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Statistical Analysis of Ozone Weekend Effect in the Largest Cities in Poland

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Abstract: This study examines O_3, NO_x, NO_2 and NO data from five large cities in Poland (Warszawa, Kraków, Łódź, Wrocław and Poznań) over a three-year period (2015-2017) to quantify the phenomenon of ozone weekend effect. The seasonal and diurnal variations of O_3 and NO_x species, showing the interdependence these two gaseous species, were presented. The number of 8-hour running average values above the threshold of 60 ppb and 1-hour above 90 ppb shows that ozone exceeded amounts are more frequent on Saturday and Sunday compared to other days of the week. The analysis of day of the week variations of O_3 indicates distinct, temporal pattern with maximum O_3 concentrations during weekend (especially on Sunday) and minimum noted on Wednesday, Thursday and Friday (depending on the station). The analysis of existence of the ozone weekend effect was performed on the basis of average O_3 concentration at the weekend and on the day of the lowest O_3 concentration during the week. Calculations were performed for the period of the whole year and for individual seasons of the year. The results of performance the non-parametric U-Mann-Whitney test indicate that differences of O_3 concentration between weekend and a specific day of the week were statistically significant for most cases, despite the significantly lower concentration of ozone precursors (NO_x). The analysis of O_x concentrations indicates that limited processes of O_3 titration by NO (ozone quenching hypothesis) are the main cause of the ozone weekend effect in the Polish cities.

Keywords: Ozone Formation, Ozone Weekend Effect, VOC/NO_x Ratio, Nitrogen Oxides

1. Introduction

Tropospheric ozone, a photochemical oxidant, is an essential, secondary pollutant in the air [1].

Ozone in the troposphere is produced by the chain of reactions involving NO_x and VOCs with the participation of solar UV radiation [2]. The cycle of ozone formation begins with the process of the photolysis of NO_2.

$$NO_2 + h\nu\ (\lambda<424\ \text{nm}) \rightarrow NO + O \quad (1)$$

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

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

Above reactions form the steady-state equilibrium for the surface ozone concentration. The photochemical net ozone production occurs when NO_2 is formed without the destruction of O_3 and the rate of photochemical ozone production is dependent on reaction of NO with peroxy radicals (HO_2 and RO_2) which are generated through the reactions of OH radicals with VOC and CO.

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

$$RO + O_2 \rightarrow R'COR'' + HO_2 \quad (5)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (6)$$

The reaction (4) is the most crucial because it generates the oxidants whilst the other reactions only replace one oxidant with another [3].

The main source of OH radicals is photolysis of O_3. This process, by using one O_3 molecule, could result in generating two OH radicals.

$$O_3 + h\nu\ (\lambda<310\ \text{nm}) \rightarrow O(^1D) + O_2 \quad (7)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (8)$$

The processes of ozone formation are complex and strongly dependent on the local VOC/NO_x ratio in the atmosphere [4]. At high VOC/NO_x ratio, OH radicals reacts predominantly with VOC producing new OH radicals and enabling O_3 formation. In these conditions ozone production is more efficient when NOx concentration increase (NO_x limited regime). At low VOC/NO_x ratio OH radicals frequently reacts with NO_2 removing radicals from the atmosphere and inhibiting production of O_3. In these conditions, O_3 production decreases when NO_x concentration increases (VOC limited regime).

Concentrations of pollutants, both primary and secondary, reveal distinct weekly patterns which are directly connected with a different human activity and consequently, result in variations of local emission level.

Phenomenon of "ozone weekend effect" (OWE) was first observed in the early 1970s in Los Angeles [5]. It is characterized by higher surface ozone concentrations at weekends in comparison to weekdays, despite limited emission of NO_x and VOC (two main precursors of surface ozone formation). The existence of OWE concerns especially urban areas with significant local pollution and additionally, it demonstrates differentiation over the course of the week [6-8].

The quantity of OWE is determined by a number of factors particularly linked with the difference in weekend/weekdays emission and the nonlinear photochemistry of ozone production strongly dependent on initial VOC/NO_x ratio. Ozone weekend effect is the greatest in locations where ozone formation takes place under lower VOC/NO_x ratio on weekdays and higher VOC/NO_x ratio at the weekends [9].

Urban areas are frequently characterized by a low VOC/NO_x ratio and it causes them to be of a VOC-limited chemical regime. During the weekend the reduction of NOx (due to a limited vehicle emission) is more efficient than the reduction of VOC, and consequently on Saturday and Sunday the VOC/NOx ratio is higher than on weekdays [9-10]. High emission of NO_x during weekdays determines the chain of reactions: $NO+O_3 \rightarrow NO_2+O_2$ (ozone titration) and following: $NO_2+OH \rightarrow HNO_3$ (OH reacts frequently with NO_2 removing radicals from the atmosphere and delays ozone formation). At the weekends the emission of NO is decreased and as a result, the processes of ozone titration are limited. Decrease of NO_x during the weekend contributes to more OH – radicals which can react with VOC and increase O_3 concentration [8]. Additionally, in the presence of VOC (simultaneously RO_2-as an effect of VOC oxidation) there is a reaction when NO_2 is produced without the consumption of ozone: $RO_2+NO_3 \rightarrow NO_2+RO$ allowing the accumulation of O_3 [4].

