Reply to comments from Referee #1 on "Representing the effects of stratosphere-troposphere exchange on 3D O_3 distributions in chemistry transport models using a potential vorticity based parameterization" by Xing et al.

We thank the reviewer for the detailed and thoughtful review of our manuscript. Incorporation of the reviewer's suggestion has led to an improved manuscript. Detailed below is our response to the issues raised by the reviewer. We also detail the specific changes incorporated in the revised manuscript in response to the reviewer's comments.

[Comment]: *The manuscript introduces a new parameterization for representing vertical, latitudinal, and seasonal variations in upper tropospheric/lower stratosphere (UT/LS) ozone within regional air quality modeling systems. The parameterization is based on regressions between modeled potential vorticity (PV) and observed ozone profiles. Observed ozone is based on measurements from 44 northern hemisphere World Ozone and Ultraviolet Radiation Data Centre (WOUDC) sites. The modeled PV is based on a 21 year (1990-2010) coupled Weather Research and Forecasting (WRF) Community Multi-scale Air Quality (CMAQ) model. The new parameterization is able to account for the significant spatial and temporal variation in O3/PV ratios above 100 hPa and thus provides a much more generalized approach then used in previous studies. The impact of the new parameterization is evaluated by comparing a set of 1 year (2006) WRF-CMAQ simulations with WOUDC and surface measurements. Results show that the new parameterization significantly reduces low biases in the UT/LS compared to simulations with a fixed O3/PV ratio of 20 ppb/PVu resulting in positive impacts at the surface in spring. However, the new parameterization increased the high bias in surface ozone during autumn, resulting in negative impacts during this period. The methodology for developing the new parameterization, results, and conclusions are clearly presented and the work is highly relevant to the air quality modeling community. Figures and Tables in the main body of the manuscript are appropriate as are the supplemental figures.*

[Response]: We thank the reviewer for the overall positive assessment of the manuscript and recognition of the implications of the results of the analysis presented.

[Comment]: *The O3/PV parameterization relies on the assumption that both O3 and PV are conserved on planetary and synoptic transport time-scales, which is appropriate at middle and high latitudes of the UT/LS. However, in the tropics, sub-grid-scale convective transport largely determines the vertical distribution of ozone while differential diabatic heating due to convective latent heating/cooling introduces a source of UT/LS PV. As a result, the slope of O3/PV verses pressure shows a great deal of scatter for latitudes less than 30N (Figure S2 in the manuscript). This introduces significant uncertainties in the O3/PV regression in the tropical UT/LS and needs to be acknowledged. As a result, the new parameterization leads to increased Normalized Mean Errors (NME) compared to the reference simulation in the tropical UT/LS (Figure 5f in the manuscript). A discussion of the appropriateness of using the new O3/PV parameterization in the tropics needs to be included in the manuscript.*

[Response]: We agree with the reviewer that in the tropics, convective transport plays a significant role in shaping the vertical ozone profile which cannot be fully represented by the UTLS PV. The uncertainties in the O_3-PV regression in the tropical UTLS as pointed by the reviewer is also suggested by the poor correlation between O_3 and PV at latitudes south of 30N (Figure S2), resulting in an increased NME in Sim-ref in the tropical UTLS (Figure 5f). We agree with the reviewer that this aspect should be further elaborated in the discussions. Following the reviewer's suggestion, in revised manuscript, we provided additional discussion of the appropriateness of using the new O_3/PV parameterization in the tropics, as below:

(Page 3 Line 31-33) "Poor correlation between O_3 and PV is found for latitudes south of 30N (Figure S2). This is in part because in the tropics, convective transport plays a significant role in shaping the vertical ozone profile. Consequently, PV alone may not be able to robustly represent UT/LS O_3 in the tropics."

(Page 5 Line 26-27) "An increased NME in Sim-ref is found in the tropical UT/LS, indicating the uncertainty in applying the new O_3/PV parameterization in the tropics."

[Comment]: *Figure 5 (d) in the manuscript shows that the reference simulation Normalized Mean Bias (NMB) exhibits the classic "C" shaped signature of convective transport and suggests that overestimates in low-level ozone lead to overestimates in tropical UT/LS ozone mixing ratios in the reference simulation. This should be discussed as well.*

[Response]: We agree that the overestimates in both low-level and UT/LS ozone mixing ratios indicates the influence of the convective transport in the tropics. At the reviewer's suggestion, we provided additional discussion in the revised manuscript, as below:

(Page 5 Line 21-24) "The overestimates in both low-level and UTLS ozone mixing ratios exhibited in the C-shaped signature in the NMB in Sim-ref is also indicative of the likely influence of convective transport on three-dimensional O_3 distributions in the tropics (e.g., Doherty et al., 2005), that is not adequately captured by the current parameterization."

Reference:

Doherty, R. M., Stevenson, D. S., Collins, W. J., and Sanderson, M. G.: Influence of convective transport on tropospheric ozone and its precursors in a chemistry-climate model, Atmos. Chem. Phys., 5, 3205-3218, doi:10.5194/acp-5-3205-2005, 2005.

[Comment]: *Page 1 line 13: The PV based function does not result in assimilation of UT/LS O3 within WRF-CMAQ. I suggest changing "numerically assimilate" to "parameterize".*

[Response]: The "numerically assimilate" has been changed to "parameterize" in the revised manuscript.

[Comment]: *Page 1 line 14: Change "parameterized" to "developed".*

[Response]: The "parameterized" has been changed to "developed" in the revised manuscript.

[Comment]: *Page 1 line 20: Change "new function" to "new parameterization"*

[Response]: The "new function" has been changed to "new parameterization" in the revised manuscript.

[Comment]: *Page 1 line 22: Change "new function" to "new parameterization"*

[Response]: The "new function" has been changed to "new parameterization" in the revised manuscript.

[Comment]: *Page 2 lines 10-26: Suggest adding a statement that co-variances between O3 and other species are not accounted for, which might introduce some inconsistencies in the chemistry*

[Response]: The statement as suggested by the reviewer has been added in the revised manuscript as below:

(Page 2 Line 25-27) "One thing should be noted that such PV based parameterization only modifies the O_3 mixing ratio, however, co-variances between O_3 and other species are not accounted for in such modifications which might introduce some inconsistencies in the chemistry in the model's UTLS."

[Comment]: *Page 2 line24: Change "numerically assimilate" to "parameterize"*

[Response]: The "numerically assimilate" has been changed to "parameterize" in the revised manuscript.

[Comment]: *Page 2 line 25: Change "parameterization" to "development"*

[Response]: The "parameterization" has been changed to "development" in the revised manuscript.

[Comment]: *Page 2 line 33: Add comment on how many vertical levels are above 100hPa*

[Response]: The information of vertical levels is added in the revised manuscript as below:

(Page 2 Line 36-37) "44 vertical layers of variable thickness between the surface and 50 hPa (approximately 3 vertical levels above 100hPa)"

[Comment]: *Page 3 line 35: Please comment on the overestimate in the amplitude of the seasonal cycle.*

[Response]: The discrepancy in the amplitude of the seasonal cycle between the parametrization and the observations arises due to the difference in the number of sites these curves are representative of. The observed curve was based on data from all sites, while the parameterized curve (red) utilized information only from locations north of 40N. We chose to base the seasonal variations only at sites >40N because that is where the seasonal variability was the strongest. We however agree that this is likely to cause some confusion. Thus we have revised figure 3 (see Figure C1) to now also include observed seasonality based on both (i) all sites, and (ii) sites at latitudes north of 40N.

We clarify it in the revised manuscript as below:

(Page 4 Line 2-6) "The seasonal variability in the O_3-PV correlation also varies with latitude. The influence of convective transport on PV in the tropics, as discussed before, also results in weaker seasonal variations in the O_3-PV correlation at low latitudes. This is seen in Figure 3, which compares the seasonal variations in this relationship inferred from (i) all sites, and (ii) sites at latitudes north of 40N. Thus to ensure that the parameterization more faithfully captures the seasonality at the higher latitudes, where it is strongest, we parameterize the temporal variations only on data at locations with latitudes north of 40N."

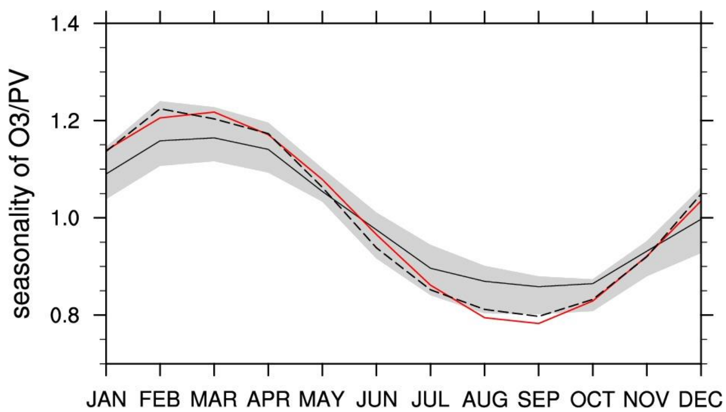


Figure C1: Seasonality of O_3/PV (Annual mean= 1, black solid line=observed mean at all sites, grey, black dash line= observed mean at sites at latitudes north of 40N, red line = fitted by function)

<u>[Comment]:</u> *Page 3 lines 36-38: How well does the new parameterization handle LS ozone loss during Arctic springtime?*

[Response]: Basically, the new parameterization is based on long-term observations, thus is able to capture the LS ozone loss which is reflected in the observation. We examined the arctic ozone trend over the past two decades and generally the new parameterization displays good performance in capturing the ozone level and its seasonal variability, as shown in Figure C2. However, it might not be able to capture the potential trend driven by factors other than PV, such as chemistry.

We have clarified this issue in the revised manuscript, as below:

(Page 4 Line 8-11) "Additionally, since only the O_3-PV correlation is considered in the parameterization, the potential trend driven by factors other than PV (e.g., chemistry) cannot be captured by the current parameterization. However, the effects of processes which are already reflected in the observation (e.g., seasonal variations such as lower stratosphere ozone loss during Spring) are implicitly captured in the parameterization."

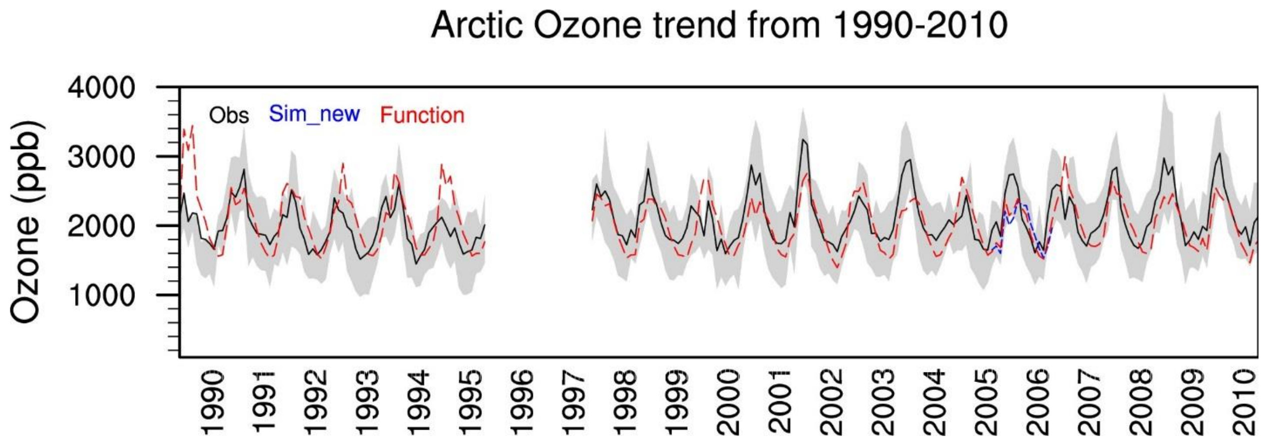


Figure C2: O_3 trend in the top layers (pressure<100hPa) in the Arctic (latitude>75N)

[Comment]: *Page 5 lines 7-12: Please comment on the role of convective transport coupling the UT/LS and lower level overestimates (see specific comments)*

[Response]: The discussion of the role of convective transport to explain the overestimates of UT/LS and lower level O3 has been added in the revised manuscript, as below:

(Page 5 Line 21-24) "The overestimates in both low-level and UTLS ozone mixing ratios exhibited in the C-shaped signature in the NMB in Sim-ref is also indicative of the likely influence of convective transport on three-dimensional O_3 distributions in the tropics (e.g., Doherty et al., 2005), that is not adequately captured by the current parameterization."

