Response to reviewer comments: Reviewer #1

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.]

Review of "Decadal change of summertime 1 reactive nitrogen species and surface ozone over the Southeast United States" by Li et al.

This manuscript investigates the ozone and reactive nitrogen changes over the southeastern US (SE) using a high-resolution global model (AM3), applied, apparently, to July and August of 2004 and 2013. They also look to see what a further 40% reduction in NOx emissions would do. (The reason I use "apparently" is that they sometimes use "summer" to say their application period, but do not specify exactly what summer entails: they should make this more clear.) As part of this study, they evaluate the model using both aircraft and ground-based, routine monitors. They find that reactive nitro- gen and ozone have both decreased in the SE, and further decreases are expected in response to a 40% NO_x reduction.

This study is both of interest to the community and, for the most part, well executed, though there are aspects that need to be corrected before it should be accepted for publication in ACP. The strength is the focus on the oxidized nitrogen species and associated chemistry. The weaknesses include an inadequate evaluation for the analysis conducted, a short application period (2 months), a potentially poor choice of years, lack of consideration of condensed phase species in their assessment and evaluation.

Specific Comments

Comment 1

(1) *Evaluation of the model is particularly important in such applications where one is trying to explain the reasons behind the observed (both in the model as well as in the ambient) changes, and, further, when using the model to extrapolate to further changes. Currently, the article relies on presenting plots with no quantitative statistical analysis. This needs to be corrected for further consideration of the article. Such an evaluation should be summarized in the main article with details in the supplemental.*

(2) *Looking at Figure 7, one sees rather considerable differences. How does this relate to other studies? If one is to assess how well the model may be relied upon to provide details of why the model may be capturing observed changes, and to what degree one can rely on the model to simulate future air quality, a more rigorous evaluation is required. One can look at the recent work done at EPA (e.g., [Simon et al., 2012]), or as part of AQMEII (e.g., [Appel et al., 2012;*

Dennis et al., 2010] [Solazzo and Galmarini, 2015]) or Environ [Emery et al., 2017] to provide the types of metrics that should be considered.

(3) *Along those lines, there are ways to adjust deposition results to account for differences in precipitation rates other than the way they have chosen, and those should be considered. They should use total deposition fields from their modeling with total deposition fields estimated by NADP (http://nadp.sws.uiuc.edu/committees/tdep/tdepmaps/).*

Response 1

(1) We now include statistical analysis of ozone and major reactive oxidized nitrogen following this reviewer's suggestion. Results are listed in the following Table 1 and included in the revised supplemental material (Table S4). Discussion of these statistics are also included in the revised manuscript in lines 331-335 as

"**Performance statistics of O_3 in the boundary layer listed in Table S4 also indicate positive biases in the model, with the fractional bias (FB) of 9.4 – 17%, fractional error (FE) of 16 – 19 %, normalized mean bias (NMB) of 9.4 – 16% and normalized mean error (NME) of 16 – 19 %.**"

and in lines 368-369 as

"**Performance metrics in Table S4 also indicate better agreement of the model with observations if hydrolysis of ISOPNB assumed.**"

(2) We performed similar statistical analysis for surface MDA8 ozone in figure 7. Results are listed in the following table and included in the revised supplemental material (Table S4). Discussion of these statistics are also included in the revised manuscript in lines 580-582 as

"**In general, AM3 overestimates surface MDA8 ozone in both years by about 16 ppb on average, with the NMB of 33 - 45 % and NME of 35 - 46 % respectively.**"

(3) We agree with the reviewer that there are other ways to account for the bias in modeled precipitation rates. However, these are beyond the scope of this manuscript. We think the direct way to minimize the bias of precipitation in the model is to compare the observed monthly average concentration of NO_3^-, with model estimates using modeled wet deposition flux of NO_3^- divided by the observed precipitation. For a better evaluation of model's performances, we performed statistical analysis of the wet deposition of NO_3^-. The text has been revised in lines 404-406 as:

"**This reduction in monthly averaged NO_3^- wet deposition flux is well captured by our model (-29 %), despite a low relative bias of 40 % in both years and NMB of - 39 – - 43 % (Table S4).**"

Total deposition fields use wet deposition measurements from the NADP NTN (used in our model evaluation) and dry deposition combined of model estimates and ambient air monitoring data. The data might introduce biases from the model. Therefore, we didn't use the total deposition estimates.

