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

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Abstract

Increasing trends of tropospheric ozone in South Korea in the last decades have reported in several studies, based on various metrics. In this study, we derived the trends of surface ozone in South Korea utilizing the daily maximum 8-hours average ozone concentrations (MDA8) measured at the surface from 2001 to 2021 and analyzed diurnal, seasonal, multi-decadal variations of this parameter at city, province, and background sites. The 4th highest MDA8 values have positive trends at 7 cities and 8 provinces throughout 2001-2021 with approximately 1-2 ppb yr^{-1} and were greater than 70 ppb after early 2010 for all sites, despite decreases of its precursor NO_2 and CO. The Seoul Metropolitan Area (SMA) and the background sites have different diurnal and seasonal characteristics of MDA8 exceedances defined in this study (percentage of the data points with MDA8 > 70 ppb among all data points). SMA have much higher exceedances during summer than spring, while the background sites have much higher exceedances during spring than summer highlighting efficient local production of ozone in SMA during summer and strong influence of long-range transport during spring. The exceedances during spring and summer are similar for the rest of sites. The peaks of exceedances occur at 4-5 PM in SMA and most of locations, while exceedances mainly occur at 7-8 PM through night at the background sites. During spring of the COVID-19 pandemic (2020-2021), the MDA8 ozone exceedances decreased for most of locations with large NO_x reductions in South Korea and China compared to 2010-2019. The large decreases of the MDA8 ozone

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exceedances occur in particular at the background sites during spring. In Gosung, Gangwondo (~600 m above sea level), the exceedances drop to ~5% from 30% in springtime during the COVID-19 pandemic. The concept of decreases of ozone in the boundary layer in Seoul and Gangwon-do to reductions in the emissions was confirmed by regional model simulations. The reductions of ozone exceedances did not occur at the major cities and provinces during summer of the COVID-19 pandemic with much smaller decreases of NO_x in South Korea and China compared to spring. This study demonstrates distinctions between spring and summer in the formation and transport of surface ozone in South Korea and the need of monitoring and modeling with focus on different processes in each season or a finer time scale.

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1. Introduction

Ozone in the low atmosphere (or troposphere) can be formed and accumulated by photochemical reactions involving nitrogen oxides and volatile organic compounds that emit from anthropogenic and natural sources (National Research Council, 1991; Monks et al., 2015). Ozone is an air pollutant harmful to public health and ecosystem and is a greenhouse gas warming the globe. Therefore, it is alarming that ozone concentrations near the surface and troposphere increase. Gaudel et al. (2018) reported rapidly increasing ozone trends from 2000 to 2014 in South Korea contrasting decreasing trends in North America and Europe utilizing available data from surface monitors, ozonesondes, and aircraft observations. Other studies also reported increasing ozone trends in South Korea for 2001-2018 (Lee et al., 2014; Shin et al., 2017; Lee et al., 2020; Yeo and Kim, 2021). Ozone in South Korea can be affected by ozone and its precursor in China. However, ozone data covering China were not included in Gaudel et al. (2018) because of lack of reported data. Recent studies highlighted rapidly increasing ozone trends in China from 2004 to 2020, particularly after 2013 (Li et al., 2019; Wang et al., 2020; Wang et al., 2022). Since the two countries are close enough to exchange ozone and its precursors, it would be essential to study the trends of ozone in South Korea associating with those in China. Particularly, spring and summer as warm season have different transport patterns and source-receptor

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relationships relevant to surface and tropospheric ozone (e.g., Cooper et al., 2010). Therefore, it would be useful to investigate ozone trends in South Korea separately for spring and summer. There were large changes in atmospheric composition during the COVID-19 pandemic (Bauwens et al., 2020; Koo et al., 2020; Seo et al., 2021). The deviations caused by the pandemic from the long-term trends would provide a valuable perspective for planning of future environmental policy to improve ozone pollution. In this study, we characterize ozone trends and exceedances in South Korea from 2001 to 2021 (including the COVID-19 period) focusing on the warm season, spring and summer. Diurnal, seasonal, and decadal changes at 7 cities, 8 provinces, and 3 background sites are studied. The causes for the large temporal changes are discussed based on regional model results.

The manuscript is organized as following. In section 2, the surface and satellite data, global and regional modeling, and other methods to utilize the data are explained. In section 3, the results are summarized as long-term trends of ozone and its precursors, characteristics of diurnal variations, and spatiotemporal variations during the pandemic. In section 4, the regional model results based on various emission scenarios are shown to identify the source-receptor relationship. Finally, the results are summarized and future research directions are suggested in the conclusions.

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2. Method

2.1. Long-term surface observational data

The hourly surface air quality monitoring data are obtained from the Airkorea website (https://www.airkorea.or.kr), including ozone (O_3), NO_2, SO_2, CO, PM_{10}, and $PM_{2.5}$ ($PM_{2.5}$ data are provided since 2015). As of March 2020, there are about 500 monitoring stations over South Korea. These routine monitor data are available for many decades and can serve as a main data set to examine long-term trends. We utilized hourly and daily maximum 8 hour-average O_3 concentrations. O_3, NO_2 and CO data are also averaged for spring and summer months. These surface monitoring data were used to investigate the impact of the COVID-19 pandemic in the Seoul Metropolitan area.

2.2. Highway toll number and mobile phone usage data

To examine changes in mobility pattern during the COVID-19 pandemic, traffic counts from the Korea Expressway Corporation daily transit data were used. The expressway transit data covering 2 years (2019 and 2020) of traffic passing toll gates were quantified from Hi-Pass (electronic toll collection system) and cash toll collection. Vehicles passing toll gates were not classified in details.

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2.3. Satellite data: tropospheric NO_2 columns

We utilized the retrievals of the tropospheric NO_2 columns from the TROPOMI on board the Sentinel-5 Precursor (S5P) satellite. S5P satellite orbits on near polar sun-synchronous orbit with equator-crossing time of 13:30 local solar time (Veefkind et al., 2012). TROPOMI provides NO_2 column measurements at unprecedented fine spatial resolution of 5 km × 3.5 km (7 km × 3.5 km prior to 5 August 2019). Level 2 data with pixels passing quality assurance > 0.5 and the cloud fraction above 40% were selected for analysis. Much stricter recommendations provided by Sentinel-5 precursor TROPOMI Level 2 product User Manual for nitrogen dioxide (Eskes et al., 2019) was not used in this analysis, to yield large enough number of sample sizes over aerosol-polluted regions. The TROPOMI data are regridded to a standard grid with a horizontal resolution of 0.1 latitude × 0.1 longitude (11 × 11 km) and monthly averaged values were derived. As the random error in the TROPOMI single-pixel uncertainties influence 40 to 60% of the tropospheric column abundance, temporal and spatial averaging may remove the random errors (Bauwens et al., 2020).

2.4. CAM-Chem model simulations

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The atmospheric component of Community Earth System model (CESMv2.2), Community Atmosphere Model with Chemistry version 6 (CAM6-chem) is developed by National Center for Atmospheric Research (NCAR) (https://www2.acom.ucar.edu/gcm/cam-chem). The CAM-chem adapted MOZART-T1 as the tropospheric chemistry mechanism (Emmons et al., 2010). The simulation used in this study was configured with 1° horizontal resolution. The sea surface temperature was prescribed, and meteorological fields were nudged to Modern-Era Retrospective analysis for Research and Applications version 2 (MERRA-2) instead of using self-produced meteorological field (https://gmao.gsfc.nasa.gov/reanalysis/MERRA-2/). The simulation was performed from 2000 to 2020 and applied CMIP6 emission inventory (2000-2014) and SSP5-8-5 emission inventory (2015-2020). The first 3 years were regarded as a spin-up. In this study, we utilized the CAM-Chem results to estimate the impact of stratospheric ozone on the surface in each season.

