Atmos. Chem. Phys. Discuss., 13, C4526–C4537, 2013
www.atmos-chem-phys-discuss.net/13/C4526/2013/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Analyzing experimental data and model parameters: implications for predictions of SOA using chemical transport models" *by* K. C. Barsanti et al.

Anonymous Referee #2

Received and published: 6 July 2013

In this work, the authors aim to increase the fidelity of "2-product" (2p) fits to SOA formation data from smog chambers by constraining them to fits obtained using another, very similar model, the volatility basis set (VBS). The basic premise, as I understand it, is as follows: when the VBS is fit to existing data it does a better job of capturing aerosol yields at low (i.e. atmospherically relevant) concentrations than does the 2p model. However, there is a desire to use the 2p model within regional and global models. Thus, the accuracy of the 2p model fits can be increased by double fitting the data, i.e. fitting observations using the VBS method and then fitting the VBS fit to the 2p model. This premise has been developed, in large part, from comparison of existing

2p and VBS fits from the literature, which seem to show generally better agreement between low SOA concentration data and the VBS model fits. However, what is not carefully considered is whether these literature fits were actually developed using identical data sets, or whether they come from different data sets: the latter is, I believe, most often the case. Rather than simply fitting the 2p model to data collected over the atmospherically relevant range, the authors instead fit the VBS model to data over the range 0-200 micrograms/mˆ3, and then fit the 2p model to "pseudo-data" generated from this fit (which I think is just a way of saying that they have fit the 2p model to the best fit curve from the VBS fit). No t surprisingly, the resulting "2p-VBS" fits look a lot more like the original VBS fits. However, I am ultimately unconvinced that this is actually leading to more accurate representation of the SOA formed at low concentrations, or at least I am not convinced that this will provide better results than if the 2p model were simply fit to the exact same data as the VBS but over a limited range of concentrations (e.g. 0-10 micrograms/mˆ3, which seems to be the range focused on in the manuscript). Ultimately, the VBS fits at low SOA concentrations are just as limited by data quality in this concentration range as are 2p fits. And when data are considered only over a narrow range of concentrations (e.g. 0-10 micrograms/mˆ3, which is effectively 2 orders of magnitude given the majority of data points considered), it is not surprising (to me at least) that the 2p and VBS models should perform similarly since both have enough free parameters to account for SOA formation over 2 orders of magnitude. By this, I mean that the 2p model has two saturation concentrations (C*'s) that are adjustable, while the VBS has 4 C*'s, but that are constrained to exist spaced by factors of 10. Thus, if data are only considered over 2 orders of magnitude the models should perform similarly. Indeed, I believe that the authors would find this to be the case if they performed 2p and VBS fits to only data where SOA concentrations range from 0 to 10 ug/mˆ3. More broadly, I have concerns that by fitting the 2p-VBS to pseudo-data generated over the range 0-200 ug/mˆ3, rather than the range of interest, that the resulting fit might be biased towards data points at higher concentrations. This concern is developed simply by looking at a few of the figures, where it is apparent that the 2p-VBS fits actually perform worse than many of the existing parameterizations in terms of their ability to match the low concentration data (in particular, high-NOx sesquiterpenes, low-NOx isoprene). I strongly encourage the authors to rethink this study and focus on data only over the atmospherically relevant range, if their goal is the development of 2p fits that are more applicable to data in this concentration range. My overall take-away from this work is that, if we want to ultimately develop parameterizations of SOA yields over the atmospherically relevant range then it is necessary to actually have more experiments conducted at low SOA concentrations. I am not convinced that the 2p-VBS method of fitting provides a way around this. Unfortunately, at this point in time I have to suggest rejection.

I have a number of additional comments, provided below, many of which are related to the issues discussed above (my apologies if this gets a bit redundant). I also demonstrate some of my points through explicit fitting of a few of the datasets presented here over only the atmospherically relevant (i.e. 0-10 ug/mˆ3) range of concentrations.

P15909/L15: The authors state the the contribution of SOA to "negative radiative forcing" may be increased if one considers formation of "brown carbon" by SOA constituents. However, this statement is either true or false, depending on what exactly the authors mean. If they mean conversion of SOA to "brown" material, this would actually decrease the negative forcing because the "brown carbon" would be absorbing, which is a positive forcing. If the authors mean that aqueous phase processing may produce OA (thus increasing PM mass), then the increase in negative forcing will be independent of whether the compounds produced are "brown" or not. In fact, if they are brown some of the increased negative forcing (from increased scattering) will be offset by the absorption by the brown components. This statement needs to be clarified.

