Response to Referee Comment 1 by Anonymous Referee #1

This paper presents high-order sensitivity analysis modeling of the impacts of emissions and stratosphere to troposphere transport on ozone. Modeling is done with a relatively recent hemispheric version of a widely-used photochemical model. While the methods are not fully novel, they pull together two relatively advanced techniques: HDDM and hemispheric modeling. Explanations are for the most part clear. I recommend publication after addressing the comments below.

Reply:

We thank the reviewer for the overall positive assessment of the manuscript and providing helpful and constructive comments. We have revised our manuscript according to the reviewer's comments and suggestions. We believe that these revisions address all points raised by the reviewer. Our point-by-point responses are provided below, and revisions are indicated in blue in the revised manuscript.

Major comments:

1. It is difficult to reconcile the concentration and zero-out contribution estimates. In Figures 6 and 7 and Table 2, concentrations are much larger than the sums of the ZOCs. For example, over most mid- and high-latitude locations in the NH top of the free troposphere (Fig 6, top, c), ozone mixing ratios are over 75 ppb, but the zero-out contributions of East Asian emissions, USA emissions, and stratospheric ozone add to less than half that much. What's the source for the rest of the O3? Sure, there will be influences from other regions, but I would have expected these to be the largest contributions and for cross-sensitivity interactions to be small. More exploration and discussion are needed on this.

Reply:

We agree with the reviewer that we should have provided additional discussion on the differences between the concentrations and the zero-out contributions for USA emissions, East Asia emissions, and stratospheric ozone in Table 2 and Figures 6-7. To examine the impacts from other regions except U.S.A. and East Asia, we have added the figure illustrating the ZOC of domain-wide emissions at surface and different altitude in Figure S5. In addition to the emissions contributions from other regions, a large part of the difference is due to the effects of initial conditions of both O_3 and other species, particularly reservoir species. To illustrate these effects, we have conducted an additional DDM simulation to investigate the sensitivity of O_3 to O_3 initial and boundary conditions. We have added new supplemental Figures S6-S9 to present these results as well as the results of the domain-wide emissions zero-out contributions over the regions and layers shown in Table 2. These figures show that the domain-wide emission zero-out contributions (Figure

S5) are larger than the U.S.A. and East Asia zero-out contributions in (Figure 6 and Table 2) (e.g. roughly 30 ppb at the top of the free atmosphere over the Pacific Time Zone (PST) region for April shown in Figure S5 vs. 3.0 + 6.5 ppb = 9.5 ppb for the U.S.A. and East Asia zero-out contributions in Table 2), pointing to the impact of emissions from these other regions on simulated ozone concentrations. Furthermore, while the contribution of O_3 initial and boundary conditions decreases over time as the domain-wide emissions zero-out contribution increases, it remains substantial throughout the analysis period. The following paragraph has been added to Section 4.3.

"Note that O_3 concentration fields and the sum of sensitivities do not generally equal each other because of nonlinearities in O_3 formation. Moreover, the zero-out contributions for U.S.A. and East Asia emissions represent only a portion of the total emissions burden, and the emissions sensitivity calculations can also be affected by initial and boundary conditions. To investigate this further, the temporal evolution of O_3 concentrations and sensitivities towards O3VORT, O3IC, O3BC and domain-wide emissions ZOC are presented in Figs. S6-9. The Figures show time series of these contributions averaged over the PST, MST, CST, and EST areas in the U.S.A. at the surface, 750 hPa, 500 hPa, and 250 hPa, corresponding to the results presented in Table 2. These figures show that the domain-wide emission zero-out contributions (Figure S5) are larger than those of zero-out contributions from U.S.A. and East Asia (Figure 6 and Table 2), pointing to the impact of emissions from other regions on simulated ozone concentrations. As expected, the impact of O3BC is small over the U.S.A due to the distance from the equatorial boundaries. At the beginning of the simulation, O_3 concentrations are dominated by initial conditions as shown by the close agreement between the O_3 concentration and O3IC curves during the first half of March. The sensitivity towards O3IC is declining throughout the simulation while O3VORT and ZOC are increasing and begin to dominate the O_3 variation by April. However, even after the one-month spin-up period, O3IC are still present over all time zones and all altitudes. In this study, we initiated the H-CMAQ simulation from the prior model simulation for 2010 (Hogrefe et al., 2018); however, this result suggest that spin-up periods longer than one month may be necessary to fully capture the effects of emissions and O3VORT contributions through calculating HDDM sensitivities over a hemispheric-scale modeling domain. Finally, Figures S6–S9 still show differences between simulated concentrations and the sum of O3VORT, O3IC, O3BC, and ZOC. Aside from the non-linearities and interactions mentioned above, this likely is also caused by contributions of initial conditions of species other than O_3 (e.g., PAN or N_2O_5) to the simulated O_3 levels."

2. The results around the perimeter (i.e., tropics) in Figure 1 are peculiar, showing negative first-order

sensitivity to VOC, positive second-order sensitivities, negative cross-sensitivity. All of these are opposite in sign to what the chemistry would typically suggest. Further investigation is needed to explore the role of boundary conditions or other factors in driving this, or if there is an error in the modeling.

Reply:

We appreciate this insightful comment. The negative first-order sensitivity to VOC and the positive second-order sensitivity to VOC and positive cross sensitivity found in Figure 1 likely were affected by the boundary conditions. To clearly state this perimeter sensitivity to VOC, we have added the following sentence in Section 4.1.

