**Response to reviewer comments: Reviewer #2**

The authors thank the reviewer for their comments that improve the quality of the paper. The reviewer comments are shown in italic fonts, the responses are in regular fonts, and revised text in bold fonts.

[The numbers in some of the reviewer's comments are added by the authors to help address the comments more clearly.]

*Title: Decadal change of summertime reactive nitrogen species and surface ozone over the Southeast United States Authors: Jingyi Li et al.*

*Summary: This article examines observations and modeling for two years with extensive field campaigns and examines decadal changes between the years. The article uses a somewhat coarse resolution (when applied to a region) and evaluates $NO_y$ species. The evaluation is mostly qualitative and the explanations for mean biases (the quantitative metric) are somewhat speculative. Overall the manuscript provides interesting insights into the decadal changes despite using short snapshots no inter-annual variation.*

*Response Overview: The manuscript provides interesting insights in reactive nitrogen speciation and trends. There are several places that need clarification or further discussion. There is at least one methodological issue (time step) that has been show to affect speciation and is not discussed.*

Specific Comments

*Overall:*

**Comment 1**
** The article uses "as shown below." and the like frequently. I recommend being more specific so that the reader can connect subsequent discussion.*

**Response 1**
We have clarified the phrase 'as shown below' all mentioned in the manuscript.

**Comment 2**
** The nomenclature for the 40% hypothetical reduction from 2013 is confusing, particularly because the 40% number is also relevant for the 2004-2013 change.*

**Response 2**
The reason we reduced $NO_x$ by 40% of 2013 as a hypothetical scenario in future (in a decade) is based on the change rate of $NO_x$ from 2004 to 2013.

**Comment 3**
** I found the introduction and subsequent discussion of AM3h confusing. Consider separating paragraphs at 248 and more clearly lay out the paragraph.*

**Response 3**
The text has been revised in lines 257-261 as:

"**Besides the base case that only includes ISOPNB for heterogeneous loss (Jacobs et al., 2014), we include two additional sensitivity tests to evaluate the potential impact of organic nitrate hydrolysis. One is "hydro_full" case including heterogeneous loss of a $C_5$ dihydroxy dinitrate (DHDN) and monoterpene nitrates from OH oxidation (TERPN1), and the other one is "no_hydro" case assuming no heterogeneous loss for any organic nitrates.**"

**Comment 4**

** DAM3 introduced in Figure 4 is an unclear nomenclature. If I understand it correctly, DAM3 is replaying the Y-axis with a subset of ANs. It is not a separate model. Why prepend the D to DAM3 and DObs?*

**Response 4**

Figure 4 has been revised as following:

