Analysis of temporal and spatial variations of ozone concentration considering traffic flow and solar radiation

Youngkook KIM [a]

[a] *The Korea Transport Institute,Sejong-si,30147,Korea*
[a] *E-mail: youngkim@koti.re.kr*

Abstract: Higher traffic flows generally lead to the increased emissions of directly emitted pollutants. In the case of ozone (O_3), a secondary pollutant, however, decreased traffic flows during weekends create favorable conditions for generating O_3, resulting in higher O_3 concentrations during weekends. In terms of spatial perspective, urban background regions have better circumstances for O_3 creation than roadside areas. The temporal and spatial conditions of O_3 generations are better in weekend and urban background regions, resulting in higher O_3 concentrations. To explain these counterintuitive phenomena, the chemistry of O_3 is reviewed and discussed with regard to the variations of hourly traffic flows and solar radiations.
Solar radiation plays a vital role in determining O_3 concentrations. The more ultraviolet (UV) radiation, the more O_3 will be generated, because solar radiation initiates the photo-dissociation of nitrogen dioxide (NO_2), followed by the reaction of atomic oxygen (O) and O_2 to generate O_3. Ambient O_3 concentrations are determined by the difference of creation and destruction rates of O_3. If the creation rate is greater than the decomposition one, then O_3 accumulation occurs. To clarify the relationship between O_3 concentration and solar radiation, hourly UV radiations are averaged over various time intervals and then used as explanatory variables in regression analysis. 6-hour mean UV radiation is identified as the best for explaining O_3 concentration.

Keywords: Ozone weekend effect; Vehicle emission; Traffic flow; Solar radiation

1. INTRODUCTION

Heavier traffic flows are known to lead to higher pollution concentrations of directly emitted pollutants, such as nitrogen oxides (NO_x), carbon monoxide, sulfur dioxide, and fine particulate matter. Several studies have shown that these concentrations vary across the week, with lower concentrations during weekends, when traffic is reduced, but that weekend ozone (O_3) concentrations are higher than during weekdays. This unexpected pattern is frequently referred to as the ozone weekend effect (OWE). Recent research regarding the OWE points to similar results on several metropolitan areas: Chicago and Philadelphia (Pun, Seigneur, & White, 2003); Azusa, CA (Fujita, Stockwell, Campbell, Keislar, & Lawson, 2003); Daegu, Korea (Jo & Park, 2005); and Southern California (Gao, 2007). Tropospheric O_3 is produced by a photochemical reaction dependent on ultraviolet (UV) radiation and forerunner chemicals, such as volatile organic compounds (VOCs) and NO_x. The formation of O_3 is a complicated and nonlinear process, depending on the concentrations of VOCs and NO_x, their mixing ratio, and the intensity of UV radiation (Derwent & Hertel, 1998; Seinfeld & Pandis, 2006).
Transportation is responsible for a substantial share of pollution emissions, including VOCs and NO_x, in urban regions (US EPA 2002). Since O_3 formation involves a photochemical process, a little understanding of O_3 chemistry should provide clues as to why higher O_3 concentrations occur during weekends.

A significant number of epidemiological studies support a positive relationship between daily mortality and O_3 concentrations (Bell, McDermott, Zeger, Samet, & Dominici, 2004; Bell & Dominici, 2008; Gryparis et al., 2004; Zanobetti & Schwartz, 2008). Considering O_3 health impacts, the World Health Organization (WHO) changed its guidelines for O_3 from 120 μg/m^3 (0.061 ppm) to 100 μg/m^3 (0.051 ppm) for a maximum 8-h mean concentration (WHO, 2006). As weekends are periods of outdoor recreation for residents of metropolitan areas, the higher O_3 concentrations are likely to result in higher O_3 exposures, possibly resulting in increased health risks.

In this research, hourly O_3 concentrations have been measured and compared for both temporal and geographical dimensions with consideration of vehicle flows and solar radiation. For the time dimension, the concentrations of weekdays and weekends are compared. O_3 concentrations have been measured at 34 air quality monitoring stations (AQMs), which were divided into two groups, urban background AQMs and roadside AQMs. For the spatial dimension, these two AQM locations were compared. Traffic count data collected at 119 traffic monitoring stations in the Seoul Metropolitan Area in 2003. We investigate why the reduced traffic during weekends leads to higher O_3 concentrations than during weekdays. The chemistry of O_3 help understand this counterintuitive phenomenon. Since solar radiation is indispensable for generating O_3, the relationship between hourly UV radiation and O_3 concentration is also investigated.

2. LITERATURE REVIEW

2.1 Ozone Creation in the Troposphere

The formation of O_3 in the troposphere depends upon the generation of ground-state atomic oxygen, $O(^3P)$ (Eq. 1). Ultra-violet (UV) radiation with wavelengths less than 290 nm is absorbed by the stratospheric O_3 layer, and thus solar radiation with wavelengths exceeding 290 nm reaches ground level, where $O(^3P)$ is produced by the photolysis of NO_2 at wavelengths in the range 290 nm ~ 424 nm (Derwent & Hertel, 1998; Seinfeld & Pandis, 2006). Ozone in the troposphere is generated by combining $O(^3P)$ with an oxygen molecule (O_2) (Eq. 2), with M a third body absorbing excessive energy and stabilizing the formed O_3 molecule.

$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad (1)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (2)$$

The main fate of tropospheric O_3 is to be used for the regeneration of NO_2, which occurs through the reaction between nitric oxide (NO) and O_3 (Eq. 3), called ozone titration (Yarwood, Grant, Koo, & Dunker, 2008). Reactions (1) ~ (3) among NO_2, O_3, and NO under the presence of sunlight reach an equilibrium, wherein the decomposition of NO_2 by sunlight and the recreation of NO_2 by ozone titration are in a steady state, called the photostationary state relation (Seinfeld & Pandis, 2006).

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (3)$$

Since the photolysis of NO_2 is the only source of O_3 creation in the troposphere, the formation of NO_2 in ways different from ozone titration provides an opportunity for O_3 to accumulate.

