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% NOx 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
$\sum$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, $\sum$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 $\sum$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 $\sum$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 NOx controls in the SE.

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

"**As an important source of organic aerosols (OA), $\sum$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	NOx 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 NOx 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.

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 C₅ 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:
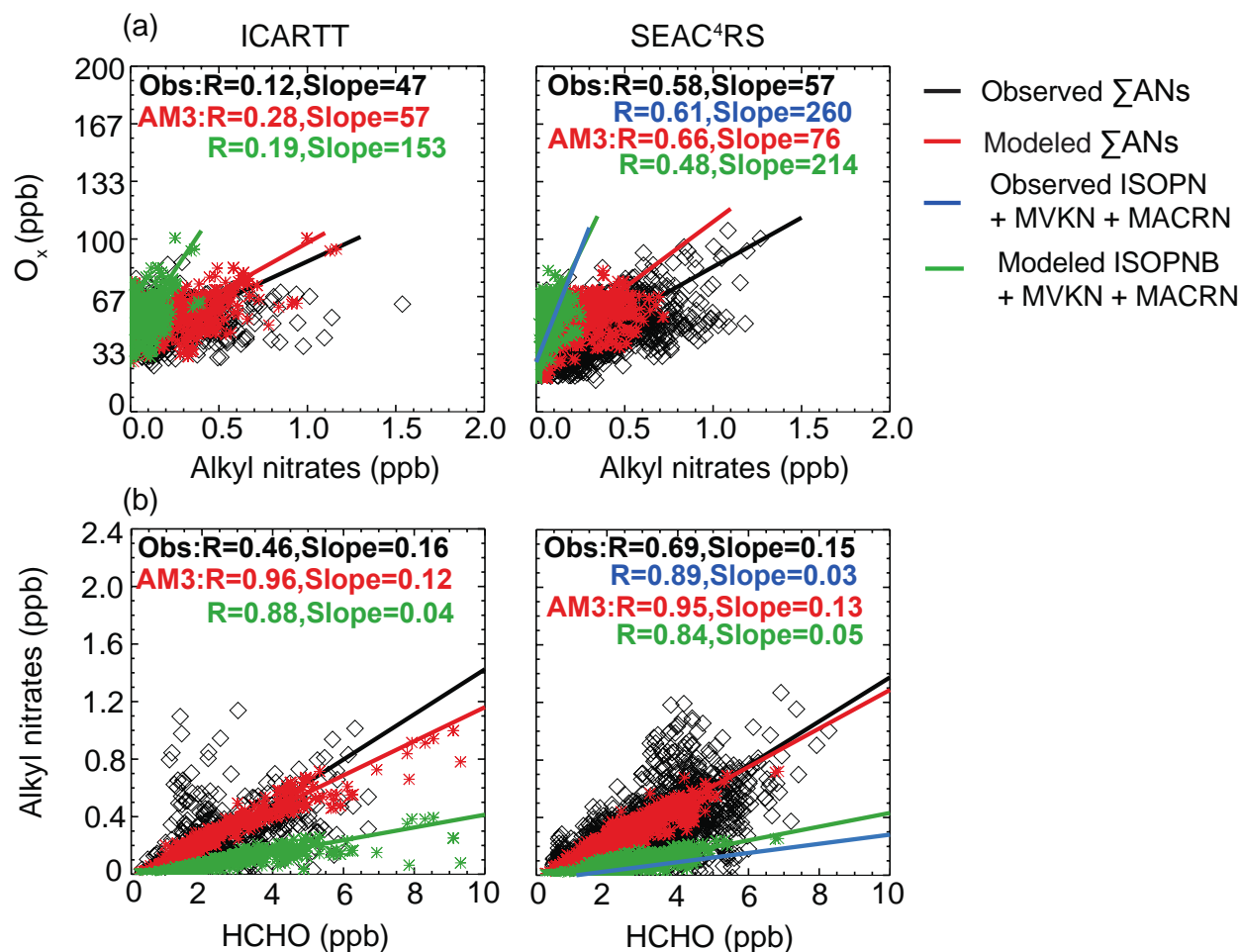
Figure 1. Figure 4 in the manuscript.

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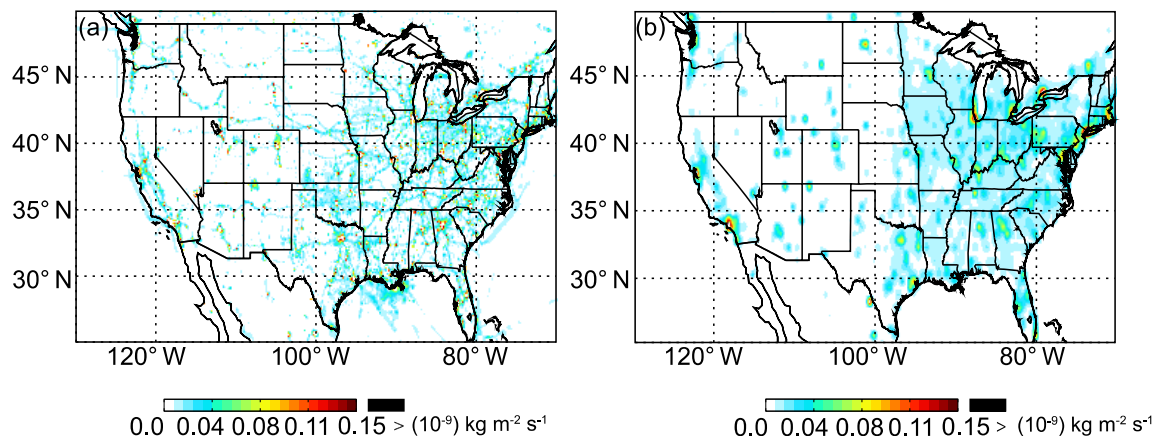
Figure 2. Anthropogenic NO_x emission rate during July-August 2013 of (a) NEI11v1 inventory and (b) RCP8.5.

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 $\sum$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 $\sum$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 $\sum$ANs (less than 10% near the surface) during SEAC^{4}RS (Fisher et al., 2016). Including small alkyl nitrates will increase modeled $\sum$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. $\sum$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.

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_x 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_y refers to reactive oxidized nitrogen not reactive nitrogen, the latter includes NH_3.
(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_x emissions are one of the major reasons that can cause the resulting reduced surface ozone and NO_y 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_y 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_x 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^{-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

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[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, $\sum$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 $\sum$ANs in 2013 used observations during SEAC[4]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_x 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 hydrolcase 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.**"

and in lines 520-522 as:

"**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)**"

Table 2. Case descriptions

Case name	Heterogeneous Loss of organic nitrates	NOx 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 NOx emissions of 2013	2013

Specific comments:

Comment 5
(1) *Page 4, "high-resolution (50x50 km^2)". 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^2) version of the GFDL AM3 global chemistry-climate model to study decadal changes of RON and O$_3$ 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_x emissions from this two versions are very similar. We now reflect this in the text in lines 176-179:

"**The resulting anthropogenic NO_x emissions (0.25 Tg N mon^{-1}) are 14 % lower than NEI11v1 emission inventory estimate of 0.29 Tg N mon^{-1} (0.28 Tg N mon^{-1} 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 ($CH_3CN \geq 225$ ppt or $HCN \geq 500$ ppt), urban plumes ($NO_2 \geq 4$ ppb or $NO_x/NO_y \geq 0.4$ (if NO_y is available)), and stratospheric air ($O_3/CO > 1.25$ mol mol^{-1}) 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 NOx 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 NOx, 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_x emissions for better comparison with NEI11 inventory. We also have included NO_x 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_x 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_x sources are concentrated.

Comment 12
(8) *Page 10, lines 370-372, what is this "regionally-averaged NO_y"? 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 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^{-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)**"

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.

Decadal change of summertime reactive oxidized nitrogen ~~species~~ and surface ozone over the Southeast United States

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Abstract

Widespread efforts to abate ozone (O_3) smog have significantly reduced nitrogen oxides (NO_x) emissions over the past two decades in the Southeast U.S. (SEUS), a place heavily influenced by both anthropogenic and biogenic emissions. How reactive nitrogen speciation responds to the reduction in NO_x emissions in this region remains to be elucidated. Here we exploit aircraft measurements from ICARTT (July-August, 2004), SENEX (June-July, 2013), and SEAC[4]RS (August-September, 2013) and long-term ground measurement networks alongside a global chemistry-climate model to examine decadal changes in summertime reactive oxidized nitrogen (RON)~~species~~ and ozone over the Southeast U.S. We show that our model can well reproduce the mean vertical profiles of major RON species and the total (NO_y) in both 2004 and 2013. Among the major RON species, nitric acid (HNO_3) is dominated (~ 42 – 45 %), followed by NO_x (31 %), total peroxy nitrates ($\sum$PNs; 14 %), and total alkyl nitrates ($\sum$ANs; 9 – 12 %) on a regional scale. We find that most RON, ~~reactive nitrogen species,~~ including NO_x, $\sum$PNs~~peroxyacetyl nitrate (PAN)~~ and ~~nitric acid (~~HNO_3~~)~~ decline proportionally with decreasing NO_x emissions in this region, leading to a similar decline in ~~exported~~ NO_y. This linear response might be~~is~~ in part due to the nearly constant summertime supply of biogenic VOC emissions in this region. Our model captures the observed relative change of RON~~reactive nitrogen species~~ and surface ozone from 2004 to 2013. Model sensitivity tests indicate that further reductions of NO_x emissions will lead to a continued decline in surface ozone and less frequent high~~extreme~~ ozone events.

1 Introduction

Since the 1990s, the U.S.A. Environmental Protection Agency (U.S. EPA) has targeted emissions of nitrogen oxides (NO_x) to improve air quality by lowering regional photochemical smog (The 1990 Clean Air Amendment). Satellite- and ground-based observations imply significant declines in U.S. NO_x emissions, with a decreasing rate of roughly - 4 % yr^{-1} after 2005 (Krotkov et al., 2016; Russell et al., 2012; Tong et al., 2015; Miyazaki et al., 2017; Lu et al., 2015; Lamsal et al., 2015). This has proven effective at lowering near-surface ozone (O_3) in the past few decades (Cooper et al., 2012; Simon et al., 2015; Hidy and Blanchard, 2015; Stoeckenius et al., 2015; Xing et al., 2015; Yahya et al., 2016). The ~~. According to U.S. EPA data, the~~ average of the annual 4th highest ~~maximum~~ daily ~~averaged~~ maximum 8-h average~~hr~~ (MDA8) ozone over 206~~212~~ sites has decreased by 31~~33~~ % from 101 ppb in 1980 to 70~~68~~ ppb in 2016~~2014~~ across the continental U.S., with more significant reductions in rural areas of the eastern U.S. in summer (Simon et al., 2015; Cooper et al., 2012). Here we use both~~combine~~ aircraft and ground-based datasets, combined with a high resolution ~~for both ozone and reactive nitrogen to evaluate a~~ chemistry-climate model, ~~used~~ to evaluate~~project future~~ responses of reactive oxidized nitrogen (RON) and surface ozone to the ~~to changes in~~ NO_x emission reductions in the Southeast U.S.~~emissions~~.

In the troposphere, ozone is produced through photochemical reactions involving NO_x and volatile organic compounds (VOCs) in the presence of sunlight. During photooxidation, a large fraction of NO_x is transformed into its reservoirs, including nitric acid (HNO_3), peroxy nitrates (RO_2NO_2~~:~~, dominated by peroxyacetyl nitrate (PAN)), and alkyl nitrates ($RONO_2$). These species, together with NO_x, are known as total reactive oxidized nitrogen ($NO_y = NO_x + HNO_3 + HONO + 2 \times N_2O_5$ + total peroxy nitrates ($\sum PNs$) + total alkyl nitrates ($\sum ANs$)). Some of these reservoir species, particularly those with an organic component, tend to be less soluble and longer lived. They may carry reactive nitrogen far from the NO_x source region (Stohl et al., 2002; Parrish et al., 2004; Li et al., 2004) and thereby affect NO_x concentrations and O_3 formation on a regional to global scale (Liang et al., 1998; Horowitz et al., 1998; Perring et al., 2013; Paulot et al., 2016; Hudman et al., 2004).

$RONO_2$ originating from biogenic VOCs (BVOCs) represents a major uncertainty in the NO_y budget, as BVOC emissions account for more than 80 % of global VOC emissions (Millet et al., 2008). To a large extent, this is due to the uncertainties in current understanding of BVOC oxidation chemistry. Biogenic $RONO_2$ species are mainly produced from the oxidation of BVOCs by OH in the presence of NO_x during daytime and by nitrate radical (NO_3) during nighttime. Laboratory and field studies show a wide range of $RONO_2$ yields from their BVOC precursors (Browne et al., 2014; Fry et al., 2014; Lockwood et al., 2010; Paulot et al., 2009; Rindelaub et al., 2015; Rollins et al., 2009; Lee et al., 2014; Xiong et al., 2015; Xiong et al., 2016; Teng et al., 2015). Another uncertainty lies in the fate of $RONO_2$, i.e. recycling $RONO_2$ into NO_x or~~versus~~ converting it to HNO_3 ~~as a NO_x sink~~ have important implications for the NO_y budget and thus O_3 production (Fiore et al., 2005; Horowitz et al., 2007; Ito et al., 2009; Perring et al., 2013; Paulot et al., 2012). This is further complicated by particle-phase~~In addition, recent field studies have shown that~~ $RONO_2$, an important component ~~is a potential source~~ of secondary organic aerosol (SOA) over the Southeast U.S. (Xu et al., 2015; Lee et al., 2016). The fate of particle-phase $RONO_2$ is unclear, with the possibility for removal by hydrolysis to form HNO_3 (Jacobs et al., 2014; Hu et al., 2011; Darer et al., 2011; Rindelaub et al., 2015; Szmigielski et al., 2010; Sato, 2008; Romer et al., 2016; Wolfe et al., 2015), photochemical aging (Nah et al., 2016; Boyd et al., 2015), and deposition (Nguyen et al., 2015) . To what extent $RONO_2$ affect the partitioning of RON and surface ozone remains to be elucidated.