2.5. WRF-Chem model simulations

The Weather Research and Forecasting (WRF) model coupled with Chemistry (WRF-Chem) is developed by National Oceanic and Atmospheric Administration (NOAA) and National Center for Atmospheric Research (NCAR) and collaborating institutes (Grell et

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al., 2005). We utilized WRF-Chem v4.4 to simulate regional meteorological fields and chemical compositions.

Our WRF-Chem set up utilizes the horizontal resolution of 28 x 28 km^2 and 60 vertical levels. The simulation period is from 24th April 12 UTC to 11st June 12 UTC. We restart the simulation at 12 UTC every day to reduce computing errors. The first 7 days of model simulation is regarded as spin-up period. The analysis period is selected as 1st May to 10th June based on local time. The Global Forecast System (GFS) Final (FNL) analysis data are used for meteorological input and boundary conditions (https://rda.ucar.edu/datasets/ds083.2/). We used The Community Atmosphere Model with Chemistry (CAM-Chem) output to the chemical boundary and first initial conditions (https://www.acom.ucar.edu/cam-chem/cam-chem.shtml) (Buchholz et al., 2019). The Model of Emissions of Gases and Aerosols from Nature (MEGAN) is used for biogenic emissions (Guenther et al., 2006).

There are 7 model sensitivity runs that adopt different emission scenarios. The control run is based on the standard EDGAR-HTAPv2 emission inventory (Janssens-Maenhout et al., 2015). “No China” case removes all anthropogenic emissions in China. “No Seoul” case eliminates all anthropogenic emissions in Seoul. There is one case that decreased Chinese VOC emissions by 50%. There are two cases that reduced Chinese NO_x

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emissions by 50%: the one case has the same VOC emissions as in the control case while the other case has the 50% reductions of VOC emissions as well. Lastly, there is one case that reduced Chinese NO_x emissions by 75%. The WRF-Chem sensitivity runs are summarized in Section 4 (discussion section).

3. Results

In this study, ozone and its precursor concentrations in 7 cities, 9 provinces, and 3 background sites in South Korea (Figure 1) are analyzed at diurnal, seasonal, and decadal time scales. Figure 2 shows the 4th highest daily maximum 8 hours-average ozone concentrations (MDA8 O_3) for the cities and provinces for ozone season (May-September) from 2001 to 2021. The 4th highest MDA8 O_3 increases by 1-2 ppb yr^{-1} for most of cities and provinces across South Korea in this period. The most of cities and provinces have the 4th highest MDA8 O_3 higher than 70 ppb after 2010 (see gray dashed line in Figures 2 and 3). The trend in Jeollanam-do is small and insignificant partly because the MDA8 O_3 was high before 2010. Widely increasing long-term ozone trends in South Korea indicate a regional nature of this pollutant, potentially influenced by Asian emissions, chemical transformations, and long-range transport. Therefore, it is imperative to understand the local and regional processes that enhance surface ozone. Ozone originated from Asia is known to be efficiently transported to North America during springtime (Jacob et al., 1999; Jaffe et al., 1999; Jaffe et al., 2003; Cooper et al., 2010; Lin et al., 2012; Langford et al.,

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2017; Jaffe et al., 2018) and summertime (Fiore et al., 2002; Liang et al., 2007) as well. Investigating seasonal differences in ozone in South Korea may provide insights on the relative importance of local and regional processes. Table 1 summarizes the abundances and differences between spring and summer ozone concentrations averaged for the peak time (10-20 LT) and the base time (01-06 LT). For the base time, the ozone concentration in spring is always higher than that in summer: differences between the two seasons range from 3.1 to 14.5 ppb. This clearly indicates the importance of large-scale influences in spring. The results are the same for the peak time except for Seoul and Gyeonggi-do: the ozone concentrations in Seoul and Gyeonggi-do in summer are slightly higher than those in spring. The differences at the peak time are small for Incheon, Daegu, and Chungcheongbuk-do, suggesting the importance of local chemistry in the areas during summer.

Figure 4 shows the ratio of ozone exceedances in summer to those in spring for the cities, provinces, and background sites. There are more exceedances in summer than in spring in Seoul, Incheon, and Gyeonggi-do indicating that local summertime ozone production is important in these areas. In contrast, in the background sites such as Kosan, Gosung, and Ulleung-do, springtime exceedances dominate, which demonstrates the importance of high springtime ozone and its transport within Asia. For the rest of the regions, springtime and summertime exceedances are comparable or springtime exceedances are slightly higher than summertime counterparts. The same conclusions are

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exhibited with diurnal variations of exceedances in Figure 5. Strongly enhanced summertime ozone exceedances are found during daytime from 13 to 20 LT, indicating efficient photochemical ozone production in this season. The peaks occurred at 17 LT in Seoul and Gyeonggi-do and one hour early at 16 LT in Incheon. Incheon is faced right to the West Sea (Figure 1). Thus, airmass flows from Incheon to Seoul under typical westerly or seabreeze condition. The late-afternoon peaks in the area (4-5 PM) and one hour late peak of exceedances in Seoul than Incheon suggest that local circulation plays an important role in a built-up and distribution of ozone within Incheon, Seoul, and Gyeonggi-do region. Springtime and summertime ozone exceedances mainly occur during daytime and night to some extents and the exceedances in the two seasons are similarly frequent in Daejeon, Pusan, and Daegu (Figure 5). It is interesting that the peaks in spring is about two hours later than those in summer for the three cities, indicating potential influence of transport in spring. Negligible exceedances from midnight to 10 LT in the three cities are due to high NO_x pollution and depletion of ozone in association with NO_x at this time. In the background sites, springtime exceedances are much larger than summertime counterparts and nighttime exceedances are as frequent as daytime counterparts. In Gosung, springtime exceedances are about 20% all day long while summertime exceedances are less than or equal to 10% (Figure 5). The altitude of the observation site in Gosung is about 600 m above sea level. This location gives a unique opportunity to examine long-range transported plumes and background information at high altitude.

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Stratospheric ozone can be deeply intruded in the low troposphere, elevating surface ozone during spring (Lin et al., 2012; Lin et al., 2015). It might be useful to understand the contribution of stratospheric ozone to surface in South Korea and its potential impacts on surface ozone trends in this region. Figure 6 shows the contribution of stratospheric ozone to the surface ozone in South Korea in each season. The stratospheric ozone influences the surface ozone in winter and spring most by 17-23 ppb from our global chemistry-climate model simulations. Approximately 37% (76%) of surface ozone in spring (winter) originated from stratosphere in South Korea according to the model (Table 2). In contrast, the influence of stratospheric ozone on the surface is minimum during summer, being about 4% of the surface ozone concentration. Therefore, it would be beneficial to derive the ozone trends and exceedances independently in spring and summer. Meanwhile, it is noteworthy that the stratospheric ozone contribution to the surface ozone does not have clear trends during 2001-2021 (not shown).

In contrast to the trends of ozone, NO_2 and CO that are ozone precursors decreased both in spring and summer from 2001 to 2021 (Table 3). NO_2 reductions are the largest in Seoul, Pusan, Daegu, and Gyeonsangbuk-do, while CO reductions are evident for a wider region. The decreasing trends of NO_2 and CO are not significant in Ulsan throughout this period. Ozone increases in South Korea despite reduction of main precursors at local scale can be attributed to the increase of long-range transport of ozone or potentially "VOC-limited" (or "NO_x-saturated") local photochemical regime of South Korea. "VOC-limited"

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regime is the condition in which NO_x (sum of NO and NO_2) concentration is high and VOC is a limiting factor to form ozone. In this case, VOC reduction would decrease ozone, while NO_x reduction would nonlinearly increase ozone. Since long-range transport from China is frequent during spring, it is useful to identify characteristics of ozone exceedance in spring separate from summer.