P15910/L14: The authors might think about adding some statement about the motivation behind the use of the VBS vs. the 2p formulations. Both end up with 4 tunable parameters, but the apparent hope in using the VBS is to increase the fidelity of the overall fit over a wider range of concentrations by constraining the volatility of the

products into reasonable "bins" and then adjusting only the yields. Thus, the VBS, compared to the 2p model, captures a wider dynamic range for the same number of fit parameters. However, it should also be noted that these methodologies are ultimately applying the same theoretical construction to the problem of fitting the data. This also does not address the fact that there are actually multiple VBS parameterizations available for use: some simply fit data using static yields, but others (when implemented in air quality models) apply an ad hoc ageing scheme.

P15910/L21: The authors refer to the work of Pankow and Barsanti as a "more detailed modeling approach." With this I do not disagree. However, my understanding of their model is that it is still reliant on comparison (or tuning) to results from chamber experiments. Thus, it doesn't seem appropriate to me to make this sound as if it is distinct from approaches that "rely on parameterizations of chamber experiments."

P15911/L4: I personally don't think that the results of Camredon et al. should be included here (at least not as presented) as a demonstration of the "high" volatility of condensation products. As written, the authors make it sound as if Camredon actually measured such products. This is not the case: the Camredon results are model results. This stands in distinct contrast to the Yu et al. results that are mentioned, which actually measured directly many of the products.

P15911/L20: I find the discussion of the Pathak et al. (2007) work to be a bit unfair to the 2p models: the "underestimation" of SOA by the 2p model at low aerosol mass concentrations was not (necessarily) the result of limitations of the 2p model, but of the concentration range considered during the fitting. Had Pathak et al. refit the overall data presented by them to a 2p model, they would have undoubtedly found better agreement at low concentrations. So, this is not a 2p limitation, but a data limitation. I think that this is important to recognize/clarify since, in essence, it provides the basis and background for the current work, which basically generates low concentration data to fit the 2p model to. Although it is clear that the authors recognize this (see for example discussion on p15912), I think that it could be expounded upon more clearly here.

Fig 1 and discussion on P15913: I will admit I am a bit confused about the relationship between Fig. 1a and Fig 1b. SOA Yield is typically defined as deltaSOA/deltaHC. Thus, there should be a linear transformation between Fig. 1a and Fig. 1b. However, if I look at where the (for example) "VBS based on Presto et al. (2005)" intercepts the actual Presto et al. (2005) data in Fig. 1a, this does not seem to correspond to the same point in Fig. 1b. What I mean more specifically is that while the gray dashed line in Fig. 1a does not intercept any of the solid gray points, it overlaps with two of the solid gray points in Fig. 1b. Further, I am having a difficult time understanding how the VBS "fit" for Presto et al. (2005) in Fig. 1a can be correct if it is truly fit to the data shown in that figure because the line doesn't actually go through any of the data points. I believe that all of this needs to be clarified. Is the fit line here not actually fit to only the data shown in the figure, but to all of the data from Presto et al. (2005)? If so, this must be stated. This is actually very important, in my opinion, because as presented I find this misleading. I say this because if I actually just take the 4 solid gray points and fit them to a 2p or VBS model, I get identical fits, so long as I apply a consistent lower bound to acceptable C* values (see Fig. 1 here). This is actually also true if I fit 2p and VBS models to the data shown as open gray squares (from a few data sources). The fits in this case are not identical, but are very, very similar (see Fig. 1 here), consistent with the findings of Shilling et al. I have actually tested this for many of the data sets presented in the model: if the 2p and VBS fits are both performed over the same data range (e.g. 0-10 ug/m^3 or the range shown in the graph), and both have the same lower limit for C* applied (1 ug/m^3, based on the VBS lower-limit C*), the fits obtained are extremely similar (see Fig. 2 here for the overall dark alpha-pinene low NOx fit and Fig. 3 for results for high-NOx sesquiterpenes, as two examples). Thus, the differences in the 2p and VBS is not in the model, but in the data used and the range considered. Given this, I have to disagree with the general premise put forward in this paper that there are "fitting advantages of the VBS approach" (L17). If 2p and VBS fits are performed for data over a narrow range of SOA concentrations the two methods will both give very

