Seo at al: Extensive spatio-temporal analyses of surface ozone and related meteorological variables in South Korea for 1999–2010, ACPD, 2014.

Abstract

Spatio-temporal characteristics of surface ozone (O_3) variations over South Korea are investigated with consideration of meteorological factors and time-scales (hyphen not needed) based on the Kolmogorov–Zurbenko filter (KZ-filter), using measurement data at 124 air quality monitoring sites and 72 weather stations for the 12 yr period of 1999–2010. In general, O_3 levels at coastal cities are high due to dynamic effects of the sea breeze while those at the inland and Seoul Metropolitan Area (SMA) cities are low due to the NO_x titration by local precursor emissions. We examine the meteorological influences on ~~the~~ O_3 using a combined analysis of the KZ-filter and linear regressions between O_3 and meteorological variables. We decomposed O_3 time-series (hyphen not needed) at each site into short-term, seasonal, and long-term components by the KZ-filter and regressed them on meteorological variables. Impact of temperature on the O_3 levels is significantly high in the highly populated SMA and inland region, ~~while that is~~but low in the coastal region. In particular, the probability of (no hyphen needed here) high-O_3 occurrence ~~doubled~~ doubles with 4 C of temperature increase in the SMA during high-O_3 months (May to October). ~~It~~ This implies that those regions will experience frequent high-O_3 events in ~~the~~ a future warming climate. In terms of short-term variation, the distribution of high-O_3 probability classified by wind direction shows the effect of both local precursor emissions and long-range transport from China. In terms of long-term variation, the O_3 concentrations have increased by +0.26 ppbv yr^{-1} on nationwide average, but their trends show large spatial variability. ~~Additional statistical analysis of the singular~~ Singular value decomposition analyses further reveal~~s~~ that the long-term temporal evolution of O_3 is similar to that of ~~the~~ nitrogen dioxide, ~~measurement~~ although the spatial distribution~~s~~ of their trends ~~are~~ is different. This study ~~would~~ will be helpful as a reference for diagnostics and evaluation of regional- and local-scale O_3 and climate simulations, and as a guide to appropriate O_3 control policy in South Korea.

1 Introduction

Surface ozone (O_3) is a well-known secondary air pollutant, which affects air quality, human health, and vegetation. High O_3 concentration has detrimental effects on respiration, lung function, and airway reactivity in human health (Bernard et al., 2001; Bell et al., 2007). In terms of mortality, Levy et al. (2005) has previously assessed that 10 ppbv increase in 1 h maximum O_3 could increase daily mortality by 0.41 %. High O_3 concentrations could also reduce agricultural production. For example, Wang and Mauzerall (2004) reported that the East Asian countries of China, Japan, and South Korea lost 1–9% of their yields of wheat, rice, and corn, and 23–27% of their yields of soybeans due to O_3 in 1990. In addition, O_3 is one of greenhouse gases of which radiative forcing is estimated as the third largest contribution among the various constituents in the troposphere (IPCC, 2007). Therefore, the spatially inhomogeneous distribution of O_3 due to its short chemical lifetime of a week to a month could induce strong regional-scale climate responses (Mickley et al., 2004).

In the recent decades, tropospheric O_3 has increased in the Northern Hemisphere mainly due to increases in anthropogenic precursors, especially nitrogen oxides (NO_x) (Guicherit and Roemer, 2000; Vingarzan, 2004). In East Asia, there have also been ~~also~~ growing concerns about elevated O_3 concentration owing to rapid economic growth and industrialization (e.g. Tang et al., 2009; Wang et al., 2009). The recent increases of O_3 in East Asia are also affected by transboundary transport of O_3 and its precursors. For example, previous modeling studies have shown that the transport of O_3 from China by continental outflow is one of the major contributions of O_3 in Japan and South Korea (Tanimoto et al., 2005; Nagashima et al., 2010). Intercontinental transport of O_3 and its precursors originated from East Asia affects O_3 concentrations and ~~related~~ air quality ~~in a remote area~~in remote areas even on a global scale (Akimoto, 2003).

Recently, several studies have focused on the relationship between O_3 levels and temperature, and suggested potential influences of the global warming and climate change on the high levels of O_3 (Jacob and Winner, 2009; Rasmussen et al., 2012; and references therein). Lin et al. (2001) calculated probability of daily ~~8 h~~ maximum 8-h average O_3 exceeding 85 ppbv for a given range of daily maximum temperatures and reported that a 3 _C increase of the daily maximum temperature doubles risk of ~~the~~ O_3 exceedances in the Northeastern United States. In addition, Ordóñez et al. (2005) showed that high temperature extremes probably led to the high occurrence of severe O_3 episodes during the summer 2003 heat wave over Europe. These results imply the potentially large sensitivity of O_3 concentration and related air quality to the temperature increases (Jacob and Winner, 2009). In the model experiments by Lin et al. (2008), both averaged O_3 concentration and frequencies of (no hyphen needed between high and O3) high-O_3 episodes in ~~the future~~ were predicted to increase in the future over the United States and East Asia. Based on climate-chemistry model experiments, Lei and Wang (2013) ~~also~~ have also shown that O_3 production increases in warmer conditions in industrial regions over the United States.

In South Korea, one of the most highly populated countries in the world, both O_3 concentration and (remove hypen again) high-O_3 episodes have increased in recent decades despite efforts to regulate emissions of O_3 precursors (KMOE, 2012). Although the increase of O_3 levels in South Korea over the last three decades is mainly regarded as the results of rapid industrialization, economic expansion, and urbanization, there are other factors to be considered to explain the long-term increase in O_3 concentration. For example, since the Korean peninsula is located on the eastern boundary of East Asia, downward transport of O_3 by the continental outflow considerably affects the high O_3 levels in South Korea (Oh et al., 2010). In addition, recent warming trend related to ~~the~~ global climate change could also be an important factor to increase O_3 concentration in South Korea. ~~The c~~Climate change is expected to increase both frequency and intensity of temperature extremes over the Korean peninsula (Boo et al., 2006). Therefore, comprehensive understanding of the various factors affecting O_3 concentration, such as local precursor emissions, transport of O_3 and its precursors from local and remote sources, and changes in meteorological fields related to ~~the~~ climate change is required to guide environmental policies.

