

Response to Referee #1

We are grateful to the reviewer for their helpful comments and guidance that have led to important improvements of the original manuscript. Our point-by-point responses are listed below. Reviewer's comments are in black font, and authors' responses are in dark blue. Page and line numbers refer to discussion paper *Atmos. Chem. Phys. Discuss.*, 15, 23231-23277, 2015.

In this manuscript, the authors uses a global chemical transport model to study the effect of changing NO_x emissions to SOA formation, using an updated volatility basis set scheme. The predicted SOA concentrations showed good agreement with observations by aerosol mass spectrometers, both in the temporal and spatial profiles. The global SOA burden was shown to be quite insensitive to NO_x changes, implying that future emission control policies on NO_x may not be effective in controlling global SOA. The manuscript is clear and well written, and fits within the scope of ACP. The comparison with observations demonstrates that the model results are robust and is a strength of this manuscript. I have some questions about the interpretation of the results, but they can be easily addressed with some minor revisions. I recommend publication of this manuscript in ACP.

Main comment:

My only major comment is the interpretation of why changes in NO_x do not lead to significant changes in global SOA. From Figs. 8 and S4, it seems to me that there simply is no significant change in beta. Since SOA yield depends critically on this branching ratio, if there is no change in beta, there is no change in relative SOA formation. To me, that seems to be the most straightforward explanation of the model results. As I understand, most areas are not NO_x-limited in the context of SOA formation, since NO_x ≫ HO₂. So a 50% reduction in NO_x (or NO) would translate to a very small change in beta. This point is further highlighted by Fig. 10, which shows no changes in SOA contributions for essentially all of the pathways. Therefore, the proposed reasons detailed in Section 5 are not as important as the lack of change in beta. I believe that if you go to greater reductions in NO_x (~90%), one might start to see changes in relative SOA formation. This does not change the conclusions of the manuscript (50% reduction in NO_x leads to no change in SOA), but I believe the reason for this is simply current NO_x is too high for HO₂ pathways to compete, even with a 50% reduction in NO_x.

Response: We agree with the reviewer that one major reason is that the change in branching ratio β is small. We've mentioned this point at several places, e.g., at P23247 L17: "The surface NO/HO₂ ratio has been greatly reduced by 67%, while the change in branching ratio β is small (-3.4 %)." As stated in Sect. 4.3, this decrease in β would lead to a shift to the HO₂ pathway thus a tendency of increase in SOA concentration. However, this increase tendency is too small and is offset by the decrease in NO₃ pathway and the reduced oxidation capacity. So this small change in β is an important reason but not the whole story.

To state clearer about the role of β , we modify the main text as follows:

At P23232 L19 (Abstract), we add: "... can be largely attributed **to a limited shift in chemical regime**, to buffering in chemical pathways...".

At P23247 L18, we add: "... the change in branching ratio is small (-4.3%), **indicating the NO concentration in the model is too high for HO₂ to compete.**"

At P23247 L21, we modify: "... the southeast US and the Amazon, both of which are mostly in the NO_x-limited regime **in terms of ozone formation** due to their large BVOC emissions (Lane et al., 2008;Malm et al., 2005), **i.e. the concentration of O₃ and OH are positively related to concentration of NO_x.**"

At P23249 L8, we add: "Due to the limited change in β , the effect of shifting to high-yield HO₂ pathway is very small."

At P23251 L14, we add: "One major reason is the very small reduction in branching ratio β thus limited shift between high- vs. low-NO_x chemical regimes."

At P23254 L6, we modify: "The fact that SOA formation is stable to changes in NO_x can be largely attributed **to limited shift in low- and high-NO_x regimes**, to buffering in chemical pathways (e.g. O₃ versus NO₃-initiated oxidation), and to offsetting tendencies in the biogenic versus anthropogenic SOA responses. "

Other comments:

- Table S1 and S2 show that the enthalpies of vaporization are different between the 2-product scheme and the VBS scheme. How much the improved agreement is due to the changes in enthalpies of vaporization?

Response: The effect of different enthalpies of vaporization (ΔH) is relatively small. We did a sensitivity test which is the same as VBS_agHigh scheme except that the ΔH is fixed at 42 kJ mol⁻¹ (same as the 2-product scheme). The annual mean SOA burden in this scheme is about 2% lower than the VBS_agHigh scheme, which is not significant. And the change in ΔH has almost no effect on the spatial distribution and vertical profile of SOA.

At P23239 L17, we add: "Changing the enthalpies of vaporization (see Table S1, S2) has no significant effect on simulated SOA burden (difference smaller than 2%)."

- What is the fossil content in SOA? Can this be used as an additional constraint for the model?

Response: In the current version CAM4-chem, organic aerosol from fossil fuel burning is regarded as primary, including both hydrophobic (OC1) and hydrophilic (OC2) organic carbon. As stated in Sect. 3.2, SOA includes anthropogenic species from oxidation of benzene, toluene and xylenes, and biogenic species from isoprene and monoterpene. Fossil content is not included in SOA in current CAM4-chem. In the model-observation comparison of total OA (Sect. 4.2.1~4.2.3), the fossil content is included.

To elucidate this point, at P23239 L6, we add: “Fossil content is regarded as POA including both hydrophobic and hydrophilic compounds and is not included in SOA in CAM4-chem.”

- How good is the assumption that POA == HOA and SOA == OOA? Could that lead to biases in predicting primary/secondary split and errors in POC estimation as described in Section 4.2.1?

Response: The assumption POA==HOA and SOA==OOA is relatively well validated from field measurements and analysis, e.g. Zhang et al., (2005), Lanz et al., (2007), Aiken et al., (2009). Based on current knowledge, we think the main reason leading to the error in POC estimation is the emission inventory and/or the assumption that all POC in the model is non-volatile. In Section 4.2.1, the overestimation of POC is clearly revealed without any assumption like POA==HOA, Because as stated in P23244 L16, the simulated POC is already larger than the observed total OC (Fig. 2).

At P23246 L13, we add the following references about the assumptions: “The observed OOA is a surrogate for SOA, and HOA is a surrogate for POA in AMS measurements (Aiken et al., 2009; Lanz et al., 2007; Zhang et al., 2005).”

- Equation (2): the ratio beta should include NO and HO₂ concentrations, and it is only because we expect k_{RO₂+NO} to be similar to k_{RO₂+HO₂} that it can simplified to equation (1)

Response: corrected.

- Pg. 23234 Line 25: add comma between Bakersfield and California, and after California

Response: corrected.

- Pg. 23240 Line 17: How is O:C ratio important in this study? I don't see any comparison of modeled O:C to observed O:C. Is it used to calculate OA:OC?

Response: We do not compare modeled and observed O:C ratios in this study because we do not have sufficient O:C observations to validate this global model. As described in Section 3.2, for POA, the current CAM4-chem tracks POC (the carbon content only in the primary particles) and we assume a POA-to-POC ratio of 1.4 when comparing to the observed total OA (Section 4.2.2). For SOA, we use the following surrogate SOA products: C₁₀H₁₆O₄ for SOA from monoterpene, C₅H₁₂O₄ for SOA from isoprene, C₆H₇O₃, C₇H₉O₃, and C₈H₁₁O₃ for SOA from benzene, toluene and xylenes, so the corresponding O:C ratios are 0.47, 0.32, 0.38, 0.34 and 0.31, respectively. The overall O:C ratio depends on the split between POA and SOA and the fraction of each SOA species.

We describe how the model treats OA:OC in Section 3.2. To be clearer about the O:C ratio, at P23239 L6, we add: “...for and xylenes, **therefore the O:C ratio is constant for each SOA species. The overall O:C ratio in total OA depends on the split between POA and SOA, and the fraction of each SOA species.**”

- Pg. 23243 Line 4 and Tables S1 and S2: it seems that the average concentrations of OA is $0.3 - 5 \text{ ug m}^{-3}$ (Table 6). I suggest using yields at a lower OA concentration instead of 10 ug m^{-3} .

Response: We choose to show the yields at 10 ug m^{-3} because this is a common choice from previous literature. Now we show the yields at both 10 and 1 ug m^{-3} as suggested by the reviewer. Please refer to the supplement for the updated tables.

- Table 4: remove f from fVBS_agHigh

Response: corrected.

- I suggest including a table of abbreviations because there are many of them used in this manuscript and a reader outside of the field will be easily confused

Response: At P23236 L2, we add: “Table 1 summarizes major abbreviations used in this study.”

Table 1. Abbreviations used in this study.

Abbreviations	Description
OA	Organic aerosol, including the mass of carbon, oxygen and other possible elements. OA = POA + SOA
OC	Organic carbon. OC = POC + SOC
POA	Primary organic aerosol
POC	Primary organic carbon.
SOA	Secondary organic aerosol.
SOC	Secondary organic carbon.
SOG	Secondary organic gas.
ASOA	Anthropogenic secondary organic aerosol.
BSOA	Biogenic secondary organic aerosol.
AVOC	Anthropogenic volatile organic compounds.
BVOC	Biogenic volatile organic compounds.
SOAM	SOA from monoterpene oxidation.
SOAI	SOA from isoprene oxidation.
MTP	Monoterpenes.
ISOP	Isoprene.
HOA	Hydrocarbon-like organic aerosol, a surrogate for POA.
OOA	Oxygenated organic aerosol, a surrogate for SOA.

Reference:

Aiken, A. C., Salcedo, D., Cubison, M. J., Huffman, J. a, Decarlo, P. F., Ulbrich, I. M. and Docherty, K. S.: and Physics Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) – Part 1 : Fine particle composition and organic source apportionment, , 9, 6633–6653, doi:10.5194/acpd-9-8377-2009, 2009.

Lanz, V. a., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C. and Prévôt, a. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, *Atmos. Chem. Phys.*, 7(6), 1503–1522, doi:10.5194/acp-7-1503-2007, 2007.

Zhang, Q., Worsnop, D. R., Canagaratna, M. R. and Jimenez, J.-L.: Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols, *Atmos. Chem. Phys.*, 5(5), 3289–2211, doi:10.5194/acp-5-3289-2005, 2005.

Response to Referee #2

We are grateful to the reviewer for their helpful comments and guidance that have led to important improvements of the original manuscript. Our point-by-point responses are listed below. Reviewer's comments are in black font, and authors' responses are in dark blue. Page and line numbers refer to discussion paper *Atmos. Chem. Phys. Discuss.*, 15, 23231-23277, 2015.

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-NO_x chemistry and reducing NO_x. 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 NO_x 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 NO_x 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 NO_x 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 NO_x 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.

Response: In the abstract, we include the main results of updated SOA model and comparison with observations. To be more sufficient, we add: "We have updated the SOA scheme in the global NCAR Community Atmospheric Model version 4 with chemistry (CAM4-chem) by implementing a 4-product Volatility Basis Set (VBS) scheme, including NO_x-dependent SOA yields and aging parameterizations. **Small differences are found for the no-aging VBS and 2-product schemes; large increases in SOA production and SOA-to-OA ratio are found for the aging scheme.** The predicted organic aerosol amounts capture both the magnitude and distribution of US surface annual mean measurements from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network by 50%, and the simulated vertical profiles are within a factor of two compared to Aerosol Mass Spectrometer (AMS) measurements from 13 aircraft-based field campaigns across different region and seasons."

We do not change the title because the effect of NO_x reduction is the main application result in this study, and this conclusion holds for every SOA scheme, no matter whether or not using VBS framework, including NO_x dependency or adding aging effects.