Two alternative reaction paths for converting NO to NO_2 are presented in Eqs. (4) and (5), where organic peroxy radicals ($RO_2\cdot$)[1] and hydroperoxy radicals ($HO_2\cdot$) react with NO to generate NO_2, without consumption of O_3. Therefore, the abundance of these two radicals in the atmosphere leads to favorable conditions for O_3 accumulation (Seinfeld, 1989).

$$NO + RO_2\cdot \rightarrow NO_2 + RO\cdot \quad (4)$$

$$NO + HO_2\cdot \rightarrow NO_2 + OH\cdot \quad (5)$$

$RO_2\cdot$ and $HO_2\cdot$ are produced in the oxidation processes of VOCs. The simplest chemical structure of VOC is methane (CH_4) and its oxidation indicates how $RO_2\cdot$ and $HO_2\cdot$ are generated. The presence of the hydroxyl radical ($OH\cdot$) initiates the oxidation of CH_4 and produces the methyl radical ($CH_3\cdot$) (Eq. 6). Then, this radical combines with oxygen (O_2) to form a methyl peroxy radical ($CH_3O_2\cdot$; $RO_2\cdot$) (Eq. 7). $CH_3O_2\cdot$ reacts with NO and creates NO_2 (Eq. 8). Subsequently, the remaining alkoxy radical ($CH_3O\cdot$; $RO\cdot$) reacts with O_2, converting it into $HO_2\cdot$ and formaldehyde (HCHO) (Eq. 9). The highly reactive $HO_2\cdot$ converts another NO molecule into NO_2 (Eq. 5). Therefore, the oxidation process of one molecule of CH_4 involves converting two molecules of NO into NO_2. As seen in Eq. (5), VOC oxidation ends with the regeneration of $OH\cdot$, leading to cyclic reactions and resulting in substantial amounts of VOC that can be degraded to generate NO_2.

$$CH_4 + OH\cdot \rightarrow CH_3\cdot + H_2O \quad (6)$$

$$CH_3\cdot + O_2 + M \rightarrow CH_3O_2\cdot + M \quad (7)$$

$$NO + CH_3O_2\cdot \rightarrow NO_2 + CH_3O\cdot \quad (8)$$

$$CH_3O\cdot + O_2 \rightarrow HO_2\cdot + HCHO \quad (9)$$

2.2 Decrease of Ozone Formation

$OH\cdot$ plays a key role in initiating the oxidation of VOCs, providing favorable conditions for the accumulation of O_3. On the other hand, $OH\cdot$ reacts with NO_2 to form nitric acid (HNO_3), removing both $OH\cdot$ and NO_2 from the atmosphere (Eq. 10). Therefore an increase of HNO_3 implies a decrease of $OH\cdot$ recycling and an elimination of NO_2 in the system, leading to a decrease in O_3 formation.

$$NO_2 + OH\cdot + M \rightarrow HNO_3 + M \quad (10)$$

Under an average urban atmosphere, the rate constants for the $NO_2 + OH\cdot$ reaction and the VOCs + $OH\cdot$ reaction are 1.7×10^4 $ppmC^{-1}\,min^{-1}$ and 3.1×10^3 $ppmC^{-1}\,min^{-1}$, respectively. Since

[1] Alkyl radicals are generally designated R·, where R represents the chemical formula for the alkyl group. The chemical formula of alkanes is C_nH_{2n+2}. Once a hydrogen atom is removed from the alkane, the involved carbon atom has an unpaired electron and the molecule becomes a highly reactive free radical. Examples of alkyl radicals include the following: methyl ($CH_3\cdot$), ethyl ($CH_3–CH_2\cdot$), n-Propyl ($CH_3–CH_2–CH_2\cdot$), isopropyl ($CH_3–\dot{C}H–CH_3$), n-Butyl ($CH_3–CH_2–CH_2–CH_2\cdot$) (Seinfeld & Pandis, 1998, pp.76, 240).

the ratio of the (NO_2 + OH·) to (VOCs + OH·) rates is around 5.5, the rates of the two reactions are equal only when the concentration ratio of VOCs to NO_2 is equal to 5.5. If the VOCs/NO_x ratio is less than 5.5, the reaction (NO_2 + OH·) dominates the system and results in slowing down the formation of O_3. Conversely, when the ratio exceeds 5.5, the reaction (VOCs + OH·) generates more intermediate products in the system, such as RO_2·, HO_2·, and recycled OH·, speeding up the formation of O_3 (Derwent & Hertel, 1998; Seinfeld & Pandis, 2006). Therefore, both the concentrations and ratio of the two precursors are important factors to determine the rate of O_3 formation.

The average O_3 concentrations during weekends are higher than during weekdays in California's South Coast Air Basin (SoCAB). Emission activity profiles, including various mobile, point, and area sources, have been collected in SoCAB, and the emission patterns of VOCs and NO_x during weekdays and weekends have been assessed. The reduction rate of NO_x in weekends is around three times greater than that of VOCs, leading to a 30% increase in the VOCs/NO_x ratio (Chinkin et al., 2003; Yarwood, Stoeckenius, Heiken, & Dunker, 2003; Yarwood et al., 2008). Undoubtedly, this phenomenon has induced an increase in O_3 concentrations (solid orange arrow). Therefore, it can be expected that SoCAB is a NO_x-saturated region. Similarly, other metropolitan regions, where lower traffic flows and higher O_3 concentrations have been observed during weekends, can be also classified as NO_x-saturated regions. In such regions, it is expected that the decreased traffic flows during weekend result in the increased O_3 concentrations.

3. EXPLORATORY ANALYSIS

The Seoul Metropolitan area is located on the mid-west side of the Korean peninsula. The area of the city is 605.41 km^2 (East-West distance: 36.78 km, North-South distance: 30.30 km), roughly equally divided by the Han River. The 2003 population was 10,276,968[2] (Seoul Metropolitan Government, 2013). The city is surrounded by mountains 600 ~ 800 meters high, with its western part close to the Yellow Sea.