The present study aims to examine the spatio-temporal characteristics of the measured O_3 variations in South Korea with consideration of three time-scales (“time scales” without hyphen) and various meteorological factors, using ground-measured data from 124 air quality monitoring sites and 72 weather stations for the 12 yr period of 1999–2010. We decomposed O_3 time-series at each measurement site into different time-scale (“time scale” without hyphen) of short-term, seasonal, and long-term components by application of the Kolmogorov–Zurbenko filter (KZ-filter) that has been used in previous studies (e.g. Gardner and Dorling, 2000; Ibarra-Berastegi et al., 2001; Thompson et al., 2001; Lu and Chang, 2005; Wise and Comrie, 2005; Tsakiri and Zurbenko, 2011; Shin et al., 2012). To investigate the meteorological impact on the O_3 levels, we applied the combined analysis of the KZ-filter and linear regression model with the meteorological variables. In the short-term timescale, the possible effects of transport from the local and remote sources on the high-O_3 episodes were explored by using the wind data. In the long-term time-scale, the singular value decomposition (SVD) with nitrogen dioxide (NO_2) measurements was additionally applied to examine the effects of varying local emissions on the long-term O_3 trend.

The remainder of this paper is structured as follows. In the next section, we describe the observational data and analysis techniques used in this study. In Sect. 3, we investigate~~d~~ the spatio-temporal characteristics of the decomposed O_3 time-series (“time series without hyphen) and its relationship with meteorological variables over South Korea. Finally, the key findings are summarized in Sect. 4.

2 Data and methodologies

2.1 Data

Hourly data of O_3 and NO_2 mixing ratios in ~~the unit of~~ ppbv units are provided for 290 air quality monitoring sites over South Korea by the National Institute of Environmental Research (NIER). The mixing ratios of O_3 and NO_2 at each monitoring site are measured

by ultraviolet ~~photometric method and chemiluminescent method~~absorption and chemiluminescence, respectively. We here analyze the O_3 time-series at 124 selected air quality monitoring sites, where continuous hourly measurements were carried out for the full 12 yr period of 1999–2010.

Hourly meteorological data at 72 weather stations of the Korea Meteorological Administration (KMA) for the same period are also used to examine the effects of meteorological factors on the O_3 variations. The meteorological variables used in this study are temperature (_C), dew-point temperature (_C), sea-level pressure (hPa), wind speed (m s^{-1}), wind direction (16 cardinal directions), relative humidity (%), and surface insolation (W m^{-2}) at the surface. Using ~~the~~ hourly data, we first calculated daily averages for O_3 (O_{3avg}), NO_2 (NO_{2avg}), temperature (T), surface insolation (SI), dew-point temperature (TD), sea-level pressure (PS), wind speed (WS), wind direction (WD), and relative humidity (RH). We also obtained daily minimum O_3 (O_{3min}), daily ~~8 h~~ maximum 8-h average O_3 (O_{38h}), and daily maximum temperature (T_{max}) from the hourly data set.

To investigate the relationship between O_3 and meteorological variables, it is desirable to use data observed at the same stations ~~are desirable to use~~. However, not all of air quality monitoring sites and weather stations are closely located in South Korea. Therefore, we assume that an air quality monitoring site can observe the same meteorological variables as those at a weather station if the distance between the two places is less than 10 km. Under the assumption, only O_3 data from 72 air quality monitoring sites and meteorological data from 25 weather stations are available to analyze the meteorological effects on the O_3 variation over South Korea. The insolation was measured only at 17 weather stations for the analysis period. Figure 1 shows geographical locations of the ground measurements used in the present study, together with colored topography based on the US Geological Survey (USGS) Digital Elevation Model (DEM).

2.2 Decomposition of O_3 time-series by KZ-filter

The KZ-filter is a decomposition method ~~to~~ than can be used to separate ~~O_3~~ time-series into short-term, seasonal, and long-term components (Rao and Zurbenko, 1994). We applied the KZfilter to the O_3 time-series by taking moving average of window length m with iterating

p times, which is denoted by $KZ_{m,p}$. The KZ-filter is basically low-pass filter ~~of~~ for removing high frequency components from the original time-series. Following Eskridge et al. (1997), the KZ-filter removes the signal smaller than the period N, which is called as the effective filter width. N is defined as follows:

$$m \times p^{1/2} \leq N \quad (1)$$

The KZ-filter method has the same level of accuracy as the wavelet transform method although it is a much easier way to decompose the original time-series (Eskridge et al., 1997). In addition, time-series with missing observations can be applicable to KZ-filter owing to the iterative moving average process.

The short-term components separated by the KZ-filter using daily O_3 time-series are not fully independent of the seasonal influence.We thus applied the KZ-filter to the daily time series of $\ln(O_3)$ as in Rao and Zurbenko (1994) and Eskridge et al. (1997). Applying $\ln(O_3)$ to the KZ-filter stabilizes variance of the short-term components because the KZ-filter can separates high-order nonlinear terms and effects into a short-term component (Highlighted sentence is not clear, please re-write) (Rao and Zurbenko, 1994; Rao et al., 1997). Note that a temporal linear trend of log-transformed data is provided as $\%\mathrm{yr}^{-1}$ because the differential of the natural logarithm is equivalent to the percentage change.

The natural logarithm of the O_3 time-series at each site denoted as $[O_3](t)$ is thus decomposed by KZ-filter as follows:

$$[O_3](t) = [O_{3ST}](t) + [O_{3SEASON}](t) + [O_{3LT}](t) \quad (2)$$

$[O_{3ST}]$ is a short-term component attributable to day-to-day variation of synoptic-scale weather and short-term fluctuation in precursor emissions. $[O_{3SEASON}]$ represents a seasonal component related to the seasonal changes in solar radiation and vertical transport of O_3 from the stratosphere whose time scale is ~~between~~ from several weeks to months. $[O_{3LT}]$ denotes a long-term component explained by changes in precursor emission, transport, climate, policy, and economy over the entire period (Rao et al., 1997; Milanchus et al., 1998; Gardner and Dorling, 2000; Thompson et al., 2001; Wise and Comrie, 2005). Tsakiri and Zurbenko (2011) showed that $[O_{3ST}]$ and $[O_{3LT}]$ are independent of each other. Also, statistical characteristics of $[O_{3ST}]$ are very close to those of white noise (Flaum et al., 1996) and therefore, $[O_{3ST}]$ is nearly detrended.