The frequency of springtime ozone exceedance increases from P1 (2002-2010) to P2 (2011-2019) in all observation sites in South Korea (Figure 7). During COVID-19, however, the frequency of exceedances significantly decreases for most of the sites: large reductions occur in Daejeon, Daegu, Chungcheongbuk-do, Gyeongsangnam-do, Gyeongsangbuk-do, Gangwon-do as well as background sites such as Kosan (Cheju Island), Gosung (Gangwon-do), and Ulleung-do. Ozone exceedances decrease from 30% to 5% in Gosung from P2 (2011-2019) to P3 (2020-2021) in spring. Gosung is close to the East Sea and is the farthest from China among the regions at a similar latitude range, but it is susceptible to long-range transported ozone because of its high elevation. NO_2 concentration does not change much from P1 to P2 across all sites. On average, there was 5% decrease from P1 to P2. In contrast, during COVID-19 (from P2 to P3), there was 25% reductions of NO_2 concentrations on average. CO concentrations also decreased by 22% from P1 to P2 and by 14% from P2 to P3. CO reductions are minor compared to NO_2 changes during COVID-19. Decreases of O_3 exceedances during COVID-19 may be associated with NO_2 decreases in this period. A notable feature is a large reduction of ozone in the background sites such as Kosan, Gosung,

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and Ulleung-do, indicating cleaner background that may be affected by emission changes in Asian sources and long-range transport. Note that there were not significant NO_2 an CO concentration changes in the background sites from P2 to P3.

During summer, ozone exceedance frequencies also increase from P1 to P2 for all sites: Chungcheongnam-do has the largest increase from 3.2% to 11.3% and Gyeonggi-do, Daejeon, Jeollabuk-do, Gyeongsangnam-do and Gyeongsangbuk-do have similar increases (Figure 8). The ozone exceedances in the background sites Kosan, Gosung, and Ulleung-do also increase in this period. NO_2 and CO concentrations decreased marginally from P1 to P2. During COVID-19, the ozone exceedance frequencies in summer increase in Seoul, Incheon, Gyeonggi-do, and Chungcheongnam-do, substantially decrease in Gangwon-do and the background sites, and remained at a similar level for the rest of sites. Because NO_2 concentrations decrease from P2 to P3 for Seoul, Incheon, Gyeonggi-do, and Chungcheongnam-do contrasting with increases of ozone exceedance, chemical regime for these regions during summer is likely to be VOC-limited (NO_x-saturated) as mentioned above. Ozone exceedance substantially decreases in the background sites from P2 to P3, indicating cleaner air at large-scale. Figure 9 shows spatial distributions of TROPOMI tropospheric NO_2 columns in spring (MAM) and summer (JJA) in East Asia and their changes from 2019 to 2020 and from 2019 to 2021. The plot shows large reductions in NO_2 columns in spring in most of China and South Korea and surrounding seas during COVID-19. Figure 10 shows changes in traffic activities in the Seoul Metropolitan Area between

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2019 and 2020. The number of cars counted at the highway tolls around this region decreased in March, April, and May in 2020 compared to 2019 by 6%. In June, this trend was reversed. The observed NO_2, SO_2, CO, PM_{10}, and $PM_{2.5}$ concentrations were also reduced during spring in 2020 compared to 2019 by 10-30%. As in Figure 9, during summer, NO_2 columns also decrease in the same region, but with limited locations and less amounts compared to spring, during COVID-19. During spring, large reductions of NO_2 in China as observed by the satellite with or without reductions of VOC are likely to contribute to substantial decreases of ozone abundances in South Korea affected by long-range transport. Meanwhile, local NO_x reductions in South Korea also can decrease ozone if NO_x reductions are large enough in the presumably "VOC-limited" chemical regime in this area. The detailed source-receptor mechanism of ozone and its precursors in each season needs to be investigated further with long-term air quality model simulations in the future. In this study, the sensitivity of the ozone concentrations in Seoul and Gangwon-do to various emission scenarios in China and South Korea are discussed for a limited time period in the next section.

4. Discussions

In this section, the WRF-Chem model simulations for the KORUS-AQ 2016 field campaign (mainly May, see Crawford et al., 2021 for details) are utilized to obtain insights about the impacts of emission changes on the ozone concentrations in Seoul and Gangwon-

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do. In Figure 11, the vertical profiles of simulated ozone from various emission scenarios are shown. The two extreme cases are "No China" and "No Seoul" cases in which all anthropogenic emissions in China and Seoul are removed, respectively. Other cases are representing 50% Chinese NO_X emission reduction only, 50% Chinese VOC emission reduction only, both Chinese NO_X and VOC emission reductions by 50%, and 75% Chinese NO_X emission reduction only scenarios. In Seoul, 50% Chinese NO_X emission reduction only scenario slightly increases ozone concentration near the surface, but decreases it above 500 m AGL (above ground level). 50% Chinese VOC emission reduction only scenario causes decrease of ozone concentration near the surface to 2000 m AGL. In the elevated layer (> 500-1000 m AGL) in Seoul, Chinese NO_X emission reductions causes more decrease of ozone concentration than Chinese VOC emission reductions. Chinese NO_X and VOC 50% emission reduction scenario led to decline of ozone concentrations near the surface to 2000 m AGL efficiently particularly above 1000 m AGL. 75% NO_X emission reduction scenario decreased ozone concentration near the surface similar to both NOx and VOC 50% reduction scenario, but this case caused the largest ozone reductions above 1000 m AGL except "No China" emission scenario. "No China" emission scenario led to 10-15 ppb lower ozone concentrations in all altitudes than the control case. "No Seoul" emission scenario led to about 20 ppb higher ozone concentration than the control case partly because of much decreased ozone depletion reacting with NO. The sensitivity test results are similar for Seoul and Gangwon-do except that all emission scenarios (including "No

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Seoul" and 50% Chinese NO_X reduction scenarios) caused decline of ozone concentrations in Gangwon-do. Either NO_X or VOC emission reductions in China clean air in Gangwon-do. The cleaning effect is largest above 500 m AGL. This may explain why the ozone exceedances sharply declined in Gosung, Gangwon-do located at ~650 m AGL during the COVID-19 pandemic (Figure 7). The sensitivity runs clearly demonstrate the long-range transport of Chinese ozone or the influence of Chinese emissions on the eastern part of Korean Peninsular such as Gangwon-do in May to beginning of June, 2016. Not only Chinese VOC emissions reductions but Chinese NO_X emission reductions help to improve ozone pollution in the boundary layer (1-3 km) in South Korea.

5. Summary and conclusions

We investigated the spatiotemporal variability of surface ozone at 7 cities, 9 provinces, and 3 background sites in South Korea from 2001 to 2021. The 4th highest MDA8 ozone concentrations increased for all cities, most of provinces and background sites for this period by 1-2 ppb yr^{-1} and they were above 70 ppb approximately after 2010. Most of South Korean monitoring sites would have been non-attainment areas for the last decade if the US EPA National Ambient Air Quality Standards were applied.

The average ozone concentrations in spring were larger than those in summer at the base time (01-06 LT) for all observation sites (on average by 6.2 ppb). This was the same for the peak time (10-20 LT) except for Seoul and Gyeonggi-do in which the summer

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average was about 1 ppb higher than the spring counterpart. The ozone concentrations in spring were on average 4.4 ppb larger than those in summer at the peak time. Higher mean ozone concentration in spring than summer can be associated with several factors. First, there are more influence of stratospheric ozone on the surface ozone in spring than summer. Our CAM-Chem simulations indicate that about 35% (5%) of surface ozone is attributed to stratospheric ozone in spring (summer). Another possibility is enhanced long-range transport of ozone from China in spring, which was not investigated systematically and statistically for multi-decadal time scales under a changing chemical and meteorological environment. A well-designed mathematical modeling approach would be helpful to disentangle multiple factors associated with background level, transport events, and chemical processes determining ozone in South Korea at a multi-decadal timescale.

