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Short and Long-Term Temporal Changes in Air Quality in a Seoul Urban Area: The Weekday/Sunday Effect

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Received: 15 March 2018; Accepted: 17 April 2018; Published: 19 April 2018

Abstract: We present evidence on the short-term differences in airborne pollution levels in terms of weekday/weekend (WD/WN) and weekday/Sunday (WD/Sun) intervals. To this end, we analyzed the hourly data of important pollutants (nitric oxide (NO), nitrogen dioxide (NO_2), ozone (O_3) and carbon monoxide (CO)) using the data acquired in the Yong-San district of Seoul, Korea from 2009 to 2013. For each week, the pollutant ratio (R_w) was estimated through either WD/WN or WD/Sun. Here, a week is defined as Sunday through Saturday, WD as Monday through Friday and WN as Sunday and Saturday. The WD/Sun R_w geometric means (and range) were 2.02 (0.27–15.5) for NO, 1.29 (0.49–5.7) for NO_2 and 0.89 (0.17–7.2) for O_3 while the fraction of R_w (WD/Sun) > 1 were 81, 71 and 38%, respectively. NO and CO levels were much higher in October through March (during Autumn and Winter) than April through September (during Spring and Summer), reflecting the potential effect of fuel consumption (e.g., in terms of use patterns of nationwide city natural gas). Thus, we provide a broader interpretation on the occurrence patterns of the major pollutants (e.g., NO, NO_2, O_3 and CO) in relation to temporal changes in man-made activities.

Keywords: oxides of nitrogen; ozone; PM_{10}; weekday-weekend effect; meteorological data

1. Introduction

The combustion of fossil fuels, especially for power generation, domestic heating and transportation purposes and so forth, is the main source of air pollution. Of these, transportation-related air pollutants (TRAPs) are most difficult to control because of the increasing vehicle usage in growing economies, especially in developing countries.

A number of natural processes (such as lightning, volcanic eruptions, bacterial activity in soil, forest fires, production of biogenic compounds and photochemical degradation of nitrogen compounds in the upper atmosphere) release considerable amounts of NO_x into the troposphere. Nonetheless, TRAP-derived NO_x (a mixture of NO and NO_2) account for most of the elevated NO_x levels observed in major cities [1]. The levels of roadside NO_x increase with traffic density, especially during 'rush hours';

hence, NO_x is a reliable marker of road-traffic emissions [2]. The higher pressures and temperatures found in internal combustion engines (especially diesels compared to natural gas furnaces for heating) favor the formation of NO from N_2 and O_2 precursors in the endothermic reaction (NIST Chemistry Webbook) [3–6].

Besides being noxious to humans, NO_x also leads to secondary atmospheric pollution, for example, the formation of aerosols and acid rain [7]. From an agricultural perspective, such secondary pollution could reduce soil and water quality, thereby hindering plant growth [8]. About 90% of the tropospheric NO_x is estimated to be from primary NO emissions whereas NO_2 is an oxidation product of NO by O_3 [9]. For the interested reader, atmospheric chemistry and physics has been comprehensively reviewed [10].

Ozone in the stratosphere is generally found at higher concentrations (e.g., at low ppm levels) than those at ground level (e.g., at ppb levels) and is important for absorbing solar UV radiation (http://www.ozonelayer.noaa.gov/science/basics.htm). However, tropospheric O_3 is a pollutant, a product of both natural and anthropogenic processes, mainly formed through the photochemical oxidation of NO, methane (CH_4), non-methane hydrocarbons (NMHCs) and carbon monoxide (CO) [11–13]. More specifically, the combined effects of volatile organic compounds (VOCs) and NO_x control on the formation of O_3 near the Earth's surface. Given the complex non-linear route of O_3 formation, its formation-removal varies day-by-day and from site-to-site depending on many factors (e.g., sunlight and VOC levels). Changes in the spatial and temporal distribution of O_3 can also be affected sensitively by meteorological factors such as ultraviolet (UV) radiation intensity, temperature (T), solar radiance (SR), wind speed (V) and relative humidity (RH). The combined effect of these natural factors can facilitate the production, loss, conversion and dispersion of atmospheric oxidants (such as O_3).

