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Photochemical Modeling of July 1994 High-Ozone Episode in the Greater Seoul Area

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Abstract

The CIT (California Institute of Technology) three-dimensional Eulerian photochemical model was applied to the Greater Seoul Area, Korea for July 24, 1994, a day of the 9-day ozone episode to understand the characteristics of photochemical air pollution problems in the area. The modeling domain was 60 km × 60 km with the grid size of 2 km × 2 km. As the base case emissions, air pollutant emission data of the National Institute of Environmental Research, Korea for the year of 1991 were used with modifications based on EKMA (Empirical Kinetic Modeling Approach) results. Comparisons between predicted and observed concentrations showed that the model predicted the peak concentration over the domain reasonably. It was found that the location of the peak ozone concentration was mainly decided by meteorological conditions. But the model could not resolve the spatial variations of concentration station by station, which was mainly caused by localized variations in emission and meteorology.

Key words : Eulerian photochemical model, July 1994 episode, Greater Seoul Area, peak concentration, local variations

1. INTRODUCTION

WHO and UNEP (1992) classified Seoul as a city having serious air pollution problems with high concentrations of sulfur dioxide and suspended particulate matter in their 1992 report. But air quality in Seoul was in the middle of change at that time. Between 1991 and 1993 the number of exceedances of SO_2 above 1-h average 250 ppb decreased from 936 to 0 and those of total suspended particulate (TSP) above 24-h average 300 g/m^3 decreased from 124 to 38 at twenty monitoring stations in Seoul.

The main cause of this change was an active fuel-change policy of the Government that forces to use clean fuels such as LNG or low-sulfur light oil instead of coal or high-sulfur heavy oil. But this change was accompanied with rapid increase of energy usage and vehicle mileage in consumer sectors. Now, emissions from transportation are dominant over those from heating, industrial activities, and power production. Emissions of nitrogen oxides (NOx) and volatile organic compounds (VOCs) become an important issue and several high ozone episodes have been reported since NOx and VOCs are precursors of photochemical ozone Between 1990 and 1997, total of 105 days recorded 1-h ozone concentrations of 120 ppb or more, that is, exceeded the ozone warning level, over about 36 monitoring stations in the Greater Seoul Area (GSA) (Ghim and Oh, 1999).

The Greater Seoul Area is the City of Seoul and surrounding areas that can exchange air mass to form a contiguous region of air quality. During the 1990s, there have been two years of high ozone episodes in GSA, 1992 and 1994. The year of 1994 was particular in that the highest two ozone concentrations, 322 ppb and 243 ppb were recorded at the Kwanghwamun monitoring station, in the middle of Seoul, on August 23 and 24. Throughout the summer of 1994 hot and arid air was stagnant over the Korean Peninsula, and daily maximum temperatures exceeded 30°C on 44 days of July and August (Ghim, 1997). It is interesting to note that only two days exceeded the ozone warning level in 1995, the lowest during the past eight years.This was similar to the year of 1989 in U.S.A. when ozone concentrations were possibly the lowest of the decade after the highest concentrations in 1988 (NRC, 1991).

In this study, a high ozone episode in July 1994 was studied by using an air quality model developed in California Institute of Technology (CIT). At first, the period including aforementioned August 23～24 with the two highest concentrations was considered. But it was concluded that these highest concentrations were too localized to be resolved in the current analysis, which was associated with low wind speeds less than 1.5 m/s in the morning (Ghim, 1997). Although GSA has a moderate capability of monitoring air quality and of collecting information on sources and emissions, it is still far from completeness needed for photochemical modeling as many areas in the world. Therefore, particular attention was paid to prepare a reasonable input for modeling from available information.

2. MODELING

2. 1 Model

The CIT airshed model is an Eulerian photochemical model that solves the atmospheric diffusion equation

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (\mathbf{u} C_i) = \nabla \cdot (\mathbf{K} \nabla C_i) + \mathrm{R}_i$$

where C_i is the ensemble mean concentration of species i, $\mathbf{u}$ is the wind velocity vector, $\mathbf{K}$ is the eddy diffusivity tensor. R_i is the rate of generation of species i by chemical reactions, and t is the time. At ground level, the boundary condition is

$$-K_{zz}\frac{\partial C_i}{\partial t} = E_i - v_g^i C_i$$

where K_{zz} is the vertical eddy diffusivity, E_i is the emission flux, and v_g^i is the dry deposition velocity for species i. A no-flux boundary condition is applied at the top of the modeling region.

