Reviewer #3

Comment [3-1]: This manuscript re-visits earlier work of Porter and Heald (2019) and extends it to examine specific factors driving observed trends in local relationships between ozone and temperature. While the idea that ozone-temperature relationships are in part fueled by the availability of NOx is not new (Wu et al., 2008; Zanis et al., 2022), the advance here involves quantification of the impact of the known NOx reductions over recent decades in the USA to weakening the ozone-temperature relationship recorded at local monitoring sites. Quantifying the role of the selected individual 'direct' and a few 'indirect' processes as represented in the GEOS-Chem model to the changes in these relationships as shown in Figures 5, 6, 7 is a useful benchmark against which future work may gauge the importance of changes in these and other processes in the coming years as well as to compare to findings in other models.

Response [3-1]: We thank the reviewer for the positive and valuable comments. All of them have been implemented in the revised manuscript. Please see our itemized responses below.

Comment [3-2]: The mean bias of the temperature fields is evaluated (line 100; Figure S1) but aren't the trends in near-surface temperature over this period more relevant to the present study? As it is, the mean biases could lead to errors in the ozone simulation as noted by Rasmussen et al. (2012).

Response [3-2]: We agree. We have added the following Table and analysis in Section 2.2 "We also compare temperature trends from MERRA-2 with observations over the period 1990-2021 (Table S1). While the overall trends are consistent, there are notable overestimation (e.g. NEUS, Plains) and underestimation (e.g. SEUS and SWUS) in different regions, which may lead to biases in interpreting the observed ozone-temperature sensitivity (as observed ozone variation responds to "true" air temperature)."

Table S1 Observed vs MERRA-2 T_{max} (daily maximum temperature) trend at summertime (June, July, August) (K/decade) from 1990 to 2021 in different regions.

	CONUS	**NEUS**	**Midwest**	**SEUS**	**Plains**	**Intermountain West**	**NWUS**	**SWUS**
OBS	0.20	0.01	0.68**	0.57	-0.09	0.48**	0.43	1.44**
MERRA-2	0.27*	0.10	0.58*	0.08	0.23	0.33	0.58	1.24**

**represents p-value<0.01, *represents p-value<0.05

Comment [3-3]: The lateral boundary conditions used to drive the regional nested simulation should be described in a bit more detail. Was this a continuous run, or was the global model also run for 1-month spin up and June plus July every 2 years?

Response [3-3]: Thank you for pointing it out. The lateral boundary conditions we used were simulated every two years, with each simulation covering June and July. The June simulation was treated as a spin-up period and thus discarded. Acknowledging the spin-up time of one month is relatively short, we conducted a separate simulation with a 6-month spin-up time and compared it with the BASE simulation. We find neglectable differences in ozone concentrations (0.3%) and $m_{\Delta O3\text{-}\Delta T\max}$ (2.3%) between the two simulations, suggesting that the spin-up time should not significantly affect our analysis and conclusions. We have revised the relevant description and added the following discussions in Section 2.4. "To demonstrate this, we conducted an additional set of experiments, starting with a global simulation at 2°×2.5° resolution from1st January 2017 to 1st August 2017. The global simulation on 1st June 2017 was then interpolated into the high-resolution nested grid to drive the high-resolution simulation from 1st June 2017 to 1st August 2017. A comparison of surface MDA8 ozone concentrations and ozone-temperature sensitivity between the two sets of simulations is shown in Figure S2. We find that the differences between the simulations with 1-month and 6-month spin-up times had only minor impacts on ozone concentrations and $m_{\Delta O3\text{-}\Delta T\max}$. The average differences between the two simulations were only 2.3% for ozone concentrations and 0.3% for $m_{\Delta O3\text{-}\Delta T\max}$, with high spatial consistency (r > 0.99). This confirms that using a 1-month spin-up time for the simulation should not affect the analysis and conclusions. However, a longer spin-up time is favorable for generating global chemical fields when sufficient computational resources are available."