The influence of human activities on local (e.g., urban) and regional (urban plus rural) air pollution has previously been investigated on a weekly basis [14–21]. Masiol et al. [22] reported 13-year trends in NO_x and O_3 levels, along with those of CO, SO_2 and PM_{10} (particulate matter of sizes < 10 μm). It has been suggested that the differences in pollution between weekday (WD: Monday through Friday) and weekend (WN: Saturday and Sunday) periods can influence the local climate in the coastal NW Atlantic region of the USA as rainfall is higher on weekends [23]. On the other hand, rainfall was reported to be higher during midweek in south east USA due in part to higher anthropogenic air pollution [24]. In an area east of the Mississippi River in the USA, the higher summer precipitation on Tuesday through Friday relative to other days were correlated with the weekly pollution cycles [25]. Also, the impact of the aforementioned meteorological factors (UV, T, SR, V and RD) on air quality was assessed in seasonal, weekly and diurnal cycles [22]. Elsewhere, Henschel et al. investigated NO_x levels in the ambient air of nine European cities between 1999 and 2010. They reported that the diurnal patterns were consistently and strongly reflected by differences in traffic densities between morning and evening; however, lower concentrations of NO_x were noticed during weekends [26]. Similar data collected from aircraft over the entire South Coast Air Basin between 1996 and 2014 also showed relative reduction in O_3 levels on weekends [27]. The airborne NO workday/Sunday effect ($R_W > \sim 2$) in New Jersey, USA was first assessed using quantile: quantile plots in 1974 [28].

Generally, industrial and transportation activities decrease during weekends (especially on Sundays in South Korea), as reflected by lower emissions. Meanwhile, PM_{10} emissions from other sources (such as households and power generation) are relatively steady irrespective of the day of the week [29]. To learn more about the weekday/weekend (*WD/WN*) and weekday/Sun effects on air quality in urban areas, we analyzed the concentration data of NO, NO_2, O_3 and CO, measured from 2009 through 2013 at Yong-san. Yong-san was chosen because of its central location in Seoul; Seoul has ~3,000,000 vehicles for a population of ~10.5 million people. In addition, Yong-san contains a US military base, the Itaewon commercial district, the Ministry of National Defense headquarters, the Hyundai Development Company and many other businesses (https://en.wikipedia.org/wiki/Yongsan_District). As continuation of our previous work [30], we sought for evident *WD/WN* effects based on the near-ground-level concentrations of airborne CO, NO, NO_2, O_3, PM_{10} and Hg in Yong-San.

The study period (2009–2013) in this work is after most of the air quality control legislation had been enacted in Korea. Carbon monoxide and sulfur dioxide levels in Seoul have remained low with a slow decline post 2007 compared to earlier years (1989–2007) when the levels were much higher with rapid decline. This study explores the weekday/weekend effect when pollution levels have remained fairly constant since 2007 [31].

Since 1985, the use of solid fuels for heating purposes (e.g., coal briquettes) has been increasingly banned and from 1999 banned in 20 regions including Seoul [31]. The "Clean Air Conservation Act," enacted in 1990, designates gaseous or granular materials that cause air pollution as "air pollutants" and requires them to be managed through monitoring and emission controls. Since then, permissible emission levels have been progressively tightened in 1999, 2005 and 2010. The tightened permissible emission levels applicable from 1 January 2015 were again announced on 31 December 2012 (http://eng.me.go.kr/eng/web/main.do).

2. Materials and Methods

2.1. Study Site Description

The concentrations of NO, NO_2 and O_3 at a site (YS) in Yong-San, Seoul, Korea (37.540041 N and 127.004820 E) were monitored from 2009 through 2013. The YS site is located east of a busy north-south main road and north of the east-west Han River. The YS site is classified as an urban air monitoring station (and operated) by the Korean Ministry of the Environment (KMOE). Yong-San has a land area of 21.87 km^2 and a population density of approximately 10,000 km^{-2}. The urban air-quality monitoring station in Yong-San is located near Yongsan-gu Hanam-dong Road 136 on the roof of a building. For the entire 260-week study period, the average, highest and lowest daily temperatures were 12.7, 31.2 and −13.7 °C, respectively.

A Seoul Metropolitan City traffic survey revealed there were ca. 3,000,000 registered cars and a human population of approximately 10,000,000 in the Seoul metropolitan area (SMA) [32]. In 2011, there were approximately 7,500,000 person.car movements per year (i.e., an occupancy of approximately 2.5 persons per car per movement and the average car traveled 37 $km \cdot day^{-1}$ [33]. The estimated number of cars in Yong-San in 2016 is approximately 65,000 (per capita basis—SMA). In Yong-San, NO_x emissions in 2009 and 2013 were 1688 and 1433 $tons \cdot y^{-1}$, respectively (URL: http://airemiss.nier.go.kr/mbshome/mbs/airemiss/index.do (in Korean)). Based on such facts, the South Korean Government has been actively implementing the advanced policies to monitor pollutant emissions (including NO, NO_2 and O_3) from traffic-related sources since 2000 via the National Air Quality Management Network (NAQMN).