similar results. The "advantages" of the VBS really only come about if one wants to fit over a wider range of SOA concentrations. Should this be surprising? I don't think so, because the 2p model can effectively deal with data over (up to) 2 orders of magnitude variation in SOA concentrations, while the (standard 4 product) VBS can deal with variations over 4 orders of magnitude. So, if data are considered over only a narrow range of concentration the two models will give essentially equivalent results. Further, I believe that the statement on P15913/L10 that refers to the "inability of the Figure 1 parameterizations to accurately capture SOA formation at low" SOA concentrations ignores the reasonably good agreement of the 2p and VBS models for the Shilling data. In other words, this sentiment is biased towards situations where things don't work rather than when they do. And, as noted above, is in my opinion confusing issues of model fidelity and data quality/fit range.

Regarding the general premise of the manuscript: The authors use VBS fits to generate "pseudo-data" to which the 2p model can be fit. This does not take into account the actual range of SOA concentrations considered when developing the VBS fits in the first place. Inherent in this is an assumption that the VBS performs better upon extrapolation to low concentrations than the 2p model. I have not seen this demonstrated in a self-consistent manner. By this I mean that I have seen where 2p and VBS fits have been compared when the fits have been performed for different data sets, but I have yet to see convincing evidence that the VBS is more robust to extrapolation than the 2p model. I do not see why the authors do not simply collect data over the "atmospherically relevant range" of concentrations and perform 2p fits directly using the data. This intermediate step of using "pseudo-data" seems to me unnecessary and, more importantly, unjustified.

Fitting of POA: I do not understand the need to use an "unconstrained" value for the enthalpy of vaporization for POA, and in particular I do not understand how this is justified. Presumably the authors generated their "pseudo-data" for POA in a similar manner to the SOA, by which I mean that they must have assumed some vaporization enthalpy to generate the data at temperatures other than 298 K. If this is the case, then I see no reason that the enthalpy in the 2p fitting should be unconstrained, since it has been inherently constrained in the construction of the pseudo-data. However, perhaps the authors made some other assumption regarding the enthalpy of vaporization for POA in the generation of the pseudo-data, although it is not clear whether this is the case. As written, I can only assume that they assumed 30 kJ/mol for POA, as for SOA, in the generation of the pseudo-data. If this is the case, then I really do not understand how the obtained larger values in the 2p fitting.

Regarding data presentation: In nearly all figures the authors limit the axes to a maximum SOA concentration of 10 micrograms/mˆ3. However, in the generation of their pseudo-data they say that they create points from 0-200 micrograms/mˆ3. By limiting the range of their graphs, it makes it exceptionally difficult for the reader to understand how much the fits are biased/controlled by data/pseudo-data at higher concentrations. Given that the not-shown region comprises a full 95% of the total range, I imagine that the data not shown exert a much more important control on the behavior at low concentrations than the actual data that exist at such low concentrations. Consider, in particular, Fig. 2. I find it very odd that the 2p-VBS fit doesn't actually pass through any of the data for the low NOx system. To me this doesn't make sense, unless there is a lot of data at higher concentrations that strongly biases the results. This is obviously the case. Why not just fit over the range that matters? At minimum, I believe that a 3rd (or 4th) panel is needed to show the data over the entire range considered in the fitting. Also, it is not made clear at all whether the other fits shown in the figures (e.g. Henze and Seinfeld and Carlton in Fig. 2 for low NOx) were actually fit to what amounts to the same dataset, or whether they effectively considered some subset of all the data available.

P15914/L13: I disagree that the 2p-VBS fits here are "fundamentally" different than the reduced (2-species) VBS fits from Shirvastava et al. (2011). The difference is that here the C* values are not constrained, while in Shrivastava et al. they are constrained.

But this is not a "fundamental" difference, only a practical difference. Further, this is a bit misleading as written since Shrivastava actually used a 1-species (not 2-species) model for SOA.

P15916/L7: The authors state: "The predicted SOA curves are particularly well-suited for illustrating the ability (or inability) of model parameters to represent SOA formation under ambient conditions." But to return to an earlier point, the authors have used data in their fitting that is far outside the range shown in the graphs. Why not just use the data over the range that is relevant to the atmosphere and remove this ambiguity? Since 2p models do not include additional "ageing" of semi-volatile vapors (unlike some versions of the VBS, although not the version under consideration here), there is absolutely no need to aim to capture the yields and partitioning at higher mass concentrations.