"It should be also noted that the positive first-order and negative second-order sensitivities to VOC found near the lateral boundary with ring-shape in the modeling domain could be the perimeter sensitivity. In this H-CMAQ modeling system, the boundary conditions are taken from the clean tropospheric background values with updates to the physical and chemical sinks for organic nitrate species (Mathur et al., 2017). For these boundary conditions, the NO concentration was set to zero, the NO_2 concentration was set to 10^{-5} ppmv, and the O_3 concentration was set to 30 ppbv. These low NO_x boundary conditions likely caused the perimeter sensitivities to VOC although it should also be noted that the absolute values of these sensitivities are small. The effect of boundary conditions is further discussed later in Section 4.3."

Minor comments on text:

p. 1, Line 32: The 250 to 50 hPa layer is actually in the stratosphere, so not "stratospheric intrusions"

Reply:

We have revised "stratospheric intrusions" to "stratospheric air mass".

p. 4, line 4: typo p. 6, line 1: It is not clear to me how the sensitivity to stratospheric O3 is being calculated.

Reply:

Section 2 mentioned our Part 1 paper, and we developed the air mass characterization technique in Part 1 paper. In contrast to this part 1 paper, this part 2 paper directly estimated the sensitivity to stratospheric O_3. In this version of CMAQ modeling system, the stratospheric O_3 is calculated using O_3/PV relationships, and DDM is applied to estimate the sensitivity to this stratospheric O_3. To address this comment, we have revised and added the explanation of DDM calculation of stratospheric O_3 as follows in Section 3.

"In addition, DDM was extended to examine the sensitivity of O_3 mixing ratios towards stratospheric O_3. A dynamic O_3/PV function considering the seasonal, latitudinal and

altitude dependencies is constructed at three vertical levels of 58, 76, and 95 hPa fitted as a 5th order polynomial function, and applicable between the range of 50 and 100 hPa (Xing et al., 2016). The sensitivity to this stratospheric O_3 is calculated by differentiating the equations used to introduce stratospheric O_3 through potential vorticity in the same matter as all other DDM sensitivity calculations. When a user specifies the desire to know the PV sensitivity, a sensitivity field corresponding to the calculation is initialized at the beginning of the model run and then updated with the derivatives in each time step and location where PV calculations occur (typically the uppermost two layers in the model). Since PV ozone in CMAQ is essentially a "replacement" of the ozone field in the top layers before the PV calculations by a scaling function, the same replacement is applied to the first-order sensitivity field. Note that the higher-order sensitivity to this stratospheric O_3 is not calculated. This sensitivity is hereafter referred to as O3VORT."

p. 6, line 10: It should be noted that because the coarse grid resolution smears out NOx, you may be missing locations where O3 is actually VOC-limited, such as urban cores with intense NOx emissions at subgrid scales.

Reply:

We have added the note to explicitly mention the limitation of this coarse-grid analysis as follows:

"Note that due to the use of a coarse horizontal grid resolution to cover the entire northern hemisphere, the simulation may not adequately capture the chemical regime in urban areas where O3 chemistry is VOC sensitive."

In addition, we have added the statement referring to our previous study as follows:

"Due to the coarse grid resolution, H-CMAQ could partly missed the VOC sensitive regime characterized over urban areas, and our previous study reported the dependency of photochemical indicators to judge the O_3 regime (e.g., $H_2O_2/(O_3+NO_2)$) on model grid resolution (Zhang et al., 2009)."

p. 6, lines 21-22: It would be more appropriate to say: "… it can be concluded that ozone is more sensitive to NOx emissions than to biogenic VOCs emissions during April 2010." Also, at some point you should note that not all NOx is anthropogenic (e.g., lightning, soils).

Reply:

We have revised this sentence according to the reviewer's comment.

p. 10, line 2: Have you identified evidence of "active convection" in the meteorological model, or is this mere speculation?

Reply:

This was our speculation, hence we have revised this sentence as follows:

"the latter may be related to active convection"

p. 12, line 29: It is difficult to follow where results are being presented on a MD8O3 or 24-hour average basis. Those sensitivities can be quite different.

Reply:

MD8O3 is not presented in this study, hence we mentioned the analysis method in the concluding section. We have revised "with other metrics (e.g., MD8O3)" into "with other metrics (e.g., MD8O3) not analyzed here".

Specific comments on figures:

Fig 1: In the caption, clarify if these are for 8-hour maximum or daily-average results.

Reply:

As we have stated in main caption, these sensitivities are monthly means computed from hourly output. We also explicitly mentioned this point in the figure caption as follows.

"The sensitivity coefficients are monthly means computed from all hourly data in April 2010."

Fig 9 and 10: Caption needs to say what the emissions changes were.

Reply:

We have revised the caption to explicitly explain these emissions changes as follows.

For figure 9:

"Perspective of changes in O_3 concentration resulting from estimated 2010-2015 emission changes over (top panel) U.S.A. and (bottom panel) East Asia at surface, bottom of free troposphere (750 hPa), middle of free troposphere (500 hPa), and top of free troposphere (250 hPa) from left to right."

For figure 10:

"Perspective of daily and monthly averaged changes in O_3 mixing ratio resulting from estimated 2010-2015 emission changes over U.S.A. (light blue bars) and East Asia (light red bars) summarized over four time zones of Pacific, Mountain, Central, and Eastern Standard Time (PST, MST, CST, and EST) in U.S.A."