Spatiotemporal variations of air pollutants (O_3, NO_2, SO_2, CO, PM_{10}, and VOCs) with land-use types

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ABSTRACT

The spatiotemporal variations of surface air pollutants (O_3, NO_2, SO_2, CO, and PM_{10}) with four land-use types: residence (R), commerce (C), industry (I) and greenbelt (G) have been investigated at 283 stations in South Korea during 2002-2013, using routinely observed data. The VOCs data at 9 photochemical pollutant monitoring stations available since 2007 were utilized in order to examine their effect on the ozone chemistry. The land-use types, set by the Korean government, were generally consistent with the satellite-derived land covers and with the previous result showing anti-correlation between O_3 and NO_2 in diverse urban areas. The relationship between the two pollutants in the Seoul Metropolitan Area (SMA) residence land-use areas was substantially different from that outside of the SMA, probably due to the local differences in vehicle emissions. The highest concentrations of air pollutants in the diurnal, weekly, and annual cycles were found in industry for SO_2 and PM_{10}, in commerce for NO_2 and CO, and in greenbelt for O_3. The concentrations of air pollutants, except for O_3, were generally higher in big cities during weekdays while O_3 showed its peak in suburban areas or small cities during weekends. The weekly cycle and trends of O_3 were significantly out of phase with those of NO_2, particularly in the residential and commercial areas, suggesting that vehicle emission was a major source in those areas. The ratios of VOCs to NO_2 for each of the land-use types were in the order of I (10.2) > C (8.7) > G (3.9) > R (3.6), suggesting that most areas in South Korea were likely to be VOCs-limited for ozone chemistry. The pollutants (NO_2, SO_2, CO, and PM_{10}) except for O_3 have decreased most likely due to the effective government control. The total oxidant values (OX = O_3 + NO_2) with the land-use types were analyzed for the local and regional (or background)

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contributions of O_3, respectively, and the order of OX (ppb) was C (57.4) > R (53.6) > I (50.7) > G (45.4), indicating the greenbelt observation was close to the background.

1. Introduction

The spatiotemporal variations in major air pollutants with the land-use types in urban or suburban areas (e.g., Kuttler and Strassburger, 1999; Flemming et al., 2005) are of great interest in densely-populated South Korea because the pollutants from local, regional, and global sources can have an impact on human health and ecosystems (e.g., Cooper et al., 2010; Gilge et al., 2010; Kim et al., 2011; Valks et al., 2011), and on climate change (WMO, 2007). The major surface air pollutants examined in this study were ozone (O_3), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), carbon monoxide (CO), particulate matter (PM_{10}) and volatile organic compounds (VOCs). Due to the high energy consumption of South Korea, the country was expected to produce substantial amounts of domestic anthropogenic pollutants (Kim et al., 2013a).

Since air pollutants could be transported from industrialized China to Korea (e.g., Li et al., 2010; Kim et al., 2011; He et al., 2012), their trends and characteristics need to be analyzed in view of international cooperation in reducing the pollutants. The impact of pollutants on a certain area can be associated with its population and emission controls, etc. (Meng et al., 2009). In order to improve the air quality in South Korea, the Ministry of Environment of Korea (MEK) monitored the major pollutants with four land-use types (residence, commerce, industry and greenbelt) set by the Ministry of Land, Infrastructure and Transport (MLIT). Please see Table 1 for the abbreviations in this study. Since the anthropogenic sources of air pollutants, such as transportation and industrial complexes, vary locally with the land-use types, it was more efficient to investigate the spatiotemporal variations of the constituents with the land-use types for our comprehensive analysis and for ultimately controlling them.

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Among the major pollutants, CO, nitrogen oxides (NO_x =NO+NO_2), PM_{10}, and some types of VOCs (e.g., BTEX; benzene, toluene, ethylbenzene, and ortho-, meta-, and para-xylenes) are primarily traffic-induced while O_3 and NO_2 are secondary trace gases formed from precursors in photochemical reactions (e.g., Kuttler and Strussburger, 1999; Masiol et al., 2014). The main sources of SO_2, the most important precursor for acid rain (Wang and Wang, 1995; Wang et al., 2001), are power plants and heavy industry. The formation of ground level O_3 also depends on the influx of stratospheric O_3, the concentrations of NO_x, NO_y (i.e., the family of reactive nitrogen species; Pandey Deolal et al., 2012), VOCs, and the ratio of VOCs to NO_x (Nevers, 2000). When the ratio of VOCs to NO_x is less than 8 to 10, decreasing NO_x tends to increase ozone formation (VOC-limited or VOC-sensitive, Larsen et al., 2003; Qin et al., 2004a). On the other hand, when the ratio is higher than 8 to 10, decreasing NO_x tends to decrease ozone formation (NO_x-limited or NO_x-sensitive). However, the value may change due to various factors (e.g., meteorology, deposition, and gas to particle conversion) (Jacobson, 2002).

Nitrogen dioxides have a substantial impact on PM_{10} through their atmospheric oxidation to aerosol nitrate, and the CO formed from the oxidation of VOCs (e.g., Wang et al., 2008), and the NO_2 emissions due to most types of anthropogenic combustion are a major O_3 precursor (Gilge et al., 2010; Lamsal et al., 2010, 2011). The SO_2 also leads to photochemical O_3 production with the NO_x and VOCs under the intense insolation (Klemm et al., 2000; Derwent et al., 2003). In other words, the photochemistry of NO-NO_2-O_3 system in the tropospheric surface layer is locally controlled by the reactions with CO and many VOCs and even SO_2 (Derwent et al., 2003; Masiol et al., 2014). Meanwhile, the PM_{10} aerosol, and the SO_2 and NO_2 gases may act as condensation nuclei or affect the formation of cloud particles in hydrological circulation (Bian et al., 2007). The PM_{10} concentrations can affect UV flux and O_3 formation (Qin et al., 2004b; Bian et al., 2007; Han et al., 2011). Therefore, controlling the amount of O_3 is difficult due to non-linear features of its formation reactions (Mazzeo et al., 2005; Jin et al., 2012). In particular, spatiotemporal variations of O_3 in South Korea have not been fully understood yet. Overall, the reactions or interactions of the above pollutants are multiple and complex.

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Masiol et al. (2014) reported on the trends and cycles of the pollutants (O_3, NO_2, SO_2, CO, PM_{10}, and BTEX) in a large city in northern Italy and they discussed their interactions. There have been dozens of previous studies on the spatiotemporal variations of some substances among the major air pollutants in terms of their cycles (diurnal, weekly and annual) and trends over South Korea. The cycles of each of the pollutants are helpful in order to understand the emission sources, human activities, photochemical processes and meteorological factors that affect it (e.g., Flemming et al., 2005; Meng et al., 2009). Seo et al. (2014) reported that the O_3 trend in South Korea from 1999 to 2010 was similar to that of NO_2 and it increased by +0.26 ppbv yr^{-1} possibly due to the local increase in anthropogenic precursor emissions and meteorological effects. Based on a model simulation, Jin et al. (2012) showed that the Seoul Metropolitan Area (SMA) was VOCs-limited for the O_3 control, while the local province outside the SMA was chemistry between VOCs-limited and NO_x-limited. However, Kim et al. (2013b) reported that in the suburban SMA, the biogenic VOCs could be the most important source of high O_3 episodes. The temporal O_3 averages in the SMA and other inland areas were low as a result of an increase in O_3 titration by NO from enhanced NO_x levels compared to those at the coastal areas sometimes due to a land-sea breeze (Ghim and Chang, 2000; Oh et al., 2006; Seo et al., 2014). In other words, the titration can slow down the O_3 accumulation in the urban (or suburban) areas due to significant concentrations of NO (Chou et al., 2006).

The long-term NO_2 trends in South Korea from 1998 to 2008 were different between Seoul and other cites with more declining trends at the Seoul sites (Shon and Kim, 2011), presumably due to the MEK effort to reduce the NO_x emissions from the SMA (Kim et al., 2013a). Diurnal and seasonal variations in the individual VOCs at a site in Seoul in 2004 were measured by Nguyen et al. (2009), provided information on the relative abundance of anthropogenic emissions compared to natural emissions. Long-term changes in the PM_{10} in South Korea in some periods between 1992 and 2010 were reported in urban areas by Kim and Shon (2011), and Sharma et al. (2014), and at the background site of Gosan by Kim et al. (2011). Meanwhile, Flemming et al. (2005) investigated the cycles of the four air pollutants (O_3, NO_2, SO_2, and PM_{10}) in Germany based on an objective air quality classification scheme of hierarchical clustering.

