scales. And yet, even when a single process has turned out not to be the smoking gun, the conclusions of these works is not that anthropogenic SOA is not important, just that the current process being tested by itself may not explain the larger budget issue. For example, Henze 2008 examines the amount of SOA produced from aromatic compounds via a specific mechanism, and these estimates shouldn't be misconstrued as representing a comprehensive model study of anthropogenic aerosol. Indeed,

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the conclusions of this work were similar to those of the present manuscript, as it notes "Consideration of additional mechanisms for formation of SOA beyond those considered here . . . would appear vital to our description of anthropogenic SOA." Similarly, the work of Farina 2010 notes that their findings "challenges the assumption that anthropogenic volatile organic compounds are not important SOA precursors on a global scale". Both works posit a total anthropogenic source possibly greater than 10 Tg / yr, so I think the wording on 5718, line 14, and again on page 5700, 22 could be adjusted. The present work moves beyond these by providing additional constraints.

5. 5711, line 17: How do you really feel about the fact that the best fit model was one in which you considered only remote sites and had SOA only from anthropogenic sources? Because we know this is a completely non-physical result, right? To me, this indicates that the inverse modeling framework is, by construction, not sufficiently sophisticated enough to capture the observations to which it is being compared, and this casts serious doubts on the rest of the analysis. Given the small amount of data, this is likely an ill-posed modeling task, which could amplify errors in the model or observations, and project these onto the solution (the source attribution). I suspect there is non-negligible error coming from representational error (see point 7) and the simplified SOA scheme (point 2), though possibly sampling plays a role (points 6a,b).

6. linear model: I have a few questions and concerns about the linear response model.

   (a) 5712, 8: Simulations 18-33 were not included as they "did not result in improved model performance." I don't follow the reasoning here. Analysis of the model output vs observations is an entirely separate step from model reduction, as the goal with developing a response model is solely to represent a complex model with a simplified model, irrespective of any obser-

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vations. Thus, to develop the best linear model, the largest space of input parameters should be explored, and weighted appropriately. Any additional information about how simulated SOA responds to changes in emissions, regardless of whether or not these SOA levels fit observations, helps the linear model characterize the global model. Regardless, there are many of the simulations in 18-33 that perform better than those in 1-17, so the distinction seems capricious. Rather, the decision about which simulations to include should depend upon the parameter uncertainty, not the model skill, as described in the next comment.

(b) While there is ample literature describing how to build representative response models by sampling the parameter space according to the uncertainty and range of the parameters themselves, the sampling method employed here seems a bit ad hoc. The range of model states sampled from also seems limited and not equal across the parameters. The weighting of these samples according to the degree to which we believe the parameter values are reasonable is also not accounted for.

(c) No evaluation of the response model vs the full model is provided. This is a fundamental omission that needs to be provided if we are to evaluate any of the findings based upon the linear response model.

(d) SOA formation is itself a nonlinear process. Can the authors estimate the degree to which the linear assumption is valid with respect to (a) the GLOMAP simulations and (b) what we know about more detailed SOA models?

7. There is considerable potential for representational error when comparing coarse global model estimates to a small number of surface observations, and it is not clear that this is handled in the best way. Throughout this work, model estimates are compared to the 47 individual AMS observations, and I don't believe this is the best use of a CTM in this context. Rather, the AMS observations should be

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aggregated so as to provide an estimate of the average concentrations within a given model grid box. The degree to which this grid box is fully / evenly sampled by the AMS observations would then be included as a "representational error" term in subsequent analysis. For example, grid boxes containing multiple AMS measurements would be given more credence than those containing just a single observation.

8. Regardless of issues of representational error or how the linear model is built, the method in which the response models are then used to optimize the sources in order to match the observations is a bit odd, and I'm not sure if it is theoretically sound. A much more standard, and possibly effective, way to find the source terms would be to construct a matrix A that contains the coefficients a - e in each column and has 47 rows, one set of coefficients for each site. If the vector of observations is d and the vector of source terms is $s = [S_M, S_I, S_A, S_{BB}, S_P]$, then the optimal values of s are obtained directly from

$$s = (A^T A)^{-1} A d$$

where here optimal means minimizing the sum of least squares. To solve for s that minimizes the NME, a similar equation could be derived, though it would be nonlinear and require an iterative solution.

If you used a standard discrete inversion method such as this, then you could also answer other questions such as: what is the uncertainty in you source estimate ($A^{-1}C_d(A^{-1})^T$) and to what degree can different source sectors be resolved given the inversion setup ($A^{-1}A$), where C_d is the error covariance matrix of the observations.

9. Fig 6: To be honest, I have a hard time believing the isoprene values. With so many observations in the NE US, Europe, and Asia, and so few in isoprene hotspots such as SE US or the Amazon, it is difficult to believe that the isoprene source distribution is being similarly represented by the AMS locations.

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10. 5716, 15: “does not greatly impact our results”. This choice gives either a biogenic source of 0 Tg / yr or of 13 Tg / yr. I would say this is a huge difference, not a negligible one. Same reaction to this comment repeated in the conclusions.

11. 5709, 5710: I know it’s consistent with what you expect that, for example, adding biomass burning will improve the performance. However, on the basis of the statistical metrics alone, this is hard to see. An r^2 of 0.0 and an r^2 of 0.03 both imply the model is largely incapable of describing the variance in the observations, and one may not be significantly better than the other. So I would perhaps place less emphasis on the differences in the correlation coefficient for any values less than $\sim$0.1, for which one might overall say the model has little correlation with the observations.

12. 5702: What about cloud processing? Is there a reason the role of this process is not mentioned here, or throughout?

3 Technical corrections

- 5702, 20: It seems odd to cite Kroll 2006 as a reference supporting enhanced SOA formation in polluted regions, as this work showed that high NOx levels were inhibiting SOA formation from isoprene in such regimes.

- 5718, 17: Perhaps some clarification is required here, as the toluene and benzene yields in Ng 2007 were much less than 80%, more like 30-40%, and even then, only under low NO_x conditions.

- 5721, 11: 2009, not 2010, for the de Gouw and Jimenez reference.

- 5701,16 and 5702, 11: I know what you mean (models that used alphas and K’s in Odum fashion), but for others the terms “traditional” and “early” are vague and

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used inconsistently. I suggest you refer to methods by the mechanisms which they represent, such as “absorptive partitioning”.

- 5704: Why not just use the EDGAR VOC emissions rather than scaling the IPCC CO emissions to match the total EDGAR amounts?
- 5705, 3: “to reduce the computational burden of our simulations”. It seems like a simplified scheme was beneficial for the sake of interpretation more than computational expense.
- 5708, 16: “no skill at capturing the spatial pattern”. Wouldn’t the r^2 value indicate skill at capturing both spatial and temporal variability?
- 5708, 16: “most likely because the spatial resolution of the global model is too coarse to resolve the urban-scale pollution.” Can this be tested by repeating the analysis leaving out the urban sites?
- 5715 and Fig. 5: Are the biomass burning values in the figure off by a factor of 10?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 5699, 2011.