2.2. Experimental Methods

The average hourly NO and NO_2 levels were monitored using chemiluminescence [30], while the O_3 levels were measured using ultraviolet (UV) photometry at 254 nm (Table S1). These techniques have a detection limit of approximately 1 ppb. The objective of the NAQMN policy is to reduce the total anthropogenic NO emissions in Seoul by 53% from 2001 (309,387 ton yr^{-1}) to 2014 (145,412 ton yr^{-1}) [34]. Hence, human activities that can contribute to the formation and distribution patterns of NO, NO_2 and O_3 have been routinely monitored. In addition, relevant meteorological parameters (e.g., including wind speed (WS), humidity (HUM), ultraviolet radiation (UV) and solar radiation (SR)) that could influence the formation of tropospheric NO_x were also monitored concurrently. Details on the analytical instrumentation are given in Table S1.

2.3. Calculation of the WD/WN or WD/Sun Effect

The average hourly concentration of a given pollutant (X) can be expressed as $[X]_{wdh}$, where w is the week number, d is the day number (i.e., Sunday = 1, Monday = 2, … Saturday = 7) and h is time (e.g., 01:00 h to 24:00 h). The first week ($w = 1$) starts at 01:00 h, Sunday, 4 January 2009. For a given week w, the *WD/WN* or the *WD/Sun* ratio, R_w can be defined by Equations (1a) and (1b), respectively:

$$R_w = \left(\frac{1}{5}\right) \times \left(\sum\nolimits_{d=2}^{6} [X]_{wd}\right) / 0.5 \times \left([X]_{w1} + [X]_{w7}\right) \tag{1a}$$

$$R_w = \left(\frac{1}{5}\right) \times \left(\sum\nolimits_{d=2}^{6} [X]_{wd}\right) / \left([X]_{w1}\right) \tag{1b}$$

where $[X]_{wd}$ is the daily average of the hourly data $[X]_{wdh}$ for a given day (d) in a given week (w). Hourly data coverage over the 5-year study period was, for example, 99.1% for NO. Daily averages ($[X]_{wd}$) were only calculated if there were 15 or more hourly data points per day.

The derived R_w values can be grouped into periods, such as yearly (i.e., w = 1–52 for 2009, w = 53–104 for 2010 and so forth where w is the week number) or by seasons, to calculate various descriptive metrics (such as the arithmetic mean (AM) (average), geometric mean (GM), the maximum and minimum, the standard deviation and etc.). Plots of the WD/WN (Equation (1a)) R_w values are shown in Figure 1 and summarized in Table S2.

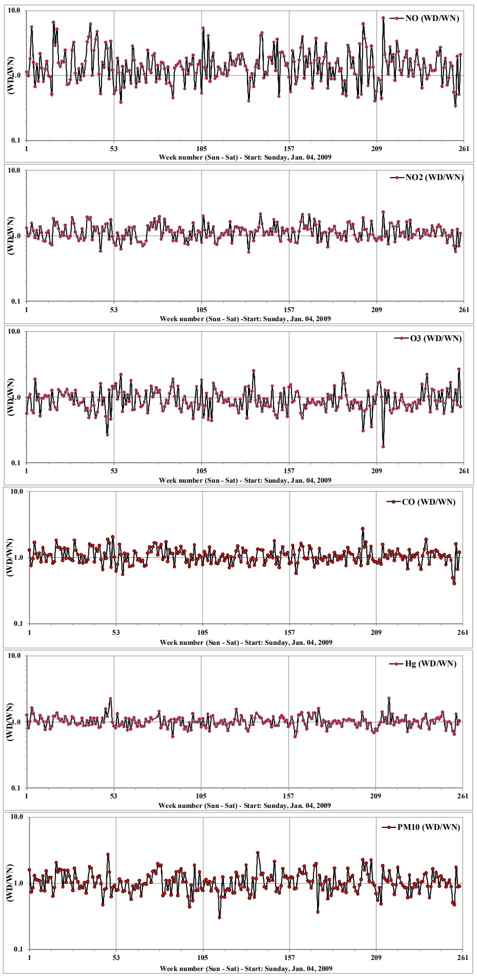

Figure 1. Comparison of the weekday-weekend ratio (R_W) plots (at weekly intervals) of NO, NO_2, O_3, CO, Hg and PM_{10} from 2009 to 2013. *Note: The y-axis scale is logarithmic to gauge whether the distribution is symmetrical with respect to the y = 1 line.*