Extensive datasets in ~~Over~~ the Southeast U.S. offer a great opportunity to study the decadal change of RON~~., photochemistry in summer is strongly influenced by both biogenic~~ and surface ozone, resulting from NO_x emission decline.~~anthropogenic emissions, implying strong sensitivity of O_3 production to changes in anthropogenic NO_x emissions (Simon et al., 2015).~~ Aircraft campaigns during the summers of 2004 and 2013, including ~~(i.e.~~ the International Consortium for Atmospheric Research on Transport and

Transformation (ICARTT) (Fehsenfeld et al., 2006; Singh et al., 2006), the Southeast Nexus (SENEX) (Warneke et al., 2016), and the Studies of Emissions and~~,~~ Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC^{4}RS) (Toon et al., 2016)~~,)~~ provide detailed characterization of tropospheric composition in this region separated by nearly a decade. 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., 2013b; Fisher et al., 2016; Yu et al., 2016; Liu et al., 2016). Together with measurements from networks, including ~~the wet deposition flux of nitrate (NO_3^-) from~~ the National Atmospheric Deposition Program (NADP) and ~~NO_y and O_3 measurements from~~ EPA Air Quality System (AQS)~~,) surface network,~~ these datasets enable~~aircraft datasets provide insights into changes in O_3 pollution and NO_y speciation over~~ a close examination of responses of RON and surface ozone to~~decadal period when~~ NO_x emissions reduction in this region.~~were declining rapidly as pollution control programs were implemented.~~

Here we use a high-resolution global 3D climate-chemistry model, the Geophysical Fluid Dynamics Laboratory (GFDL) AM3 model, with updated isoprene and organic nitrate chemistry to investigate decadal changes of RON~~NO_y (and its specific constituents)~~ and surface O_3 during summer between 2004 and 2013 over the Southeast U.S. We first evaluate the model with comprehensive measurements from three aircraft campaigns in the summer of 2004 (ICARTT) and 2013 (SENEX and SEAC^{4}RS). Model~~The model~~ estimates of nitrate wet deposition flux are also evaluated against measurements from ~~the~~ NADP; model estimates of~~for~~ NO_y are compared with~~against~~ measurements from EPA AQS to provide an additional constraint on the fate of RON~~NO_y species~~ in the model. We then investigate the repartitioning of RON~~NO_y species~~ in response to NO_x emission reductions from 2004 to 2013 on a regional scale~~.~~ From there, we examine the model estimate of decadal changes of summertime surface O_3 at 157 EPA AQS monitoring sites over the Southeast U.S. We also~~by comparing to the measurements from EPA AQS. Last, we~~ demonstrate the sensitivity of RON and MDA8 O_3 to a hypothetical~~and NO_y speciation to projected~~ NO_x emission reduction~~decreases~~ over the next decade.~~(to 2022).~~

2 Methodology

2.1 AM3 Model

We apply a high-resolution (50 x 50 km^2) version of the GFDL AM3 global chemistry-climate model to study decadal changes of RON~~O_3~~ and O_3 ~~organic nitrates~~ 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. The model configuration is to a large extent

similar to that used in ~~anothera companion~~ another paper (Li et al., 2016); and a short summary is provided below. The dynamical core, physical parameterizations, cloud and precipitation processes, and cloud-aerosol interactions mainly follow Donner et al. (2011), except that convective plumes are computed on a vertical grid with finer resolution (Paulot et al., 2016). Dry deposition in the model has been updated to use dry deposition velocities calculated in the GEOS-Chem model (Paulot et al., 2016), to reflect rapid deposition of organic nitrates and oxidized volatile organic compounds (OVOCs) (Nguyen et al., 2015). 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).

Isoprene emissions are computed in the model using the Model of Emissions of Gases and Aerosols from Nature (MEGAN). In 2004, isoprene emissions over the continental U.S. (25-50° N, 130-70° W) are computed to be 8.0 Tg C in July and August together, with a previous model estimate of 7.5 Tg C by Mao et al. (2013b). In 2013, model estimates of isoprene emissions were scaled down by 20% following Li et al. ~~Isoprene emissions are computed in the model using the Model of Emissions of Gases and Aerosols from Nature (MEGAN). In July August of 2004, the computed isoprene emissions over the continental U.S. (25-50° N, 130-70° W) are 8.0 Tg C and appear to be consistent with a previous model estimate of 7.5 Tg C by Mao et al. (2013) in the same region during this period. For 2013, we applied a 20 % reduction of MEGAN for isoprene emissions as described in Li et al.~~ (2016). The resulting isoprene ~~emissions areemission is~~ emissions are 7.7 Tg C in July-August ~~inover~~ in this region, with little difference compared to 2004. Monoterpene emissions follow Naik et al. (2013) and do not vary interannually, with a total of 4.0 Tg C in July and August.

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. As shown in Table 1, anthropogenic NO_x emissions over the continental U.S. during July-August of 2004 amount to 0.42 Tg N mon^{-1}, consistent with Hudman et al. (2007) but 11 % lower than EPA estimates of 0.47 Tg N mon^{-1} (Granier et al., 2011). For the year of 2013, we apply a 25 % reduction to the anthropogenic NO_x emissions from the RCP 8.5 projection (from base year of 2010), to best reproduce the vertical profiles of ~~RONNO_y species~~ RON during SENEX as shown below in section 4.1. This adjustment is also consistent with recent estimates of NO_x emissions over the Southeast U.S. (Anderson et al., 2014). The resulting anthropogenic NO_x emissions (0.25 Tg N mon^{-1}) are 14 % lower than NEI11v1 emission inventory estimate of 0.29 Tg N mon^{-1} (0.28 Tg N mon^{-1} from the updated NEI11v2 emission inventory), although both inventories have a similar spatial distribution (Figure S1). We also apply a diurnal variation to anthropogenic NO_x

emissions following Mao et al. (2013b). Soil NO_x emissions in our model, 3.6 Tg N yr^{-1} globally (Naik et al., 2013), are considerably lower than other model estimates, including 5.5 Tg N yr^{-1} in Yienger and Levy (1995) and 9.0 Tg N yr^{-1} in Hudman et al. (2012). As a result, the anthropogenic NO_x emissions over the continental U.S. are 0.84 Tg N for July-August of 2004, and 0.50 Tg N in July-August of 2013, with 40 % reduction from 2004 to 2013 (Table 1). This relative change in anthropogenic NO_x emissions is consistent with EPA estimates (https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data) and satellite observations . ~~The resulting anthropogenic NO_x emissions (0.25 Tg N mon^{-1}) are 14 % lower than NEI11v1 emission inventory estimate (0.29 Tg N mon^{-1}), although both inventories have a similar spatial distribution (Figure S1). Soil NO_x emissions in our model, 3.6 Tg N yr^{-1} globally (Naik et al., 2013), are considerably lower than other model estimates, including 5.5 Tg N yr^{-1} in Yienger and Levy (1995) and 9.0 Tg N yr^{-1} in Hudman et al. (2012). Lightning NO_x, calculated as a function of parameterized convection in the model following Price et al. (1997), is also lower than that of Hudman et al.~~ (2007). Compared to the NEI11v1 inventory, RCP 8.5 used in our model shows similar relative differences in both national and Southeast region. ~~by a factor of 8 over the U.S. As a result, the total NO_x emissions over the continental U.S. are 0.98 Tg N for July-August of 2004, and 0.64 Tg N in July-August of 2013 (Table 1). The 40 % reduction of anthropogenic NO_x emissions from 2004 to 2013 over the eastern U.S is consistent with EPA Air Pollutant Emissions Trends Data (https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data) and satellite observations (Krotkov et al., 2016; Lu et al., 2015).~~

2.2 Gas-phase chemistry

We apply the same isoprene mechanism as described by Li et al. (2016). A full list of the reactions can be found in Table S1. This mechanism is based on Mao et al. (2013b), but has been significantly revised to incorporate recent laboratory updates on isoprene oxidation by OH and O_3 . ~~A full list of the reactions can be found in Table S1. This mechanism is based on Mao et al. (2013), but has been significantly revised to incorporate recent laboratory updates on isoprene oxidation by OH and O_3~~ (Schwantes et al., 2015; Bates et al., 2016; Peeters et al., 2014; St. Clair et al., 2016; Bates et al., 2014; Praske et al., 2015; Müller et al., 2014; Lee et al., 2014; Crounse et al., 2011). One major feature is the suppression of δ-isoprene hydroxyl peroxy radical (δ-$ISOPO_2$) and subsequent reaction pathways in the model, as these channels are considered to be of minor importance under ambient conditions (Peeters et al., 2014; Bates et al., 2014). The fraction of $ISOPO_2$ undergoing isomerization is calculated using bulk isomerization estimates (Crounse et al., 2011). As a result, the first-generation isoprene alkyl nitrate is assumed to be β-hydroxy nitrate (ISOPNB) in the model with a yield of 10 % from the $ISOPO_2$ + NO pathway. This differs from a recent GEOS-Chem study of organic nitrates over the Southeast U.S. that assumed 9 % yield of the first-generation isoprene alkyl

240 nitrate comprised of 90 % ISOPNB and 10 % δ-hydroxy nitrate (ISOPND) (Fisher et al.,
241 2016). The treatment of β- and δ-ISOPO$_2$ will not only affect the speciation of organic
242 nitrates but also the production of O$_3$ due to different NO$_x$ recycling efficiency in their
243 secondary products. We also include updated chemistry for methylvinyl ketone (MVK)
244 (Praske et al., 2015), an updated yield of hydroxy hydroperoxides (ISOPOOH) (Bates et
245 al., 2016; St. Clair et al., 2016), fast photolysis of carbonyl organic nitrates (Müller et al.,
246 2014), and an updated ozonolysis rate of ISOPNB (Lee et al., 2014). In addition, we
247 reduce the yield of organic nitrates (MACRN) from methacrolein (MACR) oxidation
248 from 15 % to 3 %, which is estimated from the measured yield of nitrate from MVK
249 oxidation (Praske et al., 2015).

250 Another major model revision involves the treatment of ~~the~~ nighttime oxidation of
251 isoprene. Instead of following Mao et al. (2013b), we revised~~(2013), we revised the~~
252 nighttime oxidation of isoprene largely based on the Leeds Master Chemical Mechanism
253 v3.2 (MCM v3.2), allowing a more complete description of isoprene oxidation by NO$_3$.
254 In particular, MCM v3.2 suggests significant production of propanone nitrate (PROPNN)
255 from the photooxidation of the C$_5$ carbonyl nitrate, consistent with recent laboratory
256 experiments (Schwantes et al., 2015). We also updated the products of the reaction of
257 nitrooxy alkylperoxy radical (INO$_2$), the peroxy radical from isoprene oxidation by NO$_3$,
258 with HO$_2$ to reflect a lower molar yield (0.77) of C$_5$ nitrooxy hydroperoxide (INPN)
259 (Schwantes et al., 2015). The differences between MCM v3.2 and the most updated
260 version, MCM v3.3.1, in isoprene nighttime chemistry appears to be small (Jenkin et al.,
261 2015). We therefore use MCM v3.2 as the reference in this work.

262 We include a highly simplified chemistry for the oxidation of monoterpenes in this work,
263 mainly to quantify their contribution to organic nitrates. Monoterpenes are lumped into
264 one chemical species (C$_{10}$H$_{16}$) in our model. The organic nitrate yield is set to 26 % from
265 OH-initiated oxidation (Rindelaub et al., 2015) and to 10 % from NO$_3$-initiated oxidation
266 (Browne et al., 2014). Details of the monoterpene chemistry can be found in Table S2.