In this study, the KZ-filter with the window length of 29 days and 3 iterations ($KZ_{29,3}$) decomposed daily $\ln(O_{38h})$ time series at the 124 monitoring sites. $KZ_{29,3}$ removes $[O_{3ST}]$ of which the period is smaller than about 50 days, following Eq. (1). We defined the filtered time-series as a baseline ($[O_{3BL}]$) as in Eq. (3).

$$[O_3](t) = [O_{3BL}](t) + [O_{3ST}](t) \quad (3)$$

Equation (3) accounts for the multiplicative effects of short-term fluctuations on the $[O_{3BL}]$ due to the log-transformation (Thompson et al., 2001). In other words, exponential of $[O_{3ST}]$ is a ratio of the raw O_3 concentrations to the exponential of $[O_{3BL}]$, which is the baseline O_3 concentration in ppbv. Therefore, if $\exp[O_{3ST}]$ is larger than 1, the raw O_3 concentration will be larger than the baseline O_3 concentration.

$[O_{3BL}]$ is expressed as the sum of $[O_{3SEASON}]$ and $[O_{3LT}]$, as in Eq. (4) (Milanchus et al., 1998).

$$[O_{3BL}](t) = [O_{3SEASON}](t) + [O_{3LT}](t) \quad (4)$$

Since $[O_{3BL}]$ is closely associated with meteorological fields, we built a multiple regression model with available meteorological variables as in Eq. (5), following previous studies (e.g., Rao and Zurbenko, 1994; Rao et al., 1995; Ibarra-Berastegi et al., 2001). Short-term variability of meteorological variables was also filtered out by $KZ_{29,3}$.

$$[O_{3BL}](t) = a_0 + \sum_i a_i \mathrm{MET}_{BL}(t)_i + \varepsilon(t)$$
$$\mathrm{MET}_{BL}(t) = [T_{\max BL}(t), \mathrm{SI}_{BL}(t), \mathrm{TD}_{BL}(t), \mathrm{PS}_{BL}(t), \mathrm{WS}_{BL}(t), \mathrm{RH}_{BL}(t)] \quad (5)$$

In the multiple linear regression model, $[O_{3BL}]$ is a response variable and the baselines of meteorological variables ($\mathrm{MET}_{BL}(t)_i$) are predictors. Also, a_0, a_i, and $\varepsilon(t)$ denote the constant, regression coefficient of variable i, and residual of the multiple regression model, respectively.

The residual term $\varepsilon(t)$ contains not only the long-term variability of O_3 related to long-term changes in local precursor emissions but also seasonal variability of O_3 attributable to unconsidered meteorological factors in the multiple linear regression model. Thus, we applied the KZ-filter with the window length of 365 days and 3 iterations ($KZ_{365,3}$) to $\varepsilon(t)$ to extract the meteorologically adjusted $[O_{3LT}]$ of which the period is larger than about 1.7 yr as follow:

$$\varepsilon(t) = KZ_{365,3}[\varepsilon(t)] + \delta(t) = [O_{3LT}](t) + \delta(t) \quad (6)$$

In Eq. (6), $\delta(t)$ denotes the seasonal variability of O_3 related to the meteorological variables unconsidered in the multiple linear regression model and/or noise.

Finally, $[O_{3SEASON}]$ is obtained by the sum of total meteorological effects regressed on $[O_{3BL}]$ ($a_0 + \sum_i a_i MET_{BL}(t)_i$) and meteorological effects of which the period is larger than 50 days but smaller than 1.7 yr ($\delta(t)$) as in Eq. (7).

$$[O_{3SEASON}](t) = a_0 + \sum_i a_i MET_{BL}(t)_i + \delta(t) \quad (7)$$

Figure 2 shows a schematic representation of Eq. (2) using daily O_{38h} time-series at the City Hall of Seoul for the period of 1999–2010. $[O_{3SEASON}]$ in Fig. 2c clearly shows the typical seasonal cycle of O_3 in South Korea with high concentrations in spring, slight decrease in July and August, and increase in autumn (Ghim and Chang, 2000). The spring maximum of O_3 concentrations in the Northern Hemisphere is generally attributed to episodic stratospheric intrusion (Levy et al., 1985; Logan, 1985), photochemical reactions of accumulated NO_x and hydrocarbons during the winter (Dibb et al., 2003), accumulation of O_3 due to the longer photochemical lifetime (∼ 200 days) during the winter (Liu et al., 1987), and transport of O_3 and its precursors by the continental outflow (Carmichael et al., 1998; Jacob et al., 1999; Jaffe et al., 2003). On the other hand, frequent precipitation during the East Asian summer monsoon influences the decrease of O_3 concentrations in July and August (Ghim and Chang, 2000). $[O_{3LT}]$ in Fig. 2d shows that the O_3 concentrations at the monitoring site have increased in the past decade, irrespective of any change in meteorological conditions.

2.3 Spatial interpolation by AIDW method

The inverse-distance weighting (IDW) is a deterministic spatial interpolation technique for spatial mapping of variables distributed at irregular points. In this study, we adopted the enhanced version of the IDW, the adaptive inverse-distance weighting (AIDW) technique (Lu and Wong, 2008). While the traditional IDW uses a fixed distance-decay parameter without considering the distribution of data within it, the AIDW uses adjusted distance-decay parameters according to density of local sampling points. Therefore, the AIDW provides flexibility to accommodate variability in the distance–decay relationship over the domain and thus better spatial mapping of variables distributed at irregular observational points (Lu and Wong, 2008).

