Response to Reviewer #1's comments on He et al. 2019 Atmospheric Physics and Chemistry manuscript

We thank the anonymous reviewer for thoroughly reading our manuscript and providing helpful comments and suggestions, which lead a significant improvement of our manuscript. The detailed responses to major point comments are listed below (text in *italic* and black is the reviewer's comments, and the normal text highlighted in blue is our response):

*The authors presented a study on ozone pollution trend and its sensitivity to key precursors in the US over 1990 – 2015. While the lack of measurement data of ozone precursors in time and space makes it difficult to study long-term trends in ozone chemistry, increasingly available model simulations may be in place for such analysis with caution exercised. This study represents such effort. Studies like this one are needed for information of changes in ozone chemistry due to climate change and anthropogenic emissions control. I have a few comments as follows.*

Response: We appreciate the positive comments from the anonymous reviewer, and the manuscript has been revised according to these comments as listed below.
*Line numbers are based on the revised clean version of the manuscript.

*The authors stated that, to avoid introducing inconsistency for model evaluation caused by "direct comparison", they used the EPA RSIG software to visualize the observed and modeled ozone values. The question I have is how they quantified the difference between the modeled and observed values besides directly comparing the modeled value from a grid and the observed value(s) contained in that grid. Incidentally, what did "gridded" mean in "AQS station data were gridded to the CMAQ grid" in the Figure 5 caption? Didn't they just superimpose the station data on the CMAQ simulated distribution there?*

Response: The direct comparison is usually conducted through sampling the grid of CMAQ where the AQS site is located. In our previous study (He et al., 2016), we found that due to the uneven distribution of AQS monitoring sites, the direct comparison of AQS observations and our 30-km CMAQ simulations could be of problem. Figure 1 adapted from He et al. (2016) presents the case study of the CMAQ evaluation over California. AQS monitoring sites are point measurements and usually concentrated in populous urban and suburban areas such as the Los Angeles basin where high ozone levels prevail, but sparse in rural areas where ozone concentrations are generally low. Therefore, sampling CMAQ grids over locations of these AQS sites could introduce important biases. At that time, we lacked the capability to process large amount of AQS observations to our modeling grid (i.e., regrid observations to model grids), so we only raised this question. Recently, EPA added the capability in the Remote Sensing Information Gateway (RSIG) system (https://www.epa.gov/hesc/remote-sensing-information-gateway), which can calculate the gridded values of air pollutants on a selected model grid. The RSIG software applied the inverse-distance-weighted method to calculate the gridded mean (https://www.epa.gov/hesc/how-rsig-regrids-data), which is not a simple arithmetic mean of AQS observations within the grid. To explain the problem of direct comparison and the unique characteristics and advantage of RSIG, we added the following sentence in Line 215 as "*The direct comparison is usually conducted through sampling the grid of CMAQ where the AQS site*

*is located, while the distribution of AQS monitoring sites is usually uneven with more sites concentrated in populous urban and suburban areas where high ozone levels prevail. Sampling 30-km CMAQ grids over the locations of AQS measurements, i.e. direct comparison of averaged concentrations in the 900 km$^2$ CMAQ grid and pointwise AQS observations, could introduce important biases*" and in Line 222 as "*The RISG has the capability to 're-grid' the AQS observations on a selected model grid using the inverse-distance-weighted method to calculate the gridded mean concentrations (https://www.epa.gov/hesc/how-rsig-regrids-data).*"

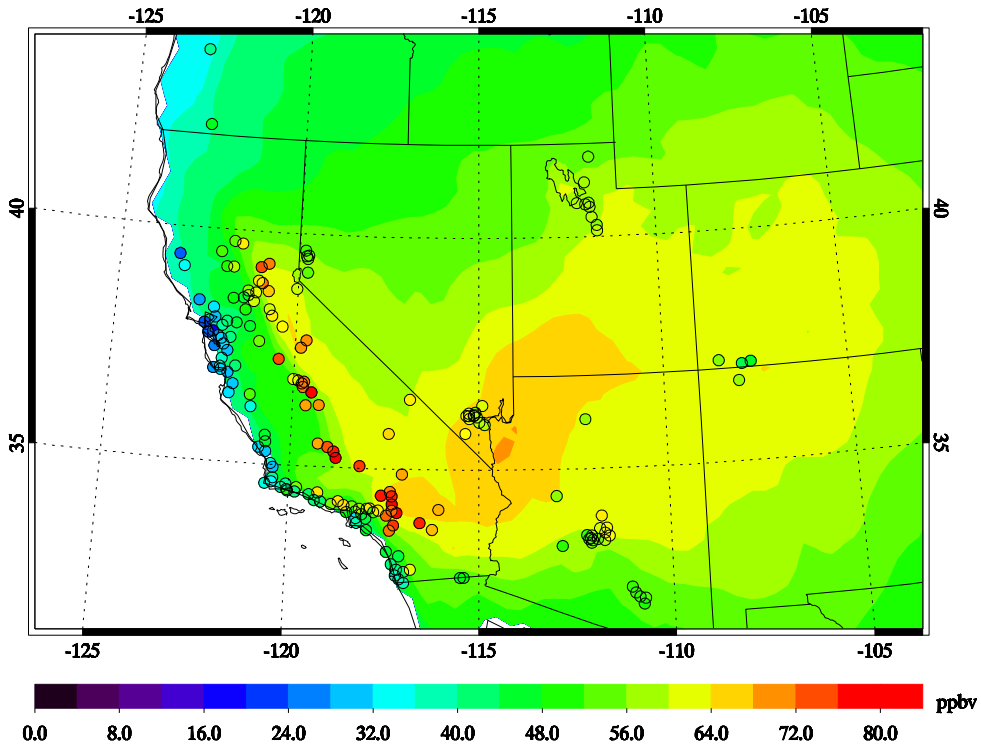



Figure 1. Comparison of EPA AQS ozone observations (color dots) and model simulations (background) in California (adapted from He et al. (2016)).

*The authors stated that in subdomains CMAQ performance exhibited large interannual variations (Table 2) and they further stated that their CWRF-CMAQ simulations showed improved performance in the Northeast and Midwest. It would be illuminating to the modeling community if they could expand on those two statements by explaining why.*

Response: We appreciate that the reviewer raised this question. Previous studies usually aggregate and average data from all modeling years into one analysis without considering interannual variations. Figure 2 shows a comparison using 2000-2015 data for the CONUS, which has better performance (NMB = -1.3%) than the year-by-year evaluation summarized in Table 2. In our manuscript, we conducted the evaluation by year for the CONUS and five subdomains, so we can identify the years with good and bad performance. With the assumption that our emissions reflect the gradual reduction of anthropogenic emissions in the past decades, the year-to-year fluctuations of model performance should be related to climate signals that control the regional ozone pollution. By doing so, we effectively reduced the impact of emissions reduction on the model performance. We are investigating the relationships between regional

climate characteristics and ozone pollution especially extreme pollution episodes, and hope to better address your question from the perspective of how extreme events affect interannual variations.

About the model improvement, we apologize that the current manuscript is not stated very clearly. These improvements were achieved through comparison with our previous study employing the CMM5-CMAQv4.7 modeling system (He et al. 2016). CMM5 is the previous generation of regional climate model, developed on the MM5 model. Our CWRF model has shown better performance for downscaling the U.S. climate and the updated CMAQ v5.2 has also improved. We have demonstrated that CWRF with more sophisticated physical processes (Liang et al., 2012) can simulate better regional climate variations in the United State including surface temperature and precipitation (Chen et al., 2016; Liu et al., 2016), especially for extreme events (Sun and Liang, 2020a; Sun and Liang, 2020b). These meteorological variables are key factors for better air quality simulations. To make these two points clear, we added following sentences and revised this paragraph in Line 233 as "*With gradual reduction in anthropogenic emissions, the fluctuations of CMAQ performance could be related to climate signals which control the regional ozone pollution. Future work is needed to identify the relationship between these regional climate variations and the U.S. ozone pollution*" and in Line 236 as "*Generally, this modeling system has substantially improved performance in the Southeast, California and Texas, and moderately improved performance in the Northeast and Midwest as compared with our previous modeling system (He et al., 2016), which significantly underestimated the U.S. ozone pollution. One reason is that CWRF with more sophisticated representation of physical processes have the capability to better simulate the U.S. climate especially surface temperature and precipitation (Liang et al., 2012; Chen et al., 2016; Liu et al., 2016; Sun and Liang, 2020b; Sun and Liang, 2020a), which are key to accurate air quality simulations. The evaluation of CMAQ performance demonstrates the capability of CWRF-CMAQ to credibly simulate historical air quality.*"

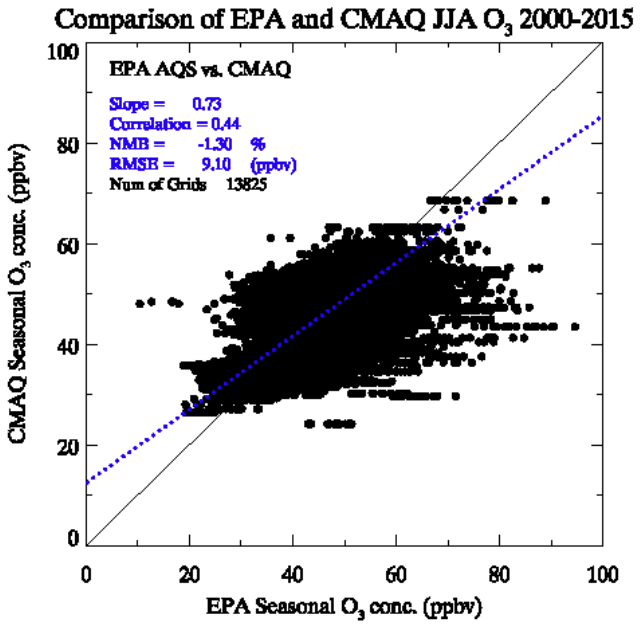



Figure 2. Similar as Figure 5b in the main article, but with data from 2000-2015

*The authors brought up an interesting point that for Baltimore and Denver the peak ozone increased in some years after 2002 although anthropogenic emissions were continuously decreasing in the past decades. From there they inferred that the increased ozone pollution on those areas "could be caused by other factors such as higher summer temperatures in certain years or enhanced stratosphere-troposphere exchange" (lines 234-244). Their Figure 4 showed the largest peak of fires emissions over a couple of years starting in 2002, which could have influenced ozone during those years. Also, were the summer temperatures really higher and STE enhanced during those couple of years? The authors might want to avoid making such sheer speculations if they had no intention to get into making these points.*

Response: Thanks for pointing out that the wildfire emissions could be an important source for the increasing summer ozone in some regions, especially Denver which could be impacted by the wildfire activities in the western United States. Another paper under review (Tao et al., *Remote Sensing*, 2020) confirmed the impacts from wildfires on air quality in the western United States. Another possibility is the change of ozone production regime, especially in Baltimore as discussed in the later section. We checked the temperature anomaly at Essex MD (AQS ID: 240053001, Fig. 3), which did not support our hypothesis. We agree that these speculations about possible high regional temperatures and STE lack evidences in current study, and removed these hypotheses in the revised manuscript.

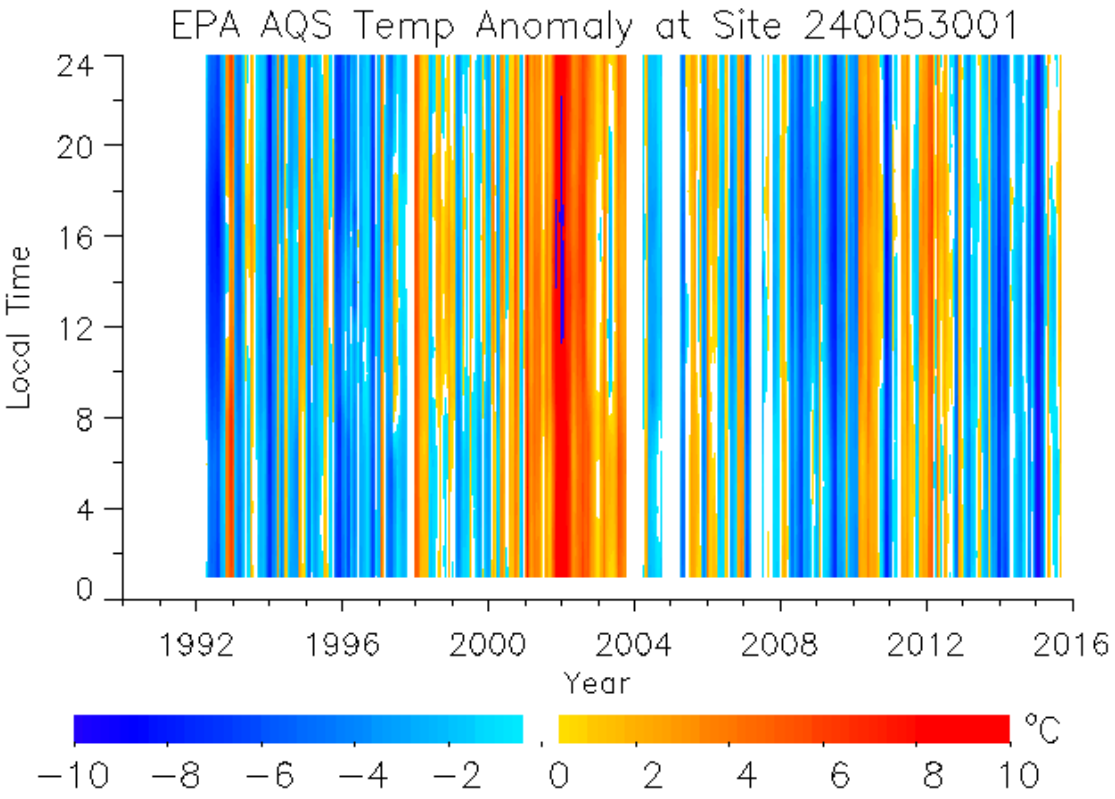



Figure 3. The AQS temperature anomaly at Essex, Maryland (Site ID: 240053001).