The weekend effect, derived from the weekly cycle, has been focused primarily on the relationship between O_3 and NO_2 in many previous studies (e.g., Brönnimann et al., 2000; Fujita et al., 2003a, 2003b; Beirle et al., 2003; Qin et al., 2004b). In these studies, they examined the weekend effect because it can be an indicator of urbanization or human activity (Atkinson-Palombo et al., 2006). For instance, the analysis of the NO_x weekly cycle could be useful in discriminating between its anthropogenic (e.g., local traffic) and natural sources (Beirle et al., 2003). The weekly cycles (or weekend/weekday effect) of O_3, NO_x, and VOCs provide insight into NO_x and VOCs limitation as well. Particularly, the analysis with the land-use types in our study can be helpful in estimating various kinds of man-made emissions (e.g., vehicles and factories, etc). Despite relatively low concentrations of O_3 precursors (NO_x and VOCs) during the weekend, 'high O_3 concentrations' at that time were observed in

California (Marr and Harley, 2002a, 2002b; Qin et al., 2004b), in remote areas (Brönnimann et al., 2000; Pudasainee et al., 2006), and in Japan (Sakamoto et al., 2005). In more detail, Beirle et al. (2003) examined the weekly cycle of the tropospheric NO_2 Vertical Column Densities (VCD) emitted by anthropogenic sources from a number of metropolises throughout the world, using satellite data from the Global Ozone Monitoring Experiment (GOME) during the 1996-2001 period. According to their report, NO_2 concentration tended to decrease on weekends when human activity was relatively low. Qin et al. (2004b) revealed that in southern California, the VOCs sensitivity at weekend, accompanied with the reduced NO_x and PM_{10} emissions, could result in enhanced O_3 formation, although this tendency was not shown in some areas close to the beach and far downstream from L.A. downtown. This result suggests that the weekend effect may vary with meteorological factors (e.g., Jacobson, 2002) and land-use types. A study on their reactive relationship (O_3, NO_2, and VOCs) with the land-use types in South Korea is required in order to explain the possible causes for the O_3 formation and to make a policy decision for either NO_x-limited or VOCs-limited regimes for the formation over the country.

As we mentioned earlier, the spatiotemporal analyses of some species among the major air pollutants have been assessed in many previous studies in terms of their cycles, trends, and interactions, although the VOCs analyses are still lacking due to the limited observations and data. To the best of our knowledge, there have not been any comprehensive studies on the spatiotemporal variation of the major air pollutants at 283 stations over South Korea associated with land-use types, using simultaneous measurement data from a dense observational network. The VOC data available since 2007 have also been utilized to examine the relative influences of VOCs and NO_2 on the O_3 change. A large number of data on the 0.1° × 0.1° or 0.25° × 0.25° spatial grids were developed to better understand the spatiotemporal variations of the pollutants with the types requires high quality, long-term observations of these reactive substances.

The purpose of this study was to comprehensively investigate the spatiotemporal variations and their consistency of the major pollutants over the four land-use types in terms of their cycles, trends, and relationships, based on simultaneous hourly observations at the stations located in urban or suburban areas in South Korea. In section 2, we briefly describe the data and measurements of the pollutants. In addition, we introduce the indices of the land surface properties derived from the satellite data to compare the four land-use types of the

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MEK. In section 3, we describe the air pollutant data on the two spatial grids: 0.1°×0.1° and 0.25°×0.25° with the characteristics of the gridded land-use type data. In section 4, the climatological pollutant averages are given for the seasons and the land-use types, respectively. The results for their cycles and trends are described in sections 5 and 6, respectively. We investigate the relationship between O_3 and NO_2 with the land-use types and discuss the results in section 7, and the weekend effect (O_3, NO_2 and VOCs) in section 8. Finally, the conclusions are provided in section 9.

2. Data and Method

The information for the surface air pollutants (O_3, CO, NO_2, SO_2, PM_{10} and VOCs) data used in this study is presented in Table 2. Hereinafter the four pollutants (CO, NO_2, SO_2, and PM_{10}) will be called 'the CNSP pollutants' in this study. The above pollutants except VOCs have been measured each hour at 283 air pollution monitoring stations of the MEK in South Korea during the period from January 2002 to December 2013 (Figs. 1a-d), while the VOCs data at 19 stations were available since 2007. The majority of observational sites were located in urban or suburban areas rather than remote areas. These pollutants were predominantly produced by mobile and stationary combustion, and/or photochemical processes (Masiol et al., 2014). Nine out of the 19 VOCs stations were selected in this study based on the criteria of better co-location of the observational sites and longer data records since 2007 (Table 2 and Fig. 1e). The VOCs at the 9 MEK photochemical stations were simultaneously observed with the other pollutants at the same sites. Figure 1f shows the locations of seven major cities in South Korea with the background map, based on the satellite-derived AVHRR land-cover types.

In order to enhance the efficiency of land-use, the MLIT classified the land of South Korea into the four land-use types as follows: 154 residential (R), 57 commercial (C), 35 industrial (I) and 37 greenbelt (G) stations (See Tables 1-2 for details). According to Article 36 of the National Land Planning and Utilization Act (http://www.law.go.kr/engLsSc.do?menuId=0&subMenu=5&query=NATIONAL_LAND_PLANNING_AND_UTILIZATION_ACT#liBgcolor2), urban or suburban areas are designated. The areas of the four land-use types have been subdivided based on Article 30 of the Enforcement Decree of the National Land Planning and Utilization Act (Please see the

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메모 [YJH9]: Referee#2, A8 Referee#3, A4 above link at http://www.law.go.kr/, keyword: National Land Planning and Utilization Act). In addition the MLIT criteria for the types are available in the supplementary data in Korean (http://www.law.go.kr/, keyword: National Land Planning and Utilization Act in Korean).

The hourly observations of the pollutants, except for the VOCs, during the 12 year period were utilized for the temporal cycle and trend analyses over the land-use types. The hourly data were arranged into 144 monthly anomaly values in order to remove the annual cycle in the time series. The anomaly value was computed by substracting the climatology (i.e., 12 year monthly mean in this study) from the monthly average in a given month. The 95% confidence intervals for the trends were calculated using the bootstrap method (Wilks, 1995). For each air pollutant anomaly data set, 10,000 new data sets were created to produce 10,000 linear trends through random sampling (e.g., Lee et al., 2013). The random sampling was conducted by drawing data out of the respective original records of the air pollutant anomalies, allowing repetition. The ± values in the trend analysis defined the 95% confidence intervals, while they stood for 1σ (standard deviation) in the concentration averages.

메모 [YJH10]: Referee#3, A1

The details of the surface air pollutants measurements including the instrumentation and methods are given in Table 3. The O_3 concentrations were measured by a Thermo 49i analyzers using the ultraviolet (UV) photometric method (e.g., Diaz-de-Quijano et al., 2009). The non-dispersive infrared method was utilized to measure the CO with a Thermo, 48CTL. The NO_2 was measured by a Thermo, 42CTL using the chemiluminescence method. The Thermo, 43CTL was used to measure the SO_2, based on the pulsed UV fluorescence method. The PM_{10} was measured by a Thermo, Model FH62-C14 (http://www.thermo.com) with the β-ray absorption method (e.g., Elbir et al., 2011). The control methods, which avoided high humidity in the measurement systems, were discussed in detail in Yoo et al. (2014).

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For the VOC observations, the water vapor in the air samples, which were collected every hour, was removed from the air using a Nafion Dryer. A total of 56 VOC species were identified and quantified using a combination of the on-line thermal desorption system (Unity/Air Server, Markes) and the GC/Deans switch/Dual FID system (Varian 3800 GC, USA). These VOC compounds could be grouped into alkyne (1), aromatic (16), olefin (10), and paraffin (29) groups (Nguyen et al., 2009). The quality check for the GC was carefully calibrated, which was routinely conducted by site managers.

Uncertainty of the measurement instruments for each pollutant is available in NIER (2010). According to the NIER's report, the minimum requirements of the measuring

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instruments for accuracy (or uncertainty) are 'less than 0.005 ppm' for O_3, NO_2, and SO_2, 'less than 0.5 ppm' for CO, and 'less than 2 % of measuring range' for PM_{10}. Also the uncertainty for VOCs is within ±20 % of true value. The uncertainties for the CO and SO_2 with respect to their typical values are relatively large compared to other pollutants (O_3, NO_2, PM_{10}, and VOCs).

In order to approximately examine the validity of the four MEK land-use types at 283 sites in South Korea, we compared them with satellite derived land-covers of both the AVHRR and MODIS in a 0.25° x 0.25° grid (Table 4). The AVHRR data were provided for 13 land covers over the globe at a 1 km x 1 km pixel resolution, time-averaged during 1981-1994 (e.g., De Fries et al., 1998; Hansen et al., 2000). The MODIS data were derived for 17 land covers over the globe at a 5 km x 5 km spatial resolution from 2002 to 2012 (e.g., Friedl et al., 2010), and they were available each year.

