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Original Research

The "Weekend Effect" on Ozone in the Warsaw Conurbation, Poland

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Abstract

The aim of our study was to examine the literature on the phenomenon of the so-called "Weekend Effect" (WE) in Warsaw and its outskirts. An analysis of the temporal and spatial distribution of ozone and nitrogen dioxide concentrations was made using hourly data on ozone and nitrogen dioxide concentrations in the period from May to September 2008 to 2012 from automatic air quality monitoring stations in Warsaw. The analysis uses data for seven stations located in different parts of the conurbation, which represent different types of areas. WE was then calculated using four methods, one of which was based on a calculation of the difference between the maximum daily ozone concentrations on weekends and the concentrations on weekdays. The results showed that most stations see higher concentrations of ozone during the weekend than on weekdays. This confirms the existence of WE, especially in the area of Granica, west of Warsaw in Kampinos National Park. At stations located within the city, average and maximum values of daily ozone concentrations are 13% and 8% higher on weekends than on weekdays, respectively, despite a reduction in NO_2 concentrations of about 20%. Analysis of the diurnal ozone and nitrogen oxide (NO_x) behaviour confirms the hypothesis that the most likely cause of the higher mean ozone levels on weekends is a reduction in ozone suppression due to lower NO_x emissions on weekend mornings. The reduction in emissions in industrial/traffic-heavy sectors on Sunday leads to a greater reduction in NO_x relative to volatile organic compounds (VOC), and thus an increase in VOC/NO_x ratios during weekends.

Keywords: "Weekend Effect" (WE), ozone, nitrogen dioxide, diurnal cycles, conurbation

Introduction

Elevated O_3 concentrations at ground level are of particular concern due to their deleterious effects on public health, various natural materials, manufactured goods, vegetation, and forests [1-4]. Ozone is present in the troposphere by way of photochemical reactions of naturally occurring geogenic and biogenic hydrocarbon emissions and nitrogen oxides, from lightning and soil processes, and from interaction with the stratosphere [5]. It is also formed by the atmospheric photochemical reactions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) [6].

The observed levels of primary pollutants show weekly patterns that directly reflect the day-to-day variations in their emissions. The pattern of secondary pollutants, on the other hand, is generally less predictable

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due to the interactions of various chemical and meteorological factors influencing chemical reactions. This is particularly true of tropospheric ozone, which is formed by nonlinear photochemical reactions involving NO_x and VOC emissions. Environmental agencies have placed considerable emphasis on ozone reduction policies based on reduced vehicle emissions, which are the main anthropogenic sources of ozone precursors. However, research remains complicated by the presence of multiple sources of precursors, the non-linear relationships between ozone and its precursors, and the influence of meteorological and climatological factors on ozone accumulation and transport [7-9].

The reduction in on-road traffic and, consequently, vehicle emissions on weekends compared to week-days has been seen as a natural experiment to examine the linkages between anthropogenic ally generated ozone precursors and ozone production. Contrary to expectations, ozone concentrations tend to be higher on weekends compared to weekdays in some places, despite the fact that VOC and NO_x emissions are typically lower on weekends. This "Weekend Effect" (WE) was first noticed in the northeastern United States [10, 11] and has been the topic of numerous research studies in the intervening three decades [12-14].

Although various hypotheses have been offered, no definitive cause of WE has been identified. The California Air Resources Board (CARB) outlined six potential causes of the effect on ozone (2003), which have been described in detail by Heuss [11, 15] and the references therein. Briefly, these are:

1. A reduction in NO_x emissions on weekends that reduces the titration of ozone.
2. A weekend change in the timing of NO_x emissions that allows for more efficient production of ozone.
3. Increased sunlight caused by a reduction in the amount of soot in the air.
4. Carry-over of airborne emissions.
5. An increase in weekend emissions, particularly from non-road-based sources, such as lawnmowers.