*I am a bit concerned with their threshold value of the O3/NOy ratio used to examine changes in the ozone formation regime. In our experience the model simulated O3/NOy ratio could differ greatly from the observed values and between simulations using different models. I am not sure if the threshold value of 15 from Zhang et al.(2009b), which used completely different models and had very different emissions and chemical environments, would be applicable. The authors need to find their own threshold value for their model simulations.*

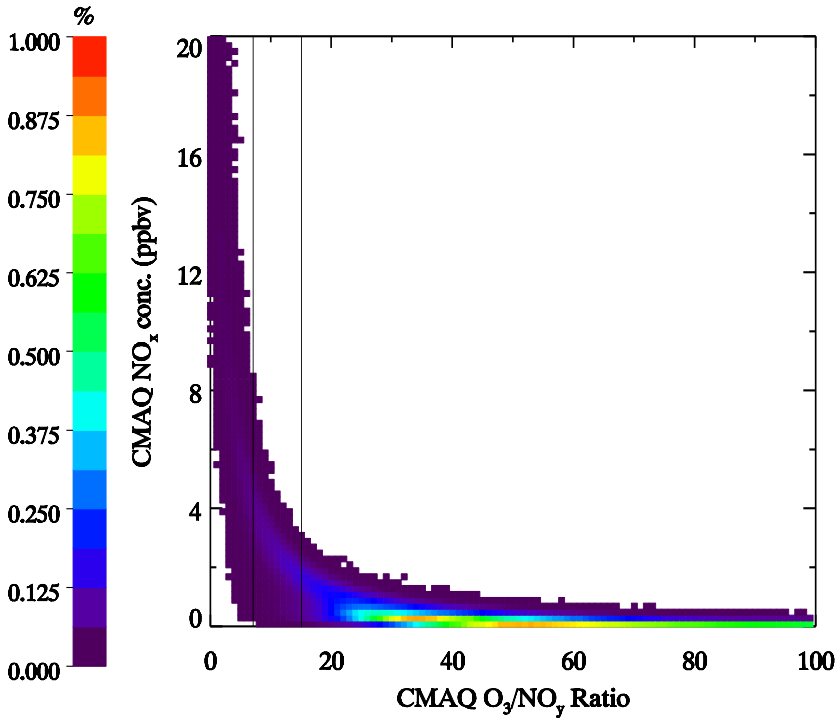
Response: Thanks for this important question. We understand that the model simulated $O_3/NO_y$ ratio could differ largely from the observed values. In our study, we could not access the long record of research-grade $NO_y$ observations from the EPA network and did not conduct long-term sensitivity experiments of CMAQ with reduced emissions rates due to limited computation resources. So we have to rely on results from the previous studies. Sillman explored the concept using photochemical indicators including $O_3/NO_y$ to identify the regime of ozone photochemical production, finding that the link between the ozone production sensitivity and these indicators is largely unaffected by changes in model assumptions, including emission rates of anthropogenic and biogenic species (Sillman, 1995; Sillman et al., 1997). Observations from urban areas of Atlanta, New York, and Los Angeles was compared with modeling results from the Urban Airshed Model at urban scales, and a threshold of 7 was proposed for using $O_3/NO_y$ ratios as the photochemical indictor (Sillman et al., 1997). Zhang et al. (2009) expanded the study to the CONUS with 1-year CMAQ simulations, suggesting a threshold of 15 for $O_3/NO_y$ ratios. Zhang et al. (2009) used previous CMAQ version 4.4 for 1-yr CONUS simulations of 2001 at a relatively coarse spatial resolution (36 km) which is close to our 30-km CONUS domain, so we adopted their proposed threshold. We agree that the current manuscript lacked the evaluation of this threshold with our modeling system, and we developed the following approach to test it.

We selected hourly $O_3$, $NO_y$, and $NO_x$ concentrations from CMAQ in the afternoon (defined as 12 pm to 4 pm) in 2014, and calculated the $O_3/NO_y$ ratios. Figure 4a shows scatter density of $O_3/NO_y$ ratios vs. $NO_x$ concentrations, which is calculated based on a 100 × 100 bins with $NO_x$ from 0-20 ppbv $NO_x$ (i.e., 0.2 ppbv per bin) and 0-100 $O_3/NO_y$ ratios (i.e., 1 per bin). In the afternoon over the CONUS, the ozone production is mainly in high $O_3/NO_y$ ratio (>15) and low $NO_x$ (less than 2 ppbv) environment, i.e., in the $NO_x$-sensitive regions by thresholds proposed by both Sillman et al. (1997) and Zhang et al. (2009). Figure 4b shows the same density plot, but the color stands for mean $O_3$ concentrations. Both low and high ozone concentrations exist in high $NO_x$ region ($NO_x$ > 4 ppbv), which are usually urban or suburban. Then we calculated the weighted ozone concentrations that equals to the product of $O_3/NO_y$ and $NO_x$ scatter density (Fig. 4a) and mean $O_3$ concentrations (Fig. 4b), which stands for the $O_3$ sensitivity with respect to $O_3/NO_y$ ratios and $NO_y$ concentrations over the CONUS (Fig. 4c). At the national scale, when the weighted ozone concentrations increase with CMAQ $NO_x$ levels, the photochemical production is $NO_x$-sensitive. The region with $O_3/NO_y$ higher than 7 and 11 both have this characteristics, while due to low probability (Fig. 4a) and urban environment (Fig. 4b) we believe the $O_3/NO_y$ threshold of 7 stands for the urban environment. Thus, the $O_3/NO_y$ ratio threshold of 15 is more proper for the CONUS scale analysis. This analysis qualitatively supports our application of results from Zhang et al. (2009).

In summary, due to limited resources and experiment design, identifying a threshold of $O_3/NO_y$ ratio is beyond the scope of this study. Using results from our CMAQ model, we proved that the threshold of 15 should be practical for our study. We added the following sentences in Line 323 as "*The usage of $O_3/NO_y$ ratio was first proposed by Sillman (Sillman, 1995; Sillman et al.,*

*1997). Sillman et al. (Sillman et al., 1997) conducted a case study of observations in urban areas (Atlanta, New York, and Los Angeles) and modeling results from the Urban Airshed Model and suggested the threshold of 7 as the transition region from VOC-sensitive environment to $NO_x$-sensitive environment. Zhang et al. (2009a; 2009b) expanded this method to the CONUS with 1-year observations and CMAQ simulations (36-km spatial resolution) and suggested a threshold of 15 for ozone pollution at the national scale. In this study, we did not have access to the long-term research grade $NO_y$ observations from the AQS network and did not conduct sensitivity experiments (due to computational resource limit) with reduced $NO_x$ emissions following Sillman et al. (1997), so we have to reply on the $O_3/NO_y$ threshold from literature. We conducted a simple evaluation of our CMAQ results and found the threshold of 7 could be more proper for urban areas and the threshold of 15 should be more applicable for our study of the whole United State (Figure S1 in the supplementary material). Please note that the $O_3/NO_y$ ratio could depend on the modeling framework, so due to the similarity of our modeling system (30-km CMAQ) and the model used in Zhang et al. (2009a; 2009b), our analysis suggests the similar threshold of 15*" and the discussion above to the supplementary material.

a)



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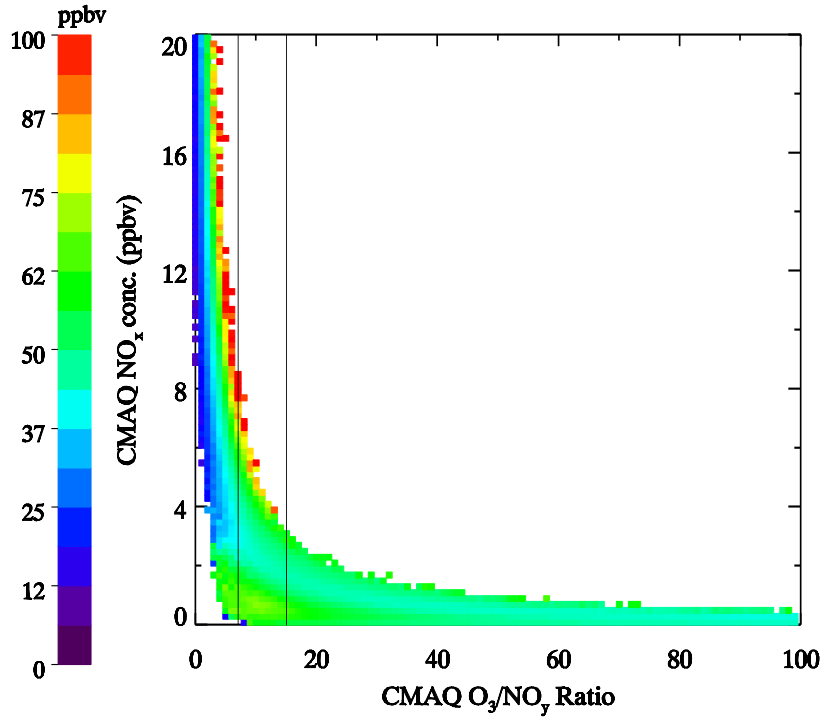
ppbv
100
87
75
62
50
37
25
12
0
CMAQ NOx conc. (ppbv)
20
16
12
8
4
0
0
20
40
60
80
100
CMAQ O3/NOy Ratio

c)

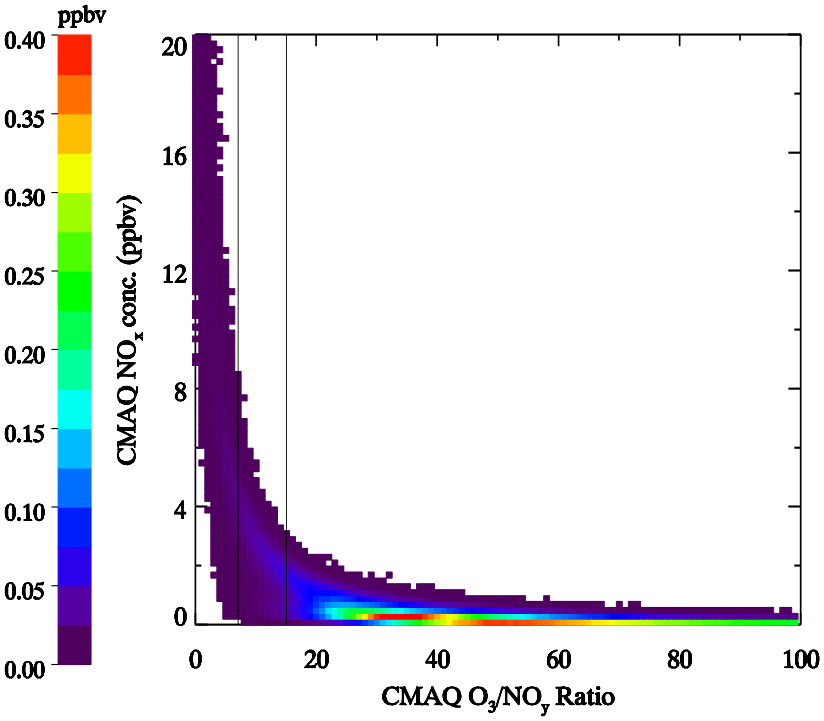
ppbv
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
CMAQ NOx conc. (ppbv)
20
16
12
8
4
0
0
20
40
60
80
100
CMAQ O3/NOy Ratio

Figure 4. Afternoon $O_3/NO_y$ ratios vs. $NO_x$ concentrations simulated by CMAQ in 2014. a) Scatter density, the color contour stands for the probability for each bin; b) $O_3$ concentrations, the color contour stands for the mean $O_3$ over the bins; c) Weighted $O_3$ concentrations. Two black lines stand for the $O_3/NO_y$ ratios of 7 and 11.

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Sun, C., and Liang, X. Z.: Improving U.S. extreme precipitation simulation: Dependence on cumulus parameterization and underlying mechanism, Climate Dynamics, to be submitted, 2020b.

Zhang, Y., Wen, X. Y., Wang, K., Vijayaraghavan, K., and Jacobson, M. Z.: Probing into regional O-3 and particulate matter pollution in the United States: 2. An examination of formation mechanisms through a process analysis technique and sensitivity study, Journal of Geophysical Research-Atmospheres, 114, 10.1029/2009jd011900, 2009.

Response to Reviewer #3's comments on He et al. 2019 Atmospheric Physics and Chemistry manuscript

We thank the anonymous reviewer for thoroughly reading our manuscript and providing helpful comments and suggestions, which lead a significant improvement of our manuscript. The detailed responses to major point comments are listed below (text in *italic* and black is the reviewer's comments, and the normal text highlighted in blue is our response):

*This manuscript presents a modeling study of the decadal ozone trend in the US. I am impressed by the significance of the results, but there are still several important issues need to be addressed before publication.*

Response: We appreciate the positive comments from the anonymous reviewer, and the manuscript has been revised according to these comments as listed below.
*Line numbers are based on the revised clean version of the manuscript.

*1 How will the results of CWRF-CMAQ differ from WRF-CMAQ? You can also use WRF to simulate decadal climate with long-term reanalysis. Better to include some description of the advantage of CWRF over WRF.*

Response: The CWRF was developed as a Climate extension of the WRF model incorporating numerous improvements in representation of physical processes and integration of external forcings that are crucial to climate scales, including interactions between land-atmosphere-ocean, convection-microphysics and cloud-aerosol-radiation, and system consistency throughout all process modules (Liang et al., 2012; Qiao and Liang, 2015; Chen et al., 2016; Liu et al., 2016; Qiao and Liang, 2016). It is built with a comprehensive ensemble of many alternate mainstream parameterization schemes for each of key physical processes. To better illustrate the advantage of CWRF, we added this short description in Line 127 of the revised manuscript.

*2 Scaling factors were used to get historical emissions. However, this will keep the spatial distribution the same at 2011 level. Why don't you use the information from other historical inventories, such as EDGAR? Could you discuss how this will affect the results?*

Response: This is a good question. The NEI2011 inventory adjusted with the ground and satellite measurements provides the best available anthropogenic emissions to the CONUS, which has also been used in the operational U.S. national air quality forecast. We used the U.S. National Emissions Trends to produce the scaling factors to generate historical emissions. It is not a perfect solution as pointed out by the reviewer that the assumption of the same spatial distribution may not be true. However, this method guaranteed that the domain total emissions would be consistent with the U.S. official emission trends, which we believe are the best available emissions for CONUS. We believe it is more important to provide total CONUS emissions constrained by the trend data than emissions with more detailed geographic distributions, when our modeling system has relatively coarse spatial resolution and integrates over 20 years. To explain our approach, we added the following sentences in Line 166 as "*Emissions of the baseline year are based on EPA NEI2011 inventory which can provide the best available anthropogenic emissions to the CONUS and are currently used in the operational U.S. national air quality forecast. The usage of APET scaling factors can guarantee the domain total emissions are consistent with the U.S. EPA emissions trend, although assuming the same spatial*

*distribution of anthropogenic emissions from year to year may not be realistic. Without a reasonable observation of actual spatiotemporal variations, it is the cost-effective approach as a first-order approximation to simulate long-term U.S. air quality driven by consistent CONUS total anthropogenic emissions that account interannual trends*".

*3 Chemical initial and boundary conditions were obtained from the default concentration profiles built in CMAQ. For long lived chemical species like ozone, long range transport and stratospheric intrusions would be important. If default concentration profiles are set, how to consider the historical changes in sources outside the US?*

Response: We understand that the ICs and BCs are important to the CMAQ performance. To reduce the impacts of ICs, we spin-up the CMAQ model for two weeks before the 5-yr continuous simulations (e.g., two weeks in December 1999 were used to create ICs for 2000-2004 CMAQ simulations). Based on our experiences in CMAQ modeling and the EPA guidance, two weeks' spin-up should be able to eliminate the influences from ICs.

The stratospheric intrusions are important for the ozone pollution in high altitude regions such as Denver, Colorado. However, the regional CMAQ does not include stratospheric chemistry, and our model top level is at 50 hPa. A potential vorticity (PV)-$O_3$ parameterization was developed recently for the hemispheric CMAQ model (Xing et al., 2016), but it is not available for the regional CMAQ version used in this study. We have discussed this shortcoming of our modeling system in the discussion section.