In the mapping of O_3 with spatial interpolation, there are ubiquitous problems such as spatial-scale violations, improper evaluations, inaccuracy, and inappropriate use of O_3 maps in certain analyses (Diem, 2003). The spatial mapping in the present study also has problems with the spatial resolution of the observations, which is not high enough to consider small-scale chemical processes and geographical complexity of the Korean peninsula (see Fig. 1). Most of the air quality monitoring sites are concentrated on the cities, and typical inter-city distances are 30–100 km in South Korea while spatial representativeness of O_3 concentration is possibly as small as around 3–4 km (Tilmes and Zimmermann, 1998) or 5 km (Diem, 2003). Despite such limits, the spatial mapping in this study is still useful because we aim not to derive an exact value at a specific point where the observation does not exist, but to provide the better quantitative understanding of O_3 and related factors in South Korea, especially focused on the metropolitan and urban areas.

3 Results

3.1 Spatial characteristics of O_3 and its trend in South Korea

Climatological daily average O_3 (O_{3avg}) and its temporal linear trends are represented in Fig. 3 and Table 1 using data from 124 monitoring sites distributed nationwide in 46 cities for the past 12 yr period. The spatial map of climatological daily average NO_2 (NO_{2avg}) is also shown in Fig. 3. In Table 1, the cities are categorized into three geographical groups: 16 coastal cities, 14 inland cities, and 16 cities in the Seoul Metropolitan Area (SMA).We separated the SMA cities from the other two groups since the SMA is the largest source region of anthropogenic O_3 precursors in South Korea. The SMA occupies only 11.8% (11 745 km^2) of the national area, but has 49% (25.4 million) of the total population and 45% (8.1 million) of total vehicles in South Korea. It is estimated that approximately 27% (291 kt) of total NO_x emissions and 34% (297 kt) of the volatile organic compounds (VOCs) emissions in South Korea are from the SMA in 2010 (KMOE, 2013). Therefore, the climatological NO_{2avg} concentration in the SMA is much higher than that in other region (Fig. 3b).

In general, O_3 concentrations are high at the coastal cities, low at the inland cities, and lowest at the SMA cities in South Korea. Along with Table 1, Fig. 3a shows that the 12 yr average of O_{3avg} is high at the southern coastal cities such as Jinhae (31.3 ppbv), Mokpo (30.3 ppbv), and Yeosu (28.1 ppbv), with the highest value at Jeju (32.6 ppbv), and low at the inland metropolitan cities such as Daegu (19.8 ppbv), Gwangju (20.5 ppbv), and Daejeon (20.7 ppbv), with lowest values at the SMA cities including Seoul (17.1 ppbv), Incheon (19.0 ppbv) and Anyang (16.8 ppbv).

Compared to the regional background concentration of 35–45 ppbv at five background measurement sites around South Korea (KMOE, 2012), the averaged O_3 concentrations in the SMA and inland metropolitans are much lower while those at the coastal cities are close to the regional background levels. In comparison with Fig. 3b, Fig. 3a shows that relatively lower O_{3avg} regions are well consistent with relatively higher NO_{2avg} regions. Substantial emissions of anthropogenic NO in the SMA and other inland metropolitans lead to NO_x titration effects even in the absence of photochemical reactions during the night, and thus the averaged O_3 concentrations are depressed by 10–20 ppbv lower than the regional background concentration (Ghim and Chang, 2000). A recent modeling study by Jin et al. (2012) has suggested that the maximum O_3 concentrations in the SMA, especially in Seoul and Incheon, are VOCs-limited. In the coastal region, on the other hand, low emissions of NO with dilution by the strong winds weaken the titration effect and result in the high O_3 concentrations. The dynamic effect of land-sea breeze is another possible factor of the high O_3 levels at the coastal cities. Oh et al. (2006) showed that a near-stagnant wind condition at the development of sea breeze temporarily contains O_3 precursors carried by the offshore land breeze during the night, and following photochemical reactions at mid-day produces O_3. The relationship between O_3 and wind speed and direction will be shown in Sects. 3.2 and 3.5 respectively.

In terms of temporal trends, the surface O_3 concentrations in South Korea have generally increased for the past 12 yr as shown in Fig. 3c and Table 1. The averaged temporal linear trend of O_{3avg} at 46 cities nationwide is +1.15% yr^{-1} (+0.26 ppbvyr^{-1}), which is comparable with observed increasing trends of approximately +0.5–2% yr^{-1} in various regions in the Northern Hemisphere (Vingarzan, 2004). Compared with previous studies in East Asia, the overall increasing trend of O_3 in South Korea is smaller than recent increasing trends over China of +1.1 ppbvyr^{-1} in Beijing for 2001–2006 (Tang et al., 2009) and +0.58 ppbvyr^{-1} in Hong Kong for 1994–2007 (Wang et al., 2009) but slightly larger than increasing trend over Japanese populated areas of +0.18 ppbvyr^{-1} for 1996–2005 (Chatani and Sudo, 2011).

Several factors that could influence the overall increase of O_3 over East Asia were suggested by the following previous studies. Tanimoto et al. (2009) suggested that the O_3 increase results from recently increased anthropogenic precursor emissions in East Asia. However, model sensitivity simulations in Chatani and Sudo (2011) indicate that the changes in East Asian emissions can explain only 30% of the O_3 trend. They have suggested the long-term variations in meteorological fields as a possible important factor although further studies are required. In particular, it is well known that insolation and temperature are important meteorological factors in O_3 variation. While insolation directly affects O_3 production through photochemical reactions, increased temperature affects net O_3 production rather indirectly by increasing biogenic hydrocarbon emissions, hydroxyl radical (OH) with more evaporation, and NO_x and HO_x radicals by thermal decomposition of peroxyacetyl nitrate (PAN) reservoir (Sillman and Samson, 1995; Olszyna et al., 1997; Racherla and Adams, 2006; Dawson et al., 2007).

The O_3 increasing trend in Fig. 3c is possibly affected by changes in meteorological variables. Figure 4 shows temporal linear trends of daily average temperature (T) and insolation (SI). Despite the spatial discrepancy between trends of O_3 (Fig. 3c) and meteorological variables (Fig. 4), both temperature and insolation have generally increased in South Korea for the past 12 yr. The spatial mean of temporal linear trend in temperature at 72 weather stations nationwide is approximately +0.09 $^{\circ}$C yr^{-1}, which is much higher than +0.03 $^{\circ}$C yr^{-1} for the Northern Hemispheric land surface air temperature for 1979–2005 (IPCC, 2007). This high increasing trend of temperature in South Korea is probably due to urban heat island effect with rapid urbanization. The averaged temporal linear trend of insolation at 22 weather stations nationwide is about +1.47Wm^{-2} yr^{-1} despite the decreasing phase of solar cycle during the 2000s. This is possibly caused by reduction in particulate matter emissions due to enhanced environment regulation in South Korea during the recent decade (KMOE, 2012).