Although the land covers of both of the satellites were obtained from different periods, the AVHRR and MODIS original types were regrouped in this study and compared for the following four land covers: forest/woods, grass/shrub, urban/built-up, and water (Table 4). The MODIS 'water' covers with the land-use types were not changed during the year period, and the covers were greater in the MEK 'industry and greenbelt' types than in the 'commerce and residence' types (Fig. 3d). In Table 4, the values with and without parentheses indicate the MODIS and AVHRR data, respectively. The MEK land-use types, set by the Korean government, were generally consistent with the satellite-derived land covers. The MEK 'greenbelt' type compared to the three other types highly corresponded to the satellite-derived 'forest/wood' (35.2-37.2 %) cover, but rarely to the 'urban/build-up' (0-16.4 %). For AVHRR, the 'water' like river dominated in the MEK types of 'greenbelt' and 'industry', while the 'urban and built' matched well with the MEK 'commerce' type (Fig. 2). The 'industry' areas were expected to be located near rivers for transportation.

메모 **[YJH13]:** Referee#1, A10

Figure 3 shows the interannual variations in the MODIS-derived land-cover types (%) versus the MEK four land-use types from 2002 to 2012. The interannual variations in the MODIS land-cover with respect to the MEK types were not significant during that time period. It is reasonable that MODIS 'forest/wood' covers were the greatest (37.2%) in the MEK 'greenbelt' type (Fig. 3a and Table 4). In the MEK 'residence' type, the MODIS 'forest/wood' cover was slightly increased, but the 'grass/shrub' cover had decreased (Fig. 3a-b). The MODIS 'urban/build-up' was at a minimum (16.4%) in the MEK 'greenbelt' and at a maximum (32.2%) in the 'commerce' (Fig. 3c and Table 4). In addition, the validity of the MEK types was investigated again in section 7 of this study in terms of the relationship between O_3 and NO_2. The inverse relationship between the two variables over the various land-use types of urban areas has been studied significantly in previous studies (e.g., Kuttler and Strassburger, 1999, their Fig. 3; http://www.sciencetime.org/ConstructedClimates/chap-4-emissions-urban-air/3-9-complicated-ozone; Masiol et al., 2014, their Fig. 5).

메모 [YJH14]: Referee#3, A7

3. Air pollutant data on the two spatial grids: 0.1°×0.1° and 0.25°×0.25°

메모 [s15]: Referee#1, A2, A4 Referee#3, A6, A10

In this study we rearranged the non-gridded pollutant data on the two spatial grids (0.1°×0.1° and 0.25°×0.25°) to examine urban characteristics of the gridded land-use type data due to the non-uniform distribution of the pollution monitoring stations. The pollutants, except for VOCs, were investigated as time-averaged in the two spatial grids after categorizing the 283 station data in the four land-use types. The stations are mostly located in the urban areas with a very sparse distribution in the rural areas (Fig. 1). The higher spatial resolution of the 0.1°×0.1° grid generally tends to represent the characteristics of large urban cities better than in suburban regions, when they were compared to those of coarser resolution (i.e., 0.25°×0.25°). For example, the more urbanized stations over the SMA contribute more to the number of the high resolution grid than that of the low resolution grid. In other words, since the number of stations are larger in the big cities (i.e., more urban features) than in the small cities (i.e., fewer urban features), the higher resolution grid displays more in the former cities than in the latter. Although this tendency is also shown in the lower resolution grids, the weighting effect of the big city characteristics is more substantial in the 0.1°×0.1° grid than in the 0.25°×0.25° grid.

Because of the difference in the numbers of stations in each grid, the grid numbers that returned the valid grid-averages of observations at the 0.1°×0.1° and 0.25°×0.25° resolutions with respect to the non-gridded 283 stations were reduced to 196 (R; 89, C; 42, I; 32, G; 33) for the 0.1°×0.1° and 146 (R; 59, C; 30, I; 25, G; 32) for the 0.25°×0.25° resolutions, respectively. Different land-use type data (e.g., two residential and three greenbelt stations) can coexist in a given grid. In this case, the pollution data in the grid have been utilized for the arithmetic average calculation for the residential and greenbelt types, respectively.

The choice of either 0.1° × 0.1° or 0.25° × 0.25° grid boxes as an optimal spatial grid scale represents a compromise based on keeping the intrinsic spatial variability of the pollutants (O_3, CO, NO_2, SO_2 and PM_{10}) of interest, namely their concentrations, at comparable levels and still having large enough total sample size, i.e. the number of grid boxes with pollutant data, for a robust computation. The variability has been examined in terms of some dimensionless measure (i.e., the ratio of standard deviation (σ) to mean ($\bar{X}$); Yoo et al., 2014) in the climatological annual average distribution of the pollutants. The $\sigma/\bar{X}$ values for the five air pollutants at the two different types of grids range from 15.0 % to 45.0 %. Since the $\sigma/\bar{X}$ values at a 0.1° × 0.1° grid are 16.3-44.0 %, they are within the range (15.0-44.9 %) at a 0.25° × 0.25° grid.

4. Climatological seasonal distributions of the pollutants: O_3, CO, SO_2, NO_2 and PM_{10}

Figure 4 shows the spatial distributions of the climatological seasonal averages of O_3 (ppb), CO (0.1 ppm), NO_2 (ppb), SO_2 (ppb) and PM_{10} (μg m^{-3}) in a 0.25° x 0.25° grid over South Korea from 2002 to 2013. The seasonal and annual averages of the five pollutants are summarized in two different types of spatial grids (0.25°×0.25° and 0.1°×0.1°) in Table 5. In the table, the standard deviation (σ) values of the five pollutants are also presented with the ± values. The distributions were highly seasonal. The peak season of O_3 in South Korea was in the spring (March, April and May) than in the summer (June, July and August) due to the summertime monsoon and clouds. The O_3 level was the lowest in the winter due to the low photolysis (Table 5). Higher concentrations of the CNSP pollutants appeared in large cities (e.g., the SMA) more often than in suburban/rural areas. However, the O_3 values were lower over the large cities than over either their outer or coastal regions due to its reaction with other air pollutants and meteorological conditions (Seo et al., 2014). According to their study, the O_3 values over the large cities were low because of the NO titration even during the night without photochemical reactions by local anthropogenic precursor emissions, while they were high in the coastal areas because of the sea breeze effect. Since O_3 and NO do not coexist at night, NO tends to be efficiently transformed into NO_2 (Mazzeo et al., 2005). The higher O_3 level in the rural areas throughout the seasons indicated the role of oxidization during the transport. Flemming et al. (2005) also reported that the high O_3 levels in the rural area could be linked to the low level of NO emissions (e.g., the VOCs role; Ahrens, 2007). It is noted that seasonal O_3 concentrations in Jeju island (Jeju station; 33.51N, 126.53S) were higher than those found inland while the opposite situations were found for the other pollutants.

The seasonal CNSP pollutant concentrations were lower in summer due to heavy rainfall (despite high but intermittent photolysis rates) than in winter, when O_3 value was the lowest (Fig. 4 and Table 5). The maximum values of the CO, NO_2 and SO_2 were shown in the winter due to the low boundary layer height (e.g., Kaiser et al., 2007) followed by the spring and the fall (see also Fig. 6c discussed later). Higher values of CO, NO_2 and PM_{10} over the SMA than in other regions were explained by the large population density and traffic emission, and industrial activity (Fig. 4). Higher NO_2 values in the SMA were also reported by Seo et al. (2014). The high SO_2 values over the coastal regions were due to the factories and power plants, and the high CO values inland were due to the active fossil fuel burning. Asian dust aerosol (e.g., PM_{10}) transported from China contributed to the spring peak in PM_{10}, and its spring maximum was due to lower amounts of precipitation than in other seasons (Table 5). These results suggest that the meteorological conditions were an important factor characterizing the seasonality of the air pollutants, while the emissions determined the magnitudes of the pollutants.

메모 [YJH16]: Referee#3, A2 Referee#3, A4

메모 [YJH17]: Referee#2, A2

메모 [YJH18]: Referee#1, A3

The amounts of CNSP pollutants were larger in a 0.1°×0.1° grid, while the O_3 values were larger in a 0.25°×0.25° grid (Table 5). In particular, the annual value for NO_2 was remarkably greater by 16% in the former than in the latter, suggesting that the vehicle emissions in the urban area were a primary source for that pollutant. On the other hand, the annual value for O_3 was smaller by 6% in the 0.1°×0.1° grid than in the 0.25°×0.25° grid, implying that the O_3 levels in the suburban/rural/coastal areas were higher than in the urban ones (Fig. 4). These features were clear in the seasonal and annual values (Fig. 4 and Table 5).