The R_W values for each species were sorted into two categories ($P = 1/R_W$ or $R = R_W$) whether R_W is <1 or >1, respectively. The definition of R_W is arbitrary; its reciprocal is also equally probable. To calculate the mean value of R_W, the GM is preferred over the AM. For example, if the AM and GM of these 3 R_W values (0.2, 1.0 and 5.0) are compared, the AM = 2.07 may imply a WD/WN effect when in fact there is none as the GM = 1.00. Generally, the GM is less sensitive to very large R_W values than an AM. The frequency count of R_W values greater or less than a selected criterion was determined (see Table S2 and Figure 2). If there is a significant WD/Sun effect, then the R_W frequency count plots of $R_W > 1$ (in Figure 2) versus 1/Rw ($R_W < 1$ in Figure 2) will be very different (e.g., NO) and if there is only a weak WD/WN or WD/Sun effect, the two distributions will be very similar (e.g., Hg). In essence, Figure 2 is transformation of Figure 1 into a frequency count plot for easier visualization of the WD/WN or WD/Sun effect. In addition, a Pearson correlation and T-test analyses were performed to find strong correlations between important variables.

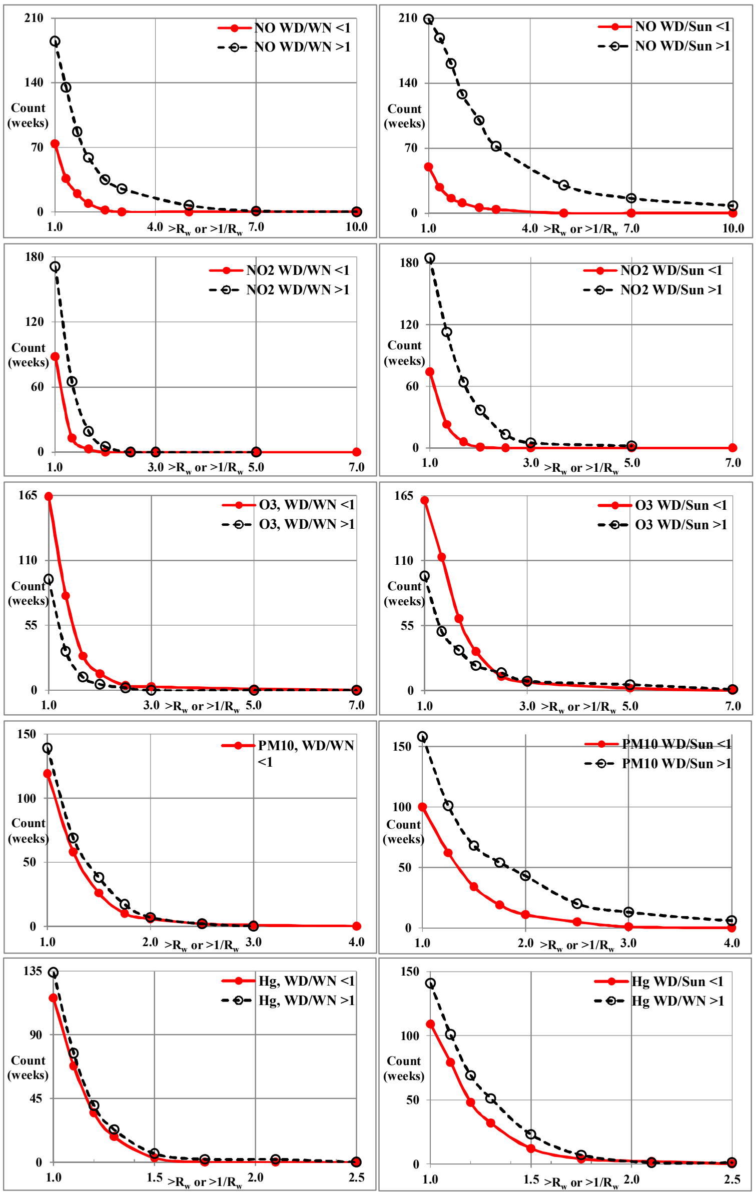

Figure 2. Number of weeks that the Weekday/Weekend or Weekday/Sunday effect ratio (R_W or $1/R_W$) is greater than a selected value (always ≥1) for NO, NO_2, O_3, Hg and PM_{10}.

3. Results and Discussion

3.1. The Weekday to Weekend (WN/WD and Weekday to Sunday (WD/Sun)) Concentration Ratios (R_w) of NO, NO_2 and O_3

The *WD/WN* (or *WD/Sun)* ratios (R_w) can provide insights on the temporal distribution of air pollutants which may lead to more reliable forecasting of pollutant levels [19,21,35]. Various factors, such as the seasons, traffic density, fuel type and usage and waste disposal activities (specifically, landfills and incineration), may give rise to differences in the *WD* and *WN* pollutant levels [21].

