Reply to the review 3 of "Changes in surface ozone in South Korea on diurnal to decadal time scale for the period of 2001-2021"

Thank you very much for your insights about trend and seasonality of background ozone values at northern midlatitude. The background ozone beyond Asia should have been discussed in the manuscript. In the revised manuscript, we included the references and mentioned this point. We also thank you for recognizing the strengths of our study. Our replies to the major concerns and specific comments are written below (the reviewer's comments in blue and our replies in black).

The reviewer's main concern was the use of surface $O_3$ data from the base time (01-06 LT) to gain information about background value because $O_3$ loss reacting with NO is dominant at this time over the highly polluted area. It is typical to ignore the data at this time when analyzing trends over polluted regions. However, in this study, we would like to utilize $O_3$ data at this time to find information about background $O_3$ because ozone is transported throughout a day and this process is very important in the region of study. The Figure R12 shows the WRF-Chem simulated surface $O_3$ in Seoul from various emission scenarios. Blue line in the plot denotes the model results only with local emissions (zero-out Chinese emissions, labeled as "No China") and black line represents the results from Control run with all emissions. The local emissions case (blue line) shows much reduced $O_3$ compared to the Control case throughout a day (including 01-06 LT). The difference between the Control case (black line) and local emissions case (blue line) at 01-06 LT indicates increase of ozone from transport from upwind sources at this time.

High $NO_x$ condition in Seoul tends to suppress the photochemical production of $O_3$ during daytime and enhance $O_3$ destruction during nighttime as exhibited in differences between black (Control case) and magenta lines (zero-out Seoul emission case, labeled as "No Seoul"). This indicates that chemistry plays a critical role in determining $O_3$ value in Seoul. Therefore, similarity of mean $O_3$ values in the Control case to clean background tropospheric $O_3$ value (climatological value) may be just a coincidence. These modeling exercises demonstrate that $O_3$ at the base time can be analyzed to derive information about background ozone even over the highly polluted (high $NO_x$) sites. The other point the reviewer commented is the impact of different $NO_x$ concentrations during spring and summer on background ozone at 01-06 LT. Because it is not daytime, differences in boundary layer height between the two seasons should be small. Lower stable boundary layer height during summer than during spring is not well theoretically supported.

