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Response to Referee #1

Brian T. Dinkelacker et al.

Author comment on "Predicted and Observed Changes in Summertime Biogenic and Total Organic Aerosol in the Southeast United States from 2001 to 2010" by Brian T. Dinkelacker et al., Atmos. Chem. Phys. Discuss.,
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(1) *This manuscript describes application of the air quality model PMCAMx to the southeastern United States from 2001 to 2010. The authors describe changes in predicted organic aerosol over the time period in response to their simulated changes in anthropogenic emissions of SO₂, NO_x and NMVOCs, in addition to biogenic emissions of isoprene, monoterpenes, and sesquiterpenes. The authors find that NO_x-dependence and partitioning have the largest influence on the anthropogenic controls on bSOA. It's my opinion this conclusion is not robustly defended and I cannot recommend publication in the present form.*

We appreciate the effort devoted by the referee to review our manuscript. In this paper we do show that a chemical transport model that includes the effects of NO_x on the gas-phase chemistry of an environment that is dominated by biogenic VOCs and the changes in the partitioning of semivolatile organic aerosol can explain reasonably well the observed changes in total organic aerosol in this area. The study investigates changes over a decade in which anthropogenic emissions of SO₂, NO_x, VOCs and organic aerosol took place. We do understand the argument of the referee that this does not necessarily prove that the simulated processes are the dominant ones. There can be scenarios in which two processes can have the same effect (e.g., lead to the oxidation of an organic molecule and transfer it to the particulate phase) and simulating just one of them is sufficient to reproduce observations. To address this issue we have rephrased this specific conclusion to explain that a model like PMCAMx simulating specific processes can reproduce the observed changes in this region that is rich in biogenic VOCs and SOA, without getting into the argument about the dominant processes.

Our responses and the corresponding changes (in regular font) follow the comments of the reviewer (in italics).

(2) *The discussion of RH dependence for SOA yield in the Introduction is lacking. Further, the lack of water pathways in the SOA model, and sole reliance on semi-volatile partitioning ... and then finding that semi-volatile partitioning in the predominant controlling mechanism lacks context and the reasoning is flawed. To my knowledge, Kamens was the first to show that changing RH in a laboratory smog chamber experiment does not necessarily change the amount of liquid water, and that water is the overriding*

controlling factor. The Kamens paper cited here has liquid water in the title. For example, in the cited Nguyen paper, there was no seed in the smog chamber experiments. They found no dependence on RH over a wide range. A dramatic change in RH in those experiments did not change liquid water changed (except maybe on the walls?). Nguyen went on to find in later controlled smog chamber experiments with inorganic seeds, where liquid water in aerosols did change, that liquid water for bSOA formation had the predominant effect and in fact seemed to be necessary. Water mattered much more so than pH in those experiments. It's odd that the water context is not discussed, in particular because the authors want to argue that partitioning is the dominant controlling mechanism, and because water pathways – neglected in this model application – are expected to contribute substantially to SOA in the region according to Carlton and Turpin.

We have followed the suggestion of the referee and extended the discussion of the RH dependence on the SOA in the Introduction section. We have also added discussion of previous work regarding the formation of SOA in the aqueous phase. In both cases all references suggested by the reviewer are now cited. We then explain that the version of PMCAMx used in this work does not include these effects that have been observed in laboratory experiments and therefore any significant discrepancies between model predictions and observations could be due to the lack of simulation of these effects.

We also recognize that the explanation of the objectives of the present work may have not been clear enough in the original manuscript. There have been numerous laboratory studies suggesting that a process may affect SOA formation and therefore OA levels in the atmosphere. These include the water related processes discussed above, pH effects, catalytic effects, photo-degradation reactions, oligomerization reactions, etc. Our approach in this paper was to simplify (instead of complicating) the model used and test if this simpler model version can explain the observed changes. The main drivers of SOA formation in the CTM version used are precursor emissions, SOA yields (with empirically derived NO_x -level dependence), NO_x and VOC effects on gas-phase chemistry, semivolatile partitioning and chemical aging reactions as described by the VBS. We do recognize that there is always additional science that one could implement in a CTM for an increased level of mechanistic accuracy. As stated in the manuscript, performance was consistent between the two periods even with significant changes in emissions. The findings suggest that the main drivers already accounted for in the model respond accordingly to those changes. We of course agree that there are processes affecting SOA formation in the atmosphere that are not accounted for in this version of the CTM – and there likely always will be. This discussion has been added to the revised manuscript.

(3) *The authors state in multiple locations that they compared their OA predictions to OA from the CSN and IMPROVE networks. This is highly problematic because neither measures OA, they measure OC. Did the authors mistakenly compare their OA predictions to OC measurements or did they use an OM:OC ratio? If they used a conversion factor what was it and was it constant? It is well established that this ratio is changing. Malm finds that the ratio is increasing. Hand et al., finds that RH problems in the laboratory are likely impacting mass measurements. Depending on the OM:OC ratio method employed, this could impact OA estimates. The authors provide no information on this, and it is difficult to surmise what potential impacts could be.*

We are well aware of difference between OC and OM and the need to convert the OC measurements to OM (or vice versa) for model evaluation. We do agree with the reviewer though that additional information is needed for this part of the analysis. We do explain in the revised manuscript the OM:OC ratios used for the conversion (they are different for the urban and the rural sites) and provide the corresponding references. It should be noted that the IMPROVE network does report OA measurements now using the OM:OC

values used in our work. We should also point out that significant effort was put into verifying the OC measurements, taking care to sort out inconsistencies in artifact corrections for historical data corresponding to different measurement codes for CSN OC. These corrections were applied appropriately to the corresponding measurement codes. A discussion of this issue has been added to the revised paper.

(4) *Line 86: could be primary.*

This is a valid point. We have rephrased the sentence to include the possibility that it may be primary anthropogenic OA too.

(5) *Application of MEGAN: did the land description change at all over the time period and if so, how was this reflected? If not, how is that choice justified?*

The differences in biogenic emissions predicted with MEGAN3 were driven by the differences in WRF predicted meteorology. There were only small changes in the land use change in the overall area over the relatively short period (a decade) between the two simulations. This is now explained in the revised paper.

(6) *Starting at Line 185: the authors state: "Anthropogenic VOC emissions decreased... which should cause a decrease in biogenic OA due to partitioning effects." This is not necessarily true. Less anthropogenic VOCs will result in less competition for OH and other radicals. Biogenic VOCs that may have blown out of the domain in the older time period simulations, may have opportunity to react and form semi-volatile species in the newer time period simulation.*

This is a valid point. We have rephrased this section mentioning the various effects that the change in anthropogenic VOCs can have on biogenic SOA. The partitioning effect due to the reduction of anthropogenic SOA is only one of these effects. There are of course other competitive effects at play in this system and a lot of them (e.g., the effect on OH mentioned) are accounted for in the SOA and gas-phase chemistry of the CTM.