

The authors sincerely thank the reviewers for their thoughtful and thorough reviews. Responses to the *reviewer comments* (in italics) appear below.

Reviewer #2

General:

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.

Yes, however, more specifically when data at low M_0 are limited. From Section 2.1: “These results suggest that the VBS approach may be better able to represent SOA formation at low Δ HC levels and M_0 , specifically when data are available but sparse.” Please also see the first part of the response to Reviewer #1, comment #2.

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.

While the best available parameters were determined by comparing 2p, VBS, and 2p-VBS parameterizations with one another and with data from different data sets, identical data sets were used to explore the assumption that the VBS approach may be better able to represent data at low M_0 , specifically when data are sparse. We considered the implicit assumptions in each method (discussed in Introduction) and then compared 2p and VBS parameterizations from identical data sets, one with many, and one with few, data points at low SOA mass loadings (Section 2.1). Section 2.1 has been revised to make this clearer.

“As introduced above, the fitted parameters are influenced both by the range in M_0 , as well as the number of data points at low M_0 . The Presto et al. (2005) data set spans Δ HC levels from 15-210 ppb and M_0 values from 7-346 $\mu\text{g m}^{-3}$ (three data points with $M_0 < 10 \mu\text{g m}^{-3}$), while Shilling et al. (2008) spans Δ HC levels from 0.3-14 ppb and M_0 from 0.1-7 $\mu\text{g m}^{-3}$ (twenty data points with $M_0 < 10 \mu\text{g m}^{-3}$). Results from Shilling et al. (2008) suggest that when sufficient data points are available at low M_0 (Figs. 1a,b) both the 2p and VBS parameterizations represented the observed yields (Fig. 1a) and captured the observed SOA formation at the lowest Δ HC levels (Fig. 1b). For the Presto et al. (2005) data set, while the observed yields at $M_0 > 50 \mu\text{g m}^{-3}$ were represented by the published 2p parameterization (not shown here, see Presto et al., 2005), observed SOA formation at the lowest Δ HC levels, 15-25 ppb, was not captured (Fig. 1b). The VBS parameterization, derived here using the Presto et al. (2005) data, was better able to represent observed SOA formation at Δ HC levels < 25 ppb in the experiments from which the parameters were derived, as well as in other chamber experiments for the same VOC+oxidant system

(Griffin et al., 1999; Cocker et al., 2001a; Presto et al., 2005; Pathak et al., 2007b; Song et al., 2007). These results suggest that, due to the lognormally-spaced fixed volatility bins, the VBS approach may be better able to represent SOA formation at low ΔHC levels and M_0 , specifically when data are available but sparse.”

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/m³, 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). Not 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/m³, 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.

We agree with the reviewer that poor data quality cannot be overcome by any fitting approach. That is the reason we spent a considerable amount of time investigating widely used parameterizations, including the data sources. We also agree with the reviewer that if sufficient data were available at low M_0 (e.g., $\leq 10 \mu\text{g m}^{-3}$) and if that data were shown to be of good quality, the 2p would perform as well as the VBS, as stated in Section 2.1. To assert this more clearly, we have modified the first paragraph of the Conclusions as follows (changes in **bold**):

“With regard to parameter fitting, VBS parameterizations may be more robust when data are sparse; however, this alone is not sufficient to overcome the limited availability **or absence** of chamber data, particularly for certain precursors, at low, atmospherically relevant ΔHC and M_0 . **With any fitting approach, the quality of the fit is only as good as the data and extrapolating outside of the data range is not recommended.**”

Please also see the response to Reviewer #1, comment #2.

And when data are considered only over a narrow range of concentrations (e.g. 0-10 micrograms/m³, 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 $\mu\text{g}/\text{m}^3$.*

We agree with this statement, only if: 1) there are sufficient data points at low M_0 ; or 2) the 2p fitting algorithm is modified to constrain the C^* values.