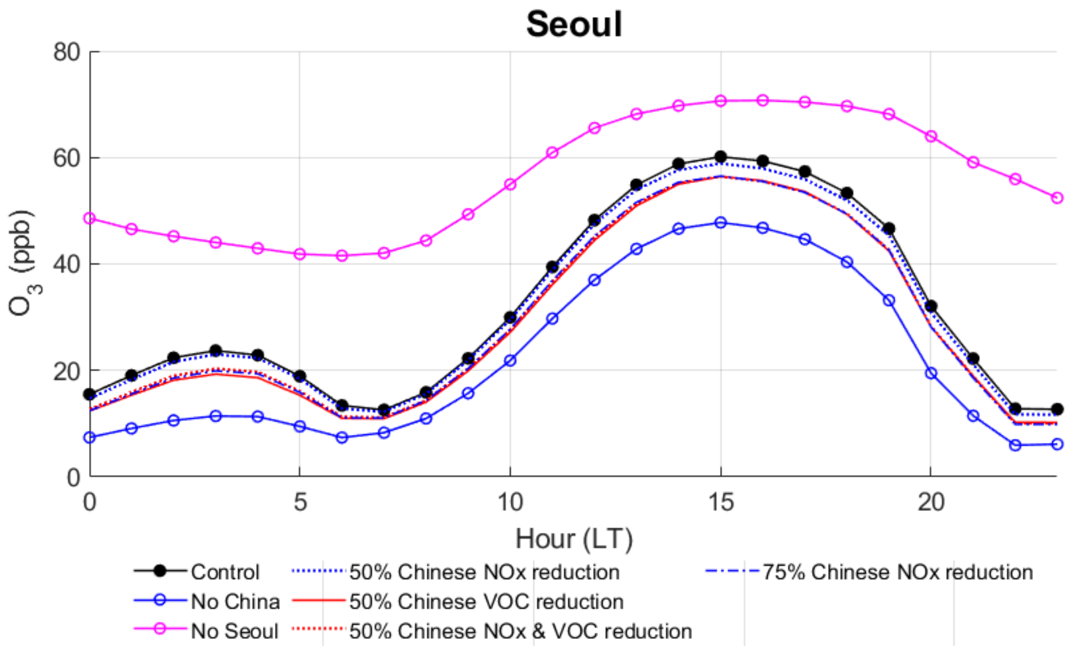

Figure R12. Diurnal variations of the model ozone concentrations at surface from various emission scenarios. The model results were averaged for the full simulation period.

The reviewer's suggestion to construct frames to analyze $O_3$ in South Korea by using the observations and chemical transport model results sounds interesting, but we are not sure if that can/should be conducted in this study. It would not be straightforward to delineate background $O_3$ (without continental influences) and to assess the impacts of local South Korean emissions and Asian mainland emissions by mainly analyzing observations for the complex atmospheric environment of South Korea. We agree with the reviewer to the point that the models like CESM constrain many important parameters to develop the model reproducing $O_3$ seasonality and trends. To rely on the models, however, the uncertainties of the models should be well accounted for. This alone is a quite challenging work. It would be interesting to conduct research the reviewer suggested. But it would require considerable times and that work would be beyond the scope of this study. In this study, we used models to help interpret observations as shown in the discussion section in the original manuscript, which is moved to the result section in the revised manuscript.

**Summary**:
This a very useful and informative paper. It has two major strengths: 1) Investigation of ozone in a region with strong local anthropogenic emissions, that also receives marine inflow with a highly polluted continent lying directly upwind of the marine area. 2) An effective incorporation of both observation and modelling based analysis. However, I believe that a major revision of the paper is required before it is ready for publication. One major need is for the authors to begin their observation-based analysis with a consideration of the ozone distribution that would be present in South Korea if there were no continental influences, i.e., if observed concentrations were due to transported baseline ozone alone. That consideration can rely on both the CESMv2.2 model calculations of these ozone concentrations (evidently shown in Figure 6), where results at ~1 km likely represent baseline ozone, and on analysis of observations as suggested below in the first major issue. This consideration would then provide a basis for understanding the continental influences, both from local South Korean emissions and from the Asian mainland emissions. Also much of the discussion is difficult to follow and requires substantial improvement; suggestions in this regard are given in the major and minor issues described below.
→ Please see the replies above.

**Major issues**:

1) I believe that the discussion based on Table 1 requires reconsideration. I assume that these are mean ozone concentrations for the peak and base time periods in spring and summer. First, I think the period names are misleading. The 10-20 LT period has higher ozone concentrations than does the 01-06 period. However, those higher (10-20 LT) ozone concentrations are similar to that expected for northern mid-latitude baseline ozone concentrations. For example, Figure 5 of Parrish et al., (2020) shows that annual mean ozone is 30 to 40 ppb in the lower 1 km of the troposphere. Figure S14 of that paper shows that ozone at Mt. Walinguan (upwind of South Korea, but at higher elevation) has mean ozone of about 45 to 60 ppb in spring and summer. To my mind, the mean ozone in Table 1 in the 10-20 LT period predominately reflects baseline ozone transported into the country; this is the reason that these mean concentrations are similar throughout the country.

→ We agree with the reviewer about the possibility of baseline ozone transported into the country, judging from similar mean values throughout the country. However, Figure R12 also illustrates various responses of surface ozone to emission scenarios in Seoul. It demonstrates that chemistry is an important factor to determine mean annual ozone in Seoul and other regions in South Korea. Therefore, we would like to avoid oversimplification of factors to determine the ozone in South Korea.

2) If the interpretation above is correct, then the lower ozone concentrations in the 01-06 period are caused by loss of ozone due to surface deposition and reaction with fresh NO emissions under a shallow nocturnal inversion. Such a diurnal cycle (low at night, higher during the day) is a ubiquitous feature of urban ozone.