Although O_3 and related meteorological variables such as temperature and insolation have recently increased in South Korea, the spatial patterns of their temporal trends do not show clear similarity. In addition, the spatial distribution of O_3 trends is rather inhomogeneous even on a metropolitan scale. For instance, Table 1 shows a wide range of O_3 trends among the SMA cities from −1.25% yr^{-1} of Gwacheon to +2.82% yr^{-1} of Seoul. The spatial inhomogeneity in O_3 trend and the trend differences among O_3, temperature, and insolation imply that the long-term O_3 trends in South Korea are not only affected by changes in meteorological conditions but also influenced by changes in local precursor emissions or transport of O_3 and its precursors. The local effects of precursor emission on the long-term changes in O_3 are further examined in Sect 3.6.

3.2 Relationships between O_3 and meteorological variables

A multiple linear regression model is here adopted to explain relationships between $O_{3\,8h}$ and each of key meteorological variables such as T_{max}, SI, TD, PS, WS, and RH. To exclude day-to-day short-term fluctuations or white noises from the original timeseries, $KZ_{29,3}$ was applied to each variable before the regression process and yielded baselines of each variable. As a result of the linear regression, squared correlation coefficients (R^2) between $O_{3\,8h}$ and each meteorological variable were calculated for 72 air quality monitoring sites distributed in 25 cities nationwide and summarized in Table 2. The nationwide average of R^2 is 0.50 for SI, 0.29 for PS, 0.22 for T_{max}, 0.14 for TD, 0.05 for RH, and 0.03 for WS, respectively. In South Korea, SI, T_{max}, and TD generally show positive correlations with O_3 levels while PS is negatively correlated with O_3 variations. Since the short-term variability in each variable is excluded, the negative correlation between O_3 and PS is related to their seasonal cycle rather than continuously changing weather system of high and low. PS in South Korea located on the continental east coast is mostly affected by the cold continental high pressure air mass during the winter when the O_3 concentrations are lowest. On the other hand, WS and RH show weak correlations with O_3 variations.

The R^2 distributions for T_{max} and SI are represented in Fig. 5. Figure 5a and b shows a common spatial pattern with high correlations at the inland and SMA cities and low correlations at the coastal cities. For instance, the average R^2 value with T_{max} for the coastal cities is only 0.07, which is much smaller than 0.36 for the SMA cities and 0.30 for the inland cities. Also, the average R^2 values with SI are 0.60 for the SMA cities and 0.58 for the inland cities, but 0.35 for the coastal cities. Despite the similar pattern between Fig. 5a and b, the R^2 values of SI are much higher than those of T_{max} because temperature affects net O_3 production rather indirectly compared to the direct influence of insolation on O_3 levels by photochemical production (Dawson et al., 2007; and references therein). The apparent R^2 differences among three regions indicate that temporal variations of O_3 at the SMA and inland cities are much more sensitive to SI and T_{max} than those at the coastal cities. The low dependence of O_3 on T_{max} and SI at the coastal cities means that the photochemical reactions of precursors are less important for determining O_3 levels there compared to the SMA and inland cities.

The meteorological effects on O_3 at the inland, coastal, and SMA cities are also examined by daily minimum O_3 (O_{3min}). In the polluted urban area, the O_3 concentration reaches near-zero minima during the night since O_3 is reduced by NO_x titration and dry deposition in the absence of photochemical reactions. However, if O_3 is persistently transported from the high-O_3 background, the concentrations will keep higher levels even at the nighttime (Ghim and Chang, 2000). Therefore, the high O_{3min} near the coast (see Fig. 6a and Table 3) implies the large influences of the background O_3 transport at the coastal cities. Previous analyses of frequency distributions of O_3 concentrations have also shown that the O_3 levels at the coastal cities such as Gangneung, Jeju, Mokpo, Seosan, and Yeosu are affected by the background O_3 transport, unlike ~~different from~~ Seoul where the effect of local precursor emission is dominant (Ghim and Chang, 2000; Ghim, 2000).

Compared to the spatial distribution of R^2 between baseline $O_{3,8h}$ and T_{max} or SI in Fig. 5a and b, O_{3min} distribution in Fig. 6a shows high O_{3min} at the coastal cities where the R^2 is low and low O_{3min} at the inland cities where the R^2 is high. These opposite patterns suggest that the meteorological effects on the O_3 production and transport effects of background O_3 are negatively correlated for the South Korean cities. The clear negative correlations are also shown in scatter plots (Fig. 6b and c). In both ~~two~~ scatter plots, the three geographical groups of cities (blue for the coastal cities, green for the inland cities and red for SMA) are well separated. Several industrial or metropolitan cities in the coastal region such as Changwon (CW), Busan (BS), and Ulsan (US) have relatively low O_{3min} compared to the rest of coastal cities. Larger NO_x emissions in these southeastern coastal cities (Fig. 3b) induce lower O_{3min} levels via NO_x titration process despite the transport effects of background O_3. Among the SMA cities, on the other hand, Ganghwa (GH) has much higher O_{3min} compared to other SMA cities. Ganghwa is a rural county located on the northwestern coast of the SMA. Therefore, both small NO_x emissions there and transport of regional background O_3 from the Yellow Sea affect the characteristics of O_3 in Ganghwa.