Reference:

Doherty, R. M., Stevenson, D. S., Collins, W. J., and Sanderson, M. G.: Influence of convective transport on tropospheric ozone and its precursors in a chemistry-climate model, Atmos. Chem. Phys., 5, 3205-3218, doi:10.5194/acp-5-3205-2005, 2005.

[Comment]: *Figure 4: Sim-new maps should be the same size as the WOUDC and Sim-ref maps.*

[Response]: We adjusted the size of Sim-new maps to be the same size as the other two in the revised manuscript.

Reply to comments from Referee #2 on "Representing the effects of stratosphere-troposphere exchange on 3D O_3 distributions in chemistry transport models using a potential vorticity based parameterization" by Xing et al.

[Comment]: *The authors derive an empirical correlation between stratospheric ozone and potential vorticity from two sets of data, with PV from the 21-year WRF simulation and ozone from WOUDC radiosondes during the same period. Specifically, they fit the ratio of ozone to PV as an order-5 polynomial function of latitude and an order-2 polynomial function of pressure (height). The temporal fitting, representing the seasonal variation, is done using a sine function with adjustable amplitude and phase. The spatial fitting is applied to the annually averaged data, so that the fitted model is given by a separable function of time and space. The applicable vertical domain is from 50-100 hPa. The parameterization is then applied to the WRF model to obtain the stratospheric ozone concentration that couples to the air quality model (CMAQ) for year-2006 simulation. The authors give two reasons why they did this study: (1) there is no stratospheric chemistry scheme available in the regional model (2) there is a wide range of measured O3/PV ratio values. The putative success of this parameterization is shown in the one-year simulation (Sim-new) where the results are compared to a reference simulation(Sim-ref) where O3/PV is simply set to be 20ppb/PVU.*

[Response]: We thank the referee for the thoughtful and detailed review of our manuscript. Incorporation of the reviewer's suggestions has led to a much improved manuscript. Below we provide a point-by-point response to the reviewer's comments and summarize the changes that have been incorporated in the revised manuscript.

[Comment]: *My overall impression is that the authors didn't give much thought in formulating their parameterization (as I explain below). Nor did the authors try to articulate clearly why fitting polynomial functions of higher orders will be better than using the linear correlation in the context of what we already know about stratospheric dynamics and mixing, the photochemical source/sink of ozone and the processes that lead to non-conservation of PV. In my view, if the authors reviewed the stratospheric mixing literature, they could have designed better parameterization and experiments.*

[Response]: We agree with the reviewer that as with most parameterizations, the development of a generalized functional relationship between O_3 and PV can be further improved. In specific, the function could be better if source and sink of O_3 involved in the stratospheric dynamics had been considered in the formulation of the function. However, the design of such a function would require an extensive effort to make the function comply with or redesign the current physics and chemistry structure in the model. It should be noted that most tropospheric chemistry-transport models do not include a representation of stratospheric chemistry in part because the vertical extent (and the resolution employed in the UT/LS) is often limited and also because typical integration time periods are inadequate to represent stratospheric chemistry impacts. The primary motivation of this study is thus to investigate the development of a practical approach to represent the potential impacts of stratosphere-troposphere exchange processes on tropospheric 3D O_3 distributions. Unlike most previous tropospheric CTM-based studies that have specified O_3 with a fixed scaling factor, here we have attempted to develop a more generalized functional relationship that can capture the seasonal and latitudinal variations in the O_3-PV correlation, especially at the higher latitudes. To our knowledge, there are no available functional relationships that can be used for this purpose. We do acknowledge that the current parameterization has some limitation and can be further improved – see for instance the revisions incorporated in response to Referee #1 comments related to representation of UT/LS O_3 in the tropics. Additionally, we feel that the suitability, evolution and performance of any parameterization should also consider practical aspects such as the model vertical grid resolution, especially in the UT/LS.

To address the reviewer's concern, we have modified the discussion in the revised manuscript as below:

(Page 7 Line 15-17) "Further improvements to the parameterization should be explored through more detailed analysis of mixing process in the UTLS, through more detailed investigation of the impact of stratospheric chemistry, and improvements in the performance of the parameterizations for conditions representative of the tropical UTLS."

[Comment]: *If the authors want to make the case that this is a simple paper based on "big data" statistical approach where the data are trained to relate one variable (PV) to another (ozone) by fitting polynomial functions with no need to discuss the underlying physics and atmospheric dynamics, the authors are then compelled to work out the uncertainty range of the coefficients in Table 1. Is the 20-year data long enough to obtain stable coefficients? If the data are split into two 10-year periods, are the coefficients very different from each other and if implemented in the simulation, would the results be very different from those in the 20-year run?*

[Response]: It is important to note that in developing the O_3-PV relationship in this study, we attempted to use all possible available data. Thus we leveraged the existence of a 21-year simulated record of PV in the UTLS with corresponding O_3 observations. The relationship developed can thus be considered to be "climatologically" representative rather than representing a specific time period or location. No particular year is used as a training data set. The choice of 2006 for model evaluation was simply based on the fact that this calendar year is also being used for many other assessments with the hemispheric CMAQ because of the availability of additional field campaign data sets (e.g., INTEX-B, IONS, TEXAQS). The good performance with the 2006 upper air observation in fact helps build greater confidence in applicability of the climatological O3-PV relationship. We have recently also completed simulations for the year 2010 and initial analysis suggest similar performance improvements.

Nevertheless, the reviewer raises a good point on the sensitivity of our methodology (and the derived coefficients in the proposed functions) to the length of the data record used. To further investigate the reviewer's question, we split the data into two 10-year periods, i.e., 1990-2000, and 2000-2010. As seen in Figure S8 (Figure C3), the differences between the coefficients derived using different data sets are relatively small. The functions based on data from 1990-2000 and 2000-2010 look quite similar to each other and both are similar to the one based on 21year period used in this study. Further to illustrate that the parameterization is not "trained" for a specific year, we leave out data for the year 2006, and used the remaining 20 years data to parameterize the function. The 2006-leave-out function looks very close to the full-21-years function, and the discrepancy between all coefficients is less than 20%. Therefore, the function parameterized in this study is not specific to a time or location, but rather designed to capture the average variability represented in the long-term record. This information is now included in the revised supplemental information material accompanying the revised manuscript.

To address the reviewer's concern, we clarify this point in the revised manuscript as below:

(Page 7 Line 6-15) “It is important to note that we attempted to use all possible available data in developing the O3-PV relationship in this study. Thus we leveraged the existence of a 21-year simulated record of PV in the UTLS with corresponding O3 observations. The relationship developed can thus be considered to be “climatologically” representative rather than representing a specific time period or location. No particular year is used as a training data set. The stability of the function has been examined by leaving out the year of 2006 for parameterization, and results show that the resulting function barely changed due to this perturbation, suggesting the function parameterized in this study is not specific to a time or location, but rather designed to capture the average variability represented in the long-term record. Figure S8 presents a comparison of the O_3-PV functions developed using different lengths of data records. As illustrated by the results, the inferred functions are quite similar across these different data sets, thereby providing some confidence in its robustness in representing the seasonal and latitudinal variations in O_3-PV.”

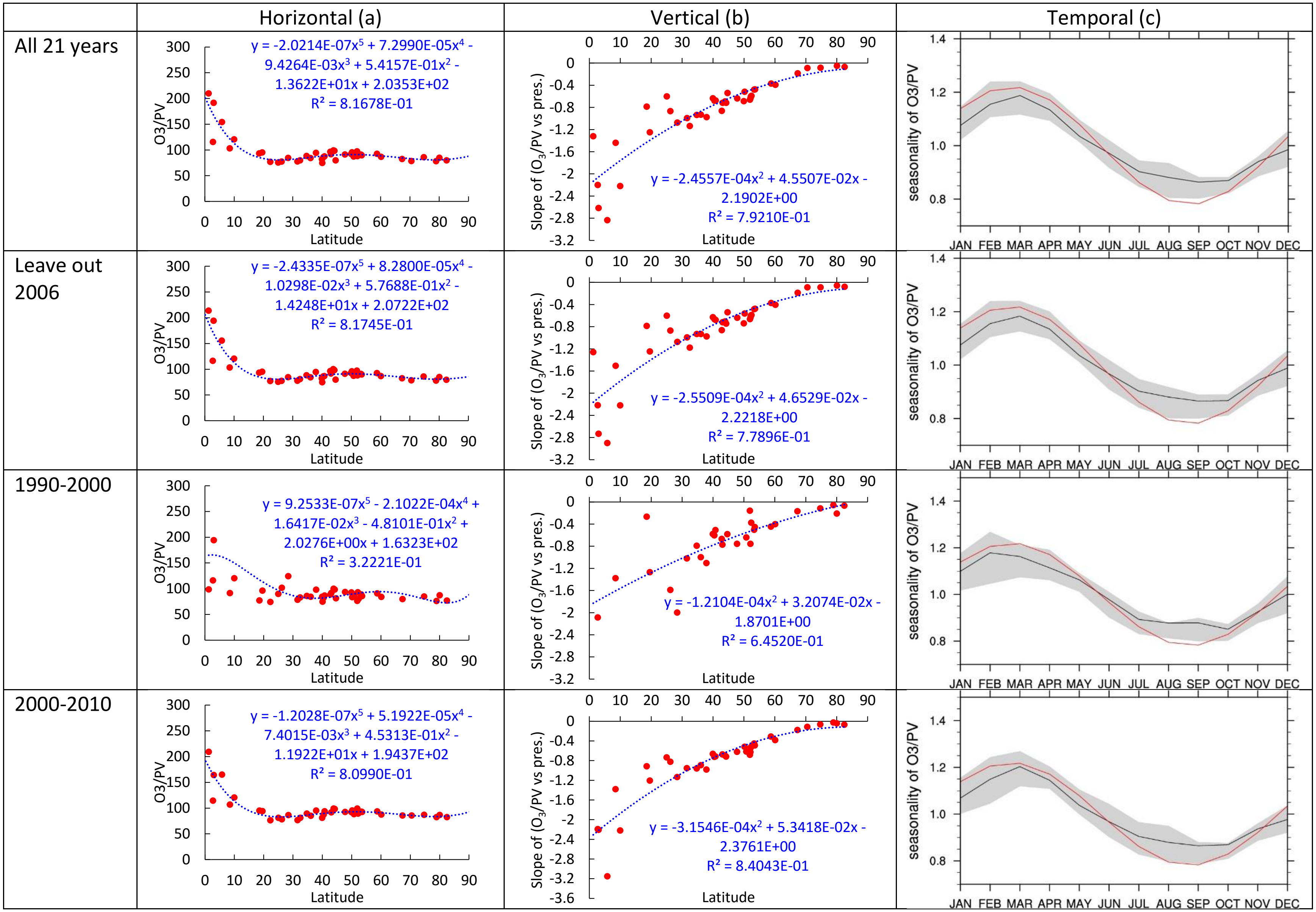


Figure C3: Sensitivity analysis for the PV function

[Comment]: *I suspect because the parameterization is confined to the region between 50 and 100hPa, for Sim-new, the free tropospheric ozone concentrations are likely biased high, particularly worse in the winter when the tropopause is the lowest. Here is my reasoning. The tropopause height changes seasonally and STE occurs at the tropopause in connection with the lowermost stratosphere. The tropopause over winter mid- and high-latitudes can be as low as 300 hPa. In other words, the parameterization completely missed the lowermost stratosphere (LMS, defined as the volume enclosed by the 380K isentropic surface/or alternatively the 100hPa isobaric surface at the top and the tropopause below) where the isentropic mixing delivers air and ozone mass across the tropopause. In my view, if one feels compelled to parameterize ozone using PV, then the crucial region where this needs to be done well is the LMS region to capture the isentropic mixing. Even we assume that the Brewer-Dobson circulation transports the correct amount of ozone to the LMS when using the authors' parameterization, and that the model does the correct mixing, one would still expect that the resulting ozone would still be biased high because of the missing midlatitude photochemical ozone loss in the LMS.*

[Response]: We agree with the reviewer that indeed a parameterization such as this could be extended to lower levels, but in this initial study we did not since most regional scale models do not have sufficient vertical resolution in the LMS. In fact early sensitivity simulations, clearly showed that model results were sensitive to the vertical resolution employed (see for instance Mathur et al., 2008; available at: https://www.cmascenter.org/conference/2008/agenda.cfm). To specify O_3-PV down to 300mb would also require a much finer vertical resolution. Nevertheless, we agree that the reviewer raises a good point that will be investigated in more detail in future studies and in further evolution of this parameterization. It should however be noted that photochemical loss for O_3 in the portions of the LMS included in the model's vertical extent, is represented based on the detailed tropospheric chemistry mechanism used in the modeling system.