→ Agreed. See the replies above (including Figure R12). Ozone in the 01-06 LT period is lower than that in the 10-20 LT period because of different chemical and physical processes involved. But there are still influence of transport in the 01-06 LT period as shown in Figure R12. Therefore, we would like to use the data in the 01-06 period.

3) To emphasize the similarity of the ozone concentrations throughout the country, and the predominant role of transported baseline ozone, I suggest that the background sites be included in Figure 3 and Table 1.

→ It was difficult to derive the trends for the background sites because some of ozone season data are missing for the sites. The data from March 31, 2011 to August 31, 2011 are missing in Gosung, Gangwon-do. The data from Mary 1, 2012 to June 8, 2012 are missing in Gosan, Jeju. The data from March 30, 2011 to June 30, 2011 are missing in Ulleung Island (in Gyeongsangbuk-do). Therefore, we limit the trend analysis for the region with multiple monitoring sites covering the full period of analysis.

4) More generally, I suggest that all tables, figures and discussion clearly address the 7 cities, 9 provinces, and 3 background sites in a consistent manner to the fullest extent possible. The discussion is often difficult to follow when varying lists of cities, provinces and sites are mentioned.

→ We presented the results for the 7 cities, 9 provinces, and 2 background sites consistently in the revised manuscript whenever possible. We omitted Gosan, Jeju Island because $NO_2$ and CO data need quality assurance from mid of 2010 to current date. The names of the sites were updated consistently throughout the manuscript. For the trend study (Figure 2 and 3), we did not include the background sites because of some missing data during ozone season.

5) The primary reason that mean ozone is generally higher in spring than in summer is that the lower troposphere baseline ozone is higher in spring than in summer, particularly in marine influenced air; e.g., see Figures 4 and 6 of Parrish et al., (2020).

→ Thank you for the reference. We explained the seasonal difference including marine influenced air in the revised manuscript and referred to Parrish et al (2020).

6) Pg. 11, lines 5-8: One reason the 01-06 LT ozone is higher in the spring is that the nocturnal inversion is tighter in the summer, so ozone loss at night is more pronounced in summer than in spring. Given the very local processes that determine the 01-06 LT ozone, for simplicity, the authors may wish to eliminate the discussion of this nighttime ozone.

→ We don't think that there are clear mechanisms driving differences in nocturnal inversion between spring and summer. See the replied above for the reason why we keep the discussions about the ozone concentrations in the 01-06 LT period.

7) A discussion of local CO and NOx trends begins near the bottom of pg. 13. These observation-based trends should be compared and discussed in relation to the trends of these species derived from the model emission inventories. This may be more relevant to NOx, since it does have more local influence than CO.

→ We listed the trends of NOx and CO emissions from linear fits of the data covering 2001-2020, obtained from Clean Air Policy Support System (CAPSS) emission inventory (https://www.air.go.kr/) (Table R7 and R8 for emission inventories and ambient concentrations, respectively). Overall, signs of slopes agree between emission inventory and ambient concentrations at least for the cities, but site-to-site variations do not agree even for the cities. And there are disagreements of signs of slopes between emission inventory and ambient concentrations for the provinces. This can be attributed to the uncertainties in long-term emission inventories of NOx and CO.

Table R7. The trends of NOx and CO emissions from linear fits of the data covering 2001-2020.