In a number of instances describing the model setup, certain important choices were not explained. E.g. Why was a high-NO_x 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.

Response: The VBS scheme we implemented in CAM4-chem is based on Pye et al. (2011), which does not include the high-NO_x isoprene pathway. To account for this omission, we performed an additional simulation that includes the high-NO_x isoprene pathway using the VBS parameters from Lane et al. (2008), and discuss the results in the Supplement.

We originally chose the POA-to-POC ratio of 2.1 based on Turpin and Lim (2001), which suggests a factor of 2.1 ± 0.2 for nonurban organic aerosols. Now, we have changed the POA-to-POC ratio to a traditionally used value of 1.4, because POA has a lower OA-to-OC ratio than nonurban aerosols (dominated by SOA). Fig. 4 to Fig. 7 and related statistics in the main text have been modified accordingly.

We do not account for the added oxygen when aging due to the large uncertainties in the aging processes and the complexity of various SOA species. The change of O/C ratio is not the focus of this study because we do not have sufficient observational evidence to validate the simulated O/C ratio in the global model. We choose a high aging parameter $k_{OH} = 4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ to provide an upper limit of SOA estimation, which would partly offset the omission of added oxygen mass during aging.

Modifications include:

At P23238 L26, we delete “and assumes a POA-to-OC ratio of 2.1...”, and add: “Later in Section 4.2, we assume a POA-to-POC ratio of 1.4 (Aiken et al., 2008; White and Roberts, 1977) to calculate modeling POA and OA to compare with observations.”

At P23239 L21, after “SOA formed from OH-initiated photooxidation of isoprene still only has one set of yields following the low-NO_x parameterizations”, we add “We do not change this isoprene-SOA parameterization to remain consistent with the VBS framework from Pye et al. (2010). Additional simulations that include the high-NO_x pathway of isoprene chemistry are discussed in the Supplement.”

At P23240 L19, after “The oxygen-to-carbon ratio (O:C) is assumed to be constant for each surrogate SOA product thus increase in SOA mass due to the addition of oxygen is not considered in the aging process”, we add: “Considering the complexity of various

SOA species and the large uncertainties in aging process, the assumption of fixed O:C ratio for each SOA product surrogate is acceptable for global model parameterizations.”

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?

Response: We performed additional simulations that include the high NO pathway for isoprene oxidation and add a discussion in the Supplement as follows.

“The VBS schemes (VBS, VBS_agHigh, etc.) that we implement into CAM4-chem as described in the main text are based on the published VBS parameterizations from Pye et al. (2010), which does not consider the high-NO_x pathway for isoprene oxidation. Here we performed an additional simulation “VBS_agHigh_isop” to evaluate the effect of this omitted pathway.

“In the VBS_agHigh_isop scheme, we add the high-NO_x branch for isoprene-oxidized SOA formation (ISOPO₂ + NO) using the parameters from Lane et al. (2008). The SOA mass yields are 0, 0.00026, 0.0195, 0.013 for C* of 0.1, 1, 10, 100 μg m⁻³, respectively, fit using a density of 1.3 g cm⁻³ to be consistent with Pye et al. (2010). Adding this pathway, the VBS_agHigh_isop scheme gives an annual mean SOA burden of 0.86 ± 0.05 Tg[C] and a net SOA production of 46.8 ± 1.9 Tg[C] per year, both of which are about 20% smaller than the VBS_agHigh scheme, and larger than the two no-aging schemes (2-product and VBS). The VBS_agHigh_isop scheme shows no significant advantage over the VBS_agHigh scheme in model-observation comparisons.

“We then performed a sensitivity run using the VBS_agHigh_isop scheme, in which anthropogenic NO emissions are reduced by 50%. Results in the southeast US and the Amazon are shown in Fig. S5. SOAM and anthropogenic SOAs through each branch behave similar to the VBS_agHigh. For isoprene oxidation in the southeast US, the HO₂ pathway increases and NO pathway decreases. While the effect of shifting to high-yield HO₂ pathway is masked due to the reduced OH concentration (about -15%, Fig. S2). The total SOA concentration decreases from 3.4 ± 0.5 to 3.0 ± 0.4 μg m⁻³. This 0.4 μg m⁻³, 10% reduction is smaller than the change in VBS_agHigh scheme (0.5 μg m⁻³, 12%), and is smaller than one standard deviation of multi-year variation, suggesting the SOA response to the NO perturbation is not significant. In the Amazon, all branches show a decrease with reduced NO. The total SOA reduction (0.1 μg m⁻³, 2%) is non-significant. These conclusions are consistent with the VBS_agHigh 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 oxidant concentration indicates a maximum at medium oxidant level of approximately 0.8×10^{12} molecules cm^{-3} . The low SOA concentration at high oxidant level might be explained by, again, the lower yields of high-NO_x pathway, which are associated with high NO_x and oxidant 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.

Response: We appreciate the reviewer’s comments about the speculations. We make several modifications in the manuscript.

In Section 4.2.3, the major influence is more OA mass to promote condensation of semi-volatile species. At P23246 L24-25, we delete “... which will increase SOA production due to the larger aerosol surface area available for condensation”, and add “which will promote condensation of semivolatiles onto pre-existing organic matter thus forming more SOA”.

In Section 4.3 and Fig. 8, we have re-examined the model outputs and find that the high SOA concentrations associated with relative low branching ratios and medium oxidant levels are mostly from tropical rainforests, where there are large emissions of precursor VOCs. Therefore we modify the paragraph as follows:

At P23248 L4, we delete “which may reflect the fact that low-NO_x pathway has higher SOA yields”, and replace by “which mostly locate in tropical rain forests with large BVOC emissions and high SOA production efficiency through the low-NO_x pathway”.

At P23248 L9, we delete “might be explained by, again, the lower yields of high-NO_x pathway, which is associated with high NO_x and oxidants levels”, and replace by “mostly occur in polluted regions where SOA production is overwhelmingly dominated by the high-NO_x (low-yields) pathway”.

Detailed Comments:

P23233, L8: remove extra period

Response: corrected.

P23234, L18,19: missing article - add “the” before “low-NO_x” and “high NO_x” or make “pathway” plural.

Response: corrected.

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.

Response: The organic nitrates can be low in volatility. The high-NO_x pathway has lower yields because organic nitrates (RONO₂) are not the dominant product of the RO₂ + NO reaction channel. The major channel is alkoxy formation (RO₂+NO->RO+NO₂) which does not directly form SOA. Our previous statement was not precise.

At P23234 L17, we delete "... their oxidation products ROOH formed from the low-NO_x pathway have a lower volatility than the oxidation products RONO₂ under the high-NO_x pathway, thus are more likely to condense to form SOA." Instead we add: "... both the ROOH groups and the RONO₂ groups can be low in volatility thus facilitating SOA formation, but RONO₂ is not the dominant product of the RO₂ + NO branch, therefore the high-NO_x pathway usually has lower yields of SOA."

P23234, L20: Delete "the"

Response: corrected.

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).

Response: We replace the word "unique" by "distinctive".

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).

Response: corrected.

P23234, L25: delete "to" before "approximately". Otherwise it reads that it comprises part of a third.

Response: corrected.

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

Response: At the beginning of the sentence, we clarify that the positive relationship between NO_x and oxidants (i.e. increase NO_x, increase OH, O₃) happens "in the NO_x-limited regime". This is part of well-understood NO_x gas-phase chemistry. Later in the manuscript (e.g. Section 4.3 and Fig. S2), we have shown the positive relationship

between NO_x and oxidants at global scale and in the two target regions, the southeast US and the Amazon, confirming that both the two regions are in the NO_x-limited regime in terms of ozone formation.

At P23234 L26, We rephrase the sentence here and add a reference book: “In the NO_x-limited regime (**in terms of O₃ formation**), the OH-initiated oxidation of CO, methane (CH₄) and other VOCs in the presence of NO_x produces O₃. Thus **in such conditions**, increasing NO_x by human activities should, in principle, lead to the increase in atmospheric oxidation capacity (OH and O₃) (**Seinfeld and Pandis, 2006**), and result in higher SOA yields.”

At P23247 L21, we modify: “...both of which are mostly in the NO_x-limited regime **in terms of ozone formation** due to their large BVOC emissions (Lane et al., 2008), **i.e. the concentration of O₃ and OH are positively related to concentration of NO_x.**”

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.

Response: we add “total **particle phase organic matter**”.

P23236, L2: “usually”? It’s this always the case?

Response: Yes the term OC always refers to organic carbon in atmospheric chemistry. We delete the word “usually”.

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.

Response: At P23236 L11, we delete “IMPROVE-OC is measured by semi-online filter analyzer”, and add “IMPROVE OC is collected using quartz fiber filters for 24 hours every third day, analyzed offline by thermal optical reflectance (TOR) (Chow et al., 1993), and corrected for an approximate positive artifact (Dillner et al., 2009). Assumptions made in this correction may not always be appropriate (Watson et al., 2009), and the potential negative artifacts due to the volatilization of particulate organics are not accounted.”

P23236, L20: Specify STP. This varies.

Response: We add: “... in standard temperature and pressure conditions (**STP: 298K, 1atm**)”.

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

Response: The 42 AMS surface measurements are summarized in Spracklen et al. (2011) and Zhang et al. (2007), and use a multiple component analysis (MCA). This MCA method uses a different algorithm to solve the same mathematical problem as the positive matrix factorization (PMF) model. There results are in general agreement (Canagaratna et al., 2007; Lanz et al., 2007).

At P23237, we add: “The HOA and OOA are determined by a multiple component analysis (MCA, Zhang et al. 2007).”

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

Response: The term “climatology” refers to normal values or multi-year average in the context of climate science, so we do not change this word usage. In chemistry-climate modeling, one commonly refers to “ozone climatology” and “aerosol climatology”.

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

Response: Reference added.

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)?

Response: We originally chose this factor of 2.1 based on Turpin and Lim (2001), which suggests a factor of 2.1 ± 0.2 for nonurban organic aerosols. Now we have changed the POA-to-POC ratio to a traditionally used value of 1.4, because as the reviewer suggested, POA has a lower OA-to-OC ratio than nonurban aerosols (dominated by SOA).

At P23238 L26, we delete “and assumes a POA-to-OC ratio of 2.1...”, and add: “Later in Section 4.2, we assume a POA-to-POC ratio of 1.4 (Aiken et al., 2008; White and Roberts, 1977) to calculate modeling POA and OA to compare with observations.”

At P23246 L3, we delete “The model underprediction of total OA is not as large as in Heald et al. (2011) probably due to the high POA-to-POC ratio of 2.1...”

Fig. 4, 5, 6 and 7 have been updated using the POA-to-POC ratio of 1.4, as well as corresponding statistics reported in the main text.

P23239, L20: Please clarify in the text why a high-NO_x 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 NO_x dependence of global SOA.

Response: At P23239 L21, after “SOA formed from OH-initiated photooxidation of isoprene still only has one set of yields following the low-NO_x parameterizations”, we add “We do not change this isoprene-SOA parameterization to remain consistent with the VBS framework from Pye et al. (2010). Additional simulations adding the high-NO_x pathway of isoprene are discussed in the Supplement.”

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.

Response: We do not account for the added oxygen when aging due to the large uncertainties in the aging processes and the complexity of various SOA species. The change of O/C ratio is not the focus of this study because we do not have sufficient observational evidence to validate the simulated O/C ratio in the global model. We choose a high aging parameter $k_{OH} = 4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ to provide an upper limit of SOA estimation, which would partly offset the omission of added oxygen mass during aging.

