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

Summary:
The authors have made marked improvements in the paper. However, the major revisions that I identified in my first review as necessary before this paper is can be published have not been adequately addressed. Until they are addressed, I cannot support publication of this paper. Those major revisions are addressed in further detail below. For the most part the minor issues identified have been addressed, but a few remaining are also listed below.

Thank for reviewing the manuscript again. We appreciate the reviewer's comments improving this manuscript. We made our efforts to address the concerns and suggestions raised by the reviewer to the best of our abilities. Our replies are written below in black.

Major issues:

1) In my judgement, the authors must begin their observation-based analysis with a consideration of the ozone distribution that would be present in South Korea if there were no local continental influences, i.e., if observed concentrations were due to transported baseline ozone alone. In my first review I suggested how this might be approached. This consideration would then provide a basis for understanding the continental influences, both from local South Korean emissions and from the Asian mainland emissions.

However, the authors have not attempted this approach. Instead they argue that "It would not be straightforward to delineate background O3 (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." This argument is not adequate. In fact the background ozone is quite readily approximated to the degree of accuracy required. As I noted in my first review, 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 6 of that paper shows that there is a small seasonal cycle (~ ± 5 ppb) in the background O3 outside of the marine boundary layer. Thus, the surface concentration that would be expected in South Korea in the absence of continental emissions is ~35-45 ppb at the spring-summer seasonal maximum; this expectation is in close accord with the peak time ozone concentrations at city and province sites throughout South Korea. To my mind, this discussion must be the starting point for the discussion of O3 concentrations throughout South Korea.

The authors also respond: "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." However, Figure R12 shows only relatively small differences in mean annual ozone at the diurnal peak times, even in Seoul, the largest city in South Korea. The Control simulation gives a maximum of ~60 ppb. No Seoul emission simulation gives ~ 70 ppb and No China emission simulation gives ~47 ppb. This clearly emphasizes my point that the ~35-45 ppb expected for background only is an excellent starting point for the discussion of the local and regional South Korean influences.

→ The reviewer suggested an interesting approach to analyze surface ozone over South Korea. We value the reviewer's opinion. Current manuscript introduced several metrics emphasizing maximum values to mean values over various time scales characterizing surface ozone over South Korea, which stimulates multiple studies in the future. A study focusing on the mean status (background value) of ozone and its deviations in South Korea that was suggested by the reviewer would be much appreciated. Unfortunately, because of large extent of current manuscript, this topic and approach suggested by the reviewer should be addressed in another manuscript.

2) In my first review I objected to the author's attempt to use the lower ozone concentrations in the 01-06 period to characterize transport of background ozone, because loss of ozone beneath the nocturnal inversion, both due to reaction with fresh local NOx emissions, but also due to surface deposition, especially to vegetated surfaces. Thus, nighttime ozone concentrations do not provide direct information regarding transported baseline ozone. However, if the authors insist upon inclusion of analysis of the data in the 01-06 period, it is essential to base that analysis of Ox = O3 + NO2 concentrations. The figure below is derived from the Seoul data that the authors included in their Figure R9. The Ox concentrations are not affected by the reaction of O3 with fresh local NOx emissions (but is affected by loss to surface deposition), providing further reactions to form NO3, N2O5 and nitrate are not important. Ox recorded during the 01-06 period is a much more accurate indicator of transported baseline ozone than is O3 itself.

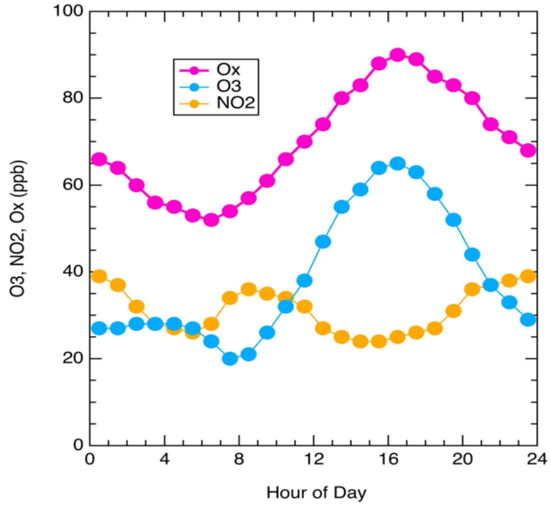

Figure 1. The diurnal variations of observed O3, NO2 and Ox averaged for the simulation period, based on reading data from the authors' Figure R9.