To clarify this issue, we have provided the following discussion in the revised manuscript as below:

(Page 7 Line 17-21) "A limitation of this study it that the current model setting lacks sufficient vertical resolution in the lowermost stratosphere. To minimize effects of artificial numerical diffusion associated with the current limited vertical resolution employed in the model, we limit the application of the parameterization to between 100-50mb. Future studies with a much finer vertical resolution, especially to adequately capture the seasonal variation in the tropopause height are suggested to further help evolve the O_3-PV parameterization and its practical use."

[Comment]: *For the reference case (Sim-ref) the specification of 20 ppb/PVU guarantees a large underestimation of stratospheric ozone as well as a large underestimation of ozone fluxes into the troposphere. It is very common in the literature that the tropopause is defined as the surface of PV= 2 PVU or Ozone =100 or 150 ppb of ozone. These isopleths are in close proximity. This is equivalent to 50-75 ppb/PVU near 150 to 300 hPa. Thus this sim-ref specification of 20 ppb/PVU is not only way too low for 50hPa as the authors already mentioned but is just too low in general. Another way to confirm my suspicion is to check the Sim-new's coefficients at zero-order (constant term) in Table 1, which I presume is the leading term. Indeed, they are 62, 151 and 203 ppb/PVU at 95, 76 and 58 hPa, much larger than 20 ppb/PVU, even near 100hPa. Thus the major finding that Sim-new corrects the negative bias of Sim-ref but overcorrects it for the autumn and winter seasons is largely expected (Page 9).*

[Response]: Yes, we agree that the 20ppb/PV unit parameterization will underestimate as it does not account for any variations in the O3-PV relationship in space and time. That precisely is the reason why we embarked on developing this parameterization.

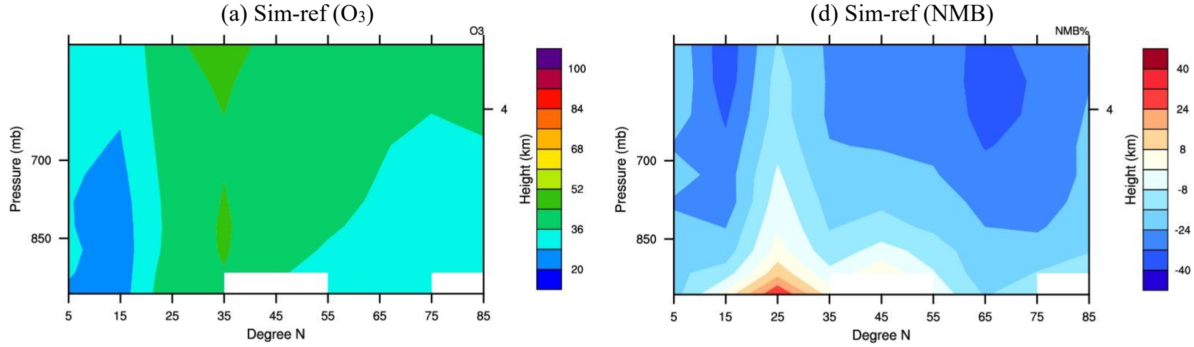
<u>[Comment]: </u>*It would be also helpful to see more comparisons of vertical profiles in the free troposphere alone between Sim-ref, Sim-new and WOUDC for the mean and variability of ozone. The log10(ozone) in Fig. 5 only gives a rough sense of magnitude dismatch, mainly that Sim-ref is too weak. The authors should zoom in on the free troposphere for more assessment.*

[Response]: The comparisons of vertical profiles in the free troposphere between Sim-ref, Sim-new and WOUDC are given in the Figure S6 (Figure C4). The free- tropospheric ozone is significantly underestimated in Sim-ref. The low bias is reduced in the new simulation with O3-PV parameterization, particularly in mid- and high- latitude regions.

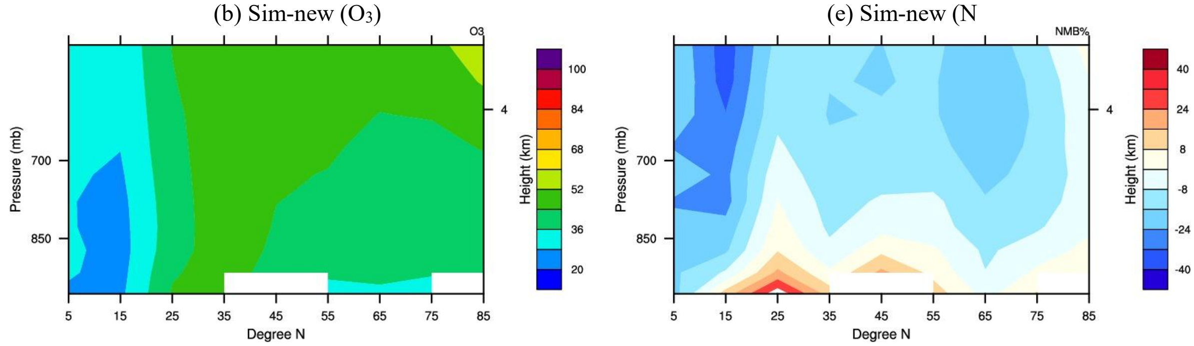
We provided the additional plots as the support information in the revised manuscript.

(Page 5 Line 27-30) “The comparison of vertical profiles in the free troposphere between Sim-ref, Sim-new and WOUDC is given in Figure S6. The free- tropospheric ozone is significantly underestimated in Sim-ref. The low bias is reduced in the simulation with the new O_3-PV parameterization, particularly in mid- and high- latitude regions.”

(a) Sim-ref (O_3) (d) Sim-ref (NMB)



(b) Sim-new (O_3) (e) Sim-new (N



MB)

(c) Obs (O3) (f) *ΔSim (NME)

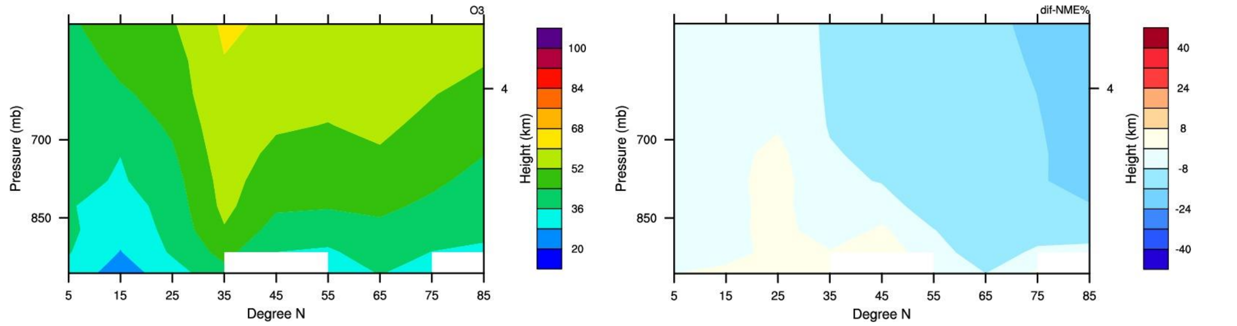


Figure C4. Zonal mean profiles of ozone and error metrics for the different cases in free troposphere (pressure>500mb). (a) Simulated ozone profile in reference case; (b) Simulated ozone profile in new case with updated O_3-PV parameterization ; (c) Observed ozone profile, the annual mean of measurement time period for each WOUDC site across the northern hemisphere; (d) Normalized Mean Bias in the reference simulation; (e) Normalized Mean Bias in the new simulation with updated O_3-PV parameterization; (d) Difference in Normalized Mean Errors between the new simulation and reference simulation (unit: ppb, 2006 Jan-Dec; NMB- Normalized Mean Bias; NME-Normalized Mean Error; *ΔSim= Sim-new minus Sim-ref in NME)

[Comment]: *It is also better to present pressure height in km or pressure in hPa instead of model layers number in Fig. 5. And more efforts are needed for caption descriptions.*

[Response]: The Y scale of Figure 5 has been changed to show both “height in km and pressure in mb” as the reviewer suggested. The figure caption has also been modified, as below:

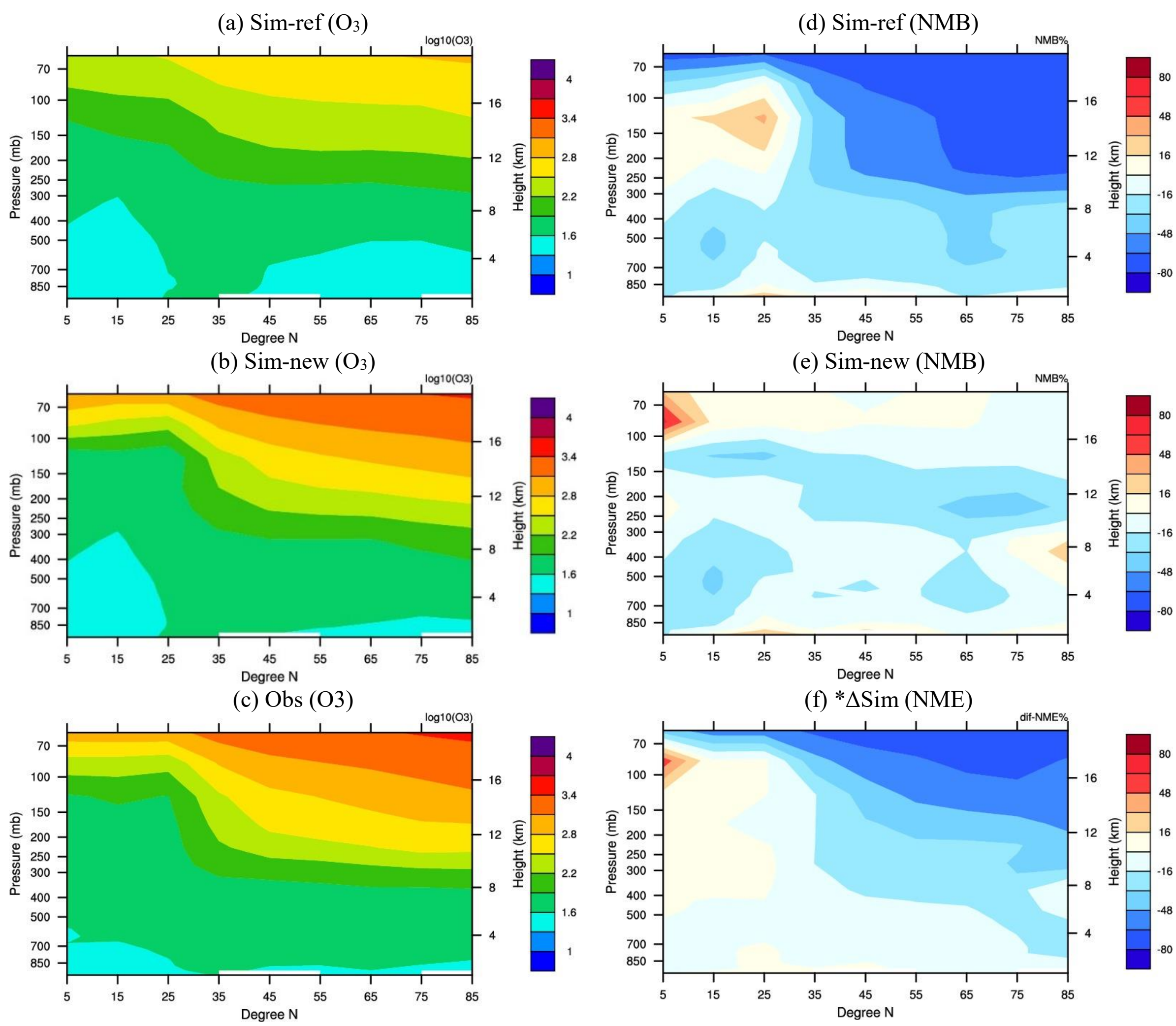


Figure C5: Zonal mean profiles of ozone and error metrics for the different cases. (a) Simulated ozone profile in reference case; (b) Simulated ozone profile in new case with updated O_3-PV parameterization ; (c) Observed ozone profile, the annual mean of measurement time period for each WOUDC site across the northern hemisphere; (d) Normalized Mean Bias in the reference simulation; (e) Normalized Mean Bias in the new simulation with updated O_3-PV parameterization; (d) Difference in Normalized Mean Errors between the new simulation and reference simulation (unit: ppb, 2006 Jan-Dec; NMB- Normalized Mean Bias; NME-Normalized Mean Error; *ΔSim= Sim-new minus Sim-ref in NME)

[Comment]: *Ultimately this paper is about surface ozone. Judged from Table 3, the surface ozone errors seem quite insensitive to the input of stratospheric ozone (Sim-ref vs Simnew). Have the authors looked into the coupling scheme between the free troposphere and the planetary boundary layer in CMAQ? Any other option for representing the boundary-layer turbulence?*

[Response]: As illustrated in Table 3 and Figure 8, errors in surface O_3 predictions are quite sensitive to the treatment of stratospheric ozone during spring. Compared to available measurements, the new O_3-PV parameterization results in much improved model performance statistics for surface O_3 during spring. The accurate representation of 3D transport mechanisms in models is critical for accurately representing the impacts of the stratosphere on lower tropospheric and boundary layer ozone – thus representation of transport by both resolved and sub-grid clouds in addition to the PBL scheme is important. The current PBL scheme in CMAQ is based on ACM2 planetary boundary layer (PBL) model (Pleim, 2007a, b). The scheme has been carefully constructed and implemented in both WRF and CMAQ to maintain consistency in the representation of mixing for both meteorological parameters as well as chemical species. It's been tested and applied in many previous studies and evaluated through comparisons with measurements of vertical profiles of various parameters. However, as suggested by the reviewer, it may be interesting to explore the use of a different PBL scheme in WRF (and CMAQ) model and will be explored in future studies.

