

# Identification and Interpretation of Representative Ozone Distributions in Association with the Sea Breeze from Different Synoptic Winds over the Coastal Urban Area in Korea

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## ABSTRACT

To aid the studies of long-term impact assessment of cumulative ozone ( $O_3$ ) exposures, the representative 8-hr  $O_3$  pollution patterns have been identified over the Greater Seoul Area (GSA) in Korea. Principal component analysis and two-stage clustering techniques were used to identify the representative  $O_3$  patterns, and numerical and observational analyses were also used to interpret the identified horizontal distribution patterns. The results yielded three major  $O_3$  distribution patterns, and each of the three patterns was found to have strong correlations with local and synoptic meteorological conditions over the GSA. For example, pattern 1, accounting for 46% of  $O_3$  concentration distributions, mostly occurred under relatively weak westerly synoptic winds. The predominant features of this pattern were infrequent high  $O_3$  levels but a distinct gradient of  $O_3$  concentration from the western coastal area to the eastern inland area that was mainly induced by the local sea breeze. Pattern 2, accounting for 31% of  $O_3$  concentration distributions, was found with higher  $O_3$  levels in the western coastal area but lower in the eastern inland area. This is due to the modified sea breeze under the relatively stronger easterly opposing synoptic wind, affecting the high  $O_3$  occurrence in the western coastal area only. However, pattern 3, accounting for 21% of  $O_3$  concentration distributions,

showed significantly higher  $O_3$  concentrations over the whole GSA mainly due to the retarded and slow-moving sea-breeze front under the weak opposing synoptic flow. Modeling study also indicated that local and synoptic meteorological processes play a major role in determining the high  $O_3$  concentration distribution patterns over the GSA.

## INTRODUCTION

Ground-level ozone ( $O_3$ ) adversely affects vegetation and human health.<sup>1</sup> In assessing plant response and health effects, the duration of exposure as well as peak concentration of  $O_3$  has been recognized to be an important factor.<sup>1-4</sup> In 1997, the U.S. Environmental Protection Agency (EPA) promulgated a new 8-hr standard for estimating multiple-hour exposures to moderate  $O_3$  concentrations, and the 8-hr standard has been used in several impact assessments using data analysis and modeling studies.<sup>5-8</sup> Multiyear photochemical model simulation is the most promising way to address the cumulative  $O_3$  exposure problem, done through precise, long-term impact studies of high  $O_3$  concentrations. However, running air quality models that cover longer-periods have generally been prohibitively complicated because of incomplete emission inventories and difficulties in constructing precise wind fields. Numerical modeling studies have suggested that, because of input demand and computational load, an episode aggregation approach by identifying several representative air quality patterns is an effective alternative to developing and running a long-term air quality model. For this reason, the air quality regimes over non-urban areas utilizing the spatiotemporal variability of daily maximum 8-hr  $O_3$  concentrations have been classified.<sup>9</sup>

Measurement studies have shown that the spatiotemporal variability of daily maximum 8-hr  $O_3$  patterns over coastal areas vary considerably due to the accumulation and transport of  $O_3$  by meteorological effects (i.e., land/sea-breeze circulation), requiring adequate quantitative photochemical as well as meteorological observations.<sup>10-14</sup> For example, in the San Francisco and Monterey Bay

## IMPLICATIONS

The GSA in South Korea has experienced the serious  $O_3$  problem caused by dense population and industrial activities. This paper focused on the episodic aggregation approaches for study cumulative  $O_3$  exposures over GSA by deriving the various spatial patterns of 8-h  $O_3$  concentration using statistical analysis, and also understanding the dynamic effects of meteorology on each pollution pattern. The quantitative interpretation associated with patterns may attribute to environment assessment for long-term as well as improvement for prediction capability of  $O_3$  over the GSA.

areas, although the spatial patterns of daily maximum 1-hr  $O_3$  concentration had been defined,<sup>15</sup> the characteristics of  $O_3$  patterns in association with meteorological conditions were not substantiated because of the limitations on the number of coastal sites. Lehman et al.<sup>9</sup> suggests that future work should involve an investigation of the dependence of  $O_3$  concentrations on meteorology for identifying  $O_3$  distribution patterns. More recently, it was shown that the timing and penetration of the sea breeze coupled with synoptic forces can play an important role in determining high  $O_3$  concentration distributions.<sup>14,16,17</sup> However, limited episodes focusing on short-term  $O_3$  exposures have been examined, and consequently the representative  $O_3$  patterns for long time periods have not yet been quantitatively elucidated.

The purpose of this paper is to identify representative spatial  $O_3$  distribution patterns on the basis of a quantitative statistical analysis of multi-year daily maximum 8-hr  $O_3$  measurements to aid in assessing cumulative  $O_3$  exposures over coastal urban areas in the Greater Seoul Area (GSA) in South Korea. Interpretations of the local circulation and synoptic conditions are attempted to explain the identified representative spatial  $O_3$  distribution patterns. As a case study, the meteorological effect on  $O_3$  level in each representative pattern was also simulated by using the MM5 (Meteorological Model generation 5; Pennsylvania State University/ National Center for Atmospheric Research [PSU/ NCAR] Mesoscale Modeling System).