The different meteorological effects on O_3 between the coastal and inland regions are further examined with wind speed. Daily average wind speed (WS) data over South Korea are averaged for 12 yr. The 12 yr averaged WS are summarized in Table 3 and presented in spatial map of Fig. 7a, which show high wind speed in the coastal region and low wind speed in the inland region. Figures 7b and c show~~s~~ that the averaged wind speeds ~~of~~ at 25 cities are positively correlated with O_{3min} and ~~are~~ negatively correlated with the coefficient of determination (R^2) between O_3 and T_{max}. In general, since the ventilation by strong~~er~~ wind speeds ~~causes the less effective~~ reduces the effect of photochemical reactions~~ due to the ventilation effect~~, the relationship between high wind speed ~~with the~~and high O_3 levels in the coastal region is attributable to the transport of background O_3. On the other hand, the weaker wind speed induces more effective photochemical reaction through the longer reaction time in stagnant condition as well as more enhanced aerodynamic resistance to dry deposition (Jacob and Winner, 2009). Therefore, the meteorological effects on the O_3 production~~s~~ become more important in the inland region where the wind speeds are lower.

3.3 Probability of O_3 exceedances related to temperature

~~Probability~~ Evaluating the probability of O_3 exceeding the air quality standard in a given range of temperature is useful to speculate about potential sensitivity of O_3 concentration to climate change (Lin et al., 2001; Jacob and Winner, 2009). ~~We here~~Here we calculate~~d~~ the probabilities ~~of high O_3 occurrence~~ that $O_{3\,8h}$ exceeds the Korean air quality standard of 60 ppbv (KMOE, 2012) as a function of the daily maximum temperature (T_{max}) for the coastal, inland, and SMA cities. Similar to the analyses in Lin et al. (2001) for the contiguous United States, Fig. 8 shows that the probabilities of O_3 exceedances increase with T_{max} at the inland and SMA cities. For example, the probability of O_3 exceedances in the SMA is almost doubled by about a 4 °C increase in T_{max} and reach 27% at 30 °C. In the coastal region, on the other hand, the probability of O_3 exceedance increases up to 12–13% with T_{max} change from 10 °C to 20 °C and does not increase significantly for T_{max} above 20 °C. This is consistent with the spatial feature of the meteorological effects on O_3 levels, which are high at the inland and SMA cities and low at the coastal cities as described in the previous section. Therefore, the probability of high O_3 occurrence will be more sensitive to the future climate change at the inland and SMA cities than at the coastal cities. In the previous modeling study by Boo et al. (2006), T_{max} over the Korean peninsula is expected to rise by about 4–5 °C to the end of 21st century owing to ~~the~~ global warming. This indicates considerable future increases in exceedances of the O_3 air quality standard over South Korea except over coastal regions.

3.4 Relative contributions of O_3 variations in different time-scales

Surface O_3 variation can be decomposed into short-term component ($[O_{3ST}]$), seasonal component ($[O_{3SEASON}]$), and long-term component ($[O_{3LT}]$) by using the KZ-filter as described in Sect. 2.2. We evaluated relative contributions of each component to total variance of original time-series. Overall, the relative contributions of $[O_{3LT}]$ in Fig. 9c are much smaller than those of $[O_{3ST}]$ in Fig. 9a and $[O_{3SEASON}]$ in Fig. 9b at all cities (Table 4). Therefore, sum of $[O_{3ST}]$ and $[O_{3SEASON}]$ account for the most of O_3 variations. In Fig. 9a and b, the relative contributions of $[O_{3ST}]$ and $[O_{3SEASON}]$ show a strong negative relationship spatially. The relative contributions of $[O_{3ST}]$ are generally larger at the coastal cities (53.1 %) ~~and small~~ than at the inland cities (45.9 %), whereas the relative contributions of $[O_{3SEASON}]$ are smaller at the coastal cities (32.8 %) ~~and large~~than at the inland cities (41.9 %). Since $[O_{3ST}]$ is related to synoptic-scale weather fluctuation by transport of O_3 (Rao et al., 1995, 1997), the large relative contributions of $[O_{3ST}]$ at the coastal cities indicate the stronger effects of the synoptic-scale transport of background O_3 there. On the other hand, $[O_{3SEASON}]$ is driven mainly by the annual cycle of meteorological factors such as insolation or temperature. Therefore, the large relative

contributions of $[O_{3SEASON}]$ at the inland cities are consistent with the higher impacts of temperature and insolation on the O_3 therein (Figs. 5 and 9b). $[O_{3LT}]$ explain less than 10% of the total variances, but its relative contribution is considerable in the southwestern part of the Korean peninsula as displayed in Fig. 9c. This is related to relatively large long-term variability or trend in the region and is further discussed in Sect. 3.6.

3.5 Short-term variation of O_3 related to wind direction

The short-term components of O_3 ($[O_{3ST}]$) account for a large fraction of total O_3 variation over South Korea. In Table 4, relative contributions of $[O_{3ST}]$ range from 32.7% to 62.5% and have a nationwide average of 49.8 %. Therefore, it is no wonder that ~~high~~(remove hyphen) high-O_3 episodes are mostly determined by day-to-day fluctuation of $[O_{3ST}]$. One considerable factor influencing the short-term variation of O_3 is wind. Shin et al. (2012) displayed $[O_{3ST}]$ on the wind speed-direction domain and showed that the effects of episodic long-range transport and local precursor emission on the ambient O_3 concentrations could be qualitatively separated from $[O_{3ST}]$.

We here further investigate the transport effect on the short-term variations of O_3 and the frequency of high-O_3 episodes using exp$[O_{3ST}]$ and wind directions (WDs). As described in Sect. 2.2, exp$[O_{3ST}]$ is a ratio of the raw $O_{3\,8h}$ concentration to its baseline concentration in ppbv (exp$[O_{3BL}]$). Thus, the $O_{3\,8h}$ concentration is higher than the baseline $O_{3\,8h}$ concentration when exp$[O_{3ST}] > 1$. We classified every single value of exp$[O_{3ST}]$ by 8 cardinal WDs during the high-O_3 season (May–October) at all available monitoring sites within each city. The probabilities of exp$[O_{3ST}] > 1$ by each WD were compared with the probabilities exceeding the South Korean air quality standard of 60 ppbv for $O_{3\,8h}$.