Ozone exceedances in this study are defined as the ratio of the data with concentrations > 70 ppb among all data, which is relevant to the US EPA standard. The ozone exceedances were more frequent in summer than spring in Seoul, Incheon, and Gyeonggi-do. The opposite was true for Jeollanam-do, Gyeongsangbuk-do, Gangwon-do, Chejudo, Ulleungdo, Daejeon, Gwangju, Kosan, and Gosung. For the rest of areas, the exceedance frequencies during spring and summer were similar. Ozone exceedances occurred most frequently at 16-19 LT (4-7 PM). However, ozone exceedances also occurred frequently during night at the background sites such as Kosan, Gosung, and Ulleungdo, indicating the possibility of strong influence of long-range transport on the surface ozone

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level at these sites.

For precursors of ozone, the multi-decadal observations of NO_2 and CO in South Korea were analyzed. NO_2 concentrations showed overall declining trends, but significant and relatively large declinations were evident only in Seoul, Incheon, Gwangju, Pusan, Daegu, Geyonggi-do, and Gyeongsagbuk-do ranging from -0.4 ppb yr^{-1} (20-25% reductions for 21 yrs in SMA) to -0.8 ppb yr^{-1} (-70% for 21 yrs in Gyeongsangbuk-do). CO concentrations also showed generally declining trends for most of sites with 13.9 ppb yr^{-1} during spring and 8.9 ppb yr^{-1} during summer. Current NO_2 (CO) concentration average was above 30 (400) ppb in SMA despite decrease of concentrations in the last two decades, still showing characteristics of highly polluted megacity. Other sites in South Korea also showed NO_2 (CO) concentration higher than 10 ppb (300 ppb) except for the background sites such as Kosan, Gosung, and Ulleungdo. VOCs are also essential ozone precursors. Ambient VOC concentrations were correlated with CO concentrations in the previous studies (Warneke et al., 2012). Therefore, high levels of CO concentration may indicate high levels of VOC concentration in South Korea. Unfortunately, multi-decadal VOC observations were not readily available for use in this study. Recent studies reported high level of aromatic and oxygenated VOC compounds in SMA during the KORUS-AQ 2016 field campaign (Crawford et al., 2021). As with many megacities in the world, high ambient NO_2 concentration raises a possibility of "VOC-limited" chemical regime (or "NOx-saturated" in many areas of South Korea. Slight reduction of NO_x (VOC) emissions would

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increase (decrease) ozone concentration in this region. Another complication comes from long-range transport of ozone out of South Korea and its trends with time.

In this study, sensitivity tests of a regional chemical model to emission changes for a limited period were conducted, suggesting that Chinese NO_X emissions reductions as well as VOC emission reductions help improve ozone pollution in South Korea. We also highlighted large reductions of ozone exceedances observed throughout all sites in South Korea in spring during the COVID-19 pandemic, with suppressed anthropogenic activities and consequently lower emissions both in China and South Korea. This hints the future direction to improve ozone pollution in South Korea and promotes further studies for projecting air quality and prioritizing actions for next decade or so.

In the future, multidecadal mathematical modeling at local to global scale as hindcast and forecast mode would be beneficial to better understand the trends of ozone in South Korea. Reliable VOC observations and intensive field campaigns similar to the KORUS-AQ 2016 would provide importance pieces to solve the puzzle of ozone in this area and help carefully monitor the changes in atmospheric composition relevant to ozone chemistry.

Code/Data availability

The surface monitor data for South Korea can be downloaded from https://www.airkorea.or.kr/web/. TROPOMI NO_2 columns are available at http://www.tropomi.eu/data-products/nitrogen-dioxide. WRF-Chem model can be

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downloaded from https://www2.mmm.ucar.edu/wrf/users/download/get_sources.html.

CAM-Chem (CESM) code is available at

https://www.cesm.ucar.edu/models/cesm2/release_download.html.

Author contribution

SWK initiates, designs, analyzes surface monitor data, and writes the manuscript, KMK, SHS, and SWK design and conduct WRF-Chem model runs, JYJ, JYJ, and SWK design and conduct CAM-Chem model runs, SHS processes the airkorea data, YSP and SHS process, analyze, and visualize TROPOMI data, and YSP and JYJ collect and analyze the highway traffic data. All authors edit the manuscript.

Competing interests

Authors declare no competing interests.

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Figure captions

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Figure 3. The same as in Figure 2 except for South Korean provinces.

Figure 4. Ratio of O_3 exceedances in Summer to exceedances in Spring. The red line indicates an one to one line. X-axis denotes names of cities, provinces, and background sites. Cities - Seo (Seoul), Inc (Incheon), DaJ (Daejeon), Gwa (Gwangju), Pus (Pusan), Uls (Ulsan), DaG (Daegu); Provinces - Gye (Gyeonggi-do), ChB (Chungcheongbuk-do), ChN (Chungcheongnam-do), JeB (Jeollabuk-do), JeN (Jeollanam-do), Che (Cheju Island), GyN (Gyeongsangnam-do), GyB (Gyeongsangbuk-do), Gan (Gangwon-do); Background sites - Kos (Kosan, Cheju Island), Ull (Ulleung Island), and Gos (Gosung, Gangwon-do). The data for 2001-2019 are utilized.

Figure 5. Diurnal O_3 exceedances. (Top) Seoul, Incheon, Gyeonggi-do, (middle) Daejeon, Pusan, and Daegu, and (bottom) Kosan, Gosung, Ulleung Island (or Ulleungdo). The data

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for 2001-2019 are utilized.

Figure 6. The contribution of stratospheric O_3 (O_{3s}) to the O_3 concentrations in each season at surface and 1 km above ground level in South Korea.

Figure 7. (top) O_3 exceedances (%), (middle) NO_2 concentrations, and (bottom) CO concentraitons in South Korean cities, provinces, and background sites during spring for 2002-2010, 2011-2019, and 2020-2021 (COVID-19). X-axis denotes names of cities, provinces, and background sites. Cities - Seo (Seoul), Inc (Incheon), DaJ (Daejeon), Gwa (Gwangju), Pus (Pusan), Uls (Ulsan), DaG (Daegu); Provinces - Gye (Gyeonggi-do), ChB (Chungcheongbuk-do), ChN (Chungcheongnam-do), JeB (Jeollabuk-do), JeN (Jeollanam-do), Che (Cheju Island), GyN (Gyeongsangnam-do), GyB (Gyeongsangbuk-do), Gan (Gangwon-do); Background sites - Kos (Kosan, Cheju Island), Ull (Ulleung Island), and Gos (Gosung, Gangwon-do).

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Figure 9. Differences in TROPOMI tropospheric NO_2 columns between 2019 and 2020 or between 2019 and 2021 (Difference = $NO_{2\ 2020\ or\ 2021}$ - $NO_{2\ 2019}$). Unit: molecules cm^{-2}

Figure 10. (Top) the number of cars passing highway tolls near the Seoul Metropolitan Area (SMA) from January to June in 2019 and 2020, (bottom) difference (%) in the toll numbers, NO_2, SO_2, CO, PM_{10}, and $PM_{2.5}$ concentrations in SMA during spring.

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Figure 11. Vertical profiles of ozone from the WRF-Chem model simulations based on various emission scenarios: (top) Seoul, and (bottom) Gangwon-do.