The most commonly used method of determining the cause of WE is to compare mean ozone concentrations on Sundays to those on Wednesdays. However, in addition to looking at mean concentrations, researchers sometimes analyze peak levels by day of the week (DOW), while still others favor analyzing only specific percentiles of cases [16]. There has been little discussion of how the choice of measurement technique and location impact WE determination and the explanation of its causes. In this paper, the WE results for the Warsaw area were calculated using four different methods and then compared.

Experimental Procedures

We used hourly data of ozone and nitrogen dioxide concentrations in the period from May to September 2008 to 2012 from seven automatic air quality monitoring stations in Warsaw. The seven stations are located in different parts of the conurbation (Fig. 1) and represent different types of areas. Four are located in the Warsaw area and are classified 'core' stations:

- Ursynów (WU) is an urban background station surrounded by high-rise buildings of various housing estates located in southwestern Warsaw, about 15 km from the city center: latitude (φ) = 52°09'N, longitude (λ) = 21°02' E, and elevation (H) = 102 m a.s.l.
- Krucza (WK) is located in the city center close to streets with high traffic, and represents the background to the city center: φ = 52°13' N, λ= 21°01' E, and H = 112 m a.s.l.
- Targówek (WT) is an urban background station located in northeastern Warsaw: φ = 52°17' N, λ = 21°02' E, and H = 85 m a.s.l.
- Podleśna (WP; data used from 2011 to 2012) is also an urban background station, and is located northwest of the city center: φ = 52°16' N, λ = 20°57' E, and H= 98 m a.s.l.

After the four core stations, the other three are located outside the city and are classified as 'fringe' stations:

- Legionowo (LE), located in close proximity to the city, is a suburban station located to the north – in close proximity to Warsaw but beyond the city's administrative boundaries: φ = 52°24' N, λ = 20°57' E, H= 95 m a.s.l.
- Granica (GR) is located west of the Warsaw conurbation, in a forested area of Kampinos National Park: φ = 52°17' N, λ = 20°27' E, H = 72 m a.s.l.
- Belsk station (BE) is located in a rural area considered to be a background station for the Warsaw region: φ = 51°50' N, λ = 20°47' E, H = 176 m a.s.l.

In addition to these seven stations, data from the Komunikacyjna district station (WKo) in the city center was used, but only for presentation of a course of NO_2 concentrations [17].

Table 1 shows average means values of ozone by day of week (DOW) for each station, the days of the week on which the mean is lowest and highest, and their locations. In addition to mean concentration by DOW, we also calculated the average peak concentration of ozone for

Fig. 1. Measurement site location.

Table 1. Mean concentrations of ozone for each day of the week in $\mu g \cdot m^{-3}$.

Station	Location	Day of the week (Sunday = 1)							Day of week means		Day occurred	
		1	2	3	4	5	6	7	Lowest	Highest	Lowest	Highest
GR	**Fringe**	55.3	55.3	55.2	53.9	54.5	55.0	54.5	53.9	55.3	4	1
WK	**Core**	56.5	55.3	54.0	53.5	54.0	55.4	54.9	53.5	56.5	4	1
WU	**Core**	58.1	56.4	56.5	55.5	55.6	57.0	56.9	55.5	58.1	4	1
LE	**Fringe**	54.8	54.1	53.7	52.5	52.9	53.7	53.9	52.5	54.8	4	1
WP	**Core**	51.7	50.3	48.7	49.1	49.3	50.6	49.6	**48.7**	51.7	3	1
BE	**Fringe**	64.2	62.5	60.9	60.7	62.0	62.2	62.4	60.7	**64.2**	4	1
WT**	**Core**	53.6	51.2	51.3	52.6	50.7	53.4	57.0	50.7	57.0	5	7

*Based on hourly readings for May-September 2008-12. **Based on hourly readings for May-September 2011-12.

each DOW (Table 2). Harmonic analysis is commonly used in the atmospheric sciences to identify the significance of cycles through a defined, fundamental period. Studies of the diurnal cycle of atmospheric phenomena, often precipitation, define the fundamental period as 24 h [18]. Studies such as ours define the fundamental period as seven days in the week [19]. Other studies examine annual cycles in monthly data with a fundamental cycle of 12 months [20].