P15917/L4: I find the sentence that begins here "In contrast…" to be quite confusing in terms of what was actually done. Also, this extrapolation of high-NOx fits to low-NOx data doesn't seem warranted when there are actual data that can be used.

General: I realize that I have been quite critical of the authors use of high concentration data and the extrapolation to low concentrations via the VBS fits and the generation of "pseudo-data". I do see that the data quality at low (i.e. atmospherically relevant) concentrations leaves something to be desired in many cases. Thus, I can see it is tempting to want to extrapolate from potentially higher-quality high concentration data sets. But it is not clear to me that extrapolation will necessarily lead to more accurate results at low concentrations. The VBS fits, and in particular the extraction of yields associated with the lowest volatility species, is dependent upon the data at these low concentrations. (In other words, if experiments were performed where SOA concentrations were all >100 micrograms/mˆ3, then the yield of the C* = 1 microgram/mˆ3 VBS species would be highly uncertain. The VBS, like the 2p model, is only as good and as useful as the data used to constrain it).

Looking at Fig. 6, and the data range considered, I do not believe that the authors are justified in including the “ALK5-Lumped Alkanes” as part of this study. The data simply do not provide the necessary constraints. I believe that this should be removed.

Sesquiterpenes: I am very concerned that the 2p-VBS fit doesn’t actually go through the data shown in Fig. 4. I do not see how this can then be a better solution than the CMAQ fit, which at least goes through the points.

P15911/L28: I don’t understand the justification for “even when limited data exist” as used here.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 15907, 2013.

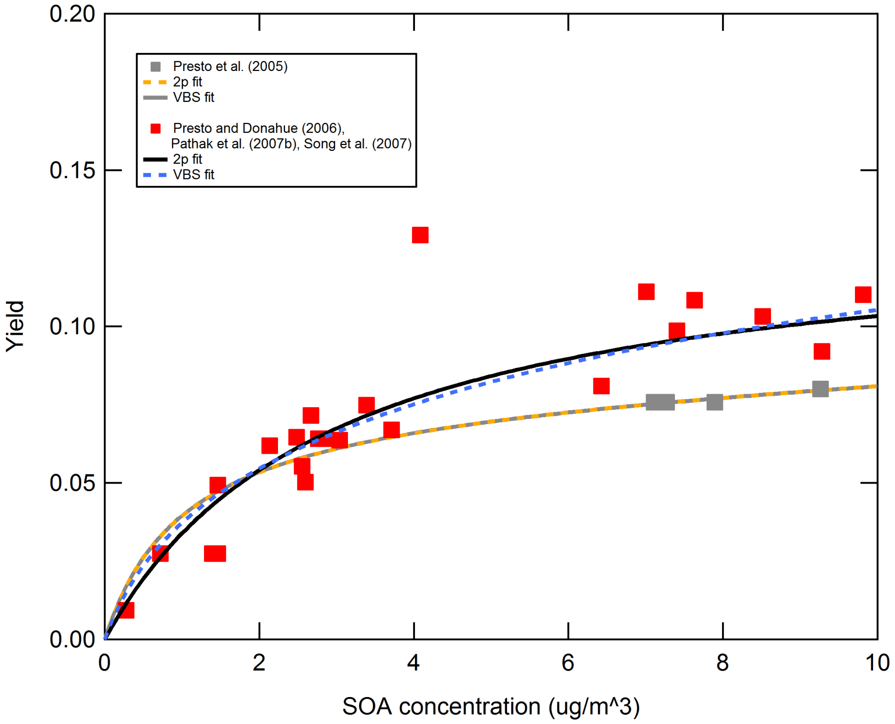

Fig. 1. Data from Fig. 1 in Barsanti et al., fit to 2p and VBS models over the range of SOA concentrations shown on the graph.