5. Diurnal, weekly and annual variations of pollutants with land-use types

Figure 5 shows the spatial distributions of climatological annual averages in a 0.25°×0.25° grid over South Korea during 2002-2013 of the surface air pollutant observations for O_3 (ppb), CO (0.1 ppm), NO_2 (ppb), SO_2 (ppb) and PM_{10} ($\mu g\ m^{-3}$) in terms of the MEK four land-use types of a) residence, b) commerce, c) industry and d) greenbelt. The distributions present unique characteristics by the four land-use types. For instance, Seoul, where both the residence and commerce types were dominant, was the most polluted with the CNSP pollutants in all of the land-use types. The CO was higher inland than in the coastal

메모 [YJH19]: Referee#1, A11, Referee#2, A12 areas and the NO_2 was higher in the major cities including Seoul, Daegu, and Busan for all of the types. The distribution of SO_2 was similar to that of NO_2, but the former was larger in the coastal area than the latter due to its industry emissions. On the other hand, O_3 levels in the greenbelt type were the highest among the four types (Fig. 5d).

Figure 6 presents the (a) diurnal, (b) weekly and (c) annual variations in the spatial averages of Fig. 5 under the MEK four land-use types as follows; residence (black circle), commerce (blue cross), industry (red square), and greenbelt (green triangle). The diurnal variations of four kinds of pollutants were investigated in the previous studies by Flemming et al. (2005) and Meng et al. (2009). The former study also showed their weekly and annual variations over different air-quality regimes, while the latter emphasized significant seasonality in their diurnal cycles. In addition, Xu et al. (2008) investigated interannual variability of the surface O_3 in its diurnal cycle in four different seasons. In this study, the diurnal cycles of the five pollutants were analyzed for the different land-use regime. The results in the figure are also summarized in Tables 6-7. Table 6 shows the magnitude order of the five pollutant concentration averages of Fig. 6 in terms of the land-use types. The numbers in the table indicate the ranking of each pollutant based on the pollutant concentration values over the types. The greater concentration values corresponded to the upper ranking numbers. Only if the orders in the two types of grids were different from each other, then those in the parentheses were given for the 0.1°×0.1° grid. Table 7 also presents the spatial mean and standard deviation of the averages in a 0.25°×0.25° grid. The values in parentheses in the table denote the mean and standard deviation in a 0.1°×0.1° grid.

The typical shapes of the diurnal, weekly and annual cycles of the five pollutants were quite similar among the different land-use types but their magnitudes were systematically different depending on the types (Fig. 6 and Tables 6-7). In other words, the rank of the pollution level by the land-use type in the weekly and annual cycles was almost the same as in the diurnal cycle (Tables 6-7). In Table 6, the magnitude order (G>R>I>C) for O_3 with the types was exactly in the reverse order for NO_2 (C>I>R>G) for all cycles, suggesting the linkage between the two pollutants. The anti-correlations between the two pollutants in the diurnal cycle were also shown in Mazzeo et al. (2005) at a green city of Argentina and Han et al. (2011) in Tianjin, China. However, the reverse order for O_3 was different from those for SO_2 and PM_{10} (I>C>R>G). It is because SO_2 and PM_{10} pollutants were not uniquely associated with vehicle emissions (Flemming et al., 2005; see also Chen et al., 2001). The

메모 [YJH20]: Referee#2, A1 (2 sentences were removed.

메모 [YJH21]: Referee#3, A2 Referee#3, A4 same order for the two pollutants with the land-use types suggested their emission sources from industrial activities rather than traffic emissions. It was interesting to note that the greenbelt area was commonly the lowest for the CNSP pollutants.

Since the primary production of O_3 was through photochemical reactions, the O_3 started to rise in the morning and showed its peak at 4 p.m. before it rapidly decreased (Fig. 6a). The O_3 level was the highest in the greenbelt and the lowest in the commerce areas, while the levels of the O_3 for the residence and industry regimes were close to each other. The diurnal cycle of the O_3 in this study agreed with that of Flemming et al. (2005). Two peaks were shown in the diurnal cycle for CO, NO_2, and PM_{10}. The first peak was due to the increasing morning traffic and industrial activity (Kuttler and Strassburger, 1999). The second peak was due to the afternoon traffic and reduced boundary layer (Lee et al., 2014) during and after sunset. The daytime minima of these species were the results of the increased boundary layer height (Ulke and Mazzo, 1998; Lal et al., 2000; Han et al., 2011) as well as the oxidation processes for the chemically and photochemically reactive CO and NO_2 of which diurnal variations were generally out of phase with those of O_3 except for the midnight period (Kuttler and Strassburger, 1999; Lal et al., 2000). The diurnal cycle of the SO_2 in the commerce type also had two peaks similar to the other pollutants (CO, NO_2 and PM_{10}). The daytime minima could be explained by the high vertical mixing of their emissions (Meng et al., 2009). According to the diurnal variations of the CO and SO_2 over a suburban site in the USA, the patterns of their diurnal cycles were changed seasonally (Chen et al., 2001). The diurnal cycles of the O_3 and NO_2 without categorizing the land-use types were shown in Fig. 6a (O_3 and NO_2), consistent with those of Han et al. (2011) in Tianjin, China.

메모 [YJH22]: Referee#3, A11

The commerce type in the daily, weekly, and annual cycles was ranked first for the CO and NO_2, but it was ranked second for the SO_2 and PM_{10} (Fig. 6 and Table 6). The industry type was ranked first for the SO_2 and PM_{10}, but it was ranked second for the NO_2. The residence type in a 0.25°×0.25° grid was ranked second with the industry regime for the CO, but it was ranked third for the NO_2, SO_2, and PM_{10}. These analyses indicated that the contribution of commerce was more important for the CO and NO_2, and that the contribution of the industry was more important for the SO_2 and PM_{10}. Since the commerce and industry types were associated with more vehicles and industrial activity, the CNSP pollutants in the residence type were lower than for these two types. Sharma et al. (2014) also reported that the

PM_{10} levels in South Korea and abroad depended on different land-use types (urban, industry, rural/suburban).

The weekly cycles were analyzed for the different land-use types (Fig. 6b). The weekly cycle of the five pollutants was more remarkable in the land-use types with industrial and commercial activities, particularly in the industry type than in the greenbelt one. The CO weekly cycle was pronounced in the commerce type as well as in the industry one. This implies that the MEK land-use types provided a reasonable discrimination between natural and anthropogenic pollutant sources. In general, on Sunday the level of the CNSP pollutants decreased but the O_3 values showed a peak. However, the degree of the Sunday pollutant values compared to those averaged for the working days from Tuesday to Friday (hereafter the working day average) varied by the pollutant species and land-use types. These Sunday low of the CNSP pollutants and the Sunday high of O_3 (so-called the O_3 weekend effect; Larsen et al., 2003) were due to the anthropogenic activity that characterized the weekly emission pattern of South Korea.

In Fig. 6b for O_3, less O_3 reduction near anthropogenic sources (e.g., the commerce and residence areas) due to the decreased NO titration could induce an enhancement of O_3 particularly in the weekly cycle (e.g., Gilge et al., 2010). The NO_2 minimum on Sunday also occurred in Hohenpeissenberg, Germany due to less anthropogenic impact on weekends than on working days (Gilge et al., 2010). In Fig. 6b, the NO_2 minimum on Sunday (24% reduction compared to the working day average) in the industry agreed with that of Beirle et al. (2003) over the industrialized regions (the USA, Europe and Japan) from the vertical column densities of tropospheric NO_2. The CO reduction on Sunday against the weekday average was the lowest (3-7%) among the CNSP due to its longer life time (e.g., Gilge et al., 2010). The PM_{10} minimum on Sunday also occurred over a neighboring country, China (Choi et al., 2008). The O_3 Sunday maximum in the industry type was enhanced by ~15% with respect to the weekday average. The weekend effect of O_3 varied with the land-use types: I (15%) > C (10%) > R (9%) > G (4%). The increasing O_3 during the weekend could be associated with: 1) the decreasing NO_2 under the VOCs-limited regime, or 2) the behavior of the VOCs (e.g., Sakamoto el al., 2005), particularly the natural ones (or biogenic) in the greenbelt. Previous studies showed an increase in the O_3 and a decrease in the NO_2 during the weekends in the U.S. and Germany (Flemming et al., 2005; Atkinson-Palombo et al., 2006).

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According to Gilge et al. (2010), anti-correlation between O_3 and NO_2 in their weekly cycles was less pronounced in summer due to photochemical O_3 production than in the other seasons.

The annual cycle of O_3 generally showed a spring-early summer maximum and a wintertime minimum (Fig. 6c). This result was consistent with that of Pochanart et al. (1999) at Oki, Japan and on a regional scale in northeast Asia. The O_3 annual variation in the greenbelt presented primary and secondary peaks in May and October, respectively, reflecting seasonal changes of the photochemical intensity and Asian monsoon (Meng et al., 2009; Sarangi et al., 2014). The double peak patterns occurred at a regional background site in nothern China in June and September, respectively (Meng et al., 2009), and at a high altitude site in north India in May and November, respectively (Sarangi et al., 2014). However, the secondary peak was not clear in the other types (residence, commerce and industry). This suggested that the O_3 production in a monthly time-scale was sensitive to the local pollutant emissions with the land-use types. The NO_2 wintertime maxima could be associated with the fossil fuel consumption and photochemical oxidation of NO to NO_2 (Shon and Kim, 2011), the lower planetary boundary layer (PBL) and photolysis rate The enhanced CO and NO_2 values in winter agreed with those of Gilge et al. (2010) over Hohenpeissenberg, Germany. Tropospheric NO_2 concentrations over South Korea also occurred in winter (at least 68%) mainly due to local emissions (Mijling et al., 2013).