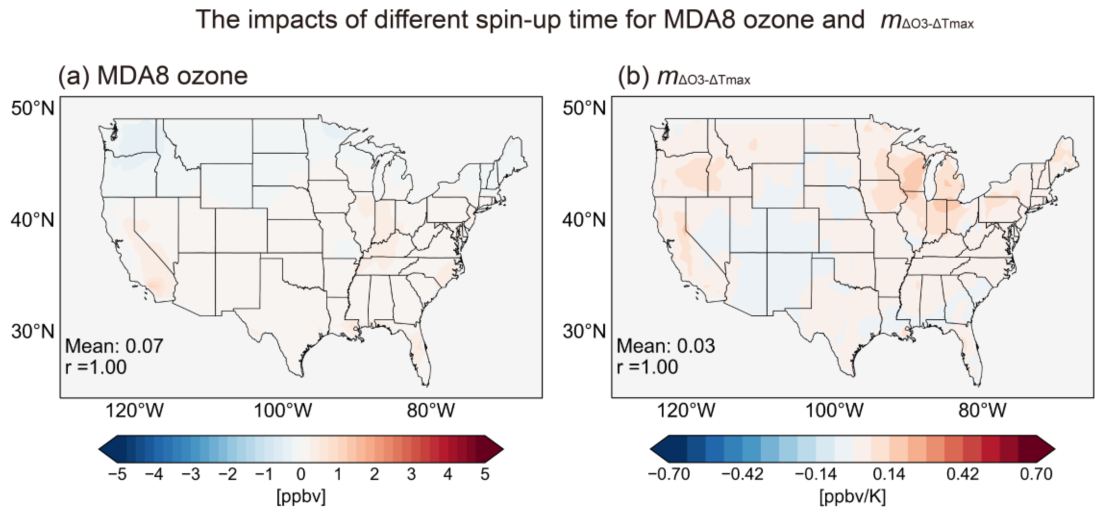

Figure S2. The impacts of different spin-up time for MDA8 ozone and $m_{\Delta O3\text{-}\Delta Tmax}$. The difference between BASE and Long spin-up time simulations in (a) MDA8 ozone and (b) $m_{\Delta O3\text{-}\Delta Tmax}$. The correlation coefficients (r) between the simulations and mean values for the CONUS sites are shown inset.

Comment [3-4]: The authors have missed some prior literature investigating how specific regional conditions shape relationships between ozone and specific meteorological variables such as temperature. Camalier et al. (2007) pointed out the weaker ozone-temperature relationship in the Southeast, which Tawfik and Steiner (2013) linked to differences in the coupling between the atmosphere and land (specifically soil moisture regimes) and suggest that surface drying is a more important predictor. Furthermore, the strong ozone-temperature relationships in the northern part of the domain has been linked to dynamics associated with the mid-latitude jet (Barnes and Fiore, 2013) and meridional transport (Kerr et al., 2020; Zhang et al., 2022). Some discussion of how the findings of this study fit in the context of those papers would be useful.

Response [3-4]: Thank you for providing the references. We have added a discussion of these studies in Section 3.1: "The higher $m_{\Delta O3\text{-}\Delta Tmax}$ in the NEUS and Midwest regions than in other regions may reflect the stronger daily variation of ozone due to rapid shift of synoptic patterns (e.g. mid-latitude cyclones) in this region during summer (Leibensperger et al., 2008). Additionally, changes in other mid-latitude dynamic systems, such as meridional movement by the mid-latitude

jet, also play a significant role in shaping the regional ozone-temperature sensitivity (Barnes and Fiore, 2013; Kerr et al., 2020; Zhang et al., 2022c). We observe a decreasing gradient in both $r_{\Delta O3\text{-}\Delta Tmax}$ and $m_{\Delta O3\text{-}\Delta Tmax}$ from north to south in the eastern United States, which aligns with previous findings (Camalier et al., 2007; Tawfik and Steiner, 2013). This observed north-to-south shift may be related to the transition in land-atmosphere coupling mechanisms due to soil moisture limitations in the southern regions (Tawfik and Steiner, 2013).”

Reference:

Barnes, E. A. and Polvani, L.: Response of the Midlatitude Jets, and of Their Variability, to Increased Greenhouse Gases in the CMIP5 Models, https://doi.org/10.1175/JCLI-D-12-00536.1, 2013.

Camalier, L., Cox, W., and Dolwick, P.: The effects of meteorology on ozone in urban areas and their use in assessing ozone trends, Atmospheric Environment, 41, 7127–7137, https://doi.org/10.1016/j.atmosenv.2007.04.061, 2007.