→ We have analyzed Ox. It is insightful to examine Ox values and their changes with seasons. Actually, NO_2 concentrations in spring are consistently, distinctively higher than those in summer, which made the comparison of Ox between the two seasons somewhat complicated. NO_2 concentrations at peak and base time in spring and summer are summarized in Table R1. Chemical lifetime of NOx is larger in spring than summer. This affects NO_2 levels during nighttime. It seems that the reviewer's concerns about seasonal changes in boundary layer height and deposition during nighttime are minor issues compared to the changes in chemical lifetime. See also our responses to major comments 4) below. Furthermore, NO_2 concentrations vary substantially with locations, which made the comparison of seasonal Ox differences among different locations somewhat complicated. In Table R2, O_X concentrations at peak and base time in spring and summer are summarized. Overall, Ox during spring is higher than that during summer and nighttime differences are prominent, which is similar to the conclusions from the analysis of O_3. Therefore, we do not change the original content. **Because we think both O_3 and Ox are useful, the analysis of NO_2 and Ox are now included in the Supporting Information following the reviewer's request (SI1, Table S6 and S7). Please refer to the changes in P15, L20 – P16, L4 in the final revised manuscript.**

Table R1. Spring and summer NO_2 concentrations in Korean metropolitan cities and provinces. Both peak time (10-20 LT) and base time (01-06 LT) averages are shown. Differences in concentrations between spring and summer ($NO_{2\ spring} - NO_{2\ summer}$) are in the parenthesis.

Location		Peak time	Base time
		Spring / Summer (difference)	Spring / Summer (difference)
City	Seoul (SUL)	36.1 / 29.5 (6.6)	36.9 / 24.6 (12.3)
	Incheon (INC)	30.5 / 24.3 (6.3)	28.5 / 19.7 (8.8)
	Daejeon (DJN)	16.1 / 12.0 (4.1)	20.5 / 13.6 (6.9)
	Gwangju (GWJ)	19.8 / 13.4 (6.4)	19.0 / 10.4 (8.6)
	Busan (BSN)	20.9 / 13.9 (7.0)	24.3 / 14.5 (9.8)
	Ulsan (ULS)	23.9 / 20.1 (3.8)	21.2 / 15.3 (5.9)
	Daegu (DGU)	24.3 / 16.6 (7.7)	26.0 / 15.4 (10.6)
Province	Gyeonggi-do (GGI)	27.3 / 20.8 (6.5)	31.2 / 20.7 (10.5)
	Chungcheongbuk-do (CCB)	18.9 / 13.6 (5.3)	20.8 / 13.7 (7.1)
	Chungcheongnam-do (CCN)	17.4 / 12.9 (4.5)	18.0 / 11.9 (6.1)
	Jeollabuk-do (JLB)	15.1 / 11.2 (3.9)	14.1 / 9.2 (4.9)
	Jeollanam-do (JLN)	17.4 / 14.0 (3.4)	14.1 / 10.5 (3.6)
	Jeju Island (JEJ)	12.0 / 8.5 (3.5)	8.5 / 6.0 (2.5)
	Gyeongsangnam-do (GSN)	18.6 / 15.0 (3.6)	18.9 / 13.3 (5.6)
	Gyeongsangbuk-do (GSB)	17.9 / 13.4 (4.5)	20.5 / 13.6 (6.9)
	Gangwon-do (GWO)	14.0 / 9.9 (4.1)	13.4 / 8.1 (5.3)
Background	Ulleung Island (ULL)	3.4 / 2.7 (0.7)	3.3 / 2.8 (0.5)
	Gosung (GSU)	4.5 / 2.6 (1.9)	4.6 / 2.8 (1.8)

Table R2. Spring and summer O_x (=O_3+NO_2) concentrations in Korean metropolitan cities and provinces. Both peak time (10-20 LT) and base time (01-06 LT) averages are shown. Differences in concentrations between spring and summer ($O_{X\ spring} - O_{X\ summer}$) are in the parenthesis.