The SO_2 maximum in January in its annual cycle was generally similar to that of SO_2 emissions from China of Wang et al. (2013) (Fig. 6c).The values of the CNSP pollutants were lowest in June-August mainly due to the washout effect during the rainy period (e.g., Flemming et al., 2005; Meng et al., 2009; Yoo et al., 2014). Despite the low washout effect of CO, its reaction with HO radical was likely to be more important for the CO sink during the warm season (Stockwell and Calvert, 1983; Novelli et al., 2003; Gilge et al., 2010). The declining tendency of the SO_2 and NO_2 emissions in boreal summer also occurred in China because of the large-scale monsoon system (Wang et al., 2013). In addition, the lifetimes of SO_2 and NO_2 in the atmosphere are substantially shorter in summer, due to dominant gas phase chemistry (e.g., faster photochemical reactions) (Levy II et al., 1999). This implies that the NO_2 transport from China to South Korea could have more impact over the Korean Peninsula during wintertime dry season than during the summer and fall (Lee et al., 2014). The springtime PM_{10} maxima in its annual variations resulted from Asian Dust and meteorological conditions (Sharma et al., 2014).

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메모 [YJH25]: Referee#1, A6

메모 [s26]: Referee#3, A12

In the annual average analyses, the urban effects of the grid difference (i.e., the pollutant value in the 0.1°×0.1° grid minus the value in the 0.25°×0.25° grid) was quantitatively the greatest in the types of 'commerce' for CO (+0.093 0.1ppm), NO_2 (+2.969 ppb), PM_{10} (+0.711 μg m^{-3}), and O_3 (-0.735 ppb); and 'industry' for SO_2 (+0.687) among the four land-use types (Table 8). This result could be explained by the emissions of vehicle in the commerce type and the emissions of factories in the industry type.

메모 [s27]: Referee#3, A12 ; A sentence was moved to conclusion (L862-864))

메모 [YJH28]: Referee#3, A4

6. Pollutant trends of O_3, NO_2, SO_2, CO, PM_{10}, and OX with respect to land-use types

Figure 7 shows the time series of the spatial averages of the monthly surface air pollutant anomalies for the five pollutant and OX concentrations in a 0.25°×0.25° grid over South Korea during the period from January 2002 to December 2013 under the following MEK land-use types: residence (black solid), commerce (blue dashed), industry (red dotted), and greenbelt (green dashed). We calculated linear trends of the pollutant anomalies with respect to each of the land-use types. The ± trend values define the 95% confidence intervals. Trend values of the pollutants are also summarized in Table 9, based on two types of analyses (the 0.1°×0.1° and 0.25°×0.25° grids) over the four land-use types of MEK of residence (R), commerce (C), industry (I), and greenbelt (G). The magnitude order for the trends of each of the pollutant over the types has been shown. It should be noted that the trend values were statistically significant except for a few of the NO_2 and SO_2 cases marked by an asterisk (*). Given the different spatiotemporal scales of the variability for the five pollutants (their scale order; CO > PM_{10} > O_3 > SO_2 > NO_x; Seinfeld and Pandis, 2006), the behavior of CO was likely to be related with the local, regional, and global effects but that of NO_2 with the local and regional ones (Gilge et al., 2010).

The CNSP pollutants in South Korea tended to decrease regardless of the land-use types but interestingly the O_3 had an increasing tendency (Fig. 7 and Table 9). Since the five pollutants showed the same trends (either positive or negative) over all of the four types, the overall trends could reflect more the effects of regional emissions than local emissions. In the O_3 formation, for instance, the local contribution related with the level of primary pollutants (e.g., titration) while the regional contribution corresponded to the background O_3 concentration (Clapp and Jenkin, 2001). The regional background was likely to be large in the greenbelt area compared to the other land-use types in view of the reduced weekly cycle

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in the greenbelt (see also Fig. 6b). The declining trends of CNSP in a 0.25°×0.25° grid by the land-use type varied with the values of -0.135~-0.247 (0.1ppm yr^{-1}) for CO, -0.042~-0.295 (ppb yr^{-1}) for NO_2, -0.036~-0.140 (ppb yr^{-1}) for SO_2, and -1.003~-1.098 (μgm^{-3} yr^{-1}) for PM_{10}.

The downward trend of PM_{10} (~2 %yr^{-1}) in this study agreed with the result (0.4-2.7 %yr^{-1}) in Sharma et al (2014) over major cities in the country during 1996-2010 (Fig. 7f and Table 9). The largest decrease for CO and SO_2 in the industry type was due to the reduced emissions from factories and power plants (Fig. 7d and e); the largest decrease for NO_2 in the residence type was associated with the reduced emission from vehicles (Fig. 7b); the commerce type was second (CO and SO_2) and third (PM_{10}); and the CNSP trends in the greenbelt type were low (third or fourth) except for PM_{10}. However, there was almost no difference in the PM_{10} declining trend between the land-use types. Kim and Shon (2011) reported that the sudden increase of PM_{10} in spring 2002 occurred due to the enhanced Asian Dust effect. The systematic decreasing trend of the CNSP pollutants suggested that the policy for air quality regulation worked successfully (Sharma et al., 2014).

In contrast to the CNSP case, it was interesting that the O_3 value in a 0.25°×0.25° grid increased with the rate of 0.352-0.501 (ppb yr^{-1}; ~1.6%) over the last 12 years although the CNSP pollutants were reduced (Fig. 7 and Table 9). This phenomenon was consistent with Mayer (1999), who reported that long-term trends of major air pollutants except for O_3 were decreasing, particularly in industrialized countries, but global O_3 levels were increasing during the early period of the twenty-first century (Cooper et al., 2010). On the other hand, the standards of the surface O_3 concentration for its government control in South Korea are less than 0.1 ppm for the O_3 average during one hour, and less than 0.06 ppm for the O_3 average during eight hours (NIER, 2010). Furthermore, one of three stages of ozone warning in the region is issued, based on the surface O_3 concentration; ozone alert for 0.12 ppm hr^{-1} or higher, ozone warning for 0.3 ppm hr^{-1} or higher, and ozone grave warning for 0.5 ppm hr^{-1} or higher concentration. While surface O_3 level varies seasonally from 0.018 ppm in winter to 0.035 ppm in spring in South Korea (Table 5), there have been 84 times for 28 areas of the ozone alert, and 83 times for 27 areas of the ozone warning on an annual basis during the 12-year period of this study (https://seoulsolution.kr/content/ozone-warning-system-ozone-warning-system-protect-citizens%E2%80%99-health?language=en). Given the increasing trends of O_3 found in this study (Fig. 7a), it will be important to understand possible factors causing such trends. Seo et al. (2014) reported an increase in the O_3 (+0.26 ppb yr^{-1}) in 46

메모 [YJH30]: Referee#3, A2
Referee#3, A4

메모 [s31]: Referee#1, A1

cities in South Korea from 1999 to 2010. Also the O_3 increase (+0.48 ppb yr^{-1}) from 1990 to 2010, which was more consistent with our results, generally occurred for all of the seasons and day/night at most of the surface monitoring sites (Lee et al., 2014). This tendency was commonly shown in the two types of spatial grid analyses, possibly due to growing background O_3 (Table 9).

메모 [s32]: Referee#3, A4

The possibility of enhanced regional (background) O_3 as well as the local effect of the O_3 titration could be supported by the significant upward trends (0.205-0.396 ppb yr^{-1}; Table 9 and Fig. 7c) of the total oxidant (OX) despite the downward trends of the O_3 precursors (e.g., NO_2, CO, and PM_{10}). Specifically the significant positive trends of the OX values (0.260-0.300 ppb yr^{-1}) in the greenbelt type in the two kinds of spatial grids suggested the increase of background O_3 induced by its inflow from the regional scale, rather than the local scale. The upward trends of the OX in the both grids were commonly more pronounced in the commerce type than the other types, but the cause was unknown.

메모 [s33]: Referee#3, A4

A positive trend of tropospheric ozone (3.1% yr^{-1}) was clearly seen over Beijing from 2002-2010 in Wang et al. (2012), who emphasized a contribution in the downward O_3 flux from the stratosphere for the period. In spite of the CNSP decreasing trends in a 0.25°×0.25° grid (i.e., less urban features), the NO_2 tendency in a 0.1°×0.1° grid (i.e., more urban features) was not evident except for the residence (Table 9). Thus, the government regulation for NO_2 might not be very successful in large cities due to its diverse sources. Xu et al. (2008) suggested that the increased variability of the surface O_3 at a station in eastern China were mainly associated with the enhanced NO_x emission near the station.