To learn more about the *WD/WN* effects, the results of NO, NO_2 and O_3 analysis were assessed on multiple temporal scales. In Figure 2, we show the *WD/WN* trend over the 5-year study period (note that the y-axis scale is logarithmic). The AM (and range) of the WD/WN data for NO, NO_2 and O_3 were 1.65 (0.34–7.7), 1.17 (0.57–2.31) and 0.96 (0.18–4.12), respectively. The corresponding GM for the WD/WN effect for NO, NO_2 and O_3 were, 1.38, 1.13 and 0.89, respectively. Out of the R_w values, a large fraction was greater than 1.0 (i.e., NO (71%), NO_2 (66%) and O_3 (36%)) for the entire 260-week study period. The *WD/WN* effect (where $R_w > 1$) was thus clearly distinguished between the pollutant species in a relative order of magnitude as NO > NO_2 > O_3.

For the entire study period, the average hourly Saturday and Sunday pollution levels were significantly different, for example, NO: 20.5 and 14.3 ppb, respectively ($p = 1.77 \times 10^{-4}$, two-tailed) and O_3: 18.9 and 22.5 ppb, respectively ($p = 6.12 \times 10^{-4}$, two-tailed). On the other hand, the average WD and Saturday pollution levels were more similar (Table 1). Similar behavior was reported in a study covering the period 1986–2007 in the Mexico City metropolitan area; the peak 3-h NO_x levels were 80 (Sun), 137 (WD) and 115 ppb (Sat). Thus, there was a strong WD/Sun effect of 1.72. and the corresponding CO WD/Sun value was 1.61. Both NO_x and CO levels peaked around 8–11 a.m. Therein, PM_{10} and O_3 showed smaller WD/Sat or WD/Sun effects [36].

The corresponding AM and GM of the WD/Sun R_w values were respectively, NO (2.73 and 2.01), NO_2 (1.41 and 1.29), O_3 (1.08 and 0.88), CO (1.22 and 1.15), PM_{10} (1.35 and 1.07) and Hg (1.08 and 1.04). The ratio of the hourly averaged WD and Sunday pollution data for the entire study period is in better agreement with the GM but not the AM of the WD/Sun R_w values, for example, NO (1.58 vs. 2.01 vs. 2.73), respectively. The presents work's YS urban site WD/Sun effect GM of 2.01 is comparable to the quantile:quantile analysis estimate of ~2.7 during the photochemical season of May through September of 1972 and 1973 at Elizabeth (an urban area), NJ, USA [28].

The influence of high road traffic density, as well as other transportation and industrial activities, on *WD* pollutant levels is more pronounced than the mere natural fluctuations at the road curbside [37,38]. From year to year, the NO and NO_2 *WD/WN* effect had shown negligible variation. Since the NO *WD/WN* pattern for each year is similar to that of NO_2, it may imply that O_3 plays a key role in the formation of NO_2; the most likely pathway is oxidation [15], as shown in Equation (2):

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2}$$

In the presence of UV light (hυ), NO and O_3 can be regenerated as shown in Equation (3):

$$NO_2 + O_2 + h\upsilon \rightarrow NO + O_3 \tag{3}$$

Table 1. Summary of airborne pollutant *WD/WN and WD/Sun* effect and meteorological data at Yong-San, Seoul, Korea (2009–2013): (a) air pollutant (WD/WN) effect, (b) air pollutant (WD/Sun) effect) and (c) meteorological (WD–WN) effect.