The chemistry is based on the LCC chemical mechanism (Lurmann *et al.*, 1987), which includes 26 differential and 9 steady-state chemical species. The dry deposition velocities are computed in the model by using a three-resistence scheme that includes turbulent transport through the atmospheric boundary layer, diffusion through a laminar sublayer, and a surface resistance to account for differences in pollutant-surface interactions. For more information, detailed description of the model can be found elsewhere (Harley *et al.*, 1993; McRae *et al.*, 1982).

2. 2 Modeling Domain

The Greater Seoul Area (GSA) is a highly populated and industrialized area with about 20 million people and 3 million vehicles, which account for a half of Korean population and 30% of the total number of vehicles in Korea, respectively. Annual emissions in GSA are estimated as 0.4 million tons of CO, 0.3 million tons of NOx and 0.06 million tons of hydrocarbons on the fuel base, which are respectively, 36%, 26%, and 40% of total emissions in Korea (Ministry of Environment, 1996). Fig. 1 shows the horizontal domain for this study, covering 60 km × 60 km with the grid size of 2 km × 2 km. As of 1997, there are of 37 monitoring stations exist within the domain including 20 in Seoul. Also there are three surface meteorological stations within the domain, and one upper air station is located just outside of the southern boundary.

The modeling domain extends to the height of 1,100 m above the ground with subdivided into 5 layers. The

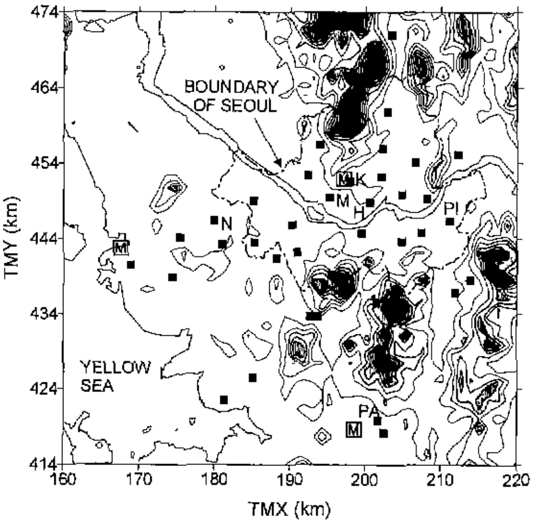


Fig. 1. Map of the Metropolitan Seoul Area showing the modeling domain. Filled contours represent topography above sea level starting from 50 m at intervals of 50 m. Solid rectangles indicate air quality monitoring stations. Among them are K, Kwanghwamun; M, Mapo; H, Hannam; N, Nae; PI, Pangi; PA, Paldal station. M indicates a surface meteorological station.

thickness of the layer are 38, 116. 154, 363, and 429 m from the ground. The horizontal domain is generally mountainous, higher in the northeast and southeast. The Yellow Sea is located in the west side. However, the west boundary of the domain could not be extended sufficiently to the west because shorelines are very complicated with many islands and it was difficult to get appropriate information on emissions for those areas.

2. 3 Emission Data

Most of emission data in Korea have been estimated by provinces with fuel usage amount and emission factors. But it is apparent that this kind of emission data is not adequate for Eulerian modeling. As the necessity of Eulerian modeling increases with concern about photochemical pollution, several groups have made efforts to prepare emission data for Eulerian modeling (Kim *et al.*, 1999). However, it was found that current available information is not sufficient to prepare a proper data set. Problems do not arise from the procedures, but from basic information that should be arranged. Nevertheless, reviewing the previous data revealed that the emission data for the year of 1991 prepared by the National Institute of Environmental Research (NIER, 1994) were most reliable. Therefore, it was decided to prepare reasonable data set by scaling the NIER 1991 data.