## METHODOLOGY

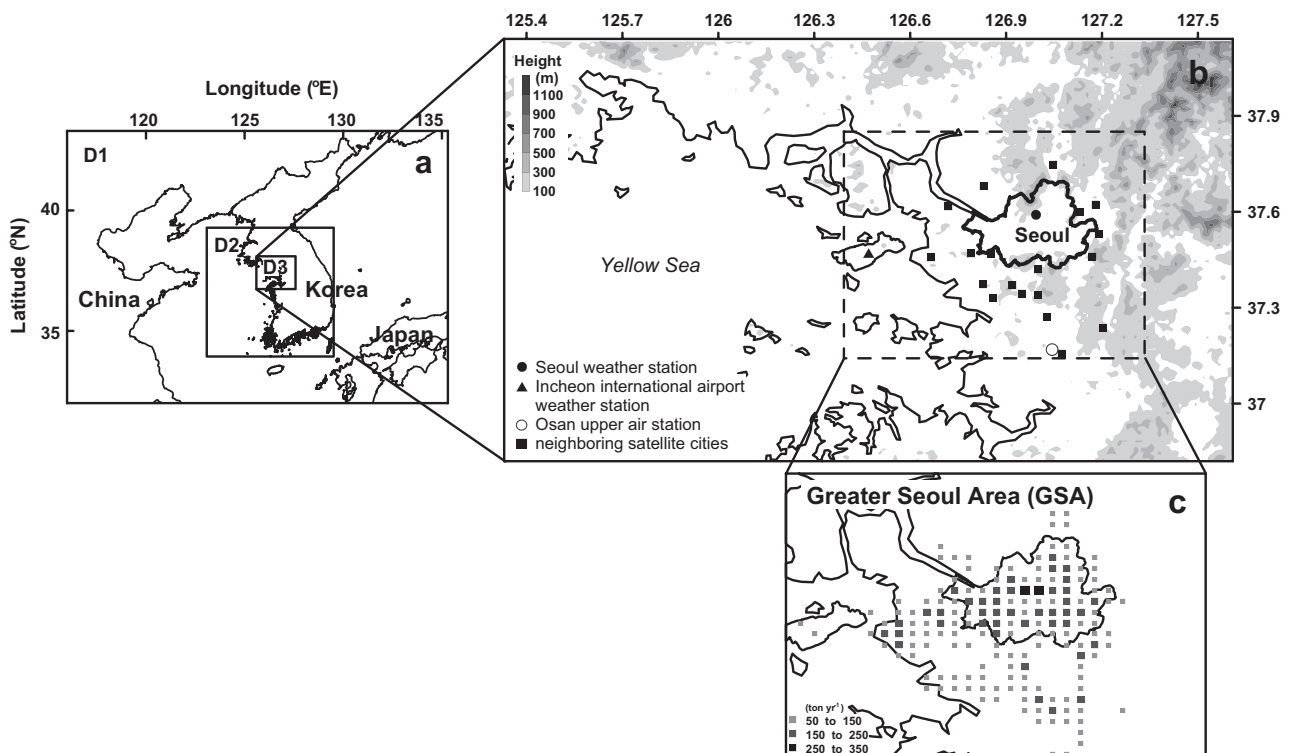
### Geographical Features in the GSA and Data

The GSA in South Korea comprises Seoul, the capital of South Korea, and its neighboring satellite cities (Figure 1).

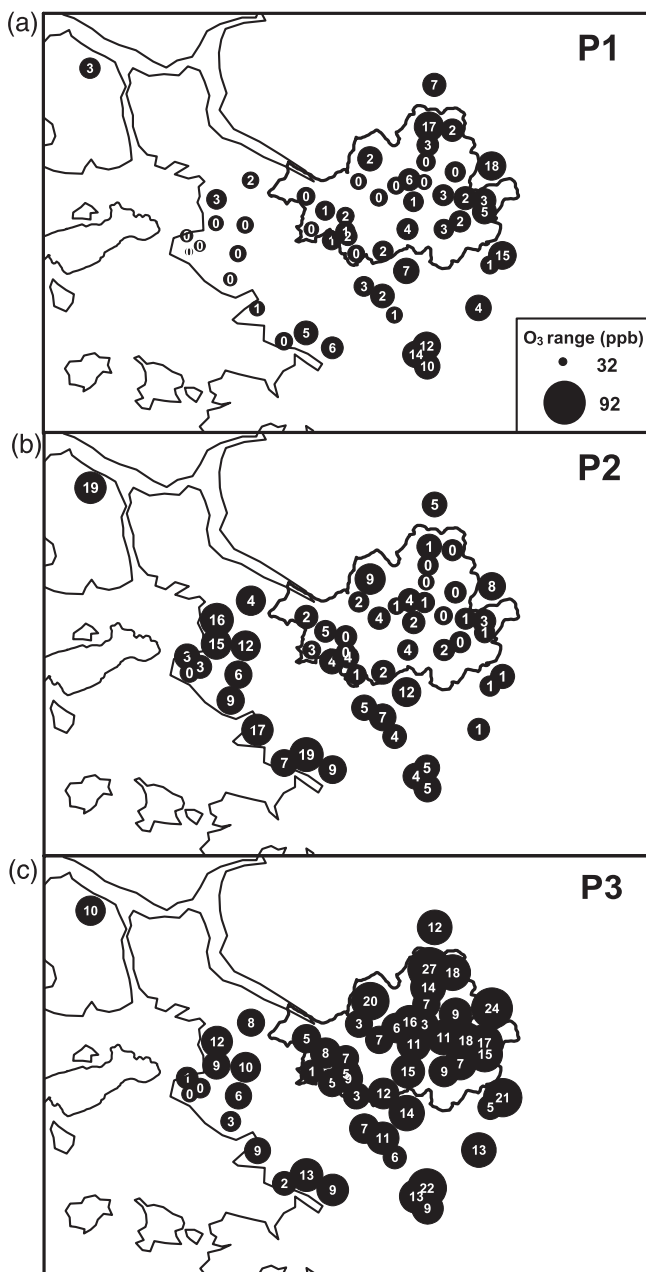
It has an area of approximately 7000 km<sup>2</sup> with 22.1 million inhabitants, accounting for approximately 45% of the total population of South Korea. Seoul, together with the industrial cities located near the western coastline, are the predominated emission sources of  $O_3$  precursors (oxides of nitrogen [ $NO_x$ ], volatile organic compounds), resulting in a steadily increasing trend of ambient  $O_3$  concentrations since the early 1990s.<sup>18</sup> The GSA is mostly surrounded by many mountains in the east and the Yellow Sea in the west, where complex local circulations occur. The sea breeze is modified by channeling through valleys and is blocked by mountains.

