

### Response to reviewer comments: Reviewer #3

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.]

#### *General comments:*

*This manuscript examines “decadal changes in summertime reactive nitrogen species and ozone over the Southeast U.S.”, and finds they “decline proportionally with decreasing NO<sub>x</sub> emissions in this region” and concludes that “this linear response is in part due to the nearly constant summertime supply of biogenic VOC emissions in this region”. There are several concerns with the overall quality of the current manuscript.*

#### **Comment 1**

*In the manuscript, some critical definition/terminology used are not accurate or ambiguous. For example, (1) NO<sub>y</sub> refers to reactive oxidized nitrogen not reactive nitrogen, the latter includes NH<sub>3</sub>.*

*(2) It seems summertime is defined in the manuscript as July-August, but the three aircraft measuring campaigns, whose observations were extensively used to evaluate the modeling results and derive the changes in observed concentrations, were conducted at, respectively, July-August, 2004, June-July, 2013, and August-September, 2013. For regulatory purpose, surface ozone is studied for a period in a year defined as ozone season, which is usually defined as April-October in the Southeast of United States.*

#### **Response 1**

The authors thank the reviewer for this important comment. We have read the manuscript thoroughly and improved any ambiguous definition/terminology that might cause confusion. Specifically, for the two examples the reviewer mentioned:

(1) We didn't include ammonium or ammonia in the analysis. We have revised the terminology 'reactive nitrogen species' to '**reactive oxidized nitrogen**' in all the places mentioned in the manuscript.

(2) We defined summertime as July-August since this is the common period covered in the three aircraft campaigns used for model evaluation. The analysis of decadal change of ozone and reactive oxidized nitrogen were based on the evaluated model results. We make this clear in the revised manuscript as "**We choose July – August as our ‘summer’ since this is the common period of all the measurements used in model evaluation.**" in lines 300-302.

#### **Comment 2**

*The decadal changes in both observation and simulations are not elucidated by using a well-designed comparison method. Reduction in NO<sub>x</sub> emissions are one of the major reasons that can cause the resulting reduced surface ozone and NO<sub>y</sub> concentrations, but it is not the only one. The method used in the manuscript is not convincing by removing other impacting factors such as meteorology and emissions reduction on other pollutants, which confounds the conclusions this manuscript makes. For example, (1) the aircraft measurements were collected at different locations and different days/months, how exactly such measurements can reveal the real changes of NO<sub>y</sub> between the two years a decade apart. (2) The model simulations were conducted for the same months for 2004 and 2013, a decade apart, but in what quantity are the impacts on species concentrations resulting from the differences in meteorology between the two years?*

## **Response 2**

(1) The authors thank the reviewer for this excellent comment. Our strategy is that if our model can well reproduce vertical profiles of RON and related species from aircraft measurements, we assume model is representative of this chemical environment and then use the model to derive the real changes between the two years a decade apart. We now add in the text (lines 517-520):

**“As RON and related species from aircraft and surface measurements are well reproduced in our model for both 2004 and 2013, we assume that the model is representative of this chemical environment, and then use the model to derive monthly mean changes between 2004 and 2013.”**

(2) We discussed about meteorology impacts on ozone changes during 2004-2013 in lines 642-657 of the original manuscript. In short, the changes of temperature and relative humidity in summers of the two years over SEUS are small according to our model, consistent with climatology data reported by Hidy et al. (2014). Decreases of ozone is mostly attributed to NO<sub>x</sub> emission reduction other than meteorology changes. The text has been revised in lines 608-620 as:

**“Our model shows marginal differences in RH (less than 1 %) and temperature (+ 2.4 K) within the PBL over the Southeast U.S. between the summers of 2004 and 2013, consistent with observed changes of RH (+ 2.7 %) and temperature (+ 2.6 K) during ICARTT and SENEX. This small variation in the model is also consistent with climatology data (Hidy et al., 2014). Camalier et al. (2007) showed that RH has a much bigger impact on summertime ozone than temperature over the Southeast U.S., suggesting little influence of meteorology on ozone trend. Using the same model but with the standard AM3 chemical mechanism, Lin et al. (2017) found that meteorology changes would have caused high surface ozone over the eastern U.S. to increase by 0.2 - 0.4 ppb yr<sup>-1</sup> in the absence of emission controls from 1988 to 2014. Therefore, we conclude that the impact of climate variability and change on O<sub>3</sub> is relatively small compared to NO<sub>x</sub> emission reductions over the Southeast U.S., consistent with previous studies (Lam et al., 2011; Hidy et al., 2014; Lin et al., 2017; Rieder et al., 2015).”**