Despite the numerous studies concerning the genesis of OWE, no definitive cause for this phenomenon has been determined. Most researchers concluded that the main cause of higher ozone concentration at the weekends is lower NO_x emission in a VOC – limited regime [11-13, 8]. Lower NO_x emission during weekend (as a consequence of limited on-road traffic) reduces the process of ozone destruction through the reaction of ozone titration: $NO+O_3=NO_2+O_2$.

In Poland, the analyses of OWE were performed for Warsaw conurbation [14] and for Mazovian Region [15]. Both studies corroborated the presence of higher concentrations of ozone during weekends than on weekdays on urban background stations. The OWE was determined to be due to the limitation of titration of ozone by NO ($NO+O_3 \rightarrow NO_2+O_2$) as a result of lower NO emission on weekend mornings.

This study reports the analysis of phenomenon of OWE in urban areas including calculations of the seasonal, weekly and diurnal variations of O_3 and NO_x, the number of O_3 exceeded amounts (8-hour running average value > 60 ppb and 1-hour average value > 90 ppb) depending on the day of the week and finally the examination of the statistical significance (existence or nonexistence) of the ozone weekend effect and determination of its plausible cause.

2. Materials and Methods

2.1. Site Description

The data analyzed in this work consists of hourly O_3, NO, NO_2, NO_x concentration values (ppb) from 5 air quality stations located in the largest cities in Poland: Warszawa – Ursynów (102 m.a.s.l.), Kraków - ul. Bujaka (223 m.a.s.l.), Łódź – Widzew (235 m.a.s.l.), Wrocław - Korzeniowskiego (114 m.a.s.l.) and Poznań - WKPPoznań2 (84 m.a.s.l.). The location of each station is depicted in Figure 1.

All 5 monitoring stations represent urban background conditions. Warszawa, the capital city of Poland and the largest metropolitan area in Poland, the only one with a population of over 1,000,000 (approximately 1,793,000 in 2020). The remaining cities represent urban areas with a population from 533,830 (Poznań) to 780, 981 (Kraków).

2.2. Analysis of Air Quality Data

The time of the analysis covers the period from January 2015 to December 2017. A 3-year measurement period is considered to be optimal for investigating the phenomenon of OWE and often used by researchers [4, 2, 13]. The fulfillment of the data completeness criteria was 75% of the hours during a day. NO was calculated as a result of subtraction of NO_x and NO_2 (NO_x-NO_2=NO). The variability of O_x oxidants (calculated as a sum of NO_2 and O_3) was also investigated. Measured data were obtained from the air pollution monitoring system set up by the Chief Inspectorate of Environmental Protection. Measurements of gaseous pollutants are made by analyzers using standard UV photometry (ozone) and chemiluminescence (nitrogen compounds) methods.