We agree that the long-range transport (LRT) through BCs can play an important role in the regional modeling of U.S. air quality. Our previous studies (He et al., 2016; He et al., 2018) show that the LRT can contribute up to 10% of ozone and $PM_{2.5}$ in the western United States; these numerical simulations are conducted in relatively short period (5 years) under multiple scenarios with fixed and dynamic LBCs. For climate studies, 5-year continuous integration is usually treated as the minimum time period, while longer simulation is preferred to better capture the climate signature. In this project, we designed a 25-yr experiment from 1990 to 2015, so CWRF downscaling can better represent the regional climate of the CONUS. Due to limited computing resources, we chose not conducting 25-yr global CTM simulations to generate dynamic LBCs conditions for CMAQ, but focused on the ozone pollution change within the United States. We understand that our approach could introduce some uncertainties in this study, and added the following sentences in Line 398 of the discussion session, "*So our current modeling system cannot take the historical changes of air pollution outside the United State into account. That is, the effect of long-range transport of air pollutants through model domain boundaries is presumed to be secondary to the long-term trends over the United States."* and In Line 403 *"With these increased air pollutant transported into the United States, our study may underestimate the impacts of domestic emission reductions to U.S. ozone pollution, especially in the West Coast and the Southwest.*".

*4 O3/NOy ratio was used as the indicator of VOC or NOx limited. The threshold of was adopted (O3/NOy < 15 indicating the VOC-sensitive regime). How to demonstrate this threshold and ratio is proper and accurate or represent the sensitivity. As model usually has difficulty in capturing the concentrations of NOy, the results might be questionable with this assumption.*
Response: We appreciate the reviewer raised this concern, which is also pointed out by the other reviewer. First, we understand that computer models have difficulty to accurately capture the

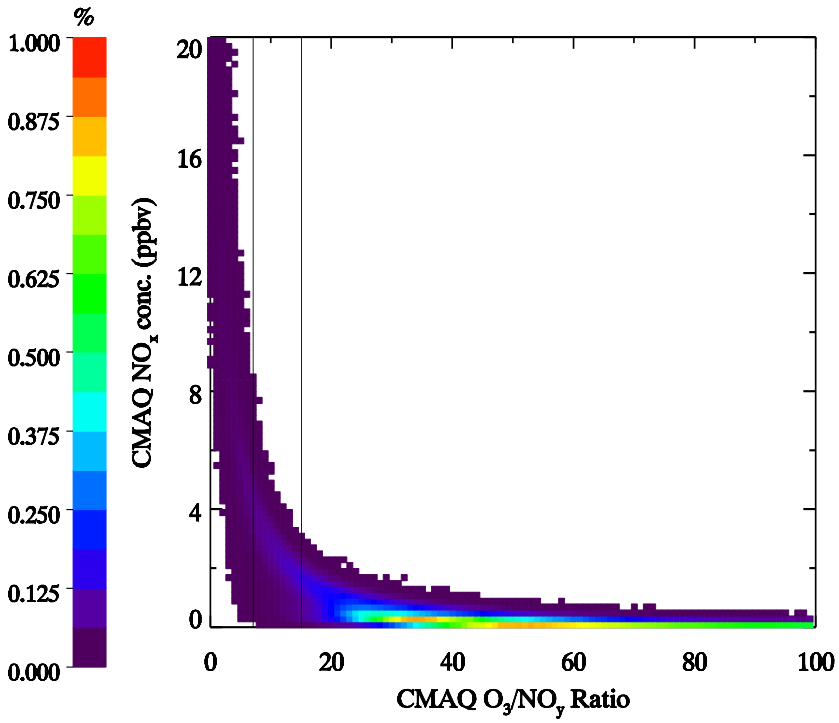
ambient $NO_y$ concentrations. In this study, because we did not access long-term research grade $NO_y$ observations from EPA, all the analysis using $O_3/NO_y$ ratios as the photochemical indicators is based purely on CMAQ simulations. So we have to rely on results from the previous studies. Sillman explored the concept using photochemical indicators including $O_3/NO_y$ to identify the regime of ozone photochemical production, finding that the link between the ozone production sensitivity and these indicators is largely unaffected by changes in model assumptions, including emission rates of anthropogenic and biogenic species (Sillman, 1995; Sillman et al., 1997). Observations from urban areas of Atlanta, New York, and Los Angeles was compared with modeling results from the Urban Airshed Model at urban scales, and a threshold of 7 was proposed for using $O_3/NO_y$ ratios as the photochemical indictor (Sillman et al., 1997). Zhang et al. (2009) expanded the study to the CONUS with 1-year CMAQ simulations, suggesting a threshold of 15 for $O_3/NO_y$ ratios. Zhang et al. (2009) used previous CMAQ version 4.4 for this 1-yr CONUS simulations of 2001 at a relatively coarse spatial resolution (36 km), which is close to our 30-km CONUS domain, so we adopted their proposed threshold. We agree that the current manuscript lacked the evaluation of this threshold with our modeling system, and we developed the following approach to test it.

We selected hourly $O_3$, $NO_y$, and $NO_x$ concentrations from CMAQ in the afternoon (defined as 12 pm to 4 pm) in 2014, and calculated the $O_3/NO_y$ ratios. Figure 1a shows scatter density of $O_3/NO_y$ ratios vs. $NO_x$ concentrations, which is calculated based on a 100 × 100 bins with $NO_x$ from 0-20 ppbv $NO_x$ (i.e., 0.2 ppbv per bin) and 0-100 $O_3/NO_y$ ratios (i.e., 1 per bin). In the afternoon over the CONUS, the ozone production is mainly in high $O_3/NO_y$ ratio (>15) and low $NO_x$ (less than 2 ppbv) environment, i.e., in the $NO_x$-sensitive regions by thresholds proposed by both Sillman et al. (1997) and Zhang et al. (2009). Figure 1b shows the same density plot, but the color stands for mean $O_3$ concentrations. Both low and high ozone concentrations exist in high $NO_x$ region ($NO_x$ > 4 ppbv), which are usually urban or suburban. Then we calculated the weighted ozone concentrations that equals to the product of $O_3/NO_y$ and $NO_x$ scatter density (Fig. 1a) and mean $O_3$ concentrations (Fig. 1b), which stands for the $O_3$ sensitivity with respect to $O_3/NO_y$ ratios and $NO_y$ concentrations over the CONUS (Fig. 1c). At the national scale, when the weighted ozone concentrations increase with CMAQ $NO_x$ levels, the photochemical production is $NO_x$-sensitive. The region with $O_3/NO_y$ higher than 7 and 11 both have this characteristics, while due to low probability (Fig. 1a) and urban environment (Fig. 1b) we believe the $O_3/NO_y$ threshold of 7 stands for the urban environment. Thus, the $O_3/NO_y$ ratio threshold of 15 is more proper for the CONUS scale analysis. This analysis qualitatively supports our application of results from Zhang et al. (2009).

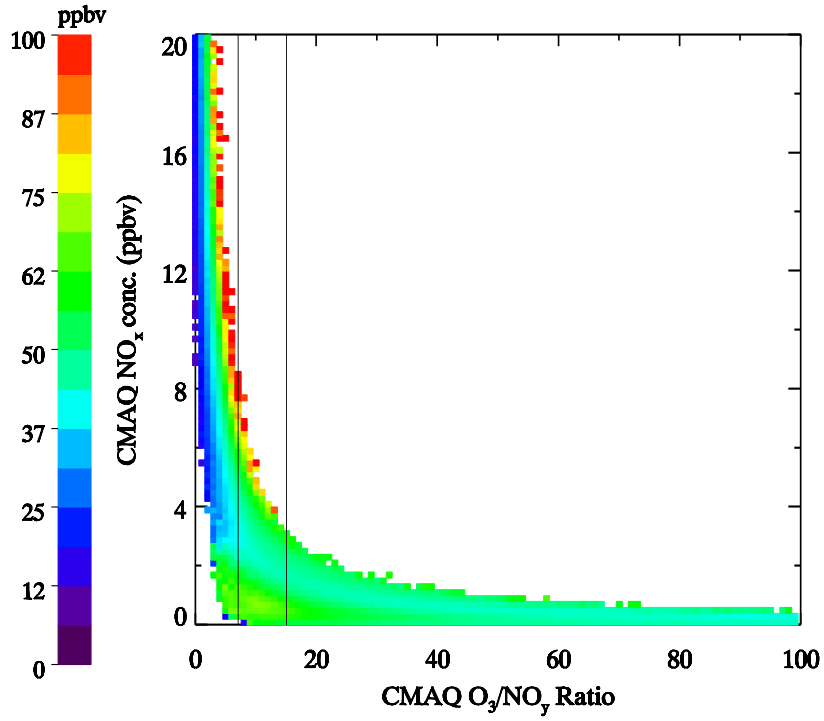
In summary, due to limited resources and experiment design, identifying a threshold of $O_3/NO_y$ ratio is beyond the scope of this study. Using results from our CMAQ model, we proved that the threshold of 15 should be practical for our study. We added the following sentences in Line 323 as "*The usage of $O_3/NO_y$ ratio was first proposed by Sillman (Sillman, 1995; Sillman et al., 1997). Sillman et al. (Sillman et al., 1997) conducted a case study of observations in urban areas (Atlanta, New York, and Los Angeles) and modeling results from the Urban Airshed Model and suggested the threshold of 7 as the transition region from VOC-sensitive environment to $NO_x$-sensitive environment. Zhang et al. (2009a; 2009b) expanded this method to the CONUS with 1-year observations and CMAQ simulations (36-km spatial resolution) and suggested a threshold of 15 for ozone pollution at the national scale. In this study, we did not have access to the long-term research grade $NO_y$ observations from the AQS network and did not conduct sensitivity experiments (due to computational resource limit) with reduced $NO_x$ emissions following Sillman*

*et al. (1997), so we have to reply on the $O_3/NO_y$ threshold from literature. We conducted a simple evaluation of our CMAQ results and found the threshold of 7 could be more proper for urban areas and the threshold of 15 should be more applicable for our study of the whole United State (Figure S1 in the supplementary material). Please note that the $O_3/NO_y$ ratio could depend on the modeling framework, so due to the similarity of our modeling system (30-km CMAQ) and the model used in Zhang et al. (2009a; 2009b), our analysis suggests the similar threshold of 15*" and the discussion above to the supplementary material.

a)



b)


ppbv
100
87
75
62
50
37
25
12
0
CMAQ NOx conc. (ppbv)
20
16
12
8
4
0
0
20
40
60
80
100
CMAQ O3/NOy Ratio

c)

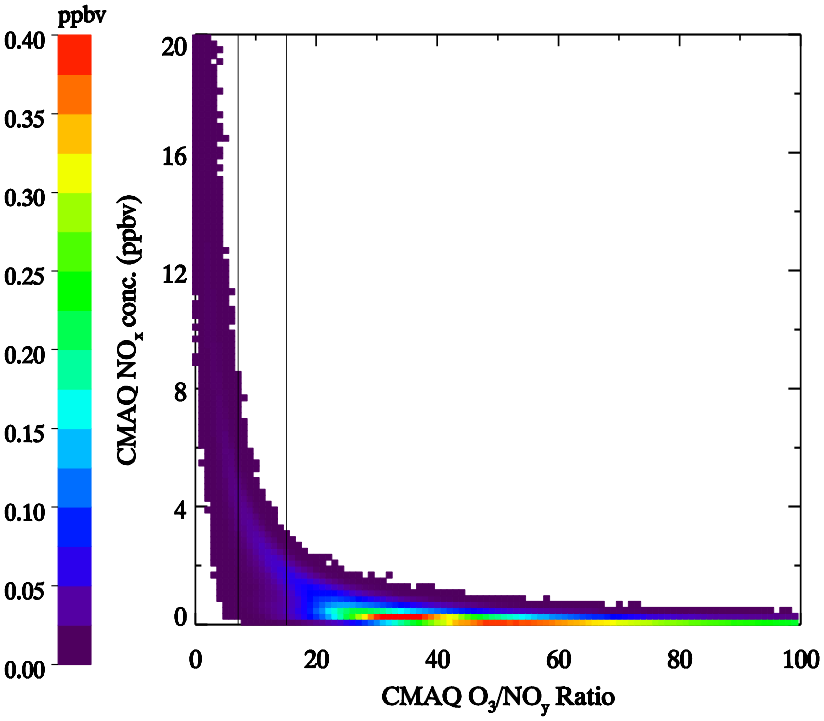

ppbv
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
CMAQ NOx conc. (ppbv)
20
16
12
8
4
0
0
20
40
60
80
100
CMAQ O3/NOy Ratio

Figure 1. Afternoon $O_3/NO_y$ ratios vs. $NO_x$ concentrations simulated by CMAQ in 2014. a) Scatter density, the color contour stands for the probability for each bin; b) $O_3$ concentrations, the color contour stands for the mean $O_3$ over the bins; c) Weighted $O_3$ concentrations. Two black lines stand for the $O_3/NO_y$ ratios of 7 and 11.

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# The long-term trend and production sensitivity change of the U.S. ozone pollution from observations and model simulations

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**Abstract**

We investigated the ozone pollution trend and its sensitivity to key precursors from 1990 to 2015 in the United States using long-term EPA AQS observations and mesoscale simulations. The modeling system, a coupled regional climate – air quality (CWRF-CMAQ) model, well captured summer surface ozone pollution during the past decades, having a mean slope of linear regression with AQS observations at ~0.75. While the AQS network has limited spatial coverage and measures only a few key chemical species, the CWRF-CMAQ provides comprehensive simulations to enable a more rigorous study of the change in ozone pollution and chemical sensitivity. Analysis of seasonal variations and diurnal cycle of ozone observations showed that peak ozone concentrations in the summer afternoon decreased ubiquitously across the United States, up to 0.5 ppbv/yr in major non-attainment areas such as Los Angeles, while concentrations at other hours such as the early morning and late afternoon increased slightly. Consistent with the AQS observations, CMAQ simulated a similar decreasing trend of peak ozone concentrations in the afternoon, up to 0.4 ppbv/yr, and increasing ozone trends in the early morning and late afternoon. ~~While a~~A monotonic decreasing trend (up to 0.5 ppbv/yr) in the odd oxygen ($O_x = O_3 + NO_2$) concentrations are simulated by CMAQ at all daytime hours. This result suggests that the increased ozone in the early morning and late afternoon was likely caused by reduced NO-$O_3$ titration driven by continuous anthropogenic $NO_x$ emission reductions in the past decades. Furthermore, the CMAQ simulations revealed a shift in chemical regimes of ozone photochemical production. From 1990 to 2015, surface ozone production in some metropolitan areas, such as Baltimore, has transited from VOC-sensitive environment (>50% probability) to $NO_x$-sensitive regime. Our results demonstrated that the long-term CWRF-CMAQ simulations can provide detailed information of the ozone chemistry evolution under a changing climate, and

may partially explain the U.S. ozone pollution responses to regional and national regulations.