## **Comment 3**

*There is no quantitative evaluation results presented for the model simulation on surface ozone. But according to the description from the manuscript: “AM3 overestimates surface MDA8 ozone in both years by about 16ppb on average”, and “MDA8 ozone averaged ... is observed to decrease by 11 ppb (23% of observed mean MDA8 ozone in July-August of 2004)”, one can deduce that the overestimation of surface MDA8 ozone in July-August of 2004 and 2013 are roughly 33% and 43%, respectively. Note that the USEPA recommends a better than 30% of mean normalized error for surface ozone performance for regulatory modeling. With worse than the EPA recommended performance, the modeling results from this study are not that meaningful for surface ozone regulation purposes.*

### **Response 3**

We have added statistical analysis of RON and surface ozone in Table 1 shown below (Table S4 in the revised supplement). We now add (lines 681-683):

**“Care should be exercised in applying the modeling results for surface ozone regulation purposes, given the high ozone bias shown in our model”.**

**Table 1.** Statistical analysis of ozone and major RON species from the base case and no\_hydro case<sup>a</sup>.

Tracers <sup>b</sup>	2004								2013							
	base				no_hydro				base				no_hydro			
	FB	FE	NMB	NME	FB	FE	NMB	NME	FB	FE	NMB	NME	FB	FE	NMB	NME
Ozone	$9.4 \times 10^{-2}$	0.16	$9.4 \times 10^{-2}$	0.16	0.11	0.16	0.11	0.16	0.17	0.19	0.16	0.19	0.17	0.20	0.16	0.20
NO <sub>x</sub>	0.19	0.55	$8.2 \times 10^{-2}$	0.59	0.25	0.56	0.14	0.61	$-3.6 \times 10^{-2}$	0.42	$-5.3 \times 10^{-2}$	0.44	$-1.3 \times 10^{-2}$	0.43	$-3.2 \times 10^{-2}$	0.45
HNO <sub>3</sub> <sup>c</sup>	$-1.4 \times 10^{-2}$ ( $7.4 \times 10^{-2}$ )	0.32 (0.41)	$5.1 \times 10^{-3}$ ( $2.6 \times 10^{-2}$ )	0.32 (0.41)	$-4.8 \times 10^{-2}$ ( $3.5 \times 10^{-2}$ )	0.33 (0.39)	$-2.2 \times 10^{-2}$ ( $6.0 \times 10^{-3}$ )	0.32 (0.38)	0.15	0.45	$5.4 \times 10^{-4}$	0.41	0.015	0.50	-0.11	0.44
PAN	0.25	0.49	0.17	0.42	0.31	0.49	0.23	0.43	$5.4 \times 10^{-2}$	0.36	$5.6 \times 10^{-2}$	0.35	$5.2 \times 10^{-2}$	0.38	$6.2 \times 10^{-2}$	0.37
ΣAN <sub>s</sub> <sup>d</sup>	-0.19	0.37	$8.9 \times 10^{-2}$	0.65	0.16	0.58	0.29	0.75	$-5.9 \times 10^{-2}$	0.57	-0.16	0.45	0.29	0.79	$-7.3 \times 10^{-3}$	0.46
NO <sub>y</sub> <sup>c</sup>	$6.4 \times 10^{-2}$ ( $6.5 \times 10^{-2}$ )	0.33 (0.40)	$6.3 \times 10^{-2}$ ( $3.8 \times 10^{-2}$ )	0.32 (0.36)	0.11 (0.12)	0.34 (0.39)	0.11 (0.10)	0.34 (0.38)	$-5.7 \times 10^{-3}$	0.27	$-4.2 \times 10^{-2}$	0.27	$-2.9 \times 10^{-2}$	0.29	$-6.0 \times 10^{-2}$	0.28
Wet deposition of NO <sub>3</sub> <sup>-</sup>	-0.40	0.50	-0.39	0.46	—	—	—	—	-0.51	0.56	-0.43	0.45	—	—	—	—

MDA8 ozone	0.30	0.32	0.33	0.35	—	—	—	—	0.39	0.40	0.45	0.46	—	—	—	—
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<sup>a</sup> Description of the two cases can be found in Table 2.  $FB = \frac{2}{N} \sum_{i=1}^N (P_i - O_i) / (P_i + O_i)$ ,  $FE = \frac{2}{N} \sum_{i=1}^N |P_i - O_i| / (P_i + O_i)$ ,

$NMB = \sum_{i=1}^N (P_i - O_i) / \sum_{i=1}^N O_i$ ,  $MNE = \frac{1}{N} \sum_{i=1}^N |P_i - O_i| / \sum_{i=1}^N O_i$ , where  $P_i$ ,  $O_i$ , and  $N$  are modeled and observed data and  $N$  is number of valid data.