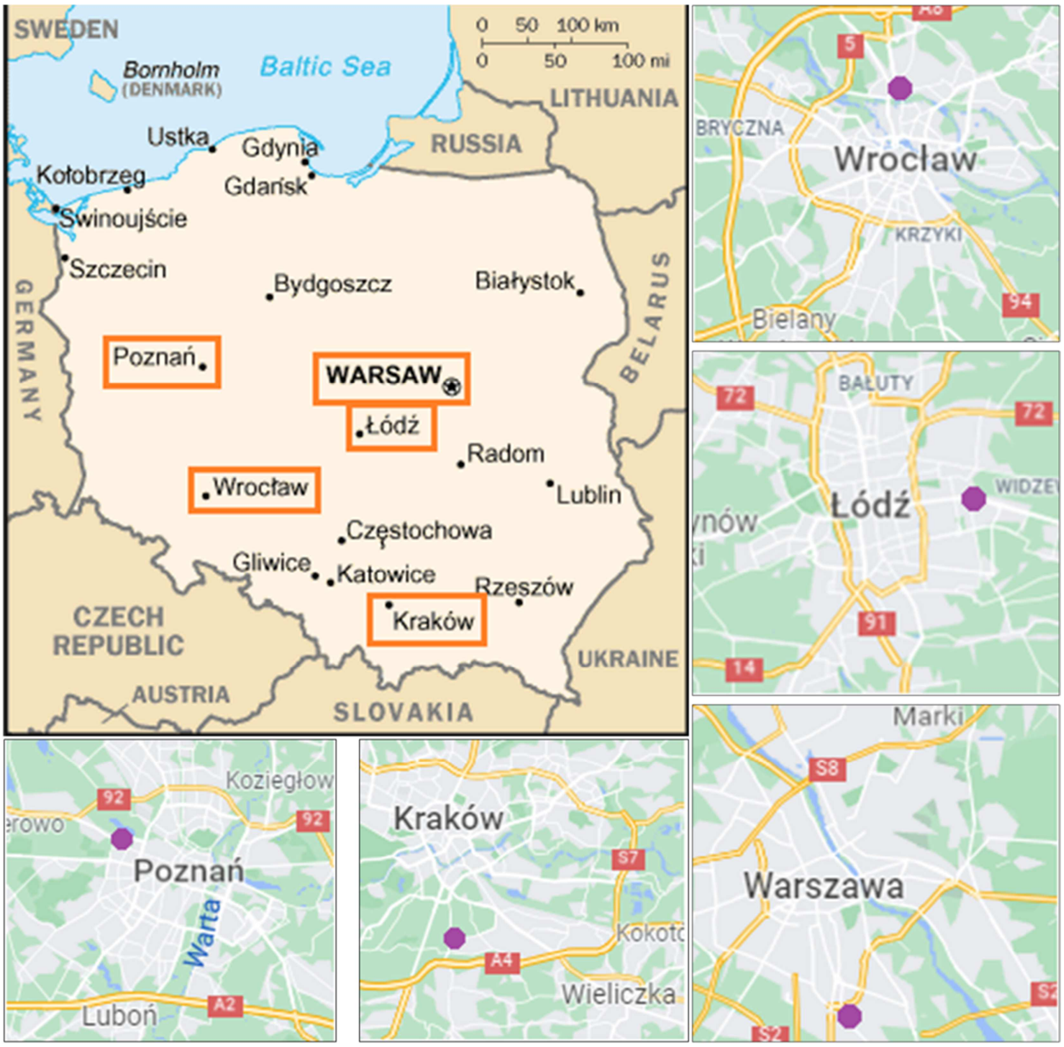

Figure 1. Map of Poland with the location of selected monitoring stations and the location of the stations within the city (purple dots). (corrected versions, source: europeetravel.com; www.maps.google.com).

3. Results

3.1. Seasonal Variation of O_3 and NO_x

The seasonal variations of O_3 are determined by many factors including: geographical location, meteorological conditions and availability of ozone precursors (especially NO_x and VOC) [16]. Intensity of chemical processes, transport and deposition are as equally important [17]. Figure 2 shows the monthly averages (calculated on the basis of daily average values) of concentrations of O_3 (on the top) and NO_x Higher concentrations of O_3 during spring and summer resulted from effective photochemical ozone production favored by high temperatures and intensive solar radiation [18]. The highest concentrations of O_3 were observed from May to August. Depending on the station the maximum was noted in May (Wrocław 34.2±7.7 ppb, Łódź 38.1±6.7 ppb), in June (Kraków 28.5±7.7 ppb) and in August (Poznań 32.5±10.4 ppb, Warszawa 32.5±9.5 ppb). The minimum values of O3 concentrations, at all stations were noted in November and ranged between 8.8±5.7 ppb (Kraków) and 13.9±6.8 ppb (Łódź). Analyzed concentration of O_3 depended on the station, the highest values were noted in Łódź and the lowest in Kraków (average value for 2015-2017 was equal to 26.6±11.9 ppb and 18.3±9.8 ppb, respectively). Additionally, all the stations present double maximum observed in May and in August with the exception of Kraków where single maximum in June was noted. Looking at NOx chart, we can see that seasonal variations in NOx were exactly inverse to those of ozone, reaching the maximum values during autumn and winter and the minimum during spring and summer. The highest values of NOx concentrations were noted in Kraków where the average value for 2015-2017 (42.0 ±36.0 ppb) were more than 3 times higher compared to Łódź (16.8 ±7.3 ppb) and more than 2 times higher than in Wrocław and Poznań (18.8±15.5 ppb and 21.6±20.7 ppb, respectively). So high values of NO_x concentrations in Kraków resulted especially from: low emission (burning low-quality coal in coal furnaces), intensive on-road emission (Kraków is one of the most popular touristic cities in Poland) and additionally, unfavorable location of the city in the Vistula River, surrounded by the terrain hills (3 sides) which hinders the effective ventilation of the city.