The  $O_3$  data used in this study were the measured daily maximum 8-hr concentrations from 54 sites (Figure 2) obtained from April to September over 7 yr (1998–2004). Hourly  $O_3$  concentrations were measured at approximately 7–15 m above ground level using an ultraviolet (UV) photometric absorption method. By taking the moving average, the 8-hr  $O_3$  concentrations were calculated from hourly  $O_3$  values at each site, and on a daily basis, daily maximum 8-hr  $O_3$  concentrations were determined. As a consequence, the daily maximum 8-hr  $O_3$  that exceeded the air quality standard of 80 parts per billion (ppb) was used. The result yielded 180 days (episodes) for this study.

Hourly meteorological data were also used. The meteorological data were gathered from 48 observation sites in total: 46 sites of Automatic Weather System (AWS, which is the automated version of the Surface Weather Observation System) and 2 specific sites labeled the Seoul weather station (SWS) and the Incheon International Airport weather station (IWS). In this study SWS (located in an inland urban area) and IWS (located in a western



**Figure 1.** (a) Three-level nested domain of MM5 model, (b) the terrain height for the magnified domain 3 and the location of meteorological stations and satellite cities near Seoul, and (c)  $NO_x$  emissions with the 3-km resolution in the GSA.

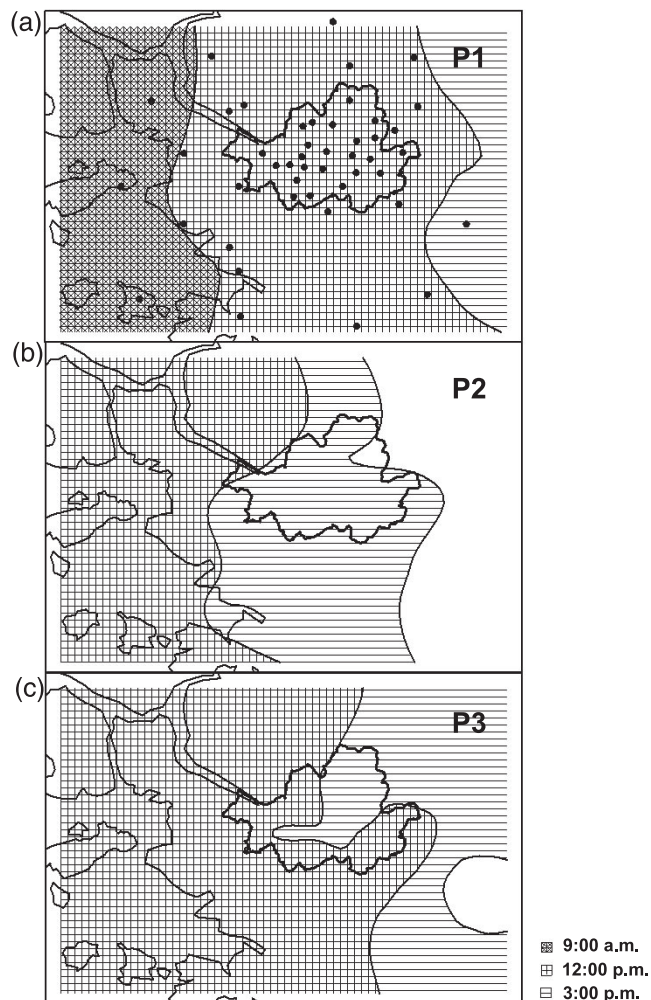


**Figure 2.** Horizontal distributions of the average daily maximum 8-hr  $O_3$  concentrations (dark circles) and the number of days exceeding the 8-hr standard (numbers within the circles) for each of the three  $O_3$  patterns (a) P1, (b) P2, and (c) P3 over the GSA.

coastal suburban area) were both used to examine the meteorological conditions associated with  $O_3$  distribution. All of the locations of the meteorological sites are denoted in Figures 1 and 3. All of the meteorological data were obtained at an altitude of approximately 10 m above ground level. In addition, the vertical wind profiles (observed twice a day) obtained at the Osan upper air station (denoted in Figure 1b) were used to identify the synoptic flow. The instruments used for both the  $O_3$  measurements and meteorological observations used in this study were regularly calibrated by the Korea Ministry of Environment and the Korea Meteorological Administration (KMA), respectively.

### Principal Component Analysis and Cluster Analysis

In this study, a three-step process consisting of principal component analysis (PCA) and two-stage cluster analysis techniques were used to identify  $O_3$  distribution patterns. Before the two-stage cluster analysis, PCA was used. As Eder et al.<sup>19</sup> described earlier, the central idea of PCA is to reduce the dimensionality of a voluminous dataset consisting of a large number of interrelated input dataset of 8-hr  $O_3$  concentrations to explain variance. Here, the size of the dataset has been reduced, and the original data matrix was reconstructed into principal components in which most of the essential information was explainable by retaining the first few principal components.<sup>20,21</sup> In this study, the daily maximum 8-hr  $O_3$  concentrations obtained at each of the 54 sites for the 180 episodes were formulated into the original matrix having a total original dimension of (180 episodes  $\times$  54 sites = 9720 observations). In formulating the matrix, the missing values were replaced by the nearest sites using a linear interpolation method. To decompose the  $O_3$  pattern more clearly, a weighting technique in the PCA procedure was applied.



**Figure 3.** Horizontal distributions of the positive u-wind components (westerly) observed at 46 AWS (black dots) at 9:00 a.m. LST, 12:00 p.m. LST, and 3:00 p.m. LST for each of the three  $O_3$  patterns (a) P1, (b) P2, and (c) P3 over the GSA.