<sup>b</sup> For ozone,  $NO_x$ ,  $HNO_3$ , PAN,  $\sum ANs$  and  $NO_y$ , observations are from ICARTT, SENEX and SEAC<sup>4</sup>RS within the boundary layer (< 1.5 km); For wet deposition of  $NO_3^-$ , observations are from NADP; For MDA8 ozone, observations are from EPA AQS data during July-August of 2004 and 2013 at monitoring stations in Figure S3.

<sup>c</sup> Statistical results of  $HNO_3$  and  $NO_y$  in 2004 (ICARTT) outside of and within the brackets used observed  $HNO_3$  measured by mist chamber/IC by University of New Hampshire and Chemical Ionization Mass Spectrometer (CIMS) by California Institute of Technology, respectively.

<sup>d</sup> Statistical results of  $\sum ANs$  in 2013 used observations during SEAC<sup>4</sup>RS.

#### **Comment 4**

*The organization and presentation of the manuscript cause a lot of confusions. (1) The authors constantly blends trends found in observations and trends found in simulations next to each other without distinguishing them clearly. (2) The purpose of the aircraft measurements and the surface observation, and the purpose of the simulations are not clearly presented. (3) A lot of qualitative statements, only supported with citations of ambiguous supporting meanings.*

#### **Response 4**

For (1) and (3), we have revised the text carefully to improve understanding of the manuscript. For (2), we now add (lines 124-128):

**“Together with measurements from networks, including the National Atmospheric Deposition Program (NADP) and EPA Air Quality System (AQS), these datasets enable a close examination of responses of RON and surface ozone to NO<sub>x</sub> emissions reduction in this region.”**

We have added descriptions of each simulation in Table 2 shown below (Table 2 in the revised manuscript), and in the text 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 including heterogeneous loss of a C<sub>5</sub> 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.”**

and in lines 520-522 as:

**“We also investigate the impacts of further decreases in NO<sub>x</sub> emissions by applying a hypothetical 40 % reduction of anthropogenic NO<sub>x</sub> emissions of 2013 but keeping other emissions and meteorology the same (“hypo” case in Table 2)**

**Table 2.** Case descriptions

Case name	Heterogeneous Loss of organic nitrates	NO <sub>x</sub> emissions	Meteorology
base	ISOPNB with a $\gamma$ of 0.005 and followed by a hydrolysis rate of $9.26 \times 10^{-5} \text{ s}^{-1}$	2004 and 2013	2004 and 2013
no_hydro	—	2004 and 2013	2004 and 2013
hydro_full	ISOPNB and DHDN with a $\gamma$ of 0.005 and followed by a hydrolysis rate of $9.26 \times 10^{-5} \text{ s}^{-1}$ ; TERPN1 with a $\gamma$ of 0.01 and followed by a hydrolysis rate of $9.26 \times 10^{-5} \text{ s}^{-1}$	2004 and 2013	2004 and 2013
hypo	Same with the base case	40 % reduction of NO <sub>x</sub> emissions of 2013	2013

*Specific comments:*

#### **Comment 5**

(1) Page 4, “high-resolution (50x50 km<sup>2</sup>)”. When conducting chemical transport modeling at regional scale, this is no way a high-resolution.

#### **Response 5**

We use a global chemistry-climate model in this work. We now revise the text in lines 144-148 as:

**“We apply a high-resolution (50 x 50 km<sup>2</sup>) version of the GFDL AM3 global chemistry-climate model to study decadal changes of RON and O<sub>3</sub> over the Southeast U.S. Chemistry-climate models provide a unique capability to both evaluate model representation of these observed changes and use that to improve future projections of air quality in the same region.”**

#### **Comment 6**

(2) Page 5 “. . . both inventories have a similar spatial distribution (Figure S1). Compare the two panels in Figure S1, apparently, the local maximum levels in the Southeast of RCP8.5 are somewhat 30% lower than the NEI2011 (no red spots are seen in the Southeast in the RCP8.5 panel). Also, why compared to NEI2011 version 1, why not the NEI2011 final version? More importantly, why don't just use NEI2011?