Vehicle flow data have been collected at road sites classified as Central Business District (CBD, 26 locations), Han River bridges (19 locations), arterial roads (36 locations), and cordon line (38 locations). The locations of the traffic count links are displayed on Figure 1. The traffic data were downloaded from the Seoul city government website[3] (Seoul Metropolitan Government, 2013).

Air pollution concentrations in 2003 have been measured at 34 air quality monitoring stations (AQMs) and are reported in both the Seoul Metropolitan government website (Seoul Metropolitan Government, 2013) and in the Annual Report of Air Quality in Korea (National Institute of Environmental Research, 2004). As illustrated in Figure 1, AQMs are distributed over the Seoul Metropolitan area, with at least one AQM in each district. Out of the 34 AQMs, 27 are classified as urban background AQMs, monitoring the average air quality and assessing whether air quality standards are attained. The other 7 AQMs are located near crowded traffic links to measure the air quality of roadsides.

In 2003, the number of weekdays was 250, thus 6,000 observations for weekdays (250 days × 24 hours). There was 52 Saturdays, 52 Sundays, and 11 national holidays in 2003. The number of observations for Saturday is 1,248. Since the behavior patterns of citizen on holidays are expected to be similar to those on Sunday, it is reasonable to include holidays in the Sunday classification. 1,512 observations are used for Sunday. There are no missing data for

[2] http://www.seoul.go.kr/v2007/publicinfo/statistics/data/4_02.html
[3] http://traffic.seoul.go.kr/archives/373

background AQMs, but, in the case of roadside AQMs, 9 missing values for weekdays and 24 missing ones for Sunday.

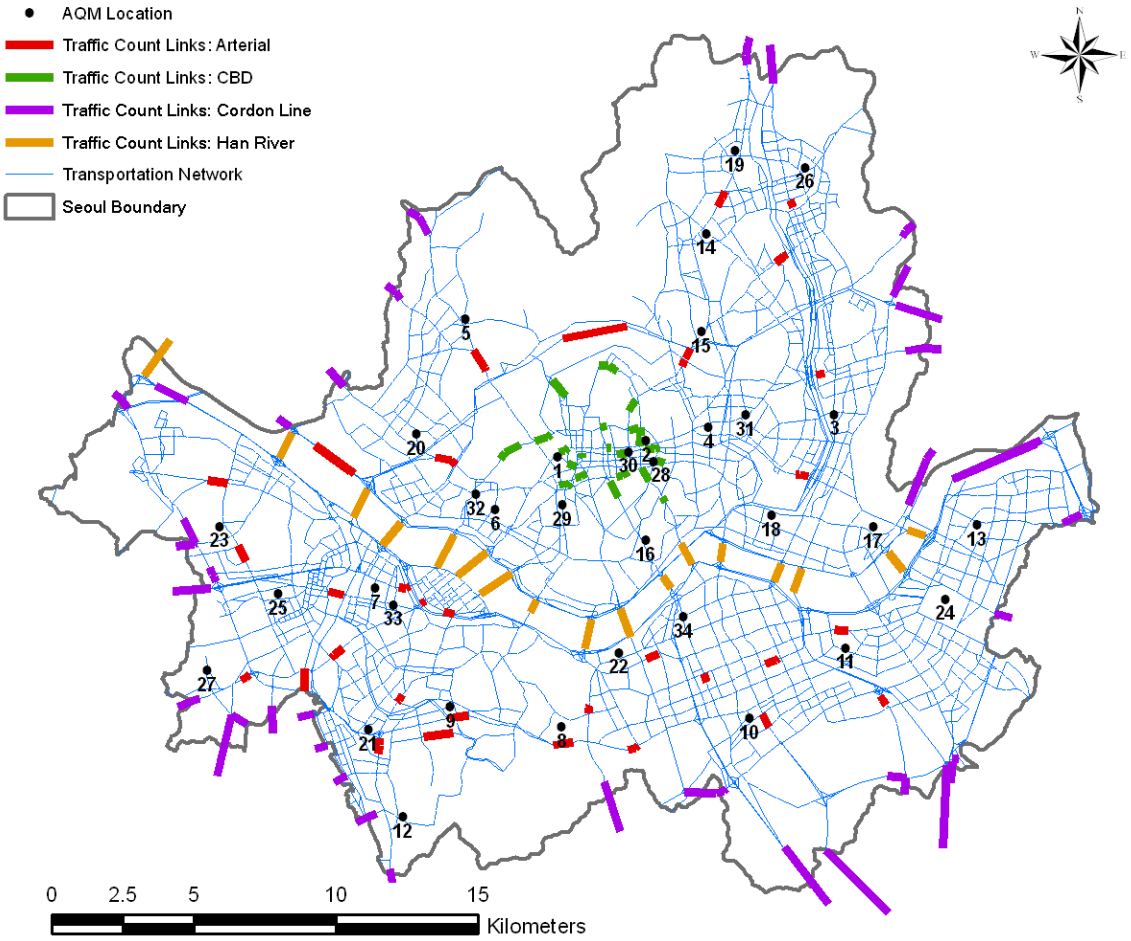

Figure 1. Location of traffic count monitoring site and AQMs in Seoul

3.1 Traffic Flows

Figure 2 shows that the hourly traffic counts during weekdays represent typical urban traffic flows, with morning and evening peaks. Saturday flows are similar to the weekday flows, except for the lowest point in the midday and evening peak. A five-day workweek system was introduced in 2000, but did not come into full effect until 2003, has the minor traffic flow differences between weekdays and Saturday. On Sunday, in contrast, counts are significantly different in terms of both daily peak and overall pattern. As expected, traffic flows on Sunday are smaller than on weekdays across all hours of the day.

The traffic flow on Sunday increases slowly in the morning, as compared to weekdays, and peaks in the late afternoon. This difference in traffic flows between weekdays and Sundays should have an influence on pollution concentrations for both directly emitted pollutants and secondary pollutants.