This weighting technique was used to produce a statistically more distinctive decomposition by relatively weighting the each observation in the input dataset.<sup>21,22</sup> In this study, the number of sites exceeding the 8-hr standard was enumerated for each episode and used as a weighting factor for all of individual observations in PCA procedure. As a result, only the first few principal components that explain a large amount of the total variation have been derived. The appropriate number of principal components that were retained was approximated using the Screen test.<sup>23</sup>

Derived from the principal components, both the hierarchical and nonhierarchical algorithms were employed as two-stage clustering techniques. As a first stage, the average linkage, which is also called a hierarchical agglomerative method, is used to determine the number of clusters in advance on the basis of the statistical indices of  $R^2$ , Pseudo-F, and Pseudo- $t^2$ . As a second stage, the initial clusters classified by average linkage are then refined by using the K-means, which provides the final solution. This two-stage algorithm was recommended because this combined approach is superior to a one-stage approach, such as only using the average linkage in terms of cluster cohesiveness.<sup>19</sup> More complete clustering algorithms are described by Eder et al.<sup>19</sup> and Davis et al.<sup>24</sup>

### Configuration of MM5 Modeling

MM5 (version 3.6) was used to analyze wind fields to explain the meteorological conditions relevant to the  $O_3$  patterns identified over the GSA. MM5 was set to use three nested grid domains: (1) the outermost domain ( $60 \times 48$  grid points) with a grid spacing of 27 km that covers northeast Asia, (2) the first nested domain ( $64 \times 61$  grid points) with a grid spacing of 9 km that covers the entire Korean peninsula, and (3) the second nested domain ( $67 \times 49$  grid points) with a grid spacing of 3 km that covers only the GSA, as shown in Figure 1. The vertical grid consists of 30 full- $\sigma$  levels with higher spacing near the ground. The lowest layer above the ground is 30 m and the top is at 100 hPa. The initial and lateral boundary conditions were obtained from the Regional Data Assimilation and Prediction System (RDAPS) that has been provided by KMA.<sup>25</sup> RDAPS consists of 3-hr interval reanalysis meteorological fields.

On the basis of the multiscale nudging technique,<sup>26</sup> analysis nudging (nudging by gridded RDAPS data) was imposed on both the outermost domain and first nested domain, whereas observational nudging (nudging by observational data) was only imposed on the second nested domain. The nudging coefficient,  $G$ , was set to  $2.5 \times 10^{-4} \cdot \text{sec}^{-1}$  for wind and temperature on the 27- and 9-km grid spacing domains, respectively, and  $4 \times 10^{-4} \cdot$

**Table 1.** Statistics for first five principal components.

	PC 1	PC 2	PC 3	PC 4	PC 5
Eigenvalue	20.15	8.65	4.93	2.49	1.96
Explained variance (%)	37.31	16.02	9.14	4.62	3.62
Cumulative explained variance (%)	37.31	53.33	62.47	67.09	70.71

**Table 2.** Statistical tests for determining number of clusters to retain.

Number of clusters	Pseudo-F	Pseudo- $t^2$	$R^2$
6	24.72	6.11	0.41
5	27.47	19.22	0.39
<b>4</b>	<b>35.32</b>	3.41	<b>0.38</b>
3	27.63	<b>39.24</b>	<b>0.23</b>
2	24.75	26.84	0.12
1	–	24.75	0.00

$\text{sec}^{-1}$  for wind on the 3-km grid. The microphysical schemes that were used were the rapid radiative transfer model (RRTM) for radiation schemes, the Grell scheme for cumulus parameterization (only used on the 27-km grid domain), and the medium range forecast (MRF) for planetary boundary layer (PBL) schemes. The model simulation was performed for 6 days from 9:00 a.m. LST (Local Standard Time) on June 4 to 12:00 p.m. LST on June 9.

## RESULTS AND DISCUSSION

### Major Patterns of 8-hr $O_3$ Pollution

Table 1 shows the results of the Screen test<sup>23</sup> in the PCA procedure, suggesting that five principal components of a matrix ( $180 \times 5$ ) could explain 70.7% of the total variance. That result suggests that by retaining only the first five principal components, a large amount of the original  $O_3$  concentration variations were explained. On the basis of these principal components, the hierarchical and nonhierarchical algorithms were both used as a two-stage clustering technique.

Table 2 summarizes the results of the average linkage analysis (hierarchical stage) from which an initial number of clusters was determined before the application of K-mean (nonhierarchical stage). In accordance with the technical guideline of cluster analysis, the number of clusters was selected from a guide at the time when both pseudo-F and pseudo- $t^2$  were maximal, with the largest drop in  $R^2$  as the number of clusters decreased<sup>20</sup> (denoted in boldface in Table 2). Given the results in Table 2, four clusters were selected and were used as input parameters to formulate the K-mean clustering. This result indicates that the original 180 episodes in total were finally grouped into four clusters. As a next and final step, the K-mean analysis was used to refine and generate the final cluster solution. The K-mean analysis used here is the iterative approach that allows all of the episodes to reclassify even after they have been grouped into the same cluster.