The emission levels were estimated by applying the NIER 1991 data to the simulation of three high-ozone days in August 1997 with EKMA (USEPA, 1989). Since EKMA relies on the box model, the emission data summed over the domain were applied with speciated VOC data measured at the downtown on the same days. Predicted ozone maximum concentrations were compared with maximum of mean diurnal variations of observed concentrations over GSA. An optimum ratio of emission data for each pollutant was determined by minimizing the differences between predicted and mean observed concentrations.

Fig. 2 shows the distribution of pollutant emissions in the modeling domain. All sources including area. line and point sources were combined on the 2 km × 2 km grid base. SO_2 emissions are usually high in the industrial area such as the west seashore and the western part of Seoul. High emission in the northeast of Seoul is from coal combustion, nearly all of which has faded out nowadays. This is because the present emission data were based on the 1991 data. On the other hand, CO and hydrocarbon emissions are high in the downtown Seoul with heavy traffic, which includes the Kwanghwamun, Mapo and Hannam stations in Fig. 1.

It is considered that diurnal variations of emissions in the summertime urban area are usually caused by traffic volume. But the monitoring results showed that the difference of traffic volume between office-going and closing hours was not large (Han *et al.*, 1995). Therefore, step changes for the diurnal variation of emissions were assumed: one and half of the hourly average emission amounts for 700~1900 LST and a half of the hourly average emission amounts for the