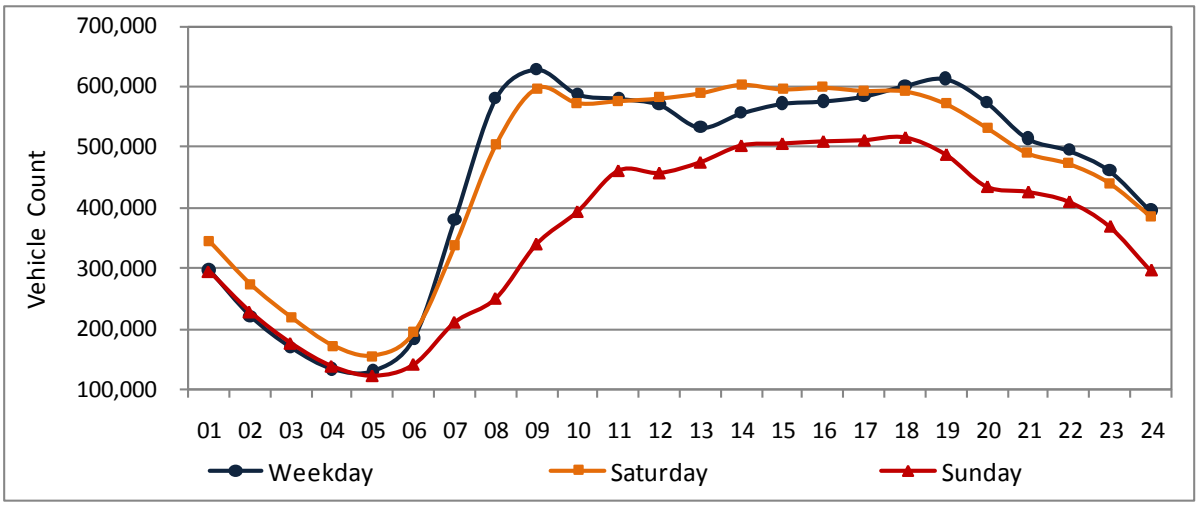

Figure 2. Hourly traffic counts during weekdays, Saturday, and Sunday in 2003

3.2 Pollutants Concentrations

The roadside AQMs are located a few meters from the curbside of major roads or junctions. The junctions are intersecting arterial roads, where heavy traffic volumes and congestion are commonly observed. Pollutant sampling tools are set up at a height of around 2.5 meters. In contrast, urban background AQMs are located away from major roadways, on the roofs of two- or three-story public buildings, such as elementary schools and public office buildings. One-hour average concentrations are calculated based on measurements every five minutes (12 readings per hour) (Korea Ministry of Environment, 2003).

Hourly-averaged pollution concentrations of O_3 and NO_2 are used for the spatiotemporal comparison. As shown in Table 1, O_3 concentrations at background AQMs are higher than those at roadside AQMs. In addition, weekdays' concentration is lower than that of Sunday. Consequently, the O_3 concentration on Sunday at the urban background site displays the highest among the four spatiotemporal combinations.

As shown in Figure 2 and 3, the hourly variations of NO_2 concentration are closely related to those of the traffic flows. The exhaust from tail pipes includes abundant fresh nitrogen monoxide(NO), which react with ambient O_3 to produce NO_2 (Eq. 3) immediately after emission. According to Derwent and Hertel (1998), over 90% of nitrogen compounds are emitted in the form of NO. Only less than 10% of nitrogen is directly emitted in NO_2 form. NO produced in the combustion process, however, mainly reacts with ambient O_3 and free radicals within a few seconds after its emission, and is transformed into NO_2. Thus, strictly, NO_2 can be classified as a secondary product, but, because of its quick and complete reaction, NO_2 can be regarded as a direct emission from vehicles. The reation between O_3 and fresh NO leads to the removal of ambient O_3 and the accumulation of NO_2 near roadside area simultaneously. Thus it is definite that high traffic flows induce high NO_2 concentrations especially at roadside areas. Shown in Table 1, the concentrations of NO_2 at the roadside areas are consistently higher than those of background records across all time dimensions.

Table 1. Descriptive statistics of O_3, NO_2 and solar radiation

Classification			N	Mean	Std. Dev.	Min.	Max.
Weekday	Background	O_3 (ppb)	6,000	13.03	13.01	1.15	85.36
		NO_2 (ppb)	6,000	39.49	15.44	7.33	130.52
	Roadside	O_3 (ppb)	5,991	8.21	6.03	1.00	48.43
		NO_2 (ppb)	5,991	50.42	15.71	9.29	142.20
	Solar radiation (MJ/㎡)		6,000	0.49	0.67	0.00	3.12
Saturday	Background	O_3 (ppb)	1,248	13.22	12.10	1.35	70.22
		NO_2 (ppb)	1,248	37.68	15.56	6.54	98.54
	Roadside	O_3 (ppb)	1,248	8.42	5.70	0.00	36.86
		NO_2 (ppb)	1,248	48.53	15.85	11.00	115.67
	Solar radiation (MJ/㎡)		1,248	0.49	0.69	0.00	2.97
Sunday	Background	O_3 (ppb)	1,512	15.19	14.42	1.27	85.27
		NO_2 (ppb)	1,512	33.98	13.52	8.15	78.85
	Roadside	O_3 (ppb)	1,488	9.65	7.34	0.86	44.86
		NO_2 (ppb)	1,488	43.70	13.53	10.17	119.29
	Solar radiation (MJ/㎡)		1,512	0.49	0.69	0.00	2.97

Figure 3 shows that the hourly NO_2 concentrations during Sunday display distinctively lower values than those during weekdays and Saturday, which is consistent with the results from several studies of California's South Coast Air Basin (Blanchard & Tanenbaum, 2003; Chinkin et al., 2003; Yarwood et al., 2008). In contrast, O_3 concentrations on Sunday are higher than those on Saturday and weekdays. Recent research has uncovered similar patterns. In Phoenix, Arizona, traffic flows are negatively correlated with ambient O_3 concentrations, with the average daily O_3 concentrations on Sunday and Saturday higher than those on weekdays (Shutters & Balling, 2006).