Item	**Species**	**All Hourly Data Average**	**Weekdays [a]**	**Weekend [a]**	**(WD–WN)**	**Units**	**WD/WN**	**WD/WN**	**WD/WN**	**%**	***t*-Test**	**Hourly Data Coverage (%)**	**Strength of**
			(MTWTF)	**(Sat, Sun)**	**Difference**		**R_w**	**R_w**	**ppb Ratio**	**of R_w**	***p* Value**		**WD/Sun Effect**
			WD	***WN***			**(AM) [b]**	**(GM) [c]**		**>1.00**	**WD:WN**		
(a)	NO	21.1 ± 21.4	22.6 ± 16.8	17.3 ± 14.7	5.3	(ppb)	1.65	1.38	1.30	71.4	1.83×10^{-4}	99.1	Strong
	NO_2	36.1 ± 13.5	37.3 ± 10.0	33.4 ± 10.1	3.9	(ppb)	1.17	1.13	1.12	66.0	1.16×10^{-5}	99.1	Moderate
	O_3	19.1 ± 11.1	18.4 ± 8.7	20.7 ± 9.9	−2.3	(ppb)	0.96	0.89	0.89	36.3	4.70×10^{-3}	99.0	Moderate inverse
	CO	527 ± 279	534 ± 241	504 ± 234	30	(ppb)	1.10	1.06	1.06	59.0	0.161	99.0	Weak
	PM_{10}	47.7 ± 30.3	47.9 ± 21.4	47.3 ± 24.0	0.6	($\mu g \cdot m^{-3}$)	1.09	1.03	1.01	53.7	0.779	99.0	Very weak
	Hg	3.1 ± 1.3	3.1 ± 1.2	3.0 ± 1.0	0.1	($ng \cdot m^{-3}$)	1.03	1.01	1.02	51.4	0.471	98.8	No evidence
(b)		*Sun*	*WD*	*Sat*	*WD-Sun*		*WD/Sun* (AM)	*WD/Sun* (GM)	*WD/Sun* ppb ratio		*Sat:Sun* *t*-test		
	NO	14.3 ± 16.6	22.6 ± 16.8	20.5 ± 20.8	8.3	(ppb)	2.73	2.01	1.58	80.7	1.77×10^{-4}	-	Strong
	NO_2	30.6 ± 12.7	37.3 ± 10.0	36.2 ± 12.7	6.7	(ppb)	1.41	1.29	1.22	71.4	1.15×10^{-6}	-	Moderate
	O_3	22.5 ± 12.6	18.4 ± 8.7	18.9 ± 10.9	−4.1	(ppb)	1.08	0.88	0.82	37.6	6.12×10^{-4}	-	Moderate inverse
	CO	488 ± 276	534 ± 241	520 ± 274	46	(ppm)	1.22	1.15	1.09	68.4	0.185	-	Weak-moderate
	PM_{10}	44.9 ± 28.6	47.9 ± 21.4	49.7 ± 33.5	3.0	($\mu g \cdot m^{-3}$)	1.35	1.07	1.07	61.2	0.085	-	Weak
	Hg	3.0 ± 1.2	3.1 ± 1.3	3.0 ± 1.2	0.1	($ng \cdot m^{-3}$)	1.08	1.04	1.03	56.4	0.871	-	No evidence
	Parameter	All hourly data average	Weekdays (MTWTF) *WD*	Weekend (Sat, Sun) *WN*	(WD–WN) difference	Units				% of (WD-Sun) >0.0			Strength of WD/Sun effect
(c)	Wind speed	2.5 ± 0.6	2.5 ± 0.4	2.5 ± 0.4	0.0	($m \cdot s^{-1}$)	-	-	-	54.1	-	99.4	No evidence
	Temperature	12.6 ± 10.8	12.6 ± 10.6	12.7 ± 10.5	−0.1	(°C)	-	-	-	49.4	-	99.8	No evidence
	Relative humidity	58.6 ± 14	58.5 ± 11	59.1 ± 11	−0.6	(%)	-	-	-	45.6	-	99.8	No evidence
	UV	3.8 ± 2.0	3.8 ± 1.6	3.8 ± 1.7	0.0	($W \cdot m^{-2}$)	-	-	-	47.5	-	99.4	No evidence
	Solar radiance	143.6 ± 78	143.8 ± 54	143.4 ± 61	0.4	($W \cdot m^{-2}$)	-	-	-	50.6	-	99.4	No evidence

[a] A week is defined as Sunday through Saturday. For each week, weekdays (WD) are defined as Monday through Friday and the weekend (WN) is defined as Sunday (first day) and Saturday (last day); [b] AM—arithmetic mean; [c] GM—geometric mean.

Several hypotheses for the O_3 weekend effect and modeling including the role of volatile organic compounds in NO_2 and O_3 formation have been discussed in detail elsewhere [36]. According to plots of hourly [NO_2] versus hourly [O_3] for weeks #73 (starting 23 May 2010) and #212 (starting 20 January 2013), [O_3] is the highest at low [NO_2] but very low at high [NO_2] (Figure S2). A Pearson correlation analysis gave large negative results, viz., −0.800 for week #73 and −0.905 for week # 212. Also shown in Figure S2 are plots of (a) [NO], (b) [NO_2], (c) [O_3], or (d) [NO_2] + [O_3] at hourly intervals. Although [NO_2] and [O_3] individually showed large temporal variations over the two 168 h periods, the sum of [NO_2] + [O_3] showed much reduced hourly variation; this observation is suspected to reflect an essentially a constant mass scenario in which NO_2 and O_3 are merely interconverted from one species to the other. These explanations indeed conform to already well-known O_3-NO_X atmospheric chemistry processes. It would have been of interest to study the effect of ozone precursors, especially volatile organic compounds (VOC), on ozone concentration. Unfortunately, there is not enough detailed information about VOC concentrations (i.e., a photochemical assessment monitoring station (PAMS)) near the monitoring station to allow this analysis. It is worth noting that at another site in Seoul (Jong-ro) equipped with PAMS, both [toluene] and [NO] were a factor up to ~3 higher on WDs compared to Sundays for most weeks [39]. A detailed kinetics study is also beyond the scope of this study.