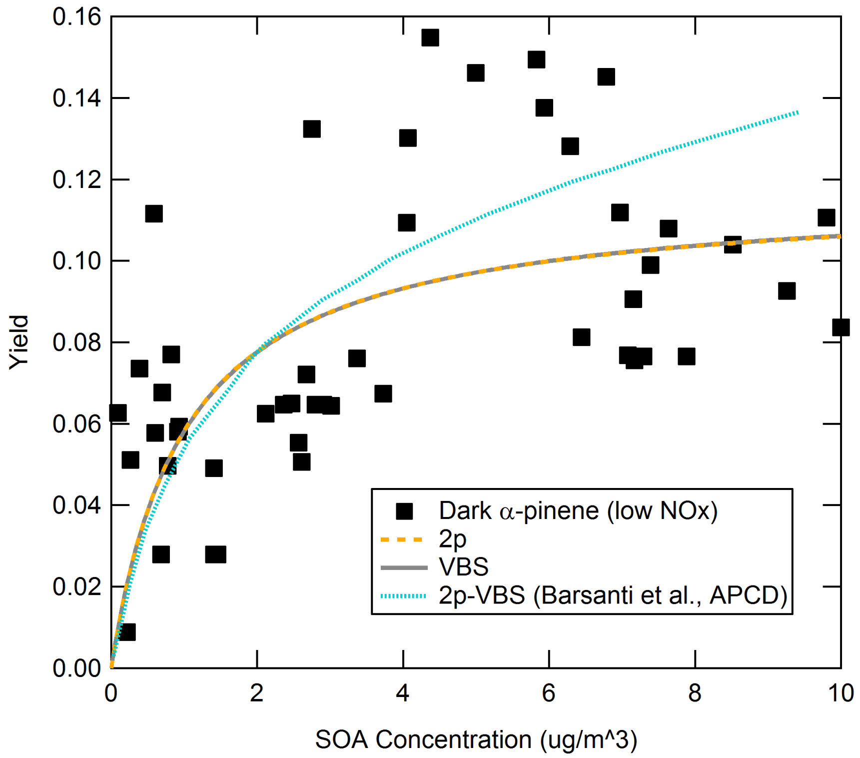

Fig. 2. Data from Fig. 3 in Barstanti et al. for low NOx dark alpha-pinene experiments, fit to 2p and VBS models over the range shown, and compared with the 2p-VBS best fit from Barsanti et al..

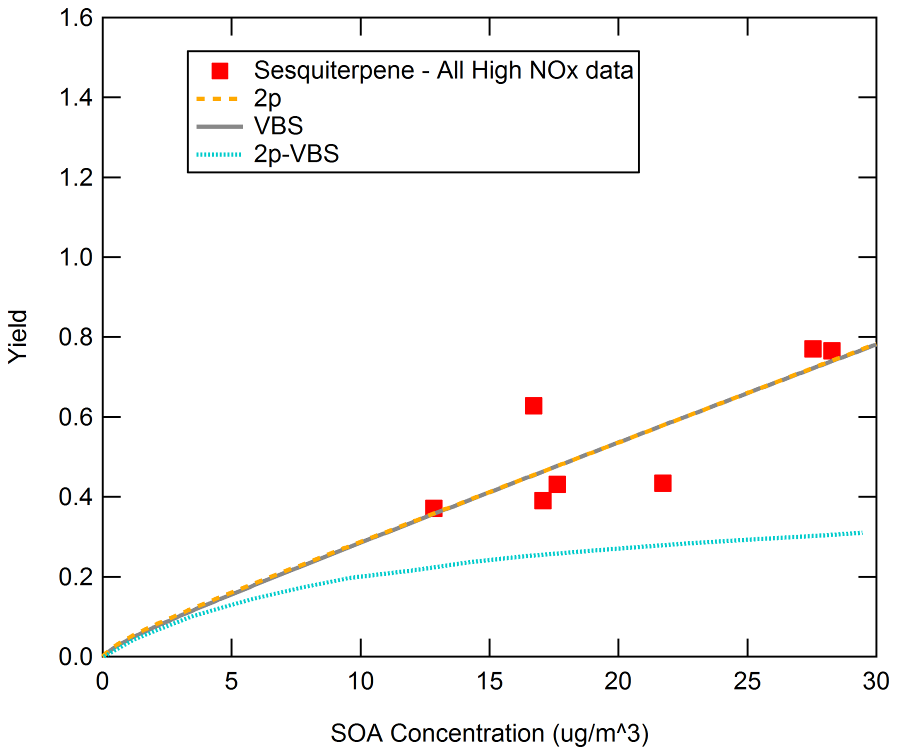

Fig. 3. Data from Fig. 4 in Barstanti et al. for high NOx sesquiterpene experiments, fit to 2p and VBS models over the range shown, and compared with the 2p-VBS best fit from Barsanti et al..