Table 1. Statistical analysis of ozone and major RON species from the base case and no_hydro case[a].

Tracers[b]	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	9.4×10^{-2}	0.16	9.4×10^{-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_x	0.19	0.55	8.2×10^{-2}	0.59	0.25	0.56	0.14	0.61	-3.6×10^{-2}	0.42	-5.3×10^{-2}	0.44	-1.3×10^{-2}	0.43	-3.2×10^{-2}	0.45
HNO_3[c]	-1.4×10^{-2} (7.4×10^{-2})	0.32 (0.41)	5.1×10^{-3} (2.6×10^{-2})	0.32 (0.41)	-4.8×10^{-2} (3.5×10^{-2})	0.33 (0.39)	-2.2×10^{-2} (6.0×10^{-3})	0.32 (0.38)	0.15	0.45	5.4×10^{-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	5.4×10^{-2}	0.36	5.6×10^{-2}	0.35	5.2×10^{-2}	0.38	6.2×10^{-2}	0.37
∑ANs[d]	-0.19	0.37	8.9×10^{-2}	0.65	0.16	0.58	0.29	0.75	-5.9×10^{-2}	0.57	-0.16	0.45	0.29	0.79	-7.3×10^{-3}	0.46
NO_y[c]	6.4×10^{-2} (6.5×10^{-2})	0.33 (0.40)	6.3×10^{-2} (3.8×10^{-2})	0.32 (0.36)	0.11 (0.12)	0.34 (0.39)	0.11 (0.10)	0.34 (0.38)	-5.7×10^{-3}	0.27	-4.2×10^{-2}	0.27	-2.9×10^{-2}	0.29	-6.0×10^{-2}	0.28
Wet deposition of NO_3^-	-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	—	—	—	—

[a] 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.

[b] For ozone, NO_x, HNO_3, PAN, ∑ANs and NO_y, observations are from ICARTT, SENEX and SEAC[4]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.

[c] 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.

[d] Statistical results of ∑ANs in 2013 used observations during SEAC[4]RS.

Comment 2

I was a bit surprised that they focus on just two months (July and August) for their analysis (and that this was not more clearly stated, if that is, indeed, the case). This, along with focusing on just one historical and one semi-current year, makes the results very sensitive to the choice of time period. Along those lines, the summer of 2013 was cold and wet in the Southeast, and the meteorological adjustment determined by EPA was relatively large (in the Southeast data available at https://www.epa.gov/airtrends/trends-ozone-adjusted-weather-conditions). This was also the case for 2004, but the concern here is the timing as the adjustments are for the season, while the modeling conducted is just two months. More analysis is needed to tell how much impact is just from the meteorology of these two years specific to the two months.

Response 2

We choose July-August for analysis is mainly because our model is evaluated in this time window by three aircraft campaigns. We make this clear in the revised manuscript in lines 300-302 as

"**We choose July – August as our 'summer' since this is the common period of all the measurements used in model evaluation**."

We agree with the reviewer that meteorology plays an important role in ozone formation. Such impact has been discussed in the original manuscript in lines 642 - 657. Specifically, the observed changes of temperature and RH between summer of 2004 and 2013 are marginal, same with model estimates. Moreover, Camalier et al. (2007) showed that summertime surface ozone over SEUS was more impacted by RH than temperature. The relative change of RH from our model (less than 1%) and observations (+ 2.7%) are very small. Therefore, influence of meteorology on decadal changes of ozone is expected to be very small. We have emphasized this in the revised manuscript 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^{-1} in the absence of emission controls from 1988 to 2014. Therefore, we conclude that the impact of climate variability and change on O_3 is relatively small compared to NO_x 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

Such an analysis, particularly when considering reactive nitrogen species, should provide additional focus on aerosol nitrate, including in the regional model evaluation. When they use the term "reactive nitrogen" are they including ammonia and ammonium? If not, they should add "oxidized".