267 **2.3 Heterogeneous loss of organic nitrates**

268 Field and laboratory studies have indicated a potential contribution to aerosol formation
269 of organic nitrates from BVOC oxidation (Ayres et al., 2015; Fry et al., 2014; Nah et al.,
270 2016; Rollins et al., 2009; Rindelaub et al., 2015; Boyd et al., 2015; Lee et al., 2016; Ng
271 et al., 2008; Fry et al., 2009; Xu et al., 2015; Lee et al., 2014; Bean and Hildebrandt Ruiz,
272 2016; Spittler et al., 2006); ~~Error! Hyperlink reference not valid.Fry et al., 2014;~~ **Error!**
273 **Hyperlink reference not valid.**~~Nah et al., 2016;~~ **Error! Hyperlink reference not valid.**~~Rollins et~~
274 ~~al., 2009;~~ **Error! Hyperlink reference not valid.**~~Rindelaub et al., 2015;~~ **Error! Hyperlink**
275 **reference not valid.**~~Boyd et al., 2015;~~ **Error! Hyperlink reference not valid.**~~Lee et al., 2016;~~
276 **Error! Hyperlink reference not valid.**~~Ng et al., 2008;~~ **Error! Hyperlink reference not valid.**~~Fry~~
277 ~~et al., 2009;~~ **Error! Hyperlink reference not valid.**~~Xu et al., 2015;~~ **Error! Hyperlink reference**

not valid.Lee et al., 2014; Error! Hyperlink reference not valid.Bean and Hildebrandt Ruiz, 2016; Error! Hyperlink reference not valid.Spittler et al., 2006). Aerosol yield depends on both the VOC precursor and the oxidant. For example, Δ-3-carene oxidation by NO_3 can produce a 38-65 % yield of organic aerosols in a smog chamber (Fry et al., 2014), which is much higher than the 1-24 % yield from NO_3-initiated isoprene oxidation (Ng et al., 2008; Rollins et al., 2009; (Error! Hyperlink reference not valid.Ng et al., 2008; Error! Hyperlink reference not valid.Rollins et al., 2009; Ayres et al., 2015). Recent chamber studies indicate a very low aerosol yield from α-pinene oxidation by NO_3 (Nah et al., 2016; Fry et al., 2014), the aerosol yield increases to ~ 18 % when α-pinene is oxidized by OH (Rollins et al., 2010; Rindelaub et al., 2015). It should be noted that these results from laboratory experiments might not be representative ofto atmospheric conditions in terms of the RO_2 reaction partner or RO_2 lifetime.

In the condensed phase, organic nitrates can undergo hydrolysis reactions producingto produce HNO_3 (Darer et al., 2011; Hu et al., 2011; Rindelaub et al., 2015; Boyd et al., 2015; Szmigielski et al., 2010; Sato, 2008; Jacobs et al., 2014; Bean and Hildebrandt Ruiz, 2016). However, the hydrolysis rate varies greatly with the structure of nitrate, and for most species remains highly uncertain, though certain trends have been elucidated, e.g. tertiary nitrates favor hydrolysis while primary and secondary nitrates are more stable (Bean and Hildebrandt Ruiz, 2016; Darer et al., 2011; Hu et al., 2011; Boyd et al., 2015). Here we assume a first-order irreversible reactive uptake for the heterogeneous loss of organic nitrates onto aerosols (R1), followed by its hydrolysis reaction returning HNO_3 and alcohols (R2) (Fisher et al., 2016):

$$RONO_2(g) \xrightarrow{k_1} AONJ(aq) \tag{R1}$$

$$AONJ(aq) + H_2O \xrightarrow{k_2} ROH + HNO_3(g) \tag{R2}$$

where $RONO_2$, AONJ and ROH represent gas- and particle-phase organic nitrates and alcohols respectively. We allow heterogeneous loss of organic nitrates to sulfate, black carbon, primary organic carbon, sea salt, mineral dust and SOA following Mao et al. (2013a). 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. We adopt an effective uptake coefficient 0.005 for ISOPNB and DHDN, and 0.01 for TERPN1, following Fisher et al. (2016), with a 3-h bulk lifetime in particle phase where $RONO_2$, AONJ and ROH represent gas- and particle phase organic nitrates and alcohols respectively. For the daytime isoprene organic nitrates (mainly from the $ISOPO_2$ + NO pathway), we only consider heterogeneous loss of ISOPNB to aerosols, since this has been detected in field and laboratory studies (Jacobs et al., 2014). Lee et al.

~~(2014) hypothesized a significant amount of C_5 dinitrate (DHDN, with a molar yield of 21 % via the ISOPNB peroxy radical + NO pathway) produced from OH oxidation of ISOPNB. Since DHDN is highly functionalized and might partition to the condensed phase forming SOA, we test the impact of this process on the estimate of NO_y speciation and O_3 concentration in a sensitivity study (AM3h, Figure S2). Aerosol formation from nighttime isoprene organic nitrates (from isoprene oxidation by NO_3) are neglected due to the low mass yields. Information about hydrolysis of daytime monoterpene nitrates (from OH oxidation of monoterpenes) is quite sparse. Two chamber studies to date have examined the hydrolysis of nitrates from α-pinene oxidation by OH (Rindelaub et al., 2015; Bean and Hildebrandt Ruiz, 2016). They found that the hydrolysis rate is dependent on relative humidity (RH) and aerosol acidity. We also examine the hydrolysis of daytime monoterpene nitrates (TERPN1) in the above sensitivity study (AM3h, Figure S2). We do not consider heterogeneous loss of nighttime monoterpene nitrates in this work due to inadequate information.~~

~~We allow heterogeneous loss of organic nitrates to sulfate, black carbon, primary organic carbon, sea salt, mineral dust and SOA following Li et al.~~ (2016) (Table S3). Details of each case are listed in Table 2.

~~. The first-order rate constant k_1 is determined using an effective uptake coefficient 0.005 for isoprene nitrates (ISOPNB in all hydrolysis cases and DHDN in AM3h, equivalent to 1.8 h lifetime in the atmosphere) and 0.01 for daytime monoterpene nitrates (TERPN1, in AM3h) following Fisher et al. (2016), which are consistent with other estimates (Wolfe et al., 2015; Marais et al., 2016). Due to the large uncertainties of lifetimes against hydrolysis, we assume a 3-h bulk lifetime for the three particle-phase nitrates following Pye et al. (2015), consistent with recent estimate of organic nitrate aerosol lifetime at a ground monitoring site in Centreville, Alabama (CTL) (Lee et al., 2016). We also conduct another sensitivity test (AM3 w/o hydro in Figure 1 and Figure 2) without accounting for the heterogeneous loss of organic nitrates.~~

3 Observational datasets

We use measurements from a series of field campaigns (2004 ICARTT, 2013 SENEX, and 2013 SEAC[4]RS) to evaluate model~~the~~ performance on~~of the model in estimating~~ O_3, NO_x, HNO_3, PAN, $\sum$ANs and NO_y over the Southeast U.S. in~~during~~ summer.

The ICARTT aircraft campaign provided a detailed characterization of tropospheric chemistry over the eastern U.S. in the summer of 2004 (July 1 - August 15, 2004). Two aircrafts~~aircraft~~, the NASA DC-8 and the NOAA WP-3D, were deployed to collect measurements of ozone, RON~~NO_y species~~, isoprene and its oxidation products. Here we focus on data including O_3, NO_x, HCHO (Tunable Diode Laser (TDL) absorption spectrometry), HNO_3 (mist chamber/IC by University of New Hampshire and Chemical

Ionization Mass Spectrometer (CIMS) by California Institute of Technology), PAN and $\sum$ANs (including gas and aerosol $RONO_2$) collected~~from 11 science flights~~ on the NASA DC-8 aircraft over the Southeast U.S. Details of the instrument operation and accuracy are summarized in Singh et al. (2006) and references therein.

Two ~~SENEX was a NOAA~~ aircraft campaigns were conducted in the summer of 2013 over the Southeast U.S. The first one is NOAA SENEX campaign, using NOAA WP-3D aircraft ~~aimed~~ to investigate the interaction between biogenic and anthropogenic emissions and the formation of secondary pollutants ~~over the Southeast U.S. in summer 2013~~ (May 27 - July 10, 2013). We focus on daytime ~~The NOAA WP-3D aircraft was launched to collect~~ measurements of ~~a variety of chemical compounds during 18 scientific flights. Here we focus on data, including~~ O_3, NO_x, HNO_3, PAN, speciated $RONO_2$ and NO_y in this work.~~from 15 daytime flights only. We also used measurements of ISOPN, methylvinylketone nitrates (MVKN) and methacrolein nitrates (MACRN) taken by University of Washington from 10 daytime flights during June 3-July 3 of the campaign.~~ Details of the instrument operation and accuracy are summarized in Warneke et al. (2016) and references therein. The second one is NASA SEAC^{4}RS campaign, which took place in August - September of 2013, with a focus on

~~Because $\sum$ANs and several speciated $RONO_2$ were not measured on the NOAA WP-3D aircrafts during SENEX, we include another aircraft campaign for model evaluation despite that this campaign has a major coverage in September of 2013. SEAC^{4}RS was a NASA aircraft campaign with the field mission based in Houston, Texas during August-September 2013, designed to examine~~ vertical transport of atmospheric pollutants from the surface to the stratosphere. Here we focus on ~~It provides comprehensive measurements of atmospheric composition in the lower troposphere over North America. Here we use~~ observations of O_3, NO_2, HCHO (laser-induced fluorescence, LIF), $\sum$ANs (including gas and aerosol $RONO_2$) and speciated $RONO_2$ collected on~~from 20~~ NASA DC-8 aircraft ~~science flights~~ to evaluate model representation~~the correlations~~ of $\sum$ANs and several~~major~~ $RONO_2$ originating from isoprene oxidation.~~ during daytime with O_x (= O_3 + NO_2) and with HCHO, respectively, as additional constraints to the model.~~ Details of the instrument operation and accuracy are summarized in Toon et al. (2016) and references therein. ~~We mainly focus on $RONO_2$ and related species from SEAC^{4}RS in this work.~~

Besides these aircraft campaigns, we also use surface observations for model evaluation, including nitrate (NO_3^-) wet deposition flux and concentration from the National Trends~~Trend~~ Network (NTN) of NADP (accessible at http://nadp.sws.uiuc.edu/data/) and surface O_3 and NO_y from EPA AQS (accessible at https://aqs.epa.gov/aqsweb/documents/data_mart_welcome.html). NTN provides the monthly NO_3^- concentration and precipitation so that the monthly mean concentration of

NO$_3^-$ and wet deposition flux could be derived for model evaluation. The AQS database provides measurements of important ambient air pollutants (O$_3$, NO$_x$, SO$_2$, PM$_{2.5}$ species, etc.) collected at monitoring sites across the continental U.S. We focus on NO$_3^-$ wet deposition fluxes at 53 NADP sites (Figure 3) and MDA8 O$_3$ at 157 EPA AQS sites (Figure S3) located in the Southeast U.S. during July - August of 2004 and 2013. NO$_y$ measurements at 10 out of the 157 AQS sites in the same episodes are compared with model estimates as an additional constraint on the decadal change of NO$_y$. We choose July – August as our 'summer' since this is the common period of all the measurements used in model evaluation.

4 Model evaluation of ozone and reactive nitrogen species

We evaluate our model against observations from aircraft campaigns in 2004 and 2013. For each of the three field campaigns, all measurements are averaged to a 1-min time resolution. Data from biomass burning (CH$_3$CN $\geq$ 225 ppt or HCN $\geq$ 500 ppt), urban plumes (NO$_2$ $\geq$ 4 ppb or NO$_x$/NO$_y$ $\geq$ 0.4 (if NO$_y$ is available)), and stratospheric air (O$_3$/CO >1.25 mol mol^{-1}) are excluded (Hudman et al., 2007) in all the analyses, as these subgrid processes may not be well represented in our model. We focus on the Southeast U.S. region, using only data within the domain of 25 - 40° N latitude and 100 - 75° W longitude for our analyses. A map of all the flight tracks of each campaign is shown in Figure S4. All model results arefor comparison with observations use model output sampled along the flight track with 1-min time resolution.

4.1 Mean vertical profiles of O$_3$ and RONreactive nitrogen species

Figure 1 shows the observed and modeled mean vertical profiles of O$_3$, NO$_x$, HNO$_3$, PAN, $\sum$ANs and NO$_y$ during ICARTT and SENEX. We use $\sum$ANs measurements from SEAC^{4}RS to evaluate model performance during summer 2013, due to the lack of $\sum$ANs measurements from SENEX. Our model results include both gas and aerosol RONO$_2$ in $\sum$ANs, although aerosol RONO$_2$ accounts for 7~11% of $\sum$ANs in the planetary boundary layer (PBLBL, < 1.5 km). 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). To investigate the impact of RONO$_2$ hydrolysis, we include two model simulations, the base case with heterogeneous loss of ISOPNB, and a sensitivity run 'no_hydro' without heterogeneous loss of organic nitrates.

Mean observed O$_3$ in the surface layer decreased from 50 ppb during ICARTT to 35 ppb during SENEX, consistent with the declining trend in surface MDA8 ozone at AQS monitoring sites (section 5.2). As we show in section 5.2, this decline in ozone is mainly

driven by NO_x emission reduction, with little influence by meteorology in the two years. Our model can reproduce the vertical gradient and the relative change of O_3 from 2004 to 2013, except for a positive absolute bias of 6 - 12 ppb in the boundary layer. 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 %. This overestimate of O_3 is higher than that reported (3 - 5 ppb) by Mao et al. (2013b) for their simulation of the ICARTT dataset, likely due to faster photolysis of carbonyl nitrates that increases the NO_x recycling efficiency from isoprene oxidation.