| Stations | | NOx (kton/yr) Slope (Correlation Coefficient) | CO (kton/yr) Slope (Correlation Coefficient) |
|---|---|---|---|
| City | Seoul | -2.35 (-0.72) | -8.02 (-0.97) |
| | Incheon | -1.14 (-0.60) | -0.74 (-0.73) |
| | Daejeon | -0.56 (-0.84) | -0.84 (-0.88) |
| | Gwangju | -0.29 (-0.63) | -0.72 (-0.94) |
| | Busan | -1.23 (-0.77) | -2.01 (-0.94) |
| | Ulsan | -1.27 (-0.90) | -0.12 (-0.37) |
| | Daegu | -0.85 (-0.74) | -1.37 (-0.87) |
| Province | Gyeonggi-do | -1.30 (-0.47) | -1.51 (-0.67) |
| | Chungcheongbuk-do | 0.52 (0.46) | 0.40 (0.40) |
| | Chungcheongnam-do | -5.32 (-0.74) | 1.49 (0.93) |
| | Jeollabuk-do | -0.66 (-0.82) | 0.61 (0.53) |
| | Jeollanam-do | 0.74 (0.57) | 1.63 (0.75) |
| | Jeju-do | 0.27 (0.64) | 0.31 (0.58) |
| | Gyeongsangnam-do | -5.47 (-0.83) | -0.09 (-0.14) |
| | Gyeongsangbuk-do | 0.78 (0.52) | 2.19 (0.76) |
| | Gangwon-do | 0.25 (0.17) | 0.95 (0.67) |

Table R8. The observed trends of $NO_2$ and CO concentrations from linear fits of the data covering 2001-2021.

| Stations | | $NO_2$<br>Spring / Summer<br>Slope (Correlation Coefficient) | CO<br>Spring / Summer<br>Slope (Correlation Coefficient) |
|---|---|---|---|
| City | Seoul | -0.77 (-0.85)/-0.72(-0.91) | -7.56(-0.77)/-5.34(-0.83) |
| | Incheon | -0.37(-0.62)/-0.50(-0.62) | -7.65(-0.71)/-4.64(-0.66) |
| | Daejeon | -0.10(-0.29)/-0.12(-0.50) | -15.53(-0.79)/-9.71(-0.64) |
| | Gwangju | -0.51(-0.85)/-0.35(-0.88) | -10.64(-0.81)/-8.00(-0.69) |
| | Busan | -0.64(-0.89)/-0.49(-0.90) | -12.32(-0.83)/-11.05(-0.81) |
| | Ulsan | -0.04(-0.08)/-0.06(-0.16) | -4.80(-0.39)/-0.75(0.07) |
| | Daegu | -0.65(-0.87)/-0.51(-0.89) | -23.49(-0.90)/-19.87(-0.87) |
| Province | Gyeonggi | -0.41(-0.66)/-0.44(-0.79) | -14.50(-0.95)/-8.82(-0.94) |
| | Chungcheongbuk | -0.18(0.39)/-0.16(-0.45) | -17.68(-0.78)/-6.49(-0.61) |
| | Chungcheongnam | -0.10(-0.30)/-0.12(-0.41) | -20.95(-0.76)/-9.33(-0.69) |
| | Jeollabuk | -0.17(-0.42)/-0.25(-0.65) | -21.33(-0.87)/-15.07(-0.85) |
| | Jeollanam | -0.21(-0.51)/-0.21(-0.58) | -5.86(-0.53)/-5.32(-0.48) |
| | Jeju Island | -0.18(-0.38)/-0.16(-0.46) | -10.74(-0.71)/-6.95(-0.50) |
| | Gyeongsangnam | -0.12(-0.31)/-0.10(-0.40) | -6.76(-0.58)/-3.92(-0.46) |
| | Gyeongsangbuk | -0.76(-0.89)/-0.49(-0.88) | -27.54(-0.82)/-17.48(-0.78) |
| | Gangwon | -0.16(-0.50)/-0.20(-0.69) | -15.31(-0.86)/-9.03(-0.71) |

8) The discussion of the COVID-19 influence on ozone (pg. 14-15) is interesting, particularly the “large reduction of ozone in the background sites”. There are other studies of the influence of COVID-19 emission reduction on background ozone at northern mid-latitudes. The findings in these other studies should be quantitatively compared to the present results.