We conducted harmonic analysis by pollutant and location to identify weekly cycles in ozone and NO_2 pollution metrics. The basic form of the harmonic equation is:

$$f(x) = \bar{X} + \sum_{r=1}^{N/2} A_r \cos(r\theta - \Phi_r) \tag{1}$$

…where f(x) is the estimated value of ozone for each DOW, $\overline{X}$ is the average value over the N = 7 observations, A_r is the amplitude of the harmonic wave (we only used the first harmonic), r is the frequency or number of times the harmonic wave is repeated over the fundamental period (equal to 1 given our exclusive use of the first harmonic fit), θ is derived as $2\pi x/N$ (where x represents intervals 1-7 through the fundamental period of seven days), and Φ_r is the phase angle of the rth harmonic, often reinterpreted as the time of maximum. We calculated WE using four methods:

Method 1 followed the standard protocol of measuring WE as the percentage difference in the mean on Sundays, minus the mean on Wednesdays, divided by the mean on Wednesdays [6].

Method 2 used the percentage difference in the peak ozone concentration on Sundays minus the peak concentration on Wednesdays, divided by the peak on Wednesdays.

Because not all minima occur on Wednesdays and not all maxima occur on Sundays (see Table 1 and Fig. 2), we used two additional methods to calculate WE.

Method 3 defined WE as the sum of the percentage difference in the mean pollution levels on Saturday and Sunday at each station compared to the lowest daily mean for ozone. This method takes into account the full weekend – not just Sunday – and also allows for minima to occur on days other than Wednesdays.

Method 4 used the amplitude of the harmonic wave that we derived to describe the weekly cycle in the pollutants, divided by the mean level. The amplitude of the harmonic wave can be envisaged as the peak variation in the weekly pollution cycle. When divided by the mean level at a particular station, the measurement represents the maximum percentage from the mean over the course of a week. We calculated the mean concentration for O_3 and NO_2 on an hourly basis for each DOW to discern if there are any differences in diurnal patterns.

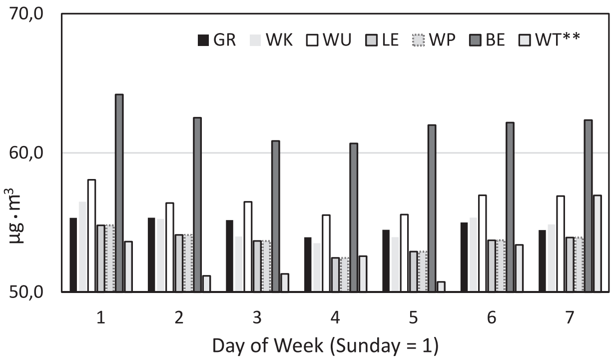

Fig. 2. Mean daily ozone concentrations for analyzed stations, based on hourly readings: May-September 2008-12; WT** 2011-12.

Results

Average means by DOW for each station and the week with the lowest and highest means, with the location, are shown in Table 1. For almost all sites, DOW levels follow a similar, roughly U-shaped pattern (Fig. 2). Concentrations are highest on Sunday, dip sharply on Mondays, remain relatively flat through Fridays, and rise sharply on Saturdays. While the patterns at each location

Table 2. Peak concentrations of ozone for each day of the week in μg·m^{-3}.

Station	Location	Day of the week, Sunday = 1							Day of week peak		Day occurred	
		1	2	3	4	5	6	7	Lowest	Highest	Lowest	Highest
GR	**Fringe**	157.6	179.9	167.0	165.1	153.6	166.8	151.1	151.1	**179.9**	7	2
WK	**Core**	157.1	148.4	145.0	144.1	158.0	171.2	151.7	144.1	171.2	4	6
WU	**Core**	155.2	142.9	142.2	138.8	153.5	164.5	155.4	138.8	164.5	4	6
LE	**Fringe**	145.6	136.6	146.2	144.1	152.7	165.5	159.7	136.6	165.5	2	6
WP	**Core**	156.8	150.0	139.0	143.6	148.0	165.0	158.0	139.0	165.0	3	6
BE	**Fringe**	149.9	140.6	142.9	140.6	160.5	145.4	167.5	140.6	167.5	4	7
WT**	**Core**	134.5	144.7	148.2	132.1	154.1	140.3	152.1	**132.1**	154.1	4	5

*Based on hourly readings for May-September 2008-12. **Based on hourly readings for May-September 2011-12.