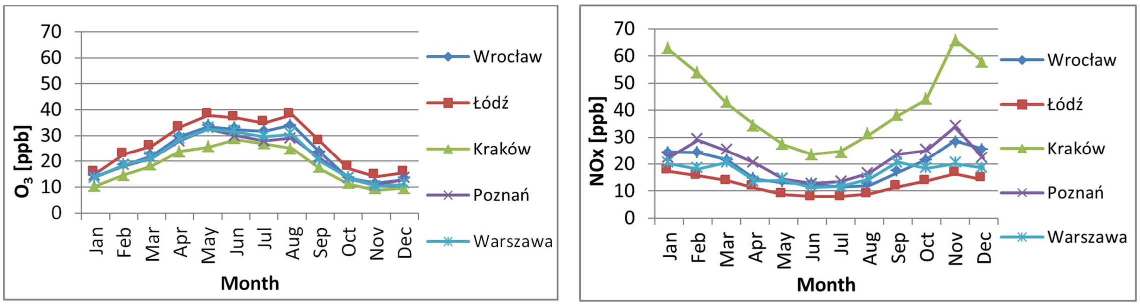

Figure 2. *Monthly average values of O_3 (on the top) and NO_x (on the bottom) for the period 2015-2017 (on the bottom) at the 5 urban stations from 2015 to 2017. At all stations a specific pattern with spring-summer maximum and autumn-winter minimum was observed.*

3.2. Diurnal Variation of O_3, NO_x, NO_2, NO

Diurnal patterns of analyzed pollutants can be explained by: emission rate of both natural and anthropogenic sources, photochemical processes between reactants, meteorological conditions such as solar radiation, temperature, relative humidity and mixing processes including vertical convections and horizontal dispersion [19-20].

The typical 24-h cycle of ozone concentration is characterized by consistently low values during night reaching the minimum just before the sunrise, steady and slow growth reaching the maximum values in the afternoon, and gradual decrease to low values during the evening. According to Fujita et al., [9] it can be divided into four phases: 1) night carryover of O_3 precursors 2) O_3 inhibition phase 3) O_3 accumulation phase 4) post maximum O_3 phase.

Figure 3 presents an example of diurnal variation in concentration of O_3, NO, NO_2 and NO_x on weekdays and weekends (2017) for Kraków station. All pollutants showed a quantitative difference between weekdays and weekend. In general the concentration of O_3 during weekends was higher while the concentration of NO, NO_2 and NO_x during the weekends was lower. Moreover the diurnal variations of NO were greater compared to NO_2, probably due to higher reactivity of NO and shorter lifetime of NO [21].

During the carryover phase, lasting from mid-night to 04:00 (CET), there is no difference of O_3 and NO_2 concentration between weekdays and weekends (approximately 13,5 ppb and 15,5 ppb respectively). NO is approximately 11% higher on weekdays. Despite the small differences the concentrations values between weekdays and weekends are very similar.

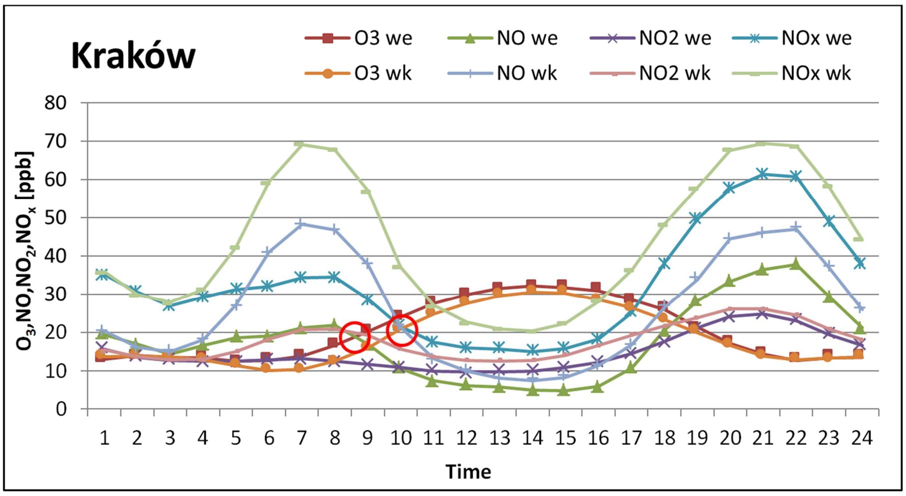

Figure 3. *Diurnal variation of O_3, NO, NO_2, NO_x on weekdays (wk) and weekends (we) for 2017 (Kraków). Red marks indicate the cross-point of NO and O_3.*