More broadly, I have concerns that by fitting the 2p-VBS to pseudo-data generated over the range 0-200 $\mu\text{g}/\text{m}^3$, 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-NO_x sesquiterpenes, low-NO_x 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.

Taking the position that for some precursors there are not sufficient data to develop robust fits at low M_0 (regardless of the approach), and that for all precursors identifying atmospherically relevant data and discarding the rest are problematic (please see response to Reviewer #1, comment #2), the VBS approach is better able to capture SOA formation at the lowest $\Delta\text{HC}/M_0$ levels. While the VBS fitting approach does not completely remove bias towards the higher mass loadings (i.e., all data points are not equally weighted, see also response to Reviewer #1, comment #2), by fixing the C^* bins in logarithmic space the VBS captures predicted SOA yields across any range of $\Delta\text{HC}/M_0$ for which data are available. For all precursors, the VBS parameterization, and by extension the 2p-VBS parameterization, captures the SOA yields across the range of $\Delta\text{HC}/M_0$ levels from which the parameters were derived.

However, as mentioned by this Reviewer, the fits are only as good as the data on which the “original” (Tsimpidi et al. 2010) VBS fits were based. Thus, following the development of the 2p-VBS parameters we did an extensive comparison between widely used 2p and VBS parameterizations, and the newly developed 2p-VBS parameterizations, to recommend a set of “best available” parameters, based on a comparison with one another and with chamber study data (Sections 3.1 and 3.2, Figs. 2-6). The best available parameters are listed in Table 3; in agreement with this reviewer, the default CMAQ parameters were retained as the “best available” for isoprene and sesquiterpenes. For some precursors, the 2p-VBS parameters did represent an improvement over the existing parameters. Also for some precursors, the ability to make an assessment was limited due to lack of data.

For the precursors that are not well represented by the 2p-VBS parameterization, there is nothing additional to be gained by performing a 2p fit on a restricted M_0 range. In some cases, SOA formation is better represented by the default parameters; in other cases there is sufficient spread in the data, and limited understanding of the reasons for that spread, that fitting one set of data over the other, or fitting all of the data with one curve cannot be justified.

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.

We absolutely agree regarding the need for more data. In our Abstract we stated: “The ability to robustly assign “best available” parameters, however, is limited due to insufficient data for photo-oxidation of diverse monoterpenes and sesquiterpenes under a variety of atmospherically relevant NO_x conditions.” And in the Conclusions: “With regard to parameter fitting, VBS parameterizations may be more robust when data are sparse; however, this alone is not sufficient

to overcome the limited availability of chamber data, particularly for certain precursors, at low, atmospherically relevant ΔHC and M_0 . “ We arrived at these conclusions after an extensive analysis of existing parameterizations (and newly developed 2p-VBS parameterizations) and available chamber data, as well as an appreciation for potential similarities and differences between chamber studies and the atmosphere, and an understanding of the representation of processes in CTMs. Such an extensive analysis, clearly linking chamber data to air quality model output, has not been published to our knowledge.

Compared to gas-phase chemical modeling, SOA modeling is unique in that SOA parameterizations are based on experiments conducted in individual laboratories under a narrow range of conditions. When employed in atmospheric models, these parameterizations are used to describe SOA formation under all atmospheric conditions. In this work we compare data from a variety of different laboratory experiments, and resulting parameterizations from a subset of those experiments, in an effort to identify the best available parameters that are most applicable to the range of conditions encountered in the atmosphere. (With gas-phase chemical modeling, community-based reaction rates are typically employed using a JPL compendium of recommended values based on years of repeated experiments in a variety of different laboratories.)

We have revised the abstract to emphasize our intent to: 1) identify a set of best-available parameters for use in the CMAQ model, including by developing a new set of parameters exploiting advantages of the VBS approach, 2) evaluate CMAQ model input using those best available parameters, and 3) guide future experiments. We also have made every effort to emphasize that while the VBS approach does in fact better represent SOA formation at low M_0 when data are sparse, the particular VBS parameterizations and by extension the 2p-VBS parameterizations, are only as good as the data from which they were derived.