We further examine mean vertical profiles of NO_x and its reservoirs in 2004 and 2013 (Figure 1). ~~Mean observed O_3 in the surface layer decreased from 50 ppb during ICARTT to 35 ppb during SENEX, consistent with the decline in surface MDA8 ozone at AQS monitoring sites during July-August from 2004 to 2013 over the Southeast U.S. as shown below. Differences in meteorology may account for some of this decline as this region was cool and wet in Summer 2013 (Hidy et al., 2014), conditions that suppress ozone formation. We show below that this impact is relatively small compared to that from NO_x emission reductions in this region. Our model can reproduce the vertical gradient of O_3 as well as the relative change from 2004 to 2013, but the model has a positive bias of upto 6 ppb and 12 ppb in the boundary layer during ICARTT and SENEX respectively. This overestimate of O_3 appears to be higher than that reported (3-5 ppb) by Mao et al. (2013) for their simulation of the ICARTT dataset, likely due to faster photolysis of carbonyl nitrates that increases the NO_x recycling efficiency from isoprene oxidation. A recent study using the GEOS-Chem model (Travis et al., 2016) shows that this regional bias can be reduced (though not eliminated) with a 53 % reduction of anthropogenic NO_x emissions from the 2011 EPA national emission inventory (NEI11v1). Despite some evidence of overestimated NO_x emissions in NEI11v1 (Souri et al., 2016; Ahmadov et al., 2015), we find that such a reduction of NO_x emissions would lead to a significant underestimate of the simulated vertical profiles of reactive nitrogen oxides in our model, as we show below. Therefore, we conclude that the bias in the vertical profile of O_3 in our model, even though the cause is not entirely understood so far, may not be solely due to biases in NO_x emissions.~~

~~We further examine mean vertical profiles of NO_x and its reservoirs in 2004 and 2013.~~ In the boundary layer along the flight tracks. ~~(Figure 1),~~ HNO_3 is the most abundant RON ~~reactive nitrogen compound~~, accounting for 40 – 46 % of NO_y, followed by NO_x (18 – 23 %), PAN (20 ~~21~~ %), and $\sum ANs$ (11 – 21 %). Between 2004 and 2013, mean observed NO_y in the boundary layer decreased by 20 %, from 2.0 ppb to 1.6 ppb, a weaker change than the 35 % reduction of total NO_x emissions (Table 1). ~~This is likely due to the different sampling regions (Figure S4) from the two campaigns. We show later that regionally averaged NO_y indicates a 34 % reduction over the Southeast U.S. from~~

~~2004 to 2013, more consistent with the emission reductions (- 35 %).~~ The responses of major RON~~reactive nitrogen compounds~~ are mostly proportional to the change in NO_x emissions, with the notable exception of $\sum ANs$. We find significant decreases in NO_x (- 35 %) and HNO_3 (- 29 %) as well as a slight decrease in PAN (- 13 %) from observations. The relative trends of HNO_3 and PAN are opposite to those found in the Los Angeles (LA) basin, where PAN decreased much faster than HNO_3 (Pollack et al., 2013). This difference results mainly from the rapid decrease of anthropogenic VOC emissions in the LA basin that also serves as major precursors of PAN. In contrast, isoprene is the major precursor of PAN over the Southeast U.S. Its~~BVOC~~ emissions show a constant supply (within 5 % differences over the two summers) in this region~~over the Southeast U.S~~. $\sum ANs$ shows a different trend from the above compounds, increasing from 0.23 ppb to 0.27 ppb (+ 17 %) near the surface.~~ (Figure 1).~~ As we show below in section 5.1, these changes (except for $\sum ANs$) are mostly consistent with model estimates on a regional average. Discrepancy in their trends of vertical profiles and regional average might be due to representative,~~ despite possible representativeness~~ errors from ~~different sampling areas during~~ the three aircraft campaigns on spatial (Figure S4) and temporal (different episodes, referring to observation data description in section 3) scales.~~(Figure S4).~~

The model can well reproduce RON~~all the NO_y species~~ in the boundary layer but tend~~tends~~ to underestimate them in the free troposphere. This is likely due to insufficient production of NO_x from lightning in the free troposphere in our model, which is 0.048 Tg N in total over North America during July - -August of 2004, lower by almost a factor of 5 compared to the value (0.27 Tg N from July 1-August 15, 2004) reported by Hudman et al. (2007). 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).

Hydrolysis of organic nitrates affects $RONO_2$ significantly in the boundary layer. ~~Underestimate of NO_x in the free troposphere might also be due to rapid conversion of NO_x to HNO_3 (Henderson et al., 2011) in the model. However, we did not adjust the model due to the high uncertainty in the estimate of lightning NO_x. 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.~~

~~Hydrolysis of organic nitrates affects $RONO_2$ significantly in the boundary layer.~~ By introducing hydrolysis of ISOPNB, we find that model relative bias of $\sum ANs$ ~~in the boundary layer~~ is reduced from + 20 % to + 2 % during ICARTT (Figure 1). Performance metrics in Table S4 also indicate better agreement of the model with observations if hydrolysis of ISOPNB assumed. However, the relative~~However, the~~ bias is increased in

magnitude from – 9 % to – 24 % during SEAC[4]RS. 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.~~.~~ Hydrolysis of ISOPNB also leads to a slight increase of HNO$_3$ (Table S4). The ~~impacts its product HNO$_3$. Although the change in HNO$_3$ is not as evident as that of RONO$_2$, model bias is slightly increased during ICARTT but improved during SENEX. We find that the~~ impact of hydrolysis of ISOPNB on boundary layer O$_3$ appears to be small. This is mainly because without hydrolysis, the dominant loss of ISOPNB is oxidation by OH, which then leads to the formation of secondary organic nitrates including MVKN, MACRN and ~~a C5 dihydroxy dinitrate~~ (DHDN.~~).~~ The majority of these organic nitrates (MVKN and DHDN) return NO$_x$ slowly due to their long lifetimes (Table S5),~~,~~ resulting in a similar effect on ozone production as hydrolysis of ISOPNB. In addition to~~Besides~~ the good agreement of ∑ANs, our model shows good agreement with speciated RONO$_2$ measured during SENEX and SEAC[4]RS, including ISOPN and the sum of MVKN and MACRN (Figure 2). We find that the large discrepancy between ∑ANs and speciated alkyl nitrates (Figure S5) can be explained by a combination of monoterpene~~terpene~~ nitrates and DHDN~~the C5 dihydroxy dinitrate~~ and nighttime NO$_3$ oxidation products from isoprene, accounting for 20 - -24 %, 14 - -17 % and 23 - -29 % of ∑ANs respectively in the boundary layer. ~~in the boundary layer. Contribution of the three types of alkyl nitrates also show different vertical trend. For clarification, all model results discussed below are from AM3 with hydrolysis of ISOPNB.~~

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.

4.2 _NO3−_ NO$_3^-$ _NO3−NO3−NO3−NO3−_ wet deposition flux and concentration

Figure 3 shows a comparison of _NO3−_ NO$_3^-$ _NO3−NO3−NO3−NO3−NO3−NO3−NO3−NO3−_ wet deposition flux between observations and model results during the summers of 2004 and 2013. The observed _NO3−_NO$_3^-$_NO3−NO3−NO3−NO3−NO3−_ wet deposition flux

539   is   calculated   by   multiplying   the   measured

540 $NO3-$ NO_3^- $NO3-NO3-NO3-NO3-NO3-$ concentration and precipitation at each

541 monitoring   site   as

542 $F_{o,i}=C_{o,i}P_{o,i}$ $Fo,i=Co,iPo,iFo,i=Co,iPo,iFo,i=Co,iPo,iFo,i=Co,iPo,i$,

543 where $F_{o,i}$ is the monthly-mean $NO3-$ NO_3^- $NO3-NO3-$ wet

544 deposition flux, $C_{o,i}$ and $P_{o,i}$ are the monthly-mean observed NO_3^- $NO3-NO3-$ concentration precipitation at

545 monitoring site i. The modeled $NO3-$ NO_3^- $NO3-NO3-NO3-NO3-NO3-$ wet

546 deposition flux includes HNO_3 and all the alkyl nitrates. Observations indicate a 24 %

547 reduction of $NO3-$ NO_3^- $NO3-NO3-NO3-NO3-NO3-$ wet deposition flux in summer

548 from 2004 to 2013 over the Southeast U.S., likely due to NO_x emission reductions. This

549 reduction in monthly averaged $NO3-$ NO_3^- $NO3-NO3-NO3-NO3-NO3-$ wet

550 deposition flux is well captured by our model (-29 %), despite ~~model has~~ a low relative

551 bias of 40 % in both years and NMB of - 39 – - 43 % (Table S4)~~.~~.

552 Since errors in modeled precipitation could strongly affect the modeled NO_3^- wet

553 deposition flux (Appel et al., 2011; Grimm and Lynch, 2005; Metcalfe et al., 2005;

554 Paulot et al., 2014; Tost et al., 2007), we also evaluate the modeled NO_3^- concentration

555 ($C_{p,i}$), which is calculated by using the modeled NO_3^- wet deposition flux ($F_{p,i}$) and

556 observed precipitation ($P_{o,i}$; $C_{p,i}=F_{p,i}/P_{o,i}$), as a separate constraint. The model shows a

557 similar declining trend from the observations with a relative bias of - 23~~18~~ % and – 41~~40~~ %

558 on NO_3^- concentration for 2004 and 2013 respectively. Our results are consistent with the

559 base case of Paulot et al. (2016), which showed that convective removal is likely

560 insufficient in AM3, leading to underestimates of both NO_3^- wet deposition flux and

561 concentrations$NO3-NO3-NO3-NO3-$.$NO3-$ Our results are somewhat different from

562 a recent GEOS-Chem study (Travis et al., 2016). They found that reducing anthropogenic

563 NO_x emissions from NEI11v1 by 53~~60~~ % can significantly improve the overestimate of

564 71 % on $NO3-$ NO_3^- $NO3-NO3-NO3-NO3-NO3-$ wet deposition flux in their model

565 during August-September of 2013. A further reduction of anthropogenic NO_x

566 emissions~~emission~~ in our model (to 0.15 Tg N mon^{-1}), as suggested by Travis et al.

567 (2016),~~in the previous study,~~ would lead to an even greater negative bias compared to

568 observations.

569 **4.3 RONO$_2$ and related species~~Chemistry~~**

570 ~~We further~~RONO$_2$ ~~can serve as either a temporary NO$_x$ reservoir by releasing NO$_2$ via~~

571 ~~photooxidation or a permanent NO$_x$ sink via hydrolysis to produce HNO$_3$. The modeled~~

572 ~~fate of RONO$_2$ affects simulated O$_3$. Therefore, it is necessary to~~ evaluate ~~the~~ RONO$_2$

573 ~~chemistry~~ and related species in this section, with a large focus on measurements from

574 ICARTT and SEAC^{4}RS. ~~to understand its speciation.~~

The major pathway for the production of daytime $RONO_2$ is the reaction of NO with RO_2

576 originating from VOC oxidation by OH:

$$RH + OH + O_2 \rightarrow RO_2 + H_2O \tag{R3}$$

$$NO + RO_2 \rightarrow (1 - \alpha)\ NO_2 + \alpha\ RONO_2 + HCHO + products \tag{R4}$$

577 where α is the branching ratio for alkyl nitrate formation. NO_2 subsequently ~~further~~

578 undergoes photolysis to produce O_3:

$$NO_2 + h\nu \overset{O_2}{\rightarrow} O_3 + NO \tag{R5}$$

579 For isoprene, α is 9 ± 4 % (for ISOPN) according to a recent study (Xiong et al., 2015).

580 For monoterpenes, specifically α-pinene, α ranges from 1 % to 26 % (Rindelaub et al.,

581 2015; Nozière et al., 1999; Aschmann et al., 2002). Here, we use 10 % for isoprene and

582 26 % for monoterpenes. ~~(Table S2), and take~~ α ~~as an average of $RONO_2$ from all the~~

583 ~~precursors.~~ As $RONO_2$ and O_3 are both produced from (R4), a correlation between them

584 is expected. We show that the model can roughly reproduce the correlation of O_x (= O_3 +

585 NO_2) vs. ΣANs during both ICARTT and SEAC^{4}RS (Figure 4), although the slope has a

586 positive relative bias of about 21 % and 33 % respectively, largely due to an overestimate

587 of O_3 in the model. ~~In particular, we find that the model shows better agreement with the~~

588 ~~observed correlation of O_x vs. daytime isoprene nitrates (the sum of ISOPN, MVKN and~~

589 ~~MACRN) than O_x vs. ΣANs during SEAC^{4}RS. This is expected since these three $RONO_2$~~

590 ~~species are directly coproduced with O_3 from (R4), but only account for a small fraction~~

591 ~~of ΣANs (Figure S5).~~ The good agreement between observed and modeled O_x vs.

592 daytime $RONO_2$ provides additional support for our treatment of the yields and fate of

593 these daytime isoprene nitrates.