Table 3 shows the number of days and 8-hr  $O_3$  statistics for each of the four identified clusters. However, as illustrated in Table 3, cluster 4 (C4) accounts for infrequent episodes because it contains only a few cases with relatively lower  $O_3$  levels. Therefore in this study we considered only three clusters (C1, C2, and C3) as representatives occupying approximately 98% (176 episodes) of the total episodes. Each of the three clusters was identified to retain noticeable differences in the characteristics of observed  $O_3$  concentrations such as  $O_3$  levels, distribution patterns, and number of stations exceeding standard

**Table 3.** Summary for statistics of the daily maximum 8-hr O<sub>3</sub> concentrations for different clusters.

Cluster	O <sub>3</sub> Pattern	Number of Days (%)	Average of the Daily Maximum 8-hr O <sub>3</sub> (ppb)	Number of Stations Exceeding 80 ppb/8 hr
C1	P1	83 (46.1)	53.3 ± 8.2	2.1 ± 1.9
C2	P2	56 (31.1)	59.9 ± 7.3	4.5 ± 4.8
C3	P3	37 (20.6)	70.8 ± 10.1	14.5 ± 8.8
C4	–	4 (2.2)	22.7 ± 7.4	1.0 ± 0.0

level. In association with the local and synoptic winds, these three clusters were used to interpret the meteorological impact on the representative O<sub>3</sub> distributions. Hereafter, clusters 1, 2, and 3 will be referred to as patterns 1, 2, and 3.

Figure 2 presents the horizontal distributions of the 8-hr O<sub>3</sub> levels and the frequency that exceeded the standard of 80 ppb for each of the three patterns. Pattern 1 (P1) accounted for approximately 46% of the total episodes and had a similar distribution pattern as the average O<sub>3</sub> distribution for special episodes related to the observed sea-breeze circulation under the westerly synoptic condition in the GSA.<sup>18</sup> In both the O<sub>3</sub> concentration and occurrence frequency exceeding the standard of 80 ppb, some gradient was found between the coastal region and the eastern inland area (Figure 2). Both the O<sub>3</sub> levels (53 ± 8.2 ppb) and number of sites exceeding the standard of 80 ppb (2.1 ± 1.9 sites) was lower than in other patterns (Table 2).

Pattern 2 (P2) accounted for 31.1% (56 episodes) of the total episodes and had a more frequent occurrence of higher O<sub>3</sub> concentrations than that of P1. This pattern particularly exhibited elevated O<sub>3</sub> concentrations over the western coastal area in comparison with P1, whereas exhibiting lower levels over the western inland area. Therefore, this is rather characterized by higher O<sub>3</sub> concentration in the western coastal area due to the convergence zone along the western coastal area formed by combining the sea breeze (westerly) and synoptic flow (easterly). Considering the relatively lower emission of O<sub>3</sub> precursors in the western coastal area, this pattern is most likely due to the impact of meteorological conditions such as surface easterly winds.

Pattern 3 (P3) accounted for 20.6% (37 episodes) of the total episodes, and had a similar pattern to P1, to some extent, except for the pollution level. It had significantly higher O<sub>3</sub> levels, reaching approximately 71 ppb on average, and severely exceeded the standard of 80 ppb (14.5 ± 8.8 sites) compared with the other two patterns. Most episodes belonging to this pattern occurred in stagnating synoptic conditions with slowly moving high-pressure systems or relatively weak easterly (or sometimes weak westerly) 850-hPa geostrophic winds over the GSA. When these synoptic conditions occur, other meteorological factors such as high temperatures, low wind speeds, and intense solar radiation, which are closely related to the high O<sub>3</sub>-forming potentials also occur.

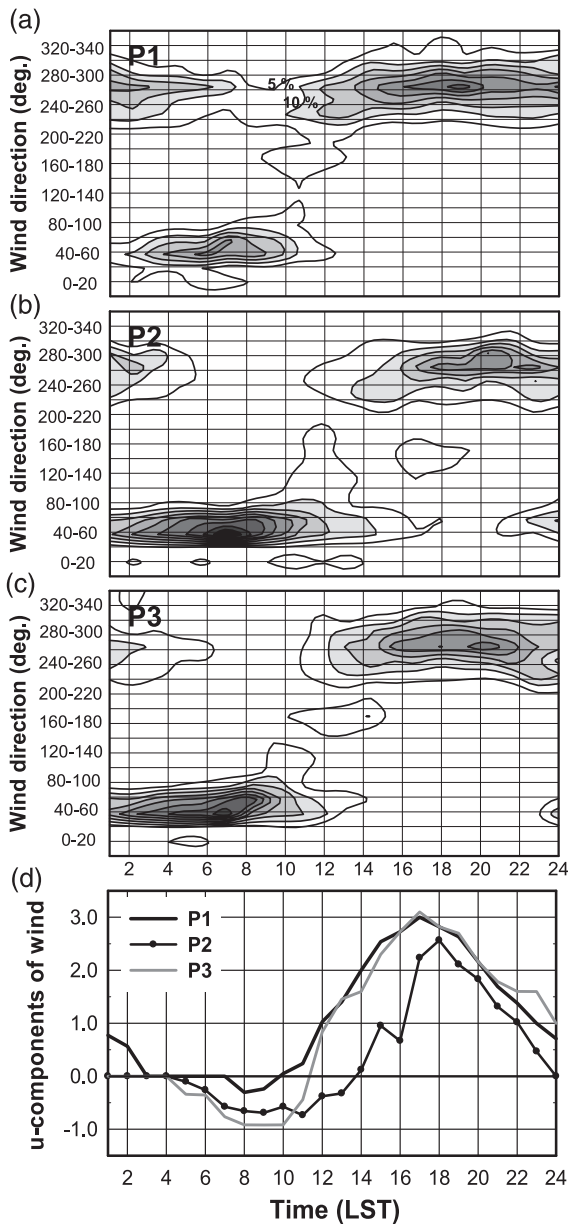
#### Association of the Sea Breeze Combined with Synoptic Flow

To examine the meteorological effects on the identified 8-hr O<sub>3</sub> concentration patterns, the correlation between

O<sub>3</sub> concentrations and meteorological measurements, including both surface and upper air observations were analyzed. Because solar radiation and temperature are crucial factors in determining photochemical production, the measurements of these two meteorological factors in each identified pattern have been compared. Comparing these meteorological factors at both SWS and IWS demonstrated that no statistical differences of meteorological parameters among all three of the patterns had occurred. For example, in each of the three patterns, the daily maximum temperature and daily solar radiation at SWS were all more than 29 °C and 18.3 MJ · m<sup>-2</sup> · day<sup>-1</sup>, respectively. These conditions indicate that there have been no significant differences in the potential for photochemical O<sub>3</sub> production, thereby indicating that the dynamic and meteorological effects of the atmosphere could be more important for the different O<sub>3</sub> patterns, rather than the generation of O<sub>3</sub> from photochemical reactions.