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/m³, then the yield of the $C^ = 1$ microgram/m³ 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).*

We are not advocating extrapolation. Presto and Donahue (2006) stated that the VBS approach is well conditioned when M_0 is within an order of magnitude of C^* . In this work, we started with the published VBS parameters of Tsimpidi et al. (2010); the lowest volatility bin was $1 \mu\text{g m}^{-3}$. If we assume consistency of approach, for each set of parameters, there was at least one data point with $0.1 > M_0 > 10 \mu\text{g m}^{-3}$. All of the pseudo-data, generated from the Tsimpidi et al. (2010) VBS curves, had the same lower limit, $M_0 > 0.1 \mu\text{g m}^{-3}$. While we did not perform a QA/QC on the data used specifically in the Tsimpidi et al. (2010) fits, we did an extensive analysis of the

resultant parameters (through analysis of the 2p-VBS parameters) by comparing them with other widely used parameters and a comprehensive list of chamber data.

Major/Minor Comments:

1. *The authors state 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.*

We thank Reviewers #2 and #3 for pointing out the poor wording of this sentence. The sentence has been revised and now reads: “...a significant contributor to negative radiative forcing on a global scale. Greater radiative forcing (Park et al., 2010), though positive in sign, may be possible if one considers the production of brown carbon by SOA constituents (Updyke et al., 2012).”

2. *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.*

In addressing the reviewer comments, in the revised manuscript we have clarified the theoretical underpinnings of the 2p-VBS parameters. We also have clarified that we are addressing only SOA formation that has been captured in chamber studies (i.e., shorter timescales) and parameterized using chamber experiments, and are not focusing on aging. While there are multiple published VBS parameterizations, they are based on different chamber experiments (e.g., Hildebrandt et al., 2011); there is no distinction between the VBS parameterizations described here and the VBS parameterizations to which ad hoc aging schemes are applied (e.g., Dzepina et al., 2011). In some applications, aging is not applied to the traditional SOA precursors (e.g., Shrivastava et al., 2011). One could investigate approaches to treat aging within a 2p framework (e.g., Shrivastava et al., 2013), which would be a follow up to this work; however, we do not believe the level of understanding is sufficient to justify such approaches at this time. Please also see responses to Reviewer #3.

3. *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.”*

The application of the carbon number-polarity grid published in Barsanti et al. (2011) did rely on tuning (of sorts) to capture SOA formation assuming the presence of a low-volatility accretion product. However, there is nothing inherent in the model that requires the use of chamber data. The model could also be applied using output from a gas-phase kinetic model (such as MCM or GECKO-A).

4. *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.*

Camredon et al. (2010) used simulation results to assign structures to peaks detected by ESI-MS and confirmed with LC-MS. To indicate that in both studies some of the compounds were positively identified and others were not, the following changes (in bold) have been made: “In dark alpha-pinene ozonolysis experiments by Yu et al. (1999), 55-95% of the SOA mass formed could be attributed to **identified and hypothesized** oxidation products that are relatively volatile, with K_p values... In more recent dark alpha-pinene ozonolysis experiments by Camredon et al. (2010), also at high M_o , all of the **proposed and identified** major monomeric oxidation products in the condensed phase have K_p values...” (see also the response to Reviewer #1, minor comment #4).