594 Another metric to evaluate $RONO_2$ chemistry is the correlation between ΣANs and

595 HCHO, as the latter is a coproduct from (R4). ~~Since HCHO can be produced from other~~

596 ~~pathways of isoprene hydroxyl peroxy radicals (ISOPO$_2$) besides (R4) (such as~~

597 ~~isomerization of ISOPO$_2$ and ISOPO$_2$ + HO$_2$), changes in the slope of ΣANs vs. HCHO~~

598 ~~may help to quantify decadal changes in isoprene oxidation pathways.~~ We show in Figure

599 4 that the model can roughly capture the observed ΣANs-HCHO slope, with an

600 underestimate by 25 % and 13 % during ICARTT and SEAC^{4}RS, respectively. The

601 underestimate is in part due to small alkyl nitrates that are neglected in the model, as

602 mentioned in section 4.1. ~~above.~~ During ICARTT, the slope estimated by AM3 is 0.12,

603 similar to the value (0.15) from a previous GEOS-Chem study using a different isoprene

604 oxidation mechanism that assumed a higher α (of ~~11~~ 4.7% from ISOPNB and 7.0 % from

both ISOPNB and ISOPND vs. 10 % of ISOPNB and zero ISOPND in AM3) and a lower yield of HCHO (66 % vs. 90 % in AM3) (Mao et al., 2013b).(Mao et al., 2013). The reason for such similarity between the two models might be two-fold: (a) the additional contribution of monoterpene nitrates to $\sum$ANs in AM3 compensates for the decrease in α from isoprene nitrates compared to GEOS-Chem and (b) the coarse grid resolution of that GEOS-Chem simulation (2 ° x 2.5 °) may lead to a higher estimate of HCHO compared to the result from a finer grid resolution (Yu et al., 2016).

Since HCHO can be produced from other pathways of isoprene hydroxyl peroxy radicals (ISOPO$_2$) besides (R4) (such as isomerization of ISOPO$_2$ and ISOPO$_2$ + HO$_2$), changes in the slope of $\sum$ANs vs. HCHO may help to quantify decadal changes in isoprene oxidation pathways. We find in Figure 4 that the observed slope of $\sum$ANs-HCHO shows very little change from 2004 to 2013. This is in part due to substantial HCHO production from isoprene oxidation under low NO$_x$ conditions (Li et al., 2016), and in part due to the buffering of $\sum$ANs in response to decreasing NO$_x$, as shown below in section 5.1.. Our model is able to reproduce such behavior. We also find in our model that the branching ratios for the reactions of ISOPO$_2$ change marginally from 2004 to 2013 over the Southeast U.S. (Figure S6). The fraction of ISOPO$_2$ + NO has decreased from 81 % in 2004 to 66 % in 2013. The fraction of ISOPO$_2$ + HO$_2$ has increased from 15 % to 28 %, and the fraction of ISOPO$_2$ isomerization has increased from 4 % to 6 %. Our result is slightly different from the results of GEOS-Chem, which found a lower contribution from the NO pathway (54 %) and higher from isomerization (15 %) during August - - September of 2013 (Travis et al., 2016).

We also compare the correlation between major daytime isoprene nitrates and HCHO during 2013, which provides a constraint on the yield of these nitrates. Our model shows a slight overestimate on the slope (Figure 4 (b)), consistent with comparison of mean vertical profiles shown in Figure 2. The computedestimated slope (5 %) in this study is different from that (2.5 %) of a recent GEOS-Chem simulation by Fisher et al. (2016). This is partially due to the different treatment of β- and δ-ISOPO$_2$ between GEOS-Chem and AM3. Another factor is that MVKN and MACRN are not allowed to hydrolyze in AM3, leading to a-higher abundanceburden of these two nitrates.

Figure 5 shows the mean vertical profiles of modeled monoterpene nitrates (MNs) and isoprene nitrates (INs) during ICARTT and SEAC^{4}RS. INs are the most abundant RONO$_2$, accounting for 76-80 % below 3 km over the Southeast U.S.., consistent with the large isoprene emissions in this region in summer (Palmer et al., 2003). In the measurements, ISOPN + MVKN + MACRN only contribute one third of the total INs (Figure S5). We show below that the discrepancy of $\sum$ANs and speciated RONO$_2$ can be explained by other daytime and nighttime INs as well as MNs in the model. More than 60 % of modeled INs originate from isoprene oxidation during daytime. The first-

generation nitrate ISOPN contributes slightly more (31 %) than the second-generation nitrates MVKN + MACRN (28 %) to the total daytime INs during ICARTT. This is different from Mao et al. (2013b)(2013) who showed a higher contribution of MVKN + MACRN than the first-generation INs, due to the different treatment of β- and δ-ISOPO$_2$. We see more ISOPN (32 %) than MVKN + MACRN (26 %) from the daytime INs during SEAC^{4}RS, consistent with Fisher et al. (2016). A large uncertainty in our model is attributed to DHDN, which contributes 32 % to the daytime INs. Fisher et al. (2016) showed less DHDN during SEAC^{4}RS since it was removed rapidly by hydrolysis (1-h lifetime) in their model. Our sensitivity test (hydro_fullAM3h, Figure S2) indicates that AM3 would significantly underestimate $\sum$ANs if we assume a similar heterogeneous loss of DHDN as ISOPN. In fact, DHDN was hypothesized originally in Lee et al. (2014) for the imbalance of nitrogen in their lab experiments, and may serve as a proxy for a large number of unidentified daytime INs. It remains unclear what the dominant loss of DHDN is. Daytime nitrates from monoterpene oxidation are another important source of $\sum$ANs in this region, accounting for 17 - 20 % (24 - 26 ppt) of the total. Fisher et al. (2016) estimate a smaller burden of MNs, of about 10 - 20 ppt due to a lower molar yield (18 % vs. 26 % in AM3) and faster hydrolysis of MNs in their model.

Nighttime chemistry contributes about 30 - 36 % of $\sum$ANs, which is dominated by isoprene oxidation as well (Figure 5). 33 - 41 % of the INs are produced during night, similar to the value (44 %) reported by Mao et al. (2013b)(2013) but with different speciation, due to the different treatment of chemistry. PROPNN contributes about 29-38 % of the total INs. PROPNN in this work is mainly produced from the oxidation of C5 carbonyl nitrate (ISN1) and C5 nitrooxy hydroperoxide (INPN) and C5 carbonyl nitrate (ISN1; (dominantly by photolysis) that are generated from isoprene oxidation by NO$_3$ during the nighttime. This is different from Fisher et al. (2016), who showed that PROPNN is partially from the δ-ISOPO$_2$ + NO pathway and partially from the oxidation of ISN1 by NO$_3$and INPN. In our model, we see a rapid increaseprompt production of PROPNN after sunrise in the boundary layer (Figure S7), consistent with observations at the Southern Oxidants and Aerosols Study (SOAS) ground site CTL (Schwantes et al., 2015). Our model overestimates the mean vertical profile of PROPNN by a factor of 3 (not shown). As our model may largely underrepresent the chemical complexity of nighttime isoprene oxidation as shown by Schwantes et al. (2015), we consider PROPNN as a proxy for other unspecified isoprene nighttime nitrates. Over allAs a result, PROPNN contributes a significant fraction of $\sum$ANs in the model, 23 - 29 % in the boundary layer as shown in section 4.1. With monoterpene nitrates and isoprene derived DHDN and nighttime NO$_3$ oxidation products taken into account, we find that model can well reproduce both observed $\sum$ANs and speciated alkyl nitrates (Figure S5)..

5 Decadal Change of PBL RONNO$_y$ species and surface ozone over SEUS

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. 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).

5.1 RON 5.1 NO$_y$ species

We first examine the simulated decadal change of RONNO$_y$ species in the boundary layer over the Southeast U.S. as shown in Figure 6. In summer of 2004, shows the model suggests thatmean modeled boundary layer concentrations of NO$_x$, HNO$_3$, ∑PNs, ∑ANs and NO$_y$ in the summer of 2004 and 2013 as well as a scenario with a further 40 % reduction from 2013 anthropogenic NO$_x$ emissions to simulate possible future emission reductions. In summer 2004, modeled NO$_y$ is mainly comprised of HNO$_3$ (45 %), NO$_x$ (31 %), ∑PNs (14 %) and ∑ANs (9 %). In response to imposing a 40 % reduction in anthropogenic NO$_x$ emissions (35 % reduction in total NO$_x$ emissions, Table 1) from 2004 to 2013, NO$_y$ declined by 34 %. This modeled response is comparable to consistent with long-term NO$_y$ measurements from the AQS surface networkdataset, which shows on average a 4542 % decrease from 2004 to 2013 over the Southeast U.S. Based on model estimates in Figure 6, most RONMost NO$_y$ species are reduced proportionally, with decreases of 38 % for HNO$_3$, 32 % for NO$_x$ and 34% for ∑PNs. The different change in ∑PNs and PAN (the majority of ∑PNs) in Figure 1 might be due to the difference in sampling regions. The only exception is ∑ANs, with a smaller decline of 19 %. As an important source of organic aerosols (OA), ∑ANs may contribute to It should be noted that the decreasechange of OA over∑ANs discussed here is different from the Southeast U.S. in the past decade (Blanchard et al., 2016).surface concentrations discussed in Section 4.1.

We conducted a sensitivity test with an additional 40 % reduction of anthropogenic NO$_x$ emissions from 2013. (Table 2). We find that NO$_y$ decreases by 29 %, with a proportional decrease in HNO$_3$, NO$_x$, and ∑PNs (Figure 6. The slower decrease of NO$_y$ is likely due to. Again, we find that ∑ANs, which decrease at a slower rate and becomes, becoming a larger fraction of total NO$_y$. The buffering of ∑ANs is consistent with previous studies (Browne and Cohen, 2012; Fisher et al., 2016), mainly due to decreasing NO$_x$ leading to lower OH resulting from decreased NO$_x$ (Figure S8) and thus a prolonged lifetimeslifetime of NO$_x$ and ∑ANs (Browne and Cohen, 2012). As shown in Figure S8, averaged noontime OH decreases by 11 % from 2004 to 2013 and by 29 % after we impose an additional 40 % NO$_x$ emission reduction from 2013 levels.

The historical NO_x emission reduction also affects reactive nitrogen export out of the boundary layer. Here we define exported nitrogen as the difference of the sources (chemical production and emissions) and sinks (chemical loss, wet and dry deposition). As shown in Table 3~~2~~, total summertime NO_y export from the Southeast U.S. boundary layer decreases proportionally, from 24.1 Gg N in 2004 to 16.6 Gg N in 2013. The NO_y export efficiency, calculated as net exported nitrogen divided by total NO_x emissions, remains roughly the same (12 %) for 2004 and 2013, comparable to~~consistent with~~ previous studies (Fang et al., 2010; Li et al., 2004; Parrish et al., 2004; Mao et al., 2013; Sanderson et al., 2008; Hudman et al., 2007). Among all exported species, NO_x contributes most of net export from the PBL (6 % of total NO_x emissions), followed by PAN (4 %) and $\sum$ANs (2 %). We emphasize in Table 3~~2~~ that a major fraction of NO_x is exported through the top of the boundary layer (convection). From a budget calculation throughout the tropospheric column over the same region, we find that despite being the same NO_y export efficiency (12 %), HNO_3 becomes the major exporter, accounting for half of NO_y export efficiency from the total column (6 %). The contributions from PAN and $\sum$ANs are roughly the same as their export from the boundary layer (4 % and 2 %). This suggests that surface NO_x ventilated through the boundary layer, converted to HNO_3 in the free troposphere and exported as HNO_3 is likely the major NO_y export mechanism over the Southeast U.S. in our model, which is in agreement with previous observations (Parrish et al., 2004; Neuman et al., 2006). PAN and $\sum$ANs together account for another half of NO_y export efficiency. As PAN and $\sum$ANs are of biogenic origin and longer lived than HNO_3, they may play a key role in influencing RON~~reactive nitrogen~~ and ozone in downwind regions (Moxim et al., 1996; Fischer et al., 2014).

5.2 Surface ozone

~~Understanding oxidation chemistry of NO_x and VOCs is essential to improve surface ozone air quality by implementing effective control strategies.~~ Since the mid-1990s, NO_x emission controls have led to significant improvement on ozone air quality over the eastern U.S. (Simon et al., 2015; Cooper et al., 2012). As NO_x emissions continue to decrease, ozone production efficiency (OPE) may increase due to the lower NO_x removal rate by OH and to some extent may compensate the ozone reduction (Sillman, 2000). Meanwhile, surface ozone production may be further complicated by the increasing importance of RO_2~~$ISOPO_2$~~ isomerization and $RO_2 + HO_2$.~~(Peeters et al., 2014).~~ Here we first evaluate our model against surface ozone observations in 2004 and 2013, and then project the future response of surface ozone to even lower NO_x emissions to examine the efficacy of near-term NO_x emission controls at lowering near-surface ozone levels.

We first examine the modeled surface ozone against observations at 157 EPA AQS monitoring sites over the Southeast U.S. in July-August of 2004 and 2013 (Figure S9). 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. This positive bias of summertime surface O_3 has been a common issue to a number of modeling studies of this region (Fiore et al., 2009; Canty et al., 2015; Brown-Steiner et al., 2015; Strode et al., 2015; Travis et al., 2016). This might be partially attributed to overestimated anthropogenic NO_x emissions from non-power plant sectors, excessive vertical mixing in the boundary layer (Travis et al., 2016) or underestimates of O_3 dry deposition (Hardacre et al., 2015; (**Error! Hyperlink reference not valid.**~~Hardacre et al., 2015;~~ **Error! Hyperlink reference not valid.**~~Val Martin et al., 2014~~). Further studies are warranted to investigate the cause of this bias in AM3.