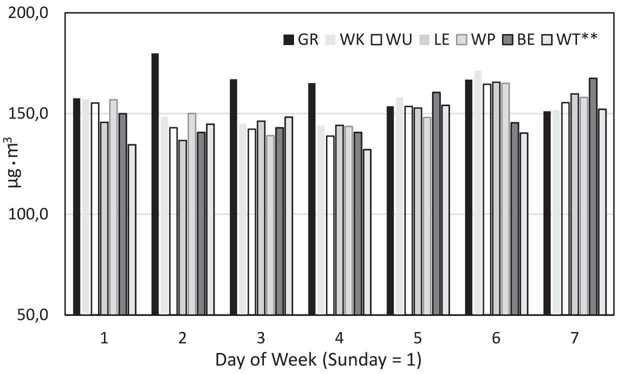

Fig. 3. Peak daily ozone concentrations for analyzed stations, based on hourly readings: May-September 2008-12.

are similar, daily means for the stations range from 48.7 μg·m^{-3} (WP on Tuesdays) to 64.2 μg·m^{-3} (BE on Sundays). In comparison to the other stations, a greater concentration of ozone was noticed at the Belsk station. The mean ozone concentrations by DOW for the fringe BE station are almost 20% higher than the concentrations at other stations, ranging from 60.7 μg·m^{-3} (on Wednesdays) to 64.2 μg·m^{-3} (on Sundays). In this analysis, the stations have a weekly cycle. In addition to the mean concentration by DOW, we also calculated the average peak concentration of ozone for each DOW (Table 2). At one of the seven sites, the highest peak occurred on Mondays (GR) 179.9 μg·m^{-3}. At four of the remaining sites, the peak occurred on Fridays (WK, WU, LE, WP). At Belsk station, the peak occurred on Saturdays (BE) and on Thursdays at the WT station.

There was more variability in the DOW on which the lowest peak occurred: Wednesday (4 stations: WK, WU, BE, WT), Monday (1 station: LE), Tuesday (1 station: WP), and Saturday (1 station: GR). These data are represented in Table 2 and Fig. 3. These differences underscore the limitations of using the standard method of quantifying WE as being the difference in ozone concentrations on Sunday and Wednesday.

Methods 1 and 2 were the percentage differences in the mean and peak for Sunday compared to Wednesday. For Method 1 (mean), these values ranged from 6% in the urban core (WK) and the fringe (BE), to 2% and 3% at the urban core (WT) and at the urban fringe (GR), respectively. However, a much wider range appeared when using the differences in the peak from 12% at the urban core (WU) to -5% at the urban fringe (GR). Notably, one urban fringe site showed a negative WE (GR). For Method 3 we considered the combined percentage difference in the mean for Saturday and Sunday from the lowest mean over the week. These values ranged from 32% at the urban fringe (GR) to 3% at the urban core (WT). With Method 4 we used the amplitude of the harmonic wave by the mean value of the harmonic. These ranged from 32% at the urban core (WT) to 5% at the urban fringe (GR) (Table 3). The goodness of fit of the weekly harmonic cycle describes the degree to which the pollutants follow a sine wave over the course of a week – the greater the fit, the closer the data are to a wave pattern. Because there are no naturally occurring seven-day cycles [19], a strong weekly harmonic cycle is a direct signal of anthropogenic activity, in this case vehicle emissions. The results show that there is a wide range in the extent to which ozone follows a weekly cycle, with

Table 3. Various measurements of ozone WE in the Warsaw conurbation, V-VIII 2008-12.