This is more obvious in Figure 3, which shows the positive u-components of wind (westerly) at the 46 AWS observation sites at 9:00 a.m., 12:00 p.m., and 3:00 p.m. LST, respectively. The leading edge of the positive u-components (which resembles a sea-breeze front) was formed at different hours in each of the three patterns. The leading edge of the positive u-components in P1 started early, with high O<sub>3</sub> concentration over the eastern part of the GSA. It was found near the western coastline at 9:00 a.m. LST and arrived at Seoul at 12:00 p.m. LST in P1. However, P2 appears later than P1, with relatively higher O<sub>3</sub> concentrations over the western GSA. This suggests that the identified O<sub>3</sub> patterns were closely related to the onset of the sea-breeze front and its propagations, and therefore the wind fields in each of the three patterns derived by sea-breeze development and penetrations had great capabilities to explain the pattern of O<sub>3</sub> concentrations over the GSA.

Figure 4 shows the diurnal variation of wind direction as well as medians of the u-component at SWS, and Figure 5 presents the distributions of the u-components at 850 hPa at 9:00 a.m. LST obtained from the Osan upper air station in each of the three patterns. According to Figures 4 and 5, the diurnal variation of the winds was largely governed by the sea breeze in the morning together with a synoptic westerly flow that prevents the development of the sea breeze. For example, it should be noted for P1 that the obvious westerly sea breeze reached Seoul at around 10:00 a.m. LST induced by the westerly synoptic flow (Figure 3) with a low wind speed (57% for u-component ranging from 0 to 5 m · sec<sup>-1</sup>). Therefore, with an onshore synoptic force such as that in Figure 5,



**Figure 4.** Diurnal variations of wind direction (%) for (a) P1, (b) P2, and (c) P3. (d) The u-component of wind at SWS for each of the three O<sub>3</sub> patterns (P1, P2, and P3). The positive u-component of wind is westerly.

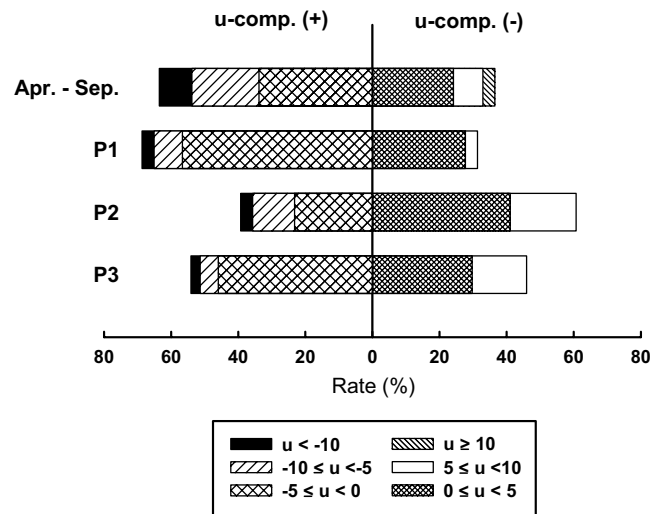
the sea-breeze development was initiated earlier and progressed over the GSA until evening.<sup>27</sup> Thus it is obvious that the polluted air over the western GSA was transported by the early sea breeze, and led to high O<sub>3</sub> concentrations over the eastern GSA where there are no heavy emission sources.<sup>28-30</sup> In this manner, the O<sub>3</sub> distributions with the distinct east-west gradient of O<sub>3</sub> in P1 were inseparably connected to the development of the sea breeze under the onshore synoptic flow.

On the contrary, P2 shows a rather different wind flow. The positive u-component was not found inland until 12:00 p.m. LST in P2 (Figure 3). Only after 12:00 p.m. LST did it gradually start to extend inland. In Figure 4, the diurnal variation of winds at SWS shows the retarded sea breeze when the easterly wind was prevalent

until approximately 2:00 p.m. LST. These surface wind patterns indicate that there is a strong possibility that the development of the sea breeze was suppressed by synoptic forces,<sup>31</sup> although both P1 and P2 have similar inland surface temperatures. Figure 5 also shows the offshore synoptic flow frequently observed in P2 (68.7%), which all support the association of a sea breeze with an opposing synoptic flow giving rise to late sea breeze.

Ding et al.<sup>16</sup> have also shown that the sea breeze delayed by the offshore synoptic flow is an important factor in high concentrations of O<sub>3</sub> in coastal areas. The recirculation of polluted air originating from coastal source areas is also suggested in association with a late sea breeze,<sup>17,32</sup> which makes it possible for the O<sub>3</sub> levels along the coast to increase. In the same manner, O<sub>3</sub> levels over the western coastal area in P2 were found to increase similarly, due to the late sea breeze resulting from its interaction with the offshore synoptic flow. Thus, in this pattern, the prevailing easterly synoptic winds lasting until the early afternoon are well characterized by a high potential to enhance O<sub>3</sub> concentration patterns in the western GSA, as has been demonstrated in previous studies.