## 1. Introduction

Tropospheric ozone ($O_3$) is one of the major air pollutants, regulated by the U.S. Environmental Protection Agency (EPA), that pose myriad threats to public health and the environment (Adams et al., 1989; WHO, 2003; Ashmore, 2005; Anderson, 2009; Jerrett et al., 2009). It is also an important greenhouse gas due to the absorption of thermal radiation, affecting the climate (Fishman et al., 1979; Ramanathan and Dickinson, 1979; IPCC, 2013). The major source of tropospheric ozone is photochemical production from ozone precursors such as carbon monoxide (CO), volatile organic compounds (VOCs), and nitrogen oxides ($NO_x$) at the presence of sunlight (Crutzen, 1974; Seinfeld, 1991; Jacob, 2000; EPA, 2006), while downward transport of stratospheric air mass contributes substantially to ozone concentrations in upper troposphere (Levy et al., 1985; Holton et al., 1995; Stevenson et al., 2006). In the past decades, ozone pollution in the United States has been reduced substantially due to regulations on anthropogenic emissions of ozone precursors (Oltmans et al., 2006; Lefohn et al., 2008, 2010; Cooper et al., 2012; He et al., 2013; Cooper et al., 2014), although some studies suggested no trend or slight increases at some rural areas (Jaffe and Ray, 2007; Lefohn et al., 2010; Cooper et al., 2012). Most of these analyses focused on peak ozone concentrations, e.g., daily maximum 8-hour average ozone (MDA8), during summer, but studies on trends in seasonal and diurnal patterns of ozone pollution are limited. He et al. (2019) analyzed measurements from four monitoring sites in the eastern United States and found different ozone trends between rural and urban sites from the late 1990s to the early 2010s including some increases at certain hours, suggesting effects of national regulations could be regionally dependent. Thus, it is important to extend our study to

other regions of the United States in a longer time period.

The non-monotonic trends in United States ozone pollution could be caused by the complex non-linear chemistry of ozone production involving $NO_x$ and VOCs (Logan et al., 1981; Finlayson-Pitts and Pitts, 1999; Seinfeld and Pandis, 2006). With continuous reduction of anthropogenic emissions of ozone precursors mainly $NO_x$ and VOCs in the United States, we need to better understand the photochemical regime change for local ozone production (i.e., ozone production sensitivity), because air pollution regulations could have different effects under $NO_x$-sensitive and VOC-sensitive environment (Dodge, 1987; Kleinman, 1994). For instance, under a VOC-sensitive photochemical regime, the decrease of $NO_x$ emissions has limited impacts on improving ozone pollution. Previous studies have developed photochemical indicators to identify the ozone production sensitivity (Sillman, 1995; Sillman et al., 1997; Tonnesen and Dennis, 2000b, 2000a; Sillman and He, 2002). Sillman (1999) found the ratio of VOCs and $NO_x$ ($VOC/NO_x$) has a typical value less than 4 for the VOC-sensitive environment and higher than 15 for the $NO_x$-sensitive regime. Observation-based studies of ozone production sensitivity relied on research grade measurements of ozone precursors and photochemical intermediates that are not routinely measured by air quality management agencies such as the U.S. EPA. These species include reactive nitrogen compounds ($NO_y$), nitric acid ($HNO_3$), and hydrogen peroxide ($H_2O_2$), normally observed during field campaigns (e.g., Shon et al., 2007; Peng et al., 2011) which only covered limited areas in certain periods. Studies based on air quality models (AQM) could identify the ozone production regimes at regional scales (Sillman et al., 1997; Sillman and He, 2002; Zhang et al., 2009a; Zhang et al., 2009b; Xie et al., 2011), but the simulation periods were usually short (less than one year) and thus could not capture the long-term change in ozone production sensitivity.

Regional AQMs are widely used for investigating the U.S. air quality (Tagaris et al., 2007; Tang et al., 2009; Hogrefe et al., 2011; Pour-Biazar et al., 2011; He et al., 2016a; He et al., 2018). They incorporate finer resolutions, more detailed emissions, and more explicit chemical mechanism than global chemical transport models to better resolve characteristics of tropospheric and surface dynamics, physical and chemical processes essential for air quality. Our group has developed and used coupled regional climate-air quality models to study air quality variations under a changing regional climate (Huang et al., 2007; Zhu and Liang, 2013; He et al., 2016a; He et al., 2018). Our previous studies showed the model's ability to capture the decadal U.S. air quality change (e.g., Zhu and Liang, 2013). In this study, we coupled the latest Climate-Weather Research Forecast (CWRF) and the EPA Community Multiscale Air Quality (CMAQ) models. CWRF has demonstrated substantial improvement in downscaling regional climate and extremes (Liang et al., 2012; Chen et al., 2016; Liu et al., 2016; Liang et al., 2019; Sun and Liang, 2020a; Sun and Liang, 2020b) and thus can provide more realistic weather conditions for AQMs to produce more credible air quality simulations.

To supplement the limited observations in both spatial coverage and chemical species, we conducted a continuous 26-yr CWRF-CMAQ simulation from 1990 to 2015 for a more rigorous analysis of long-term U.S. ozone trend. The model performance of the U.S. air quality was first evaluated against gridded ozone observations. The ozone seasonal variations and diurnal cycles were then extracted to determine the observed long-term trend. The model simulations were subsequently analyzed to explain the observed ozone trends and change in ozone production sensitivity.

## 2. Observations and model simulations

### 2.1 Long-term EPA observations

Hourly measurements of surface ozone concentrations from 1990 to 2015 were available from the EPA Air Quality System (AQS) database (https://www.epa.gov/outdoor-air-quality-data). They have been examined following the EPA guidance including the quality assurance and quality control. The locations and durations of AQS monitoring sites have changed substantially due to logistics and requirements to cover the regions sensitive to air pollution. Figure 1 shows that more than 2000 sites which reported ozone measurements ~~from~~ during the period of 1990 to 2015. To alleviate the impacts from missing data and short durations, we selected 640 sites that had ozone observation records longer than 20 years. Hourly ozone observations were processed following the approach described in He et al. (2019) to create the long-term seasonal and diurnal records for these stations.

### 2.2 Regional climate modeling

CWRF (Liang et al., 2012) was driven by the European Centre for Medium-Range Weather Forecasts ERA-Interim reanalysis (ERI, Dee et al., 2011) to downscale regional climate variations during 1989-2015 with the first year as the spin-up and not used. We adopted the well-established CWRF North American domain with a 30-km grid spacing (Fig. 1), covering the Contiguous United States (CONUS) and neighboring southern Canada, northern Mexico and adjacent oceans. The CWRF was developed as a climate extension of the WRF model (Skamarock et al., 2008) incorporating numerous improvements in representation of physical processes and integration of external forcings that are crucial to climate scales, including interactions between land-atmosphere-ocean, convection-microphysics and cloud-aerosol-

radiation, and system consistency throughout all process modules (Liang et al., 2012; Qiao and Liang, 2015; Chen et al., 2016; Liu et al., 2016; Qiao and Liang, 2016). CWRF is built with a comprehensive ensemble of many alternate mainstream parameterization schemed for each of key physical processes. ~~The CWRF incorporated advanced representations of key physical processes and integrations of external forcings crucial to climate scales (Liang et al., 2012)~~. It has been vigorously tested in North America and Asia showing outstanding performance to capture regional climate characteristics (Yuan and Liang, 2011; Chen et al., 2016; Liu et al., 2016; Liang et al., 2019). The CWRF downscaling has been shown to provide realistic meteorological fields and regional climate signals that can be cordially used to drive the CMAQ for long air quality simulations. Major CWRF physics configurations include the semi-empirical cloudiness parameterization of Xu and Randall (1996), the cloud microphysics scheme of Tao et al. (1989), the short wave and long wave radiation scheme of Chou et al. (2001), the ensemble cumulus parameterization (Qiao and Liang, 2015, 2016; Qiao and Liang, 2017), and the planetary boundary layer scheme of Holtslag and Boville (1993). Hourly CWRF outputs were processed using a modified Meteorology-Chemistry Interface Processor (MCIP, version 4.3) for CMAQ simulations.

### 2.3 Emissions preparation

To prepare anthropogenic emissions, we chose 2014 as the baseline year. This year's emissions were modified from the National Emissions Inventory 2011 (NEI2011). The modifications was based on measurements from the Ozone Monitoring Instrument (OMI) onboard satellite Aura, the ground-based AQS network, and the *in-situ* continuous emissions monitoring in power plants (Tong et al., 2015; Tong et al., 2016). The so modified NEI2011

inventory was processed using the Sparse Matrix Operator Kernel Emissions (SMOKE) version 3.7 (Houyoux et al., 2000). Emissions from on-road, off-road, and area sources were placed at the model layer closest to the surface. Emissions from point sources, e.g., stacks from power plants, were distributed vertically based on stack height and plume rise. The plume rise was estimated based on the method in Briggs (1972). The inventory pollutants were speciated according to the carbon bond chemical mechanism version 5 (CB05) and AERO5 aerosol mechanism. To fill the gap where NEI2011 data were not available, the Emissions Database for Global Atmospheric Research (EDGAR v3, http://edgar.jrc.ec.europa.eu/) at a 1° × 1° resolution developed by the Joint Research Centre of European Commission was adapted. Figure 2 shows an example of 2010-2015 mean $NO_x$ emissions distribution over the modeling domain. Daily mean $NO_x$ emissions have high values in urban areas of cities such as Los Angeles, Chicago, and the northeast corridor from Washington D.C. to Boston.

To project emissions from the baseline year into all individual years, we used the scaling factors from Air Pollutant Emissions Trends (APET) ~~Data~~ data compiled by the U.S. EPA (https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data). Emissions of the baseline year are based on EPA NEI2011 inventory which can provide the best available anthropogenic emissions to the CONUS and are currently used in the operational U.S. national air quality forecast. The usage of APET scaling factors can guarantee the domain total emissions are consistent with the U.S. EPA emissions trend, although assuming the same spatial distribution of anthropogenic emissions from year to year may not be realistic. Without a reasonable observation of actual spatiotemporal variations, it is the cost-effective approach as a first-order approximation to simulate long-term U.S. air quality driven by consistent CONUS total anthropogenic emissions that account interannual trends. Figure 3 shows the emission

177 evolution from 1990 to 2015. Since 1990 anthropogenic emissions of $NO_x$, CO, sulfur dioxide
178 ($SO_2$), and VOCs had steady decreasing trends, with $SO_2$ experiencing the largest reduction. On
179 the other hand, anthropogenic $PM_{2.5}$ and $NH_3$ emissions stayed mostly flat since the early 2000s.
180 The wildfire emissions were based on the Global Fire Emissions Database, Version 4 with
181 small fires (GFEDv4s, Randerson et al., 2017; van der Werf et al., 2017). The 0.25° × 0.25°
182 degree resolution GFEDv4s data were projected onto the modeling domain and speciated into the
183 CB05 and AERO5 species. GFEDv4s had a monthly resolution from 1997 to 2000 and daily
184 resolution from 2000 onward. Figure 4 illustrates the fire emissions evolution during 1990 to
185 2015 relative to 2014. Fire emissions have large interannual variations, with high emissions in
186 1998, 2002, 2013, and 2015, and low emissions in 2001, 2004, and 2014. We developed a
187 method to merge the aforementioned anthropogenic and wildfire emissions into the
188 temporalized, gridded and speciated data ready for CMAQ.
189 The biogenic emissions were calculated on-line within CMAQ based on the Biogenic
190 Emissions Landuse Database, Version 3 (BELD3, https://www.epa.gov/air-emissions-
191 modeling/biogenic-emissions-landuse-database-version-3-beld3). The 1-km resolution BELD3
192 data with spatial distribution of 230 vegetation classes over the North America were processed
193 through the Spatial Allocator developed by the Community Modeling and Analysis System
194 (CMAS) center (https://www.cmascenter.org/sa-tools/) to generate the gridded vegetation
195 distribution over the study domain. Table 1 lists the 5-yr mean variations of daily major ozone
196 precursor (CO, $NO_x$, and NMVOCs) emissions in the modeling domain and five subdomains.
197 The emission data show regionally dependent reductions. For instance, compared with 2000-
198 2004, the $NO_x$ emissions in 2005-2009 decreased by ~36% averaged in the CONUS, while 38%
199 and 35% reductions existed in states of California and Texas.

### 2.4 Air quality modeling

The EPA CMAQ model version 5.2 (EPA, 2017) was selected to simulate the U.S. air quality variations driven by CWRF meteorological fields (Section 2.2) and constructed emissions (Section 2.3). Major chemical mechanisms include the Carbon Bond 6 revision 3 (CB6r3) gas phase chemical scheme with updated secondary organic aerosol (SOA) and nitrate chemistry (Yarwood et al., 2010) and the latest AERO6 aerosol scheme (EPA, 2017), which improved U.S. air quality simulations over previous chemical mechanisms (Appel et al., 2016). Chemical initial and boundary conditions were obtained from the default concentration profiles built in CMAQ (EPA, 2017). Simulations were conducted continuously for each 5-year segment (e.g., 1990-1994, 1995-1999, etc.) with two-week spin-up in December prior to each starting years to speed up simulation turn around. Hourly concentrations of ozone and its key precursors such as nitric oxide (NO) and nitrogen dioxide ($NO_2$) were saved for subsequent analyses.

## 3. Results

### 3.1 Evaluation of CMAQ performance

Our previous studies showed that the direct comparison of observation data from monitoring sites and CMAQ results in 30-km grid could introduce inconsistency for evaluating the model performance (He et al., 2016a). The direct comparison is usually conducted through sampling the grid of CMAQ where the AQS site is located, while the distribution of AQS monitoring sites is usually uneven with more sites concentrated in populous urban and suburban areas where high ozone levels prevail. Sampling 30-km CMAQ grids over the locations of AQS measurements, i.e. direct comparison of averaged concentrations in the 900 $km^2$ CMAQ grid and pointwise AQS observations, could introduce important biases. So we applied the EPA Remote

Sensing Information Gateway (RSIG) software (available at https://www.epa.gov/rsig) to map the site observations onto our CMAQ grid. The RISG has the capability to 're-grid' the AQS observations on a selected model grid using the inverse-distance-weighted method to calculate the gridded mean concentrations (https://www.epa.gov/hesc/how-rsig-regrids-data). Figure 5 compares summer (JJA) mean MDA8 ozone in 2014 between gridded AQS observations and CMAQ outputs and shows that the model can well capture the U.S. ozone pollution, except underestimation in urban areas such as the Los Angeles basin.

Table 2 summarized the statistics ~~for~~ of CMAQ performance ~~of~~ simulating the summer ozone concentrations during 2000 - 2015 in CONUS and subdomains. Linear regression analyses of MDA8 ozone result in a mean slope value of 0.75 for CONUS, i.e., CMAQ slightly underestimates ozone over the United States. In subdomains, CMAQ performance exhibits large interannual variations. For instance, in Texas the linear regression slope and correlation coefficient ranges from 0.58 to 0.97 and 0.55 to 0.86, respectively. With gradual reduction in anthropogenic emissions, the fluctuations of CMAQ performance could be related to climate signals which control the regional ozone pollution. Future work is needed to identify the relationship between these regional climate variations and the U.S. ozone pollution. Generally, this modeling system has substantially improved performance in the Southeast, California and Texas, and moderately improved performance in the Northeast and Midwest as compared with our previous ~~study~~ modeling system (He et al., 2016a), which significantly underestimated the U.S. ozone pollution. One reason is that CWRF with more sophisticated representation of physical processes have the capability to better simulate the U.S. climate especially surface temperature and precipitation (Liang et al., 2012; Chen et al., 2016; Liu et al., 2016; Sun and Liang, 2020a; Sun and Liang, 2020b), which are key to accurate air quality simulations. ~~These~~

~~results~~The evaluation of CMAQ performance demonstrates the capability of CWRF-CMAQ to credibly simulate historical air quality.