From approximately 05:00 the ozone inhibition phase begins. Fresh emission of NO (corresponding with morning traffic rush hour) inhibit O_3 formation via the efficient process of O_3 titration ($O_3+NO \rightarrow NO_2+O_2$). Additionally O_3 production is limited by the reaction of NO_2 with OH radicals [22]. Due to definitely more intensive on-road emission by automobiles on weekdays the mean NO concentration is twice as large on weekdays compared to weekends (approximately 20 ppb and 40 ppb respectively). The maximum 1-hour value of NO on weekdays is equal to 48 ppb and 22 ppb on weekends. NO_2 concentration values stays on similar level as during previous phase, both on weekdays and at the weekends (18 ppb and 13 ppb respectively). O_3 concentration following low values reaches minimum at 05:00-06:00 during weekends (13 ppb) and 06:00-07:00 during weekdays (10 ppb). Reaching O_3 minimum early in the morning, just before the sunrise, is caused mainly by intensive processes of O_3 titration and the lack of photochemical ozone production (absence of solar radiation). The time after the morning NO peak, when lines of NO and O_3 concentration intersect with each other is the end of inhibition phase and start of O_3 accumulation period. The conversion of NO to NO_2 using peroxy radicals begins the cycle of ozone production. It is of the essence that the point of intersection and simultaneously the start of O_3 accumulation phase is approximately 1,5 hour earlier at the weekend compared to weekdays (approximately 09:10 on weekends and 10:40 on weekdays). The duration of accumulation phase is limited by the time of O_3 maximum (14:00 on both weekends and weekdays). The daytime increase and maximum of O_3 concentration is the result of photochemical reactions of O_3 precursors with the presence of solar radiation [23]. The duration of O_3 accumulation phase was estimated as a difference between the time of O_3 maximum and the time of O_3-NO intersection. This value is equal to 04:50 hour for weekends and 03:20 hour for weekdays. The shorter length of ozone inhibition phase at the weekend is a result of significantly lower NO emission values on weekend mornings. When O_3 reach peak values the NO and NO_2 records the lowest concentrations during a day reaching 5,5 ppb and 9,7 ppb on weekends and 7,5 ppb and 12,7 ppb on weekdays, respectively. In this phase the NO_x accumulation is negligible due to high photochemical consumption. From 14:00 up to mid-night there is a phase of O_3 reduction, mainly due to a decline of photolysis rate (less intensive solar radiation) and due to titration of O_3 by NO (new NO emitted during evening traffic rush hour). O_3 concentration values during approximately 8 hour decreases by 20 ppb and 17 ppb at the weekend and on weekdays, respectively.

During weekends the evening peak of NO and NO_2 is approximately 40% higher in magnitude than the morning peak. This difference can result from a different activity of society during non working days (shifted more to afternoon and evening because no need to drive to work in the morning). Classical bimodal traffic pattern: home-work, work-home in these days is changed. In the case of weekdays the NO concentration values during morning and evening peaks is comparable while NO_2 is 22% higher during the evening peak.

Generally, concentrations of NO_x and O_3 is negatively correlated. Such a dependence may indicate a probable VOC-sensitive nature of urban areas. In these conditions the decrease of NO_x and increase of VOC results in growth of O_3 formation. High concentration of NO_x consumes available OH radicals limiting the oxidizing potential of NO_2 and VOC, main ozone precursors [24].

3.3. Day of Week Analysis of Ozone Exceedances

Data of O_3 concentration for the period 2015-2017 from all stations were analyzed to examine the number of 8-h running averages and number of 1-h averages when target threshold (60 ppb) and information threshold (90 ppb) (respectively), established to protect human health, were exceeded depending on the day of the week (Figure 4).

The statistics presented in the Figure 4 show that the greatest number of 8-h averages exceeding the target of 60 ppb was noted at Łódź station (375) and the lowest at Warszawa station (146). There is a distinct temporal pattern, with a number of exceeded amounts increased during weekend (especially on Sunday) and continued at the beginning of next week (Monday), what is clearly depicted especially in Łódź, Kraków and Poznań. At all stations (with the exception of Warszawa) the maximum number of 8-h averages with concentrations of $O_3 > 60$ ppb was observed on Sunday. This pattern can be explained by the limited local emission of NO_x during the weekends. The sum of exceeded amounts noted at the weekend (Saturday and Sunday) ranged between 35% (Warszawa) and 44% (Poznań) of total exceeded amounts calculated for all the week. The information threshold (> 90 ppb) was exceeded only in 2015 at 3 out of 5 stations: Wrocław, Poznań and Kraków. The number of episodes was 9, 3 and 4 respectively, whereas the vast majority of cases: 8, 2 and 2 (respectively) were noted at the end of the week (Friday, Saturday and Sunday).