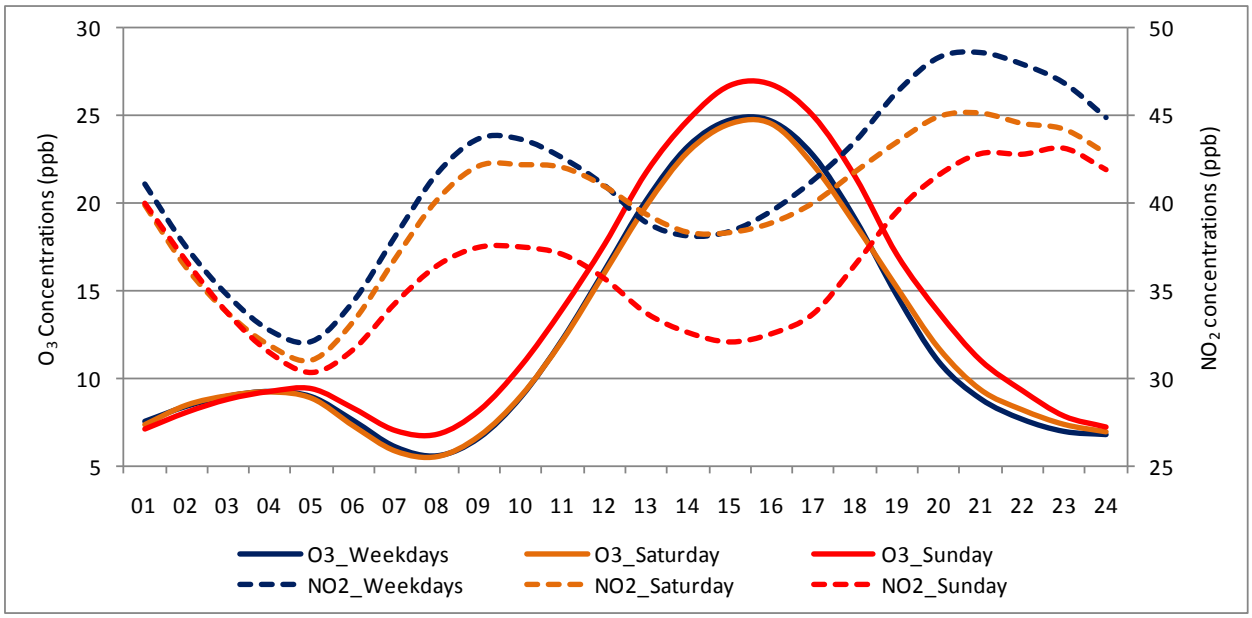

Figure 3. Comparisons of hourly O_3 and NO_2 concentrations between weekdays, Saturday, and Sunday

The counts of traffic flow and the concentrations of a directly emitted pollutant (NO_2) and a secondary pollutant (O_3) measured during weekdays and weekends in Seoul, display consistent results with these recent studies. It is logical to infer that decreased vehicle flows lead to decreased NO_x emissions. The decreased NO_x emissions on Sunday generates a favorable condition for the accumulation of O_3.

3.3 Traffic Flow and O_3 Concentration

In previous section, we observe that the O_3 concentrations at roadsides are lower than those at background AQMs. Across the seasons, as shown in Figure 4 and 5, O_3 concentrations monitored at the urban background AQMs are higher than those of roadside AQMs. Several studies have reported that heavily traveled roadside areas are less polluted by O_3 than urban background regions (Jo & Park, 2005; Kim & Guldmann, 2011), and that average concentrations of O_3 at rural and non-urban sites are higher than those at urban sites (Gregg, Jones, & Dawson, 2003; Yang & Miller, 2002). Average O_3 concentrations over 2003 ~ 2006 at urban, suburban and rural sites in central Taiwan were equal to 24 ppb, 27 ppb, and 29 ppb, respectively (Tsai, Wang, Wang, & Chan, 2008). A comparison of daily maximum O_3 concentrations in urban (Bridgeport and New Heaven), suburban (Danbury, East Hartford, Greenwich, Middletown, Madison, and Stratford), and rural (Stafford) areas in Connecticut, USA indicates a difference of 10 ppb or more between non-urban and urban sites (Yang & Miller, 2002). The annual average O_3 concentrations at sites in New York City and surrounding rural areas also support these results: O_3 concentrations in rural areas are significantly higher (28 ppb) than those at urban sites (16 ppb). Empirical research based on observational data reports consistent patterns of O_3 concentrations, higher in less traffic flow and lower in heavily travelled areas.