Leibensperger, E. M., Mickley, L. J., and Jacob, D. J.: Sensitivity of US air quality to mid-latitude cyclone frequency and implications of 1980–2006 climate change, Atmospheric Chemistry and Physics, 8, 7075–7086, https://doi.org/10.5194/acp-8-7075-2008, 2008.

Kerr, G. H., Waugh, D. W., Steenrod, S. D., Strode, S. A., and Strahan, S. E.: Surface Ozone-Meteorology Relationships: Spatial Variations and the Role of the Jet Stream, Journal of Geophysical Research: Atmospheres, 125, e2020JD032735, https://doi.org/10.1029/2020JD032735, 2020.

Tawfik, A. B. and Steiner, A. L.: A proposed physical mechanism for ozone-meteorology correlations using land–atmosphere coupling regimes, Atmospheric Environment, 72, 50–59, https://doi.org/10.1016/j.atmosenv.2013.03.002, 2013.

Zhang, X., Waugh, D. W., Kerr, G. H., and Miller, S. M.: Surface Ozone-Temperature Relationship: The Meridional Gradient Ratio Approximation, Geophysical Research Letters, 49, e2022GL098680, https://doi.org/10.1029/2022GL098680, 2022.

Comment [3-5]: Uncertainties in the model and their implications for the conclusions could be discussed more clearly. For example, the underlying assumption is that the model represents all important processes driving ozone-temperature relationships. The BB4CMIP emissions have spurious variations associated with the introduction of GFED emissions (satellite data) after 1997 (Fasullo et al., 2022), which might lead to problems for ozone trends in regions strongly influenced by fire. The dry deposition scheme only includes stomatal deposition variations with with meteorology (line 150) but non-stomatal pathways may also respond to temperature (Clifton et al., 2022).

Response [3-5]: Thank you for pointing out this issue. We have added a discussion on the model uncertainties in Section 4: "Nevertheless, there is significant room for improving the ability in capturing the ozone-temperature relationship in the chemical transport model. The GEOS-Chem simulations do not account for the response of anthropogenic NO_x and VOCs emissions to temperature. Recent studies have shown that these emissions can increase simulated regional ozone-temperature sensitivity by up to 7% and 14% (Kerr et al., 2019; Wu et al., 2024). The parameterization of several temperature-dependent processes is limited or even missing in the model. For example, the dry deposition scheme used in this study lacks the temperature response of non-stomatal pathways (Clifton et al., 2020), which could introduce uncertainty in simulated $m_{\Delta O3\text{-}\Delta Tmax}$ particularly in vegetation-rich regions such as the southeastern United States. Additionally, according to the BDSNP scheme used in this study, soil NO_x emissions are modeled as an exponential function of temperature between 0 and 30 °C, remaining constant at temperatures above 30 °C. However, some studies have reported continuous increases in soil NO_x emissions at temperatures higher than 30 °C in regions such as California (Oikawa et al., 2015; Wang et al., 2021). The absence of other temperature-dependent natural emissions, such as soil Nitrous acid (HONO) (Tan et al., 2023), may also lead to an underestimation of ozone responses to extreme temperatures in the GEOS-Chem simulations. Uncertainties in the biomass burning emission inventory (Fasullo et al., 2022) limit the accuracy of ozone-temperature sensitivity simulations in fire-impacted regions, such as the mountainous western United States. The 50 km resolution of the model may not fully capture sub-grid meteorological variations, which can play an important role in reproducing extreme conditions at site-level scales. Our study demonstrates that ozone-temperature sensitivity is highly responsive to changes in emissions, emphasizing the importance of more accurate anthropogenic emissions inventory for interpreting the ozone-temperature relationship. Further efforts are needed to enhance the model's ability to capture long-term trends in the ozone response to temperature (including underlying weather conditions and transport patterns), and to better unravel the mechanisms driving the observed ozone-

temperature relationship, in particular the role of transport and ventilation.”

Reference:

Clifton, O. E., Fiore, A. M., Massman, W. J., Baublitz, C. B., Coyle, M., Emberson, L., Fares, S., Farmer, D. K., Gentine, P., Gerosa, G., Guenther, A. B., Helmig, D., Lombardozzi, D. L., Munger, J. W., Patton, E. G., Pusede, S. E., Schwede, D. B., Silva, S. J., Sörgel, M., Steiner, A. L., and Tai, A. P. K.: Dry Deposition of Ozone Over Land: Processes, Measurement, and Modeling, Reviews of Geophysics, 58, e2019RG000670, https://doi.org/10.1029/2019RG000670, 2020.