Location		Peak time	Base time
		Spring / Summer (difference)	Spring / Summer (difference)
City	Seoul (SUL)	70.5 / 65.1 (5.4)	57.5 / 42.1 (15.4)
	Incheon (INC)	65.1 / 57.4 (7.7)	53.6 / 39.9 (13.7)
	Daejeon (DJN)	57.3 / 49.0 (8.3)	43.3 / 32.7 (10.6)
	Gwangju (GWJ)	59.7 / 48.8 (10.9)	47.5 / 34.4 (13.1)
	Busan (BSN)	61.2 / 48.1 (13.1)	54.6 / 36.9 (17.7)
	Ulsan (ULS)	62.6 / 53.5 (9.1)	47.0 / 34.0 (13.0)
	Daegu (DGU)	63.9 / 54.2 (9.7)	50.0 / 35.0 (15.0)
Province	Gyeonggi-do (GGI)	64.8 / 59.3 (5.5)	52.0 / 38.7 (13.3)
	Chungcheongbuk-do (CCB)	61.0 / 53.0 (8.0)	45.6 / 34.3 (11.3)
	Chungcheongnam-do (CCN)	58.7 / 50.6 (8.1)	47.6 / 35.0 (12.6)
	Jeollabuk-do (JLB)	53.4 / 46.2 (7.2)	40.8 / 32.8 (8.0)
	Jeollanam-do (JLN)	59.9 / 49.1 (10.8)	47.1 / 34.6 (12.5)
	Jeju Island (JEJ)	61.3 / 42.7 (18.6)	52.5 / 34.6 (17.9)
	Gyeongsangnam-do (GSN)	62.9 / 55.0 (7.9)	47.8 / 35.2 (12.6)
	Gyeongsangbuk-do (GSB)	63.0 / 51.4 (11.6)	49.0 / 34.2 (14.8)
	Gangwon-do (GWO)	58.5 / 49.0 (9.5)	41.3 / 28.6 (12.7)
Background	Ulleung Island (ULL)	60.0 / 46.6 (13.4)	59.2 / 45.9 (13.3)
	Gosung (GSU)	62.8 / 45.7 (17.1)	62.7 / 47.9 (14.8)

3) In my first review I suggested that the background sites be included in Figure 3 and Table 1 in order to emphasize the similarity of the ozone concentrations throughout the country, and the predominant role played by transported baseline ozone. The authors have not made that inclusion; they argue that missing data require that exclusion. However, the data are missing only for periods of only 1 to 4 months out of 21 years. Such minor periods of missing data do not significantly compromise trend analyses. The great value of the background sites for comparison with other south Korean sites is shown in the authors' Figure R11 which clearly demonstrates that peak, mid-day mean ozone concentrations are very similar (in both the observations and model simulation) at the largest South Korean urban area (Seoul) and one of the background sites (Gosung). In my view, it is imperative that all tables, figures and discussion clearly address the 7 cities, 9 provinces, and 2 background sites in a consistent manner to the fullest extent possible. I do understand that measurements of precursor species may not be available from background sites, and thus cannot be included. However, on lines 12-15 of page 30 in the Conclusions Section the authors state: "The 4th highest maximum daily 8-hour average (MDA8) ozone concentrations showed an increasing trend in all cities, most provinces, and background sites during this period, with a yearly increase of 1-2 ppb." Certainly the data from the background sites must be shown in the paper to support that conclusion. The

increasing trend at background sites should also be included in the similar sentence in the Abstract (lines 8-9, page 2).

→ Agreed. We added the trends of the 4th highest MDA8 ozone from 2001 to 2021 for the background sites to Table 1. Although there are missing data during the ozone season, the 4th highest MDA8 ozone values were calculated for these sites. Because of this limitation and low certainty, the plots of the trend of the 4th highest MDA8 ozone for the background sites are not presented in Figure 2 or 3. In Table 1, the trends for 2001-2019 are also shown for the background sites because the increasing trends for this shorter period (prior to the COVID-19 pandemic) are more certain. Averages of ozone, NO_2, and Ox for the background sites at peak and base time for spring and summer are added to Table 2 and Supporting Information (Table S6 and S7). Because of discontinuity of the data, the trend of NO_2 and CO for the background sites are not shown in Table 3 and 4 in the final revised manuscript. We note this information in the Table captions for Table 1, 3, and 4. **Please refer to the changes in P13, L20 – P14, L8 and P15 L5-6, P15 L 11-13 and Table 1 and 2 in the final revised manuscript and Table S6 and S7 in SI1.**