Station	Location	Method 1	Method 2	Method 3	Method 4
		(%)			
GR	**Fringe**	3	**-5**	32	5
WK	**Core**	6	9	9	11
WU	**Core**	5	12	9	9
LE	**Fringe**	4	1	7	8
WP	**Core**	5	9	10	12
BE	**Fringe**	6	7	6	11
WT**	**Core**	2	2	3	32

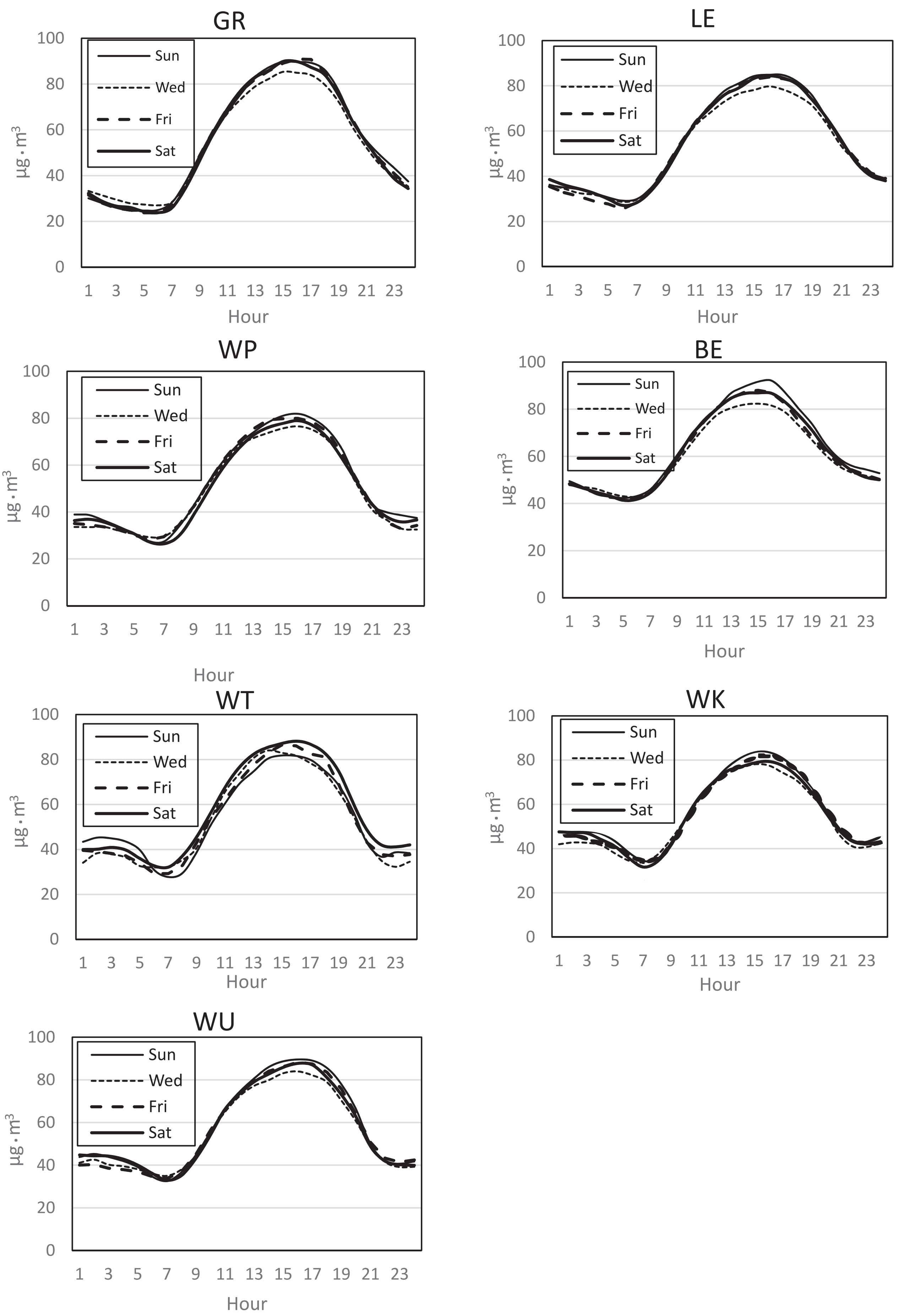

Fig. 4. Diurnal ozone concentrations (mean level for V-IX 2008-12 with the exception of WT station mean level for summer 2011-12).