Reference:

Pleim, J. E.: A Combined Local and Nonlocal Closure Model for the Atmospheric Boundary Layer. Part I: Model Description and Testing, J. Appl. Meteorol. Clim., 46, 1383–1395, doi:10.1175/JAM2539.1, 2007a.

Pleim, J. E.: A Combined Local and Nonlocal Closure Model for the Atmospheric Boundary Layer. Part II: Application and Evaluation in a Mesoscale Meteorological Model, J. Appl. Meteorol. Clim., 46, 1396–1409, doi:10.1175/JAM2534.1, 2007b.

Representing the effects of stratosphere-troposphere exchange on 3D O_3 distributions in chemistry transport models using a potential vorticity based parameterization

Jia Xing[1, 2], Rohit Mathur[1], Jonathan Pleim[1], Christian Hogrefe[1], Jiandong Wang[1, 2], Chuen-Meei Gan[1], Golam Sarwar[1], David C. Wong[1], Stuart McKeen[3]

[1]The U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, USA
[2]School of Environment, Tsinghua University, Beijing, 100084, China
[3]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 809309, USA

Correspondence to: Rohit Mathur (mathur.rohit@epa.gov)

Abstract. Downward transport of ozone (O_3) from the stratosphere can be a significant contributor to tropospheric O_3 background levels. However, this process often is not well represented in current regional models. In this study, we develop a seasonally and spatially varying potential vorticity (PV)-based function to parameterize upper tropospheric / lower stratospheric (UTLS) O_3 in a chemistry transport model. This dynamic O_3-PV function is developed based on 21-year ozonesonde records from World Ozone and Ultraviolet Radiation Data Centre (WOUDC) with corresponding PV values from a 21-year Weather Research and Forecasting (WRF) simulation across the northern hemisphere from 1990 to 2010. The result suggests strong spatial and seasonal variations of O_3/PV ratios which exhibits large values in the upper layers and in high latitude regions, with highest values in spring and the lowest values in autumn over an annual cycle. The newly-developed O_3/PV function was then applied in the Community Multiscale Air Quality (CMAQ) model for an annual simulation of the year 2006. The simulated UTLS O_3 agrees much better with observations in both magnitude and seasonality after the implementation of the new parameterization. Considerable impacts on surface O_3 model performance were found in the comparison with observations from three observational networks, i.e., EMEP, CASTNET and WDCGG. With the new parameterization, the negative bias in spring is reduced from -20 to -15% in the reference case to -9 to -1%, while the positive bias in autumn is increased from 1 to 15% in the reference case to 5 to 22%. Therefore, the downward transport of O_3 from upper layers has large impacts on surface concentration and needs to be properly represented in regional models.

1. Introduction

Accurate characterization of distribution of tropospheric ozone (O_3) is of great interest because it is not only impacts human ecosystem health, but also affects the earth-atmosphere radiation balance and global climate. In addition to its well-known sources from the photochemistry involving NO_x and VOC, O_3 in the troposphere can also originate from stratosphere-to-troposphere exchange in tropopause folds and in cut-off lows (e.g., Danielsen,1968; Bamber et al., 1984; Holton et al., 1995) which become important during periods of significant downward transport or deep stratospheric intrusions (Roelofs and Lelieveld, 1997; Stohl et al., 2000; McCaffery et al., 2004; Zanis et al., 2014; Neu et al., 2014). The contribution of stratosphere-to-troposphere exchange to troposphere column O_3 is estimated to be 20-50% of all sources across the globe (Lelieveld and Dentener, 2000) and the fraction is becoming larger due to reductions in O_3 precursor emissions and climate change (Collins et al., 2003). Quantification of O_3 contributions from the stratosphere-to-troposphere exchange is crucial for air quality management strategies.

Accurate O_3 vertical profiles are also essential for specifying lateral boundary conditions (LBCs) used in regional air quality simulations to capture the amount of O_3 imported to a region (Lam and Fu, 2010). A dynamical model representation of free-tropospheric O_3 variability becomes necessary for regional model applications conducted over large spatial domain and long simulation periods wherein sufficient opportunities exist for exchange between the boundary layer and free troposphere. LBCs traditionally derived from global model simulations, often can suffer from uncertainties associated with the simulation biases at global scale and inconsistent downscaling methodologies. In order to reduce such uncertainties and to adequately represent variability in the free troposhpere, a dynamic representation of the upper tropospheric / lower stratospheric (UTLS) O_3 is desirable in regional models.

Potential vorticity (PV) has often been used as an indicator for air mass exchange between the stratosphere and the troposphere due to its strong positive correlation with O_3 and other tracers transported from the lower stratosphere to upper troposphere (Danielsen,1968; Browell et al., 1987; Ancellet et al., 1994). Previous studies used a linear scaling with a constant O_3/PV ratio to parameterize the influence of stratosphere-to-troposphere exchange on O_3 near the tropopause (Ebel et al, 1991; Carmichael et al, 1998; McCaffery et al, 2004). However, the reported O_3/PV ratios vary depending on location, season, and altitude. For example, Browell et al (1987) suggested the average ratio between O_3 mixing ratios and PV is 50.2 ppb/PVu (1 PV unit = 10^{-6} m^2 K kg^{-1} s^{-1}) from a study conducted over southern Nevada and California in April, 1984, while Ancellet et al (1994) suggested that the O_3 to PV ratios in the tropopause fold were 30-40 ppb/PVu at an European sounding station during November 1990. Carmichael et al (1998) suggested a O_3/PV ratio in the range 50-100 ppb/PVu at two sites in East Asia during spring, with smaller values at lower altitudes. Roelofs and Lelieveld (2000) reported a strong seasonal variation of O_3/PV ratio ranging from 36-76 ppb/PVu with the largest in spring and the lowest in autumn based on MOZAIC data across North America and Europe. Clearly, the O_3/PV ratio varies significantly as a function of location, altitude and time. However, to date, the spatial and temporal variations of O_3/PV ratio have not been not well quantified.

This study aims to analyze the relationship between PV and UTLS O_3 over a large spatial and temporal scale and then to derive a spatially and temporally varying PV-based function to parameterize UTLS O_3 in a chemistry transport model. One thing should be noted that such PV based parameterization only modifies the O_3 mixing ratio, however, co-variances between O_3 and other species are not accounted for in such modifications which might introduce some inconsistencies in the chemistry in the model's UTLS. The method of development of the O_3-PV function is described in section 2. The evaluation of the new function through a model simulation is presented in section 3, and summarized in section 4.

2. Method

2.1 Ozonesonde observations and PV data

A 21-year air quality simulation across the northern hemisphere from 1990 to 2010 has been conducted in our previous study (Xing et al., 2015) by using the Weather Research and Forecasting (WRF) coupled with the Community Multiscale Air Quality (CMAQ) model. Throughout the simulation, WRF was nudged towards NCEP/NCAR Reanalysis data and NCEP ADP operational global surface and upper air observational weather data as described in Xing et al. (2015). The model domain covers the northern hemisphere (see Figure 1) with a horizontal grid of 108 km×108 km resolution and 44 vertical layers of variable thickness between the surface and 50 hPa (approximately 3 vertical levels above 100hPa) (Mathur et al., 2012, 2014).

The model configuration and evaluation is detailed in Xing et al (2015). Anthropogenic emissions are derived from EDGAR (Emission Database for Global Atmospheric Research, version 4.2) and biogenic emissions are derived from GEIA (Global Emission Inventory Activity) (Guenther et al., 1995; Price et al., 1997). The model performance in the simulation of gaseous and particle concentrations was evaluated thorough comparison with several ground observation networks.

Ozonesonde observations were obtained from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC). A total of 44 sites (noted as red dots in Figure 1) across the northern hemisphere were selected after applying screening criteria which required at least one complete year covering all 12 months. The O_3/PV ratio used in this study is calculated by using the O_3 mixing ratio from WOUDC divided by the PV estimated from WRF.

2.2 Parameterization of O_3-PV correlations

We parameterize the O_3/PV ratio as a combination of one spatial function and one temporal function, as shown below:

$$O_3/PV = F(spatial) \times \mathrm{G}(temporal) \quad (1)$$

The spatial function is parameterized through an analysis of O_3/PV correlations with latitude and air pressure on an annual average basis. The spatial distribution of the O_3/PV ratio at three vertical levels (58, 76 and 95 hPa) is presented in Figure S1. At the top layer (58hPa), most sites exhibit a consistent O_3/PV ratio around 80 ppb/PVu, while larger values are noted in low latitude (<20°N) regions where PV is small. At lower altitudes (i.e., 76, 95hPa), the O_3/PV ratio decreases to around 50 ppb/PVu. The O_3/PV ratio against latitude on each of the three levels is fitted by a 5[th] order polynomial function, as below:

$$F_{p_0}(lat) = a(0) + a(1) \times lat + a(2) \times lat^2 + a(3) \times lat^3 + a(4) \times lat^4 + a(5) \times lat^5; lat = abs(latitude) \quad (2)$$

The values of $a(0)$- $a(5)$ are summarized in Table 1.

Decrease in the magnitude of the O_3/PV ratio with decreasing height is evident across the sites. In addition, significant decreases are exhibited in low latitude regions. Figure S2 displays the slope of the O_3/PV ratio vs. pressure at different latitudes. These slopes are estimated from the slope of the O_3/PV ratio at three vertical layers (i.e., 58, 76 and 95 hPa), i.e.

$$F(lat, p_x) = F_{p_0}(lat) + f(lat) \times (p_x - p_0); p_x \in (50hPa, 100hPa), p_0 = 58.56hPa \quad (3)$$

A 2[nd] order polynomial function is then used to fit the latitude-dependent decreasing rate of O_3/PV vs. pressure (i.e., vertical heights), as follows:

$$f(lat) = \min[(b(0) + b(1) \times lat + b(2) \times lat^2), 0] \quad (4)$$

The values of $b(0)$- $b(2)$are summarized in Table 1.

To examine the pressure- and latitude- dependent spatial function, we compared the measurement-based and function-fitted O_3/PV values in Figure 2. Generally, the new function is able to capture the variation of O_3/PV ratio at different horizontal and vertical locations. Large values are seen in upper layers and in low latitude regions. The correlation coefficients (R) between measurement-based and function-fitted values are 0.5-0.9 and normalized mean biases (NMB) are within ±15%. Poor correlation between O_3 and PV is found for latitudes south of 30N (Figure S2). This is in part because in the tropics, convective transport plays a significant role in shaping the vertical ozone profile. Consequently, PV alone may not be able to robustly represent UTLS O_3 in the tropics.