Figure 10 shows exp$[O_{3ST}]$ in the SMA cities (Seoul, Incheon, Suwon, and Ganghwa) with probabilities of exp$[O_{3ST}] > 1$ and $O_{3\,8h} > 60$ ppbv for each WD. In Seoul, high-O_3 episodes are occurred most in northwesterly although westerly and northeasterly winds predominate during the high-O_3 season (Fig. 10a and b). The high probability of high-O_3 in northwesterly in Seoul is similar to those in other neighboring cities in

SMA, where the predominant probability also appears in northwesterly wind in Incheon located in the west of Seoul (Fig. 10c and d), westerly wind in Suwon in the south of Seoul (Fig. 10e and f), and Ganghwa in the northwest of Seoul (Fig. 10g and h).

Sea–mountain breeze can explain the prevalence of high-O_3 episodes under west or northwesterly winds in the SMA. In the western coast of the SMA, there are many thermoelectric power plants (see triangles in Figs. 11 and 12) and industrial complexes ~~where~~ which directly emit a large amount of O_3 precursors. Heavy inland and maritime transportation in those regions ~~are~~ is also an important source of NO_x and hydrocarbon emissions.

Since the SMA is surrounded by the Yellow Sea in the west and mountainous region in the east (see Fig. 1), the westerly sea breeze ~~are~~ is well developed under O_3-conducive meteorological conditions such as high temperature and strong insolation with low wind speed (Ghim and Chang, 2000; Ghim et al., 2001). In addition, locally emitted precursors and transported background O_3 from the west are trapped in the SMA due to the westerly sea breeze and the mountainous terrain in the east of the SMA. Therefore, the O_3 concentrations in the SMA increase in such O_3-conducive meteorological conditions with near-westerly winds.

Another factor to increase the high-O_3 probabilities in the near-westerly winds is long-range transport of O_3 and its precursors from China. For example, Ghim et al. (2001) reported some high-O_3 cases in the SMA, which result from the transport of O_3-rich air with strong westerly wind at dawn under overcast conditions. Oh et al. (2010) also showed that the elevated layer of high O_3 concentration over the SMA is associated with the long-range transport of O_3 from eastern China. As the mixing layer thickens over the SMA, the O_3 concentration can increase by up to 25% via vertical down-mixing process (Oh et al., 2010). Recently, Kim et al. (2012) showed that westerly winds also transport O_3 precursors such as NO_2 and carbon monoxide (CO) from China to South Korea.

Interestingly, the high-O_3 probability in Ganghwa (Fig. 10g and h) shows bimodal distribution with another peak in easterly wind. Considering that Ganghwa is a rural

county on the northwestern coast of the SMA, the double peak of high-O_3 probability in easterly and westerly winds shows the effects of both local and long-range transport.

We extended the above $\exp[O_{3ST}]$ and WDs analysis to 25 cities over South Korea. The nationwide view of the high-O_3 probabilities is represented by the probabilities of $\exp[O_{3ST}] > 1$ and $O_{3\,8h} > 60$ ppbv by each wind direction during the high-O_3 season (May–October). Figures 11 and 12 show spatial maps of the probabilities of $\exp[O_{3ST}] > 1$ and $O_{3\,8h} > 60$ ppbv, respectively. As indicators of major precursor emission point source, we marked 26 of major thermoelectric power plants with triangles on the map. In general, the most of the thermoelectric power plants are located in the western coast of the SMA and southeastern coastal region of the Korean peninsula. Thermoelectric power plants are important sources of NO_x in South Korea, accounting for 13% (140 kt) of total NO_x emission nationwide (KMOE, 2013). Considering that industrial complexes over South Korea are mostly concentrated near the power plants, the area with triangles in Figs. 11 and 12 represents major sources of O_3 precursors.

In Figs. 11 and 12, the both probabilities of $\exp[O_{3ST}] > 1$ and $O_{3\,8h} > 60$ ppbv are generally high on a national scale in the near-westerly wind conditions (Figs. 11f–h and 12f–h). The prevailing westerly wind of the synoptic-scale flow transports O_3 and its precursors from China to South Korea and thus increases the probability of high-O_3 episodes as well as high O_3 concentrations. However, on a local scale, the high probability regions of high-O_3 correspond to downwind of the thermoelectric power plants. For example, the high probabilities of high-O_3 in the southeastern part of South Korea, downwind of power plants along the southeastern coast, also appear even in the easterly or southerly wind (Figs. 11c–e and 12c–e). Therefore, the spatial features of the high-O_3 probabilities in each wind direction could be associated with both local effect of precursor emission and long-range transport from the continent.

3.6 Long-term variation of O_3 and local precursor emissions

~~Temporal~~ The temporal linear trend of baseline ($[O_{3BL}]$) is almost the same ~~with~~ as that of the original time- series (“time series” separated and without hypen)
since short-term component ($[O_{3ST}]$) is nearly detrended. Therefore, the O_3

trend can be represented as a sum of the seasonal component ($[O_{3SEASON}]$) and longterm component ($[O_{3LT}]$) trends. The spatial trend distributions of $[O_{3BL}]$ and its two separated components of seasonal and long-term components are shown in Fig. 13.

It is noted that the period used in Fig. 13 is shorter than the total period of original data because of truncation effect in the KZ-filter process. The long-term component obtained by the KZ-filter of $KZ_{365,3}$ loses 546 days at the beginning and end of original time-series.

The increasing trends of O_3 are generally high in the SMA and southwestern part and low in the southeastern coastal region of Korean peninsula (Fig. 13a). This spatial inhomogeneity of the O_3 trends over South Korea is mainly contributed by the longterm component trends (Fig. 13c) rather than the seasonal component trend (Fig. 13b). Therefore, the large spatial variability in local precursor emissions induced the spatial inhomogeneity of O_3 trends in South Korea. On the other hand, relatively homogeneous distribution of the seasonal component trends implies that meteorological influences on the long-term changes in O_3 have little regional dependence nationwide.

Since the spatially inhomogeneous O_3 trends are related to the local precursor emissions, we also tried to investigate their relationship with NO_2 measurement data. To detect temporally synchronous and spatially coupled patterns between the long-term variations of O_3 and NO_2, we applied the SVD to $[O_{3LT}]$ and the long-term component of NO_2 ($[NO_{2LT}]$). $[NO_{2LT}]$ was simply obtained by applying the KZ-filter of $KZ_{365,3}$ to the log-transformed NO_2 time-series. The SVD is usually applied to two combined spacetime data fields, based on the computation of a temporal cross-covariance matrix between two data fields. The SVD identifies coupled spatial patterns and their temporal variations, with each pair of spatial patterns explaining a fraction of the square covariance between the two space-time data sets. The square covariance fraction (SCF) is largest in the first pair (mode) of the patterns, and each succeeding mode has a maximum SCF that is unexplained by the previous modes.