A large fraction of the NO *WD/WN* and WD/Sun R_w ratios were >1, contrary to those of the O_3; an indication of the influence of parameters other than emissions from vehicles and natural gas heating system. It is commonly believed that the major source of curbside NO is from internal combustion engines and this may be true for April through October (Figure S1) as natural gas use (mainly for building heating purposes) is at its lowest in the warmer months. Nationally, between December 2011 and December 2013, city gas demand ranged from a high of 2924 k·ton in January 2013 (average monthly temperature = −3.2 °C) to a low of 917 k·ton in September 2013 (average monthly temperature = 21.5 °C (http://www.kesis.net/). The per-capita city gas demand in Yong-san or Seoul is assumed to be very similar to the national per-capita demand. For monthly temperatures between 21–28 °C, the national city gas demand was 949 ± 33 k·ton·month^{-1}; for monthly temperatures below 21 °C, national demand followed this relationship: $=6.08 \times 10^6/(273 + T) - 19{,}800$ k·ton·month^{-1} ($p = 0.991$) where T (−3.8 to 20.6 °C) is the monthly temperature in Yong-san). The high NO *WD/WN and WD/Sunday effect* indicates the possibility that traffic density and industrial activities were at their lowest on weekends and Sundays. However, the estimated NO_x emissions from 65,000 cars in Yong-san Gu (assuming 0.08 g·NO_x·km^{-1} (Euro-4 standard, gasoline) and 37 km·day^{-1}) is only 70 ton·yr^{-1} compared to total NO_x emissions of ~1500 ton·yr^{-1} in Yong-san Gu (URL: http://airemiss.nier.go.kr/mbshome/mbs/airemiss/index.do (in Korean)). In South Korea, the monthly consumption of gasoline (~1000 k·ton·month^{-1}) and diesel (~2000 k·ton·month^{-1}) has been very stable over the period May 2011 to April 2017 unlike city gas demand (KESIS, URL: http://www.kesis.net/). Thus, the major NO and CO emission sources are suspected to be from the combustion of city natural gas in the colder months of the year.

3.2. Influence of Meteorological Parameters on Weekday/Sunday Effect (R_w) for NO, NO_2, O_3 and CO

Based on our previous work [30], we attempted to identify whether one or more meteorological parameters are correlated with the observed *WD/Sunday* profiles. Table S2 summarizes the Pearson correlation analysis data for selected pollutants versus Sunday temperature, UV, wind speed, relative humidity and solar irradiance data. In general, the meteorological parameters had very little positive influence on R_w values, for example, for NO, the R_w:temperature, $r = -0.08$. and O_3, the R_w:temperature, $r = -0.04$. The strongest positive influence was seen for wind speed, NO_2:Wind ($r = 0.45$), NO:Wind ($r = 0.34$) and CO:Wind ($r = 0.35$) and that for O_3:Wind was negative ($r = -0.35$). This is possibly because higher wind speed ensures better dispersal mixing of the air in the tropopause. There was, however, some modest negative influence; for example, O_3 (R_w):UV, $r = -0.29$ unlike the daily concentration data where the correlation is strongly positive, [O_3]:UV, r = 0.65 thus some apparent inconsistencies exist for unknown reasons.

3.3. PM_{10} and Hg WD/WN Effect

Airborne mercury is also of interest because it has different source to many of the other pollutants examined. Because no weekday/weekend effect was observed, we can conclude that the sources are not the same as the other pollutants for which a weekday/weekend effect. This indicates that in this location in Seoul, mercury is mostly a background pollutant with most contributions from background levels and long-term transport and not heavily influenced by local emissions. PM_{10} shows minimal WD/WN or WD/Sun effect again suggesting the NO and PM_{10} emissions are from different and unrelated sources.