Surface O_3 concentrations over the Southeast U.S. decline substantially from 2004 to 2013 in response to the large NO_x emission reduction (Simon et al., 2015). MDA8 ozone averaged across all the monitoring sites is observed to decrease by 11 ppb (23 % of observed mean MDA8 ozone in July-August of 2004) resulting from approximately 40 % reductions of anthropogenic NO_x emissions (35 % reduction in total NO_x emissions).~~)~~ ~~across the continental U.S.~~ This strong sensitivity of surface ozone to NO_x emission reflects the linear relationship between ozone production rate and NO_x concentrations when NO_x is low (Trainer et al., 2000)~~.~~. In contrast, the sensitivity of surface ozone to NO_x emissions appears to be weaker in the 1980s. Jacob et al. (1993) found that summertime afternoon ozone over the eastern U.S. is only reduced by 15 % with a 50 % reduction of anthropogenic NO_x emissions from 1985 levels, suggesting a lower OPE when NO_x concentrations were high. We attribute this transition from a low OPE in the 1980s to high OPE in 2000s to the extended lifetime of NO_x resulting from NO_x emission reductions. Our model is able to capture this strong NO_x - O_3 sensitivity, with the mean MDA8 ozone reduced by 10 ppb from 2004 to 2013. We find that a further 40 % reduction of anthropogenic NO_x emissions with identical meteorological conditions ~~and non-anthropogenic emissions in 2013~~ could lead to an additional 9 ppb decrease, a similar magnitude to the change from 2004 to 2013. ~~Meanwhile, any increase in OPE over the past decade appears to be small and to have little impact on net ozone production, leading to a continued high sensitivity of surface ozone to NO_x emission reductions in the near future.~~

We further investigate the impact of temperature and moisture on surface O_3 from 2004 to 2013. While several studies suggest that surface O_3 increases with ambient temperature (Jacob and Winner, 2009; Bloomer et al., 2010; Wu et al., 2008; Steiner et al., 2010), Cooper et al. (2012) showed that this temperature related impact is weak during the period of 1990-2010 across the U.S.A~~USA~~. Recent studies suggest that relative humidity (RH) or vapor pressure deficit (VPD) may play an important role in ozone variability through soil-atmosphere or biosphere-atmosphere coupling (Kavassalis and Murphy, 2017; Camalier et al., 2007; Tawfik and Steiner, 2013). 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.(Hidy et al., 2014). 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 19881999 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).

Decreasing NO_x emissionsemission also reduces the frequency of highextreme O_3 pollution events. Figure 7 shows the probability density function of observed and modeled MDA8 ozone at each monitoring site during July-August of 2004 and 2013, and the probability density function of modeled MDA8 ozone under a hypotheticalfuture scenario with another 40 % reduction in anthropogenic NO_x emissions compared to 2013. We show that the lowest O_3, about 20 ppb in current model simulations, remains invariant with NO_x emission changes over the Southeast U.S., consistent with observations (Figure 7 (a)). Meanwhile, the high tail of MDA8 ozone events has shifted from more than 100 ppb in 2004 to about 85 ppb after the 40 % reduction of anthropogenic NO_x emissions from 2013. A similar shift is found in observations. The narrowing of the range of O_3 with decreasing NO_x is consistent with the observed trends reported by Simon et al. (2015). We also find that further reductions of NO_x emissions will reduce both median O_3 values and the high tail, suggesting that fewer highextreme ozone events will occur under continued NO_x emission controls in the future.

6 Conclusions and Discussions

Near-surface ozone production over the Southeast U.S. is heavily influenced by both anthropogenic and biogenic emissions. We investigate the response of NO_y speciation to such NO_x reduction to the significant NO_x emission controls (about 40 % reductionreductions) in this region over the past decade, in light of the fast-evolving understanding of isoprene photooxidation. This knowledge is needed to predict nitrogen and ozone budgets in this region and elsewhere in the world with similar photochemical environments. Here we use extensive aircraft and ground observations, combined with a global chemistry-climate model (GFDL AM3), to examine decadal changes in NO_y abundance and speciation as well as in surface O_3 mixing ratios over the Southeast U.S. between the summers of 2004 and 2013. We then use the model to infer future NO_y

832   speciation and surface ozone abundances in response to further NO_x emission controls in

833   this region.

834   We first evaluate the model with aircraft and surface observations. When we apply the

835   estimated 40 % reductions in anthropogenic NO_x emissions from 2004 to 2013, our

836   model reproduces the major features of vertical profiles of NO_x, HNO_3, PAN, $\sum$ANs and

837   NO_y observed during aircraft campaigns over the Southeast U.S. in the summers of 2004

838   and 2013. By including recent updates to~~on~~ isoprene oxidation, our model can largely

839   reproduce the vertical profiles of $\sum$ANs and several speciated alkyl nitrates, as well as

840   their correlations with O_x and HCHO, ~~(Figure 4),~~ lending support to the model

841   representation of isoprene oxidation. On the other hand, we show that a~~the~~ discrepancy

842   between measured $\sum$ANs and speciated $RONO_2$~~,~~ can be explained by a combination of

843   monoterpene~~terpene~~ nitrates, dinitrates and nighttime NO_3 oxidation products from

844   isoprene. We also show that modeled ozone appears to be insensitive to hydrolysis of

845   ISOPNB, because its photooxidation, mainly by OH, also returns little NO_x.

846   Major RON~~NO_y species~~ decline proportionally as a result of NO_x emission reductions in

847   the Southeast U.S., except for~~that $\sum$ANs decline at~~ a slower rate in $\sum$ANs. The slower

848   decline of $\sum$ANs reflects the prolonged lifetime of NO_x when it is decreasing.~~.~~ Our model

849   suggests that summertime monthly averaged NO_x, HNO_3, PAN, and NO_y decline by 30-

850   ~~-~~40 %, in response to 40 % reduction~~reductions~~ in anthropogenic NO_x emissions from

851   2004 to 2013. ~~The slower decline of $\sum$ANs reflects the prolonged lifetime of NO_x with~~

852   ~~decreasing NO_x.~~ This proportional decrease is likely~~to a large extent~~ driven by high

853   concentrations of biogenic VOCs, the major precursor of PAN~~VOC~~ in this region that

854   change little in magnitude from 2004 to 2013. In contrast, Pollack et al. (2013) find a

855   faster PAN decrease than HNO_3 in the LA basin over the past several decades, partly due

856   to the decrease in anthropogenic VOC emissions that are major PAN precursors.

857   Deposited and exported NO_y decline with NO_x emission reductions. The model also

858   shows a decrease of NO_3^- wet deposition flux by 29 % from 2004 to 2013, consistent with

859   observations from the NADP network (- 24 %). We find from model calculations that the

860   NO_y export efficiency remains at 12 % in both 2004 and 2013, leading to a proportional

861   decrease of exported NO_y. The dominant NO_y export terms include NO_x or HNO_3, each

862   accounting for 6% of the total exported NO_y, followed by $\sum$PNs (4 %) and $\sum$ANs (2 %).

863   The response~~Response~~ of surface ozone to NO_x emission reductions reveals a strong ~~O_3-~~

864   NO_x – O_3 sensitivity in summertime over the Southeast U.S. Observations from EPA

865   AQS surface network suggest that mean MDA8 ozone during July-August has decreased

866   by 23%, from 48 ppb in 2004 to 37 ppb in 2013.~~, a 23 % decrease.~~ Despite a positive

867   absolute bias of up to~~upto~~ 12 ppb in boundary layer ozone and ~~a bias of~~ 16 ppb in surface

868   MDA8 ozone, our model shows a 10 ppb decrease of surface MDA8 ozone from 2004 to

869 2013, very close to the observed 11 ppb decrease from the EPA data. The bias of ozone
870 in our model is not entirely attributed to uncertainties in NO_x emissions, as the
871 overestimate suggested by earlier work would lead to an underestimate of NO_y (Travis et
872 al., 2016). Care should be exercised in applying the modeling results for surface ozone
873 regulation purposes, given the high ozone bias shown in our model. We. More
874 importantly, we find from model calculations that modeled MDA8 O_3 will continue to
875 decrease by another 9 ppb assuming anthropogenic NO_x emissions are reduceddecreased
876 by 40 % from the 2013 levelslevel with meteorology and other emissions kept the
877 sameconstant. In addition, further NO_x emission reduction leads to less frequent
878 highextreme ozone events. (Figure 7). This continued strong sensitivity of surface O_3 to
879 NO_x emissions can guide the development of effective emission control strategies for
880 improving future air quality.

Data availability

882 Observational datasets and modeling results are available upon request to the
883 corresponding author (jmao2@alaska.edu).

Author contributions

885 This was largely a collaborative effort. R. C. Cohen, J. D. Crounse, A. P. Teng, P. O.
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887 Ryerson, P. Veres, J. M. Roberts, A. Neuman, J. B. Nowak, G. M. Wolfe, T. F. Hanisco,
888 A. Fried, H. B. Singh, J. Dibb contributed to the collection of aircraft observations in
889 2004 and 2013; J.Mao and J.Li conceived the study; J.Li and J. Mao performed analysis
890 and modeling; J.Li, J.Mao, A. M. Fiore, R. C. Cohen, P. O. Wennberg, J. D. Crounse, J.
891 A. Thornton, A. Neuman, J. B. Nowak, J. Peischl, J. Dibb, F. Paulot, L. W. Horowitz and
892 G. M. Wolfe wrote the paper with input from all coauthors.