Response 3

We did include aerosol organic nitrate in ∑ANs and stated in several places (i.e. lines 287-288, lines 308-309, and lines 340-341) in the original manuscript. There are high uncertainties in the kinetics of organic nitrate aerosol formation such as the hydrolysis rate of different organic nitrates. Evaluation of this mechanism is beyond the scope of our work. For model evaluation of inorganic nitrate aerosols, unfortunately, this cannot be accomplished since their formation is not included in the current version of AM3. Moreover, Ng et al. (2017) has reviewed the global distribution of particulate nitrates, finding that the major component over the Southeast U.S. is organic nitrates. Therefore, inorganic nitrate aerosols were ignored in this work. We didn't include ammonia or ammonium in our analysis either. For clarification, we have revised the terminology 'reactive nitrogen species' to "**reactive oxidized nitrogen**" in all the places mentioned in the manuscript. We also add following sentences in lines 319-322:

"**We do not consider inorganic nitrates in particle phase in this analysis, due to lack of thermodynamic model for inorganic aerosols in current version of AM3. This simplification is expected to have minimal effects, as they only account for a small fraction of aerosol nitrates in the Southeast U.S. (Ng et al., 2017).**".

Comment 4

There is a logical mismatch in the current paper. They state that there is a linear relationship between ozone and NOx emissions (line 627). This indicates a constant OPE. However, they also state that there is a transition from low to high OPE (line 633), though, admittedly, they do not say that after transitioning to a high OPE, it does not become constant. However, the discussion of OPE suffers from their not actually calculating an OPE. I might suggest removing much, if not all, of the OPE discussion unless they can bolster it further. If they do not remove this section, line 639: stating that OPE has increased very little and had little impact on net ozone production needs more definitive evidence.

Response 4

We have removed this discussion as the reviewer suggested.

Comment 5

I might suggest they integrate some of their findings with those in Blanchard et al., "ACP (2016) "Effects of emission reductions on organic aerosol in the southeastern United States". While this article is focused on organic aerosol, it relates to NO_x controls in the SE.

Response 5
We add discussion in lines 534-536 as:

"**As an important source of organic aerosols (OA), ∑ANs may contribute to the decrease of OA over the Southeast U.S. in the past decade (Blanchard et al., 2016).**"

Comment 6
Line 66: EPA still targets VOC emissions. (Look at the reductions in mobile VOCs over the period of interest!). Over the 2004 to 2013 period, how much of the ozone reduction is due to NO_x vs. VOC controls? Do mobile emission reductions have a big impact in the rural areas under investigation here?

Response 6
We find that modeled ozone in summer in the Southeast U.S. is insensitive to VOC emissions from mobile sources, because VOCs in the Southeast U.S. is predominantly of biogenic origin.

Comment 7
There should be more discussion about the potential reasons for model bias following the work by Travis et al., (2016), and how this paper fits into that discussion.

Response 7
We now add in lines 386 – 395:

"**Given the good agreement between observed and modeled RON in both 2004 and 2013, we find that the ozone bias, shown in Figure 1, cannot be completely explained by an overestimate of anthropogenic NO_x emissions. A recent GEOS-Chem study (Travis et al., 2016) shows that the ozone bias in their model can be largely reduced by scaling down anthropogenic NO_x emissions. 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. Such a reduction would be also inconsistent with the relative changes in EPA estimates of NO_x emissions shown above. Indeed, other processes, such as ozone dry deposition, may also contribute to this bias and warrant further investigation."**

Comment 8
(1) Abstract: The final sentence states that 'further reductions of NOx emissions will lead to...less frequent extreme ozone events', however, the paper does not address extreme ozone events, just averages. This should be removed.
(2) Some reorganization of the paper could help improve its interpretation. A few suggestions: 1. The operational evaluation of the model and discussion of trends over time overlap (e.g., lines 343-363 and 488-499 discuss changes over time). I recommend splitting the evaluation section into 'operational' and 'dynamic' subsections (see Dennis et al. 2010 for an example). The dynamic

evaluation section can address observed/modeled changes as related to emissions reductions, but the bulk of the discussion on this point should be reserved for its own section (currently section 5). (3) 2. Define metrics used for comparison. 'Bias' is used here in both absolute (e.g., line 352) and relative (e.g., line 401) In the paragraph from lines 488-499, for example, the authors combine discussion of operational and dynamic evaluation, observed changes in response to emissions, and comparisons with previous modeling efforts.

Response 8

(1) We have revised 'extreme' ozone events to 'high' ozone events in all the places mentioned in the manuscript.

(2) We thank the reviewer for introducing these two evaluation types. Since our work starts with model evaluation in both 2004 and 2013 for aircraft and surface datasets, operational and dynamic evaluation are closely coupled in section 4. We find it difficult to split into operational and dynamic evaluations.