4) In my first review I mentioned that 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. The authors disagree, and respond that they "don't think that there are clear mechanisms driving differences in nocturnal inversion between spring and summer." I am not a meteorologist, but is has been my understanding that atmospheric stability is at a minimum in spring and significantly greater in summer – hence tighter inversion layers in summer. I believe that this may be clearly shown in the authors' Table R5, which shows that mean wind velocity is generally higher in spring than in summer at all of the stations considered. The nocturnal inversion is much more sharply defined in calm than in windy conditions. Regardless of my meager meteorological expertise, if the authors really wish to compare nighttime ozone concentrations between spring and summer, it is their responsibility to demonstrate that the nocturnal boundary layer dynamics do not change between seasons to a degree large enough to affect that comparison – they have not provided that demonstration. Again, given the very local processes that determine the 01-06 LT ozone, including the unaccounted for effects of surface deposition, and for the reasons discussed in my point 2) above, I recommend that the authors eliminate the discussion of this nighttime ozone; this discussion does not seem to be central to the main points of the paper. Notably, the analysis discussed in Section 3.2.1 is not mentioned either in the Abstract or in Section 4 Conclusions.

→ Understanding of stably stratified turbulence is limited and parameterization of stable boundary layer and its height is challenging (Cuxart et al., 2006; Fernando and Weil, 2010). There are currently several issues in practical applications of the state-of-the-art model and observations in association with stable boundary layer height. The boundary layer height from typical global and mesoscale models are not readily comparable to the observed nocturnal boundary layer heights. For example, the stable boundary layer from ceilometer reflects the observed vertical profiles of aerosols rather than thermal and mechanical turbulence structure. Meanwhile, the stable boundary layer height from WRF model output is subject to the definition of the model critical Richardson number and is not readily comparable to observations of boundary layer height during nighttime. Detailed discussions about the definitions of stable boundary layer height that is determined by stability and wind shear are beyond the scope of this paper.

According to Kim and Park (1996), seasonal changes in nighttime wind speed, stability, and friction velocity (a measure of turbulence intensity) between spring and summer over Seoul Metropolitan Area were small. The seasonal changes in nighttime dry deposition velocity of NO_2 over this area were also very small. Please refer to the figures below (Figure 5, 6, 7, and 10 from Kim and Park, 1996). However**, in final the revised manuscript, we included the NO_2 and Ox analysis in the Supporting Information following the reviewer's comments (SI1 Table S6 and S7).** Please see also our response to the reviewer's major comment 2).

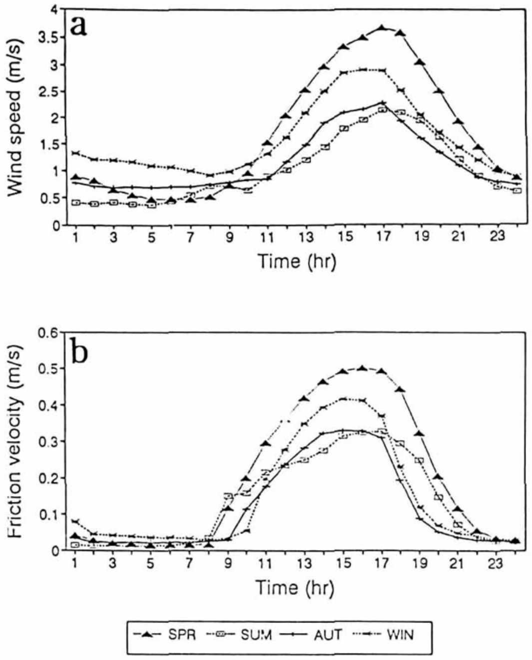

Fig. 5. The dirunal variations of seasonal mean (a) wind speed (m/s) and (b) friction velocity (m/s).

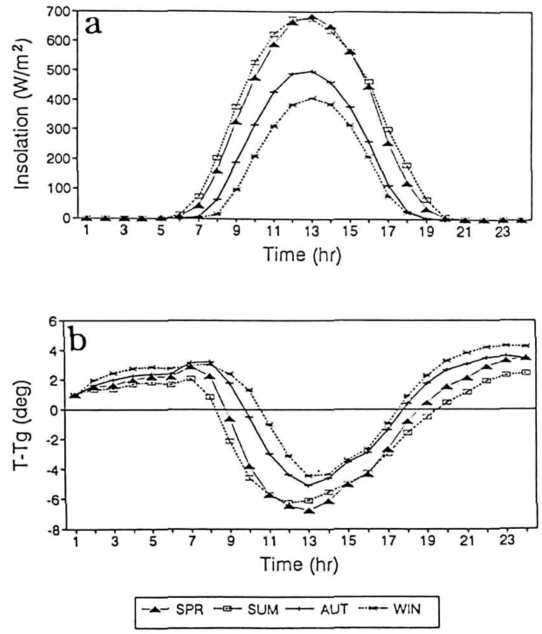

Fig. 6. The same as in Fig. 5 except for (a) solar radiation (W/m2) and (b) temperature difference between surface temperature and ground temperature (deg).