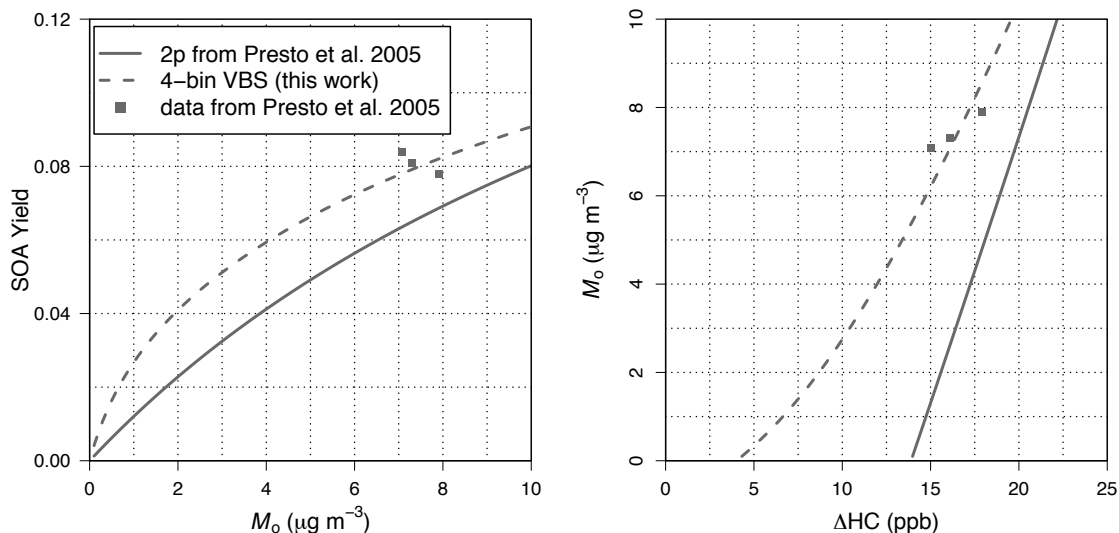
5. *I find the discussion of the Pathak et al. (2007) work to be a bit unfair to the 2p models: the “underestimation” of SOA by the 2p model at low aerosol mass concentrations was not (necessarily) the result of limitations of the 2p model, but of the concentration range considered during the fitting. 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.*

We have revised the paragraph. It now reads: “With the 2p fitting approach, the relatively volatile products that are formed in significant quantities in experiments with high ΔH_C levels (and thus high M_o) “mask” the presence of lower volatility products formed with much lower α values. Thus, lower volatility products may not be adequately represented by K_p values derived from high M_o chamber experiments, though such lower volatility products may explain all SOA formation in the atmosphere. Evidence for this has been provided by

low M_o chamber experiments. For example Pathak et al. (2007a) reported, also for dark α -pinene ozonolysis experiments, that existing 2p parameters significantly underestimated SOA at low mass loadings (see also Presto and Donahue (2006)). As described in Presto and Donahue (2006), the VBS fitting approach has some advantages over the 2p fitting approach that are achieved by fixing the volatility bins (C^* values) based on experimental and/or ambient M_o ranges and fitting only the α values. For a typical 4-species basis set (e.g., $C^* = \{0.1, 1, 10, 100\} \text{ mg m}^{-3}$) the number of free parameters, four, is the same as with the 2p approach; however, the VBS parameters are much less covariant because the volatility space is fixed. Also because of the fixed logarithmically-spaced volatility bins, VBS parameters may be better able to represent SOA formation at low M_o , specifically when limited data exist.”

6. *I will admit I am a bit confused about the relationship between Fig. 1a and Fig 1b. SOA Yield is typically defined as $\Delta\text{SOA}/\Delta\text{HC}$. 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.*

In Fig. 1a, $M_o/\Delta\text{HC}$ vs. M_o is plotted, in Fig 1b, M_o vs. ΔHC . Because ΔHC appears in the denominator in 1a and the sum of ratios does not equal the ratios of the sums, the transformation between 1a and 1b is not linear. However, the reviewer did identify an error in Fig. 1; the data points intercepting the parameterization curves should be consistent. The reported SOA yields from Presto et al. (2005) were corrected for temperature in Fig. 1a, while the M_o values were not similarly corrected. We have corrected the error in the revised manuscript (retaining the reported temperature of $T = 295 \text{ K}$). The two panels are now consistent, as illustrated in the plot below. We have carefully checked all other figures to confirm no similar error(s) had been made. We regret the error, but note that it does not change the discussions and conclusions of the study. We thank the reviewer for catching this detail.