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Location		Peak time	Base time
		Spring / Summer (difference)	Spring / Summer (difference)
City	Seoul	34.4 / 35.6 (-1.2)	20.6 / 17.5 (3.1)
	Incheon	34.6 / 33.1 (1.5)	25.1 / 20.2 (4.9)
	Daejeon	41.2 / 37.0 (4.2)	22.8 / 19.1 (3.7)
	Gwangju	39.9 / 35.4 (4.5)	28.5 / 24.0 (4.5)
	Pusan	40.3 / 34.2 (6.1)	30.3 / 22.4 (7.9)
	Ulsan	38.7 / 33.4 (5.3)	25.8 / 18.7 (7.1)
	Daegu	39.6 / 37.6 (2.0)	24.0 / 19.6 (4.4)
Province	Gyeonggi-do	37.5 / 38.5 (-1.0)	20.8 / 18.0 (2.8)
	Chungcheongbuk-do	42.1 / 39.4 (2.7)	24.8 / 20.6 (4.2)
	Chungcheongnam-do	41.3 / 37.7 (3.6)	29.6 / 23.1 (6.5)
	Jeollabuk-do	38.3 / 35.0 (3.3)	26.7 / 23.6 (3.1)
	Jeollanam-do	42.5 / 35.1 (7.4)	33.0 / 24.1 (9.4)
	Cheju Island	49.0 / 35.0 (14.0)	43.7 / 29.2 (14.5)
	Gyeongsangnam-do	44.3 / 40.0 (4.3)	28.9 / 21.9 (7.0)
	Gyeongsangbuk-do	45.1 / 38.0 (7.1)	28.5 / 20.6 (7.9)
	Gangwon-do	45.6 / 39.5 (6.1)	31.5 / 24.0 (7.5)

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Table 2. Surface and stratospheric O_3 concentrations and their ratio in Korea simulated by CESM. The concentrations and ratios for the altitude of 1 km are shown in parenthesis.

Season	Surface O_3	Stratospheric O_3 (O_{3S})	Ratio (O_{3S}/O_3) (%)
DJF	30.4 (46.2)	23.2 (26.4)	76.2 (57.2)
MAM	45.3 (64.2)	16.7 (21.4)	36.9 (33.3)
JJA	45.9 (53.9)	2.0 (3.0)	4.3 (5.6)
SON	36.3 (51.1)	9.8 (12.1)	26.9 (23.8)

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Table 3. The observed trends of NO_2 and CO concentrations from linear fits of the data covering 2001-2021.

Stations		NO_2 Spring / Summer Slope (Correlation Coefficient)	CO Spring / Summer Slope (Correlation Coefficient)
City	Seoul	-0.72 (-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)
	Pusan	-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)
	Cheju	-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)

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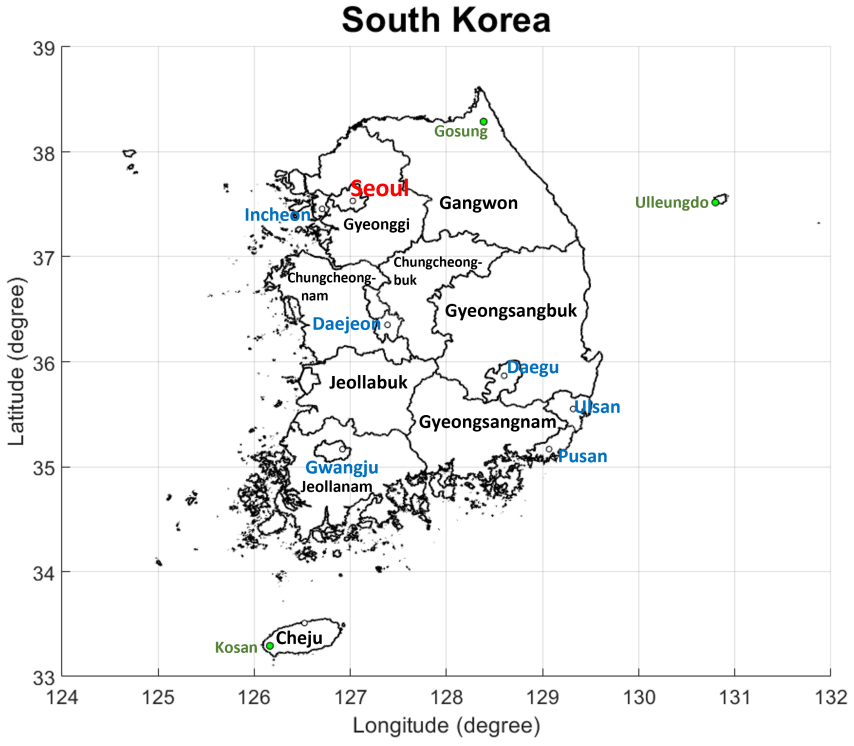

Figure 1. The locations of cities, provinces, and background sites in South Korea.

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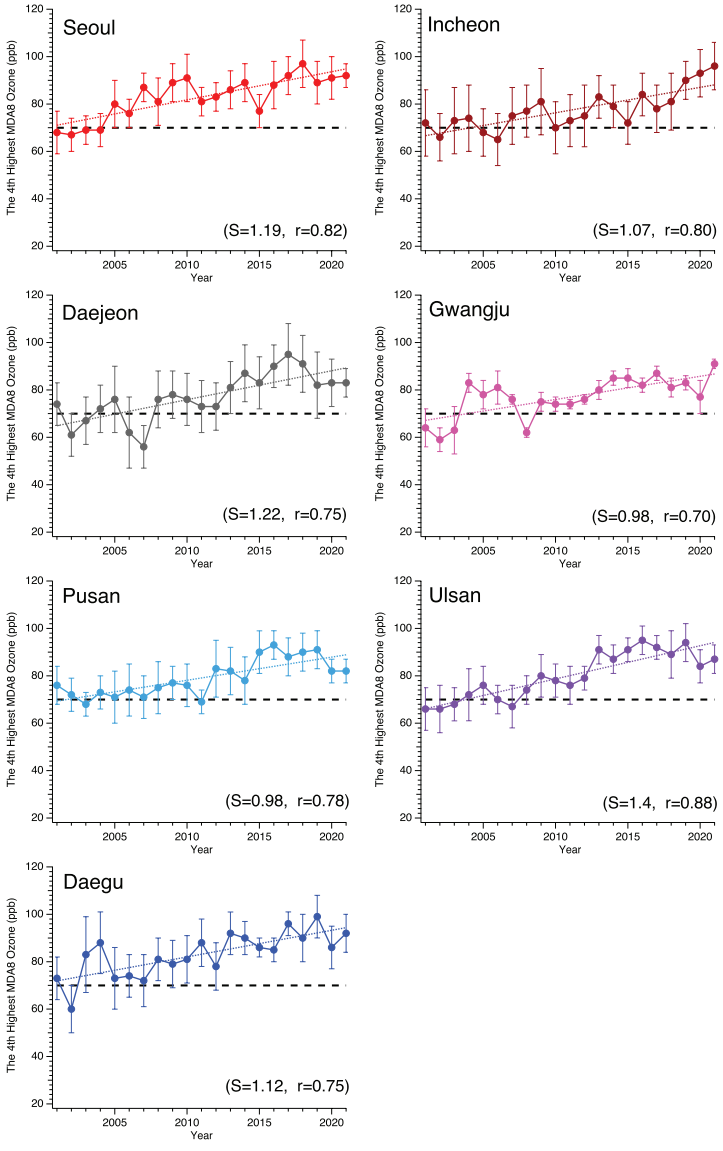

Figure 2. The trend of the 4th highest daily maximum 8 hours average (MDA8) O_3 concentrations in the South Korean metropolitan cities from 2001 to 2021. Only the data for May-September (ozone season) are used. Bars denote standard deviations among the sites within the city. The slopes (S) and correlation coefficients (r) from linear fits are shown in parentheses. Grey dashed line indicates 70 ppb that is the air quality standard defined by the US Environmental Protection Agency.