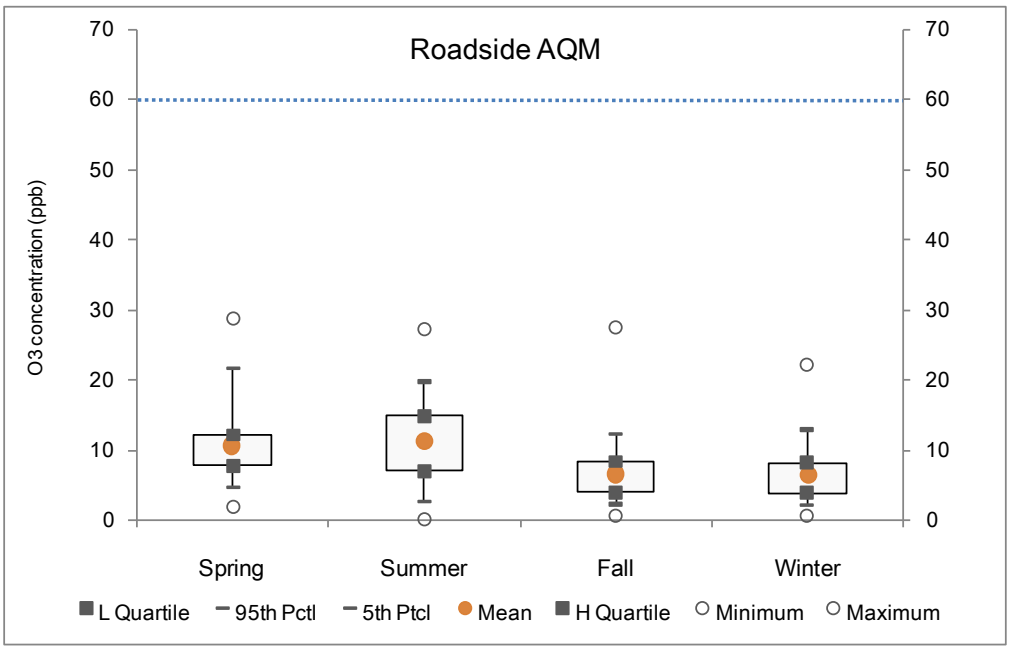

Figure 4. Box-plot of daily O_3 concentrations at roadside AQMs

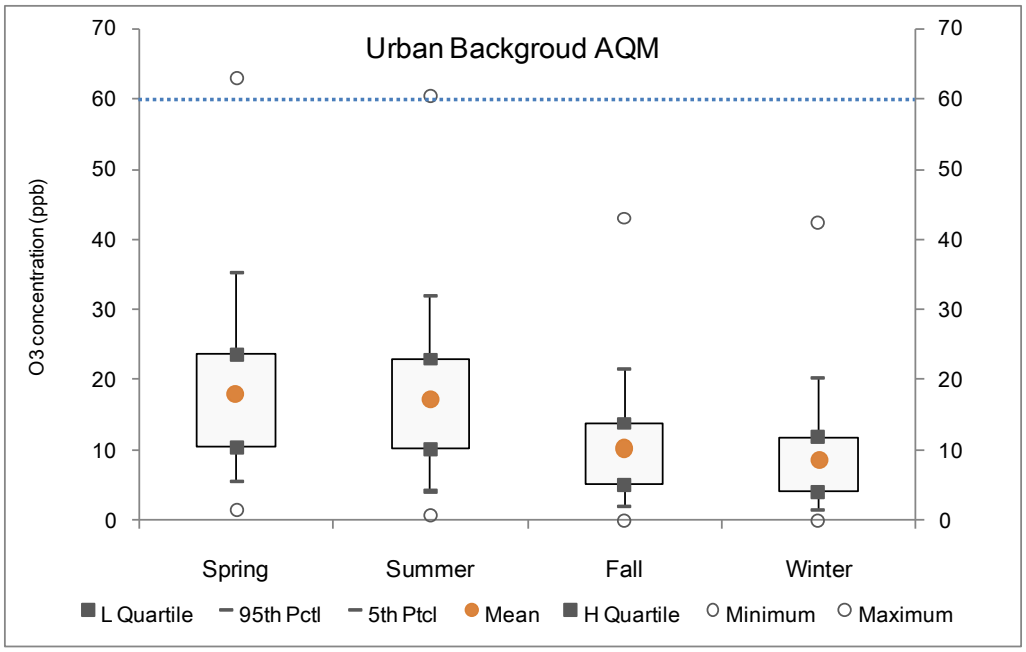

Figure 5. Box-plot of daily O_3 concentrations at urban background AQMs[4]

As discussed in the O_3 chemistry section, the areas near heavy traffic flows are abundant in fresh NO emission and the concentrations of O_3 are significantly affected by the ozone titration process (Eq. 3). Some daily and hourly concentrations at background AQMs violate O_3 standards, while all the concentrations monitored at roadside AQMs are within the standards. In Korea, summer is the rainy season, thus even radiation in summer is stronger than those of the other seasons but the actual intensity of arrived radiation to the earth surface may not. Particularly, May is known to have the most favorable meteorological conditions for O_3 formation, subsequently higher O_3 concentrations are observed in spring season.

3.4 Solar Radiation and O_3 Concentration

Among diverse meteorological factors, solar radiation plays an important role in determining O_3 concentrations. In particular, UV radiation is indispensable for generating O_3, thus it is necessary to focus on the relationship between intensity of UV radiation and O_3 concentration. The intensity of UV radiation plays an important role in the formation of O_3, because solar radiation initiates the photodissociation of NO_2 (Eq. 1), followed by the reaction of ground-state atomic oxygen and O_2 to generate O_3 (Eq. 2). As illustrated in Figure 6, hourly-averaged O_3 concentrations during May 2003 have a pattern similar to UV radiation, but with a time lag. As expected, the peak of solar radiation occurs around 1:00 PM, but O_3 concentration peaks at 4:00 PM. The three-hour time lag between the two peaks may be explained by the rate differences between the creation and destruction of O_3. Since ambient O_3 concentrations are determined by rates of creation and decomposition, the rate of creation is greater than that of decomposition, and then the accumulation of O_3 will occur. The time lag suggests that the creation rate exceeds the decomposition rate until 4:00 PM. To elucidate the relationship between UV radiation and O_3 concentration, a moving average method could be considered.

[4] The dotted line indicates the 8-hr standard for O_3 concentration: 60 ppb/8hr.