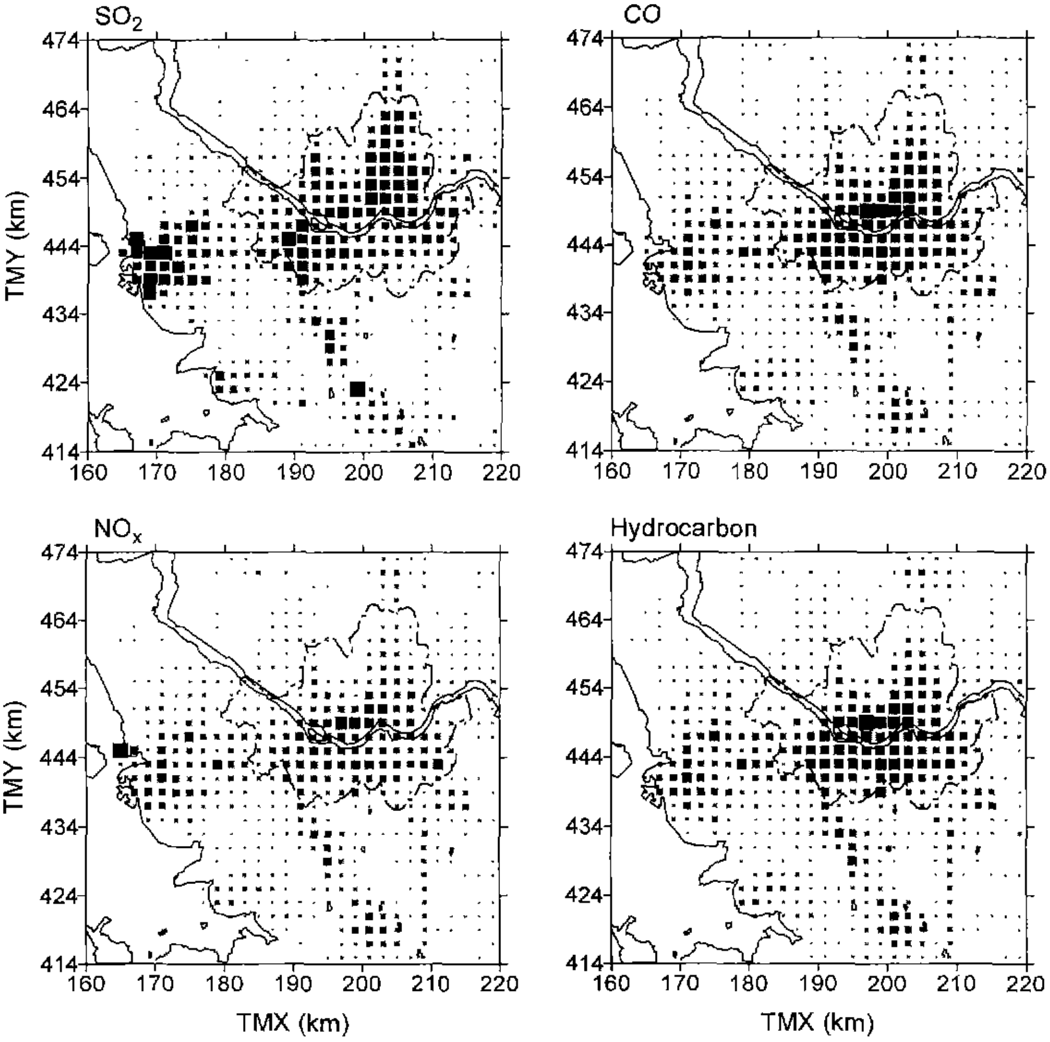


Fig. 2. Pollutant emission distributions. The largest emission is SO_2 35 g/s, CO 277 g/s, NOx 39 g/s, and hydrocarbon 34 g/s.

remaining 12 hours. Weekly variation of the emission was not considered

2. 4 Simulation Day

The July 1994 episode lasted for 9 days from July 21 to 29. During the episode, peak 1-h concentrations varied from 119 to 188 ppb, and peak 8-h concentrations varied from 82 to 142 ppb (Ghim and Oh, 1999). Among 9 days, July 24 was selected for the case of clear sky (cloud cover, 0.18), high temperature (daily maximum temperature, 38.4°C), and possible effect of pollutant transport (mean wind speed, 1.8 m/s). On July 24, eight monitoring stations including 6 stations in Seoul reported exceedances of 1-h ozone concentration over 100 ppb, the air quality standard. Peak 1-h concentration over the domain was 175 ppb at 1500 LST at the Nae station, located slightly west from the western boundary of Seoul as shown in Fig. 1. Simulation started from July 22, and the first two days were devoted for the spin-up period.

2. 5 Meteorological Data

Three-dimensional wind fields were generated diagnostically with the routine contained in the CIT model by using the monitoring data from surface meteorological stations and upper air stations operated by the Korea Meteorological Administration. In order to eliminate the boundary effects during the wind field estimation, wind field domain was set larger than the domain in Fig. 1. by 40 km in each direction as recommended by Kim *et al.* (2000). Other surface meteorological variables such as temperature and humidity were interpolated by using the Barnes (1973) scheme. Clear conditions were assumed for ultra-violet solar radiation. Mixing height was inferred from the vertical profile of potential temperature measured by upper air sounding at the Osan Airforce Base, located about 40 km south of Seoul. The minimum mixing height was assumed to be 200 m.

2. 6 Landuse Data

Landuse data were obtained from the Korea Forestry Research Institute to determine the surface roughness and the ground properties for quantifying the deposition processes. Average surface roughness length was estimated according to Lee (1997).

2. 7 Boundary and Initial Conditions

Upwind conditions employed by Harley *et al.* (1993) were used at all horizontal boundaries. Several boundary conditions including the use of measured concentrations were tested. It was confirmed that the influence of boundary conditions was only retained near the boundaries.

Two-day spin-up employed in the current analysis was sufficient to remove the effect of initial conditions from the domain. But initial data from criteria pollutants were prepared by interpolating the measured data at the monitoring stations in order to help the model adapted to the prescribed conditions. For VOC, concentrations measured at the downtown in August 1997 were used with assuming the same distribution with CO by considering a close relationship between the two (Kuebler *et al.*, 1996).

3. RESULTS AND DISCUSSION

Two step approaches were taken as follows. First, the base-level emission case was tested in order to evaluate the model's ability to represent general features of the photochemical air pollution on the simulation day. Second, effects of controlling VOC and NOx emissions were investigated at each monitoring station in order to characterize photochemistry over the GSA.

3. 1 Base Run

Fig. 3 shows comparisons of the predicted and observed concentrations for ozone, NO, NO_2 and CO at the Hannam station. The Hannam station is located at the downtown with heavy traffic as shown in Figs. 1 and 2, thus can be considered as the typical downtown station. On July 24, 1994, ozone daily maximum at the Kwanghwamun station, where the highest concentrations were usually recorded as seen on August 23~24, 1994, was well below 50 ppb. Fig. 3 shows that the level of predicted daily maximum ozone at the Hannam station is comparable to the observed one but the predicted maximum time is delayed compared with the observed one. Predicted concentrations generally show similar variations with the observed ones in the first half of the day, but show delayed increase for ozone and overestimation for NO_2 and CO. It is interesting to note that these phenomena are prominent at the western and southern parts of Seoul, the reason of which will be discussed later.