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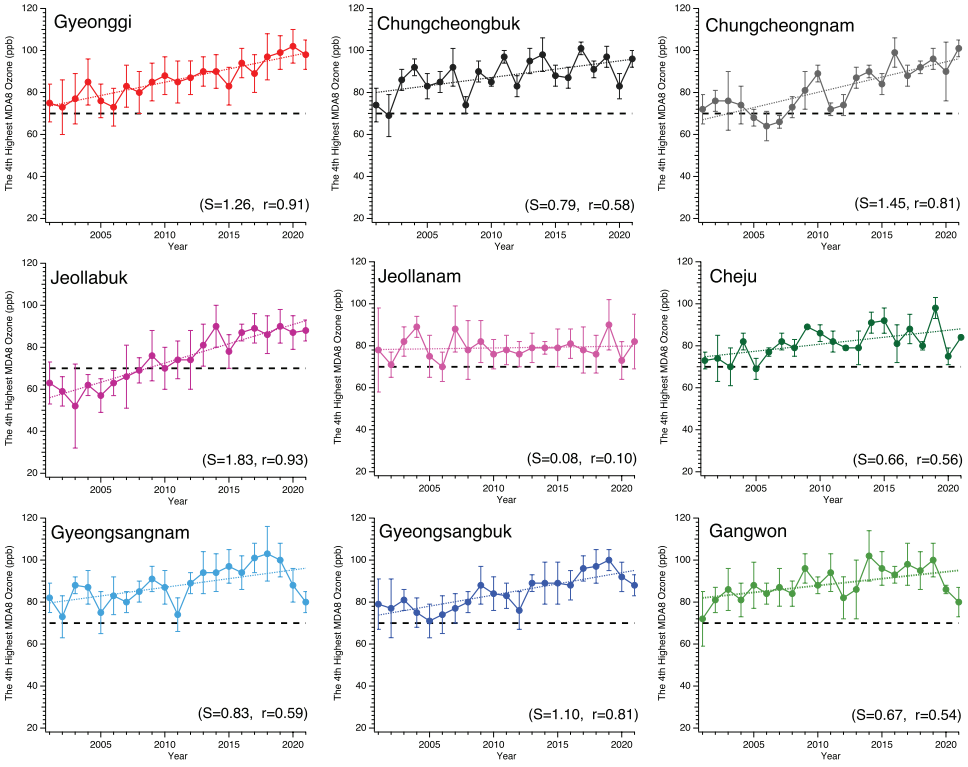

Figure 3. The same as in Figure 2 except for South Korean provinces.

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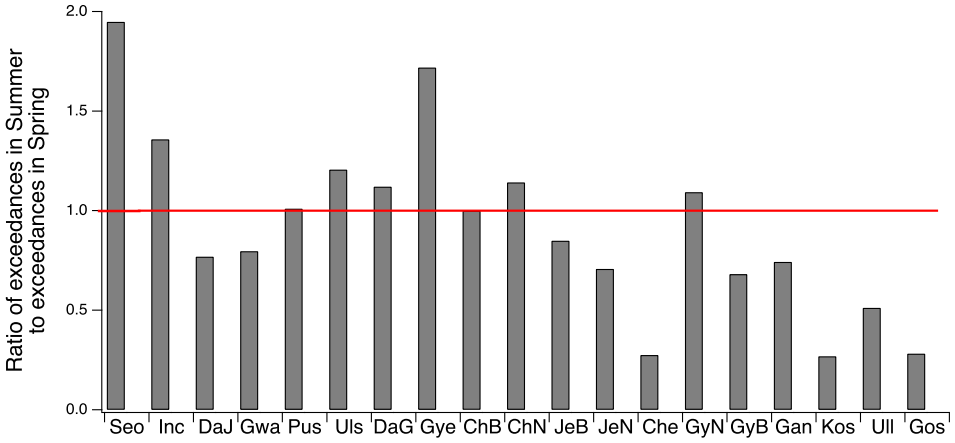

Figure 4. Ratio of O_3 exceedances in summer to exceedances in spring. The red line indicates an one to one line. X-axis denotes names of cities, provinces, and background sites. Cities - Seo (Seoul), Inc (Incheon), DaJ (Daejeon), Gwa (Gwangju), Pus (Pusan), Uls (Ulsan), DaG (Daegu); Provinces - Gye (Gyeonggi-do), ChB (Chungcheongbuk-do), ChN (Chungcheongnam-do), JeB (Jeollabuk-do), JeN (Jeollanam-do), Che (Cheju Island), GyN (Gyeongsangnam-do), GyB (Gyeongsangbuk-do), Gan (Gangwon-do); Background sites - Kos (Kosan, Cheju Island), Ull (Ulleung Island), and Gos (Gosung, Gangwon-do). The data for 2001-2019 are utilized.

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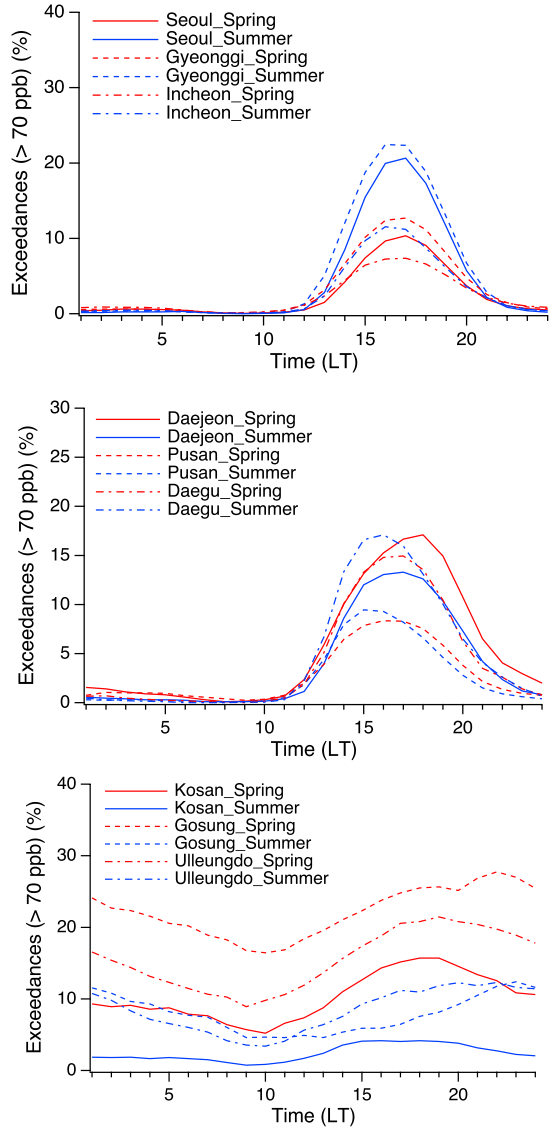

Figure 5. Diurnal O_3 exceedances. (Top) Seoul, Incheon, Gyeonggi-do, (middle) Daejeon, Pusan, and Daegu, (bottom) Kosan, Gosung, Ulleung Island (or Ulleungdo). The data for 2001-2019 are utilized.

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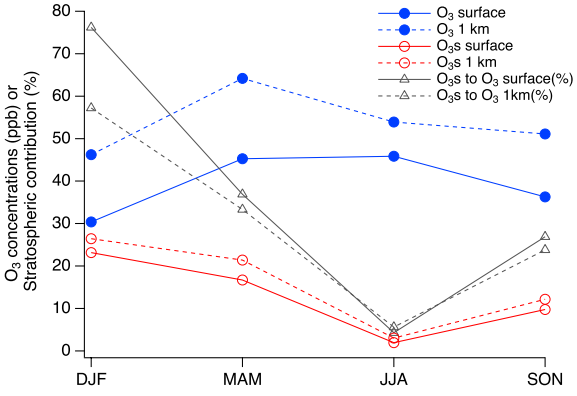

Figure 6. The contribution of stratospheric O_3 (O_{3s}) to the O_3 concentrations in each season at surface and 1 km above ground level in South Korea. The plotted values are extracted from the CESMv2.2 results.