### **Response 6**

We have compared NEI2011 version 1 with the final version NEI2011 version 2. NO<sub>x</sub> emissions from this two versions are very similar. We now reflect this in the text in lines 176-179:

**“The resulting anthropogenic NO<sub>x</sub> emissions (0.25 Tg N mon<sup>-1</sup>) are 14 % lower than NEI11v1 emission inventory estimate of 0.29 Tg N mon<sup>-1</sup> (0.28 Tg N mon<sup>-1</sup> from the updated NEI11v2 emission inventory),...”**

As this work focuses on the relative change of RON and related species from 2004 to 2013 in a global climate-chemistry model, we find it difficult to interpret model results in 2004 using NEI2011. We now state in the text in lines 167-170:

**“Anthropogenic emissions follow the Representative Concentration Pathway 8.5 (RCP 8.5) projection (Lamarque et al., 2011) for both 2004 and 2013, to compare the model to observations in a consistent fashion and also enable future projection of air quality in this region.”**

### **Comment 7**

(3) Figure S3, why Florida surface ozone data were not included? This study is for the Southeast, which should include Florida.

### **Response 7**

We didn't include ozone data in Florida to avoid influences of ocean impacts (such as emissions, circulation, etc.).

### **Comment 8**

(4) Page 9, lines 329-331, why aircraft measurements for biomass burning and urban plumes are excluded for the model evaluation?

### **Response 8**

This is because these cannot be well represented on the scale of model. We have explained this in the revised text in lines 306-309 as

**“Data from biomass burning (CH<sub>3</sub>CN ≥ 225 ppt or HCN ≥ 500 ppt), urban plumes (NO<sub>2</sub> ≥ 4 ppb or NO<sub>x</sub>/NO<sub>y</sub> ≥ 0.4 (if NO<sub>y</sub> is available)), and stratospheric air (O<sub>3</sub>/CO >1.25 mol mol<sup>-1</sup>) are excluded (Hudman et al., 2007) in all the analyses, as these subgrid processes may not be well represented in our model.”**



### **Comment 9**

- (5) 1. Page 9, lines 334-335, “. . . use model output sampled along the flight track with 1-min resolution”. How exactly this has been done?
2. What are the time-steps of the model?
3. What are the time intervals of the model outputs?
4. Is this necessary since all the presented comparisons are for monthly averaged values anyway?
5. Is there any statistical metrics calculated for the comparisons at the 1-min resolution?

### **Response 9**

1. We mapped model outputs with observations at different locations (i.e. latitude, longitude and pressure) and local sampling time (for example, 8:12 CST sampling time corresponds to model estimate during 8:00-9:00 CST).
2. The chemistry and transport time step of the model is 20 mins. We now add “**The current time step for chemistry and transport in our model is 20 mins.**” in lines 155-156.
3. The output time interval of the model in this study is 1 hour for chemical tracers and 1 month for depositions of these tracers.
4. We used 1-min time resolution average of measurements to sample model output to better capture the locations of aircraft as well as atmospheric composition. This is the best way to compare the model with aircraft measurements.
5. We have calculated NMB, NME, FB, and FE using aircraft measurements and model estimates and included the results in Table S4 in the revised supplement.

### **Comment 10**

- (6) 1. Table 1 and table 2, “Monthly averaged”, or two month (July-August) averaged?
2. Table 1, Why not present the NO<sub>x</sub> emissions for the Southeastern US too, instead of for only North America totals?
3. Are they still 40% reduction for the Southeast only?
4. Also, how about those numbers of emissions amounts for the Southeast only used in the model compared to the NEI 2011 final version inventory?
5. Also, what about anthropogenic emissions pollutants other than NO<sub>x</sub>, such as VOC, CO etc.?

### **Response 10**

1. ‘Monthly averaged’ in the original Table 1 and Table 2 are two-month averaged for July and August.
2. We calculated national total NO<sub>x</sub> emissions for better comparison with NEI11 inventory. We also have included NO<sub>x</sub> emissions over the Southeast U.S. in Table 1 in the revised manuscript as well.
3. 40% reduction was applied to eastern U.S. that contributes 74% of the national total NO<sub>x</sub> emissions.
4. The comparison between NEI 2011 and RCP 8.5 shows similar relative differences in both national and Southeast region. We now add this in the text in lines 188-190

**“Compared to the NEI11v1 inventory, RCP 8.5 used in our model shows similar relative differences in both national and Southeast region.”**

5. The dominate VOC precursor of summertime ozone in the Southeast U.S. is biogenic isoprene. Contributions of anthropogenic VOCs and CO are quite small compare to isoprene on summertime ozone in this region. Therefore, we didn't compare anthropogenic VOCs and CO from NEI2011 inventory and that from our model.

#### **Comment 11**

*(7) Figure 7, there are bumps at around 30ppb in the 2013 simulations, but not seen from the 2004 simulation and any observations. Why those bumps?*

#### **Response 11**

We are unclear about the cause of those bumps. We find that those values appear to be related to urban and suburban areas where NO<sub>x</sub> sources are concentrated.