Competing interests

894 The authors declare that they have no conflict of interest.

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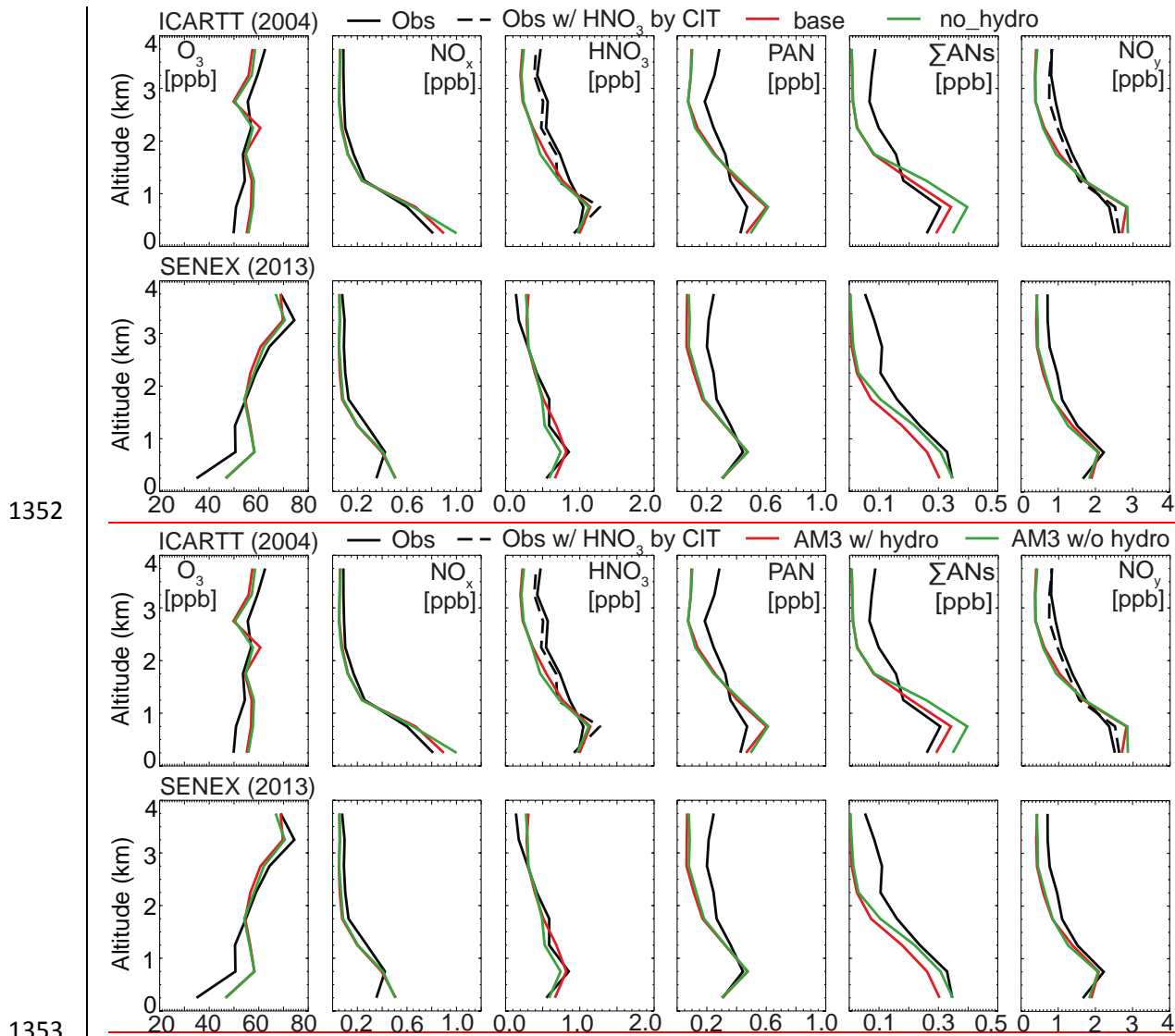
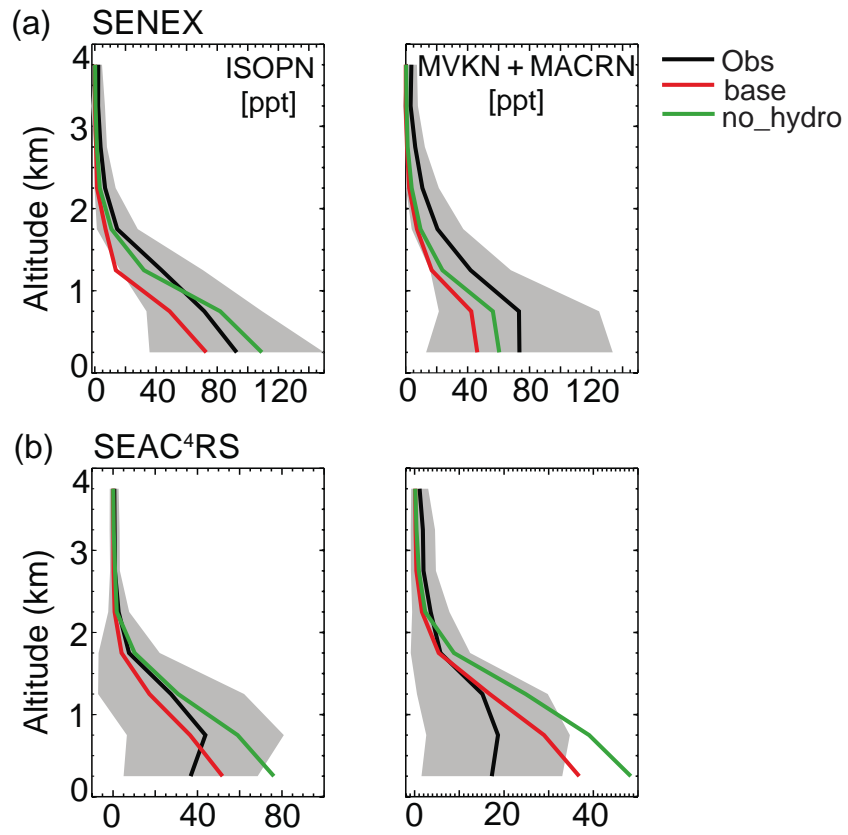
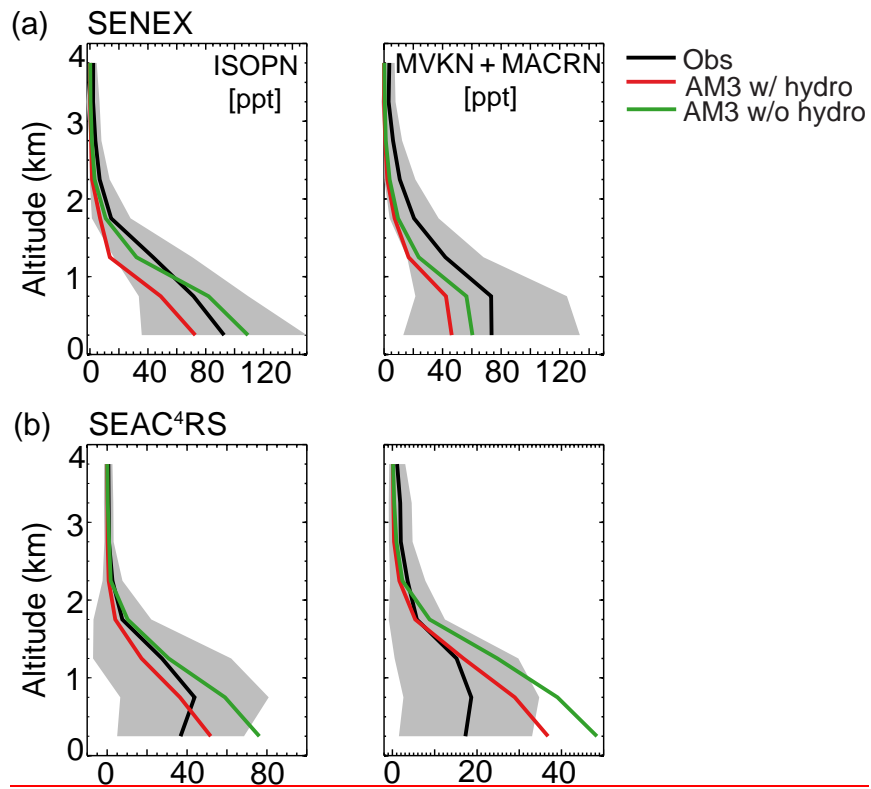
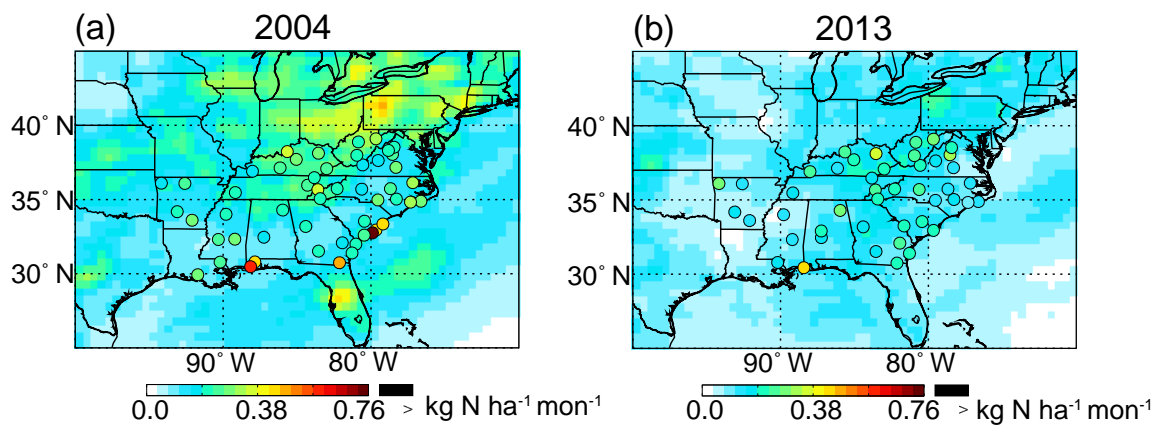
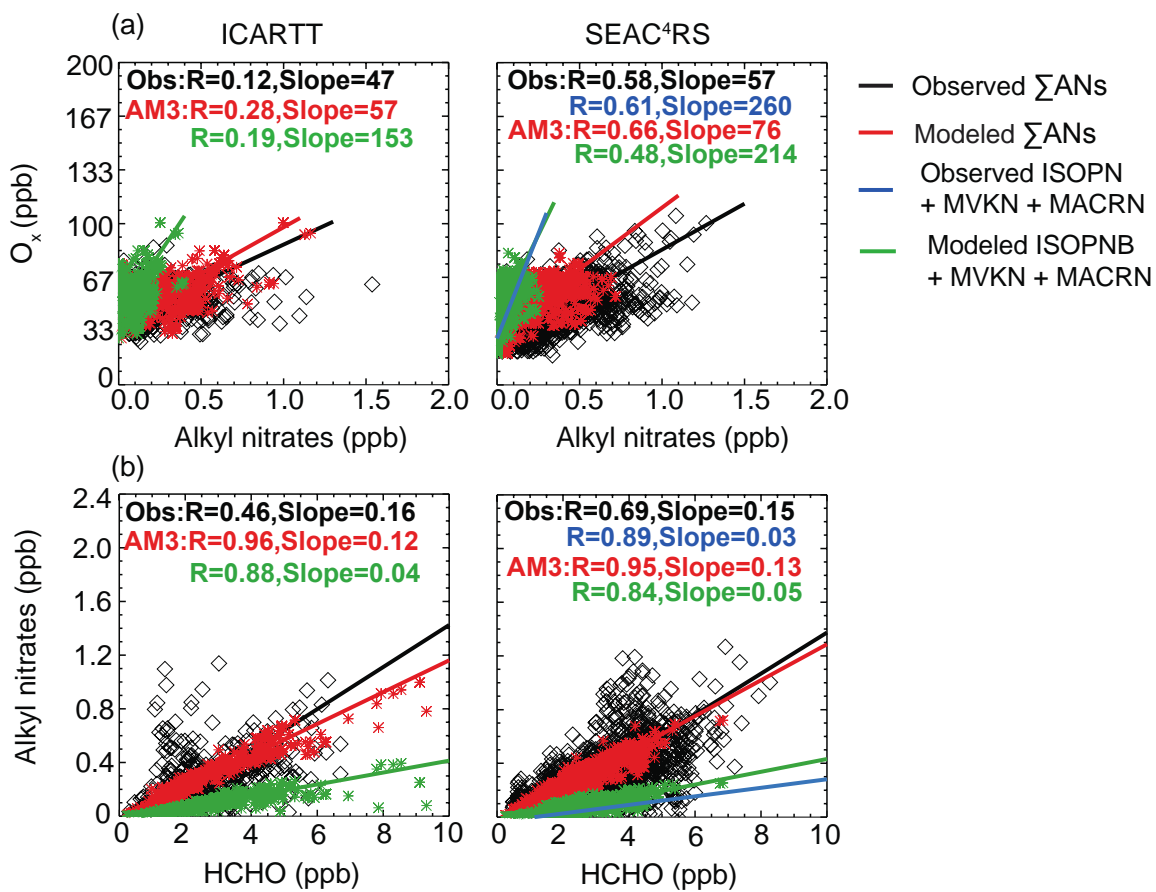


Figure 1. Mean vertical profiles of ozone and reactive oxidized nitrogen species from observations during ICARTT (top row) and SENEX (bottom row) over SEUS (25 - 40° N, 100 - 75° W) during daytime, and model estimates from AM3 with hydrolysis of ISOPNBalkyl nitrates (red) and AM3 without hydrolysis of alkyl nitrates (green). The soliddashed and dashedsolid black lines in the HNO_3 of ICARTT represent measurements collected using mist chamber/IC by University of New Hampshire (UNH) and Chemical Ionization Mass Spectrometer by California Institute of Technology (CIT), respectively. NO_y from ICARTT is calculated as the sum of NO_x, HNO_3 (w/ UNH in the solid line and w/ CIT in the dashed line), PAN and total alkyl nitrates (ΣANs). ΣANs in the bottom row are from SEAC^{4}RS.

1366   **Figure 2.** Mean vertical profiles of ISOPN and MVNK+MACRN during (a) SENEX and
1367   (b) SEAC[4]RS over SEUS (25 - -40° N, 100 - -75° W). Black lines are the mean of
1368   observations. Red and green lines are the mean of modeled results with hydrolysis of
1369   ISOPNB and without hydrolysis of alkyl nitrates respectively. Grey shades are the one
1370   standard deviation ($\pm\sigma$) of averaged profiles of the measured tracers.

1371

1372 **Figure 3.** Nitrate wet deposition flux (kg N ha⁻¹ mon⁻¹) from NADP (circles) and AM3
1373 (background) during July - -August of 2004 and 2013.

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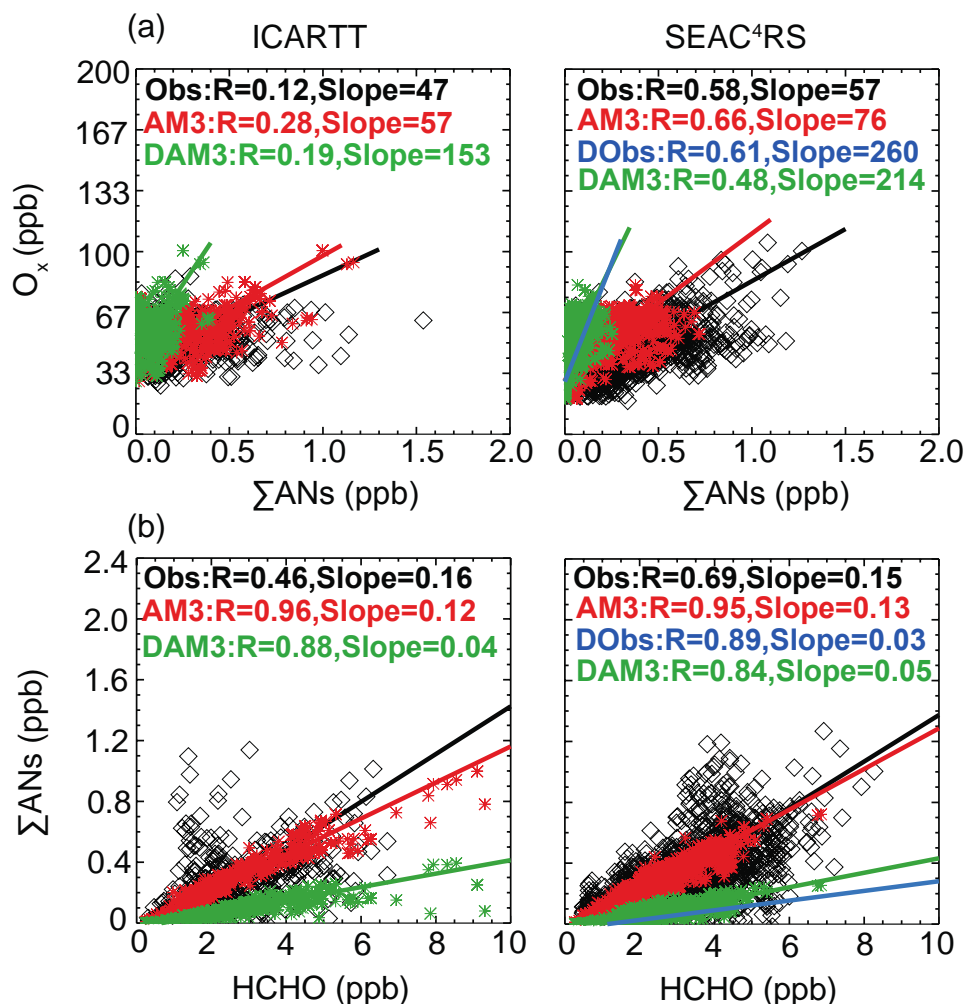


Figure 4. O_x versus $\sum$ANs correlation (top; (a)) and $\sum$ANs versus formaldehyde
correlation (bottom; (b)) within the boundary layer (< 1.5 km) during ICARTT (left) and
SEAC[4]RS (right). Observations are in black diamonds; model estimates from AM3 with
ISOPNB hydrolysis are in red symbols. Green symbols ~~(DAM3)~~ represent the correlation
using modeled ISOPN + MVKN + MACRN. Blue symbols ~~(DObs)~~ represent the
correlation using observed ISOPN + MVKN + MACRN from SEAC[4]RS. Solid lines are
the reduced major axis regression lines.