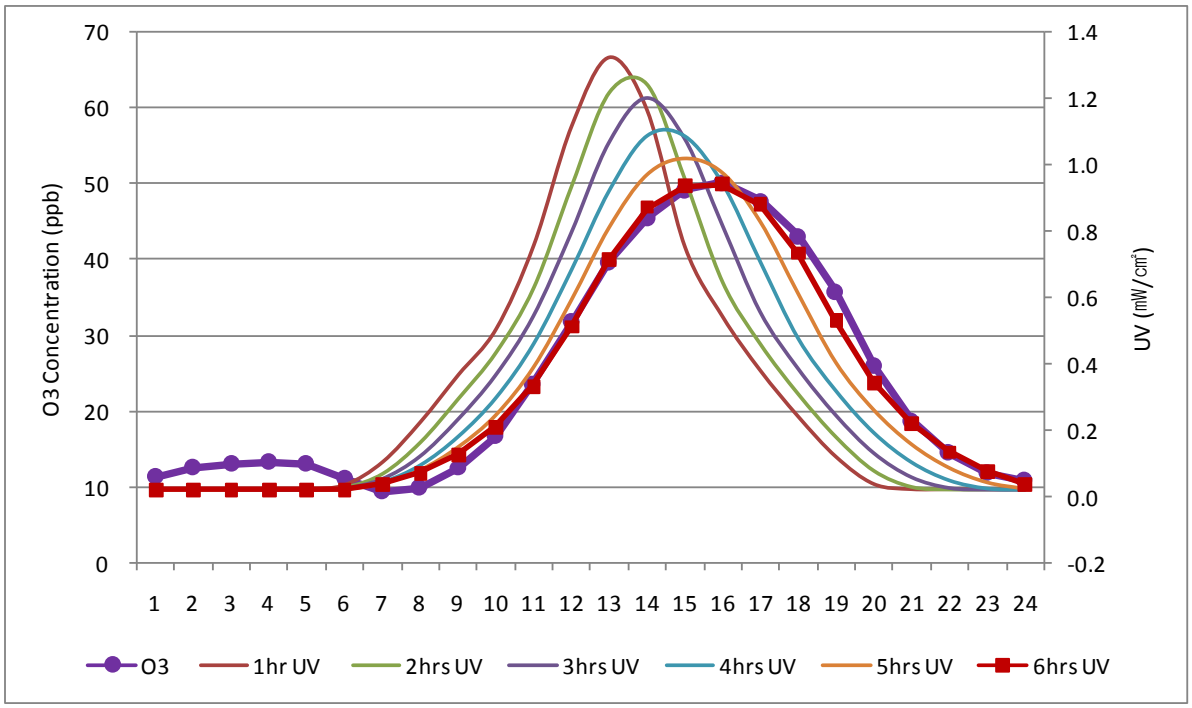

Figure 6. Comparison between hourly O_3 concentration and moving average of UV radiation

4. REGRESSION ANALYSIS BETWEEN OZONE AND UV RADIATION

The previous descriptive analysis suggests that hourly measured solar radiations are not appropriate to explain hourly O_3 concentrations because of the time lag between these two data sets. To account for the time lag effect on O_3 regression model, the explanatory variable, solar radiation, is averaged over 1 to 8 hours, and then they are used as an explanatory variable in turn.

Define C_h as the hourly O_3 concentration at specific hour h, and UV^{ma} as the moving average of solar radiation. Since the data of pollution and radiation cover the entire year of 2003, the total number of data to estimate each regression model is 8,760.

$$C_h = \alpha + \beta\, UV^{ma} \tag{11}$$

where,

C_h : hourly O_3 concentration at specific hour h, and
UV^{ma} : moving average of solar radiation.,

The explanatory power of solar radiation can be assessed by comparing the t value of the estimated Eq. (11). The regression results are presented in Table 2. Each regression model is estimated with 8,760 (24 hrs × 365days) observations and, as shown in the table, all estimated parameters are statistically significant.

As expected, solar radiation has strong positive effects on O_3 concentration. The explanatory power of solar radiation varies with the values of moving average. The t value of explanatory variable increases until 6-hour average and then it decreases, indicating the hourly

accumulation rate of O_3 is different and the value of 6-hour average UV is best fitting to explain O_3 concentration. Figure 6 also shows these statistical results visually.

Table 2. Regression results between O_3 and hourly average UV radiation

UV Radiation	Parameter	Std. Error	t value	P>|t|	R^2
1-Hour avg.	8.17	0.13	61.13	0.00	0.299
2-Hour avg.	9.40	0.13	73.36	0.00	0.381
3-Hour avg.	10.49	0.12	84.91	0.00	0.452
4-Hour avg.	11.43	0.12	94.49	0.00	0.505
5-Hour avg.	12.21	0.12	100.50	0.00	0.536
6-Hour avg.	12.80	0.13	101.86	0.00	0.542
7-Hour avg.	13.19	0.13	98.69	0.00	0.527
8-Hour avg.	13.39	0.14	92.27	0.00	0.493

5. CONCLUSION

This study investigates the spatiotemporal variations of O_3 concentrations with regard to traffic flow and solar radiation. The chemistry of O_3 creation and destruction is reviewed. During any given hour, under assumed steady-state meteorological conditions, O_3 concentrations are determined by the rates of O_3 creation and destruction. The concentration of O_3 is affected not only the level of precursors' concentration but their mixing ratio. The change of VOCs and NO_x ratio across spatial and temporal dimensions is the possible reason for the high O_3 concentration on Sunday at the urban background regions. Since solar radiation is a key factor to generate ozone, UV radiation is adopted as an explanatory variable to explain O_3 concentration. The hourly plot of O_3 concentration and solar radiation show that there are significant time gaps between these two data sets. Thus, a simple moving average method is applied to the hourly solar radiation data and eight sets of moving average are tested, resulting in 6-hour running average is best to explain O_3 concentration.

The regression coefficients β is statistically significant at the 1% level for all models. Even though the greatest R^2 of model reaches up to 0.54, it is difficult to use this regression model as impact analysis, that is, predicting the increase in concentrations resulting from a given increase of UV radiation ($\Delta C = \beta.\Delta UV$). For the reasons that follow, with given same UV radiation, the level of O_3 concentration may be significantly different along the rate of O_3 titration and the level of NO_2 concentration.

REFERENCES

Bell, M. L., & Dominici, F. (2008). Effect modification by community characteristics on the short-term effects of ozone exposure and mortality in 98 US communities. *American Journal of Epidemiology, 167*(8), 986-997.