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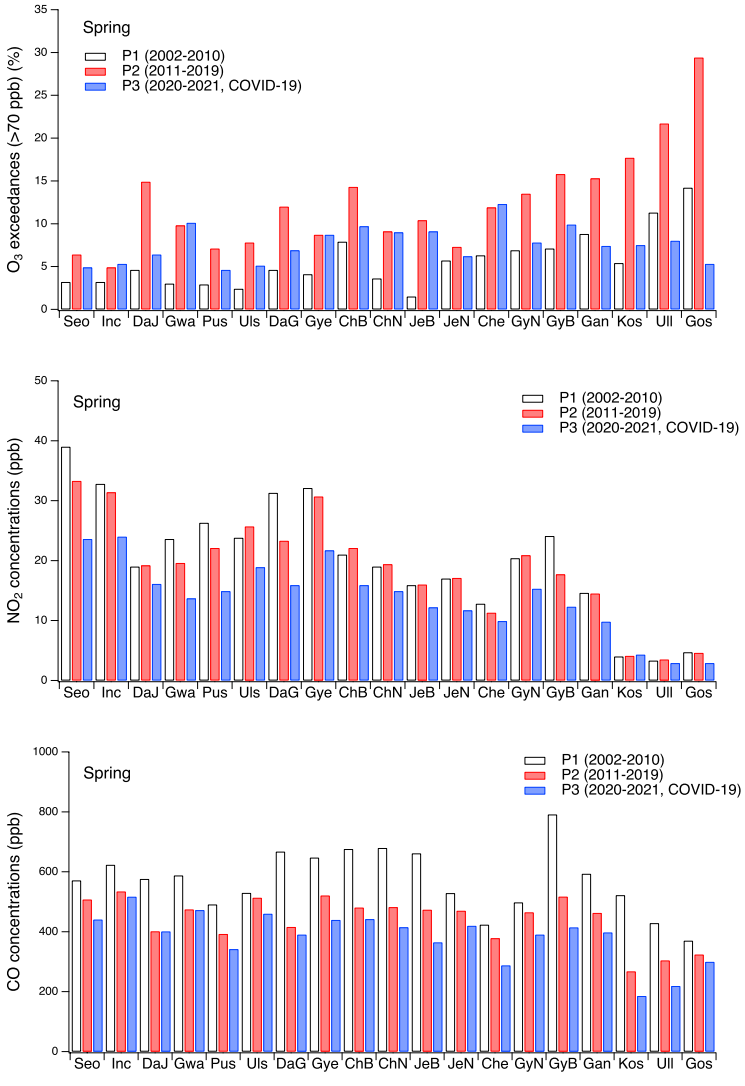

Figure 7. (Top) O_3 exceedances (%), (middle) NO_2, and (bottom) CO concentrations in South Korean cities, provinces, and background sites during spring for 2002-2010, 2011-2019, and 2020-2021 (COVID-19). X-axis denotes names of cities, provinces, and background sites. Cities - Seo (Seoul), Inc (Incheon), DaJ (Daejeon), Gwa (Gwangju), Pus (Pusan), Uls (Ulsan), DaG (Daegu); Provinces - Gye (Gyeonggi-do), ChB (Chungcheongbuk-do), ChN (Chungcheongnam-do), JeB (Jeollabuk-do), JeN (Jeollanam-do), Che (Cheju Island), GyN (Gyeongsangnam-do), GyB (Gyeongsangbuk-do), Gan (Gangwon-do); Background sites - Kos (Kosan, Cheju Island), Ull (Ulleung Island), and Gos (Gosung, Gangwon-do).

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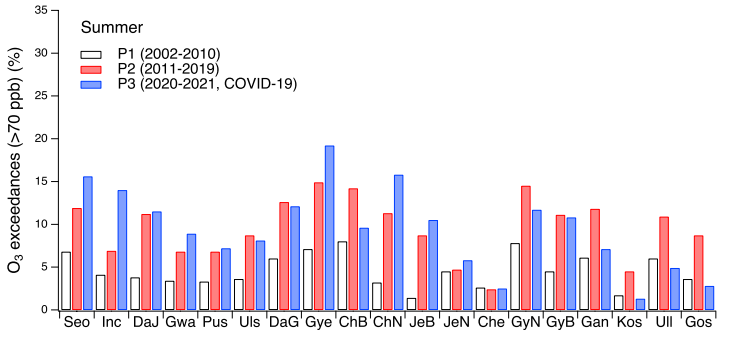

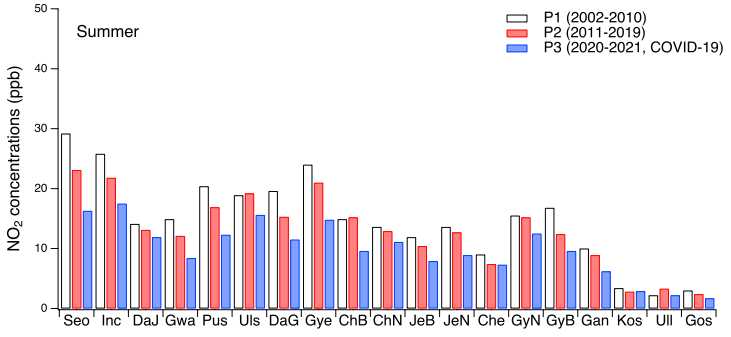

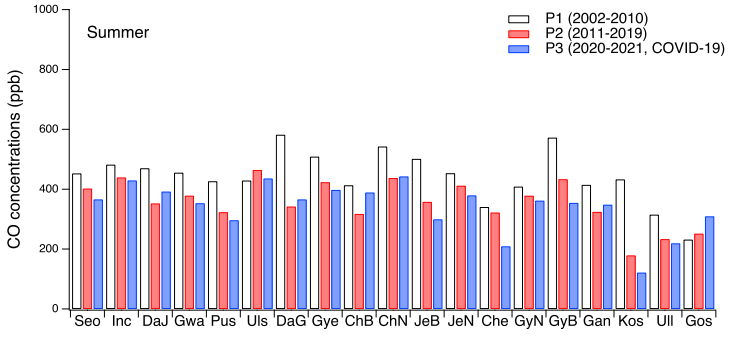

Figure 8. The same as Figure 7 except for summer.