However, P3 shows a different O<sub>3</sub> pattern in Figure 3. Positive u-components reached Seoul at 12:00 p.m. LST and then moved eastward in the afternoon. The change to westerly components at SWS occurred earlier than P2 but later than P1, as shown in Figure 4, although the wind fields of P3 seem similar to P2. This similarity implies that O<sub>3</sub> and its precursors can accumulate over western GSA under the easterlies, with low wind speed (less than 2 m · sec<sup>-1</sup> at SWS) during the morning. After midday, P3 became similar to P1 in the magnitude of the positive u-component, which means accumulated pollutants can be transported eastward when the photochemical production of O<sub>3</sub> was maximized by the optimal photochemical conditions. As a result, extremely high O<sub>3</sub> levels covering the entire GSA were found in this pattern (Figure 2).



**Figure 5.** Occurrence frequency (%) of u-component at the 850-hPa level observed at the Osan upper air station at 9:00 a.m. LST for each of the three O<sub>3</sub> patterns (P1, P2, and P3). The positive u-component of wind is westerly.



### A Case Study for Major O<sub>3</sub> Patterns

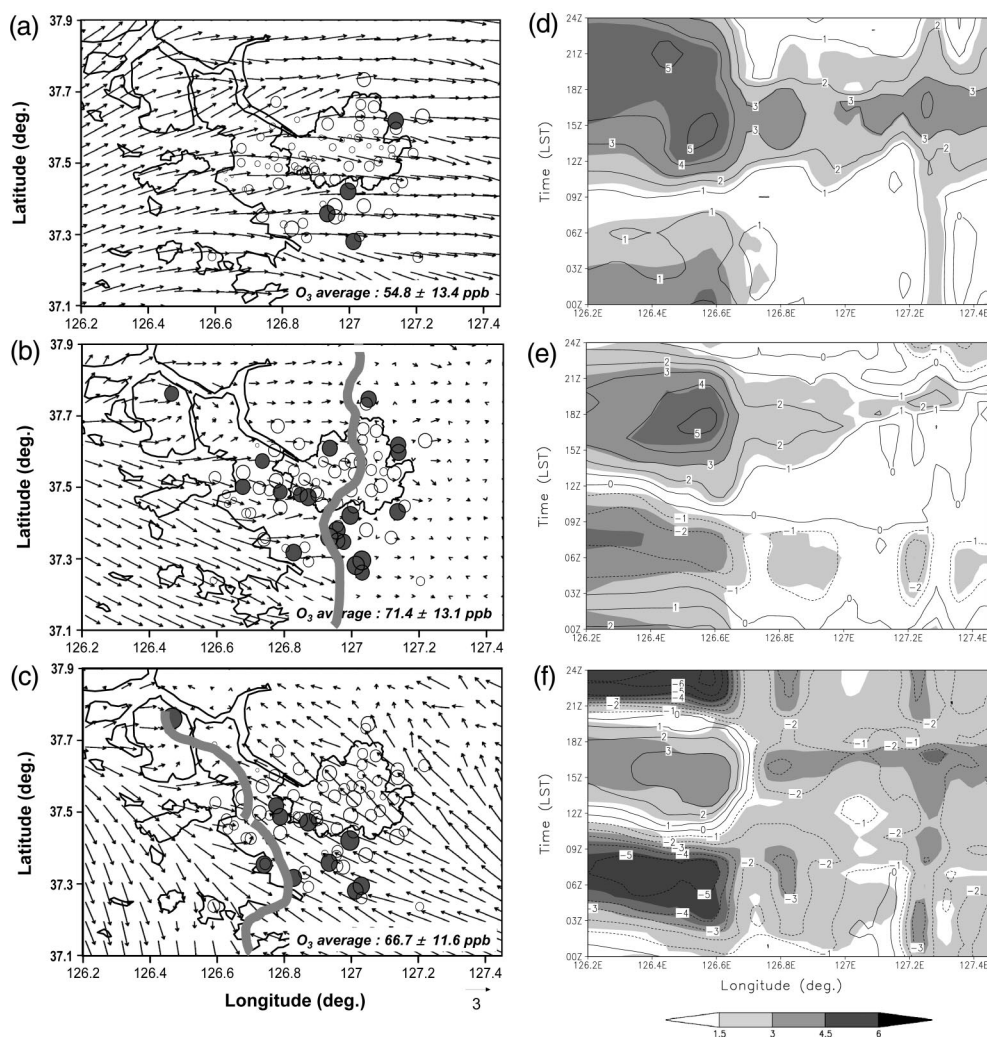
To verify the effects attributed to the sea breeze associated with each O<sub>3</sub> pattern, a numerical simulation using MM5 was performed for three typical cases (June 5, 8, and 9, 2003). During this period, each of the three identified O<sub>3</sub> patterns occurred with the substantiated change of both surface wind and synoptic flow. Both high daily maximum temperatures (29–31 °C) and strong solar radiation (23.2–23.5 MJ · m<sup>-2</sup> · day<sup>-1</sup>) at SWS were observed.

Figure 6, a–c, shows the maximum 8-hr O<sub>3</sub> concentrations observed at air monitoring sites as well as the simulated surface wind fields with sea-breeze front lines at 3:00 p.m. LST. Figure 6, d–f, shows the longitude-time cross-section for u-components of simulated surface wind and wind speed. The cross-section was taken over the latitude of 37.6° E across the center of Seoul. The simulated horizontal wind fields (not shown) reproduce diurnal variations in winds with reasonable accuracy. For example, the simulations at SWS have a minor discrepancy from observations in wind direction and speed with a root

mean square error of 19° and 0.5 m · sec<sup>-1</sup> on average, respectively.

On June 5, relatively higher O<sub>3</sub> concentrations were observed in the eastern and southern part of the GSA. Four monitoring sites (shaded circles) reported high O<sub>3</sub> levels exceeding 80 ppb/8 hr, as illustrated in Figure 6a. Under a high pressure system located over the Yellow Sea, north-westerly synoptic flow enhanced the surface westerly (positive u-component)<sup>33</sup> after 0900 LST and then rapidly penetrated further inland (Figure 6d) causing dominant westerly surface winds of 4 m sec<sup>-1</sup> over the entire GSA at 3:00 p.m. LST. These wind fields made the quick transportation of the pollutants emitted at the western coastal area in the morning possible causing relatively higher 8-hr O<sub>3</sub> concentrations on the eastern part of the GSA.<sup>11,29,30</sup> This feature is well characterized in P1, as described in the previous section.