The O_3 levels, which were related to the spatial variability in the local precursor emissions, were expected to vary with the land-use types. Seo et al. (2014) revealed that the long-term trends of the local precursor emissions on O_3 in South Korea could affect the O_3 trends locally, and in the country, significant enhancement of the background O_3 negatively affected the air quality. In order to understand the negative relationship in trend between O_3 and CNSP pollutants, particularly NO_2, we have investigated the relationship (i.e., correlation and weekly cycle) among O_3, NO_2 and VOCs with the land-use types further in sections 6 and 7. In this study, we focused on two issues: 1) which condition in view of the O_3 control in South Korea was more dominant, the VOCs-sensitivity or NO_2-sensitivity? 2) Did this condition significantly depend on the land-use types and the weekly cycles of the pollutants? The negative relationship between O_3 and NO_2 is expected in the VOCs-limited condition.

Local effect of the pollutants compared to the regional (i.e., background) effect can be shown, based on their weekly variations at each station of the four land-use types.

7. Correlation between O_3 and NO_2 with land-use types

As shown in Fig. 7, the increasing O_3 trend was the opposite of the decreasing CNSP trends. The O_3 trends could be affected by interannual variations of the pollutant emissions (e.g., NO_x and VOCs) from their various sources and of the meteorological conditions (Kim et al., 2006). In view of the 'O_3 control' strategy, the relationship between O_3 and NO_x (and the VOCs) was examined in many previous studies (e.g., Mazzeo et al., 2005; Han et al., 2011). There were various factors affecting the O_3: 1) local precursor emissions (e.g., NO_2, VOCs, and CO, etc.); 2) O_3 transport and its precursors from the local and remote sources; and 3) meteorological conditions (Seo et al., 2014). In this study we focused on the relationships on the local (grid) and regional (nationwide) scales in South Korea.

Figure 8 shows scatter diagrams of the O_3 versus NO_2 from the monthly anomalies of Fig. 7 in South Korea under the four land-use types: a) residence (black circle), b) commerce (blue cross), c) industry (red square) and d) greenbelt (green triangle). The sample number in the monthly anomaly time series of each pollutant was 144 during 2002-2013. The temporal correlation coefficient (r) between the anomalies of the two pollutants was given together with the regression dotted line. The correlations in the residence and commerce types were statistically significant at a significance level of $p < 0.01$ (i.e., either $r > 0.194$ or $r < -0.194$). The correlation was also significant at $p < 0.05$ (i.e., either $r > 0.137$ or $r < -0.137$) in the industry type, but not significant in the greenbelt type due to the least NO_2 emissions. Therefore, these results indicated that the NO_2 emissions from vehicles in the residence and commerce areas were highly related to the O_3 change on the long-term time scale (Fig. 8a-b). Also the NO_2 probably affected the O_3 in the industry type. The above results agreed with those of Seo et al. (2014) who reported that the long-term O_3 variation over South Korea was similar to that of NO_2, but their trends were spatially different.

Figure 9 presents the relationship between O_3 and NO_2 in terms of the climatological annual averages over South Korea during 2002-2013 under the MEK four land-use types of: residence (R), commerce (C), industry (I), and greenbelt (G). The relationship was derived from the data all of the 283 stations, which were individually specified by one land-use type among the four types (Fig. 9a). Since the stations of residence were located nationwide (i.e., more than a half of all the stations), the relationship could be spatially different due to the population-related traffic emissions. Furthermore, the NO_2 decreasing trends in a 0.1°×0.1° grid (Table 9) were found significant only in the residence area, but not in the other types, despite the government control efforts (e.g., Shon and Kim, 2011). Note that the pollutant trends in a 0.25°×0.25° grid were given in Fig. 7, where the NO_2 trends were significant except for the commerce among the four land-use types. In order to further investigate the relationship within the residence areas based on the population size, we subdivided the locations of the 154 residence-type stations of Fig. 1a by the three regions (Fig. 9b) as follows: i) the capital city of the country, Seoul (red circle), ii) the SMA (green circle) except for Seoul, and iii) outside of the SMA (blue circle). Therefore, the SMA is composed of i) Seoul and ii) the SMA except for Seoul. The 20% and 50% portions of the entire population in South Korea (~50.5 million in 2014) lived in Seoul and the SMA, respectively. There were more traffic emissions in the SMA than outside of the SMA, particularly in the residence types.

메모 [YJH34]: Referee#2, A5, Referee#3, A13

A very strong correlation ($p < 0.01$) of PM_{10} with the CO and NO_2 in their monthly dataset time series (Fig. 7) was likely to be associated with the traffic emission sources (see also Shon and Kim, 2011; Sharma et al., 2014). The correlations (0.42-0.56) in the residence and commerce were greater than those (0.32-0.47) in the greenbelt and industry, which was probably due to the vehicle emissions. In other words, more traffic emissions, which were related to the population density, were expected in Seoul than in the SMA excluding the capital city. The residence and commerce types were dominant in Seoul (Fig. 1a-b), while the residence and industry types predominantly existed in the SMA (Fig. 1b and d). Figure 9c is the same as Fig. 9a except for excluding the data in the SMA residence areas. Figure 9d is the same as Fig. 9a except for the O_3 and NO_2 relationships in the residence only over the three different regions shown in Fig. 9b. In Fig. 9d, the relationships over the three regions are shown in three colors, respectively.

The NO_2 value was the highest in the commerce areas over South Korea (Fig. 9a and c; Table 10). The NO_2 concentration was estimated in the following order: Commerce (C; 31.3) > Residence (R: 25.9) > Industry (I: 24.3) > Greenbelt (G: 13.3) (Fig. 9a). However, when the NO_2 (ppb) values in the region excluding the 74 SMA residence stations were examined, the order of the residence and industry areas was different from the previous case as follows:

메모 [YJH35]: Referee#3, A3

I (24.3) > R (20.3) (Fig. 9c). This result suggested that there were more NO_2-related traffic emissions (5.6 ppb) in the SMA residence areas than in the nationwide residence areas (Fig. 9a and c). The maxima (30.2 ppb) of the O_3 concentrations occurred in the greenbelt areas, while their minima were shown in the commerce areas (Fig. 9a and c). The order of magnitude of the O_3 was the opposite of that of the NO_2, showing an inverse relationship between the two pollutants (see also Han et al., 2011).

The traffic-induced pollutants were mainly NO, CO and PM_{10}, as well as VOCs, and the secondary trace gases of O_3 and NO_2 could be formed from these precursor substances during the photochemical reactions (Kuttler and Strassburger, 1999). They reported the inverse relationship of the O_3 versus NO_2 within the urban areas (Essen, Germany) with the following five land-use types: motorway, the main and secondary roads, residence and greenbelt. The three types of the roads and motorway could correspond to the commerce areas in our study, particularly in the urban area (e.g., the SMA). Overall, our results were consistent with those of Kuttler and Strassburger (1999) who showed that the higher O_3 concentration was formed in urban green areas in the summer during intensive solar radiation, due to the relatively low share of NO in the total concentrations of NO_2 in the greenbelt areas. However, an inverse relationship has been also found in winter (Table 10). The consistency in the relationship of O_3 versus NO_2 between the two studies supported the validation of the MEK classification method for the four land-use types. According to the monthly mean analysis of Xu et al. (2008) at a background station in eastern China, the negative correlation between O_3 and NO_x was found in the lowest 5% of ozone in cold season than in the highest 5% in warm season. Overall, the inverse relationship in Fig. 9a and c of this study, which systematically showed in the O_3 magnitude order (G > R > I > C; see also Table 6 in a 0.25°×0.25° grid) over the stations excluding the SMA residence areas in a non-grid, agreed well with the previous studies, suggesting that the four MEK land-use type classification was made reasonably.

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As shown in Figs. 1a and 9a, the number of nationwide residence stations was the largest among the four land-use types. The spatial dependence of the O_3 versus NO_2 relationship over the three different residence types (Fig. 9b; Seoul, the SMA except for Seoul, and Outside of the SMA) where the amounts of traffic emissions were expected to be different due to the number density of automobiles per unit area (as shown in Fig. 1d) was interesting to note. Furthermore, relatively short-lived NO_2 compared to the other pollutants

(CO, PM_{10}, O_3, and SO_2) in this study was used as a good indicator to reflect local and regional anthropogenic effects (Gilge et al., 2010). Although the SMA included Seoul, the residence region was separated into two sub-regions in this study in order to analyze the difference in the pollutants between them (Fig. 9d and Table 10). Heavier traffic generally occurred in Seoul than in the rest areas in the SMA. The NO_2 (ppb) concentrations in the residence areas over South Korea were estimated in the following order: Seoul (35.5±2.53) > SMA except for Seoul (31.7±4.03) > Outside of the SMA (20.3±4.94) (Fig. 9d). In the residence, there were pronounced reductions in the mean and standard deviation values of NO_2 due to the greater distance from the main traffic-induced pollution sources in the SMA including Seoul. The order of the O_3 (ppb) concentrations was the opposite of that for the NO_2 as follows; Outside of the SMA (25.0±4.03) > SMA except for Seoul (19.8±1.74) > Seoul (18.6±1.30). As a result, the MEK residence type, which had large variations in the two pollutant concentrations, could be required to be subdivided in the future in view of the O_3 versus NO_2 relationship. However, the difference in the concentrations between the two regions within the SMA (i.e., Seoul and the SMA except for Seoul) was relatively small compared to that between the SMA and outside of the SMA, due to the their transport over the geographically neighboring locations.