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.

We agree and have revised for clarity. We have added the following text in section 2.1: “Figures 1a and 1b illustrate the relationship between chamber M_0 and Δ HC levels and predicted SOA yields and mass concentrations using 2p and VBS fitting approaches for dark α -pinene ozonolysis experiments (**shown only for $M_0 \leq 10 \mu\text{g m}^{-3}$** , see supplementary material Table S1 for a descriptive list of all experimental data **including full M_0 and Δ HC ranges**.)” And “The Presto et al. (2005) data set spans Δ HC levels from 15-210 ppb and M_0 values from 7-346 $\mu\text{g m}^{-3}$ (three data points with $M_0 < 10 \mu\text{g m}^{-3}$), while Shilling et al. (2008) spans Δ HC levels from 0.3-14 ppb and M_0 from 0.1-7 $\mu\text{g m}^{-3}$ (twenty data points with $M_0 < 10 \mu\text{g m}^{-3}$).” Please also see responses under “General”.

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 $\mu\text{g/m}^3$ or the range shown in the graph), and both have the same lower limit for C^* applied (1 $\mu\text{g/m}^3$, 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.*

We (in our responses) and others (Matsunaga and Ziemann, 2010; Henry et al., 2012) have articulated the need for conducting chamber experiments over a wide range of experimental conditions. Regarding the figures this reviewer presents, published 2p parameterizations used in CMAQ and other CTMs were not developed constraining product volatility. Thus, when data at low M_0 are sparse, the VBS approach will better represent the data and there is an opportunity to provide improved parameters, as demonstrated in this work. There is no additional (and arguably lesser) benefit to be gained by simply refitting the data. For example, looking at Figure 4 for sesquiterpenes, we recommend using the CMAQ default

parameters over those of the VBS from Tsimpidi et al. (2010) and Pye et al. (2010). Given the spread and uncertainties in the data at low M_o , additional fitting would not produce an objectively better fit when one considers that the selection of atmospherically relevant data points requires subjective judgment.

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.

We agree. We have replaced the “Fig. 1 parameterizations” with “some chamber-based”.

- 7. 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.*

Please see previous responses, as well as responses to Reviewer #1, comment #2.

- 8. 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.*

This was not clear in the original manuscript and has now been revised. The pseudo-data were generated using the published VBS parameters at $T=298$ K and ΔH_{vap} (which varies with C^* and ranges from 46 to 112 kJ mol⁻¹) reported in Shrivastava et al (2008) and Grieshop et al. (2009). To generate pseudo-data at $T=272$ and $T=314$ K, we used the reported ΔH_{vap} values to account for the temperature dependence of C^* . In 2p-VBS fitting procedure, $\Delta H_{\text{vap},1}$ and $\Delta H_{\text{vap},2}$ were treated as fitting parameters instead of being fixed so that

the 2p-VBS curves reproduced the VBS curves at all three temperatures. (For non-POA species, ΔH_{vap} is fixed at 30 kJ mol^{-1} , following Pathak et al. 2007b.)

9. *Regarding data presentation: In nearly all figures the authors limit the axes to a maximum SOA concentration of 10 micrograms/m³. However, in the generation of their pseudo-data they say that they create points from 0-200 micrograms/m³. 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.*

The intent of the fitting 2p-VBS parameters is to reproduce the VBS yields curves. By using a large number (~800) of pseudo-data points from 0.1 to 200 mg/m³, we were able to reproduce the VBS yield curves, both at the low and high M_0 range, as the example in Figure S1 shows. Thus, the 2p-VBS fits are not biased by pseudo-data at higher concentrations. No additional error is introduced by the 2p-VBS fit over the VBS parameterization; the original error associated with the VBS fits is retained. In Sections 3.1 and 3.2 we discuss the reasons that the VBS (and by extension 2p-VBS) may/may not agree with other parameterizations and/or chamber data.