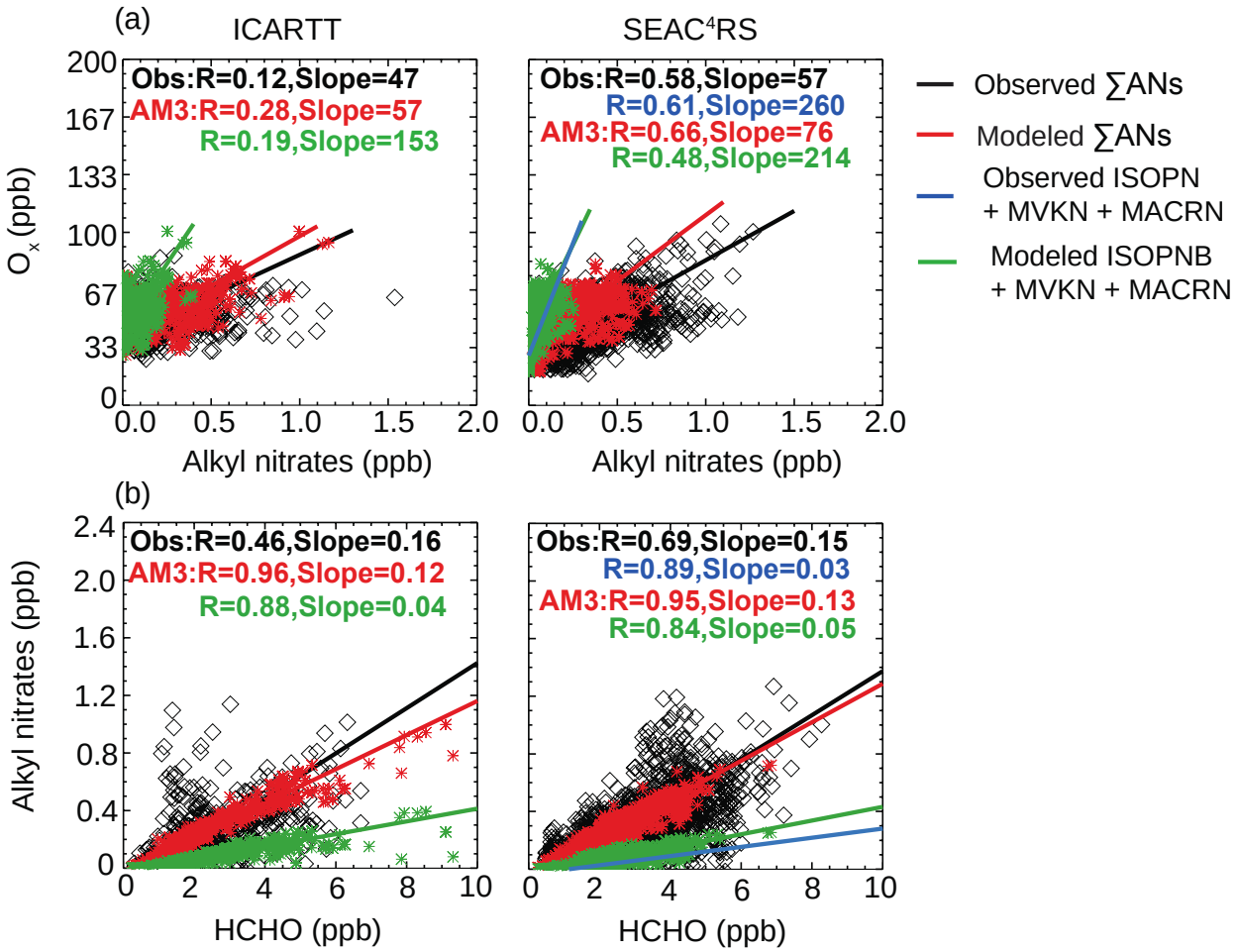


**Figure 1**. Figure 4 in the manuscript.

**Comment 5**

** Emissions are reported for the CONUS and average annual rates (1/mo), but spatial allocation and temporal allocation may be important to understand how they affect the region/time being reported.*

**Response 5**

We show in the following Figure 2 (Figure S1 in the original supplement) that $NO_x$ emissions in our model exhibit a similar spatial pattern to the one in NEI11v1 inventory. We apply a diurnal variation to anthropogenic $NO_x$ emissions in the model. This has been clarified in the revised text in lines 180-181:

"**We also apply a diurnal variation to anthropogenic $NO_x$ emissions following Mao et al. (2013b).**"