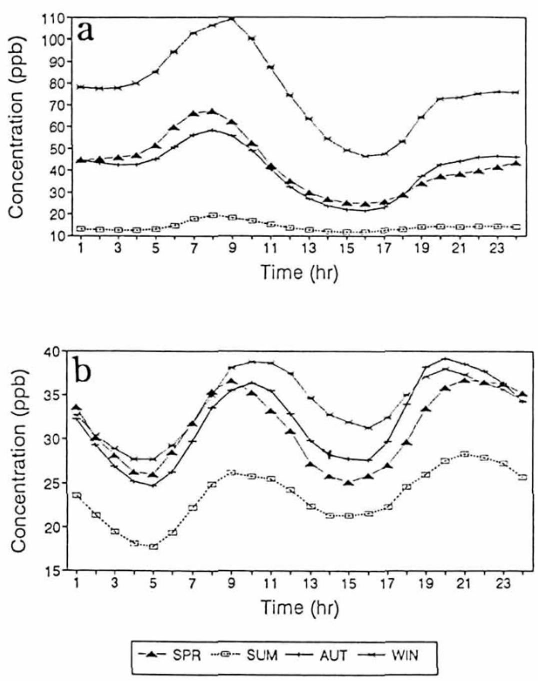

Fig. 7. The diurnal variations of mean (a) SO_2 and (b) NO_2 concentration (ppb).

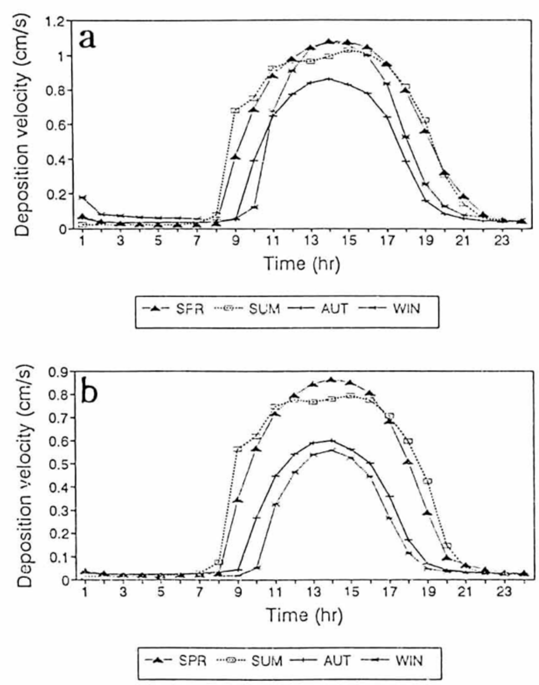

Fig. 10. The same as in Fig. 7 except for (a) SO_2 and (b) NO_2 dry deposition velocity (cm/s)

5) The Conclusions section requires some modifications. Specifically:

- On page 31, lines 4-7 has the sentence: "The majority of ozone exceedances occurred between 16-19 LT (4-7 PM). Interestingly, exceedances also occurred frequently at night in background sites such as Gosung and Ulleung Island, indicating a strong influence of long-range transport on surface ozone levels in these locations." I suggest that the final phrase "in these locations." be changed to "over South Korea". The only reason that nighttime exceedances are not seen at most sites in South Korea is that loss of ozone to fresh NOx emissions at night reduce the ozone concentrations below the concentration of transported background ozone.

→ We agree with you about underlying causes for reduced ozone during nighttime at most sites in South Korea. However, here, we wanted to highlight the Gosung and Ulleung Island sites for frequent nighttime exceedances, which is different from highly polluted cities like Seoul. Therefore, we kept the original content.

- Page 31, lines 13-14 has the sentence: "Therefore, it is not clear what drove increase of ozone exceedances over South Korea from P1 to P2." I disagree; I believe that it is abundantly clear that the increases in ozone exceedances in South Korea can be attributed to increased anthropogenic emissions in China. This certainly follows from the following sentence which states: "We observed significant reductions in ozone exceedances across all monitoring sites in South Korea during the spring of the COVID-19 pandemic (period P3, 2020-2021), which was attributed to decreased anthropogenic activities and subsequent lower emissions in both China and South Korea." This discussion should be clarified.