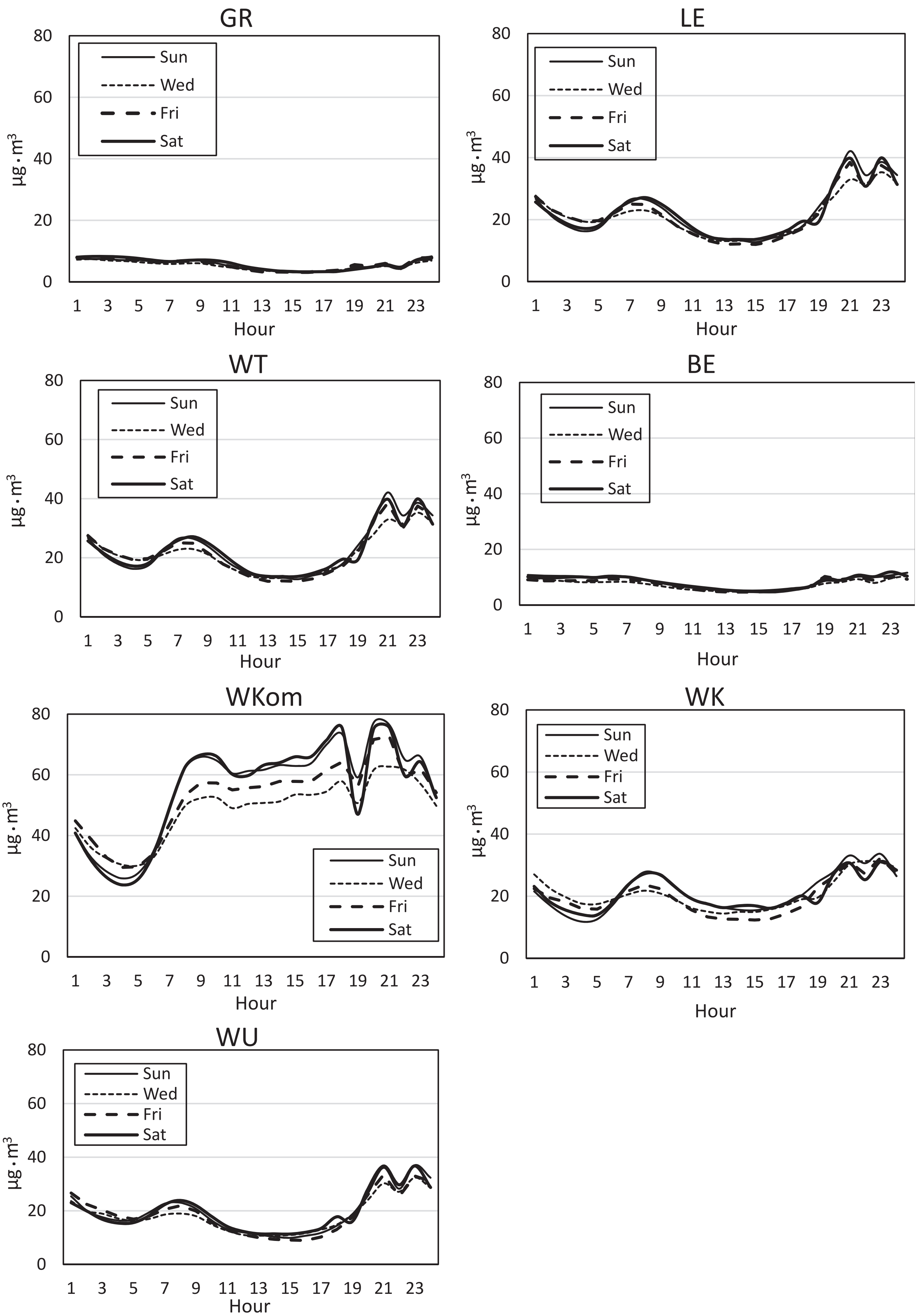

Fig. 5. Diurnal nitrogen dioxide concentrations (mean level for V-IX 2008-12).

