We thank the reviewers for their comments. The response below and the corresponding changes to the manuscript have helped improve the manuscript. We have highlighted the reviewer comments in blue, our response in red and the changes in the manuscript in *italic red*.

<u>Response to comments made by reviewer 2</u>

1) The model does not take into account the influence of vapor wall-losses on SOA formation, although the influence is substantial. What is the impact of this neglect on the paper's conclusion? For example, would the similar SOA amount obtained from BaseM and SOM models still hold? Since the vapor losses on the wall compete with vapor's oxidations or/and its condensation. The inclusion of vapor losses on the wall may increase the oxidation rate and change the oxidation products' distribution, so the proportion of SOA generated from later-generation products might become larger so that the influence of multi-generation oxidation on SOA concentrations become more important than that shown in current conclusion.

The reviewer is correct to point out that vapor wall-losses are an important experimental artifact that potentially bias model predictions of ambient OA. Accounting for vapor wall-losses could also lead to a substantially different product distribution with varying contributions from different SOA precursors. In order to study the influence of vapor wall-losses in detail, we have performed 3-D model simulations using vapor wall-loss corrected parameterizations, the findings of which are submitted in a companion paper (Cappa et al., 2015) that precisely discuss the issues the reviewer brings up. Here, we briefly respond to the reviewer's queries but would like to point the reviewer to the other paper for more details.

Accounting for vapor wall losses leads to more SOA being formed in the model, compared to when vapor wall losses are not accounted for. In Cappa et al. (2015), this was demonstrated through simulations conducted using the SOM in which separate parameterizations were used that were either corrected for or not corrected for the influence of vapor wall loss during the data fitting. In that work, we also attempted to perform simulations using a BaseM-like model that had been corrected for vapor wall losses such that comparison between BaseM and SOM simulations could help elucidate the potential synergistic effects between vapor wall loss and multi-generational ageing alluded to by the reviewer. However, it was found that it was not possible to develop a robust 2-product parameterization that could be used in the 3D simulations due to the 2-product approach having insufficient resolution to represent the SOA products in volatility space, which led to very poor constraints in modeling the SOA at very low OA concentrations. We concluded that the BaseM would need to be redone with a higher resolution in volatility space, i.e. a four or six-product approach; this additional work has been left for future studies.

In both the eastern US and the South Coast Air Basin, accounting for vapor wall-losses resulted in much larger enhancements in SOA concentrations when the absolute OA concentrations were lower (e.g., rural/remote locations). This finding might imply that multigenerational aging plays an increasingly important role when accounting for vapor wall-losses, especially in remote/rural locations. However, it will be hard to discern this fact until a Base-type model is run with sufficient resolution in volatility space.

For reference, we note that the companion paper (Cappa et al., 2015) was mentioned on Page 25845, Line 17.

2) Not clear to me how the authors discriminate the low NOx scenario and the high NOx scenario in the model. Is there any threshold to cut off them? Does the NOx range used for the low NOx scenario match those measured at Smoky Mountain Site? And the NOx for the high NOx scenario fit those at Urban sites?

At present, we do not consider a dynamic response of NO_x on SOA formation. Rather, we perform two simulations that use SOM parameters determined from separately fitting to chamber observations for experiments conducted under 'low' and 'high' NO_x conditions. These results capture the maximum uncertainty inherent in modeling the NO_x dependence of SOA formation. In the manuscript we argue that

"While most 3-D models include schemes to simulate the NO_x dependence of SOA formation, these schemes remain ad hoc as they are based on limited experimental measurements and also rely on the ability of the model to accurately predict radical concentrations (RO_2, HO_2) or VOC-to-NO_x ratios. In this work, the model predictions from the low- and high-yield simulations bound the NO_x-dependent uncertainty in SOA concentrations and we recommend that future work examine this issue in much more detail."

The NOx range used in smog chamber experiments to derive parameters for the low NOx scenario was 0-5 ppb which does approximately correspond to the NOx concentrations predicted at remote locations such as the Smoky Mountains (see Fig 3 below). The NOx concentration used in toluene smog chamber experiments for the high NOx scenario was ~50 ppb, which approximately matches the concentrations at urban sites (see Fig 3). The NOx range used in smog chamber experiments for other parent VOCs under the high NOx scenario was 100-400 ppb, which is higher than current atmospheric concentrations in the US. The VOC / NOx ratio was maintained at atmospherically relevant levels during these experiments and so the smog chamber results still capture the first order behavior of the "high NOx" system. Models that attempt to smoothly interpolate between the low NOx and high NOx cases (e.g. CMAQ) or that bound the limiting behavior between these cases (this work) could both benefit from new experiments performed at atmospherically relevant "high NOx" concentrations.
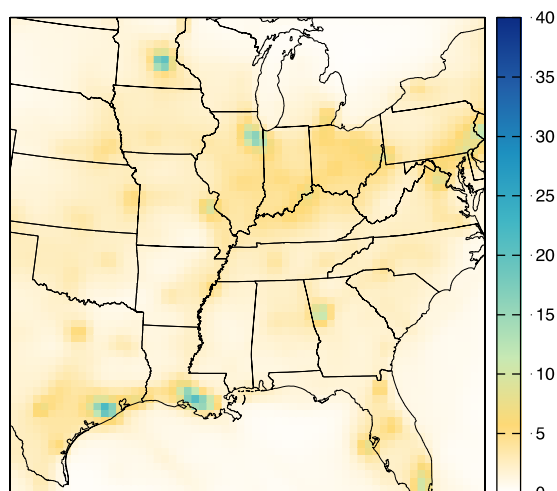

Figure 3: Daily-averaged NO_x concentrations (ppb) on August 20th, 2015 in the eastern US.