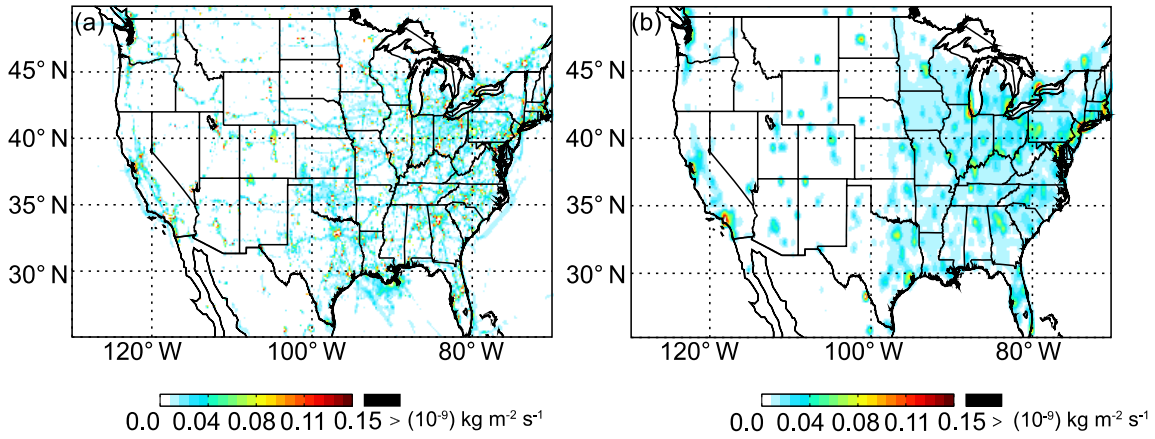


**Figure 2**. Anthropogenic $NO_x$ emission rate during July-August 2013 of (a) NEI11v1 inventory and (b) RCP8.5.

**Comment 6**

** The "discrepancy" introduced on lines 413-415 and explained in Figure S5 seems like a major point. Consider moving Figure S5 into the main text. Even if the figure stays in the supplement, describe the "discrepancy" and make a citation to clarify.*

**Response 6**

Our focus is the comparison of major RON species and the total ($NO_y$). As ∑ANs only accounts for a small fraction of $NO_y$ and there are high uncertainties in $RONO_2$ chemistry, we intend to show the figure in supplement and explain the 'discrepancy' in the caption of the figure as:

"**The discrepancy between ∑ANs and sum of ISOPN, MVKN and MACRN is attributed to monoterpene nitrates and a C5 dihydroxy dinitrate (DHDN) and nighttime $NO_3$ oxidation products from isoprene.**"

**Comment 7**

** The OPE discussion covers a long time-range (1993 to near present day), and ultimately is suggested to be "small and to have little impact". Consider moving this discussion to the conclusions and tightening the language.*

**Response 7**
We have removed the OPE discussion in the text following Reviewer #1's suggestion (Comment 4) to avoid confusion.

**Comment 8**
** The balance between $NO_x$ and products has been shown to be sensitive to computational time step at the surface[1]. How has this been treated in AM3?*

**Response 8**
We agree with the reviewer on the impact of computational time on $NO_y$ speciation. The current computational time step is 20 minutes. With this setting, our model can well reproduce the vertical profiles of all the major reactive oxidized nitrogen. We have emphasized this in lines 155-158 of the revised manuscript as

"**The current time step for chemistry and transport in our model is 20 mins. We show below in section 4.1 that, with the current setting, our model can well reproduce the vertical profiles of RON. Sensitivity of RON to operator duration should refer to Philip et al. (2016).**"

Line by line:

**Comment 9**
*140 - I did not see transport/chemistry time steps. Time steps have been shown to affect chemical partitioning[1], and likely export form. Please report this information and consider the implications on the export speciation outcome.*

**Response 9**
Please refer to Response 8.

**Comment 10**
*359 - I do not think you show how reactive nitrogen oxides would change with a 53% reduction. see below... where?*

**Response 10**
This has been explained as "We find that if we reduce anthropogenic $NO_x$ emission in our model by another 40 %, from 0.25 Tg N $mon^{-1}$ to 0.15 Tg N $mon^{-1}$ as suggested by Travis et al. (2016), simulated $NO_y$, $HNO_3$ and PAN decrease by 30 %, 33 % and 30 % respectively, leading to a noticeable underestimate for these nitrogen reservoirs." in lines 393-397 of the original manuscript. This sentence has been moved and revised in lines 390-392 of the current version of manuscript as:

"**We find that a similar reduction of anthropogenic $NO_x$ emissions in 2013, from 0.25 Tg N $mon^{-1}$ to 0.15 Tg N $mon^{-1}$, would lead to an underestimate of $NO_y$, $HNO_3$ and PAN by 30 %, 33 % and 30 %, respectively.**"