### 3.2 Long-term ozone trend in AQS observations

We applied a box-averaging technique (He et al., 2016b; He et al., 2019) to analyze ozone measurements at the selected AQS monitoring sites (Fig 1). This approach used an hour by month box to calculate the mean 24-hr diurnal cycle of ozone for each month. Then we calculated the climatology mean over 24 hours by 12 months and the respective anomaly for each month at each AQS site. Figure 6 shows samples of long-term mean ozone concentrations and anomalies at four non-attainment cities: Baltimore, Maryland; Los Angeles, California; Denver, Colorado; and New York City (NYC), New York. The hour by month climatology (left column of Fig. 6) shows that the peak ozone concentrations in the afternoon during the ozone season (April to September) have been reduced significantly in these cities. However, ozone concentrations in the morning (8 am to 12 pm, all local time hereafter) and at night (8 pm to 8 am) increased slightly. These results confirm the effectiveness of recent emission controls which were designed to reduce the peak ozone. But the expansion of ozone at moderate levels (40-50 ppbv), which are higher than the natural background of U.S. ozone (Fiore et al., 2002; Fiore et al., 2003; Wang et al., 2009; Lefohn et al., 2014), could cause negative health impacts.

The anomaly (right column of Fig. 6) shows large variabilities of ozone concentrations because the ozone production is significantly impacted by regional climate (e.g., temperature, precipitation) with interannual and decadal variations. Large ozone reduction occurred after 2003 when the EPA $NO_x$ State Implementation (SIP) call was implemented (He et al., 2013). The anomalies at Los Angeles (Fig. 6b) and NYC (Fig. 6d) shows decreases of the peak ozone in the

afternoon of summer and increases in other times and seasons. For Baltimore and Denver, the peak ozone was not monotonically reduced, but increased in some years after 2002. Given the continuous reduction of anthropogenic emissions in the past decades, the increased ozone pollution in these areas could be caused by other factors ~~such as higher summer temperatures in certain years or enhanced stratosphere-troposphere exchange (for Denver at the high altitude area)~~, which need further investigations in the future.

We used the linear regression analysis to calculate the slope, correlation (R), and p-value of ozone trend at each local hour. Figure 7 shows ozone trends (slope, unit of ppbv/yr) at AQS sites which are statistically significant ($R^2 > 0.5$, and $p < 0.05$) in the early morning (8 am), at noon (12 pm), in the afternoon (4 pm), and in the evening (8 pm). Consistent results with the four cities (Fig. 6) are found ubiquitously. The peak ozone at noon and in the afternoon generally had a decreasing trend in CONUS, up to 0.5 ppbv/yr, confirming the improved air quality due to regulations, while ozone in the early morning and late afternoon increased slightly at most of monitoring sites. However, AQS sites in the Bay area (San Francisco, California) and Denver had stronger positive trends in the day time. The possible explanations include the trans-pacific transport of ozone and its precursors to the U.S. West Coast (Hudman et al., 2004; Huang et al., 2010; Lin et al., 2012b) and stratosphere-troposphere exchange of ozone to high altitude region (Langford et al., 2009; Lin et al., 2012a).

### 3.3. Ozone trends derived from CMAQ simulations

We applied the same box-averaging technique to hourly surface ozone simulations in CONUS and conducted the linear regression analysis to estimate the ozone trend at each model grid (Fig. 8). Compared with ozone trends derived from AQS observations (Fig. 7), the

CMAQ model successfully captured the spatial pattern and magnitude of change in ozone pollution. For instance, at 4 pm LT, CMAQ simulated up to 0.4 ppbv/yr decrease in surface ozone in the eastern United States and south region of California state. However, CMAQ simulated statistically insignificant trends (white color in Fig. 8c) at 4 pm LT in the Bay area, Los Angeles, and Denver where AQS observations showed increasing trends (Fig. 7c). The discrepancy occurred because our model used the static chemical lateral conditions (LBCs) that did not include the change of trans-Pacific transport of air pollutants, which were known to elevate the background ozone in the West Coast. Also CMAQ does not contain stratospheric chemistry and hence cannot account the contribution of downward transport of stratospheric ozone to the high altitude region.

Consistent with trends derived from AQS observations, CMAQ also simulated increasing ozone trends in the early morning (8 am LT, Fig. 8a) and late afternoon (8 pm LT, Fig 8d), especially in urban regions such as Los Angeles and Chicago. He et al. (2019) found ozone increases from observations at four sites in the eastern United States and a possible cause suggested by the reduced NO-$O_3$ titration through examining the trend in odd oxygen ($O_x = O_3 + NO_2$). Due to known interferences from nitrogen compounds such as $NO_x$ and organic nitrates to standard $NO_2$ measurements employed by EPA (Fehsenfeld et al., 1987; Dunlea et al., 2007; Dickerson et al., 2019), the analysis of $O_x$ required research grade $NO_2$ analyzer (e.g., photolytic $NO_2$ conversion) which are not available in current AQS network. Thus, our simulations provide a unique opportunity to expand such study to the whole CONUS.

Trends in $O_x$ concentrations simulated by CMAQ at 8 am, 12 pm, 4 pm, and 8 pm show a consistent decreasing trend over the modeling domain, up to 0.5 ppbv/yr reductions in the eastern United States (Fig. 9). The result confirms our hypothesis that the reduced NO-$O_3$ titration

elevated surface ozone concentrations in the early morning and late afternoon when the photochemical production of ozone is low or not active. Nowadays, ~~The~~ the ~~current~~ EPA ozone standard focuses on peak ozone concentrations, i.e., MDA8 ozone which usually has maximum values at noon or in the early afternoon, so the damage from additional ozone exposure from these elevated ozone concentrations in the early morning and late afternoon is not considered under the current environment policy. These increased ozone levels could offset the benefit from reduced peak ozone in past decades, which needs further investigations to provide scientific evidence for future policy decision.

### 3.4 Change in photochemical regime

With the continuous reduction of ozone precursor emissions, changes in the complex $O_3$-$NO_x$-VOC chemistry are anticipated. We used the $O_3/NO_y$ ratio as the indicator to study the photochemical regime change in the U.S. surface ozone production. The usage of $O_3/NO_y$ ratio was first proposed by Sillman (Sillman, 1995; Sillman et al., 1997). Sillman et al. (Sillman et al., 1997) conducted a case study of observations in urban areas (Atlanta, New York, and Los Angeles) and modeling results from the Urban Airshed Model and suggested the threshold of 7 as the transition region from VOC-sensitive environment to $NO_x$-sensitive environment. Zhang et al. (2009a; 2009b) expanded this method to the CONUS with 1-year observations and CMAQ simulations (36-km spatial resolution) and suggested a threshold of 15 for ozone pollution at the national scale. In this study, we did not have access to the long-term research grade $NO_y$ observations from the AQS network and did not conduct sensitivity experiments (due to computational resource limit) with reduced $NO_x$ emissions following Sillman et al. (1997), so we have to reply on the $O_3/NO_y$ threshold from literature. We conducted a simple evaluation of our

CMAQ results and found the threshold of 7 could be more proper for urban areas and the threshold of 15 should be more applicable for our study of the whole United State (Figure S1 in the supplementary material). Please note that the $O_3/NO_y$ ratio could depend on the modeling framework, so due to the similarity of our modeling system (30-km CMAQ) and the model used in Zhang et al. (2009a; 2009b), our analysis suggest the similar threshold of 15.

The threshold of 15 proposed by Zhang et al. (2009b) was adopted to identify the VOC-sensitive or $NO_x$-sensitive regime, i.e., $O_3/NO_y < 15$ indicating the VOC-sensitive regime. For each local hour, we calculated the probability when $O_3/NO_y$ is lower than 15 in every month. Figure 10 shows the probability of VOC-sensitive regime at 2 pm in July of 1995, 2005, and 2015. Most regions dominated by the VOC-sensitive chemistry are urban or suburban where anthropogenic $NO_x$ emissions are relatively high as compared with anthropogenic and/or biogenic VOCs emissions, such as the Los Angeles basin, the Northeast corridor (Washington D.C.-Baltimore-Philadelphia-NYC), and the Chicago metropolitan area. Noting that these maps are created based on ozone photochemical production simulated at the surface level, so the distributions are slightly different from recent studies using satellite data (Duncan et al., 2010; Jin et al., 2017; Ring et al., 2018).

We calculated the mean probability of VOC-sensitivity (2 pm in July) in a 3 × 3 CMAQ grid in metropolitan areas of Baltimore, Los Angeles, and NYC from 1990 to 2015 (Fig. 11). CMAQ simulations suggest the transition from VOC-sensitive regime to $NO_x$-sensitive regime in these urban areas. There were interannual variabilities in the probability of VOC-sensitive photochemistry in Baltimore (~50%) and NYC (~80%) in the 1990s and the early 2000s. After the EPA 2003 $NO_x$ SIP call, anthropogenic $NO_x$ emissions decreased substantially leading to reduced ozone pollution in the eastern United States (He et al., 2013), so the photochemical

production of surface ozone is expected to gradually become $NO_x$-sensitive. In 2015, ozone photochemical production in Baltimore was dominated by $NO_x$ emissions (only ~20% probability of VOC-sensitive), while NYC had higher probability (>50%) of VOC-sensitive chemistry. In Los Angeles, ozone chemistry slowly leaned to $NO_x$-sensitive, but until 2015 the local ozone production was still controlled by VOCs emissions. In regions with VOC-sensitive photochemistry in summer, reduction in $NO_x$ emissions had a limited impact on the local rate of ozone production until the photochemistry of ozone production became $NO_x$-sensitive. Our analysis can partially explain the different responses of ozone pollution in major U.S. cities to national air quality regulations during the past decades (Cooper et al., 2012) and can provide some insights for future policy decision.

## 4. Conclusions and Discussion

EPA AQS observations in the United States from 1990 to 2015 were analyzed to study the trend in surface ozone seasonal variations and diurnal cycles. We ~~showed~~ found that the peak ozone concentrations in the afternoon decreased significantly, especially in major non-attainment regions, but the concentrations in the early morning and late afternoon increased slightly. Regional climate-air quality model captured the long-term records of U.S. ozone pollution and suggested that the increased ozone was caused by reduced NO-$O_3$ titration due to the continuous reduction of $NO_x$ emissions. Model simulations also showed changes in ozone photochemical regime. The U.S. urban/suburban areas generally transited from the VOC-sensitive regime in the early 1990s to more $NO_x$-sensitive regime recently. But ozone production in some cities such as NYC and Los Angeles are still substantially impacted by VOC emissions. The current national and regional regulations focus on the MDA8 ozone concentrations mainly determined by the

peak ozone in the afternoon. Our study revealed the elevated ozone concentrations in the early morning and late afternoon which must be considered for their impacts on public health. ~~While~~ When $NO_x$ emissions are currently the main target of national and regional control measures, our study suggested that regulations on anthropogenic VOCs emissions could be important in certain regions. This study can improve our understanding about the effectiveness of regulations in the past decades and will provide scientific evidence for future policy decision.

Ozone production is highly non-linear, so accurate emissions are essential to simulate its long-term variations. Due to limited resources, we scaled the anthropogenic emissions from a baseline year (2014) to the 1990s using factors derived from the national trend data to construct consistent emissions for the CONUS with respect to the EPA data. This scaling cannot accurately reflect the detailed regional-dependent regulations for individual state such as the 2012 Health Air Act in Maryland (He et al., 2016b). Also, because the GFED data were only available after 1997, the contribution of wildfire emissions to ozone pollution was not included in model simulations between 1990 to 1996. Thus, we anticipated some uncertainties in ozone simulations in the early 1990s. Our model also has limitations to reproduce ozone records in high altitude regions such as Denver because of lacking the stratospheric chemistry in CMAQ and missing the effect of stratosphere-troposphere exchange to surface ozone. Lastly, due to limited resources, our experiments used static chemical LBCs for CMAQ, which excluded the long-range transport of air pollutants into the United States. So our current modeling system cannot take the historical changes of air pollution outside the United State into account. That is, the effect of long-range transport of air pollutants through model domain boundaries is presumed to be secondary to the long-term trends over the United States. For some West Coast regions such as the state of California, the trans-Pacific transport had been enhanced in the past decades and could play a

more important role in determining the local air quality. With these increased air pollutant transported into the United States, our study may underestimate the impacts of domestic emission reductions to U.S. ozone pollution, especially in the West Coast and the Southwest. To accurate evaluate the contribution from trans-boundary emission, dynamic LBCs from a global chemical transport model is needed in the future study.

## Author contribution

H.H., X.L., and Z.T. designed the experiment; H.H. and C.S. developed the CWRF-CMAQ system and performed the CWRF modeling; Z.T. and D.T. prepared the emission data; H.H. conducted the CMAQ simulations; H.H., Z.T., and C.S. analyzed the data; H.H. prepared the manuscript with contributions from all co-authors.