Fig. 4 shows the predicted distribution of daily maximum ozone concentration together with the observed one at the monitoring stations. The model predicts that high ozone cloud over 120 ppb covers large area, centered on the southwest of Seoul boundary. The model also predicts relatively low daily maximum ozone at the center of Seoul, where emissions are high. As a

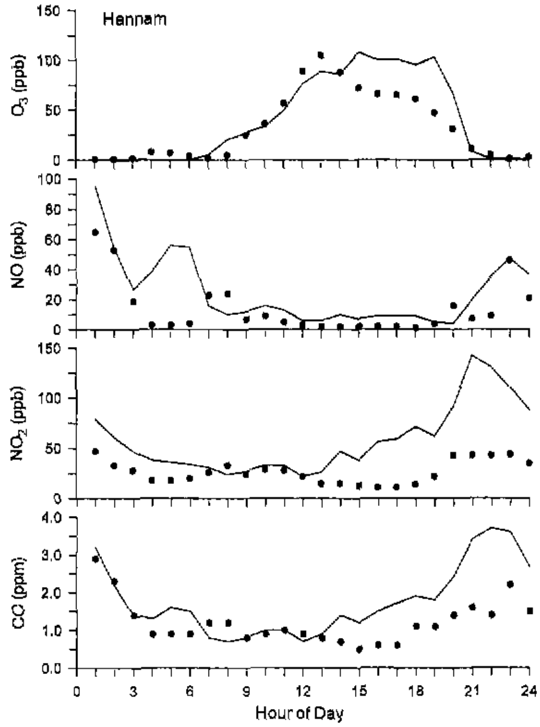


Fig. 3. Comparisons of predicted and observed concentrations for ozone, NO, NO_2 and CO at the Hannam station. Solid line indicates predicted concentration and solid circle indicates observed concentration.

whole, predicted ozone cloud is too broad compared with observed daily maximum which varies from 25 ppb to 175 ppb within the same region. This clearly demonstrates the limitation of the current modeling that cannot resolve the local variations in the study area. The local variations may include emission variations coming from complicated landuse associated with high population density, and wind field variations that could not be accounted during diagnostical estimation with measurement data from several meteorological stations.

Nevertheless, the predicted peak 1-h concentration, 150 ppb is not much different from the observed peak 1-h concentration, 175 ppb at the Nae station. Moreover, the model predicts the location of the peak concentration within a few kilometers. This means that the occurrence of peak concentration at the Nae station was not a local event, but a domain-wide event.