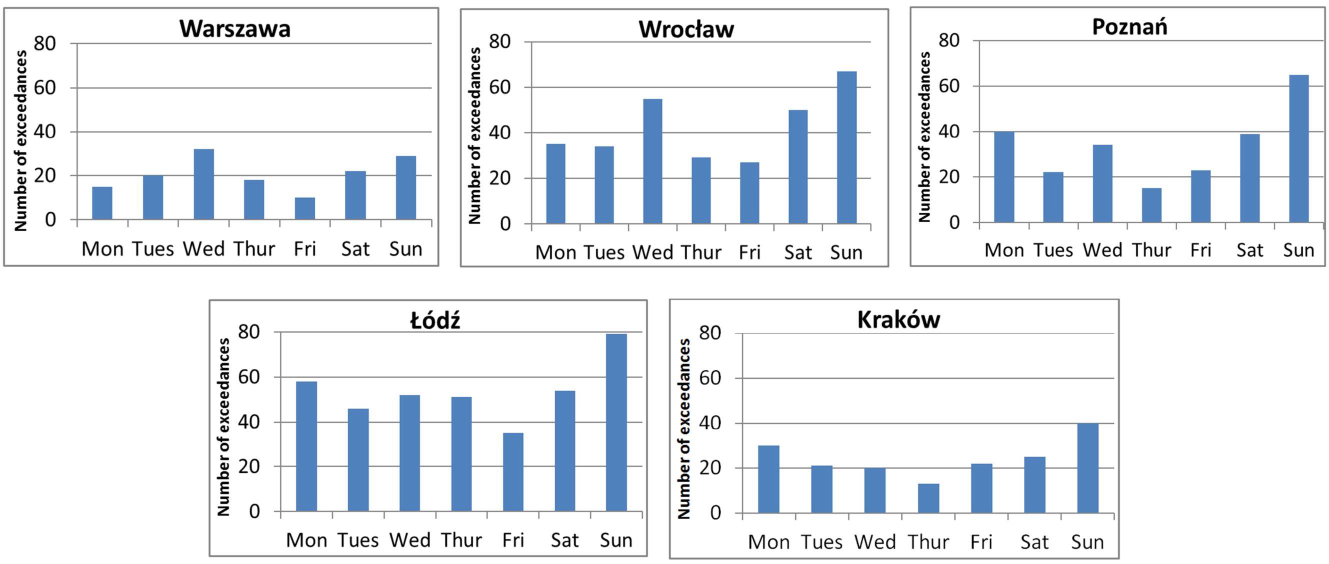

Figure 4. *Number of episodes (calculated as a 8-hours moving avarage value of ozone concentration > 60ppb) on each day of the week at all urban stations for the period from 2015 to 2017.*

3.4. Weekend/Weekday Variations of O_3 and NO_x

The mean concentration of ozone by day of the week for each station are presented in Table 1.

For all cities, weekly ozone variation unveil a similar U-shaped pattern (the highest values on Sunday, rapid decrease on Monday, minimum on Wednesday, Thursday or Friday and stable increase up to next Sunday). Although the pattern at each station is comparable the values of daily means vary widely depending on a location. The highest concentrations, noted on Sunday, ranged from 21.0±9.6 ppb in Kraków to 29.3±10.9 ppb in Łódź. The lowest values in Poznań and Warszawa were noted on Wednesday (20.4±10.2 ppb and 20.3±10.3 ppb, respectively), in Wrocław and Łódź on Thursday (21.7±11.9 ppb and 25.3±12.3 ppb, respectively) and in Kraków on Friday (reaching 17.0±10.3 ppb). In spite of the significant differences in diurnal ozone concentrations the magnitudes of difference between the day with the highest and the lowest values were comparable and ranged between 3.8 ppb (Poznań) and 4.7 ppb (Wrocław). This may indicate an existence of OWE on a similar level in all cities. Figure 5 presents the weekly cycle of O_3 and NO_x for each station during the period 2015-2017.

Table 1. *Average diurnal concentration of O_3 (together with standard deviation) for the period 2015-2017. The minimum and maximum values during the week are bolded.*

	Ozone [ppb]				
	Wrocław	Łódź	Kraków	Poznań	Warszawa
Mon	23.1±11.0	26.9±11.3	17.8 ± 9.6	21.7 ± 10.1	22.2± 10.6
Tue	21.9±11.3	25.9±12.0	17.8 ± 9.7	21.1 ± 11.0	21.2± 10.8
Wed	21.8±11.4	25.7± 11.9	17.9 ± 9.5	20.4 ± 10.2	20.3± 10.3
Thu	21.7±11.9	25.3± 12.3	17.9 ± 9.9	20.6 ± 10.7	20.9± 10.4
Fri	22.1±11.4	25.6± 12.1	17.0± 10.3	20.4 ± 10.6	20.7± 10.7
Sat	25.3±11.6	27.8± 12.3	18.7 ± 9.8	22.9 ± 11.0	23.0± 11.1
Sun	26.4±10.6	29.3± 10.9	21.0 ± 9.6	24.2 ± 9.8	24.2± 10.0