Fasullo, J. T., Lamarque, J.-F., Hannay, C., Rosenbloom, N., Tilmes, S., DeRepentigny, P., Jahn, A., and Deser, C.: Spurious Late Historical-Era Warming in CESM2 Driven by Prescribed Biomass Burning Emissions, Geophysical Research Letters, 49, e2021GL097420, https://doi.org/10.1029/2021GL097420, 2022.

Kerr, G. H., Waugh, D. W., Strode, S. A., Steenrod, S. D., Oman, L. D., and Strahan, S. E.: Disentangling the Drivers of the Summertime Ozone-Temperature Relationship Over the United States, J. Geophys. Res. Atmos., 124, 10503–10524, https://doi.org/10.1029/2019JD030572, 2019.

Oikawa, P. Y., Ge, C., Wang, J., Eberwein, J. R., Liang, L. L., Allsman, L. A., Grantz, D. A., and Jenerette, G. D.: Unusually high soil nitrogen oxide emissions influence air quality in a high-temperature agricultural region, Nat Commun, 6, 8753, https://doi.org/10.1038/ncomms9753, 2015.

Tan, W., Wang, H., Su, J., Sun, R., He, C., Lu, X., Lin, J., Xue, C., Wang, H., Liu, Y., Liu, L., Zhang, L., Wu, D., Mu, Y., and Fan, S.: Soil Emissions of Reactive Nitrogen Accelerate Summertime Surface Ozone Increases in the North China Plain, Environ. Sci. Technol., 57, 12782–12793, https://doi.org/10.1021/acs.est.3c01823, 2023.

Wu, W., Fu, T.-M., Arnold, S. R., Spracklen, D. V., Zhang, A., Tao, W., Wang, X., Hou, Y., Mo, J., Chen, J., Li, Y., Feng, X., Lin, H., Huang, Z., Zheng, J., Shen, H., Zhu, L., Wang, C., Ye, J., and Yang, X.: Temperature-Dependent Evaporative Anthropogenic VOC Emissions Significantly Exacerbate Regional Ozone Pollution, Environ. Sci. Technol., https://doi.org/10.1021/acs.est.3c09122, 2024.

Wang, Y., Ge, C., Garcia, L. C., Jenerette, G. D., Oikawa, P. Y., and Wang, J.: Improved modelling of soil NOx emissions in a high temperature agricultural region: role of background emissions on NO2 trend over the US, Environ. Res. Lett., 16, 084061, https://doi.org/10.1088/1748-9326/ac16a3, 2021.

Comment [3-6]: Why does the model miss the observed decline in the slope after 2010 in Figure 5b? Figure S7 suggests this is occurring in the SEUS and Midwest; some of the literature referenced may be helpful for additional context in interpreting the differences across regions from the perspective of the processes that dominate in different regions.

Response [3-6]: We find that overestimation of $m_{\Delta O3\text{-}\Delta Tmax}$ after 2010 is likely due to the uncertainty in anthropogenic NO_x emissions. We have added the following discussion in Section 3.2: "The simulated ozone-temperature sensitivity for 2013–2017 shows an overestimation, particularly in the SEUS and Midwest regions (Figure S8). Christiansen et al. (2024) suggested that the CEDS inventory overestimates post-2010 anthropogenic NO_x emissions, especially in the eastern United States, which may lead to overestimation of ozone-temperature sensitivity in these regions. The GEOS-Chem model also misses several pathways in describing the responses of ozone to temperature, such as the responses in anthropogenic emission and land-atmosphere interaction through soil and vegetation. This will be discussed in detail in Section 4."

Reference:

Christiansen, A., Mickley, L. J., and Hu, L.: Constraining long-term NOx emissions over the United States and Europe using nitrate wet deposition monitoring networks, Atmospheric Chemistry and Physics, 24, 4569–4589, https://doi.org/10.5194/acp-24-4569-2024, 2024.

Comment [3-7]: The focus on NYS in Section 3.4, while interesting, appears arbitrary. What is the rationale for choosing this state? Are the correlations between ozone and temperature particularly strong there?