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## Tables and Figures

**Table 1.** Summary of multiyear mean average of daily CO, $NO_x$, and NMVOCs emissions in the CONUS and five subdomains. (Unit: mol/km$^2$ per second) Please note that our California and Texas subdomains include more area than the states of California and Texas.

| **CONUS** | | | | | **Southeast** | | |
|---|---|---|---|---|---|---|---|
| Year | CO | $NO_x$ | NMVOCs | | CO | $NO_x$ | NMVOCs |
| 1990-1994 | 32.9 | 1.24 | 0.94 | | 47.2 | 1.43 | 1.03 |
| 1995-1999 | 26.2 | 1.18 | 0.76 | | 37.4 | 1.36 | 0.85 |
| 2000-2004 | 18.9 | 1.26 | 0.69 | | 26.4 | 1.46 | 0.72 |
| 2005-2009 | 12.3 | 0.94 | 0.60 | | 16.9 | 1.07 | 0.59 |
| 2010-2015 | 8.0 | 0.60 | 0.46 | | 11.0 | 0.66 | 0.45 |
| **California** | | | | | **Northeast** | | |
| 1990-1994 | 18.3 | 1.22 | 0.57 | | 110.3 | 3.29 | 2.12 |
| 1995-1999 | 14.6 | 1.16 | 0.46 | | 87.2 | 3.16 | 1.68 |
| 2000-2004 | 10.6 | 1.23 | 0.40 | | 62.1 | 3.41 | 1.43 |
| 2005-2009 | 7.1 | 0.91 | 0.35 | | 40.3 | 2.56 | 1.25 |
| 2010-2015 | 4.6 | 0.56 | 0.26 | | 25.9 | 1.62 | 0.93 |
| **Texas** | | | | | **Midwest** | | |
| 1990-1994 | 22.6 | 1.21 | 1.26 | | 58.2 | 1.88 | 1.41 |
| 1995-1999 | 18.1 | 1.15 | 1.03 | | 46.3 | 1.80 | 1.14 |
| 2000-2004 | 13.0 | 1.20 | 1.01 | | 33.4 | 1.92 | 0.98 |
| 2005-2009 | 8.4 | 0.91 | 0.92 | | 22.0 | 1.44 | 0.85 |
| 2010-2015 | 5.5 | 0.60 | 0.73 | | 14.3 | 0.91 | 0.63 |

**Table 2.** Summary about the comparison of JJA MDA8 ozone concentrations from AQS observations and CMAQ simulations during 2000-2015 in the CONUS and subdomains. Slope and Correlation (Corr. R) are calculated for each year based on linear regression analysis. Please note that our California and Texas subdomains include more area than the states of California and Texas.

| **Year** | Slope | Corr. R | NMB | RMSE | **Year** | Slope | Corr. R | NMB | RMSE |
|---|---|---|---|---|---|---|---|---|---|
| **CONUS** | | | | | | | | | |
| **2000** | 0.73 | 0.37 | -6.9 | 10.5 | **2008** | 0.70 | 0.54 | -5.4 | 8.4 |
| **2001** | 0.80 | 0.61 | -7.7 | 8.7 | **2009** | 0.78 | 0.35 | -1.6 | 8.5 |
| **2002** | 0.71 | 0.63 | -8.6 | 9.2 | **2010** | 0.75 | 0.51 | -6.2 | 8.4 |
| **2003** | 0.81 | 0.60 | -4.3 | 8.4 | **2011** | 0.77 | 0.42 | -7.1 | 9.2 |
| **2004** | 0.85 | 0.39 | 1.3 | 8.9 | **2012** | 0.67 | 0.60 | -10.7 | 9.3 |
| **2005** | 0.87 | 0.54 | -7.3 | 8.8 | **2013** | 0.70 | 0.50 | -1.8 | 7.9 |
| **2006** | 0.77 | 0.48 | -7.6 | 9.1 | **2014** | 0.72 | 0.44 | -3.0 | 7.6 |
| **2007** | 0.70 | 0.60 | -6.1 | 8.0 | **2015** | 0.73 | 0.41 | -4.2 | 7.7 |
| **California** | | | | | | | | | |
| **2000** | 0.70 | 0.67 | -19.3 | 15.2 | **2008** | 0.63 | 0.53 | -18.0 | 14.8 |
| **2001** | 0.72 | 0.63 | -18.1 | 14.8 | **2009** | 0.67 | 0.61 | -19.0 | 13.5 |
| **2002** | 0.80 | 0.55 | -15.5 | 14.4 | **2010** | 0.62 | 0.55 | -19.0 | 14.1 |
| **2003** | 0.80 | 0.55 | -20.1 | 16.2 | **2011** | 0.68 | 0.57 | -17.0 | 13.3 |
| **2004** | 0.78 | 0.51 | -19.2 | 16.1 | **2012** | 0.64 | 0.63 | -21.4 | 14.9 |
| **2005** | 0.78 | 0.54 | -19.0 | 15.3 | **2013** | 0.64 | 0.60 | -17.9 | 13.5 |
| **2006** | 0.80 | 0.61 | -20.5 | 15.6 | **2014** | 0.69 | 0.56 | -21.9 | 14.8 |
| **2007** | 0.69 | 0.65 | -16.0 | 12.9 | **2015** | 0.72 | 0.61 | -22.3 | 14.2 |
| **Texas** | | | | | | | | | |
| **2000** | 0.60 | 0.77 | -20.4 | 11.8 | **2008** | 0.62 | 0.74 | -10.5 | 6.6 |
| **2001** | 0.58 | 0.62 | -19.6 | 11.5 | **2009** | 0.73 | 0.78 | -17.1 | 8.7 |
| **2002** | 0.70 | 0.72 | -10.4 | 6.6 | **2010** | 0.65 | 0.77 | -9.4 | 5.3 |
| **2003** | 0.64 | 0.78 | -8.8 | 6.5 | **2011** | 0.52 | 0.83 | -22.7 | 12.1 |
| **2004** | 0.97 | 0.55 | -7.2 | 5.8 | **2012** | 0.53 | 0.86 | -17.8 | 9.4 |
| **2005** | 0.70 | 0.78 | -21.5 | 11.4 | **2013** | 0.53 | 0.74 | -11.6 | 6.9 |
| **2006** | 0.66 | 0.83 | -20.5 | 11.3 | **2014** | 0.66 | 0.72 | -5.0 | 4.7 |
| **2007** | 0.77 | 0.84 | -4.0 | 3.9 | **2015** | 0.76 | 0.61 | -10.1 | 5.8 |
| **Southeast** | | | | | | | | | |
| **2000** | 0.61 | 0.41 | -20.5 | 13.3 | **2008** | 0.52 | 0.77 | -13.4 | 8.3 |
| **2001** | 0.64 | 0.70 | -7.7 | 6.2 | **2009** | 0.88 | 0.52 | -2.7 | 4.2 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **2002** | 0.56 | 0.77 | -14.1 | 9.5 | **2010** | 0.69 | 0.75 | -7.8 | 5.1 |
| **2003** | 0.65 | 0.77 | -0.7 | 4.7 | **2011** | 0.84 | 0.62 | -13.5 | 8.2 |
| **2004** | 0.81 | 0.59 | 3.2 | 4.4 | **2012** | 0.62 | 0.73 | -9.4 | 6.1 |
| **2005** | 0.54 | 0.64 | -8.8 | 6 | **2013** | 0.74 | 0.70 | 7.0 | 4.1 |
| **2006** | 0.74 | 0.60 | -14 | 9 | **2014** | 0.84 | 0.40 | 0.9 | 4.0 |
| **2007** | 0.56 | 0.71 | -14.1 | 9 | **2015** | 0.71 | 0.44 | -2.6 | 4.2 |
| **Northeast** | | | | | | | | | |
| **2000** | 0.50 | 0.25 | 7.9 | 7.0 | **2008** | 0.46 | 0.11 | -0.5 | 5.8 |
| **2001** | 0.46 | 0.28 | -3.6 | 6.0 | **2009** | 0.67 | 0.23 | 13.7 | 7.3 |
| **2002** | 0.51 | 0.13 | -8.5 | 8.3 | **2010** | 0.49 | 0.10 | -0.4 | 5.6 |
| **2003** | 0.85 | 0.16 | 3.0 | 5.3 | **2011** | 0.47 | 0.31 | 3.2 | 5.9 |
| **2004** | 0.81 | 0.21 | 10.0 | 6.6 | **2012** | 0.55 | 0.17 | -2.9 | 5.3 |
| **2005** | 0.84 | 0.11 | 2.5 | 5.8 | **2013** | 0.78 | 0.45 | 11.6 | 6.4 |
| **2006** | 0.45 | 0.21 | 3.0 | 6.0 | **2014** | 0.60 | 0.33 | -4.8 | 5.1 |
| **2007** | 0.48 | 0.19 | -0.7 | 5.6 | **2015** | 0.49 | 0.11 | 2.2 | 5.1 |
| **Midwest** | | | | | | | | | |
| **2000** | 0.41 | 0.25 | 3.4 | 5.9 | **2008** | 0.44 | 0.25 | 3.5 | 4.7 |
| **2001** | 0.55 | 0.30 | -2.3 | 4.9 | **2009** | 0.54 | 0.22 | 14 | 7.2 |
| **2002** | 0.45 | 0.27 | -5.2 | 7.0 | **2010** | 0.57 | 0.12 | 2.4 | 5.3 |
| **2003** | 0.66 | 0.25 | -0.1 | 4.7 | **2011** | 0.45 | 0.21 | 1.1 | 5.6 |
| **2004** | 0.68 | 0.44 | 13.9 | 7.5 | **2012** | 0.46 | 0.19 | -11.6 | 8.3 |
| **2005** | 0.76 | 0.15 | -4.4 | 5.6 | **2013** | 0.74 | 0.18 | 4.9 | 4.0 |
| **2006** | 0.50 | 0.17 | 0.3 | 5.0 | **2014** | 0.64 | 0.20 | 5.7 | 4.1 |
| **2007** | 0.39 | 0.20 | -0.6 | 5.6 | **2015** | 0.68 | 0.27 | 8.7 | 4.7 |

704 NMB: Normalized Mean Bias (Unit: %)
705 RMSE: Root Mean Square Error (Unit: ppbv)
706

**Figure 1.** Locations of EPA AQS sites for surface ozone monitoring during 1990-2015. Red dots stand for monitoring sites with more than 20 year record. Black dots show the locations of monitoring sites have short data records which are not used in this study. The map shows the CWRF-CMAQ 30-km domain and five subdomains sensitive to air pollution. CA: California (including nearby parts of Nevada, Arizona and Oregon); TX: Texas (including nearby parts of Louisiana, Arkansas, and Oklahoma); SE: Southeast; NE: Northeast; MW: Midwest. Please note that our CA and TX subdomains include more area than the states of California and Texas.

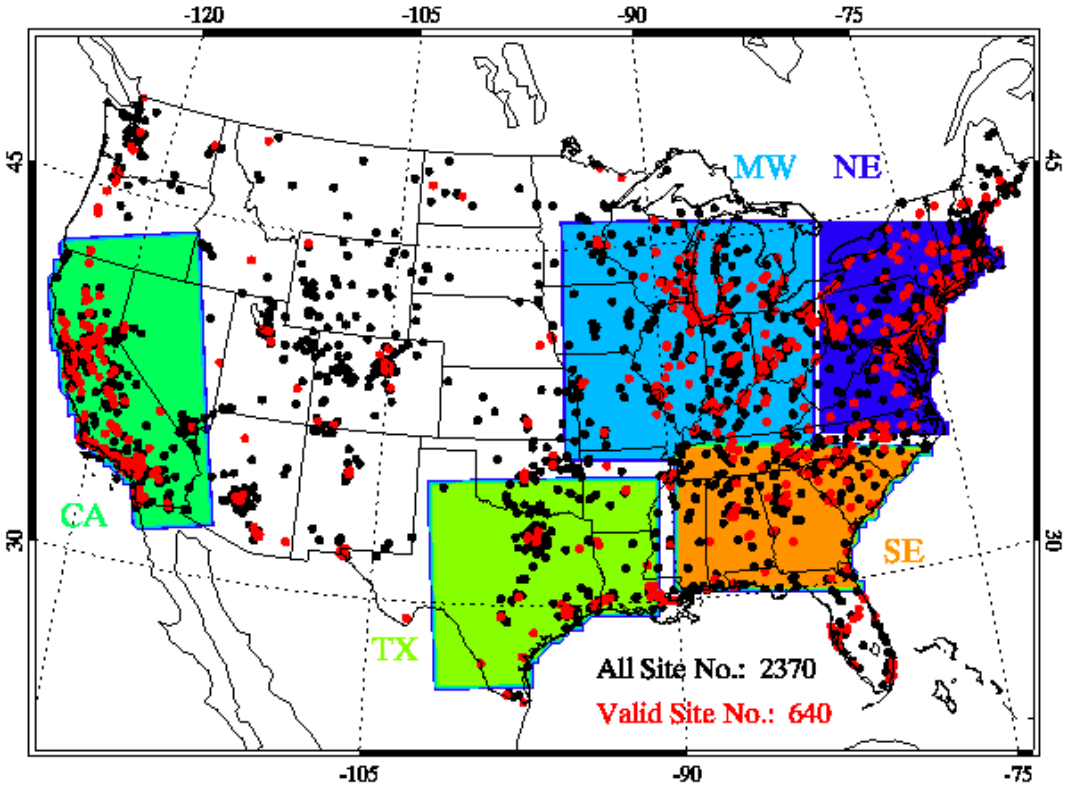
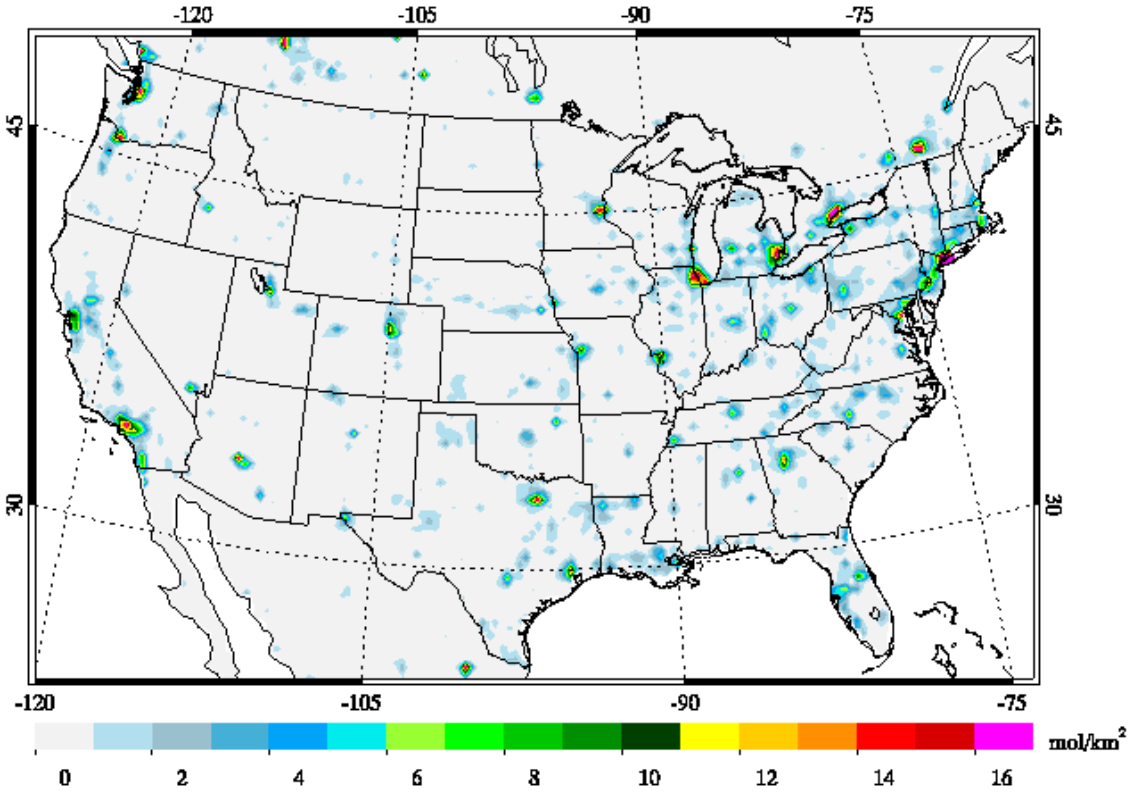


**Figure 2.** Averaged daily $NO_x$ emissions between 2010 and 2015 in the modeling domain (Unit: mol/km$^2$ per second).



718 **Figure 3.** Anthropogenic emission evolution relative to 2014 in the modeling domain from 1990
719 – 2015.