3.4. Other Studies on the WD/WN Effect

Although 16 similar studies on the *WD/WN* effect were published from 1995 to 2014 [15–21,35,36,40–45], our current work has identified a strong relationship (and interdependence) between the NO, NO_2, O_3 and CO WD/WN and WD/Sun effect and the meteorological parameters. Of the aforementioned 16 references, it was noted that the concentrations of specific air pollutants (i.e., SO_2, NO_x and PM_{10}) are nearly constant on weekdays (*WD*) but were approximately 40–60% lower on weekends (*WN*) in southwestern Germany [46]. Prior to this, Mayer had established the differences between weekday and weekend levels of NO, NO_2 and O_3, as well as other air pollutants that were routinely monitored for temporal variability, at an official air-quality monitoring station in the Bad Cannstatt district of Stuttgart between 1981 and 1993 [47]. The *WD/WN* effect was strongly influenced by motor traffic in Stuttgart, a large city in southern Germany with a population of approximately 500,000. More recently, the diurnal NO_x levels were found to exhibit two peaks during weekdays at 6–8 am and 4–8 pm, which were attributed to rush-hour traffic [17]. During weekends, only a single, afternoon peak was observed, which can be attributed to higher rates of leisure activities.

4. Conclusions

We investigated for evidence of the weekday/weekend (*WD/WN*) and weekday/Sunday (*WD/Sun*) effects of pollution levels based on the temporal distribution of NO, NO_2, O_3 and CO at an urban (Yong-San) air-quality monitoring station in the Seoul megalopolis. The data strongly indicate that the NO *WD/WN and WD/Sunday* ratios may be due in part of lower NO emissions (reduced diesel vehicle movements and natural gas use) on Saturdays and Sundays relative to weekdays. The weekly NO and O_3 levels have a poor Pearson correlation (r = −0.60) and there is a ~6-month phase difference between NO and O_3 minima and maxima. On the other hand, the NO:City gas use pair has the highest Pearson correlation of r = 0.82 of all such studied pairs. There were no unexpected observations with regard to the intra- or inter-year level, *WD/WN* or WD·Sun (R_w) ratio for each pollutant. The geometric mean of the WD/Sun (or WD/WN) weekly effect and the hourly averaged pollution data (weekday, Saturday and Sunday) is the most reliable means to determine the existence of any WD/Sun or WD/WN effect; the arithmetic mean is the least reliable and therefore strongly discouraged. We plan to examine other sites throughout South Korea for the spatial distribution of oxides of nitrogen, ozone and particulate matters in the future, over a decade. Based on our study, it is recommended that the political decision makers should implement policies to reduce pollutant emissions more effectively during weekdays from major man-made sources in the Republic of Korea. If total NO emissions are reduced, then airborne [NO], [NO_2] and [O_3] should all decrease as they are coupled through chemical reactions.

Supplementary Materials: The following are available online at http://www.mdpi.com/2071-1050/10/4/1248/s1. Table S1. Basic information regarding instrumentation used for measuring three target pollutants (NO, NO_2 and O_3) and meteorological data; Table S2. Number of weeks that the Weekday/Sunday effect ratio (R_w or $>1/R_w$) is greater than a selected value (always ≥ 1) for NO, NO_2, O_3, Hg and PM_{10} using the Microsoft Excel COUNTIF facility; Table S3. Pearson correlation analysis of the daily mean data, Weekday/Sunday effect (R_w) for NO, NO_2, O_3 and CO with selected meteorological data and monthly data (NO, CO, temperature and city gas demand; Figure S1. The mean weekday (Monday through Friday) [NO] (top panel) versus mean Sunday [NO] levels (middle panel) for each week. The bottom panel shows the weekday/Sun effect (R_w) of NO for each week; Figure S2. Plots of [NO_2] versus [O_3] and [NO], [NO_2], [O_3] or [NO_2] + [O_3] at every hour for weeks #73 (WD/Sunday effect = 12.0) and #212 (WD/Sunday effect = 0.27).

Acknowledgments: The authors acknowledge support from a National Research Foundation of Korea (NRF) grant funded by the Ministry of Science, ICT and Future Planning (No. 2016R1E1A1A01940995). K.-H.K. also acknowledges support made by the Korea Ministry of Environment (MOE) (2015001950001) as part of "The Chemical Accident Prevention Technology Development Project."

Author Contributions: Initially, A.A.A. analyzed the data, conducted the literature survey, drafted the main manuscript text and prepared the Tables and Figures. Later, J.E.S. re-analyzed the data, conducted a literature survey and made major revisions to the manuscript text, Tables and Figures. J.E.S. (assistant principal investigator) and K.-H.K. (principal investigator) reviewed and edited the draft manuscript for scientific content. In addition, J.E.S. and K.-H.K. performed the overall internal review (with assistance from the other authors, viz., J.W.S., K.V., E.-C.J., J.H. and R.J.C.B.).

Conflicts of Interest: The authors declare no conflict of interest.

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