the degree of fit from 45% (WP, GR) to 87% (LE). Ozone levels are highest at the fringe Granica and Belsk stations, where Ellis et al [6] have shown that ozone accumulates.

Discussion of Results

The analysis of diurnal patterns for ozone by DOW at the urban core and fringe sites shown in Fig. 4 reveals a similar pattern: a peak on Sunday (LE, WP, WU, BE) or Friday (WK, GR) or Saturday (WT) at 16:00, high carry-over of around 40 $\mu g \cdot m^{-3}$ in the evening of the next day from 22:00 onwards at that level until 07:00 the next morning, after which the levels increase. Fig. 4 shows data from the urban and fringe samples.

Comparable charts of urban and fringe sites are similar. Both the highest and the lowest values of ozone concentration were recorded for the GR, BE, and LE fringe stations, while levels during the week follow a similar pattern, with Saturdays and Sundays taking higher morning dips than weekdays.

The diurnal pattern of NO_2 at the urban core site in WK and at WKo is very specific (Fig. 5). From Monday to Friday diurnal patterns are very similar to the lowest values of concentration for Wednesday. Pearson correlation coefficients of the hourly readings by DOW ranged 0.97-0.99. The most distinct differences occur on Saturday and Sunday mornings at approximately sunrise (05:00), when NO_2 levels rise rapidly until 9:00, remaining at a relatively high level (70-80 $\mu g \cdot m^{-3}$ for WKo) until late evening (21:00). The values of NO_2 concentrations and their variations at the urban stations located away from the city centre and at the fringe stations are much lower. There are two characteristic peaks that are lower in the morning (8:00) and higher in the evening (21:00; in contrast, a very steady course of concentration occurs at GR and BE stations). In these cases, the concentration remains at a constant low level (10 $\mu g \cdot m^{-3}$) all day and throughout the week (Fig. 5).

The analysis indicates that all of the stations considered present higher ozone levels during the weekend than on weekdays. At the urban core stations, the daily mean ozone concentration and daily maximum ozone peaks are 13% and 8%, respectively – higher than those on weekdays, despite a reduction in NO_x levels of approximately 20%. Moreover, at all stations the mean percentage difference in ozone levels is always twice as high between Sundays and weekdays as it is between Saturdays and weekdays. Analysis of diurnal ozone and NO_x behaviour confirms the hypothesis that the most likely cause of higher mean weekend ozone levels is a reduction in ozone suppression due to lower NO_x emissions on weekend mornings. The reduction in emissions from industrial/traffic-heavy sectors on Sunday (and to a lesser extent on Saturday) leads to greater reduction in NO_x relative to VOC, and thus higher VOC/NO_x ratios on weekends [7]. This is an important result, as higher VOC/NO_x ratios in VOC-limited areas increase the efficiency and rate of ozone formation on weekends [9]. In addition, the reduced weekend NO_x emissions from automobiles during the morning period reduce the extent of ozone inhibition by titration of ozone with NO, allowing ozone to accumulate earlier in the day during the weekend. Our results suggest that control strategies involving only a decrease in NO_x levels may not be sufficient to reduce high ozone levels in this area. Further studies on the role of VOC species and on atmospheric transport and dispersion dynamics, by means of more detailed measurements and photochemical models, are necessary [7]. The WE phenomenon has been observed in many other polluted urban atmospheres, where changes in VOC/NO_x ratios that occur on weekends lead to higher ozone concentrations on weekends [21-24].