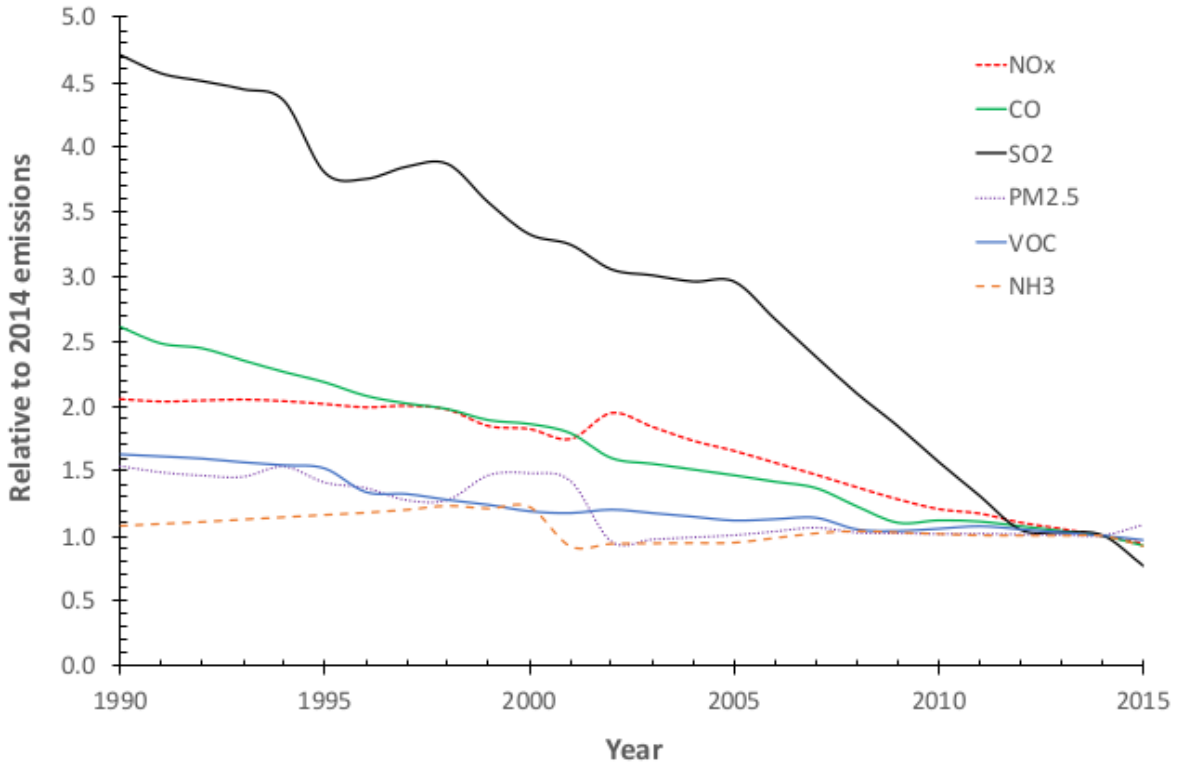



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**Figure 4.** Fire emission evolution relative to 2014 in the modeling domain from 1990 – 2015. Noting that GFED fire emissions are not available before 1997.

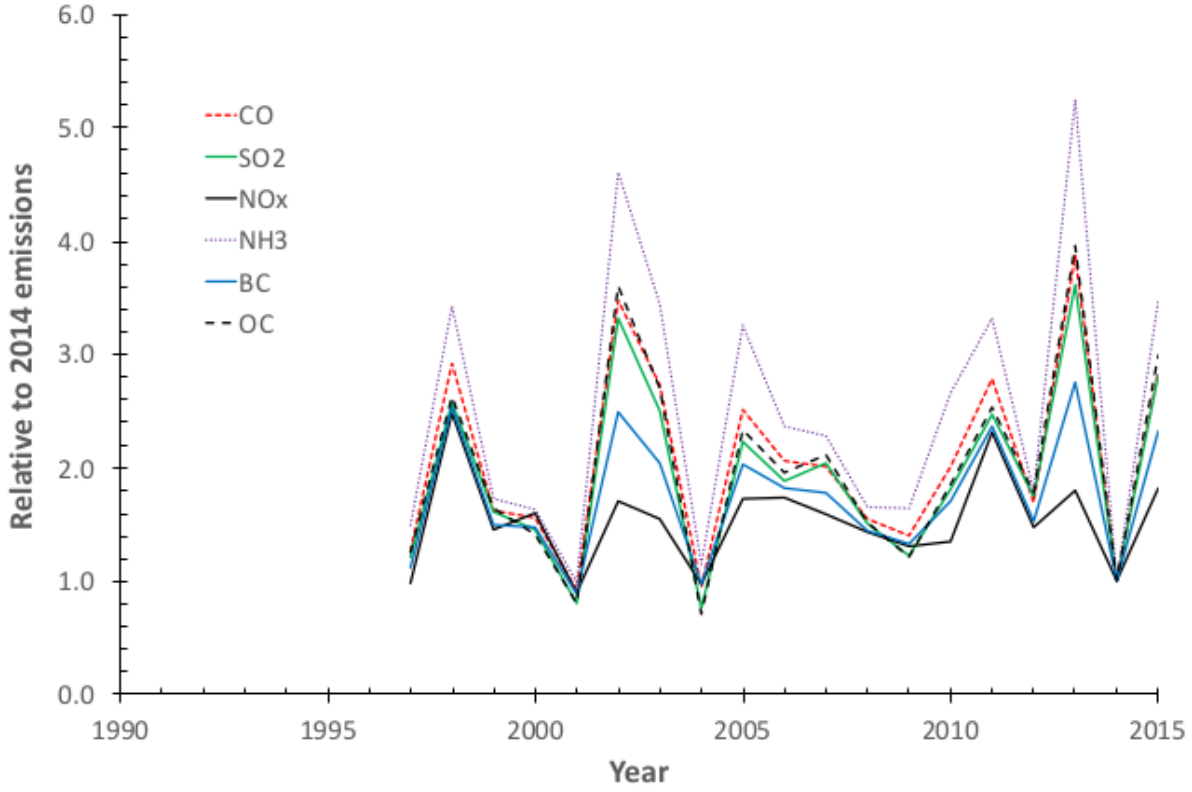
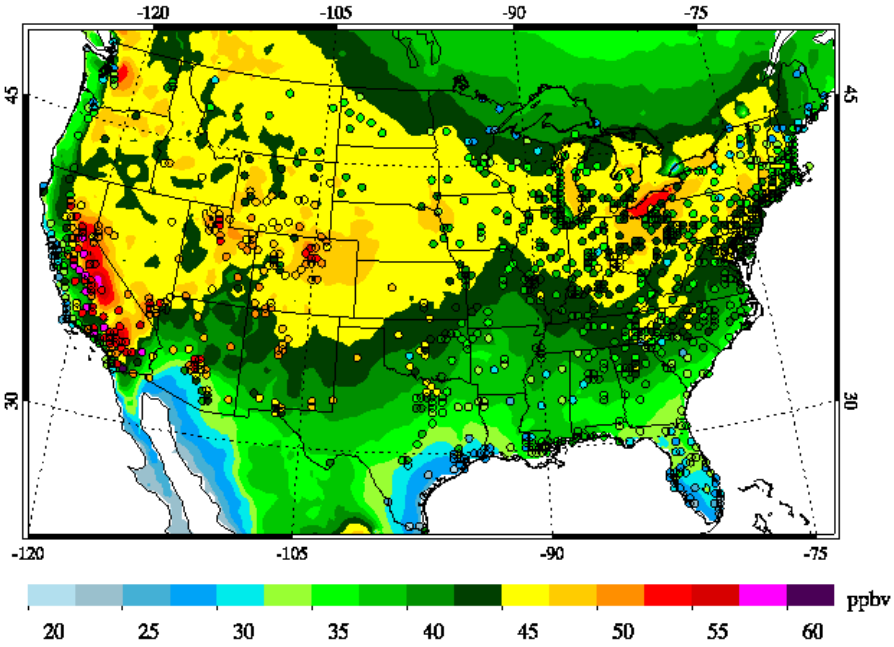


**Figure 5.** Comparison of summer MDA8 ozone concentrations from EPA AQS observations and CMAQ simulations in 2014. AQS station data were gridded to the CMAQ grid using the EPA RSIG software. a) Contour plot, the background stands for the CMAQ outputs and the dots stand for gridded AQS observations; b) Scatter plot of the gridded AQS observations and co-located CMAQ outputs.

a)




b)

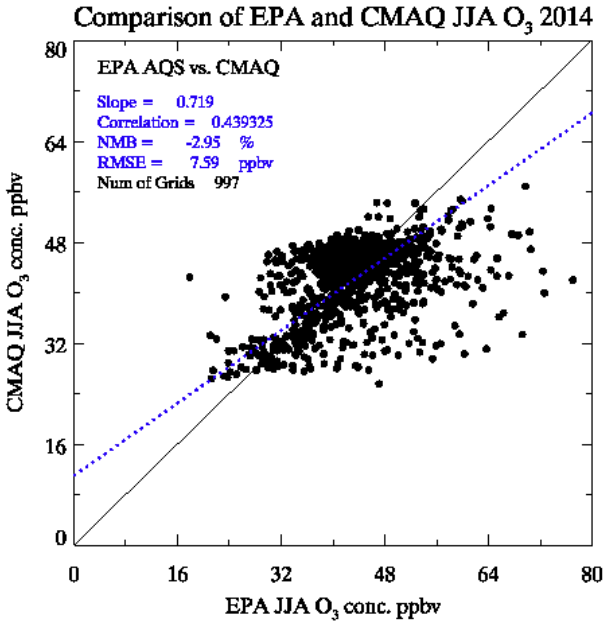


**Figure 6.** The box-averaging analyses of AQS ozone observations at selected sites from 1990-2015. a) Essex, Maryland (suburban Baltimore, AQS ID 240053001); b) Pasadena, California (downtown Los Angeles, AQS ID 060372005); c) Denver, Colorado (downtown Denver, AQS ID 080310014); d) Staten Island, New York (suburban New York City, AQS ID: 360850067). Left column shows the monthly mean, right column shows the anomaly values. White patches stand for missing data or not sufficient data for the box-averaging analysis.

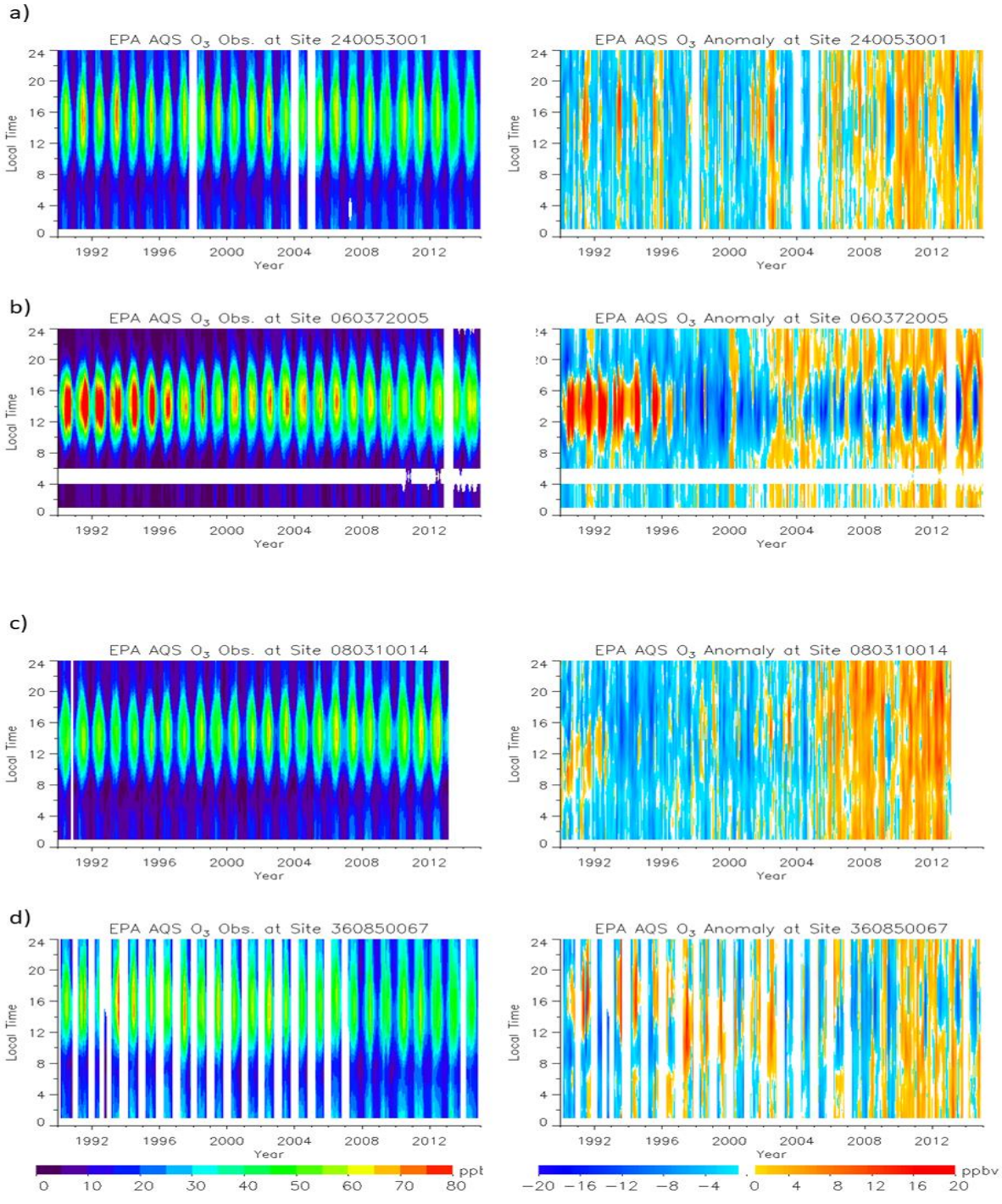


**Figure 7.** Trend in ozone observations at selected EPA AQS sites during 1990-2015 (Unit: ppbv/yr). a) at 8 am; b) at 12 pm; c) at 4 pm; d) at 8 pm (all local time). We only show the sites with statistically significant linear trend in the plots.