→ Thank you for introducing publications. In the revised manuscript, we refer the study by Steinbrecht et al. (2021) that reported about 7% reductions of mid-latitude free atmosphere ozone concentrations in 2020 from the climatology value covering 2000-2020. Our study focused on the analysis surface ozone over South Korea that substantially increased for the period of 2000-2020. Thus, it is not straightforward to quantitatively compare the anomaly in 2020 from climatology in this study with that in Steinbrecht et al. (2021). It is still worthwhile to mention agreement in declining ozone concentration/exceedances during COVID in our study and Steinbrecht et al (2021).

9) I find the discussion beginning on line 14, page 13 and continuing to the end of the Results section on page 16 to be very confusing, with many topics discussed in a disjointed manner. Please revise and clarify this discussion. Any topic that cannot be clearly and concisely explained without speculation should be eliminated.

→ Agreed. There are indeed many topics. Following your suggestions, to clarify the contents, we made several subsections with appropriate titles within the results section. The discussion section is also incorporated into the result section. The titles for the subsections in the results section in the revised manuscript are written below.

3.1 Surface ozone trends

3.2 Difference between spring and summer: background value, exceedance, stratospheric influence, and precursor concentrations

  3.2.1 Background values at the base and peak times

  3.2.2 Ozone exceedances

  3.2.3 Influence of stratospheric ozone

  3.2.4 Long-term trends of surface $NO_2$ and CO concentrations

3.3 Changes detected during the COVID-19 pandemic (2020-2021) compared to 2002-2019

  3.3.1 Changes in ozone exceedances and local precursors during springtime

  3.3.2 Changes in ozone exceedances and local precursors during summertime

  3.3.3 Changes in precursor concentrations at a regional scale during spring and summer: TROPOMI tropospheric $NO_2$ columns

3.4. Impacts of changes in East Asian emissions on surface/boundary layer ozone in South Korea: a modeling analysis

  3.4.1. Changes in surface/boundary layer ozone due to emissions reductions: East Asian region

  3.4.2. Vertical sensitivity of ozone changes in South Korea to East Asian emission Reductions

  3.4.3. Comparisons with recent modeling research

10) Similarly, the Section 4 discussion section is difficult to follow. The authors should aim to convey the main points of the modeling results as clearly and concisely as possible. The last two sentences of the section appear to be the main points; they should be clearly and concisely supported by the preceding discussion.

→ The discussion section is now incorporated into the results section for better support of the content and a smooth connection. We emphasized the last two sentences by reorganizing the results section and adding more explanations.

11) The Summary and Conclusions section will need to be rewritten when the issues identified here are addressed. Specifically:

- The ozone in the 01-06 LT period is so affected by local conditions that it should not be included in the 2nd paragraph of this Section.

→ Please see our replies above. We kept using data at 01-06 LT to get information about background/transport.

- Page 19, discussion beginning on line 17 should be improved. If there is strong influence of long-range transport on the surface ozone at the background sites, then that influence must also be present at all sites throughout South Korea. That influence is not apparent at night at most sites due to rapid nighttime loss of ozone at most sites.

→ Please see our replies above. Even with rapid nighttime loss of ozone at most sites, there is still information about long-range transport. We would like to maximize the use of the data at 01-06 LT.

- An explanation should be given as to why there is such large regional differences in overall percentage decline in $NO_2$. Perhaps this can be related to the model emission inventory?

→ There are many sources of $NO_2$ besides mobile sources in South Korea, such as power plant and industries. Thus, decline of $NO_2$ varies at the monitoring sites that have different source profiles. As mentioned, uncertainty in the emission inventory is generally large and was not extensively estimated.

**Minor issues**:

1) Pg. 4, Line 11: Four references are given for papers that have previously reported increasing ozone trends in South Korea. Two of those are missing from the reference list. The introduction should briefly summarize what these papers found, and discuss the advances that the authors' make in this paper beyond what is known from those earlier papers.