At P23240 L19, we add: “Considering the complexity of various SOA species and large uncertainties in aging process, the assumption of fixed O:C ratio for each SOA product surrogate is acceptable for global model parameterizations.”

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.

Response: The major influence is more OA mass to promote condensation of semi-volatile species.

At P23246 L24-25, we delete “... which will increase SOA production due to the larger aerosol surface area available for condensation”, and add “which will promote condensation of semivolatiles onto pre-existing organic matter thus forming more SOA”.

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.

Response: We performed additional simulations and discuss the effect of including the high-NO isoprene chemistry in the Supplement. Please see the response earlier in this document, which include: “... For isoprene oxidation in the southeast US, the HO₂

pathway increases and NO pathway decrease. While the effect of shifting to high-yield HO₂ pathway is masked due to the reduced OH concentration (about -15%, Fig. S2)...”.

P23250, L2: make “consider” plural

Response: corrected.

P23250, L5: change “interference” to “influence”?

Response: corrected.

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

Response: This is because the reduction in NO₃ is not as large as 50% due to the NO_x gas-phase chemistry. In the southeast US, the 50% reduction in anthropogenic NO emission is equivalent to 45% in total NO emission, and leads to a 49% decrease in atmospheric NO_x (=NO+NO₂) and only a 24% decrease in NO₃ concentration.

At P23250 L7, we add: “This reduction in NO₃-branch compared to its normal value is relatively small because the decrease in NO₃ concentration is only 24%.”

Figure 1: Some white contour line labels are missing.

Response: corrected.

Reference:

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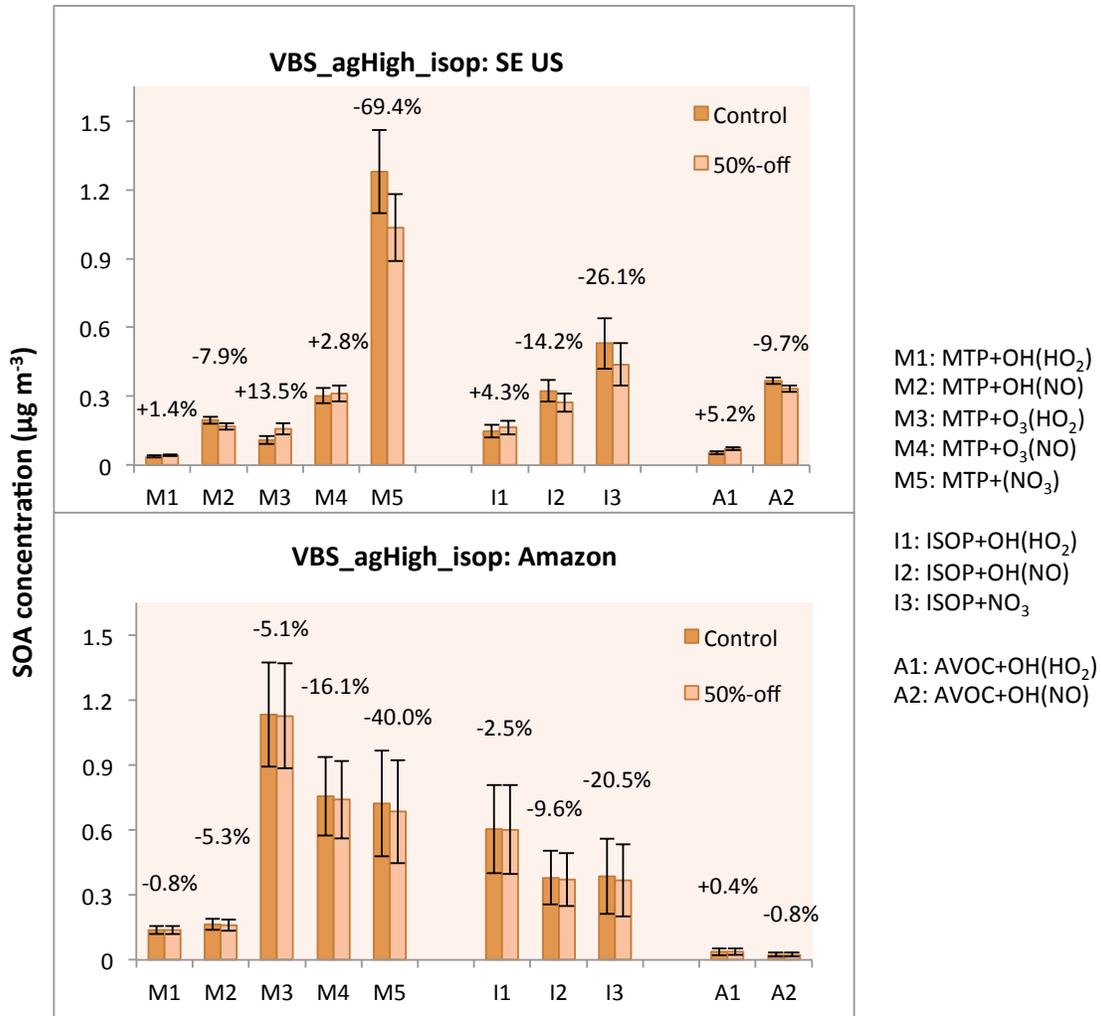


Figure S5. Annual mean surface SOA concentration ($\mu\text{g m}^{-3}$) in the control run and the sensitivity run (with 50% anthropogenic NO emission off) from different pathways using the VBS_agHigh_isop scheme, averaged over the southeast U.S. [32°-40°N, 95°-77°W] and the Amazon [17°S-5°N, 77°-55°W]. The numbers above each bar denote the relative contributions (%) of each SOA formation pathway to the total SOA concentration change. The sum of all numbers equals -100% due to the overall decrease in total SOA.

1 **Limited effect of anthropogenic nitrogen oxides on secondary organic**
2 **aerosol formation**

3

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1 **Abstract**

2 Globally, secondary organic aerosol (SOA) is mostly formed from emissions of biogenic
3 volatile organic compounds (VOCs) by vegetation, but can be modified by human
4 activities as demonstrated in recent research. Specifically, nitrogen oxides
5 ($\text{NO}_x = \text{NO} + \text{NO}_2$) have been shown to play a critical role in the chemical formation of low
6 volatility compounds. We have updated the SOA scheme in the global NCAR
7 Community Atmospheric Model version 4 with chemistry (CAM4-chem) by
8 implementing a 4-product Volatility Basis Set (VBS) scheme, including NO_x -dependent
9 SOA yields and aging parameterizations. Small differences are found for the no-aging
10 VBS and 2-product schemes; large increases in SOA production and SOA-to-OA ratio
11 are found for the aging scheme. The predicted organic aerosol amounts capture both the
12 magnitude and distribution of US surface annual mean measurements from the
13 Interagency Monitoring of Protected Visual Environments (IMPROVE) network by 50%,
14 and the simulated vertical profiles are within a factor of two compared to Aerosol Mass
15 Spectrometer (AMS) measurements from 13 aircraft-based field campaigns across
16 different region and seasons. We then perform sensitivity experiments to examine how
17 the SOA loading responds to a 50% reduction in anthropogenic nitric oxide (NO)
18 emissions in different regions. We find limited SOA reductions of 0.9 to 5.6%, 6.4 to
19 12.0% and 0.9 to 2.8% for global, the southeast US and the Amazon NO_x perturbations,
20 respectively. The fact that SOA formation is almost unaffected by changes in NO_x can be
21 largely attributed to a limited shift in chemical regime, to buffering in chemical pathways
22 (low- and high- NO_x pathways, O_3 versus NO_3 -initiated oxidation) and to offsetting
23 tendencies in the biogenic versus anthropogenic SOA responses.

1

2 **1. Introduction**

3

4 Organic aerosols (OA) account for a substantial fraction of atmospheric fine particulate
5 matter, and can have significant impacts on both air quality (Huang et al., 2014; Zhang et
6 al., 2007) and climate (Carslaw et al., 2010). Previous research suggests that organic
7 compounds make up between 10%~90% of the total aerosol mass at continental mid-
8 latitudes and in tropical forests (Andreae and Crutzen, 1997; Kanakidou et al., 2005;
9 Putaud et al., 2010; Seinfeld and Pankow, 2003). Aside from primary organic aerosols
10 (POA) that are directly emitted into the atmosphere, another major fraction of OA is
11 composed of secondary organic aerosols (SOA), which are formed through chemical
12 transformation of anthropogenic and biogenic volatile organic compounds (AVOCs and
13 BVOCs). AVOCs include aromatics, alkanes and alkenes of about 25, 44 and 38 TgC per
14 year, respectively, from industrial processes, fossil fuel use, biomass burning and road
15 vehicles (Williams and Koppmann, 2007). Isoprene and monoterpenes are the dominant
16 BVOC emissions with estimated global source strengths of about 500 TgC per year and
17 150 TgC per year, respectively (Guenther et al., 2012). POA can also re-evaporate upon
18 dilution and participate in the chemical oxidation processes leading to the formation of
19 SOA (Robinson et al. 2007).

20

21 Biogenic SOA (BSOA) is usually regarded as natural aerosol and as such cannot be
22 addressed by emission control legislation. Recent research implied that anthropogenic
23 compounds facilitate BSOA formation, thus providing the possibility to control BSOA by

1 regulating the emission of other precursor pollutants like AVOCs, POA and nitrogen
2 oxides (Carlton et al., 2010; Emanuelsson et al., 2013; Hoyle et al., 2011; Lin et al., 2013;
3 Rollins et al., 2012; Volkamer et al., 2006). For example, Carlton et al. (2010) have
4 shown that in the southeast US, up to 50% of the total BSOA surface atmospheric loading
5 is attributed to controllable pollution emissions. Spracklen et al. (2011) found that at the
6 global scale the model with a large human-interfered SOA source was the most consistent
7 with observations, which includes a maximum of 10% SOA (10 Tg year^{-1}) from fossil
8 sources, and the extra is mostly likely due to an anthropogenic pollution enhancement of
9 BSOA. The potential impacts of human activities are visible in every step of BSOA
10 formation: the amount of naturally emitted BVOCs through land use and land cover
11 change, the oxidative transformation of BVOCs to semivolatiles through altering
12 atmospheric oxidants concentrations, and the partitioning behavior to the aerosol phase
13 through modifying the load and miscibility of pre-existing organic aerosol (Hoyle et al.,
14 2011).