→ As the reviewer mentioned, it is likely that the increases in ozone exceedances in South Korea from P1 to P2 are attributed to increased anthropogenic emissions in China. However, we would like to conclude this after completion of our long-term model simulations and analysis covering this period. And it would be also important to address the impact of the climate changes (e.g., large positive temperature anomaly in 2010's) on changes in ozone concentrations over South Korea. Following the reviewer's comments, in the final revised manuscript, we stated "The observed increase in ozone exceedances from P1 to P2 in South Korea may be partially attributed to the rise in anthropogenic emissions originating from China. More modeling experiments covering the P1 to P2 period would help identify the main factors behind the ozone increases. It is important to investigate not only changes in anthropogenic emissions but also the impact of climate change on ozone variations during this period". **Please refer to changes in P32 L10-L15 in the final revised manuscript.**

Minor issues:

1) Table 1: I presume that the tabulated ozone concentrations are means over all days in each season. This should be stated in the Table caption.

→ We clarified this information. A sentence "Data during typical ozone season (May-September) are used" are added to **the caption in Table 1**.

2) The description of the two models indicates that different anthropogenic emission inventories are used in the two models. The authors have now given a brief discussion regarding how well these inventories compare (their Table R9), but they include that discussion only in their response to the reviewers' comments. This is very important discussion; it should also be included in the paper itself, possible in the Supplementary Material.

→ Following the reviewer's suggestions, we included the Table R3 in this reply to **the Supporting Information (SI1 Table S5)**. The discussions are shown in the note attached to the table.

3) Pg. 14, line 1 contains the term "Asian emissions". I think more specificity is required here. Perhaps "Chinese emissions" or East Asian emissions".

→ Corrected to "East Asian emissions". **Refer to P14, L9 in the final revised manuscript.**

References

Cuxart, J., and Coauthors, 2006: Single-column model intercomparison for a stably stratified atmospheric boundary layer. Bound.-Layer Meteor., 118, 273–303, doi:10.1007/s10546-005-3780-1.

Fernando, H. J. S., and J. C. Weil, 2010: Whither the stable boundary layer? A shift in the research agenda. Bull. Amer. Meteor. Soc., 91, 1475–1481, doi:10.1175/2010BAMS2770.1.

Kim, S.-W. and S.-U. Park, 1996: Estimation of dry acidic deposition in the Seoul Metropolitan Area, Journal of Korean Meteorological Society, 32, 2 (In Korean).

Reply to the reviewer 4 of the revised manuscript "Changes in surface ozone in South Korea on diurnal to decadal time scale for the period of 2001-2021"

We thank you for reviewer's time and helpful comments. Our replies are written in black.

The second version of the manuscript has improved, and most of the referees' comments have been correctly addressed by the authors.

I think that a figure presenting the atmospheric transport is missing. While a Lagrangian analysis would be valuable but maybe out of the scope of this paper, one possibility is to overlay on maps of Figure 9 the seasonal average wind vectors to have a better sense of the mean transport in spring and summer.
→ We added the wind vectors for each season in **Figure 9 and Supporting Information (SI3 Figure S2 and S5)**. We have a plan to pursue a Lagrangian analysis for another manuscript.

Concerning the conclusion, the last sentences present some perspectives on how to improve our understanding of the ozone trends in South Korea. It is my opinion that a network of ozonesondes at a few key locations (Seoul, Gosung, a background site) with the capability of a weekly launch would be important to understand the evolution of ozone for the next decade. It will be complementary (and much cheaper) than a large field campaign like KORUS-AQ . If the authors agree, they could add a few sentences on the value of monitoring ozone with ozonesonde launches on a regular basis.
→ Agreed. We added "Monitoring ozone within the boundary layer and at higher altitudes is crucial for enhancing our understanding of ozone trends in South Korea. A network of ozonesondes at multiple sites with the capability of weekly launches would be a valuable complement to a large field campaign" to the **last paragraph of the final revised manuscript**.

Technical comments:
I don't understand Figure 4. What kind of ratio is presented here exactly?
→ First, we calculated the exceedances in each season. Here, the exceedances are defined as the fraction of hourly ozone concentration greater than 70 ppb among all available data. What is plotted is the ratio of exceedances in summer to exceedances in spring. In the final revised manuscript, we included this detail in **the caption of Figure 4**.

Figure 5: You should use the same naming convention as in the previous figures: province and background sites.
→ Agreed. We used the same naming convention in **Figure 5** as much as possible in the final revised manuscript.