Response [3-7]: In Section 3.4, we focus on the impact of ozone pollution on human health under high-temperature conditions. We selected New York State (NYS) as an example because of its strong ozone-temperature correlations and high population density. This allows us to explore how emission reductions have led to a significant decrease in ozone concentrations during high-temperature events due to in the declined ozone-temperature sensitivity. We also found that this phenomenon is widespread across other regions (Figure 9b).

Comment [3-8]: The goal of Figure 9 is very interesting, but additional work would help strengthen the analysis. What are the trends in the 0-10% temperature bin values as compared to the 90-100% bins? These are likely sampling very different meteorological conditions. How does the metric used in this figure compare to the linear fit between daily ozone and temperature?

Response [3-8]: In the discussion of ozone mitigation benefit in Section 3.4, we compared the ozone-temperature relationship under different emission scenarios for the 2013-2017 climate conditions, with both sets of simulations using the same meteorological conditions (so no trends in temperature is involved). As you mentioned the 0-10% and 90-100% temperature bins represent significantly different meteorological conditions across regions (Figure R1a). We compared the ozone mitigation benefit, as defined in our study, with the reduction in ozone-temperature sensitivity calculated using the decreased $m_{\Delta O3\text{-}\Delta Tmax}$, and found that the two metrics are nearly identical (Figure R1b). We further analyzed the probability of ozone exceedance under high-temperature conditions before and after emission reductions, emphasizing the impact of the benefit by reducing $m_{\Delta O3\text{-}\Delta Tmax}$ in section 3.4: "This benefit significantly reduces the probability of ozone exceedance (MDA8 ozone > 70 ppbv) during high-temperature conditions (above the 90th percentile of T_{max}), from 70% (estimated from the 1995E simulation) to 28% (from the BASE simulation)."

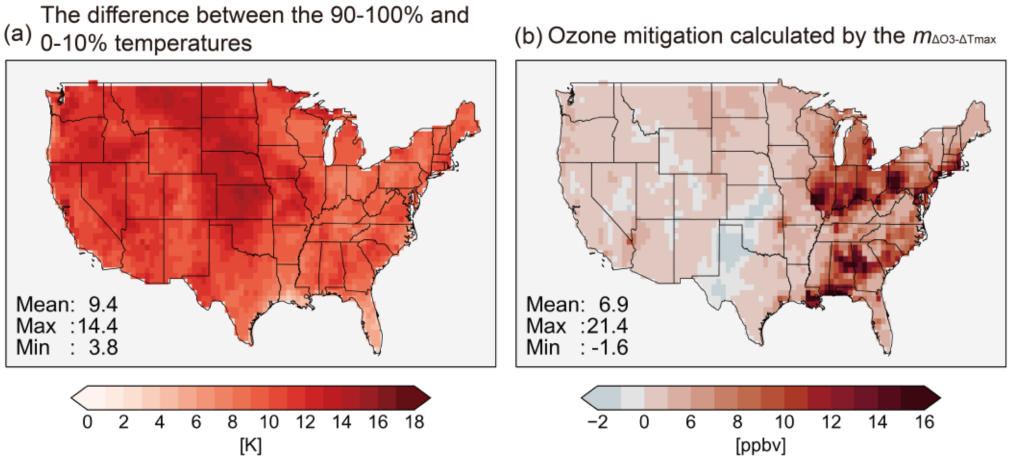

Figure R1. (a) The distribution of the difference between the 0-10% and 90-100% temperatures bins. (b) Distributions of ozone mitigation benefit in July due to the decreased $m_{\Delta O3\text{-}\Delta Tmax}$, estimated as the difference $m_{\Delta O3\text{-}\Delta Tmax}$ between the 1995E and BASE multiplied by the temperature difference from the 0-10% to 90-100% bins at each grid in July (2013,2015 and 2017). Mean, max, and min

values for the 608 sites are shown inset.

Comment [3-9]: The data availability statement regarding the model simulations, which are critical to the conclusions drawn in the paper, does not appear to align with current best practices in sharing data for open science. Will the authors provide at least the datasets behind their figures, or a limited set of diagnostics from their simulations in a public repository to allow future studies to easily re-visit and extend their findings?

Response [3-9]: We agree. Upon acceptance, we will update the Data Availability section accordingly to include a link to the repository and ensure that all relevant data is accessible for further research.