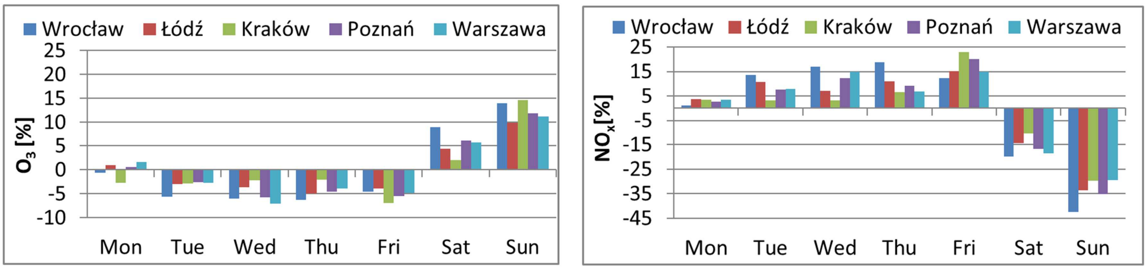

Figure 5. *The weekly variation of the concentration of O_3 (on the top) and NO_x (on the bottom) presented as a percentage differences of average value for all week (line 0-y axis) and for each day of the week.*

The height of bars is a percentage difference between average value for all week and average value for individual days. Average value for all week was taken as a 0 value on the y axis. The mean values of ozone for each station are as follows: 23.2±11.4 ppb at Wrocław, 26.7±11.9 ppb at Łódź, 18.3±9.8 ppb at Kraków, 21.6±10.6 ppb at Poznań and 21.8±10.6 ppb at Warszawa. Mean values of NO_x were equal to: 18.9±15.5 ppb, 12.3±7.3 ppb, 42.1±36.0 ppb, 21.5±20.7 ppb and 16.8±11.8 ppb respectively. In case of O_3, positive deviations were noted on weekend at all stations wherein on Sunday values of deviations were at least twice as high as on Saturday reaching maximum values 14% and 14,6% at Wrocław and Kraków respectively. Additionally, in Łódź, Poznań and Warszawa positive deviations were noted also on Monday, albeit their values were negligible (up to 1,6%). On the other days of the week (Tue-Fri) negative deviations (up to 7%) were noted. Analogical differences from the weekly average, as for O_3, were calculated for NO_x. Negative deviations were noted on weekend at all locations. The highest values were noted on Sunday (from 30% in Warszawa and Kraków to 42% in Wrocław). On Saturdays values oscillated between 10% (Kraków) and 20% (Wrocław). On weekdays positive deviations were noted, whereas the highest values for 4 stations (with the exception of Wrocław) were recorded on Friday. It is probably related to increased on-road traffic on that day, linked with the end of the working week and driving targeting leaving the city.

3.5. Statistical Analysis of the Ozone Weekend Effect

Calculations presented so far confirm the main assumption of OWE definition that is the existence of higher O_3 concentrations at the weekend with simultaneously lower concentrations of NO_x (at all stations). Furthermore they are the basis for the selection of method measuring the OWE. The standard method used for quantifying the existence of OWE is to compare the concentration of ozone on Sunday to those measured on Wednesday [25]. Analyzing Table 1, it can be stated that for all urban sites the highest value of O_3 concentrations occurred on Sunday, but the lowest O_3 concentration on Wednesday occurred only for 2 out of 5 analyzed sites (Poznań and Warszawa). For the remaining stations, the weekly minimum occurred on Thursday (Wrocław and Łódź) and on Friday (Kraków). These differences indicate limitations of the most common method of determining the ozone weekend effect.

For the purpose of this work the existence of OWE was determined as a difference (in ppb) between the concentration of ozone at the weekend (average value for Saturday and Sunday) and the concentration of ozone on the day of the week when O_3 concentration was the lowest (in this work referred to as weekly minimum). Depending on the station it was Wednesday (Poznań, Warszawa), Thursday (Wrocław, Łódź) and Friday (Kraków).

For every week of the 3-year measuring period and for every station the daily average of O_3 concentration for the weekend (Saturday - Sunday) and for Wednesday, Thursday and Friday (depending on the city) was prepared to calculate the weekend - weekly minimum differences. Then the averages of all weekends and appropriate days of the week were grouped into sets of data for different seasons during the analyzed period: spring (March - May), Summer (June - August), Autumn (September - November), Winter (December - February).