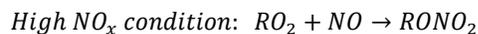
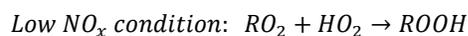
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16 Among the multiple human-induced influences, nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$, emitted
17 from many fossil-fuel driven activity sectors) play a critical role in SOA formation
18 through several aspects. First, through the competitive chemistry of organo-peroxy
19 radicals (RO_2) formed from oxidation of AVOC and BVOC precursors, which can react
20 mainly with NO at high NO_x or hydroperoxyl (HO_2) and peroxy radicals (RO_2) at low
21 NO_x conditions (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012). Calculating the
22 SOA yield dependence on NO_x is challenging because the OH/O_3 ratio depends on the
23 VOC/NO_x ratio (Presto et al., 2005). Lane et al. (2008) suggested that SOA yields could

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1 be calculated by a linear combination of the “pure” mass yields scaled by the strength of
2 each branch. In many SOA models (e.g. Heald et al., 2008; Lane et al., 2008; Pye et al.,
3 2010), the representative reactions for each branch are:



4 For AVOCs like light aromatics (Ng et al., 2007) and BVOCs like isoprene (Kroll et al.,
5 2006) and monoterpenes (Presto et al., 2005), both the ROOH groups and the RONO₂
6 groups can be low in volatility thus facilitating SOA formation, but RONO₂ is not the
7 dominant product of the RO₂ + NO channel, therefore the high-NO_x pathway usually has
8 lower yields of SOA. Second, NO_x can influence SOA formation through nighttime
9 nitrate radical (NO₃) chemistry. This pathway has a distinctive chemical signature due to
10 the high yields of organic nitrate (RONO₂), which also forms during daytime
11 photooxidation in the presence of NO but with a lower yield. The importance of NO₃-
12 initiated SOA formation have been confirmed by chamber experiments (Griffin et al.,
13 1999; Ng et al., 2008) and field studies, e.g. in Bakersfield, California, NO₃-chemistry
14 contributed approximately a third of the nighttime increase in total OA (Rollins et al.,
15 2012). Finally, NO_x levels can impact the atmospheric oxidation capacity. In the NO_x-
16 limited regime (in terms of O₃ formation), the OH-initiated oxidation of CO, methane
17 (CH₄) and other VOCs in the presence of NO_x produces O₃. Thus in such conditions,
18 increasing NO_x by human activities should, in principle, lead to the increase in
19 atmospheric oxidation capacity (OH and O₃) (Seinfeld and Pandis, 2006), and result in
20 higher SOA yields. For example, using a chemical transport model PMCAMx, Lane et al.
21 (2008) suggested that a 50% reduction in NO_x emissions could decrease predicted

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1 | ground-level BSOA by an average of $0.5 \mu\text{g m}^{-3}$ in the eastern US by lessening the
2 | atmospheric oxidant levels.

3

4 | Due to the multiple impacts of NO_x on SOA formation, it is important to understand how

5 | NO_x emission controls alter the particulate matter, atmospheric loading. The goal of this

6 | study is to improve the SOA scheme in a global climate-chemistry model by

7 | incorporating a 4-product Volatility Basis Set (VBS) framework (Pye et al., 2010), which

8 | has 4 representative volatility bins to better represent the volatility distribution of all

9 | semivolatiles in the atmosphere than the default 2-product scheme (Heald et al., 2008;

10 | Odum et al., 1996). The model is then used to investigate the impacts of anthropogenic

11 | NO_x emission reduction on SOA formation. Section 2 describes the observational

12 | datasets used in this study. In Section 3, we describe the default and updated SOA

13 | parameterizations embedded within the global chemistry-climate model framework. We

14 | perform control simulations using six different model configurations, including the

15 | default 2-product scheme and the updated SOA scheme with and without NO_x -dependent

16 | yields for monoterpene, and with and without simplified SOA aging parameterizations.

17 | Section 4 shows the results. The control simulations are evaluated and assessed against

18 | several observational datasets. Then, we perform sensitivity simulations to probe the

19 | impacts of a global 50% anthropogenic NO emission reduction on SOA production. We

20 | conduct this experiment as a simplified potential future scenario based on the 50% NO_x

21 | emission reduction from power plants in the southeast US by pollution control programs

22 | in the past decade (Frost et al., 2006; Kim et al., 2006). Section 5 summarizes the

23 | findings of this study.

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2 Terminology and Data sets

Table 1 summarizes major abbreviations used in this study. The term OA refers to the total particle phase organic matter including carbon, hydrogen, oxygen and other possible elements. The term OC refers to only the mass of carbon in these organic compounds. Both OA and OC are used based on different measurement techniques. Similarly, primary organic carbon (POC) is the carbon mass in POA; secondary organic carbon (SOC) is the carbon mass in SOA. In this study the term SOA (secondary organic aerosol) and SOG (secondary organic gas) refer to particle phase and gas phase, respectively.

2.1 IMPROVE OC measurements. The US total OC dataset is from the Interagency Monitoring of Protected Visual Environments (IMPROVE, Hand et al., 2011). IMPROVE OC is collected using quartz fiber filters for 24 hours every third day, analyzed offline by thermal optical reflectance (TOR) (Chow et al., 1993), and corrected for an approximate positive artifact (Dillner et al., 2009), Assumptions made in this correction may not always be appropriate (Watson et al., 2009), and the potential negative artifacts due to the volatilization of particulate organics are not accounted. We choose 120 surface sites from IMPROVE network that are within the bottom layer in corresponding model grids. The original 3-day data from 2005 to 2009 has been averaged to seasonal and annual mean values. OC concentrations from sites within the same model grid cell (1.9°×2.5° latitude by longitude) are averaged for comparison to modeled OC concentrations in corresponding model grid cells.

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2 **2.2 Aircraft-based OA measurements from Aerosol Mass Spectrometer (AMS).** The

3 OA datasets come from 13 aircraft field campaigns that took place between 2005 and
4 2009 (Heald et al., 2011). In these campaigns, total OA density was measured using AMS
5 in standard temperature and pressure conditions ([STP: 298K, 1atm](#)), and provides fast on-
6 line submicron aerosol composition (Canagaratna et al., 2007). For each field campaign,
7 the 1-minute raw data is averaged temporally and horizontally along the flight track for
8 comparison to the simulated monthly mean OA vertical profile in corresponding month
9 and location in the model. Each observed OA profile is further averaged vertically to a
10 single value for comparison to the simulated OA concentration averaged over the same
11 range of altitudes.

12

13 **2.3 Surface OA/OOA/HOA measurements from AMS.** We select 42 surface AMS

14 measurements in 2000-2008 from previous studies (Spracklen et al., 2011; Zhang et al.,
15 [2007](#)) that differentiate between hydrocarbon-like OA (HOA, a surrogate for POA from
16 combustion and biomass burning) and oxygenated OA (OOA, a surrogate for SOA from
17 all sources). [The HOA and OOA are determined by a multiple component analysis](#)
18 [\(MCA, Zhang et al. 2007\).](#) The averaged OOA, HOA and OA data for each campaign
19 have been compared to the simulated monthly mean SOA, POA and total OA in the
20 corresponding model grid. Most of these measurements were taken before 2005. We did
21 not perform simulations in this period due to the lack of GEOS-5 meteorological data
22 (described in Section 3.1). Therefore the model results are averaged from 2005 to 2009 as
23 a climatology to compare with this observational dataset.

1

2 **3. Modeling framework**

3

4 **3.1 CAM4-chem model.** The global Community Atmosphere Model Version 4 with
5 chemistry (CAM4-chem) is part of the Community Earth System Model (CESM, version
6 1.2.2) (Tilmes et al., 2015). Here, we employ CAM4-chem in its specified dynamics
7 mode, in which CAM and the Community Land Model (CLM) are driven by offline
8 Goddard Earth Observing System Model Version 5 (GEOS-5) reanalysis meteorological
9 fields (available since 2004). The prescribed sea surface temperature and sea ice data are
10 from the Climatological/Slab-Ocean Data Model (DOCN) and Climatological Ice Model
11 (DICE) as other components of CESM. In this configuration, CAM4-chem is run in a
12 Chemistry-Transport Model mode, such that direct comparison can be performed without
13 having to consider variability associated with internally generated meteorology. CAM4-
14 chem includes interactive simulation of O₃-NO_x-CO-VOC and bulk aerosol chemistry
15 (based on the MOZART-4 chemical mechanism) as described in Lamarque et al., (2012).
16 The default 2-product SOA scheme is described in Sect. 3.2 and in Heald et al. (2008).
17 Updates performed for the purpose of this study are discussed in Section 3.3 and 3.4. The
18 emission of isoprene and monoterpenes are calculated online by Model of Emissions of
19 Gases and Aerosols from Nature (MEGAN-2.1), which is embedded in CLM (Guenther
20 et al., 2012). The anthropogenic, biomass burning and other (except biogenic) emissions
21 in CESM are as described in Lamarque et al. (2012). These consist of anthropogenic
22 emissions from the Precursors of Ozone and their Effects in the Troposphere (POET)
23 inventory for 2000 (Granier et al., 2005), with Asia replaced by Regional Emission

1 inventory for ASia (REAS-v1) for each year (Ohara et al., 2007). The biomass burning
2 emissions are from GFED-v2 (van der Werf et al., 2006) for 2005-2008 and from the Fire
3 INventory of NCAR (FINN-v1) for 2009 (Wiedinmyer et al., 2010). All the SOA
4 schemes discussed in this study consider that SOA are only generated from oxidization of
5 gas-phase VOCs. The SOA formation from organic compounds emitted originally in the
6 condensed phase is not considered. Simulations are performed with a 30 minute time
7 step, a horizontal resolution of $1.9^\circ \times 2.5^\circ$ and 56 levels from the surface to
8 approximately 40 km.

9

10 **3.2 Default SOA parameterization**

11 In CAM4-chem, the default SOA formation follows the 2-product approach (Odum et al.,
12 1996). Each parent VOC is oxidized to generate 2 semivolatile surrogates, which can
13 partition into pre-existing organic particles including both POA and SOA. The
14 partitioning of the semivolatile products is described by absorptive partitioning theory
15 into carbonaceous aerosol material (Donahue et al., 2006; Pankow, 1994). CAM-chem
16 tracks POC in its emission, transport and deposition module. Later in Section 4.2, we
17 assume a POA-to-POC ratio of 1.4 (Aiken et al., 2008; White and Roberts, 1977) to
18 calculate modeling POA and OA to compare with observations. The model simulates
19 anthropogenic SOA (ASOA) from NO_x -dependent OH-initiated oxidation of
20 anthropogenic aromatics (benzene, toluene and xylene), BSOA from the OH-initiated
21 oxidation of isoprene, and the ozonolysis, OH- and NO_3 -initiated oxidation of
22 monoterpene (Table 2). The surrogate SOA products are assumed to be: $\text{C}_{10}\text{H}_{16}\text{O}_4$ for
23 SOA from monoterpene (SOAM), $\text{C}_5\text{H}_{12}\text{O}_4$ for SOA from isoprene (SOAI), $\text{C}_6\text{H}_7\text{O}_3$,

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1 C₇H₉O₃, and C₈H₁₁O₃ for SOA from benzene, toluene and xylenes, therefore the O:C
2 ratio is constant for each SOA species. The overall O:C ratio in total OA depends on the
3 split between POA and SOA, and the fraction of each SOA species. Fossil content is
4 regarded as POA including both hydrophobic and hydrophilic compounds and is not
5 included in SOA in CAM4-chem. The default 2-product model in CAM4-chem only
6 applies low-NO_x yields parameterization for all OH- and O₃-initiated BSOA formation.
7 The SOA mass yields (summarized in Table S1) are from Heald et al. (2008) and
8 references therein.