#### **Comment 12**

*(8) Page 10, lines 370-372, what is this “regionally-averaged NO<sub>y</sub>”? It seems jumped from the observations to simulations here?*

#### **Response 12**

This sentence has been removed to avoid confusion.

#### **Comment 13**

*(9) Page 10, line 369, “This is likely due to the different sampling regions (Figure S4) from the two campaigns”. If this is the case, then why you can trust the other derived reduction numbers from comparing the observations form the two campaigns? And why you can trust the changes derived from these observations to represent the real changes in the Southeastern US as a region?*

#### **Response 13**

All the analysis exhibited in section 4.1 is mainly for evaluation of our model by comparison with measurements during the three aircraft campaigns. As the flight tracks, although were not exactly identical, were all within the Southeast U.S. region, reduction numbers derived from these sampling data represent the general trend in this region to some extent.

Our strategy is that if our model can well reproduce vertical profiles of RON and related species from aircraft measurements, we assume model is representative of this chemical environment and then use model to derive the real changes between the two years a decade apart. This is showed in section 5. We have clarified this in the revised manuscript in lines 517-520 as:

**“As RON and related species from aircraft and surface measurements are well reproduced in our model for both 2004 and 2013, we assume that the model is representative of this**

chemical environment, and then use the model to derive monthly mean changes between 2004 and 2013.”

#### Comment 14

(10) 1. Page 18, lines 649-651. What are the quantitative differences in both simulated and observed RH and temperature between 2004 and 2013 in July-August?

2. What about the differences in cloud cover, precipitation etc. that also impact on ozone formation? 3. Lines 654-657, this statement, for changes between 2004 and 2013, is not supported by convincing evidence. How exactly the citation in lines 651-654 supports this statement? Since this is also the base for deriving the major finding: “reactive nitrogen species and ozone over the Southeast U.S.”, “decline proportionally with decreasing  $\text{NO}_x$  emissions in this region”, solid demonstration of this statement is needed.

#### Response 14

1. Based on observations (ICARTT and SENEX), changes of temperature and RH are + 2.6 K (291.5 - 294.1 K) and + 2.7 % (68.9 - 71.6 %), respectively. Our model predicts + 2.4 K (290.0 - 292.4 K) and - 0.88 % (77.3 - 76.4 %) of changes for temperature and RH. Therefore, our model can well capture this trend of meteorology. It also proves that decreases of ozone over the Southeast U.S. from 2004 to 2013 is not attributed to meteorology. We reflect this in the revised text in lines 608-611 as:

**“Our model shows marginal differences in RH (less than 1 %) and temperature (+ 2.4 K) within the PBL over the Southeast U.S. between the summers of 2004 and 2013, consistent with observed changes of RH (+ 2.7 %) and temperature (+ 2.6 K) during ICARTT and SENEX.”**

2. There are no observations of cloud cover and precipitation from aircraft measurements. Based on measurements from NADP, there are no significant changes of observed precipitation between 2004 and 2013 in July-August (total precipitation of 14.6 m in two months). Our model showed good agreement with observations, with 13.1 m for 2004 and 15.3 m 2013.

3. Lin et al. (2017) found 0.2 – 0.4 ppb/yr increase of ozone due to meteorology changes. this is not significant compared to observed 1.1 ppb/yr decrease of ozone. Camalier et al. (2007) also showed that summertime ozone over the Southeast U.S. is more affected by RH that mostly varied little during 2004-2013, according to both observations and model estimates. We have revised the text in lines 612-620 as:

**“Camalier et al. (2007) showed that RH has a much bigger impact on summertime ozone than temperature over the Southeast U.S., suggesting little influence of meteorology on ozone trend. Using the same model but with the standard AM3 chemical mechanism, Lin et al. (2017) found that meteorology changes would have caused high surface ozone over the eastern U.S. to increase by 0.2 - 0.4 ppb yr<sup>-1</sup> in the absence of emission controls from 1988 to 2014. Therefore, we conclude that the impact of climate variability and change on O<sub>3</sub> is relatively small compared to NO<sub>x</sub> emission reductions over the Southeast U.S., consistent with previous studies (Lam et al., 2011; Hidy et al., 2014; Lin et al., 2017; Rieder et al., 2015)”**

Reference:

Camalier, L., Cox, W., and Dolwick, P.: The effects of meteorology on ozone in urban areas and their use in assessing ozone trends, *Atmos. Environ.*, 41, 33, 7127-7137, 2007.