The temporal function is parameterized through an analysis of O_3/PV ratios using seasonal cycles derived from monthly mean values. As seen in Figure 3, the O_3/PV ratio exhibits significant seasonal variations over an annual cycle. Consistent with Roelofs and Lelieveld (2000), the highest O_3/PV ratios occur in spring and the lowest ratios in autumn. A trigonometric function equation is used to represent the seasonality of the O_3/PV ratio, as below:

$$G(mfrc) = 1 + sin\big(12° \times (mfrc \times 30 + c(0))\big) \times c(1)\ ; mfrc = \frac{JulianDay}{365} \quad (5)$$

The values of $c(0)$ and $c(1)$are summarized in Table 1. The fitted function generally captures the seasonal variation of O_3/PV, as seen in Figure 3. The seasonal variability in the O_3-PV correlation also varies with latitude. The influence of convective transport on PV in the tropics, as discussed before, also results in weaker seasonal variations in the O_3-PV correlation at low latitudes. This is seen in Figure 3, which compares the seasonal variations in this relationship inferred from (i) all sites, and (ii) sites at latitudes north of 40N. Thus to ensure that the parameterization more faithfully captures the seasonality at the higher latitudes, where it is strongest, we parameterize the temporal variations only on data at locations with latitudes north of 40N.

One should note that the parameterization is based on limited air pressure values, thus it is only applicable for conditions within the range from 50 to 100 hPa. Additionally, since only the O_3-PV correlation is considered in the parameterization, the potential trend driven by factors other than PV (e.g., chemistry) cannot be captured by the current parameterization. However, the effects of processes which are already reflected in the observation (e.g., seasonal variations such as lower stratosphere ozone loss during Spring) are implicitly captured in the parameterization. By combining the spatial and temporal functions, the newly-developed O_3/PV function has been incorporated in the WRF-CMAQ model.

2.3 Application and evaluation

Simulations for the entire year of 2006 were conducted using the WRF-CMAQ model with the newly-developed O_3/PV function (denoted as "Sim-new"), with a three month spin-up period (October-December in 2005). O_3 mixing ratios in the upper layers only (for air pressure smaller than 100hPa) are scaled based on the time varying modeled PV values and the function detailed in section 2.2. The simulated O_3 in the lower layers are then impacted by the modeled dynamics such as downwards transport.

A reference case (noted as "Sim-ref") is conducted by using a previously developed time- and space-invariant scaling ratio of 20 ppb/PVu derived from limited ozonesonde measurements from the IONS network and model PV estimates over the CONUS during summer 2006 (Mathur et al., 2008). The model simulations for which this 20 ppb/PVu scaling ratio was originally developed had a top level pressure of 100 hPa. Therefore, UTLS O_3 is expected to be underestimated in Sim-ref since the O_3/PV should be larger than 20 ppb/PVu when the top pressure of the model configuration is 50 hPa as in this study, particularly in high latitude regions and during spring time.

To investigate the influence of downward transport of O_3 through the stratosphere-to-troposphere exchange, we conducted a controlled case (noted as "Sim-off") in which no UTLS O_3 were simulated (i.e., the O_3/PV function was turned off). The difference between Sim-new and Sim-off represents the impacts of downward transport of O_3 from the upper layers.

All other model options are identical in Sim-new, Sim-ref and Sim-off. The model configuration follows that described by Xing et al (2015). The anthropogenic emissions were derived from EDGAR. Biogenic VOC and lightning NO_x emissions were obtained from GEIA. Sarwar et al. (2015) reported that halogen chemistry and enhanced O_3 deposition over sea-water can affect tropospheric O_3 mixing ratios. Thus, we included the impact of halogen chemistry and enhanced O_3 deposition in the marine environment in all three cases.

The observed data used for the evaluation is summarized in Table 2. The WOUDC global ozonesonde measurements in 2006 are used for comparison with the predicted O_3 vertical profile. Surface O_3 measurement networks, including the European Monitoring and Evaluation Programme (EMEP, http://www.emep.int), the Clean Air Status and Trends Network (CASTNET, http://epa.gov/castnet/) and the World Data Centre for Greenhouse Gases (WDCGG, http://ds.data.jma.go.jp/gmd/wdcgg/) including a few sites in Asia and Europe, are used for comparison with the predicted surface O_3 concentrations. Only data at sites that covered more than 75% of entire year are selected for the comparison, except in the case of CASTNET because most sites have no O_3 records in winter (criteria set as at least 50% coverage).

3. Results and discussion

3.1 Comparison with O_3 sonde data from WOUDC

Figure 4 displays the observed and simulated annual mean O_3 for three groups of layers, i.e., upper layers at pressure <100hPa, middle layers at 300-500hPa and low layers at >800hPa, across the northern hemisphere. Seasonal comparisons for each group of layers are given in Figure S3-S5 (Spring = MAM, Summer = JJA, Autumn = SON, and Winter = DJF). Compared to the reference case (i.e., Sim-ref), the case with new-function (i.e., Sim-new) exhibits better agreement with observed UTLS O_3, especially in high latitude regions where O_3 levels are high. The statistics of model performance for simulated O_3 are summarized in Table 3. Both cases exhibit large R (>0.9) due to the strong correlation between UTLS O_3 and PV. However, the O_3 at high layers is significantly underestimated in Sim-ref, especially during spring (by -75%) when the UTLS O_3 is the highest across the year. The application of the dynamic O_3/PV function significantly improves the model performance for simulated O_3, as indicated by the significantly reduced NMB and the Normalized Mean Errors (NME) and slightly increased R-values in Sim-new. Such improvements are also evident in the simulated O_3 in the middle layers. The NMB-range is reduced from about -37 to -17% in Sim-ref to about -17 to -1% in Sim-new. Changes in lower-layer O_3 are also noticeable. Because of the greater O_3 burden in upper layers, higher O_3 is seen at low layers in Sim-new compared to Sim-ref. Such increase of low-layer O_3 improves the model performance by reducing the negative biases in spring and summer from -15 and -9% in Sim-ref to -5 and -1% in Sim-new, but deteriorates the model performance in Autumn as positive biases increase from 9% in Sim-ref to 15% in Sim-new. In winter, such increase of low-layer O_3 results in an overestimation of 13% in Sim-new from an underestimation of -7% in Sim-ref.

The observed and simulated O_3 vertical profiles at the 44 WOUDC ozonesonde monitor sites are compared in Figure 5. The simulated O_3 in Sim-new has better agreement with the WOUDC observations across most layers and latitudes. The most significant improvement is seen in the high latitude regions (latitude>45°) where the UTLS O_3 is significantly underestimated in Sim-ref by up to -75% (Figure 5d), as the NMB is reduced to a moderate level (within ±30%) in Sim-new. The overestimates in both low-level and UTLS ozone mixing ratios exhibited in the C-shaped signature in the NMB in Sim-ref is also indicative of the likely influence of convective transport on three-dimensional O_3 distributions in the tropics (e.g., Doherty et al., 2005), that is not adequately captured by the current parameterization. The NME in Sim-new is reduced by 10% - 70% (Figure 5f), though the overestimation of near-surface O_3 in low latitude regions (latitude<45°) becomes even more evident in the Sim-new due to more downward transport of O_3 from the upper layers. An increased NME in Sim-ref is found in the tropical UTLS, indicating the uncertainty in applying the new O_3/PV parameterization in the tropics. The comparison of vertical profiles in the free troposphere between Sim-ref, Sim-new and WOUDC is given in Figure S6. The free- tropospheric ozone is significantly underestimated in Sim-ref. The low bias is reduced in the simulation with the new O_3-PV parameterization, particularly in mid- and high- latitude regions.

Comparisons of O_3 seasonal variations are displayed in Figure 6. With the application of dynamic O_3/PV function, the Sim-new results in better performance (with larger R values) in seasonality as well as magnitude at all layers for both low and high latitude regions compared to the Sim-ref case. More importantly, the dynamic O_3/PV function derived from the seasonal variation of UTLS O_3, also improves the model performance in the simulation of the seasonality of low-layer O_3, suggesting the importance of accurate representation of downward transport of UTLS O_3 to the ground. In summer, the slight overestimation of high-layer O_3 but underestimation of middle-layer O_3 is noticeable in high latitude regions, which might be associated with the underestimation of downward transport of O_3 among those layers. A better vertically resolved model structure with higher resolutions may improve representation of dynamics near the tropopause and help reduce such discrepancy in the simulation of downward transport of UTLS

O_3.

3.2 Comparison with surface O_3 observation networks

Increased UTLS O_3 burden leads to more downward transport of O_3 to the surface. To investigate such impacts on the model performance in simulation of ground-level O_3 concentrations, we compared the simulated surface O_3 from two cases, i.e., Sim-ref and Sim-new, with observations from three surface networks. The observed surface daily maximum 8-h average O_3 (noted as "8h-max O_3"), the NMB in Sim-ref, and the difference between the NMEs from two simulations (i.e., NME in Sim-new minus Sim-ref) are presented in Figure 7 (for EMEP), Figure 8 (for CASTNET) and Figure S7 (for WDCGG). Statistics of the comparison are summarized in Table 3.

For EMEP sites in Europe, the 8h-max O_3 concentration in spring and summer is higher than in fall and winter. The Sim-ref underestimates O_3 by -15% in spring but overestimates O_3 by +15% in autumn. The application of dynamic O_3/PV function reduces the low biases (NMB is reduced from -15% to -1%) in spring but increases the high biases (NMB is increased from +15% to +22%) in autumn, because of more O_3 downward transport from upper layers. In summer and winter, the overall performance in O_3 simulations changes from slight underestimation (NMB = -7% to -0.3%) to slight overestimation (NMB = +3% to +15%). In most cases, better performance in Sim-new is noticeable at sites where the O_3 is underestimated in Sim-ref (See Figure 7).

Similar results are presented at CASTNET sites across the United States, as seen in Figure 8. The 8h-max O_3 in the simulation of Sim-ref is largely underestimated by -17% and -10% respectively during spring and summer when the O_3 is the highest across the year. The sim-new exhibits relatively better results, as the NMB is reduced to -9% and -8% respectively in spring and summer (see Table 3). In addition, lower NMEs and larger Rs are noted in Sim-new compared to Sim-ref. During autumn, O_3 is mostly overestimated at the eastern sites in the Sim-ref case and such overestimation becomes more pronounced in Sim-new, as the NMB is increased from +5% in Sim-ref to +8% in Sim-new. However, the performance for surface O_3 improved at the western U.S. sites in Sim-new. The O_3 in winter is underestimated by -10% in Sim-ref but overestimated by +6% in Sim-new.

At the WDCGG sites in Asia and Europe (see in Figure S6), the underestimation of O_3 during spring and winter is evident in Sim-ref. Better representation of UTLS O_3 and its subsequent downward transport in Sim-new improves the model performance, as the NMB is reduced from -20% (spring) and -17% (winter) to -8% (spring) and -0.03% (winter). The overestimation of O_3 in autumn becomes greater in Sim-new, as the NMB is increased from +0.8% to +5%.

3.3 Impacts on surface O3 from the downward transport

The relative change from the Sim-off to Sim-new, as displayed in Figure 9, can be used to investigate the influence of exchange process between the free troposphere and boundary layer on surface O_3 concentrations. High impacts are evident in high latitude regions where UTLS O_3 is high. Also the exchange between the free troposphere and boundary layer is much stronger during spring and winter. The increasing percentages from Sim-off to Sim-new in east China, the U.S., Europe and the northern hemisphere are estimated to be about 7.4%, 13.3%, 16.4% and 11.5%, respectively, on an annual basis. The downward transport from upper layers has even larger impacts on surface O_3 during spring and winter, and the increasing percentages in four regions are, respectively, about 10.5%, 17.0%, 21.0% and 15.1% in spring, and 15.4%, 25.5%, 32.3% and 20.4% in winter.

4. Summary and conclusion

A seasonally and spatially varying PV-based function was developed from an investigation of the relationship between PV simulated by WRF and UTLS O_3 derived from the WOUDC sonde observations over a 21-year period across the northern hemisphere. This new generalized dynamic O_3/PV function is successfully applied in the WRF-CMAQ model to parameterize O_3 in the upper troposphere. The implementation of the new function significantly improves the model's performance in the simulation of UTLS O_3 in both magnitude and seasonality compared to observations, which then enables a more accurate simulation of the vertical distribution of O_3 across the northern hemisphere. These can then be used to derive more realistic vertically and temporally varying LBCs for regional nested model calculations. It is important to note that we attempted to use all possible available data in developing the O_3-PV relationship in this study. Thus we leveraged the existence of a 21-year simulated record of PV in the UTLS with corresponding O_3 observations. The relationship developed can thus be considered to be "climatologically" representative rather than representing a specific time period or location. No particular year is used as a training data set. The stability of the function has been examined by leaving out the year of 2006 for parameterization, and results show that the resulting function barely changed due to this perturbation, suggesting the function parameterized in this study is not specific to a time or location, but rather designed to capture the average variability represented in the long-term record. Figure S8 presents a comparison of the O_3-PV functions developed using different lengths of data records. As illustrated by the results, the inferred functions are quite similar across these different data sets, thereby providing some confidence in its robustness in representing the seasonal and latitudinal variations in O_3-PV. Further improvements to the parameterization should be explored through more detailed analysis of mixing process in the UTLS, through more detailed investigation of the impact of stratospheric chemistry, and improvements in the performance of the parameterizations for conditions representative of the tropical UTLS. A limitation of this study is that the current model setting lacks sufficient vertical resolution in the lowermost stratosphere. To minimize effects of artificial numerical diffusion associated with the current limited vertical resolution employed in the model, we limit the application of the parameterization to between 100-50mb. Future studies with a much finer vertical resolution, especially to adequately capture the seasonal variation in the tropopause height are suggested to further help evolve the O_3-PV parameterization and its practical use.