10 3.3 Updated SOA scheme

11 We update the SOA model to include a 4-product VBS scheme, which has 4 semivolatile
12 surrogates for each parent VOC species. The saturation concentrations (C*) at 295K for
13 the 4 product groups are 0.1, 1, 10, 100 μg m⁻³, respectively. This VBS has a wider range
14 of volatilities than the default 2-product parameterization that can better represent the
15 volatility distribution of atmospheric semivolatiles. Another goal of implementing this
16 VBS framework is to facilitate implementation of advanced processing including the
17 aging effect. Changing the enthalpies of vaporization (see Table S1, S2) has no
18 significant effect on simulated SOA burden (difference smaller than 2%). In addition to
19 the current reactions used in the 2-product model, we have added the NO_x-dependent
20 pathway for SOA formation from monoterpenes and the NO₃-initiated oxidation of
21 isoprene into the VBS (see Table 2). SOA formed from OH-initiated photooxidation of
22 isoprene still only has one set of yields following the low-NO_x parameterizations. We do
23 not change this isoprene-SOA parameterization to remain consistent with the VBS

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1 [framework from Pye et al. \(2010\). Additional simulations that include the high-NO_x](#)
2 [pathway of isoprene chemistry are discussed in the Supplement.](#) The SOA mass yields
3 (summarized in Table S2) are from Pye et al. (2010) and references therein.

4
5 In the 4-product VBS model, the partitioning between the high-NO_x (RO₂+NO) and low-
6 NO_x (RO₂+HO₂) pathway is determined by the branching ratio β (Pye et al., 2010):

$$\beta = \frac{[NO]}{[NO] + [HO_2]}$$

7 Thus, 100×β% of the parent hydrocarbon channels through the high-NO_x pathway, and
8 100×(1- β)% of the parent hydrocarbon channels through the low-NO_x pathway. This
9 format of β is a simplification of:

$$\beta = \frac{\sum k_{RO_2+NO} \times [NO]}{\sum k_{RO_2+NO} \times [NO] + \sum k_{RO_2+HO_2} \times [HO_2]}$$

10 where k_{RO_2+NO} and $k_{RO_2+HO_2}$ represent the reaction rate coefficients of RO₂+NO and
11 RO₂+HO₂, respectively.

12
13 Field studies that quantified the elemental composition of OA indicate the importance of
14 aged oxygenated OA (Aiken et al., 2008; Chen et al., 2011; Heald et al., 2010). Several
15 regional modeling studies have found the “aging” process necessary to produce
16 reasonable OA mass (Athanasopoulou et al., 2013; Hodzic and Jimenez, 2011; Knote et
17 al., 2015; Lane et al., 2008; Tsimpidi et al., 2010). In this study we implement a
18 simplified aging parameterization into the global model to provide a rough assessment of

1 the SOA sensitivity in VBS to the effect of aerosol aging. At every model time step, each
2 gas-phase SOA product except for the lowest volatility product ($C^*=0.1\mu\text{g m}^{-3}$) is
3 assumed to be further oxidized by OH with a reaction rate constant k_{OH} of $4\times 10^{-11}\text{ cm}^3$
4 $\text{molec}^{-1}\text{ s}^{-1}$ (Atkinson and Arey, 2003; Tsimpidi et al., 2010), which reduces its volatility
5 by an order of magnitude. The oxygen-to-carbon ratio (O:C) is assumed to be constant
6 for each surrogate SOA product thus increase in SOA mass due to the addition of oxygen
7 is not considered in the aging process. Considering the complexity of various SOA
8 species and the large uncertainties in aging process, the assumption of fixed O:C ratio for
9 each SOA product surrogate is acceptable for global model parameterizations. The aging
10 rate $k_{\text{OH}}=4\times 10^{-11}\text{ cm}^3\text{ molec}^{-1}\text{ s}^{-1}$ is at the high end of previously suggested parameters
11 (Lane et al., 2008). We do simulations with and without this aging parameterization to
12 quantify the possible range of global SOA strengths, and do additional simulations (see
13 Section 3.4) to examine the effect of different aging parameters.

14

15 Particle-phase SOA as well as gas-phase SOG are removed from the atmosphere by wet
16 and dry deposition. Dry deposition follows a resistance-in-series formulation (Heald et
17 al., 2008; Wesely, 1998). SOA and other soluble aerosols are removed by both in-cloud
18 scavenging and below-cloud washout (Barth et al., 2000; Lamarque et al., 2012).

19

20 **3.4 Experiment setup**

21 In this study, we apply six different treatments of SOA formation, as summarized in
22 Table 2. ‘2-product’ is the default SOA model; ‘VBS’ and ‘VBS_agHigh’ are the updated
23 4-product VBS scheme with and without the aging effect. ‘VBS_agHigh’ applies the high

1 aging rate $k_{OH}=4\times 10^{-11}$ cm³ molec⁻¹ s⁻¹ to all species, thus presumably providing the
2 higher bound of simulated SOA loadings. These three schemes (2-product, VBS and
3 VBS_agHigh) are the main SOA schemes that we use to compare with observations
4 (Section 4.2) and study the sensitivity to NO_x perturbations. For each of the three
5 schemes, we perform one control run and one sensitivity run in which anthropogenic NO
6 emissions are reduced by 50% (Section 4.3). We perform additional simulations to
7 explore the impact of different aging and NO_x-dependency parameterizations:
8 ‘VBS_agLow’ applies a lower k_{OH} of 5.2×10^{-12} cm³ molec⁻¹ s⁻¹ (Hu et al., 2013) to all
9 species, which is close to the lower limit suggested by other studies (Hodzic and Jimenez,
10 2011; Spracklen et al., 2011); ‘VBS_agAVOC’ applies $k_{OH}=4\times 10^{-11}$ cm³ molec⁻¹ s⁻¹ to
11 AVOCs only, as suggested by some studies that ASOA ages longer than does BSOA
12 (Lee-Taylor et al., 2015). ‘VBS_lowNO_x’ is the same as ‘VBS’ except that all SOAM is
13 assumed to be formed through the low-NO_x (RO₂+HO₂) pathway. This ‘VBS_lowNO_x’
14 scheme is done to isolate the influence of the NO_x-dependent pathway for SOAM
15 formation, which is not considered in the default 2-product settings. All simulations are
16 conducted for the years 2004 to 2009 with offline meteorology from GEOS-5 reanalysis
17 and specific monthly anthropogenic emissions. The year 2004 result is discarded as spin-
18 up.

19

20 4. Results

21

22 4.1 Comparison of various SOA schemes

1 The annual mean zonally averaged SOA concentration is shown in Fig. 1. The tropical
2 maximum in the lower troposphere is due to large year-round Amazonian BVOC
3 emissions coupled with extensive seasonal biomass burning that provides ample pre-
4 existing POA onto which the semivolatiles can condense. The second surface maximum
5 in the northern hemisphere mid-latitudes 30°-60° is mostly attributed to (1) summertime
6 BVOC emissions from broadleaf deciduous forest in the temperate and boreal zones,
7 especially the southeast US, which has very high BVOC emissions in the summer
8 (Guenther et al., 2006), (2) plentiful supply of anthropogenic and biomass burning
9 emitted POA, and (3) large amounts of AVOC emissions from human activities. In most
10 simulations, indicated by the white contour lines in Fig. 1, the BSOA from isoprene and
11 monoterpenes oxidation accounts for more than 70% of the total SOA in most latitudes
12 and altitudes, which actually includes both ‘naturally-formed’ and ‘anthropogenically-
13 influenced’ BSOA. The rest is ASOA from the oxidation of AVOCs. In the
14 VBS_agAVOC run, ASOA accounts for a larger fraction in Northern Hemisphere mid-
15 latitudes than other simulations ranging from 30% to 50% because in this scheme aging
16 process is only applied to ASOA.

17

18 | Table 3 details the annual global SOA budget in each control experiment. Compared to
19 the default 2-product approach, the VBS scheme predicts a smaller global annual burden
20 of SOA (19% lower than the 2-product), although the surface concentration is 11%
21 higher with compensating lower concentrations at higher elevations. Due to the higher
22 yields in the VBS (see Table S1 and S2), more parent hydrocarbon is consumed near the
23 source location and less is transported to upper troposphere relative to the 2-product

1 scheme. Their different volatility also contributes to the difference in SOA
2 concentrations. Table 3 suggests a shorter SOA lifetime of 8.9 days in the VBS than the
3 lifetime of 11.4 days in the 2-product scheme due to the larger wet-deposition flux, which
4 is consistent with the higher surface concentration. The SOA global burden in the
5 VBS_lowNO_x run is 14% higher than the VBS. This is consistent with the fact that the
6 high-NO_x (RO₂+NO) channel is less SOA-producing comparing to the low-NO_x
7 (RO₂+HO₂) channel. The yields of SOAM at 10 μg m⁻³ under high- and low-NO_x are
8 0.09 and 0.19, respectively (Table S2).

9

10 For present climate, the differences in annual burden between the 2 VBS models without
11 aging effect (VBS and VBS_lowNO_x) and the 2-product model are relatively small
12 (<20%), because for most parent hydrocarbon species they are fitted into the same
13 chamber data (see Heald et al. (2008), Pye et al. (2010) and references therein). In
14 contrast, in VBS_agHigh, adding the aging effect accelerates the shift of volatile mass
15 towards lower volatility bins and hence more mass in the particle phase, and results in an
16 overall doubling of the net SOA (particle phase) production, which is important for SOA
17 environmental impacts. We find that the SOA production is sensitive to the assumed OH
18 oxidation rate constant (k_{OH}) for aging of the semivolatile intermediates. For example,
19 using VBS_agLow scheme with a lower k_{OH} of 5.2×10⁻¹² cm³ molec⁻¹ s⁻¹ (Hu et al.,
20 2013), the annual mean SOA production rate would be 44.6±2.0 Tg[C] year⁻¹, in
21 comparison to a production rate of 58.6±2.4 Tg[C] year⁻¹ in the VBS_agHigh scheme
22 with k_{OH} = 4×10⁻¹¹ cm³ molec⁻¹ s⁻¹, and a production rate of 28.6±1.6 Tg[C] year⁻¹ in the
23 VBS scheme without aging parameterization. This single aging parameter represents the

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1 multi-generational aging of hundreds of thousands oxidation intermediate species that are
2 involved in the SOA formation (Lee-Taylor et al., 2015) and is currently not well
3 characterized for individual precursors and chemical environments. In the rest of this
4 study, we will use the three schemes, 2-product, VBS and the VBS_agHigh, to compare
5 with observations and explore the NO_x-dependent effects.