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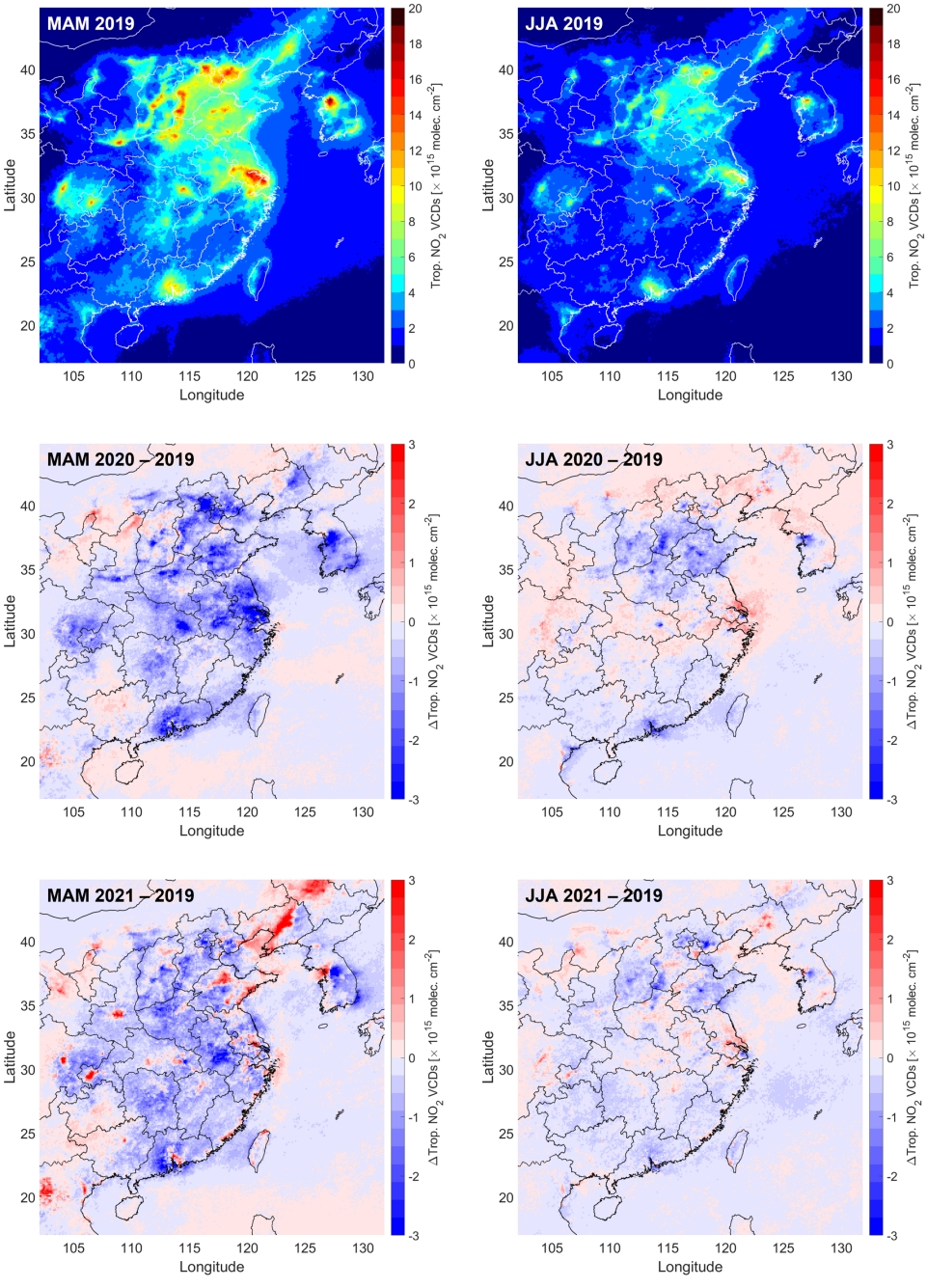

Figure 9. Differences in TROPOMI tropospheric NO_2 columns between 2019 and 2020 or between 2019 and 2021 (Difference = $NO_{2\ 2020\ or\ 2021}$ - $NO_{2\ 2019}$). Unit: molecules cm^{-2}

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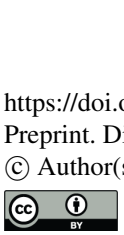

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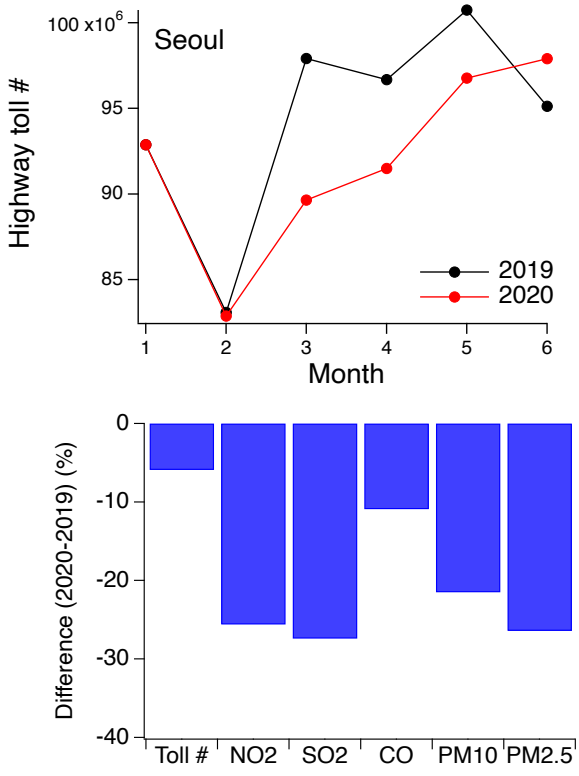

Figure 10. (Top) the number of cars passing highway tolls near the Seoul Metropolitan Area (SMA) from January to June in 2019 and 2020, (bottom) difference (%) in the toll numbers, NO_2, SO_2, CO, PM_{10}, and $PM_{2.5}$ concentrations in SMA during spring.

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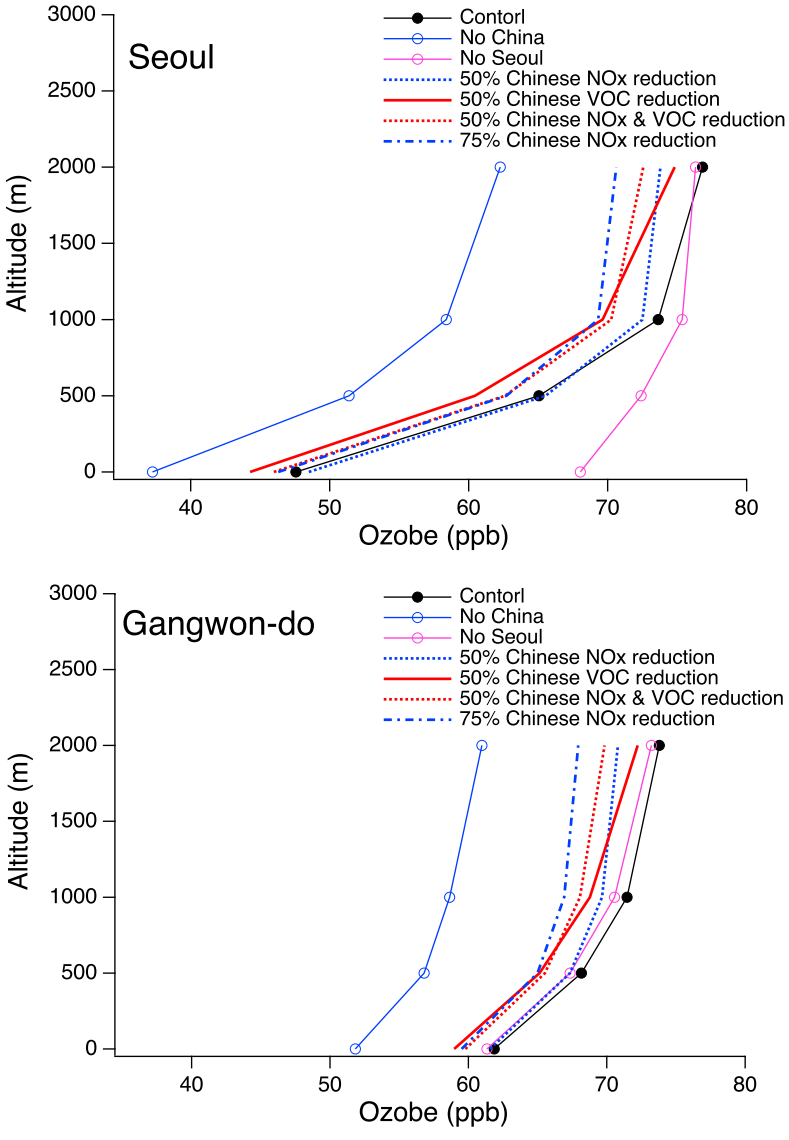

Figure 11. Vertical profiles of ozone from the WRF-Chem model simulations based on various emission scenarios: (top) Seoul, and (bottom) Gangwon-do.