Summary and Conclusions

Our analysis indicates that all of the stations present higher ozone levels during the weekend than on weekdays. The four methods used for calculating the WE produce considerably different results that vary with location type:

– Method 1 shows a positive Weekend Effect for all types of stations based on mean ozone concentrations by DOW.
– Method 2 uses peak ozone concentration by DOW, and shows a more pronounced WE. For fringe stations LE and WT, peak ozone concentrations show either a muted WE, no effect, or the opposite effect (at the GR station) – that is, the levels are lower on weekends.
– For method 3, which looks at the combined Saturday and Sunday mean ozone concentrations compared to the lowest mean level, WE ranges from 3% to 10% in the urban core, and from 6% to 32% at the urban fringe. This basis of calculation takes into account the fact that the highest peak concentrations of ozone occur mainly on Saturdays.
– Method 4 describes the degree to which mean levels of ozone by DOW follow a cycle.

Methods 1, 3, and 4 are all based on mean ozone concentrations of ozone by DOW. Method 2 is based on peak ozone concentration (as can be seen in Fig. 1, mean concentrations of ozone are evidently higher for the BE fringe site on weekends). The diurnal patterns of ozone and NO_2 shown in Figs 4 and 5 show that the most likely cause of higher means of ozone on weekends is a reduction in ozone titration as a result of reduced vehicle emissions and hence NO_2 levels.

The four methods used to calculate WE give different results in relation to the stations analyzed. In the results for Method 1, based on the analysis of average values of ozone concentrations for all stations, WE is indicated by values greater than 0. The highest values (5% to 6%) were recorded for the urban stations (Krucza, Ursynów and Podleśna), and the station representing the agricultural area (Belsk). Slightly lower values (3% to 4%) were recorded for the stations located on the outskirts of the conurbation (Legionowo and Granica). Similar results were obtained with Method 4, which is based on the values predicted from the equation harmonic function. In this case, WE at the urban stations is 9% to 12%, and for the stations located on the outskirts, 5% to 8%.

A similar structure as found in Method 1 results can be seen in the ratios calculated using Method 2, which is based on an analysis of the maximum concentration values. The highest values (9% to 12%) were recorded for the urban stations (Krucza, Ursynów, and Podleśna) and the lowest (7%) for the Belsk agricultural station. WE does not occur at the stations located on the outskirts of the city, and this is indicated in the results as values lower than 1% for Legionowo, and even negative values (-5% at Granica).

The results of the Method 3 calculations for average ozone concentrations on weekends and weekdays indicate WE occurring at the urban stations (9% to 10%, Belsk) located in the rural area, and at Legionowo on the outskirts (6% to 7%). In comparison with the other stations, the result obtained for Granica (on the fringes) is substantially different (32%). Results for particular stations indicate that for Granica there is a very wide variance: from no WE (calculated with Method 2), to a very strong WE (calculated with Method 3). This wide variation in results also holds true for Targówek. According to Methods 1, 2, and 3, a low WE is indicated, while Method 4 returns a WE of 32%.

The diurnal patterns of ozone and NO_2 given in Figs 4 and 5 show that the most likely cause of higher ozone on weekends is a reduction in ozone titration as a result of reduced vehicle emissions, and hence NO_2 levels [25, 26]. Analysis of diurnal ozone and NO_x behaviour confirms the hypothesis that the most likely cause of higher mean weekend ozone levels is a reduction in ozone suppression due to lower NO_x emissions on weekend mornings. The reduction in emissions from industrial/traffic-heavy sectors on Sundays (and to a lesser extent, Saturdays) leads to a greater reduction in NO_x relative to VOC, and thus higher VOC/NO_x ratios on weekends. This is an important result, as higher VOC/NO_x ratios in VOC-limited areas increase the efficiency and rate of ozone formation on weekends [9]. In addition, the reduced weekend NO_x emissions from automobiles during the morning period reduce the extent of ozone inhibition by titrating ozone with NO, allowing ozone to accumulate earlier in the day on weekends. Our results suggest that control strategies that involve only decreased NO_x levels may not be sufficient to reduce high ozone levels in this area.

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