→ The missing references were added. We clarify the contribution of our study compared to the previous study. In reply to the Reviewer 1, we wrote "The published works on the trend of surface ozone in South Korea presented the ozone metrics such as annual mean of hourly ozone, annual mean of MDA8 ozone, annual mean of daily maximum hourly ozone, and frequency of hourly concentrations greater than 120 ppb. The trends based on those metrics have already been published (e.g., Yeo and Kim, 2021). Since the US EPA National Ambient Air Quality Standard (NAAQS) for ozone is 70 ppb, as the fourth-highest MDA8 ozone concentration, averaged across three consecutive years, and the recent study by Wang et al. (2022) adopted the 4th highest MDA8 ozone concentrations as one of the metrics for study of Chinese ozone pollution, it would be nice to have analyses adopting the 4th highest MDA8 ozone for a global comparison. The EPA standard is also designed for public health protection. Exceedances presented in our study are similar to the frequency exposed to MDA8 ozone > 70 ppb (relevant to EPA standard)". This state some of our contributions to ozone analysis over South Korea, compared to the previous studies. This study reveals characteristics of newly defined exceedances (hourly O3 concentration > 70 ppb) that captured large changes of ozone during COVID and emphasizes long-range transport of ozone over eastern part of South Korea such as Gangwon-do and Ulleung-Island.

2) There are minor problems with the English usage, which should be corrected by editing by a native English speaker.

→ We improved English for the revised manuscript with the aid of a native speaker without changing contents.

3) Page 5, line 9 mentions that 8 provinces are studied; however Table 1 lists 9 provinces. Please develop a list of cities, provinces, and background sites, and consistently use that list throughout the paper.

→ We kept listing 9 provinces in the main text, tables, and figures in the revised manuscript.

4) In the Figure 1 caption, the different colors used for the city province and site names should be described. Also it is not clear exactly what is being plotted here: Is each symbol the mean 4th highest (MDA8) over all sites in the city or province? Confidence limits should be given for all derived slopes.

→ In the revised manuscript, we explained the meaning of different colors in Figure 1. In Table 1 in the revised manuscript, we showed slope, standard deviation, P-value, and signal-to-noise value. The information about all sites in the city or province is shown in the Supporting Information.

5) In the description of the two models evidently different anthropogenic emission inventories are used in the two models (CMIP6 for 2000-2014 and SSP5-8-5 for 2015-2020 in CAM-Chem and WRF-Chem and EDGAR-HTAPv2). There should be a brief discussion regarding how well these inventories compare, and if any problems arise

from using perhaps incompatible emissions in the two models. Also mention should be made regarding whether these inventories correctly simulate the emissions reductions during the COVID-19 period.

→ CMIP6 is based on EDGAR v4.2 or v4.3.2 described in Feng et al. (2020). SSP5-8.5 and EDGAR-HTAP v3 can be compared for the KORUS-AQ campaign period in 2016, as the WRF-Chem simulations were conducted during the period. In this reply, we compared $NO_x$ emissions of SSP5-8.5, EDGAR-HTAP v3, v2, and KORUS v5. In Table R9, over China, SSP5-8.5 NOx emissions are slightly larger than those in KORUS v5 and are lower than those in EDGAR-HTAP v3. SSP5-8.5 has much lower NOx emissions over South Korea and SMA, compared to EDGAR-HTAP v3. “No SMA” simulations with WRF-Chem may help estimate the uncertainty in the simulated $O_3$ originated from the emission discrepancy. “No SMA” increases $O_3$ concentrations over South Korea (SMA) by 1.87 (22.1) ppb.

We acknowledge the emission differences for the two models. However, we are conducting research utilizing CAM-Chem and WRF-Chem separately for different purposes. Separate papers for different models are in review and in preparation. In this study, we utilized the results from CAM-Chem to analyze the contribution of stratospheric ozone to tropospheric ozone and use WRF-Chem model to investigate the impacts of anthropogenic emission changes on local and regional air quality. Thus, one-to-one comparison of the two models are beyond the scope of this study.