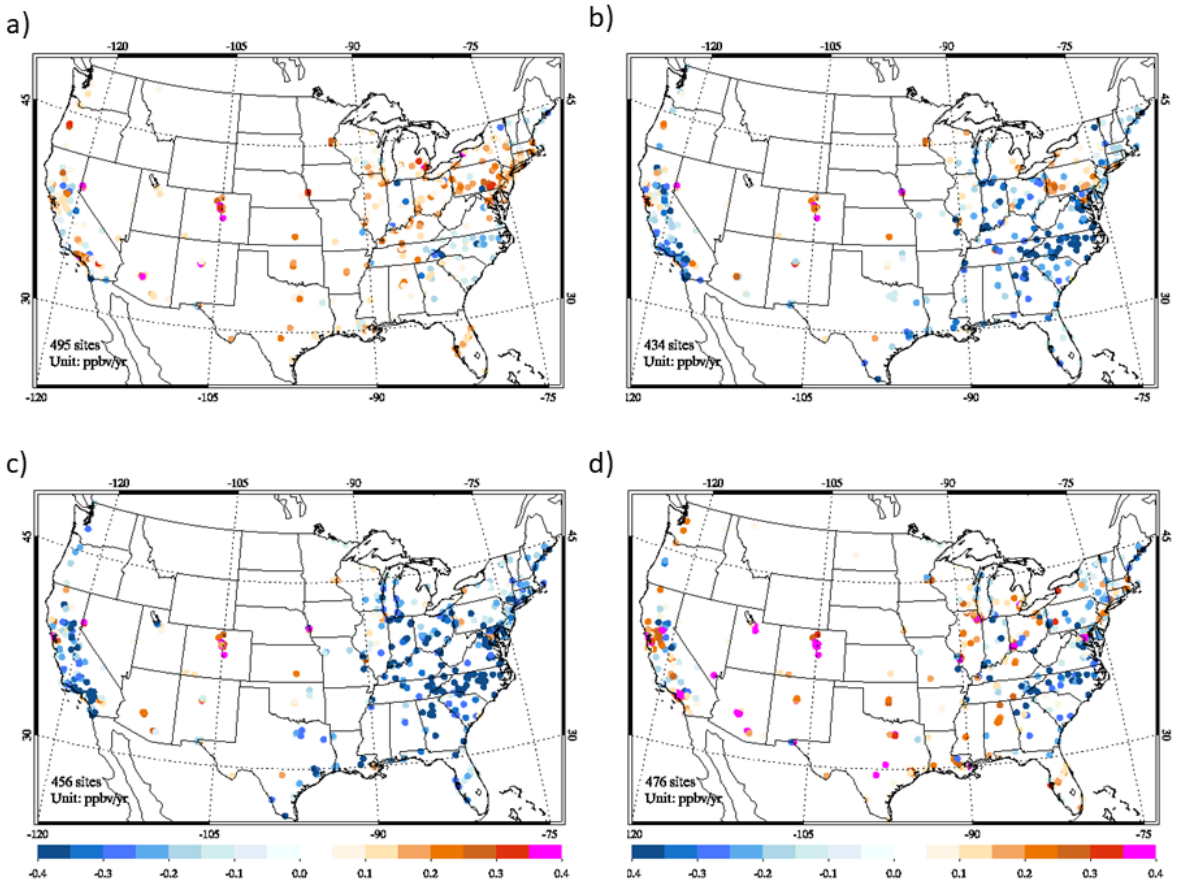


**Figure 8.** Trends in ozone simulations from CMAQ during 1990-2015 (Unit: ppbv/yr). a) at 8 am; b) at 12 pm; c) at 4 pm; d) at 8 pm (all local time). We only show CMAQ grids with statistically significant linear trend in the plots.

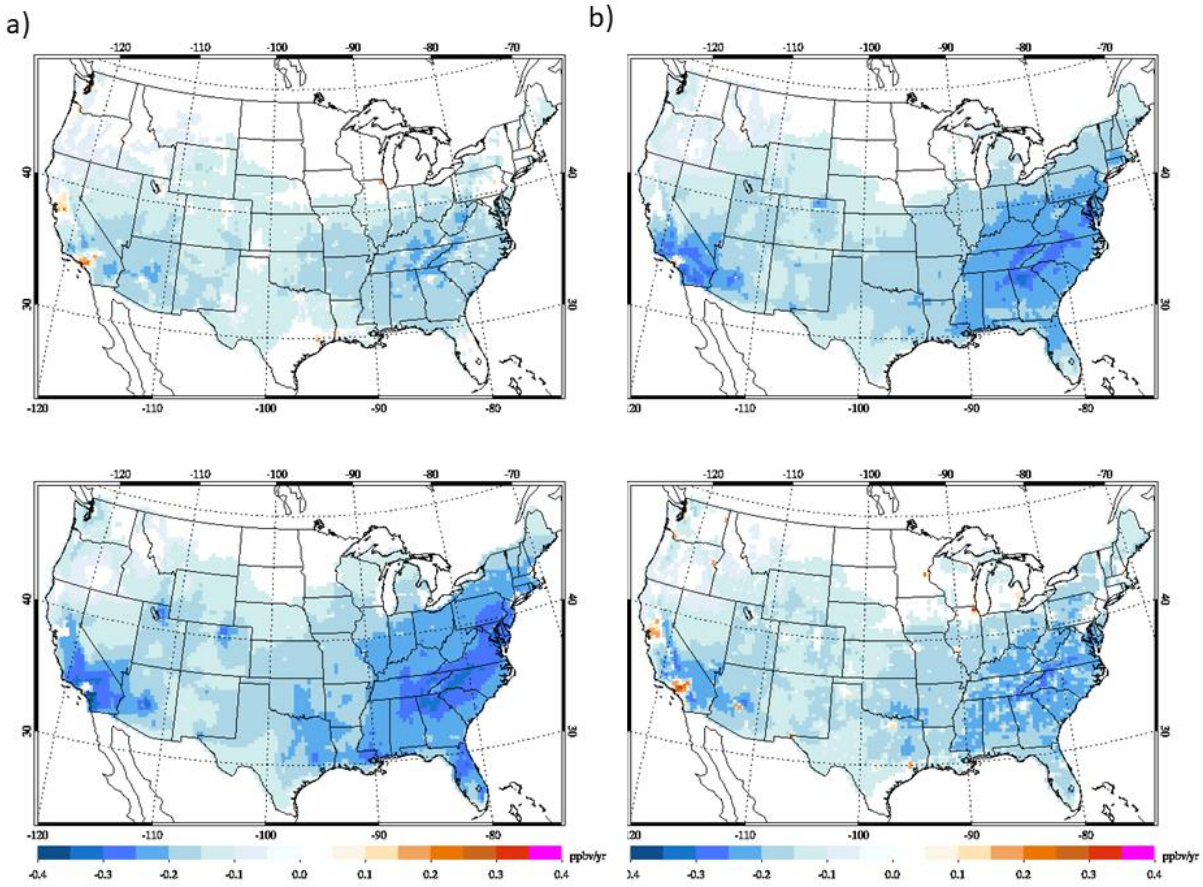


**Figure 9.** Trend in $O_x$ ($O_x = O_3 + NO_2$) simulated by CMAQ during 1990-2015. a) at 8 am; b) at 12 am; c) at 4 pm; d) at 8 pm (all local time). We only show CMAQ grids with statistically significant linear trend in the plots.

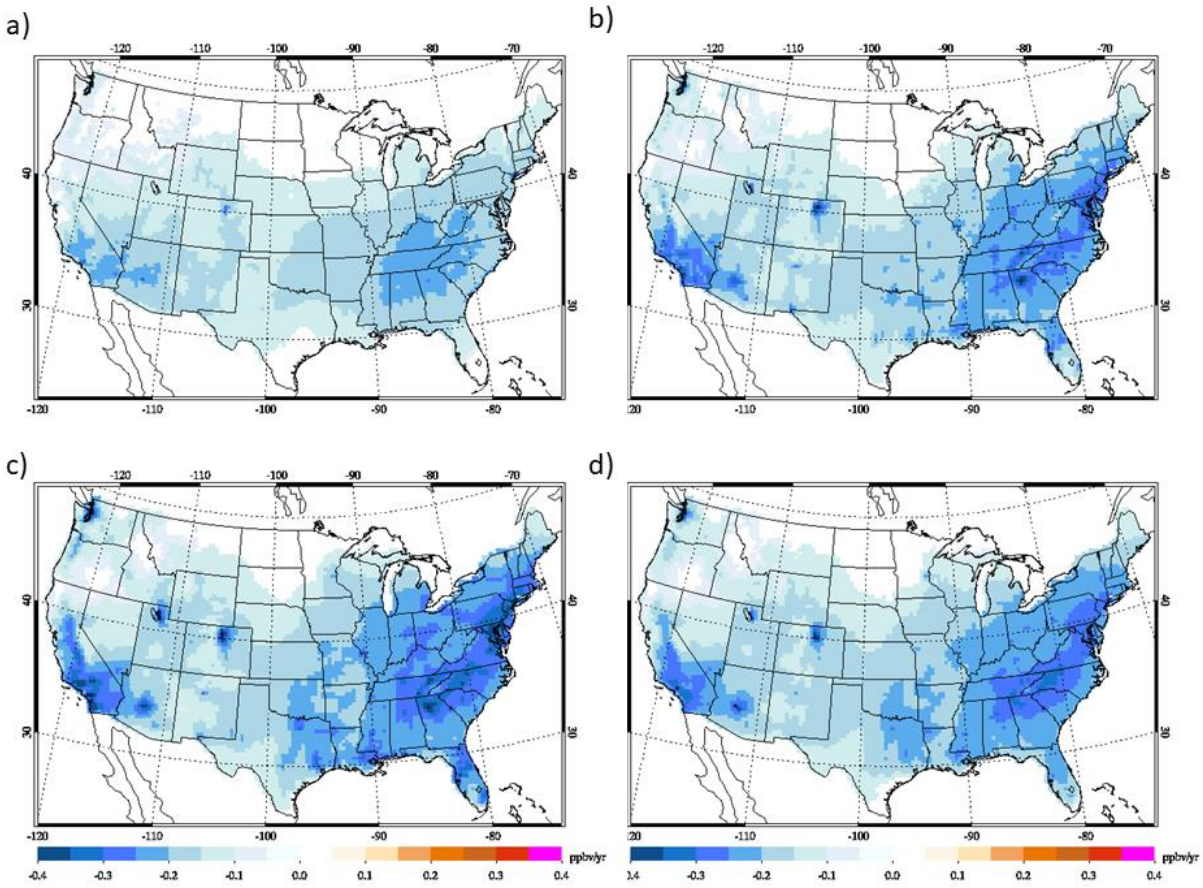
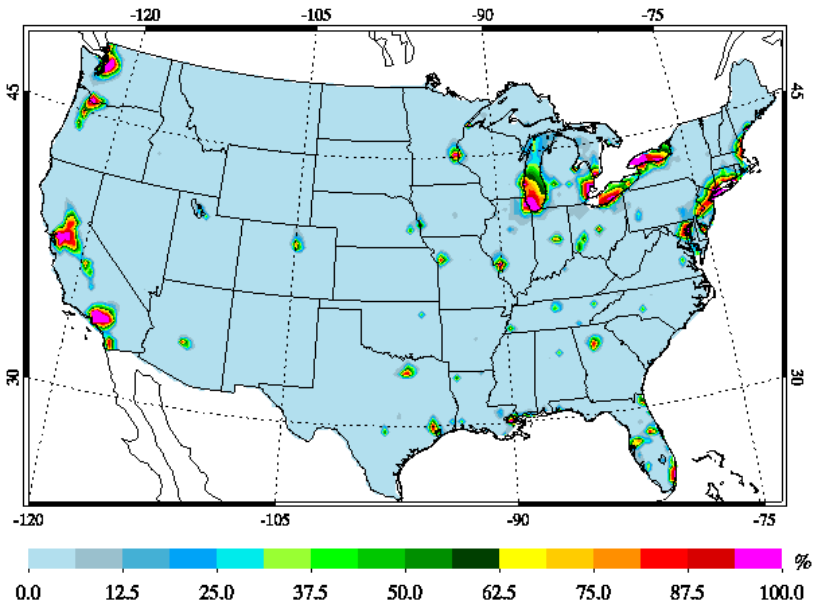
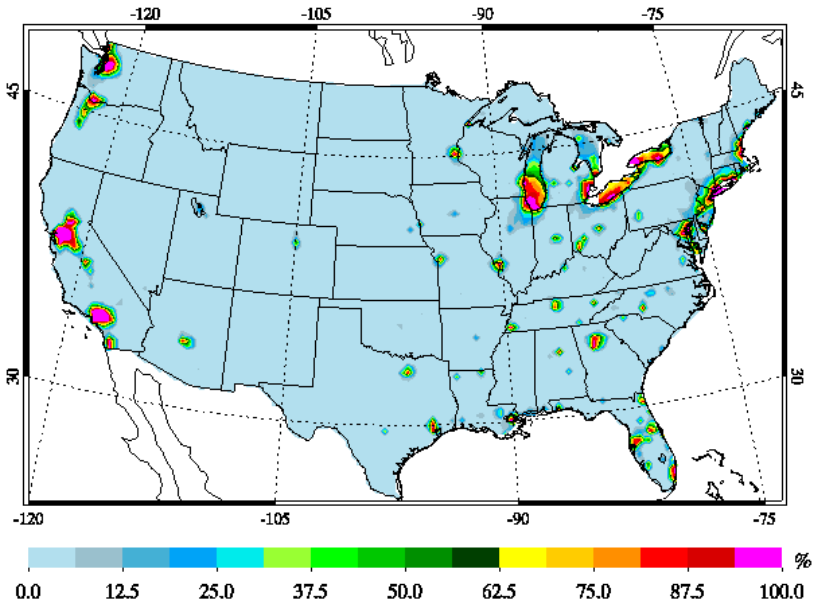


**Figure 10.** Probability of VOC-sensitive photochemical ozone production (i.e., $O_3/NO_y < 15$) in the CONUS simulated by CMAQ at 2 pm local time in July, a) 1995; b) 2005; and c) 2015

a)




b)



762 c)

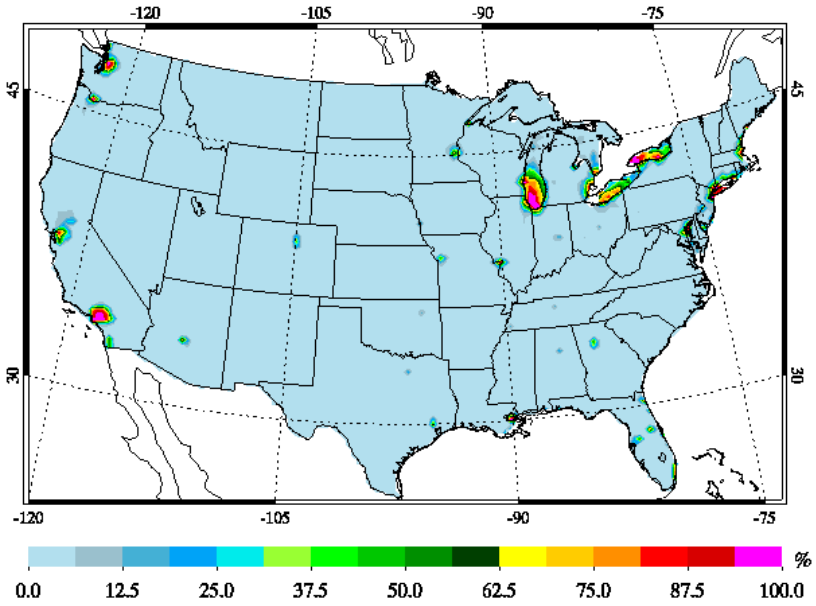



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**Figure 11.** Long-term trends in probability of VOC-sensitive photochemical production of surface ozone in three major urban areas at 2 pm in July. Probability is calculated using averages of 3 × 3 grids centered at downtown.