6

7 **4.2 Evaluation of OA in CAM4-chem simulations**

8 **4.2.1 Comparison with the IMPROVE network OC observations**

9 The IMPROVE surface observations and the model outputs are averaged from 2005 to
10 2009. Modeled OC concentrations are calculated as the sum of primary carbon (directly
11 emitted and transported in the model) and the carbon contained in each SOA species that
12 is calculated assuming the surrogate SOA products described in Section 3.2. Fig. 2(a) and
13 Fig. 3 show the model-IMPROVE comparison of annual mean surface total OC
14 concentrations using the model 2-product, VBS and VBS_agHigh. The total OC in the 2-
15 product and the VBS are similar to each other and are close to the IMPROVE OC
16 magnitude. They capture the observed spatial distribution within 50% ($r^2=0.45$ and 0.47 ,
17 respectively). They capture the low OC values in middle and west inland area, and high
18 OC values in the southeast US where considerable BVOC is emitted from forest as well
19 as POC and AVOC emitted from economic sectors. In the northeast US and some coastal
20 polluted regions in California, OC is greatly overestimated by the models. Fig. 2(c)
21 indicates large simulated POC concentration in these regions while IMPROVE total OC
22 (=POC+SOC) is even not as large as the simulated POC concentrations. Therefore the
23 positive bias of the two no-aging simulations in the northeast US is likely due to an

1 overestimate of POC emissions in the inventory, or due to the assumption that all POA
2 are non-volatile once emitted and stay in the particle phase until deposition. The fact that
3 IMPROVE sites are predominantly located in remote clean regions might also contribute
4 to this discrepancy. In Fig. 2(b) the white contour lines illustrate the annual mean fraction
5 of SOC in total OC. Table 4 summarizes the fractions in each season. In the two no-aging
6 models, annual mean SOC-to-OC ratio ranges from 20% to 30% in the northeast US and
7 40% to 60% in the southeast US. Even in summer, the ratio does not exceeds 50% in the
8 northeast US and 70% in the southeast US, which is lower than the suggested values from
9 Ahmadov et al. (2012) and Shrivastava et al. (2008). The aging experiment VBS_agHigh
10 increases the SOC-to-OC ratio greatly (68% and 81% in summertime northeast and
11 southeast US) and overestimates OC across the entire US due to large SOA formation
12 from aging, which is consistent with previous studies that the aging coefficient we apply
13 here ($k_{OH} = 4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) is at the high end of suggested aging rates. The
14 VBS_agHigh scheme slightly improves the replication of spatial distribution of annual
15 mean OC concentrations ($r^2=0.53$ as compared to 0.45 and 0.47 in the 2-product and VBS
16 schemes) but not in summer ($r^2=0.13$, Table 5). Assuming only ASOA ages, the
17 VBS_agAVOC scheme does not improve the simulated spatial distribution ($r^2=0.48$ in
18 annual average and $r^2=0.18$ in summer, Table 5).

19

20 4.2.2 Vertical profiles of OA from aircraft-based AMS measurements

21 To assess the simulated OA vertical profile in these models, we select 13 aircraft
22 campaigns that had available AMS measurements between 2005-2009. The comparison
23 of vertical profiles is shown in Fig. 4. The VBS_agHigh scheme provides a higher OA

1 concentration than the other two no-aging simulations. Overall, the inter-model
2 differences are smaller than the model-observation differences. In biomass burning
3 influenced regions, the observed OA profile is usually associated with large variations at
4 elevated altitude, indicating sporadic fire plumes. For example, for the AMMA campaign
5 (west Africa), the aircraft tracked biomass-burning plumes, thus giving several maxima
6 of observed mean OA at multiple altitudes. In this case, the observed median value at
7 each layer is a more reliable value for evaluation of the simulations (Heald et al., 2011).
8 The simulated OA profiles in these fire-influenced regions are close to the observed
9 median OA profiles and all are within one standard deviation of observations except at
10 site DODO (west Africa). The enhanced observed concentrations in DODO in the upper
11 troposphere indicate strong deep convection. The discrepancies are likely caused by
12 biases in sub-grid meteorology and vertical transport rather than the chemical formation
13 of SOA or POA emissions. Polluted regions have high OA concentrations at the surface.
14 All three of the simulations capture both the vertical distribution characteristics and
15 magnitude of concentration with the largest model-observation difference within $5 \mu\text{g m}^{-3}$.
16 ³. OA in remote sites is close to zero. The models capture OA at IMPEX (west North
17 America and east Pacific) and OP3 (Borneo) sites but overestimate at TROMPEX (Cape
18 Verde) and VOCALS-UK (south Pacific). Generally, the simulated OA profiles are all
19 within a factor of 2 of the observed magnitude, indicating a reasonable model
20 performance across different regions and seasons. Fig. 5 compares OA concentrations
21 averaged across each entire campaign. All the three simulations underestimate observed
22 OA in most campaigns, except in remote sites TROMPEX (Cape Verde) and VOCALS-
23 UK (eastern south Pacific ocean). The VBS_agHigh scheme has the lowest root-mean-

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1 square difference (rmsd) of 1.45, and captures 56% of observed OA mean concentrations,
2 as compared to 50% and 52% in the 2-product and VBS schemes.

4 4.2.3 OA, SOA and POA from surface AMS measurements

5 The observed OOA is a surrogate for SOA, and HOA is a surrogate for POA in AMS
6 measurements (Aiken et al., 2009; Lanz et al., 2007; Zhang et al., 2005). We use 42
7 short-term surface AMS measurements (Spracklen et al., 2011; Zhang et al., 2007) and
8 classify their locations into four groups: North America (17 sites), Europe (12 sites), East
9 Asia (12 sites) and Amazon (1 site). Most of these measurements were taken before 2005.

10 The 2005-2009 monthly mean model results have been averaged into a climatology to
11 compare to the observations, which may lead to large model-observation differences. Fig.
12 6 compares the measured and simulated OA, OOA(SOA) and HOA(POA). The
13 comparisons between observations and simulations show large discrepancies (in opposite
14 directions) for primary and secondary species. POA is identical in the three simulations.

15 Consistent with the comparison with the IMPROVE network in Section 4.2.1, the models
16 overestimate POA in most regions especially in North America, which will promote
17 condensation of semivolatiles onto pre-existing organic matter thus forming more SOA.

18 The SOA concentration in the two no-aging models, 2-product and VBS, are close to
19 observed OOA in North America and are lower in other regions. By including the aging,
20 the VBS_agHigh simulation increases SOA concentration, leading to an overestimation
21 in North America and still an underestimation in most other regions. The total OA
22 concentrations in all the models exceed observed OA in North America. In Fig. 7 we plot
23 the comparison of SOA(OOA)-to-OA ratios from the observations and simulations. The

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1 2-product and VBS models significantly underestimate the observed OOA-to-OA ratios
2 that range from 0.4 to 1. The VBS_agHigh model makes an improvement but is still
3 lower than the observations due to the large amount of simulated POA. Overall, the inter-
4 model differences are smaller than the model-observation differences. These conclusions
5 are consistent with Section 4.2.1 and 4.2.2.

6

7 **4.3 The impact of anthropogenic NO_x pollution on surface SOA**

8 For each of the 2-product, VBS and VBS_agHigh schemes, we perform a control run and
9 a sensitivity run in which the anthropogenic NO emissions are reduced by 50% to explore
10 the impact of NO_x pollution on surface SOA concentrations. Other NO sources including
11 biomass burning and soil emissions are not changed. The 50% reduction in anthropogenic
12 NO emissions leads to a 36% decrease in annual mean total NO emissions and a 38%
13 decrease in surface NO_x concentrations at global scale (Fig. S1). The global surface level
14 of oxidants OH, O₃ and NO₃ decrease by 13%, 8% and 29%, respectively (Fig. S2). The
15 surface NO/HO₂ ratio has been greatly reduced by 67%, while the change in branching
16 ratio ($\beta = \frac{NO}{NO+HO_2}$) is small (-3.4%), indicating the NO concentration in the model is too
17 high for HO₂ to compete. The spatial distribution and probability density function of β
18 are plotted in Fig. S3 and Fig. S4. We choose a polluted and a clean region as examples:
19 the southeast US [32°-40°N, 95°-77°W] and the Amazon [17°S-5°N, 77°-55°W], both of
20 which are mostly in the NO_x-limited regime in terms of ozone formation due to their
21 large BVOC emissions (Lane et al., 2008), i.e. the concentration of O₃ and OH are
22 positively related to concentration of NO_x. We examine the dependence of annual mean
23 surface SOA concentrations on β and oxidants level at the global scale, and over the

1 southeast US and the Amazon regions in Fig. 8. The comparison of the sensitivity (red)
2 and the control runs (green) indicates that the 50% reduction in anthropogenic NO
3 emissions leads to a small decrease in β , oxidation level and SOA concentrations. In Fig.
4 8, the small SOA concentrations associated with small β values ($\beta < 0.6$) mostly happen
5 over the ocean (not shown) or polar regions where VOC precursors hardly exist and NO_x
6 concentrations are low. In the range $0.6 < \beta < 1.0$, the common regime over land, the
7 highest SOA concentrations occur at relatively lower β values, which mostly locate in
8 tropical rain forests with large BVOC emissions and high SOA production efficiency
9 through the low-NO_x pathway. The influences of β and oxidant level are tightly related
10 because high β indicating high NO_x is usually associated with high concentrations of
11 oxidants. The dependence of SOA on oxidant concentration indicates a maximum at
12 medium oxidant level of approximately 0.8×10^{12} molecules cm⁻³. The low SOA
13 concentrations at high oxidant level mostly occur in polluted regions where SOA
14 production is overwhelmingly dominated by the high-NO_x (low-yields) pathway.
15
16 The SOA production in response to NO_x perturbations is complex as described in Section
17 1. For example, in the VBS_agHigh scheme, we consider monoterpene SOA (SOAM)
18 coming from NO₃-initiated oxidation and the low- and high-NO_x pathway for both OH-
19 and O₃-initiated oxidation. As shown in Fig. 9, with a 50% reduction in anthropogenic
20 NO emissions, total surface SOAM concentration decreases, dominated by the decrease
21 in NO₃-oxidation branch. This decrease in total SOAM mass is a result of addition or
22 cancellation of various changes in each branch, and the relative importance of different
23 branches may alter with different regions. One interesting phenomenon is that when NO_x

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1 emissions are reduced, the low-NO_x OH- and O₃-initiated oxidation branches form less
2 SOAM mass in the Amazon, but more SOAM in human-influenced regions like mid-
3 latitude broadleaf forest in the southeast US, coastal Asia and boreal forest in northern
4 Europe. To further understand and quantitatively evaluate the complex NO_x influence on
5 SOA formation, we examine the predicted change in surface SOA concentrations in
6 different pathways in response to the decrease in anthropogenic NO emissions, as
7 illustrated by Fig. 10. Table 6 details the relative contribution of each pathway to the total
8 SOA change. The results for various SOA types i.e. aromatic SOA, isoprene SOA and
9 monoterpene SOA are discussed below.

10

11 **4.3.1 Anthropogenic SOAs from benzene, toluene and xylenes: ASOA**

12 ASOA in the three models are assumed to form from OH-initiated oxidation, including
13 both low-NO_x and high-NO_x pathways, i.e. AVOCs+OH(HO₂) and AVOCs+OH(NO). In
14 the southeast US as shown in Fig. 10, all models predict an increase in the low-NO_x
15 pathway and a decrease in the high-NO_x pathway. This is because the model assumes
16 linear interpolation between low- and high-NO_x pathways based on the branching ratio
17 (Section 3.3). When NO_x is reduced, more AVOCs are oxidized under the low-NO_x
18 pathway, which has higher yields (see Table S1 and S2). Due to the limited change in β ,
19 the effect of shifting to high-yield HO₂ pathway is very small. The total ASOA formation
20 depends on both the low-/high-pathway partitioning and the oxidation capacity, thus can
21 either increase (e.g. 2-product, VBS) or decrease (VBS_agHigh). In the Amazon, the
22 ASOA changes follow the same pattern as in the southeast US, but their relative
23 contributions are very small due to the low concentrations of AVOCs and anthropogenic

1 NO_x. The contributions of ASOA changes to total SOA change (defined as
2 $\frac{\text{change in ASOA}}{|\text{total SOA change}|}$) ranges from -3.7% to 9.2% in southeast US and from -0.6% to 1.0% in
3 the Amazon.