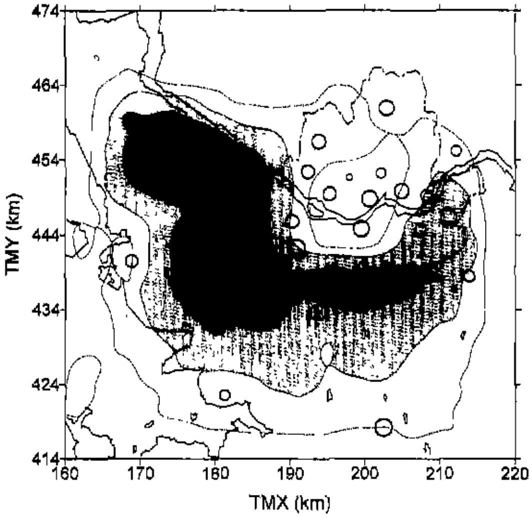
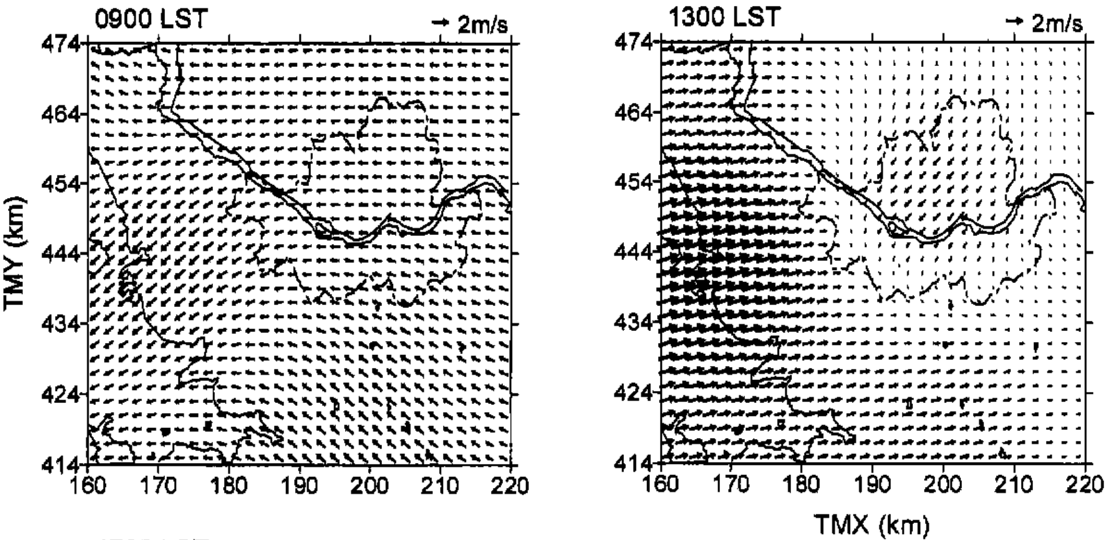


Fig. 4. Predicted and observed daily maximum ozone concentrations. Filled contours represent predicted maximum starting from 120 ppb at intervals of 10 ppb. The size of open circle represents observed concentration from 25 ppb to 175 ppb.

In order to interpret the occurrence of peak concentration at the Nae station, several representative wind fields are given in Fig. 5. In the morning, easterlies are dominant over the domain; between 1200 LST and 1500 LST, strong westerlies are developed starting from the west seashore; after 1600 LST, weak easterlies and northeasterlies are covered over the domain. With these variations of the wind field, pollutant transport can be estimated as follows. In the morning, ozone precursors produced in Seoul move to the west of Seoul by esterlies. In the afternoon, precursors produced from the industries near the west seashore start to move to the east along with strong westerlies, but they cannot move further because of weak winds over Seoul, and become stagnant near the west boundary of Seoul, at the Nae station.

The concentrations of air pollutants at the Nae station were also high on this day, daily average concentrations of NO, NO_2 and CO were 79 ppb, 48 ppb, and



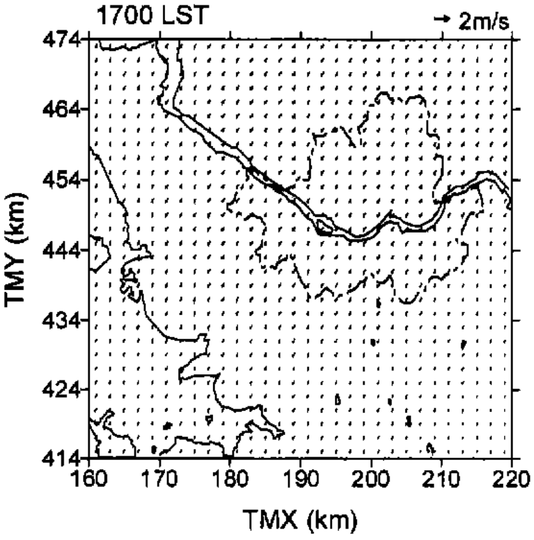


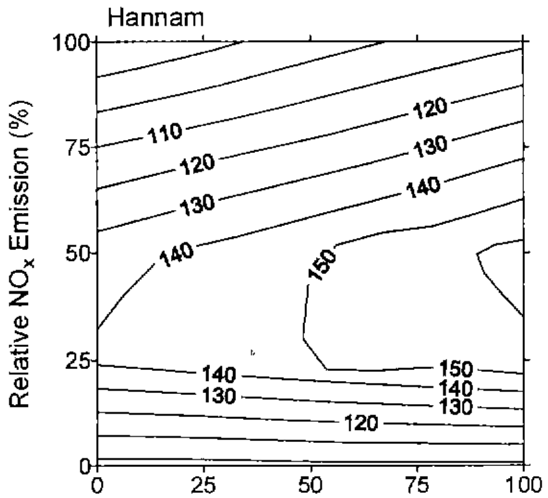
Fig. 5. Variations in the predicted wind field on July 24, 1994.