Comment [3-10]: Line 12: In what applications are ozone-temperature relationships being used to predict the impacts of future climate change? The overall weak correlations (Figure 2; Table S1; low r values indicate that even at best less than half the variance is captured) suggest this is not a very useful metric for prediction.

Response [3-10]: Thank you for your comment. High ozone-temperature sensitivity often indicates a region's heightened risk of climate penalties. While this metric may not precisely predict the exact increase in ozone due to climate change, it still serves as a useful reference for assessing potential risks in future scenarios. To more accurately convey our point, we have replaced "predict" with "infer."

Comment [3-11]: line 67: It seems relevant to compare the r-values for model versus observations too.

Response [3-11]: We agree. We have revised as: "<u>In this study, we analyze the present-day (2017-2021) and long-term trends (1990-2021) in the summertime surface ozone-temperature relationship in the continental US.</u>"

Comment [3-12]: Lines 114-115: What type of linear regression method is used to quantify the trend?

Response [3-12]: We used a univariate linear regression based on the least squares method to quantify the long-term trend in ozone-temperature sensitivity.

Comment [3-13]: Lines 137-142. The discussion of BDSNP is very confusing. The scheme is described but then line 141 suggests it isn't used, "but here we do not implement this scheme...". Please explain more clearly.

Response [3-13]: We apologize for the confusion. Our intention was to highlight that the current parameterization scheme for soil NO_x has certain limitations, which may introduce additional uncertainties into the study's results. We have moved this discussion to Section 4, where we provide a more comprehensive overview of the potential model uncertainties.

Comment [3-14]: Figure 2. The color bar hides the relatively weak correlations across much of the country.

Response [3-14]: The color bar of $r_{\Delta O3\text{-}\Delta Tmax}$ ranges from -0.2 to 1.0, so light colors indicate weak correlations. We find that 568 of 608 sites are with p-value<0.1, as indicated by the borders.

Comment [3-15]: Figures 3b & 4. Are the values plotted meaningful in regions where the correlations are weak? It may be worth considering a screening that only plots for p-values above some threshold (0.10?).

Response [3-15]: Following your suggestion, we have revised the Figure 3b to include only sites with $r_{\Delta O3\text{-}\Delta Tmax}$ p-values<0.01.

Comment [3-16]: In Figure 4, the errors on the values of the slopes seem fairly large for the individual months (a lot of scatter).

Response [3-16]: We agree. The scatter in the slope values for individual months is due to the

model's weaker ability to capture the ozone-temperature response relationship in certain regions. Our intention is to provide an objective representation of the model's performance. We hope that future developments in atmospheric chemistry transport models will help reduce the bias.

Comment [3-17]: Lines 423-236. The increasing role of soil NOx on U.S. air quality has been noted in some other recent work as well; see for example Guo et al. (2018) and Geddes et al. (2022). Guo et al. (2018) also suggest that soil NOx may be contributing to ozone biases in GEOS-Chem.

Response [3-17]: Thank you for pointing this out. We have cited these references in Section 3.3.

Comment [3-18]: In Section 4, it would be useful to summarize how NOx has declined over this period, and whether the largest drops in the slopes/correlations have occurred in locations where anthropogenic NOx has decreased the most.

Response [3-18]: Thank you for pointing this out. We have added a description in the main text: "During the period from 1990 to 2021, anthropogenic NO$_x$ emissions in the United States decreased by approximately 69%, and the eastern United States, where stricter anthropogenic emission controls were implemented, is the core region where ozone-temperature sensitivity has declined the most."

Comment [3-19]:

Line 132 and elsewhere: biologic à biogenic?

Line 191 caption of Figure 2 black boarder à border

Line 255 least à smallest or weakest

Line 278 transportation à transport

Line 384 caption of Figure 8 temperature-indirect à temperature-direct ?

Response [3-19]: Thank you for pointing it out. We corrected them accordingly.

Comment [3-20]: Line 442 what is "ozone migration"?

Response [3-20]: We have corrected it.

Comment [3-21]: Line 468. Is this a spatial correlation of the slopes from the model vs observations?

Response [3-21]: This is the ratio of the ozone-temperature sensitivity trends between model (-0.28 ppbv/K/decade) and the observations (-0.67 ppbv/K/decade).