Bell, M. L., McDermott, A., Zeger, S. L., Samet, J. M., & Dominici, F. (2004). Ozone and short-term mortality in 95 US urban communities, 1987-2000. *The Journal of the American Medical Association, 292*(19), 2372-2378.

Blanchard, C. L., & Tanenbaum, S. J. (2003). Differences between weekday and weekend air pollutant levels in southern california. *Journal of the Air & Waste Management*

Association, 53(7), 816-828.
Cardelino, C. A., & Chameides, W. L. (1990). Natural hydrocarbons, urbanization, and urban ozone. *Journal of Geophysical Research, 95*, 13971-13979.
Chinkin, L. R., Coe, D. L., Funk, T. H., Hafner, H. R., Roberts, P. T., Ryan, P. A., et al. (2003). Weekday versus weekend activity patterns for ozone precursor emissions in California's south coast air basin. *Journal of the Air & Waste Management Association, 53*(7), 829-843.
Derwent, R. G., & Hertel, O. (1998). Transformation of air pollutants. In J. Fenger, O. Hertel & F. Palmgren (Eds.), *Urban air pollution : European aspect*. Dordrecht; Boston: Kluwer Academic Publishers.
Gregg, J. W., Jones, C. G., & Dawson, T. E. (2003). Urbanization effects on tree growth in the vicinity of New York City. *Nature, 424*(6945), 183-187.
Gryparis, A., Forsberg, B., Katsouyanni, K., Analitis, A., Touloumi, G., Schwartz, J., et al. (2004). Acute effects of ozone on mortality from the "air pollution and health: A European approach" project. *Am.J.Respir.Crit.Care Med., 170*(10), 1080-1087.
Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., & Fall, R. (2000). Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. *Atmospheric Environment, 34*(12-14), 2205-2230.
Jo, W., & Park, J. (2005). Characteristics of roadside air pollution in Korean metropolitan city (Daegu) over last 5 to 6 years: Temporal variations, standard exceedances, and dependence on meteorological conditions. *Chemosphere, 59*(11), 1557-1573.
Kim, Y. and Guldmann, J.M., 2011. Impact of traffic flows and wind directions on air pollution concentrations in Seoul, Korea, *Atmospheric Environment*, *45*(16), 2803-2810.
Korea Ministry of Environment. (2003). *2003 environment white paper*. South Korea:
Lamb, B., Guenther, A., Gay, D., & Westberg, H. (1987). A national inventory of biogenic hydrocarbon emissions. *Atmospheric Environment, 21*(8), 1695-1705.
Lau, J., Hung, W. T., Cheung, C. S., & Yuen, D. (2008). Contributions of roadside vehicle emissions to general air quality in Hong Kong. *Transportation Research Part D, 13*(1), 19-26.
National Institute of Environmental Research. (2004). *Annual report of air quality in Korea 2003*. Seoul, Korea: Ministry of Environment.
Pun, B. K., Seigneur, C., & White, W. (2003). Day-of-week behavior of atmospheric ozone in three U.S. cities. *Journal of the Air & Waste Management Association, 53*(7), 789-801.
Rinne, H. J. I., Guenther, A. B., Greenberg, J. P., & Harley, P. C. (2002). Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature. *Atmospheric Environment, 36*(14), 2421-2426.
Roorda-Knape, M. C., Janssen, N. A. H., de Hartog, J., Van Vliet, P. H. N., Harssema, H., & Brunekreef, B. (1999). Traffic related air pollution in city districts near motorways. *The Science of the Total Environment, 235*(1-3), 339-341.
Russell, A., Milford, J., Bergin, M. S., McBride, S., McNair, L., Yang, Y., et al. (1995). Urban ozone control and atmospheric reactivity of organic gases. *Science, 269*(5223), 491-495.
Sanderson, M. G., Jones, C. D., Collins, W. J., Johnson, C. E., & Derwent, R. G. (2003). Effect of climate change on isoprene emissions and surface ozone levels. *Geophysical Research Letters, 30*
Seinfeld, J. H. (1986). *Atmospheric chemistry and physics of air pollution*. New York: Wiley.

Seinfeld, J. H., & Pandis, S. N. (2006). *Atmospheric chemistry and physics: From air pollution to climate change, 2nd ed.* New York: John Wiley & Sons, Inc.

Seoul Metropolitan Government. (2010). *Air pollution monitoring data.* http://www.seoul.go.kr/info/organ/subhomepage/env/statistics/11366_index.html

Shutters, S. T., & Balling, R. C. (2006). Weekly periodicity of environmental variables in Phoenix, Arizona. *Atmospheric Environment, 40*(2), 304-310.

Steiner, A. L., Tonse, S., Cohen, R. C., Goldstein, A. H., & Harley, R. A. (2006). Influence of future climate and emissions on regional air quality in California. *Journal of Geophysical Research, 111*

Tsai, D., Wang, J., Wang, C., & Chan, C. (2008). A study of ground-level ozone pollution, ozone precursors and subtropical meteorological conditions in central Taiwan. *Journal of Environmental Monitoring, 10*(1), 109-118.

WHO. (2006). *WHO air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide, global update 2005,summary of risk assessment*. Geneva, Switzerland: WHO Press.

Yang, J., & Miller, D. R. (2002). *Trends and variability of ground-level O_3 in Connecticut over the period 1981-1997*

Yarwood, G., Grant, J., Koo, B., & Dunker, A. M. (2008). Modeling weekday to weekend changes in emissions and ozone in the Los Angeles basin for 1997 and 2010. *Atmospheric Environment, 42*(16), 3765-3779.

Yarwood, G., Stoeckenius, T. E., Heiken, J. G., & Dunker, A. M. (2003). Modeling weekday/weekend ozone differences in the Los Angeles region for 1997. *Journal of the Air & Waste Management Association, 53*(7), 864-875.

Zanobetti, A., & Schwartz, J. (2008). Mortality displacement in the association of ozone with mortality: An analysis of 48 cities in the United States. *Am.J.Respir.Crit.Care Med., 177*(2), 184-189.