Impacts on ground-level O_3 concentrations from the implementation of this dynamic function were evaluated through the comparison with three observation networks: EMEP, CASTNET and WDCGG. Compared to Sim-ref, more O_3 is transported downward to the surface due to a larger UTLS O_3 burden in Sim-new in which the dynamic O_3/PV function was applied. The implementation of the new dynamic function results in better performance in O_3 simulations in spring when O_3 is underestimated in Sim-ref relative to all networks, but worse performance in autumn when O_3 is overestimated in Sim-ref at most sites; the overestimation in autumn in Sim-ref suggests that processes other than free-troposphere-to-boundary-layer exchange are dictating this model bias.

The O_3 downward transport has strong spatial and temporal variations, as its impact is more evident in high latitude regions and during spring. Impacts of the downward transport can contribute to the background surface O_3 concentrations by 7.4%, 13.3%, and 16.4% in east China, the U.S. and Europe, respectively, on an annual basis and with even larger contributions in spring. Thus, the improvement of UTLS O_3 simulation is important to provide a better assessment of background O_3 levels.

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Table 1: Parameterization of the O_3/PV ratio correlation function

Nth of vector		0	1	2	3	4	5
	p (hPa)						
Horizontal (a)	58.56	203.53	-13.622	0.54157	-9.4264×10^{-3}	7.2990×10^{-5}	-2.0214×10^{-7}
	76.40	151.22	15.762	0.86918	1.8049×10^{-2}	1.8418×10^{-4}	-7.1408×10^{-7}
	95.62	62.217	-1.4435	3.0439×10^{-2}	5.8000×10^{-4}	-1.5410×10^{-5}	8.2912×10^{-8}
Vertical (b)	58 to 96	-2.1902	4.5507×10^{-2}	-2.4557×10^{-4}			
Temporal (c)	58 to 96	2	0.22				

Table 2: Summary of ozone observations used for comparison with WRF-CMAQ simulations

	Network	Region	Number of sites	Record frequency	Date Sources
Vertical profile	WOUDC	Global	44	Several hourly data per month	http://www.woudc.org/
Ground	WDCGG	Global	12	Hourly	http://ds.data.jma.go.jp/gmd/wdcgg/
	US-CASTNET	United States	51	Daily 8-hour maxima	http://epa.gov/castnet/
	EU-EMEP	Europe	117	Hourly	http://www.emep.int/

Table 3: Statistics of model performances in ozone simulations

Network	Season			Sim-ref				Sim-new			
Vertical hour-specific O_3		N pairs	Obs (ppb)	MB (ppb)	NMB (%)	NME (%)	R	MB (ppb)	NMB (%)	NME (%)	R
WOUDC- High layers (pressure<100hPa)	Spring	249	1516.53	-1135.39	-74.87	67.43	0.90	26.07	1.72	**21.05**	**0.94**
	Summer	243	1176.71	-776.68	-66.01	58.97	0.93	84.47	7.18	**22.58**	0.93
	Autumn	246	1155.66	-763.60	-66.08	59.30	0.92	**-30.03**	**-2.60**	**17.67**	**0.96**
	Winter	243	1458.05	-1073.49	-73.63	63.86	0.91	**-77.13**	**-5.29**	**23.25**	**0.95**
WOUDC- Middle layers (300hPa<pressure<500hPa)	Spring	504	72.27	-26.52	-36.70	34.63	0.67	**-9.71**	**-13.44**	**21.78**	*0.61*
	Summer	492	73.08	-19.79	-27.09	27.93	0.56	**-12.06**	**-16.51**	**21.37**	**0.70**
	Autumn	498	59.45	-9.99	-16.80	18.91	0.66	**-4.29**	**-7.21**	**16.97**	**0.68**
	Winter	487	58.07	-15.28	-26.30	24.45	0.67	**-0.60**	**-1.04**	**18.52**	**0.74**
WOUDC- Low layers (pressure>800hPa)	Spring	1260	43.15	-6.65	-15.41	26.48	0.52	**-0.43**	**-1.00**	**22.98**	0.52
	Summer	1222	39.65	-3.45	-8.71	27.43	0.72	**-2.10**	**-5.28**	**25.84**	**0.74**
	Autumn	1241	34.66	3.22	9.28	25.91	0.61	*5.18*	*14.93*	*28.89*	**0.62**
	Winter	1229	33.80	-2.23	-6.60	56.00	0.33	4.33	12.80	*63.92*	**0.40**
Surface 8h-max O_3		N pairs	Obs ($\mu g\ m^{-3}$)	MB ($\mu g\ m^{-3}$)	NMB (%)	NME (%)	R	MB ($\mu g\ m^{-3}$)	NMB (%)	NME (%)	R
EU-EMEP	Spring	10539	95.22	-14.31	-15.03	20.71	0.46	**-0.67**	**-0.70**	**17.73**	*0.41*
	Summer	10663	96.44	-0.24	-0.25	22.29	0.66	2.62	2.71	*22.36*	0.66
	Autumn	10469	69.26	10.07	14.54	34.33	0.55	*14.89*	*21.50*	*40.33*	*0.53*
	Winter	10173	64.65	-4.82	-7.45	35.63	0.46	9.85	15.23	*45.33*	**0.48**
US-CASTNET	Spring	3919	113.03	-19.54	-17.28	20.76	0.52	**-9.61**	**-8.50**	**15.69**	**0.53**
	Summer	4456	115.58	-11.36	-9.83	19.48	0.62	**-9.48**	**-8.20**	**18.81**	**0.63**
	Autumn	3279	89.21	4.60	5.16	22.21	0.59	*7.54*	*8.45*	*23.70*	*0.58*
	Winter	1094	89.23	-9.09	-10.18	16.46	0.47	5.09	5.71	**15.31**	0.47
WDCGG	Spring	1023	114.50	-22.46	-19.61	23.52	0.53	**-9.34**	**-8.16**	**17.25**	**0.57**
	Summer	1021	100.30	-1.62	-1.62	33.93	0.55	0.80	0.79	**32.57**	**0.60**
	Autumn	948	91.22	0.72	0.79	29.38	0.46	*4.55*	*4.99*	*30.42*	0.46
	Winter	939	84.84	-14.16	-16.69	36.49	0.49	0.02	0.03	**36.16**	*0.48*

Note: **bold**= better performance in Sim-new than Sim-ref; *italic*= worse performance in Sim-new than Sim-ref

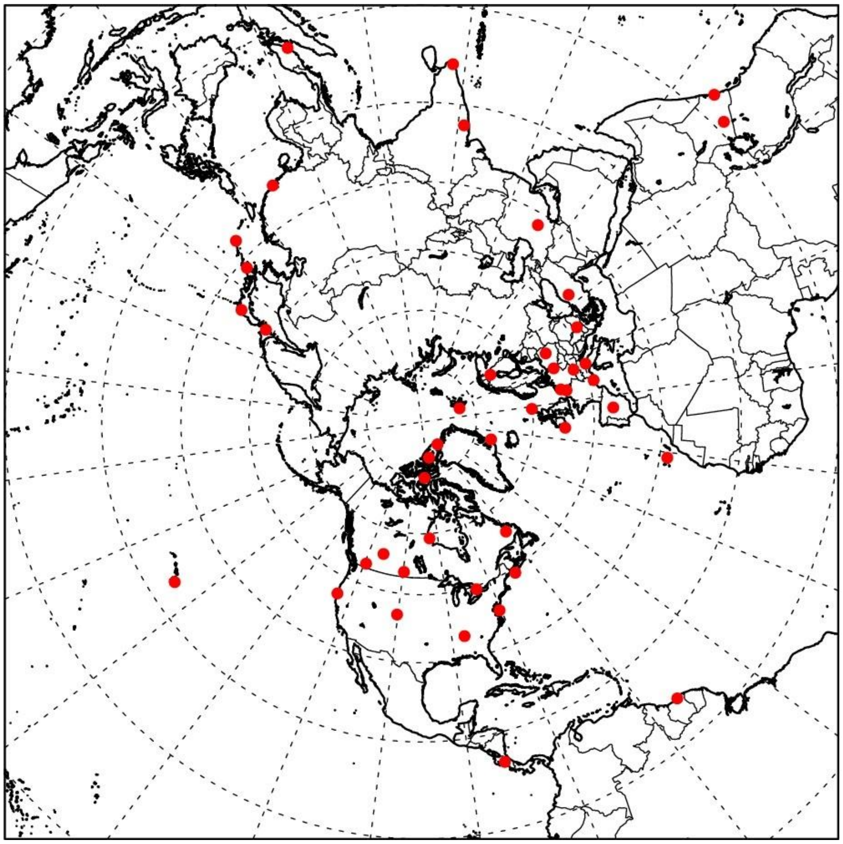

Figure 1: Simulation domain and spatial locations of the 44 WOUDC sites used in this study

1st (top) layer (mid-layer pressure=58hPa) 2nd layer (mid-layer pressure=76hPa) 3rd layer (mid-layer pressure=95hPa)

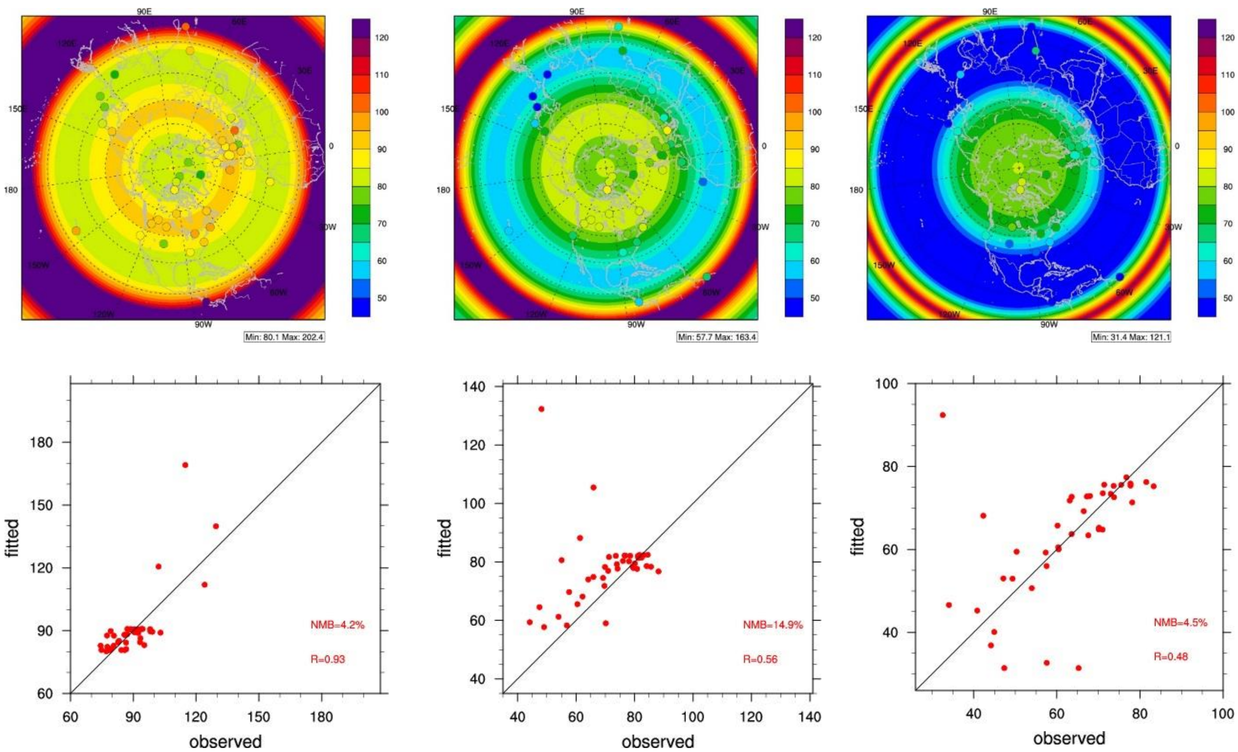

Figure 2: Sensitivity of O_3/PV to spatial location (ppb/PVu)