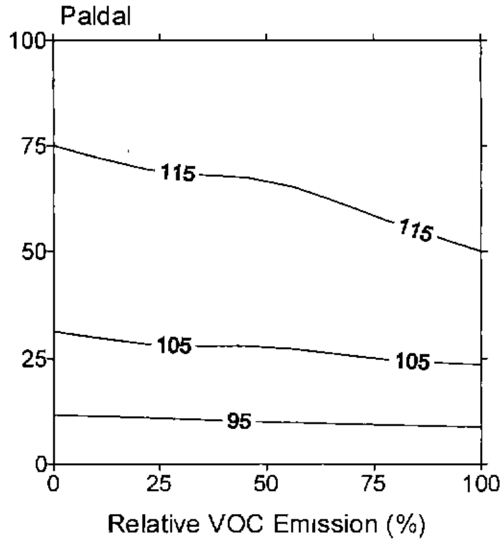
1.7 ppm respectively, which were far higher than monthly averages of 3 ppb, 10 ppb, and 0.2 ppm, respectively. The fact that three stations among 6 stations exceeding ozone 1-h standard in Seoul were located in the western part of Seoul also supports the aforementioned mechanism of pollutant transport being dominant process for high ozone concentration at the area.

However, this movement of pollutants over the domain also predicted higher concentrations of primary pollutants above the observed ones at the western and southern parts of Seoul. Actually, two phenomena are observed in the model prediction: they are overprediction of several primary pollutants in the afternoon and delayed maximum of ozone concentration. The first one is prominent at the western and southern parts of Seoul and was explained by the general movement of pollutants. But the second one is general over the domain. Although the two phenomena are not closely related in the model prediction, it is surmised that they are linked each other since redundancy of primary pollutants could result in prolonged production of ozone. This probably could be corrected if more accurate information on levels and diurnal variations of emissions be available.

3. 2 Effects of VOC and NOx Control

NOx reduction generally reduces ozone daily maximum, but can increase it in the downtown with high level of NOx. This is due to releasing of OH radicals to react with VOCs to produce photochemical ozone, rather than to consuming OH radicals by NO_2. However, in the downwind areas of major VOC and NOx sources, NOx reduction can effectively reduce ozone concentration because NOx generally reacts more





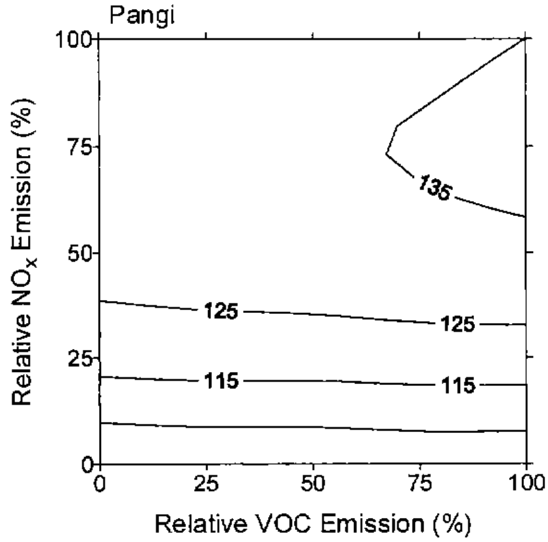


Fig. 6. Ozone isopleths at three representative sites with low, high and moderate VOC/NOx ratios. Site locations are shown in Fig. 1.

rapidly than VOCs to yield a NOx limiting condition (NRC, 1991).