Table R9. The area sum emissions in Eastern China (27.7-40°N, 115-123°E), South Korea (34.5-38°N, 126-130°E), and Seoul Metropolitan Area (SMA: 37.2-37.8°N, 126.5-127.3°E) in May 2016 for NOx.

| **NOx emission** (unit = mols/s) | **SSP5-8.5** | **EDGAR-HATP v3** | **EDGAR-HATP v2** | **KORUS v5** |
|---|---|---|---|---|
| China | 6638 | 9034 | 10063 | 5482 |
| South Korea | 303 | 1097 | 990 | 886 |
| SMA | 26 | 214 | 196 | 191 |

Feng, L., Smith, S. J., Braun, C., Crippa, M., Gidden, M. J., Hoesly, R., Klimont, Z., van Marle, M., van den Berg, M., and van der Werf, G. (2020). The generation of gridded emissions data for CMIP6. Geoscientific Model Development, 13, 461-482, doi.org/10.5194/gmd-13-461-2020

6) Page 10, line 11-12: For greater accuracy, I suggest changing "… increases by 1-2 ppb yr-1 for most of cities and provinces across South Korea …" to "… increases by 1.0-1.5 ppb yr-1 for most cities and provinces across South Korea …"

→ We changed it to 1.0-1.5 ppb $yr^{-1}$.

7) Page 10, line 12-13: For greater accuracy, I suggest changing "The most of cities and provinces have the 4th highest MDA8 O3 higher than 70 ppb after 2010." to "In nearly all cities and provinces, the 4th highest MDA8 O3 has been higher than 70 ppb since 2010 or earlier."

→ Thank you for your suggestion. We replaced the original sentence by the one the reviewer suggested.

8) I suggest vertical lines be added to Figure 4 to separate the cities, provinces, and background sites from each other. Similarly for Figures 7 and 8. Also simplify the figure captions.

→ We noted cities, provinces, and background sites with labels and lines in Figure 4, 7, and 9. The names of the location were redefined and were used consistently throughout the manuscript.

9) The discussion illustrated in Figures 4, 5 and 7 is based on "exceedances"; however, I cannot find where "exceedance" is defined in the paper. Please define. (I assume it is a day when MDA8 ozone exceeds 70 ppb).

→ Agreed. The mistakes in the abstract were corrected. The definition of exceedances is clarified in the abstract. In this study, exceedance is defined as hourly $O_3$ > 70 ppb.

10) Figure 5 needs to be clearly explained. If an exceedance is based on MDA8, how can there be a diurnal cycle, since there is only one MDA8 per day? Is this percent of days with ozone above 70 ppb in a given hour? I suggest using the same ordinate scale in all 3 graphs, so that the comparison is made easy for the reader. Also the general description of the sites included in the 3 graphs should be given; i.e., top = Seoul area, middle = secondary cities, bottom = remote sites.

→ Please see the reply above for minor point (9). We also used the same ordinate scale for Figure 5. The general description of the sites is included in the figure caption as suggested by the reviewer.

11) It seems that the information included in Table 2 and Figure 6 are identical; I suggest that Table 2 be eliminated.

→ Agreed. We deleted Table 2 in the original manuscript and moved to the Supporting Information for the readers who may want to obtain the details.

12) Please give units for the slopes in Table 3; confidence limits should be given for the derived slopes. Also please give the slopes for the background sites for comparison, if those data are available.

→ The units are shown in the table caption. The results from statistical analysis are included in the revised manuscript. Because of discontinuous record of the data, the slopes for the background sites are not shown.

13) Figure 11 – x-axis labels have typo.

→ Corrected.

14) Page 20 – Please define SMA

→ SMA (Seoul Metropolitan Area) was defined in Page 2 in the original manuscript.

References:

Parrish, D.D., et al. (2020), Zonal similarity of long-term changes and seasonal cycles of baseline ozone at northern mid-latitudes. J. Geophys. Res.: Atmos., doi: 10.1029/2019JD031908.

References

Feng, L., Smith, S. J., Braun, C., Crippa, M., Gidden, M. J., Hoesly, R., Klimont, Z., van Marle, M., van den Berg, M., and van der Werf, G. (2020). The generation of gridded emissions data for CMIP6. Geoscientific Model Development, 13, 461-482, doi.org/10.5194/gmd-13-461-2020