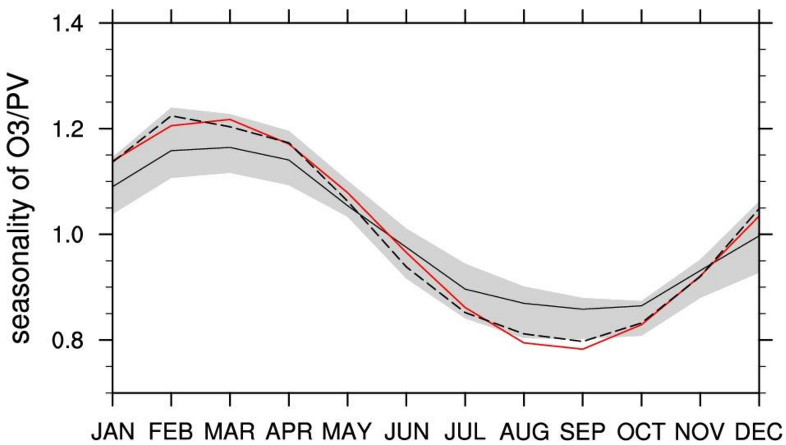

Figure 3: Seasonality of O_3/PV (Annual mean= 1, selected pressure < 60 hPa, black solid line=observed mean at all sites, grey shadows represent 25% to 75% of observed records, black dash line= observed mean at sites at latitudes >40N, red line = fitted by function)

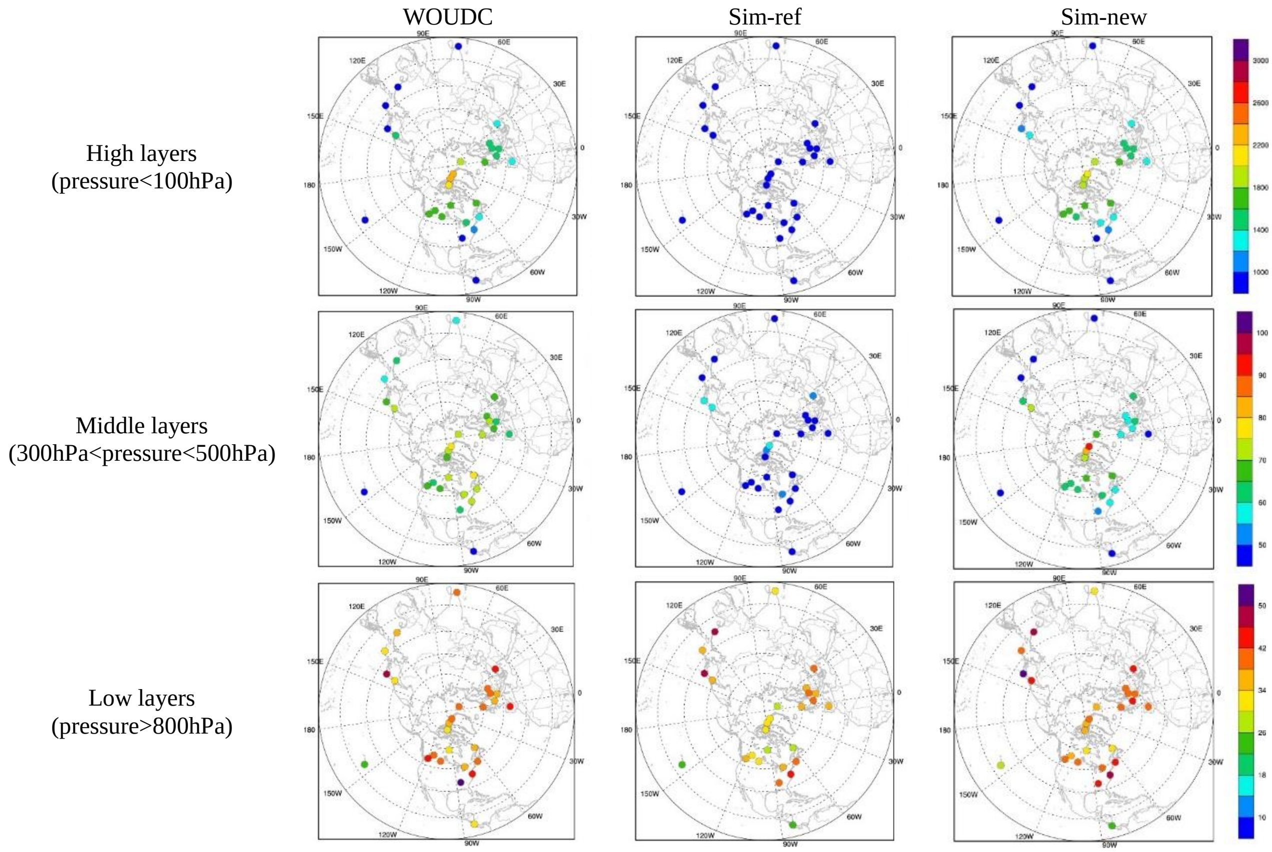

Figure 4: Ozone spatial distributions (annual mean of measurement time period for each WOUDC site, ppb, 2006 Jan-Dec)

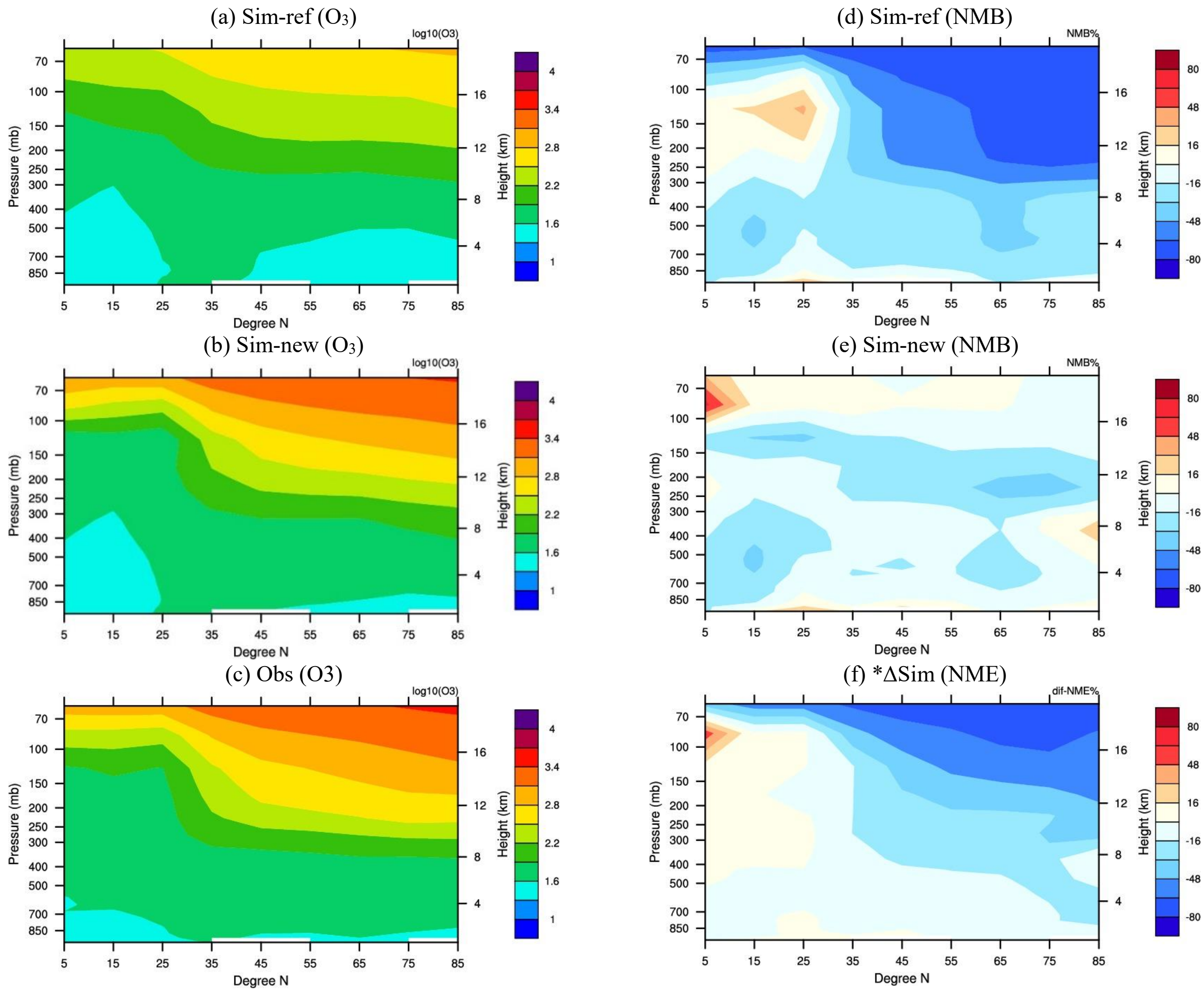

Figure 5: **Zonal mean profiles of ozone and error metrics for the different cases. (a) Simulated ozone profile in reference case; (b) Simulated ozone profile in new case with updated O_3-PV parameterization ; (c) Observed ozone profile, the annual mean of measurement time period for each WOUDC site across the northern hemisphere; (d) Normalized Mean Bias in the reference simulation; (e) Normalized Mean Bias in the new simulation with updated O_3-PV parameterization; (d) Difference in Normalized Mean Errors between the new simulation and reference simulation (unit: ppb, 2006 Jan-Dec; NMB- Normalized Mean Bias; NME-Normalized Mean Error; *ΔSim= Sim-new minus Sim-ref in NME)**

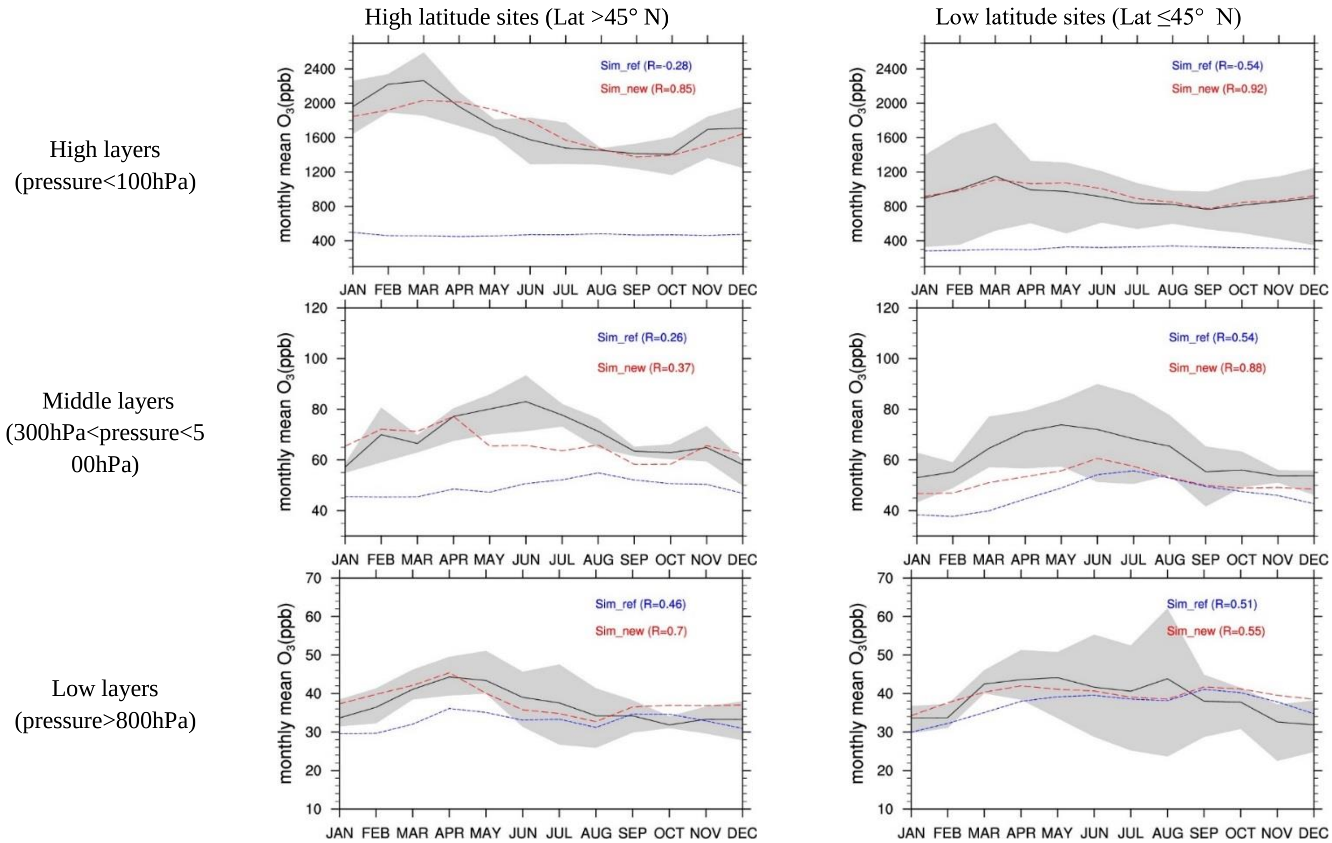

Figure 6: Ozone seasonal variations (44-site averages of monthly mean of measurement time period for each WOUDC site, ppb, 2006 Jan-Dec, black lines represent observations, blue lines represent Sim-ref, red lines represent Sim-new, grey shadows represent 25th and 75th percentiles of observations)

