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 NOx 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 NOx changes, implying that future emission control policies on NOx 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 NOx 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 $NO \gg HO_2$. 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 NOx leads to no change in SOA), but I believe the reason for this is simply current NO_x is too high for HO_2 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/HO_2 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 HO_2 pathway thus a tendency of increase in SOA concentration. However, this increase tendency is too small and is offset by the decrease in NO_3 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 HO_2 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 O_3 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 HO_2 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. O_3 versus NO_3-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 HO_2 concentrations, and it is only because we expect k_RO_2+NO to be similar to k_RO_2+HO_2 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: $C_{10}H_{16}O_4$ for SOA from monoterpene, $C_5H_{12}O_4$ for SOA from isoprene, $C_6H_7O_3$, $C_7H_9O_3$, and $C_8H_{11}O_3$ 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 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 μg m^{-3} because this is a common choice from previous literature. Now we show the yields at both 10 and 1 μg 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.