On the following 2 days (June 6 and 7), there were no interesting distributions of O<sub>3</sub> concentrations because of little precipitation and low temperatures. However, on



**Figure 6.** Simulated horizontal wind fields at 10 m above ground level at 3:00 p.m. LST, with the observed daily maximum 8-hr O<sub>3</sub> concentrations (left panels), and longitude-time cross-section of u-wind components (shaded area denotes wind speed in m · sec<sup>-1</sup>) along the latitude of 37.6° (right panels) on June 5 (a and d), June 6 (b and e), and June 9 (c and f) in 2003. The size of circles in left panels indicates the average concentrations varying from 30 to 120 ppb. Shaded circles and thick shaded lines in the left panels indicate the sites exceeding the 8-hr O<sub>3</sub> standard and the location of the sea-breeze front estimated from the convergence of winds, respectively.

the next day (June 8), very high concentrations (average:  $71.7 \pm 13.2$  ppb/8 hr) were observed throughout the GSA and  $O_3$  exceeding 80 ppb occurred at 20 sites, with a maximum 8-hr  $O_3$  concentration of 96.5 ppb (Figure 6b). The synoptic features showed that, as the North Pacific High gradually expanded toward the Korean peninsula, the weak southeasterly flow ( $\sim 5 \text{ m} \cdot \text{sec}^{-1}$  at the Osan upper air station) prevailed at the 850-hPa level on that day. This pattern well represents P3. Furthermore, low wind speed (i.e.,  $< 1.5 \text{ m} \cdot \text{sec}^{-1}$ ) was simulated inland in the morning due to its influence on offshore flow (Figure 6e). This implies that these local and synoptic meteorological conditions contributed to the high accumulation of  $O_3$  and its precursor over the entire GSA. The positive u-component slowly expanded inland after 11:00 a.m. LST and was near Seoul's center ( $127^\circ \text{E}$ ) at 3:00 p.m. LST. Because the slowly moving sea breeze transported it, much higher  $O_3$  concentrations could occur in the downstream area rather than in the high emission areas. In addition, on the basis of potential temperatures observed over Seoul during June 6–9, significant increases in  $O_3$  concentrations occurred, in part because of the lower mixing height ( $\sim 1.5 \text{ km}$ ) at 3:00 p.m. LST than that of other days,<sup>34</sup> which led to a weak dilution of the primary emissions within the mixing layer.<sup>35,36</sup>

On June 9, a southeasterly synoptic flow was strengthened by an increasing pressure gradient under the North Pacific High ( $\sim 10 \text{ m} \cdot \text{sec}^{-1}$  on an 850-hPa level over the Korean peninsula). The  $O_3$  level rapidly decreased (average:  $66.9 \pm 11.6$  ppb/8 hr) with only nine sites in the southwestern GSA area exceeding the 8-hr standard (Figure 6c). It is clear that the positive u-components with calm conditions ( $< 1.5 \text{ m} \cdot \text{sec}^{-1}$ ) were at shoreline after midday but did not extend further inland during the day, as shown in Figure 6f. This condition corresponds to P2, in which  $O_3$  levels in the western GSA were influenced by the transport of pollutants from inland high emission areas. Thus, the recirculation of air loaded with  $O_3$  or its precursors frequently occurred with the late sea breeze, apparently leading to higher  $O_3$  concentrations in the coastal GSA area.<sup>17,31,37</sup>

## CONCLUSIONS

It is generally believed that multiyear simulation of a photochemical simulation of a photochemical model is needed because  $O_3$  standards for protecting crops and other vegetation are assessed ideally on the basis of cumulative  $O_3$  exposures. For this purpose the identification of the cumulative observed  $O_3$  statistics was attempted over the coastal GSA. Also, numerical and observational analyses were applied to interpret the dependency of identified horizontal surface 8-hr  $O_3$  pollution distribution patterns on meteorological variables.

By employing the PCA and two-stage clustering techniques on the basis of a daily maximum 8-hr  $O_3$  concentration for a 7-yr period from 1998 to 2004, three major patterns of surface 8-hr  $O_3$  pollution distribution were identified. Each pattern showed a different horizontal gradient and level of  $O_3$  concentration, with a strong correlation with the transport and the accumulation of pollutants under the different meteorological conditions. In particular, the measurements of surface/upper wind

fields showed the different ranges and timing of sea-breeze penetration due to the different synoptic flows and played an important role in determining the 8-hr  $O_3$  patterns. In a case study of three typical days, the effects of the early and late developing sea breeze under onshore and offshore synoptic flow were reconfirmed. These synoptic flows had the behavior of pollutants, resulting in quite different patterns of daily maximum 8-hr  $O_3$  concentrations. Through this study, an emphasis was also put on the role of meteorological or dynamic processes that control  $O_3$  distributions over a coastal urban area. For example, three 8-hr  $O_3$  pollution patterns were clearly identified by unique meteorological and synoptic conditions. Therefore, their associations with the development of sea breezes under the different synoptic winds were able to be well substantiated by the characteristics of typical high  $O_3$  concentration episodes.

In this study, we derived statistical daily maximum 8-hr  $O_3$  concentration patterns representing real meteorological conditions. These representative patterns were found to be consistent with the characteristics of a typical episode in Korea. They will be used to quantify longer-term  $O_3$  exposures, to assess their impact, or to generate estimates for protecting human health and vegetation in the GSA. In addition, detailed photochemical modeling approaches covering multiyear simulations will be tested to further confirm the reliability of the results derived in this study.

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