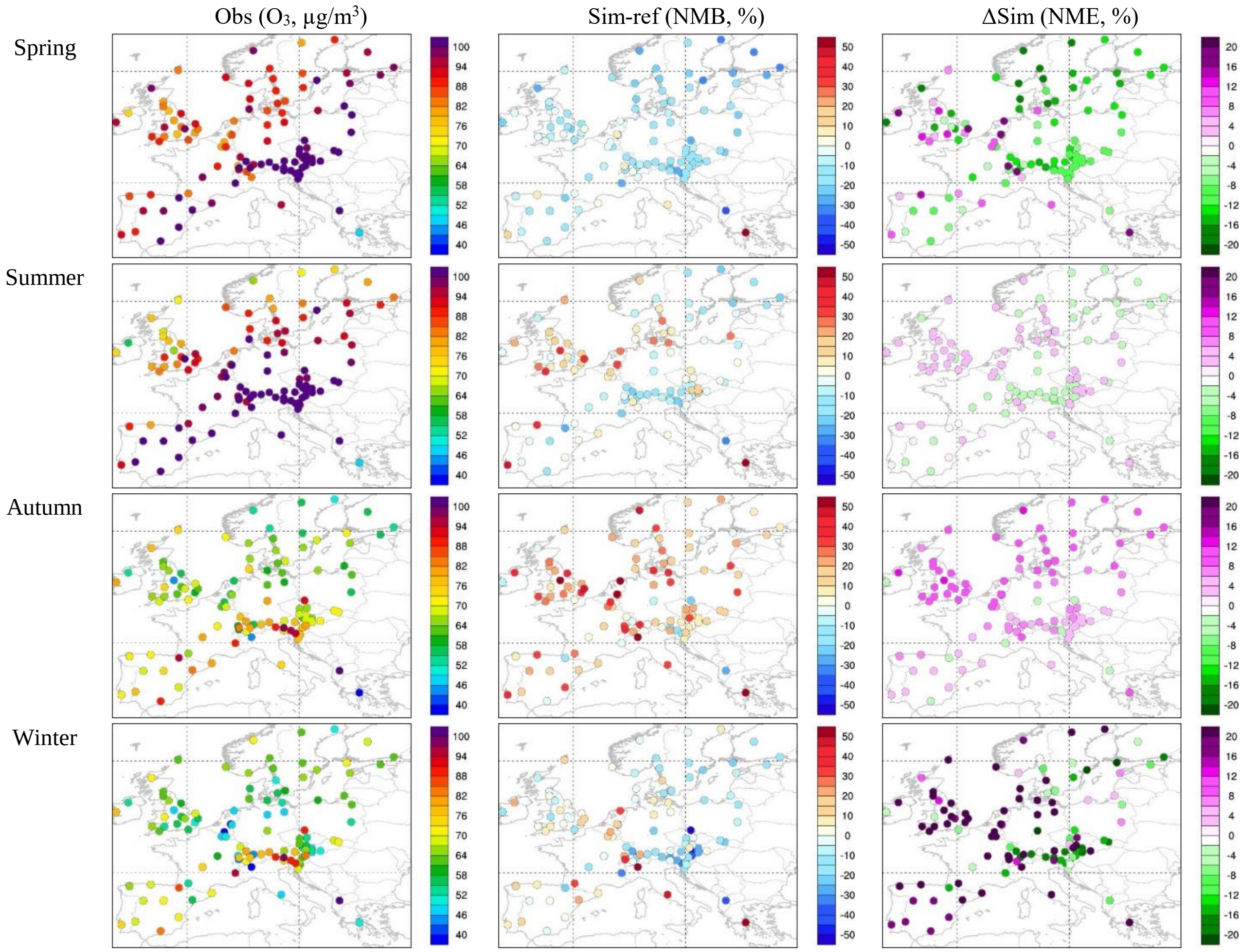

Figure 7: Comparison with EMEP surface daily maximum 8-h average O_3 concentrations (ΔSim= Sim-new minus Sim-ref in NME)

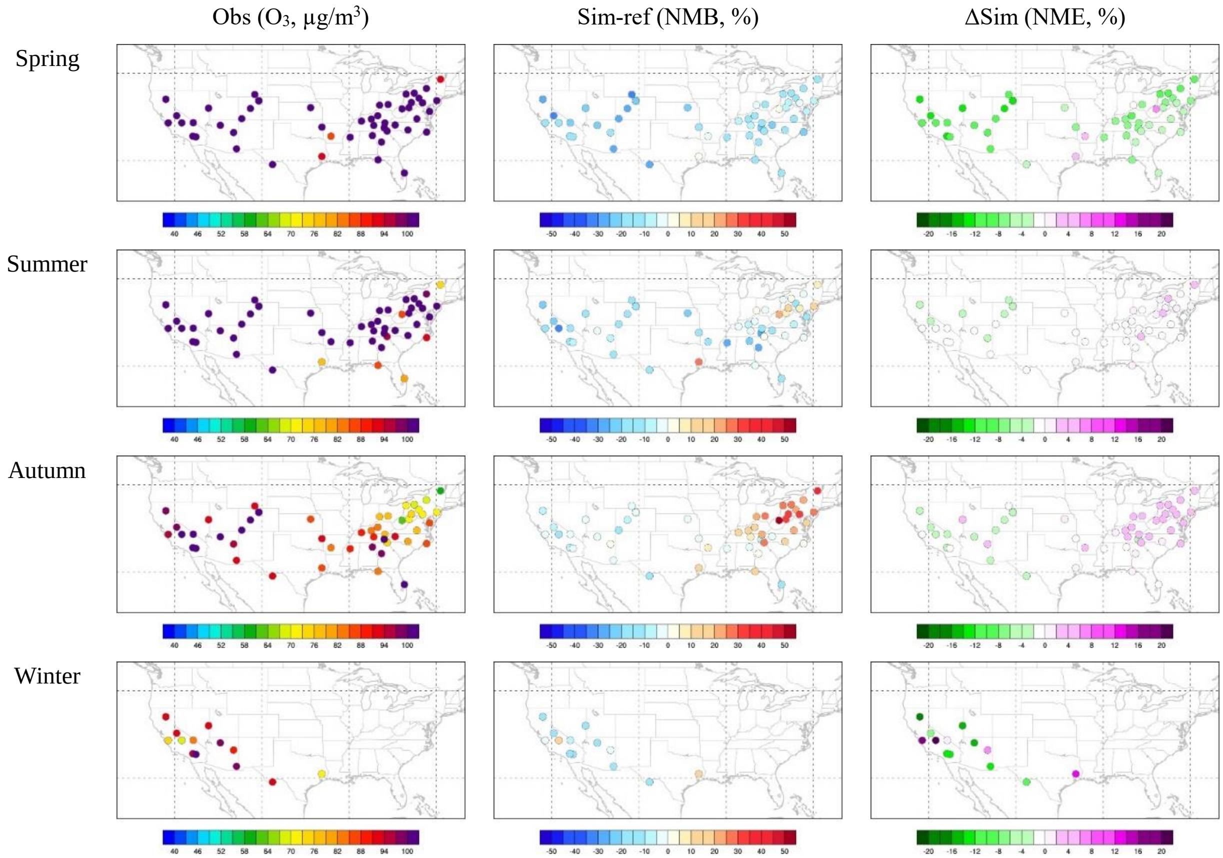

Figure 8: Comparison with CASTNET surface daily maximum 8-h average O_3 concentrations (ΔSim= Sim-new minus Sim-ref in NME)

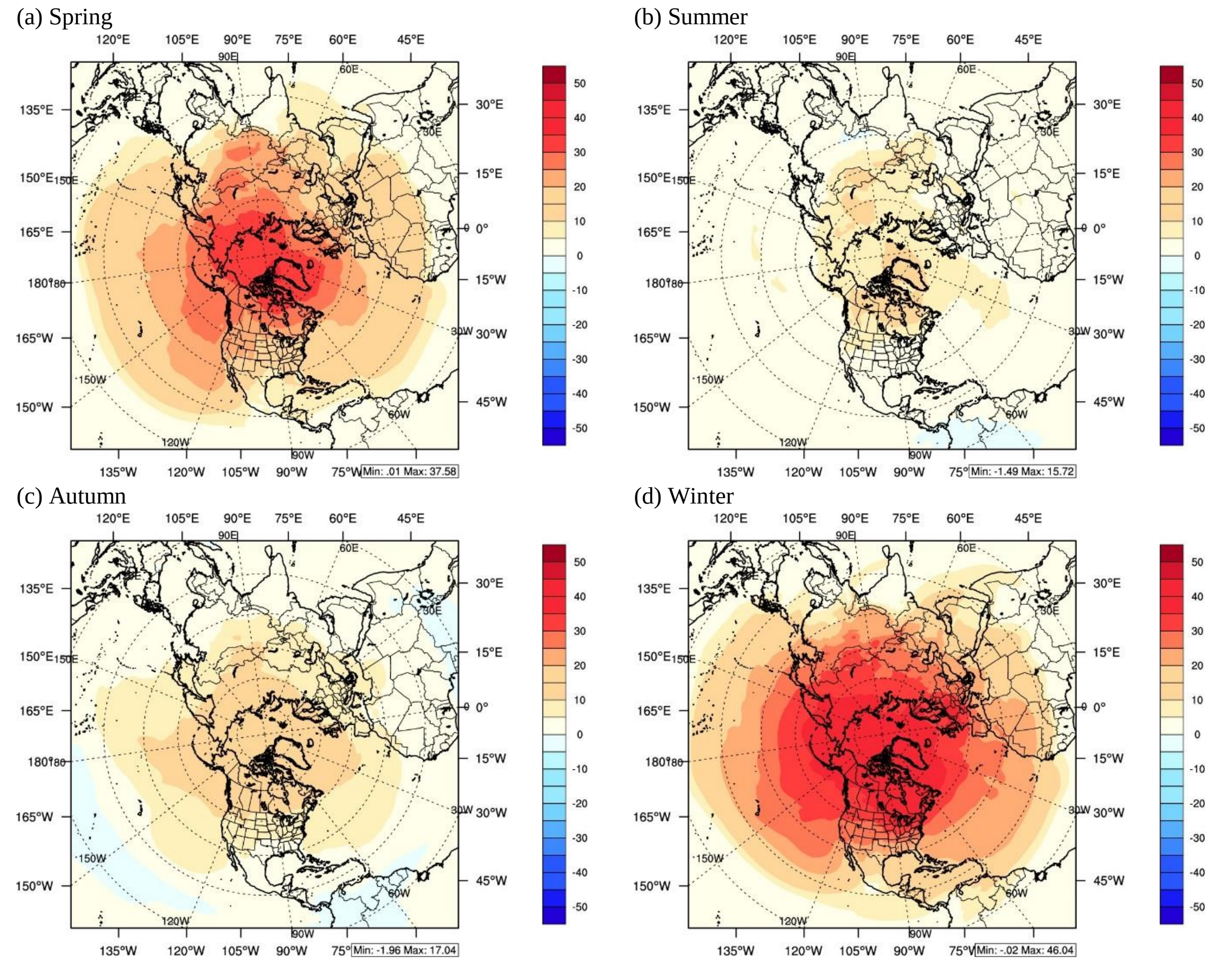

Figure 9: Relative changes in surface O_3 due to dynamic O_3/PV function (unit:%, *changes = (Sim-new minus Sim-off) / Sim-new)