In order to understand the photochemical characteristics of the domain, VOC and NOx emissions were reduced to 75%, 50%, 25%, and none from the base level emissions, and maximum ozone concentrations were calculated at each monitoring station. By examining the ozone isopleths, the monitoring stations could be classified into three groups: (1) with low VOC/NOx ratio suspected as a highly polluted area, (2) with high VOC/NOx ratio, probably located in the downwind side, and (3) with moderate VOC/NOx ratio. Fig. 6 presents ozone isopleths at three typical sites, whose locations were given in Fig. 1.

As was mentioned earlier, the Hannam station is located in the downtown. Daily maximum ozone increases with NOx reduction until NOx emission reaches about 40% of the base level. Both VOC and NOx reduction also increase maximum ozone. Only VOC reduction is effective. The Paldal station is located 35 km south of Seoul. At this station, maximum ozone can be effectively reduced by NOx reduction. Although not efficient, VOC reduction can also decrease maximum ozone. The Pangi station is located at the eastern part of Seoul. The ratio of VOC/NOx is slightly low for the present, but becomes lower when polluted air mass is transported from Seoul center with westerlies.

Fig. 7 shows the distribution of three groups of the monitoring stations. One station outmost in the north was excluded because it was considered to be influenced by the boundary effects. Total 29 stations among 36 stations, including 18 stations in Seoul, have low VOC

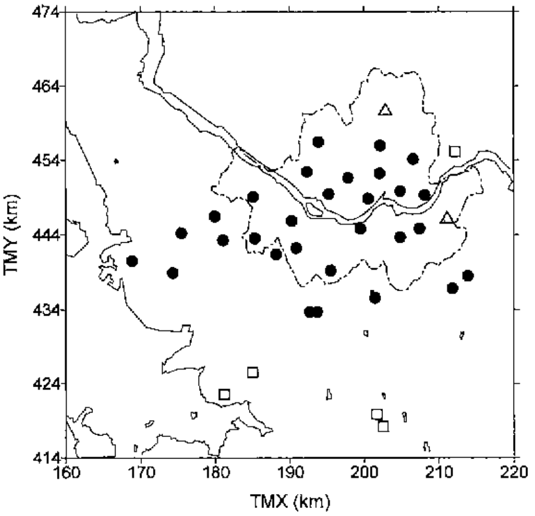


Fig. 7. Classification of the monitoring stations by VOC/NOx ratios. Solid circle represents a low ratio, open rectangle, a high ratio, and shaded triangle, a moderate ratio.

/NOx ratios. Five stations have high VOC/NOx ratios. These stations are located in the outer region of GSA. Two stations with moderate VOC/NOx ratios are located at the northern and eastern parts of Seoul, respectively. But as you might expect, grouping stations with moderate VOC/NOx ratios is rather ambiguous in comparison with grouping stations with low and high VOC/NOx ratios. In general, the stations with low VOC/NOx ratios are located at the center of Seoul with high emissions as well as near the western and southern boundary of Seoul. The region outside the western and southern boundary of Seoul shows high ozone concentrations in the model prediction in spite of relatively low emissions. This indicates that photochemical characteristics of a site are influenced by both emission characteristics and meteorological patterns.

4. CONCLUSIONS

In order to understand the characteristics of photochemical air pollution problems in the Greater Seoul Area, spatial and temporal variations of ozone concentration on a day of July 1994 ozone episode were studied with the CIT model. The model could predict domain-scale variations of ozone concentration. More precisely, the model predicted the location of peak concentration over the domain within a few kilometers, and predicted a reasonable value of peak concentration. The model also showed photochemical characteristics of a site, viewed from ozone isopleths in terms of the VOC/NOx ratio, depended not only on the emission characteristics but also on the meteorological patterns.

Nevertheless, the model could not resolve highly variable ozone concentrations observed within a few kilometers, which should have been due to local effects. In comparison with observed ones, predicted concentrations of several primary pollutants were high in the afternoon near west and south of Seoul where the pollutants were predicted to be merged, and predicted time of ozone maximum was generally delayed. As a whole, the results in this study warranted further studies on photochemical air pollution in GSA, especially areas of emissions and meteorological data. With these improvements, photochemical air quality modeling can be utilized to elucidate air quality characteristics in the area and to develop cost-effective control strategies to reduce ozone levels.

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