**Comment 11**

*387 - If lightning N had "likely ... insufficient production", why is it also too uncertain to change? Is there a similar reference for 2013?*

**Response 11**
High uncertainties associated with the production rate of $NO_x$ by lightning is partially due to lightning $NO_x$ production per flash, altitude of lightning $NO_x$ in models and impacts of temperature. Therefore, it is difficult to adjust lightning $NO_x$ in our model. We have revised the text in lines 362-365 as:

"**This underestimate can be improved by scaling up lightning emission by a factor of 5-10 (Fang et al., 2010). We do not adjust the lightning $NO_x$ emissions in this work due to its high uncertainty (Ott et al., 2010; Pickering et al., 1998).** "

**Comment 12**
*402 - The low bias may be good for SEAC$^4$S, but it would also be bad for ICARTT. This sentence reads as though there is a tidy explanation.*

**Response 12**
We have modified the text in lines 371-373 as:

"**This low bias can be partially due to neglecting small alkyl nitrates, which could contribute 20 - 30 ppt to ∑ANs (less than 10% near the surface) during SEAC$^4$RS (Fisher et al., 2016). Including small alkyl nitrates will increase modeled ∑ANs a bit in ICARTT as well.**"

**Comment 13**
*446 - The discussion of implemented chemistry seems to belong in section 2.*

**Response 13**
We have shortened the discussion in Section 2 as the reviewer suggested, particularly on heterogeneous chemistry.

**Comment 14**
*459 - R5 is not the exclusive fate of NO2. This should be more clear and consistent in the narrative. Perhaps using Ox would simplify and correct the narrative.*

**Response 14**
We have explained $O_x$ to connect R5 to the narrative in lines 432-433 as

"**We show that the model can roughly reproduce the correlation of $O_x$ (= $O_3$ + $NO_2$) vs. ∑ANs during both ICARTT and SEAC$^4$RS (Figure 4), ....**"

**Comment 15**
*508,510 - Not clear here if you are referencing simulated or observed abundances.*

**Response 15**

This is simulated abundances. We have stated in line 508-509 of the original manuscript as "Figure 5 shows the mean vertical profiles of modeled monoterpene nitrates (MNs) and isoprene nitrates (INs) during ICARTT and SEAC$^4$RS."

**Comment 16**
*542 - "prompt production" is often used as a technical term in chemical mechanisms to mean implemented without the intermediate, perhaps rate limiting, reaction. If this is implemented as "prompt production", then it seems inappropriate to say that you "In our model, we see prompt production." please clarify.*

**Response 16**
The text in lines 505-506 has been revised as:

"**In our model, we see a rapid increase of PROPNN after sunrise in the boundary layer (Figure S7), …**"

**Comment 17**
*562 - This sentence and what precisely it references is unclear. I'm assuming 561,562 is observations. The differences from the model are calculable from Figure 6, but not immediately available. Clarify and or add numbers to the text.*

**Response 17**
This sentence has been explained as "**Based on model estimates in Figure 6, most RON are reduced proportionally ...**" in lines 530-531 of the revised manuscript.

**Comment 18**
*702,705 and elsewhere - The Pollack study is compared to this study several times. The differences. I am not sure why this is important to the conclusions.*

**Response 18**
The trend of RON, specifically PAN, is not only dependent on changes of $NO_x$ but also on that of VOC precursors. Pollack study exhibited a different conclusion from our study on PAN trend, likely due to different VOC precursors in the two studied regions.

Reference:

[1] Philip, S., Martin, R. V., and Keller, C. A.: Sensitivity of chemistry-transport model simulations to the duration of chemical and transport operators: a case study with GEOS-Chem v10-01, Geosci. Model Dev., 9, 5, 1683-1695, 2016.

[2] Mao, J., Paulot, F., Jacob, D. J., Cohen, R. C., Crounse, J. D., Wennberg, P. O., Keller, C. A., Hudman, R. C., Barkley, M. P., and Horowitz, L. W.: Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry, J. Geophys. Res., 118, 19, 11,256-211,268, 2013.