(3) We have revised 'bias' all mentioned in the manuscript to 'absolute bias' or 'relative bias' correspondingly, if needed.

Comment 9

Lines 567-575: why does the response of NO_y concentration change from linear (from 2004-2013) to nonlinear with further emissions reductions?

Response 9

We now clarify this in lines 539-540 of the revised manuscript as:

"**The slower decrease of NO_y is likely due to $\sum$ANs, which decrease at a slower rate and becomes a larger fraction of NO_y.**".

Comment 10

Change all mentions of 'future' 40% reduction in NO_x emissions to 'hypothetical' reduction (e.g., line 661). This analysis was performed partly to investigate the hypothesis that NOx emissions are overestimated, and there's no proof that the future will bring continued reductions. Also, I believe this model run was performed with 2013 meteorology, but this should be made clear.

Response 10

We have replaced all the 'future' 40% reduction in NO_x emissions to 'hypothetical' reduction in the revised text. We also include the following sentence in lines 520-522:

"**We also investigate the impacts of further decreases in NO_x emissions by applying a hypothetical 40 % reduction of anthropogenic NO_x emissions of 2013 but keeping other emissions and meteorology the same ("hypo" case in Table 2).**"

A table with descriptions of all the cases performed is added in the revised manuscript (shown below).

Table 2. Case descriptions

Case name	Heterogeneous Loss of organic nitrates	NO_x emissions	Meteorology
base	ISOPNB with a γ of 0.005 and followed by a hydrolysis rate of 9.26×10^{-5} s^{-1}	2004 and 2013	2004 and 2013
no_hydro	—	2004 and 2013	2004 and 2013
hydro_full	ISOPNB and DHDN with a γ of 0.005 and followed by a hydrolysis rate of 9.26×10^{-5} s^{-1}; TERPN1 with a γ of 0.01 and followed by a hydrolysis rate of 9.26×10^{-5} s^{-1}	2004 and 2013	2004 and 2013
hypo	Same with the base case	40 % reduction of NO_x emissions of 2013	2013

Comment 11

In the discussion or Data sections, add some mention of reliability/consistency of measurements as a basis for model evaluation across the decade

Response 11

We have added a few sentences about the reliability of measurements in lines 120-124:

"**These data have been widely used to evaluate model estimates of RON and ozone (Singh et al., 2007; Pierce et al., 2007; Perring et al., 2009; Fischer et al., 2014; Hudman et al., 2007; Henderson et al., 2011; Hudman et al., 2009; Edwards et al., 2017; Baker and Woody, 2017; Travis et al., 2016; Mao et al., 2013; Fisher et al., 2016; Yu et al., 2016; Liu et al., 2016).**"

Comment 12

Line 715: Change upto to 'up to'

Response 12

All the typos have been corrected.

References:

Appel, K. W., S. Roselle, G. Pouliot, B. Eder, T. Pierce, R. Mathur, K. Schere, S. Galmarini, and S. T. Rao (2012), Performance Summary of the 2006 Community Multiscale Air Quality (CMAQ) Simulation for the AQMEII Project: North American Application, in Air Pollution Modeling and Its Application XXI, edited by D. G. Steyn and S. T. Castelli, pp. 505-511, doi:10.1007/978-94-007-1359-8_84.

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.

Dennis, R., et al. (2010), A framework for evaluating regional-scale numerical photochemical modeling systems, Environ. Fluid Mech., 10(4), 471-489, doi:10.1007/s10652-009-9163-2.

Emery, C., Z. Liu, A. G. Russell, M. T. Odman, G. Yarwood, and N. Kumar (2017), Recommendations on statistics and benchmarks to assess photochemical model performance, J. Air Waste Manage. Assoc., 67(5), 582-598, doi:10.1080/10962247.2016.1265027.

Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, Atmos. Chem. Phys., 17, 3, 2103-2162, 2017.

Simon, H., K. R. Baker, and S. Phillips (2012), Compilation and interpretation of photochemical model performance statistics published between 2006 and 2012, Atmos. Environ., 61, 124-139, doi:10.1016/j.atmosenv.2012.07.012.

Solazzo, E., and S. Galmarini (2015), Comparing apples with apples: Using spatially distributed time series of monitoring data for model evaluation, Atmos. Environ., 112, 234-245, doi:10.1016/j.atmosenv.2015.04.037.