Specific comments
1) Page 25840-25841. In a natural way, multi-generational VOC oxidations for SOA formation should be explicitly modeled using detailed gas-phase chemical mechanisms. And there are some studies using such type of SOA model, from the box model to the global model (e.g., Valorso et al., 2011; Lee et al., 2011; Utembe et al., 2011; Lin et al., 2012). This type of model should be discussed in the introduction part.

We have now included and discussed the literature referenced by the Reviewer:

" Chemically explicit models have seldom been used in 3D modeling (e.g. Johnson et al. (2006), Chen et al. (2006), Ying and Li (2011)) due to their heavy computational burden, although some studies have used reduced complexity forms for 3D modeling (e.g. Utembe et al. (2011), Lin et al. (2012)) or have implemented them for box modeling studies (e.g. Lee-Taylor et al. (2011)).

2) Page 25845, line 5. Missing a period after "(2015a)".

Corrected.

Page 25847, line 4-5. Are the SOA concentrations shown for Base model predicted with acid-catalyzed enhancement of isoprene SOA? If so, what would it affect the results if the enhancement was not included? Note that the BaseM model excludes this enhancement.

Yes, the Base model predictions include the acid-catalyzed enhancement of isoprene SOA and as the reviewer points out the BaseM does not. The acid-catalyzed pathway contributes a very small amount of SOA to the total OA mass (see Figure below that shows domain-wide concentrations of acid-catalyzed SOA in SoCAB and the eastern US). The SOM was not parameterized to consider the acid-catalyzed pathway (as only low RH experiments were fit) and hence the BaseM (which served as a reference for the SOM to investigate the effect of multigenerational aging) also did not include the acid-catalyzed pathway. The work has focused on multi-generational aging in the gas-phase however future work will be directed towards parameterizing particle-phase aging that would include acid-catalyzed pathways.

Page 25848, line 12. Where is the Fig. S1? I could not find it in the Supplement.

The wrong supplement was attached to the discussions paper. This will be corrected during the final submission; Figure S.1 (updated to Figure S.2 in revised manuscript) shown below.
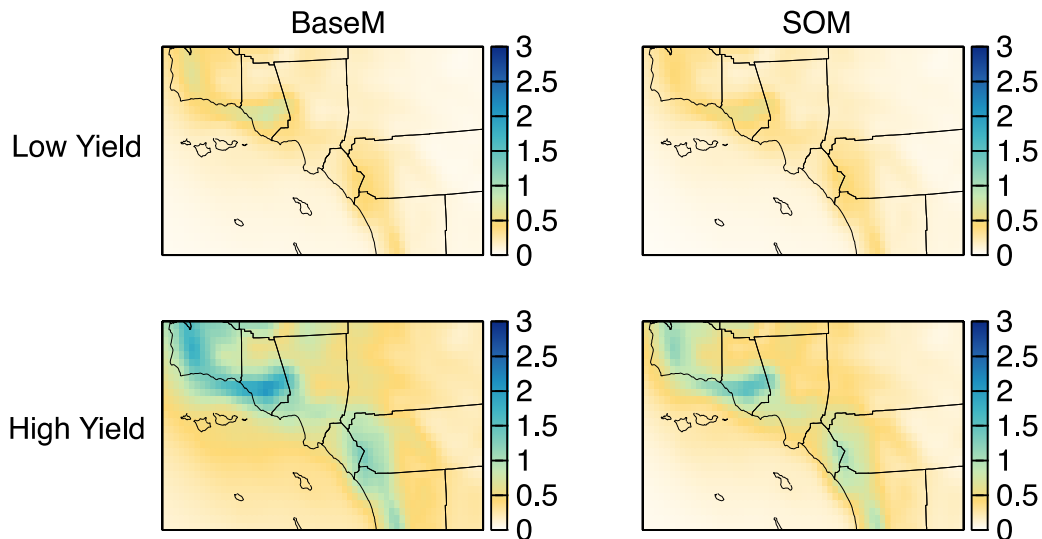
Figure S.2: 14-day averaged SOA concentrations in SoCAB for the BaseM and SOM simulations for the low-yield and high-yield parameterizations.

Page 25852, line 24. Fig. 4 should be Fig.5, and Fig.5 shown in the later text should be Fig.4. The context in the paper does not match the figure shown. Switch the Fig.4 and Fig.5.

Corrected.

Page 15854, line 15-18. The model does not consider the SOA contributions from IVOCs, whereas some other models that managed to close model-measurement gaps include the IVOC SOA as well as the simple OH aging mechanism. Is that possible this SOA enhancement comes from IVOCs oxidation, not from the double-counting effect. i.e., the aging mechanism is added on top of existing parameterizations?

We agree with the reviewer that IVOCs could potentially be an important source of additional SOA formation. One should view the 'double-counting' from ad hoc addition of OH ageing and contributions from IVOCs as, to first order, additive processes. They are not mutually exclusive, i.e. considering one does not preclude the other. In the current study, we did not consider the SOA contributions from IVOCs in this work since their emissions and potential to form SOA remain uncertain (although some new data from Carnegie Mellon University appear promising for inclusion in 3-D models). In this manner, we are able to focus solely on the role that multi-generational ageing plays in determining SOA concentrations from VOCs under different model frameworks (e.g. SOM versus COM-type). On page 25854, lines 15-18, we argue that COM-type aging schemes have been included in 3-D models simultaneously with S/IVOC oxidation and hence have not been studied in isolation. Here, we separate these effects. So while IVOCs could be important sources, our conclusions about COM-type aging schemes remains robust.

In the Supplement, Sect. Cascading Oxidation Model (COM), "It is described in Table S.2" should be Table S.3.

Corrected.

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