8. Weekend effect of the O_3, NO_2, VOCs, OX, and VOC/NO_2 with land-use types

Since the O_3 formation at the surface can depend on two major precursors (i.e., NO_x and VOCs; Larsen et al., 2003) and the ratio of the NO_x and VOCs (e.g., Pudasainee et al., 2006), the relationship among these three pollutants (O_3, NO_2 and VOCs) was examined in the weekly cycles of many previous studies (e.g., Gilge et al., 2010). The impact of the VOCs emission controls on the O_3 trend in northwest Europe was discussed in Derwent et al. (2003). Both the VOC emission data and the observations of atmospheric concentrations of VOCs in South Korea were lacking compared to those of the O_3 and NO_2, and thus the VOC observational sites and records were sparse (as shown in Fig. 1e and Table 2). Figure 10 shows the weekly variations in the VOCs (green triangle), O_3 (red square) and NO_2 (blue rectangle) concentrations at 9 photochemical air pollution monitoring stations in South Korea since 2007 under the MEK four land-use types. The land-use types at the stations available for simultaneous observations (O_3, NO_2, and VOCs) were 4 residences (the sites of Bulgwang,

메모 [YJH37]: Referee#1, A13

메모 [s38]: Referee#3, A4

Daemyoung, Gocheon and Goowol), 3 greenbelts (Seokmo, Taejong and Gwanin), a commerce area (Simgok) and an industry area (Joongheung).

The weekly cycle of the three pollutants was conspicuous in the residence and commerce areas (Fig. 10a-e). In the areas, the NO_2 and VOCs values were higher by 20-33% on the weekdays than on the weekends due to variations in anthropogenic activity, while the O_3 value was higher by 17-21% on the weekends. The VOCs increase on weekdays in the residence (Bulgwang) was probably due to vehicle emissions (e.g., Anthwal et al., 2010). The so-called weekend effect has been reported by Marr and Harley (2002a, 2002b) and Fujita et al. (2003a, 2003b) over the LA basin with higher O_3 concentrations on the weekends than on the weekdays. Marr and Harley (2002b) also found the weekly patterns of the lower NO_x and VOCs during weekend, out of phase with the higher O_3. Qin et al. (2004b) revealed that VOCs-limited condition for O_3 production and the NO_x-emission reduction in weekend could be associated with the weekend effect of O_3 in Southern California. In contrast to the residence and commerce areas, however, the weekly cycles of the three pollutants are not clear in the greenbelts and industry areas (Fig. 10f-i). In view of the negligible weekly cycle in the industry areas (Fig. 10f), the primary source for the cycle was traffic emission rather than the industrial factory activity. Since the industry station at Joongheung was located near the coast (Fig. 1e; red square), it could also have been influenced by meteorological factors (e.g., sea breeze). In addition, more observations for the industry and commerce types were required for detailed analysis, because the photochemical (VOCs) data in the two types were only available at a single station, respectively (Fig.10 e-f). In summary, more local effect influenced on the three pollutants in the residence and commerce areas, while regional (background) effect dominated in the greenbelt and industry areas.

It is interesting to note that the averages of the three pollutants at Simgok in the commerce (Fig. 10e) were highly contrast with those at Seokmo (Fig. 10g) in the greenbelt type. In other words, the O_3 level among the nine stations (Fig. 10) was the highest at Seokmo but relatively low at Simgok. However, the NO_2 and VOCs values had an opposite tendency with the O_3 case, showing their high values at the former (commerce) site and their low values at the latter (greenbelt) site. According to the study of Seo et al. (2014), larger NO_x emissions over the metropolitan cities in the short-term and seasonality showed lower O_3 minima because of NO_x titration and a nocturnal NO_y chemical process. They also

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reported that the higher O_3 level near the Seokmo greenbelt (i.e., Ganghwa) were induced due to lower NO_x emissions and the regional O_3 influxes from both the Yellow Sea (and China) and the SMA.

The decrease of local VOCs reduced O_3 with a reasonable amount of NO_2, and the ratio of VOCs to NO_x (i.e., VOC/NO_x) was an important factor for the O_3–control strategy (Marr and Harley, 2002a, 2002b; Fujita et al., 2003a, 2003b). Decreasing NO_x tended to increase O_3 formation when the VOC/NO_x ratio was less than the threshold values of 8-10 (Larsen et al., 2003). In addition, decreasing NO_x tended to decrease O_3 formation when the ratio was greater than the threshold values. In this study, the NO_2 value instead of NO_x was introduced for an approximate calculation of the ratio. The amounts of NO_2 approximately corresponded to 77-95% of the amount of NO_x over a background station in northern China (Meng et al., 2009). Therefore, the ratios used in this study (i.e., VOC/NO_2) may be overestimated, compared to those of VOC/NO_x. The inter-relationship among the three pollutants was statistically examined in view of the individual role of NO_2 and VOCs for the O_3 control in this study. Figure 11 shows the scatter diagrams of the long-term averages of the a) VOCs vs. NO_2, b) O_3 vs. VOCs, c) O_3 vs. NO_2, and d) O_3 vs. VOC/NO_2 at the photochemical stations under the following four land-use types; residence (black circle), commerce (blue cross), industry (red square), and greenbelt (green triangle). The correlation coefficient and the dotted regression line were also given. The spatial coefficients were statistically significant for the cases of O_3 vs. NO_2 at $p < 0.01$ (i.e., $r < -0.750$; Fig. 11c) and for VOCs vs. NO_2 at $p < 0.05$ (i.e., $r > 0.583$; Fig. 11a). Meanwhile the correlations were not significant for the other two cases (O_3 vs. VOCs, and O_3 vs. VOC/NO_2) (Fig. 11b and d). The significant positive correlation between the VOCs and NO_2 might have been due to their common anthropogenic sources (e.g., transportation and industrial activities, etc). Nine VOC values in Fig. 11a-b were systematically separated by their types in view of magnitude. However, the residence values for the NO_2 and O_3 cases were not distinct from the industry case, due to their broad-range values in the residence areas (Fig. 11c). Overall, the pollutant values at the 4 residences and 3 greenbelts are systematically clustered in the 2-dimensional domains of Fig. 11, supporting the idea that the MEK land-use types are reasonable.

메모 [s40]: Referee#2, A6

Figure 12 presents weekly variations of the OX and VOC/NO_2 values at each of the 9 photochemical stations of Fig. 10. The equally-weighted averages with respect to the four land-use types were also given for the OX and VOC/NO_2 in Fig. 12a-b (the grey cross dashed line), respectively. The weekend effect of OX in the residence and commerce was evident, while it was negligible in the greenbelt area (Fig. 12a). This contrast suggested the reduction of order of OX (ppb) is C (57.4) > R (53.6) > I (50.7) > G (45.4) (Table 11). The weak weekly cycle of OX in the greenbelt may be associated with the OX background level, although there was about a 9 ppb difference in OX between the greenbelt stations.

The average of VOC/NO_2 (the grey cross dashed line) did not show a clear weekly cycle (Fig. 12b). The weekly cycles of the ratio were almost negligible except for some stations. The industry type at Joongheung had a minimum on Tuesday in the weekly cycle, and its cause was unknown. Some weekend effects of the reduced ratio (i.e., the decrease on Saturday-Monday) at Daemyoung and Gocheon in the residence area occurred possibly due to the NO_2 reduction from less anthropogenic traffic emission. The ratio values tend to be relatively low in the greenbelt (2.0-5.3) and residence (2.6-3.5) areas. The four type average was 6.6 (Table 11). Based on the average result at the photochemical stations, the VOCs-limited chemistry over South Korea was more common than the NO_x-limited one in the industry (Joongheung). As a result, except for the Joongheung station, the NO_2 decrease in weekend could result in the enhanced O_3 production at the other eight stations in South Korea. This phenomenon was more conspicuous in the residence and commerce areas (5 stations) due to the weekly cycle of anthropogenic vehicle emission than in the greenbelt areas (3 stations). The ratio result in this study over the SMA was consistent with that of Jin et al. (2012) who reported that the areas of the Seoul and Incheon cities were VOCs-limited using the Ozone Isopleth Plotting Package for Research (OZIPR) model. Also in the model study, 24 areas in Gyeonggi-do where approximately included the SMA except the two cities was equally either VOCs-limited or neutral. However the modelling had some limitations due to inaccuracy in emission inventories and transport.