5 4.3.2 Isoprene SOA: SOAI

6 In our current models, the isoprene only has one set of yields for OH-initiated daytime
7 oxidation following low-NO_x parameterization, and is oxidized by NO₃ during the night
8 (the latter is not considered in the 2-product model). The OH-oxidation is the dominant
9 branch to form SOAI in both regions. When anthropogenic NO emissions are halved,
10 both OH- and NO₃- initiated branches decrease in the southeast US and the Amazon due
11 to reduced atmospheric OH and NO₃ levels, respectively. The contributions of SOAI
12 changes ($\frac{\text{change in SOAI}}{|\text{total SOA change}|}$) are -46.8% to -73.0% and -30.8% to -43.0% in the two
13 regions.

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15 4.3.3 Monoterpene SOA: SOAM

16 Monoterpenes are oxidized by OH, O₃ and NO₃ in all models but the 2-product model
17 only considers the low-NO_x pathway (Table 2). In the southeast US with large human
18 influence, the surface SOAM formation is largely attributed to NO₃-initiated oxidation as
19 indicated by most models, which dominates the reduction in response to reduced NO_x.
20 This branch itself contributes to the total SOA change ($\frac{\text{change in SOAM from NO}_3\text{-oxidation}}{|\text{total SOA change}|}$)
21 by -48.9% to -65.3%. This reduction in NO₃-branch compared to its normal value is
22 relatively small because the decrease in NO₃ concentration is only 24%. In the VBS and
23 VBS_agHigh models, the partitioning between high- vs. low-NO_x pathway determines

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1 the tendency of increasing yielding from the low-NO_x pathway and decreasing yielding
2 through high-NO_x pathway. The OH-oxidation in the southeast US follows such
3 tendency. However, the SOA formed from both high- and low-NO_x pathway of
4 ozonolysis increases. One possible explanation is the “buffering” between O₃- and NO₃-
5 initiated oxidation, both of which mostly happen at night. Compared to the control run,
6 NO₃ is significantly lower in the sensitivity run, thus more monoterpenes would be
7 oxidized by O₃ under both low- and high- NO_x conditions. Adding up the changes in all
8 branches, the SOAM change contributions to total SOA change are about -36.1% to -
9 60.7%. In the Amazon pristine environment, most branches demonstrate a slight
10 reduction in SOAM in all models. Since the absolute magnitude of anthropogenic NO_x is
11 small, the major influence of the NO_x might be the decline in level of atmospheric
12 oxidants: OH, O₃ and NO₃ decrease by 14%, 6% and 16%, respectively. Despite the
13 minor lessening of oxidation capacity, the SOAM reduction and total SOA reduction are
14 negligible.

15

16 **4.3.4 Summary of surface SOA concentration change**

17 The changes in total SOA concentration at the surface in different regions are
18 summarized in Table 7. In both human-influenced and clean regions, the 50% reduction
19 in anthropogenic NO emissions leads to a decline of BSOA, which dominates the overall
20 SOA decrease. The ASOA could either rise (in models without aging parameterization)
21 or decline (in models with aging considered). Among the multiple effects of NO_x, BSOA
22 is mostly influenced by changes in NO₃-initiated oxidation. Both BSOA and ASOA are

1 also influenced by the change in atmospheric oxidation capacity and the partitioning
2 between high- vs. low-NO_x pathways.

3

4 The annual mean total surface SOA reductions in the southeast US, the Amazon and
5 global average range from 119 to 518, 30 to 153, 3.6 to 43 ng m⁻³, respectively. The
6 corresponding percentage reductions are 6.4 to 12.0%, 0.9 to 2.8% and 0.9 to 5.6%.
7 These changes are comparable with previous estimates (Carlton et al., 2010; Lane et al.,
8 2008), but all are smaller than the magnitude of one standard deviation, indicating that
9 such changes are not statistically significant compared to interannual variations caused by
10 climate and emission variations. The column concentrations of tropospheric SOA are also
11 examined (results not shown here), and the conclusion still holds – no significant change
12 of SOA column concentration when anthropogenic NO emissions are reduced by 50%.

13 One major reason is the small reduction in branching ratio β thus limited shift between
14 high- vs. low-NO_x chemical regimes. The fact that SOA is stable in response to
15 anthropogenic NO_x changes is also attributed to the buffering of various branches (e.g.
16 increased ozonolysis and decreased NO₃-oxidation), the partitioning between low- and
17 high-NO_x pathways and the offset from opposite tendencies of BSOA and ASOA
18 responses (in the no-aging models).

19

20 **5. Summary**

21

22 NO_x plays a complex role in the chemical formation of SOA. The complexity includes
23 the competition between NO and HO₂ to react with RO₂, its substantial influence on

1 atmospheric oxidation capacity, and the nighttime NO₃ direct oxidation of isoprene and
2 monoterpenes. In this study, we have updated the SOA scheme in the global chemistry-
3 climate model CAM4-chem to include a 4-product VBS scheme that has a broader
4 representation of volatility distribution, and quantitatively evaluated and explained the
5 multiple impacts of anthropogenic NO_x on SOA at global scale.

6

7 We updated the SOA scheme in CAM4-chem to a 4-product VBS scheme. Compared to
8 the default 2-product model, the VBS scheme has 11% higher surface SOA
9 concentration. While the total annual mean SOA burden is 19% smaller (0.69±0.03
10 Tg[C] as compared to 0.85±0.04 Tg[C]) and lifetime is shorter (8.9±0.2 days as
11 compared to 11.4±0.4 days). Due to the different volatility and higher yields of SOA in
12 the VBS, more VOC is oxidized near surface and less is transported to higher levels, and
13 more SOA is washed out near surface. We explored an aging parameterization with a
14 constant reaction rate with OH ($k_{OH}=4\times 10^{-11}$ cm³ molec⁻¹ s⁻¹, the higher-limit in previous
15 studies), which almost doubles the net annual SOA production and significantly increases
16 the SOA concentration both at surface and in the lower free troposphere. The global SOA
17 burden with aging considered (i.e. VBS_agHigh scheme) increases to 1.08±0.06 Tg[C]
18 and the corresponding lifetime is 6.7±0.1 days. By applying a lower aging reaction rate
19 ($k_{OH}=5.2\times 10^{-12}$ cm³ molec⁻¹ s⁻¹, the lower-limit in previous studies), we found that the
20 simulation of SOA is quite sensitive to the assumed k_{OH} . Despite the significance to SOA
21 formation and properties, the aging effect is still poorly understood at the global scale.
22 Further laboratory and process-modeling constraints at different conditions are needed.

23

1 The simulated total OC concentrations in the 2-product and the VBS models without
2 aging are similar, and they capture the magnitude and distribution of annual mean surface
3 OC concentrations in the US from the IMPROVE network by 45-47%, but overestimate
4 OC in the polluted northeast US and west coastal regions. The models with an
5 implementation of aging (VBS_agHigh) slightly improve the replication of annual mean
6 spatial distribution ($r^2=53\%$), but overestimate the magnitude. All three models perform
7 poorly in summertime. Compared to AMS measurements from 13 aircraft-based field
8 campaigns, the simulations of OA vertical profiles are within a factor of 2 across
9 different regions and seasons. The VBS_agHigh scheme performs better than the two no-
10 aging models to reproduce these observed OA concentrations ($r^2=56\%$, $rmsd=1.45$).
11 Further climatological comparisons with surface AMS observations indicate reasonable
12 simulated total OA concentrations but overestimation of POA in some polluted regions,
13 which is consistent with the comparison to the IMPROVE network. This overestimation
14 of POA may come from higher biased POC from emission inventory in certain regions
15 (e.g. the northeast US). If so, it would partially conceal the fact that the current
16 parameterized SOA yields and overlooking of aging in the two no-aging models actually
17 lead to the SOA underestimation. Another possible explanation might be POA re-
18 evaporation and subsequent conversion to SOA (Robinson et al., 2007), indicated by the
19 lower fraction of SOA-to-OA ratio in simulations than the AMS observations. Generally,
20 the inter-model differences are smaller than the model-observation differences. We
21 believe that the updated SOA model (e.g. VBS, VBS_agHigh) is superior to the default
22 one because we implemented the NO_x -dependent SOA formation of monoterpenes,
23 whose absence is a major drawback of the default model. The VBS framework also

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1 facilitates inclusion of important processes like aging and the future implementation of
2 size-resolved calculations. The model-observation discrepancies come from several
3 reasons: ~~(1)~~ potential loss of POA due to evaporation and subsequent SOA formation
4 which is currently not considered in this study; ~~(2)~~ uncertainties in chamber-derived SOA
5 yields due to wall losses (Zhang et al., 2014); ~~(3)~~ lack of constraints on dry deposition of
6 organic gases (Hodzic et al., 2014; Knote et al., 2015) or unaccounted photolysis
7 reactions during aging of organics (Hodzic et al., 2015). Other non-chemistry reasons
8 include: (1) the site-level measurement versus coarse model grid (1.9°×2.5°); (2) specific
9 observation time period (days to weeks) versus simulated monthly mean values; (3) sub-
10 grid meteorology (e.g. convection events) that the model cannot capture; (4) large
11 uncertainties related to fire activity (e.g. biomass burning plumes).

12

13 Finally, we performed sensitivity experiments to examine how the SOA loading responds
14 to a 50% reduction in anthropogenic NO emissions in different regions. The BSOA
15 generally decreases due to the reduction in NO₃-initiated reaction and the reduced
16 atmospheric oxidation capacity, while the ASOA increases in the two no-aging models
17 mainly because of the increased partitioning to the low NO_x pathway, more AVOCs are
18 oxidized through the low-NO_x pathway that has higher yields. In the aging model, ASOA
19 decreases due to the more important effect of reduced oxidation capacity. Decreases in
20 the total surface SOA concentrations are 6.4 to 12.0%, 0.9 to 2.8% and 0.9 to 5.6% for
21 the southeast US, the Amazon and global NO_x perturbations, respectively, which,
22 however, are not significant. The fact that SOA formation is stable to changes in NO_x can
23 be largely attributed to limited shift in low- and high-NO_x regimes, to buffering in

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1 | chemical pathways (e.g. O₃ versus NO₃-initiated oxidation), and to offsetting tendencies
2 | in the biogenic versus anthropogenic SOA responses. Our results, based on the global
3 | chemistry-climate model CAM4-chem with simplified SOA schemes, indicate that air
4 | quality control on anthropogenic NO_x may not have substantial impacts on organic
5 | aerosol loadings at large regional scales. Further modeling studies including both
6 | process-based and parameterized schemes need to be done to carefully examine the NO_x
7 | impact on SOA formation.

8

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16 |

17 **Disclaimer**

18 Any opinions, findings and conclusions or recommendations expressed in the publication
19 are those of the author(s) and do not necessarily reflect the views of the National Science
20 Foundation.

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1 **Table 1. Abbreviations used in this study.**

Abbreviations	Description
<u>OA</u>	<u>Organic aerosol, including the mass of carbon, oxygen and other possible elements. OA = POA + SOA</u>
<u>OC</u>	<u>Organic carbon. OC = POC + SOC</u>
<u>POA</u>	<u>Primary organic aerosol.</u>
<u>POC</u>	<u>Primary organic carbon.</u>
<u>SOA</u>	<u>Secondary organic aerosol.</u>
<u>SOC</u>	<u>Secondary organic carbon.</u>
<u>SOG</u>	<u>Secondary organic gas.</u>
<u>ASOA</u>	<u>Anthropogenic secondary organic aerosol.</u>
<u>BSOA</u>	<u>Biogenic secondary organic aerosol.</u>
<u>AVOC</u>	<u>Anthropogenic volatile organic compounds.</u>
<u>BVOC</u>	<u>Biogenic volatile organic compounds.</u>
<u>SOAM</u>	<u>SOA from monoterpene oxidation.</u>
<u>SOAI</u>	<u>SOA from isoprene oxidation.</u>
<u>MTP</u>	<u>Monoterpenes.</u>
<u>ISOP</u>	<u>Isoprene.</u>
<u>HOA</u>	<u>Hydrocarbon-like organic aerosol, a surrogate for POA.</u>
<u>OOA</u>	<u>Oxygenated organic aerosol, a surrogate for SOA.</u>

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Table 2. Summary of SOA treatments in CAM4-chem model runs.