The first three leading SVD modes (singular vectors) of the coupled O_3 and NO_2 long-term components account for the SCF with 94.6% of the total, of which the first, second, and third modes are 63.7 %, 23.6 %, and 7.3% respectively. Figure 14 displays the expansion coefficients (coupled spatial patterns) and their time-series of the first mode along with spatial map of the $[NO_{2LT}]$ trends. The dominant first mode of the O_3 and NO_2 long-term components (Fig. 14a and b) is very similar to the spatial distributions of $[O_{3LT}]$ trends (Fig. 13c) and $[NO_{2LT}]$ trends (Fig. 14c) respectively. In Fig. 14d, the strong coherence in the time-series is observed between the first modes of the $[O_{3LT}]$ and $[NO_{2LT}]$ with a correlation coefficient of 0.98. The results of SVD analysis suggest that the long-term variations of O_3 and NO_2 in South Korea have similar temporal evolutions with different spatial patterns.

The differences in spatial patterns of $[O_{3LT}]$ and $[NO_{2LT}]$ as shown in Fig. 14a and b are required to be further investigated. Since the VOCs emissions from industry, transportation, and the solvent usage in construction are large in South Korea (KMOE, 2013), further analyses of VOCs measurements are needed. On top of that, especially in South Korea, biogenic precursor emissions are also potentially important for the analysis due to dense urban vegetation in and around metropolitan areas. Therefore, there remains the limitation of our current data analysis due to ~~insufficient emission analyses and measurement data of the~~ the lack of both VOC emission data and observations of atmospheric concentrations of VOCs~~ and NO_x~~ in South Korea.

4 Conclusions

This study has investigated various spatio-temporal features and inter-relationship of surface O_3 and related meteorological variables over South Korea based on ground measurements for the period 1999–2010. A general overview of surface O_3 in terms of spatial distributions and its temporal trend is provided based on its decomposed components by the KZ-filter.

In South Korea, the O_3 concentrations are low at the inland and SMA cities due to the NO_x titration by anthropogenic emissions and high at the coastal cities possibly due to the dynamic effects of the sea breeze. The averaged O_3 levels in South Korea have ~~been~~ increased for 1999–2010 with an averaged temporal linear trend of +0.26 $ppbv yr^{-1}$

(+1.15% yr^{-1}). The recent increase of the O_3 levels, which is common in the Northern Hemisphere and East Asia, may result from the recent increase of anthropogenic precursor emissions in East Asia and the long-term variations in meteorological effects.

We applied a linear regression model to investigate the relationships between O_3 and meteorological variables such as temperature, insolation, dew-point temperature, sea-level pressure, wind speed, and relative humidity. Spatial distribution of the R^2 values shows high meteorological influences in the SMA and inland regions and low meteorological influences in the coastal region. The high meteorological influences in the SMA and inland regions are related to effective photochemical activity, which results from large local precursor emissions and stagnant conditions with low wind speeds. On the other hand, the low meteorological influences in the coastal region are related to large transport effects of the background O_3 and ventilation and dry deposition with high wind speeds.

In the SMA and inland region, the high-O_3 probability ($O_{3\,8h} > 60$ ppbv) increases with the daily maximum temperature rise. Specifically in the SMA, the most populated area in South Korea, the probability of the O_3 exceedances is almost doubled for about 4 °C increase in daily maximum temperature and reached 27% at 30 °C. It is noted that the variations in O_3 exceedance probabilities according to the maximum temperature show an approximate logarithmic increase in the SMA and inland regions. It thus implies that these regions will experience more frequent high-O_3 events in the future climate conditions with the increasing global temperature.

The O_3 time-series observed at each monitoring site can be decomposed into the short-term, seasonal, and long-term components by the KZ-filter. Relative contributions of each separated component show that the short-term and seasonal variations account for most of the O_3 variability. Relative contributions of the short-term component are large at the coastal cities due to influence of the background O_3 transport. In contrast, those of the seasonal component are large at the inland cities due to the high meteorological influences on the O_3 variations.

The transport effects on the short-term component are shown in the probability distributions of both high short-term component values and O_3 exceedances for each wind direction. During the high-O_3 season (May–October) in South Korea, the probabilities of both high short-term component O_3 and O_3 exceedances are higher in the near-westerly wind condition rather than in other wind directions. For the short-term time-scale, the eastward long-range transport of O_3 and precursors from China can cause the nationwide high probabilities of O_3 exceedances in the near-westerly wind condition. However, the high probabilities of O_3 extreme events in downwind regions of the thermoelectric power plants and industrial complexes are related to local transport of O_3 precursors which apparently enhances the O_3 levels.

The distribution of O_3 trends in South Korea is spatially inhomogeneous. Although the relative contributions of the long-term components are much smaller than those of other two components, such spatially inhomogeneous distribution of O_3 trend is mainly contributed by the long-term component O_3 trends rather than the seasonal component O_3 trend related to the long-term change of meteorological conditions. It is because the long-term change of the local precursor emission has a localized effect on the long-term O_3 change. SVD between O_3 and NO_2 shows that the long-term variations of O_3 and NO_2 in South Korea have similar temporal evolutions with different spatial patterns. The results of SVD analysis clearly demonstrate the influences of local precursor emissions on the long-term changes in O_3. However, the precise interpretation of the large spatially inhomogeneous distribution in the long-term component O_3 trend is limited due to lack of VOC measurements data.

The KZ-filter is a useful diagnostic tool to reveal the spatio-temporal features of O_3 and its relationship with meteorological variables. General features revealed by the KZ-filter analysis will provide a better understanding of spatial and temporal variations of surface O_3 as well as possible influences of local emissions, transport, and climate change on O_3 levels in South Korea. Our analyses would also be helpful as a reference for the evaluation of chemistry transport models and furthermore for establishing appropriate O_3 control policy.