Figure 13 and Table 11 summarized the long-term surface air pollutant averages (O_3, NO_2, OX, VOCs, and VOC/NO_2) at the 9 photochemical stations over South Korea since 2007 in terms of the four MEK land-use types. The values (O_3, NO_2, VOCs, and VOC/NO_2) in the bar graph in the figure were shown in the colors of orange, blue, grey and red, respectively. The OX values were given with the symbol 'diamond' in green. The OX value, composed of NO_2-independent and NO_2-dependent parts, was utilized in order to understand the regional background O_3 concentration (i.e., the NO_2-independent one) (Mazzeo et al., 2005; Han et al., 2011). According to their studies, the OX values did not necessarily

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메모 [YJH42]: Referee#1, A15

correlate to the levels of local primary pollution (i.e., NO_x-dependent). The residence values of the NO_2 and VOCs were 3-4 times greater than the greenbelt values. The NO_2 (ppb) concentrations in the four land-use types were estimated to be in the following order: Commerce (C; 35.5) > Residence (R; 31.8) > Industry (I; 19.7) > Greenbelt (G; 9.9). The VOCs (ppbC) order was C (308.3) > I (199.6) > R (112.2) > G (31.2). Therefore, the anthropogenic sources of the VOC pollutants in the commerce and industry areas were likely to be more dominant than the natural ones. Nguyen et al. (2009) also reported the relative abundance of anthropogenic VOCs emissions compared to natural ones at a site in Seoul in 2004. The VOC order in the residence and commerce areas was different from NO_2 order, probably due to the different anthropogenic sources for the two different pollutants. On the other hand, the greenbelt and industry O_3 averages were greater than the residence and commerce ones by approximately 50%. The order for O_3 (ppb) was G (35.3) > I (31.0) > C ≈ R (21.8-22.0), which was almost opposite to the NO_2 case.

The ratio values of the VOC/NO_2 (3.6-8.7) in the residence, greenbelt, and commerce areas were generally smaller than the threshold values, while the ratio in the industry was the largest (10.2) of the four types (Table 11 and Fig. 13). The order for the ratio was I (10.2) > C (8.7) > G (3.9) > R (3.6). Therefore, the 8 stations except for the industry area among the 9 photochemical stations belonged to the VOCs-limited range which was defined as having the ratio value of less than 8 to 10 (see also Larsen et al., 2003). The industry station corresponded to the NO_x-limited chemistry. Higher O_3 levels on weekends (except in industry) could be associated with lower NO_2 values on weekends under the VOCs-limited O_3 formation regime. This tendency was also shown in the greenbelt as well as in the residence and commerce areas, although not as evident as the residence and commerce. This result was similar to the analysis of Marr and Harley (2002b) in California. They found that a shift in O_3 formation from NO_x-limited to VOCs-limited condition in the region could result from the reduction of VOCs more than that of NO_x. Based on the number of individual land-use type stations and their distribution over South Korea (Fig. 1), the VOCs control strategy for the O_3 reduction in this country was overall more effective than the NO_x control strategy. However, since the sample number of the photochemical stations in this study was limited particularly in the commerce and industry areas, the strategy could be shifted with the land-use types and more photochemical station data were needed for a more rigorous result. On the other hand, the VOCs-limited condition was also shown in Shanghai, China (Tie et al., 2013).

On the other hand, according to the one-dimensional photochemical study of Liu et al. (2012) in Beijing, China, the reduction of either NO_2 or VOCs could induce the decrease of O_3 production in the transition regime from VOCs-limited to NO_x-limited, which was more pronounced in the PBL. Lower VOCs in greenbelt areas than other land-use types in Fig. 10 indicate a weak contribution of the anthropogenic VOCs in greenbelt areas. Therefore the competing role between biogenic- and anthropogenic sources highly depends on the location and conditions.

The OX values ranged from a minimum (45.4 ppb) in the greenbelt areas to a maximum (57.4 ppb) in the commerce area, indicating less variability than the other pollutant values (O_3, NO_2, and VOCs) (Fig. 13 and Table 11). This result agreed with the analysis of Mazzeo et al. (2005) at a green area of Argentina. The OX values in some areas in Taiwan were almost constant in previous studies (Chen et al., 2002; Chou et al., 2006). This result suggested that the 'NO_x-titration' effect (e.g., Chou et al., 2006) was an important mechanism for the O_3 change. The temporal O_3 levels in the SMA and some inland areas were lower than those in the greenbelt and coastal areas due to NO_x titration effect (Kuttler and Strassburger, 1999; Ghim and Chang, 2002; Seo et al., 2014). The titration could have occurred locally even during nighttime without photochemistry from the nitrate formation and dry deposition by anthropogenic precursor emissions, and the higher O_3 values in the greenbelts related to the lower titration and the lower oxidization of NO (i.e., dilution) during the transport (Seo et al., 2014). Since local sources of both anthropogenic and biogenic hydrocarbons affected the oxidation (Kuttler and Strassburger, 1999; Clapp and Jenkin, 2001), their share needs to be further examined using, for instance, VOCs. Thus, O_3 formation in its weekly cycle could increase during weekend despite the reduced total (i.e., anthropogenic+natural) VOCs, because of their different species (Marr and Harley, 2002b).

9. Conclusion

We have comprehensively investigated the spatiotemporal variations in the surface air pollutants (O_3, NO_2, SO_2, CO, and PM_{10}) with the MEK four land-use types of residence, commerce, industry and greenbelt over South Korea from 2002 to 2013, using routinely observed hourly data at 283 stations. The variations were analyzed in terms of the cycles (diurnal, weekly, and annual) of the pollutants, their trends and inter-relationship. The VOCs

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Also, Referee#2, A3

data at 9 photochemical stations available since 2007 were also utilized in order to examine their effects on the ozone chemistry. The CNSP pollutants were overall larger in a 0.1°×0.1° grid (i.e., more urban characteristics), while the O_3 values were larger in a 0.25°×0.25° grid (i.e., more suburban/rural). The land-use types were generally consistent with the satellite-derived land covers and with the previous result (Kuttler and Strassburger, 1999) of an anti-correlation between the O_3 and NO_2 in diverse city areas. The relationship between the two pollutants in the SMA residence areas was substantially different from that outside of the SMA, probably due to the local difference in the vehicle emissions.

메모 [s45]: Referee#3, A12, from L480

The highest concentrations of air pollutants in the cycles were found in the industrial areas for SO_2 and PM_{10}, in the commercial areas for NO_2 and CO and in the greenbelt areas for O_3, respectively. The CNSP pollutants, except for O_3, were generally higher in the big cities during the weekdays while the O_3 showed its highest values in the small cities during the weekends. The weekly cycle and trends of the O_3 were out of phase with those of the NO_2, particularly in the residential and commercial areas. Regardless of the land-use types, the CNSP pollutants had significantly decreasing trends in contrast with the O_3 uptrend, probably due to the effective government controls (Kim and Shon, 2011).

메모 [YJH46]: Referee#1, A17

메모 [YJH47]: Referee#3, A2, A4

The weekly cycles of the pollutants were locally sensitive to the land-use types, while their long-term trends were most commonly similar to the types and regional areas. Total oxidant values (OX) with the land-use types were analyzed for the local and regional (or background) contributions of O_3, and the OX (ppb) order was C (57.4) > R (53.6) > I (50.7) > G (45.4), emphasizing the importance of the local part. However, the elevated O_3 over South Korea in the short-term could be due to both local anthropogenic precursors (NO_x and VOCs, etc) and their transport from China (Seo et al., 2014). In addition, the local wind could affect the ozone level over the SMA and Seoul (Ghim and Chang, 2000). The values of the VOC/NO_2 ratio for each of land-use types turned out to be in the order of I (10.2) > C (8.7) > G (3.9) > R (3.6), which suggested that most of the areas (~70 %) in South Korea have to be under VOCs-limited sensitivities for ozone chemistry.

Complete observations of the pollutants from intensive field campaigns and their monitoring are required in the future together with their profile measurements (e.g., Han et al., 2009) for their reduction. In view of the O_3 control, the inter-relationships between the pollutants (O_3, NO_x, VOCs, PM_{10}, and CO) and their seasonal washout and vertical mixing have to be further investigated. The regional transport of the pollutants from China (e.g., Kim

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et al., 2012), accurate assessment on their emission inventories, the meteorological condition (temperature, cloud and aerosol, air masses, etc) on the pollutants, and the relative impact of anthropogenic and biogenic VOCs on O_3 chemistry are beyond the scope of this study, but they need to be studied in the future.

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