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SOA scheme	Reactions to form SOA	Description
2-product	MTP+OH(HO ₂); MTP+O ₃ (HO ₂); MTP+NO ₃ ; ISOP+OH(HO ₂); AVOCs+OH(HO ₂); AVOCs+OH(NO).	Default 2-product scheme; SOA mass yields summarized in Table S1 (Heald et al., 2008).
VBS	MTP+OH(HO ₂); MTP+O ₃ (HO ₂); MTP+OH(NO); MTP+O ₃ (NO); MTP+NO ₃ ; ISOP+OH(HO ₂); ISOP+NO ₃ ; AVOCs+OH(HO ₂); AVOCs+OH(NO).	Updated 4-product VBS scheme; SOA mass yields summarized in Table S2 (Pye et al., 2010)
VBS_lowNO _x	MTP+OH(HO ₂); MTP+O ₃ (HO ₂); MTP+NO ₃ ; ISOP+OH(HO ₂); ISOP+NO ₃ ; AVOCs+OH(HO ₂); AVOCs+OH(NO).	Same as VBS, but assuming all monoterpene SOA (SOAM) is formed under low-NO _x conditions
VBS_agHigh	Same as VBS	Same as VBS, with multi-generational aging applied to all species; $k_{OH}=4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.
VBS_agLow	Same as VBS	Same as VBS, with multi-generational aging applied to all species; $k_{OH}=5.2 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.
VBS_agAVOC	Same as VBS	Same as VBS, with multi-generational

		aging applied to ASOA only; $k_{OH}=4\times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.
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1 | Table 3. Summary of simulated annual mean global budget of SOA (particle-phase).

	Burden Tg[C]	Net SOA production Tg[C] year⁻¹	Lifetime Day	Wet deposition Tg[C] year⁻¹	Other losses (by SOA dry deposition) Tg[C] year⁻¹
2-product	0.85±0.04	27.3±2.1	11.4±0.4	-24.4±1.8	-2.9±0.3
VBS	0.69±0.03	28.6±1.6	8.9±0.2	-25.3±1.4	-3.3±0.3
VBS_lowNO_x	0.79±0.03	33.7±1.8	8.5±0.2	-29.8±1.5	-3.9±0.3
VBS_agHigh	1.08±0.06	58.6±2.4	6.7±0.1	-52.1±2.1	-6.5±0.4
VBS_agLow	0.96±0.05	44.6±2.0	7.8±0.1	-40.0±1.7	-4.8±0.3
VBS_agAVOC	0.75±0.03	31.5±1.6	8.6±0.2	-27.8±1.4	-3.7±0.3

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1 | **Table 4. Fraction of SOC in total OC (%) in the southeast US and the northeast US.**

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		Annual	MAM	JJA	SON	DJF
Northeast US	2-product	24%	15%	45%	20%	6%
	VBS	28%	19%	49%	23%	8%
	VBS_agHigh	45%	33%	68%	39%	12%
<hr/>						
Southeast US	2-product	39%	29%	62%	32%	8%
	VBS	44%	34%	67%	37%	10%
	VBS_agHigh	63%	55%	81%	56%	18%

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1 | **Table 5. Coefficients of determination (r^2) of IMPROVE measurements versus**
2 | **simulated total OC.**

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	Annual	MAM	JJA	SON	DJF
2-product	0.45	0.40	0.18	0.41	0.42
VBS	0.47	0.42	0.18	0.43	0.42
VBS_agHigh	0.53	0.54	0.13	0.49	0.45
VBS_agAVOC	0.48	0.45	0.18	0.44	0.44

3

1 | **Table 6. The relative contributions (%) of each SOA formation pathway to the total**
 2 | **SOA concentration change in the southeast US and the Amazon, defined as**
 3 | $\frac{\text{SOA change in each pathway}}{|\text{total SOA change}|}$. The sums of all numbers in each simulation equal -100%
 4 | because the total SOA change in the sensitivity runs compared to the control runs are
 5 | always negative. The reaction denotations are the same as defined in Figure 10.

		M1	M2	M3	M4	M5	I1	I2	A1	A2
SE US	2-product	-10.4		+15.0		-65.3	-46.8		+10.6	-3.1
	VBS	+2.9	-13.5	+29.5	+8.8	-63.8	-40.3	-32.7	+13.7	-4.5
	VBS_agHigh	+1.0	-5.3	+8.9	+2.0	-48.9	-35.1	-18.9	+3.5	-7.2
Amazon	2-product	-5.1		-0.2		-65.0	-30.8		+1.4	-0.4
	VBS	+0.4	-7.8	+5.9	-15.8	-45.1	-16.2	-21.9	+0.9	-0.5
	VBS_agHigh	-1.4	-4.3	-9.5	-13.9	-27.2	-30.4	-12.6	0.0	-0.6

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1 | **Table 7. Changes in surface SOA concentrations due to a 50% reduction in**
 2 | **anthropogenic NO emissions.** Total SOA changes from each model are listed for global
 3 | average, the southeast U.S. and the Amazon.

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		Concentration in Control run (ng/m³)	Standard deviation (ng/m³)	Concentration change in sensitivity run (ng/m³)	Percentage change
SE US [32°-40°N, 95°-77°W]	2-product	1638	248	-119	-7.3%
	VBS	2005	286	-127	-6.4%
	VBS_agHigh	4331	594	-518	-12.0%
<hr/>					
Amazon [17°S-5°N, 77°-55°W]	2-product	3360	1383	-30	-0.9%
	VBS	3884	1197	-46	-1.2%
	VBS_agHigh	5390	1542	-153	-2.8%
<hr/>					
Global average	2-product	358	40	-3.6	-1.0%
	VBS	393	37	-3.6	-0.9%
	VBS_agHigh	774	52	-43	-5.6%

4

1 **Figure captions**

2 **Figure 1. Annual mean zonally averaged SOA concentration ($\mu\text{g m}^{-3}$) (shown as**
3 **colored shades) and the fraction of biogenic SOA (%) (shown as white contours) in**
4 **CAM4-chem for different SOA treatments.**

5 **Figure 2. Annual mean surface concentrations (units: $\mu\text{g[C]} \text{ m}^{-3}$) of (a1)~(a3) total**
6 **organic carbon (OC=POC+SOC), (b1~b3) secondary organic carbon (SOC) and (c)**
7 **primary organic carbon (POC).** The data is averaged from 2005 to 2009. In (a1)~(a3),
8 scatters are IMPROVE observations and color shades are simulated total OC from the
9 model 2-product, VBS and VBS_agHigh. In(b1)~(b3), white contours indicate the
10 fraction of SOC in total OC (%), ranging from 30% to 70% with an interval of 10%. (c)
11 shows simulated POC, which is identical in the 3 simulations.

12 **Figure 3. Comparison of averaged annual mean surface OC concentrations ($\mu\text{g[C]}$**
13 **m^{-3}) between IMPROVE measurements and the 3 simulations: 2-product, VBS and**
14 **VBS_agHigh.** Different colors indicate sites in different regions. In each subplot, the
15 dash line is 1-to-1 line. The coefficients of determination (r^2), root-mean-square-
16 difference (rmsd) and the model-to-observation slope (k) are included.

17 **Figure 4. Comparison between observed vertical profile of OA concentration ($\mu\text{g m}^{-3}$)**
18 **from 13 AMS field campaigns and the 3 model simulations: 2-product, VBS and**
19 **VBS_agHigh.** The campaign information is summarized in Heald et al. (2011) (Fig. 1
20 and Table 1 therein). The error bars are one standard deviation of the binned observations
21 for each 0.5 km interval. The grey shades are simulated POA assuming a POA-to-POC
22 ratio of 1.4. The model simulations are sampled for the corresponding months and
23 locations for each campaign. The location and location type for each campaign is
24 included in each subplot.

25 **Figure 5. Comparison between averaged OA concentration ($\mu\text{g m}^{-3}$) from 13 AMS**
26 **field campaigns and the 3 model simulations: 2-product, VBS and VBS_agHigh.** The
27 campaign information is summarized in Heald et al. (2011) (Fig. 1 and Table 1 therein).
28 All data in each campaign are temporally, horizontally and vertically averaged to a single
29 value, and compared to the model outputs averaged over the same period and location.

30 **Figure 6. Comparison of surface AMS measurements (units: $\mu\text{g m}^{-3}$) and three**
31 **simulations. First column: total OA; second column: SOA(OOA); third column:**
32 **POA(HOA).** The coefficients of determination (r^2) and root-mean-square-difference
33 (rmsd) are included in each subplot. The observed oxygenated OA (OOA) is a surrogate
34 for SOA from all sources. The observed hydrocarbon-like OA (HOA) is a surrogate for
35 POA from combustion and biomass burning. Simulated POA is identical in the three
36 simulations. In POA-HOA comparison, data points with observed HOA smaller than 0.01
37 $\mu\text{g m}^{-3}$ have been set to 0.01 $\mu\text{g m}^{-3}$ to be shown in the plots.

38 **Figure 7. Comparison of observed OOA-to-OA ratio from surface AMS**
39 **measurements and simulated SOA- to-OA ratio from the 2-product, VBS and**

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1 **VBS_agHigh schemes.** The coefficients of determination (r^2) and root-mean-square-
2 difference (rmsd) are included in each subplot.

3 **Figure 8. Dependence of annual mean surface SOA concentration ($\mu\text{g m}^{-3}$) on**
4 **branching ratio and oxidants level at global scale, in the southeast US and the**
5 **Amazon.** The control runs and the sensitivity runs using VBS and VBS_agHigh schemes
6 are shown. The 2-product results are similar to the VBS results (not shown). Data points
7 over ocean are excluded. Note that the scales for the southeast US and the Amazon are
8 different from the global subplots.

9 **Figure 9. Changes in surface monoterpene SOA (SOAM) concentration ($\mu\text{g m}^{-3}$) in**
10 **the sensitivity run with 50% reductions in anthropogenic NO emissions compared to**
11 **the control run using VBS_agHigh scheme.** The total SOAM change is shown in (a).
12 The SOAM change in each formation branch is denoted as: (b1): MTP+OH(HO_2) (low-
13 NO_x OH-photooxidation); (b2): MTP+OH(NO) (high- NO_x OH-photooxidation); (b3):
14 MTP+ O_3 (HO_2) (low- NO_x ozonolysis); (b4): MTP+ O_3 (NO) (high- NO_x ozonolysis); (b4):
15 MTP+ NO_3 (NO_3 -initiated oxidation).

16 **Figure 10. Annual mean surface SOA concentration ($\mu\text{g m}^{-3}$) in the control runs and**
17 **the sensitivity runs (with 50% anthropogenic NO emission off) from different**
18 **pathways, averaged over the southeast U.S. [32° - 40°N , 95° - 77°W] and the Amazon**
19 **[17°S - 5°N , 77° - 55°W].**