We recognize that, based on this and other comments, we have not done a sufficient job differentiating the theoretical underpinnings of the 2p-VBS parameters from the parameters themselves (which are influenced by the specific VBS parameters on which they were based). We have addressed this to a greater extent in the revised manuscript.

Regarding the low NOx isoprene 2p-VBS fit, it does not pass through the data because the VBS parameterization was not based on data. From our paper, Section 3.1.1: “For the low-NOx conditions, the 2p-VBS underpredicted SOA yields compared to chamber observations (Fig. 2a) and was not able to reproduce the observed SOA formation at the lowest ΔHC levels (Fig. 2b) (chamber data: Kroll et al., 2005, 2006; Chan et al., 2006; Chhabra et al., 2010). The low-NOx 2p parameterizations of Henze and Seinfeld (2006) and of Carlton et al. (2009) were in better agreement with the observations (Kroll et al., 2006, Chhabra et al., 2010); **both of which were derived directly from chamber data**. In contrast, Lane et al. (2008a) **extrapolated the low-NOx VBS parameterization from the high-NOx VBS parameterization** as follows: the high-NOx VBS parameters (Lane et al., 2008a; Tsimpidi et al., 2010), based on the “3p” parameterization of Pandis et al. (1991), were adjusted using an M_0 -dependent yield correction from the α -pinene experiments and parameterizations of

Pathak et al. (2007a). It is thus not unexpected that the low-NO_x 2p-VBS parameterization was not able to represent observed SOA formation, particularly at the lowest ΔHC levels.”

10. *P15914/L13: I disagree that the 2p-VBS fits here are “fundamentally” different than the reduced (2-species) VBS fits from Shrivastava 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.*

The differences between the 1-species parameters from Shrivastava et al. (2011) and the 2p-VBS parameters developed here go beyond constraining/not constraining the C* values. Shrivastava et al. (2011) did not fit data (or as in our work pseudo-data) to represent chamber observations. We have clarified that only 1-species was used to represent the traditional volatile precursors. Please also see response to Reviewer #3, comment #4.

11. *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.*

Please see responses above.

12. *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-NO_x fits to low-NO_x data doesn’t seem warranted when there are actual data that can be used.*

We agree.

1: Efforts now have been made to clarify that no extrapolations between high and low NO_x parameters were performed in this work, and that any such discussion details the methods used to obtain the parameters reported by Tsimpidi et al. (2010). (See also the response to Reviewer #1, minor question #7).

2: We stated in the conclusion that we do not think extrapolating between high- and low-NO_x conditions produces reliable parameters. As noted in the introduction, it was our intention to detail the often overlooked connections between experimental conditions, parameter optimizations, and model predictions. In order to do this, we carefully examined the origins of the VBS parameters reported in Tsimpidi et al. (2010), our starting point, which was not (in all cases) straightforward. We admit to being surprised at some of our findings and believe that there is a need to publish these findings as guidance for future measurement and modeling studies.

13. *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.*

Similarly to above, it was our intent to point out where improvements can be made in the links between laboratory experiments and model simulations. We agree that the alkanes are one area where much more data are needed. Nonetheless, alkanes are included as a precursor in such models and SOA formation is represented using either 2p or VBS parameters.

14. *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.*

Agreed. In Table 3 we note which sets of parameters were determined to be the “best available” based on the comparison with many published chamber studies. For sesquiterpenes, the CMAQ parameters were determined to be the best available.

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

This has been revised to: “specifically when limited data exist”.

References:

Dzepina et al., *Environmental Science & Technology*, 45: 3496-3503, 2010

Henry et al., *Environmental Science & Technology*, 46: 12347-12354, 2012

Matsunaga and Ziemann, *Aerosol Science & Technology*, 44: 881-892, 2010