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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Limited effect of anthropogenic nitrogen oxides on Secondary Organic Aerosol formation" *by* Y. Zheng et al.

Anonymous Referee #2

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This paper describes a modeling study of SOA formation and aging using the NCAR CAM4-chem model implementing a new 4-product VBS scheme with different aging parameterizing and comparing to the standard 2-product model, turning on and off aging or high/low-NOx chemistry and reducing NOx. The differences in total OA, type of OA (POA/HOA, SOA/OOA), spatial and vertical distributions, changes in relative contributions from the different VOC-type + low/high NOx pathways are compared within the model and to IMPROVE filter and online AMS aircraft measurements. Small differences (and slight improvement with comparisons) are shown for using the 4-product model and large increases in SOA are shown for the aging scheme. 50 percent NOx reductions result in insignificant changes for global, SE US, and Amazonia SOA. Discussions of compensating effects on oxidants and SOA yields are discussed to explain

the lack of overall sensitivity to NOx reductions.

The manuscript is generally well written and describes a clear and straightforward modeling study exploring basic chemical parameterizations and comparisons to observations. This manuscript warrants publication in ACP after relatively minor revisions.

General comments followed by a detailed list of comments are below.

General/Main Comments:

The title and abstract should include more about the results from the different VBS schemes, aging, and comparison to measurements. The NOx sensitivity study is really only one part of the study. as presented in the paper. The summary reflects a better balance of the overall study investigations and results.

In a number of instances describing the model setup, certain important choices were not explained. E.g. Why was a high-NOx isoprene pathway not included? Why use such a high, unjustified value of OM/OC for POA? Why is oxygen not added during aging? Such omissions make the reader wonder if the agreement and differences are more of an artifact of such choices rather than a reflection of the actual SOA chemistry in the atmosphere.

Can the authors add a short discussion of the significance of omitting high-NO pathway for isoprene oxidation and how that may be effecting the results?

There are a handful of instances where the authors speculate on the reasoning for specific model output results.

For example in Section 4.2.3, it stated: "Consistent with the comparison with the IMPROVE network in Sect. 4.2.1, the models overestimate POA in most regions especially in North America, which will likely increase SOA production due to the larger aerosol surface area available for condensation."

Or in Section 4.3 it is stated: "The dependence of SOA on oxidants concentration

indicates a maximum at medium oxidants level of approximately 0.8e12 molecules cm-3. The low SOA concentration at high oxidants level might be explained by, again, the lower yields of high-NOx pathway, which is associated with high NOx and oxidants levels."

It would seem that rather than speculate on such causes/effects, these hypotheses can be tested with sensitivity studies using the model and speculation should be reserved for instances when there is no further information available. The authors have done a nice job of presenting, deconstructing and discussing much of the results however cases like these examples (and a few others) seem to stop short of using the information the model provides to the full extent possible. I.e. the answer to these speculations is most certainly available from the model – whereas, whether what is happening in the model truly represents certain processes in the atmosphere could be speculated upon.

Detailed Comments:

P23233, L8: remove extra period

P23234, L18,19: missing article - add "the" before "low-NOx" and "high NOx" or make "pathway" plural.

P23234, L17-19: Is generally true? According to the Pankow SIMPOL model (see Table 1 in Kroll and Seinfeld, Atmos Environ 2008) nitrate functional groups lower vapor pressure more than hydroperoxy groups.

P23234, L20: Delete "the"

P23234, L20: "unique chemical signature" seems a bit strong/misleading. As pointed out later in that sentence, RONO2 are formed through a different (and often comparable pathway).

P23234, L25: make "contributes" past tense. This is not necessarily generally true for that location (i.e. study was done in spring/summer. Certainly may not be the case in winter).

P23235, L25: delete "to" before "approximately". Otherwise it reads that it comprises part of a third.

P23234, L26-L2 next page: This logic is a bit non-sequitur in that it notes the effect of NOx on O3 in low-NOx conditions followed a statement that seems to rely on low-NOx conditions dominating (i.e. increase NOx, increase OH, O3). Such a statement should not be made without presenting evidence to support such a connection.

P23236, L1: "total organic matter" could be confused by some as including gas-phase. Clarify that is meant to apply only to the particle phase.

P23236, L2: "usually"? It's this always the case?

P23236, L11-12: Can you provide a reference for the IMPROVE-OC filter analysis? I thought that was an offline technique where the filters were brought back to the lab for analysis. This is not a minor detail as leaving filters around for extended periods, transporting, and analyzing later may impose substantial biases due to evaporation of semi-volatiles or unwanted chemistry. Also, say what the method actually is so the reader doesn't have to go dig up the documentation to get a general sense.

P23236, L20: Specify STP. This varies.

P23237, L5-7: Provide references for PMF factors.

P23237, L12: As a climatological AVERAGE? Climatology by itself is the study of climate.

P23238, L25: should probably cite Donahue 2006 also since the C* formulation is being used rather than the Pankow one.

P23238, L26: POA-to-POC of 2.1? Primary OA has a much lower ratio (near 1 for HOA and 1.5-1.7 for BBOA, see Aiken et al. 2008 EST and the many papers that followed). You mean overall OM/OC OA, mostly dominated by OOA (SOA)?

P23239, L20: Please clarify in the text why a high-NOx isoprene parameterization is

not included. This seems like it could be a major omission, especially considering that this study primarily is an investigation of the NOx dependence of global SOA.

P23240, L17-19: Why is oxygen not added when aging? Presumably the underlying mechanism for lowering the volatility is primarily by the addition of oxygenated functional groups. This would seem to underestimate the mass and the O/C of the SOA formed.

P23246, L24-25: Is surface area really the more important affect or rather OA mass? Obviously higher surface area can help outcompete deposition to the surface of the earth which is part of the model. However, OA mass will promote condensation of higher volatility species. Please clarify. If not obvious from the data, it seems like something that could be probed with the model.

P23249, L22-23: If a high-NO isoprene chemistry were included in the model and produced less SOA there couldn't there be a compensating effect of increasing SOA by shift from the NO to the HO2 pathway. Can the authors discuss this possibility? The isoprene low-NO pathway is clearly an important contribution to the total SOA production in all regions and models.

P23250, L2: make "consider" plural

P23250, L5: change "interference" to "influence"?

P23250, Section 4.3.3: Can the authors comment on why NO3+monoterpene SOA decreases so little with the 50

Figure 1: Some white contour line labels are missing.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 23231, 2015.