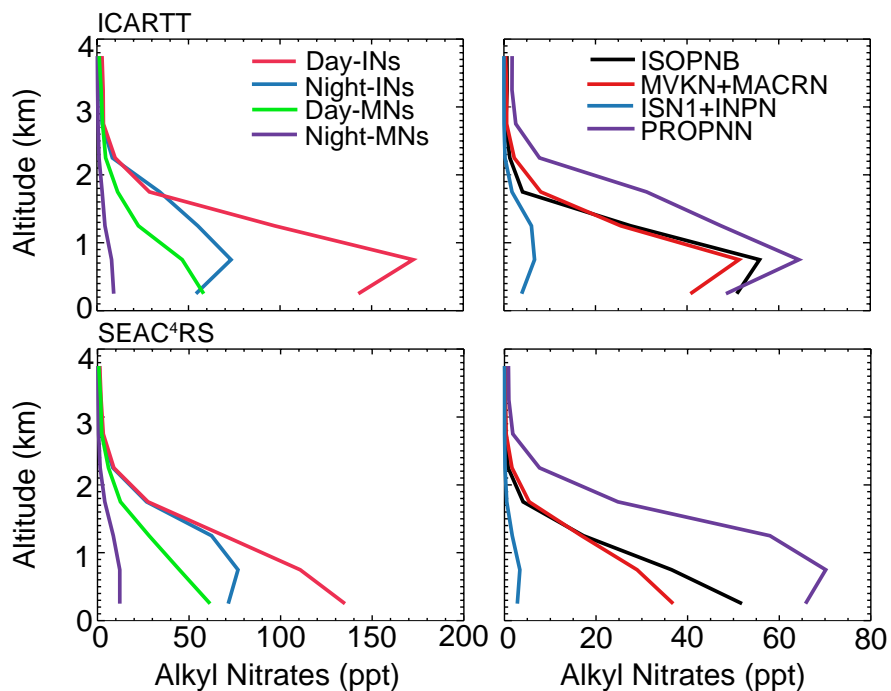
1383

1384

Figure 5. Mean vertical profiles of modeled alkyl nitrates from isoprene and monoterpene oxidation (left) and major isoprene nitrate species (right) during ICARTT (top row) and SEAC⁴RS (bottom row) from AM3 with hydrolysis of ISOPNB.

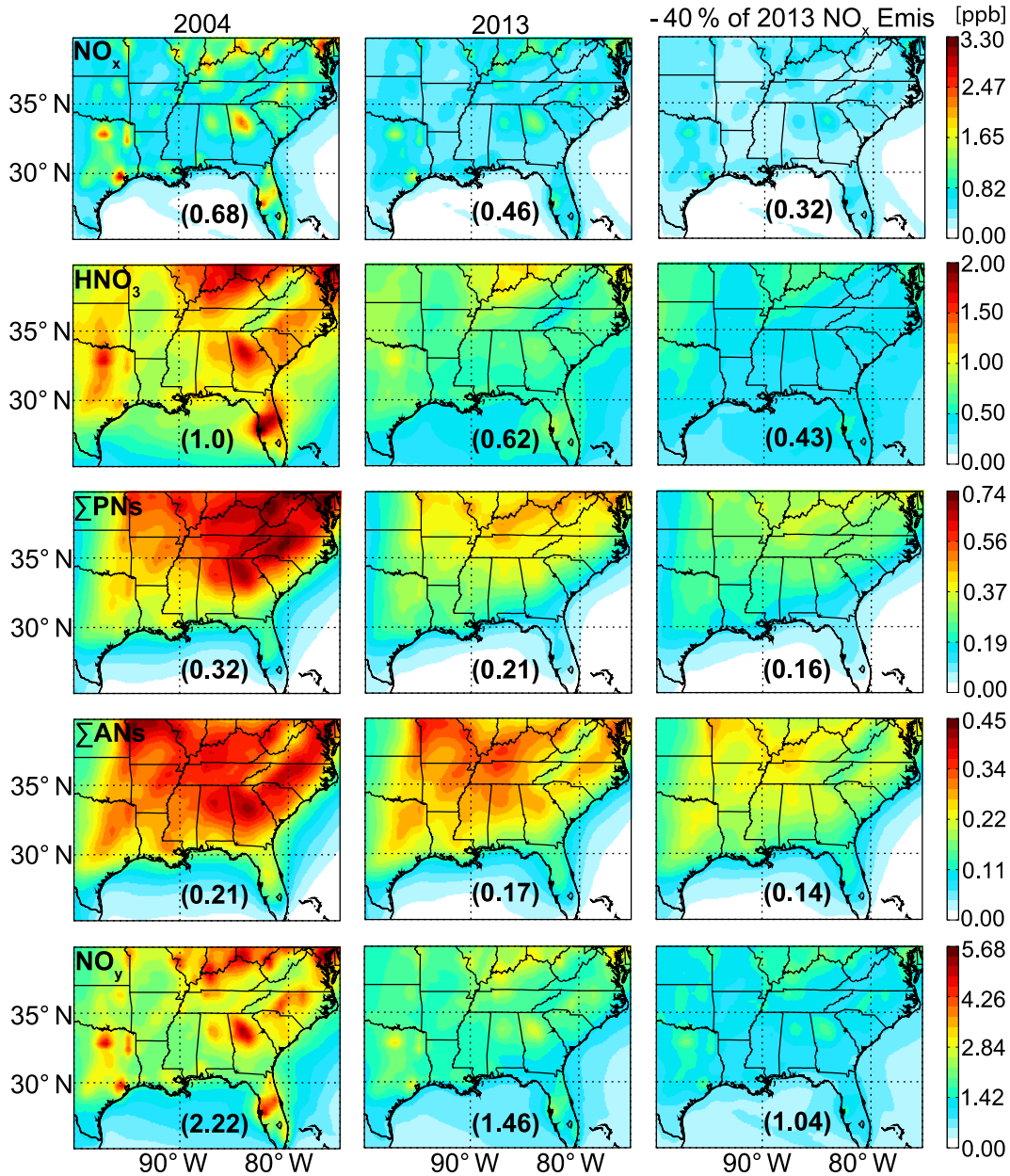
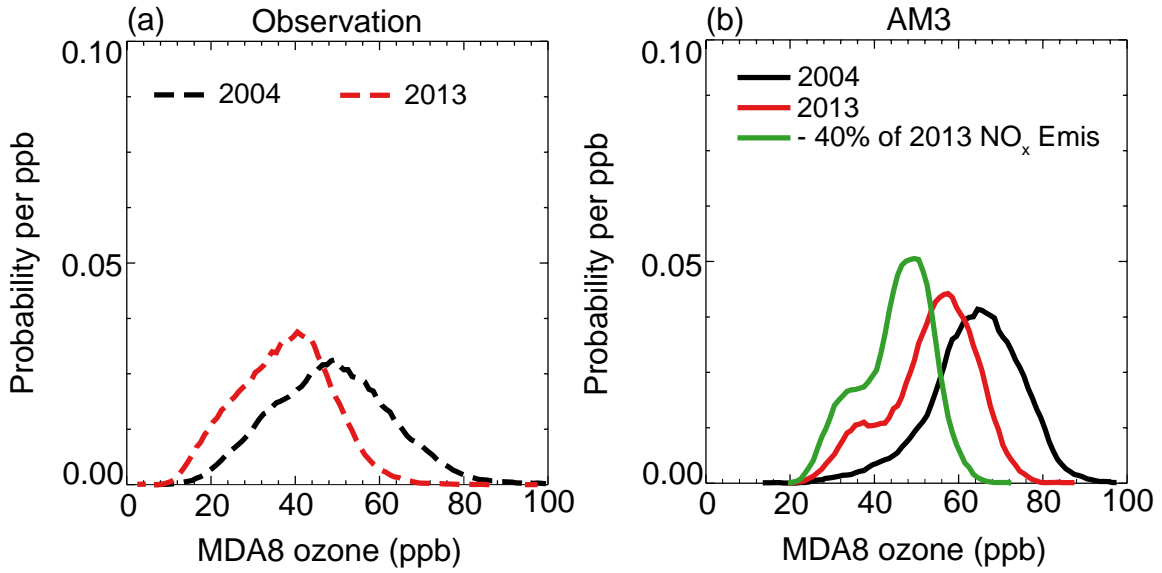



Figure 6. Modeled mean NO_x, HNO_3, total peroxy nitrates ($\sum PNs$), total alkyl nitrates ($\sum ANs$) and NO_y averaged over the boundary layer (< 1.5 km) of the Southeast U.S. during July - August of 2004 (left), 2013 (middle), and a scenario assuming 40 % reduction of 2013 anthropogenic NO_x emissions (right). Numbers in parentheses indicate mean concentrations over the plotted region. Note different color scales represent the concentration of each species.

1395
1396 **Figure 7.** Observed (a) and simulated (b) probability density function of MDA8 ozone at
1397 AQS monitoring sites in Figure S3 during summer of 2004, 2013, and a scenario with 40 %
1398 reduction in the anthropogenic NO_x emissions of 2013.

1399

1400 **Table 1.1.** Monthly averaged NO_x emissions in July-August of 2004 and 2013 over
1401 North America (25-50° N, 130-70° W) and over the Southeast US (25-40° N, 100-75° W)
1402 in brackets in AM3.in AM3.

Source Type	2004 (Tg N)	2013 (Tg N)
Anthropogenic	0.42 (0.19)	0.25 (0.11)
Biomass Burning	8.4×10^{-3} (2.8×10^{-3})	8.4×10^{-3} (2.8×10^{-3})
Soils	2.9×10^{-2} (9.5×10^{-3})	2.9×10^{-2} (9.5×10^{-3})
Aircraft	8.8×10^{-3} (2.9×10^{-3})	8.0×10^{-3} (2.8×10^{-3})
Lightning	0.02 (0.01)	0.02 (0.01)
Total	0.49 (0.22)	0.32 (0.14)

1403

1404

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

1405

1406 **Table 3.2.** Monthly NO_y budget in the boundary layer (< 1.5 km) of the Southeast United States for July-August of 2004, 2013 and a
1407 scenario with 40 % reduction of anthropogenic NO_x emissions of 2013[a].

	2004					2013					- 40 % of 2013 Anthropogenic NO_x Emis				
Species	Emission	Chem (P-L)	Dry Dep	Wet Dep	Net Export	Emission	Chem (P-L)	Dry Dep	Wet Dep	Net Export	Emission	Chem (P-L)	Dry Dep	Wet Dep	Net Export
NO_x	208.7	-172.4	21.8	–	14.5	132.6	-105	14.2	–	13.4	88.3	-69.6	9.2	–	9.5
ΣPNs[b]		15.2	5.7	–	9.5		10.3	3.9	–	6.4		7.7	3.0	–	4.7
ΣANs		24.3	14.3	6.2	3.8		19.4	11.4	4.7	3.3		15.4	9.1	3.9	2.4
day[c]		13.8	8.7	3.6	1.5		12.0	7.5	3.0	1.6		10.2	6.3	2.6	1.3
night[d]		10.5	5.6	2.6	2.4		7.4	4.0	1.7	1.7		5.3	2.8	1.3	1.1
HNO_3		131.7	77.8	57.6	-3.7		74.2	45.6	35.1	-6.5		45.8	29.2	25.6	-9.0
NO_y					24.1					16.6					7.6

1408 [a]We define the boundary of Southeast US is 25-40° N, 100-75° W. All budget terms are in Gg N.
1409 [b]ΣPNs includesinclude PAN, peroxymethacryloyl nitrate (MPAN), and a C5 hydroxy peroxyacyl nitrate (C5PAN1) produced by
1410 oxidation of ISN1.
1411 [c]Alkyl nitrates produced from oxidation of isoprene and monoterpenes by OH.
1412 [d]Alkyl nitrates produced from oxidation of isoprene and monoterpenes by NO_3.