Table 2. *Weekend – the lowest day of the week differences of O_3 (together with standard deviation), where: We-mean O_3 concentration on weekend; Min – mean O_3 concentration on the lowest day of the week; We – Min – difference in ppb, percentage difference; p-value (U-Mann-Whitney test) ([a]) – p<0,005 ([b]) – p<0,1.*

	O_3 [ppb]			
	We	**Min**	**We-Min**	**p**
2015-2017 Entire period				
Wrocław	25,8±10,7	21,7±11,9	4,0 (16%)	0,003*
Łódź	28,6±11,1	25,4±12,3	3,2 (11%)	0,031*
Kraków	19,8±9,2	17,0±10,3	2,8 (14%)	0,009*
Poznań	23,6±9,9	20,4±10,2	3,2 (14%)	0,007*
Warszawa	23,7±10,1	20,2±10,3	3,5 (15%)	0,005*
2015-2017 Spring				
Wrocław	31,1±7,5	26,0±8,2	5,1 (16%)	0,005*
Łódź	34,2±7,3	30,3±7,9	3,9 (11%)	0,025*
Kraków	23,8±5,8	19,7±7,7	4,1 (17%)	0,011*
Poznań	28,5±7,1	26,7±7,3	1,8 (6%)	0,173
Warszawa	28,8±6,6	25,5±7,5	3,3 (12%)	0,036*
2015-2017 Summer				
Wrocław	34,9±7,2	33,1±7,7	1,8 (5%)	0,266
Łódź	38,0±8,8	36,7±9,1	1,3 (3%)	0,424
Kraków	27,8±7,5	27,0±8,1	0,8 (3%)	0,542
Poznań	31,2±7,7	27,6±8,2	3,7 (12%)	0,043*
Warszawa	32,3±7,5	29,4±7,9	2,9 (9%)	0,158
2015-2017 Autumn				
Wrocław	18,9±8,2	15,3±10,8	3,6 (19%)	0,069**
Łódź	21,9±8,3	19,2±11,3	2,7 (12%)	0,028*
Kraków	13,8±6,4	11,2±7,0	2,6 (19%)	0,088*
Poznań	17,6±7,6	13,3±7,4	4,3 (24%)	0,022*
Warszawa	17,1±6,9	12,5±6,9	4,6 (27%)	0,006*
2015-2017 Winter				
Wrocław	18,0±7,7	12,7±7,7	5,3 (29%)	0,005*
Łódź	20,4±7,2	15,9±7,7	4,5 (22%)	0,012*
Kraków	13,3±7,4	10,1±8,0	3,2 (24%)	0,015*
Poznań	16,8±7,3	14,1±8,1	2,8 (16%)	0,126
Warszawa	16,4±7,7	13,5±7,5	2,9 (18%)	0,079**

Table 3. *Weekend – the lowest day of the week differences of NOx (together with standard deviation), where: We-mean NOx concentration on weekend; Min – mean O_3 concentration on the lowest day of the week; We – Min – difference in ppb, percentage difference; p-value (U-Mann-Whitney test) (*) – p<0,005 (**) – p<0,1.*

	NO_x [ppb]			
	We	**Min**	**We-Min**	**p**
2015-2017 Entire period				
Wrocław	13.0±7.9	22.4±17.4	-9.5 (-73%)	0.000[a]
Łódź	9.4±4.2	13.6±7.2	-4.3 (-46%)	0.000[a]
Kraków	33.9±23.3	51.7±45.4	-17.9 (-53%)	0.000[a]
Poznań	15.9±10.2	24.2±28.3	-8.2 (-52%)	0.000[a]
Warszawa	12.8±6.8	19.3±13.5	-6.5 (-51%)	0.000[a]
2015-2017 Spring				
Wrocław	11.1±5.1	19.1±14.8	-8.0 (-72%)	0.000[a]
Łódź	8.4±2.4	12.4±4.2	-4.0 (-48%)	0.000[a]
Kraków	28.5±18.1	43.3±25.7	-14.8 (-52%)	0.002[a]
Poznań	14.7±8.0	18.4±12.1	-3.7 (-25%)	0.079[b]
Warszawa	11.9±4.8	19.2±9.0	-7.3 (-61%)	0.000[a]
2015-2017 Summer				
Wrocław	8.7±2.7	12.8±5.5	-4.0 (-46%)	0.000[a]

	NO_x [ppb]			
	We	Min	We-Min	p
Łódź	6.6±1.8	9.0±3.2	-2.4 (-37%)	0.000[a]
Kraków	22.4±6.5	30.3±13.8	-7.9 (-35%)	0.013[a]
Poznań	11.6±5.0	15.9±8.3	-4.4 (-38%)	0.006[a]
Warszawa	10.5±4.6	14.0±6.0	-3.5 (-34%)	0.002[a]
2015-2017 Autumn				
Wrocław	14.4±7.6	26.5±17.5	-12.1 (-84%)	0.000[a]
Łódź	10.2±3.3	16.4±8.4	-6.2 (-60%)	0.001[a]
Kraków	36.9±20.2	56.6±45.1	-19.7 (-53%)	0.061[b]
Poznań	19.5±13.1	32.2±35.9	-12.7 (-65%)	0.099[b]
Warszawa	13.9±7.2	23.8±20.7	-10.0 (-72%)	0.013[a]
2015-2017 Winter				
Wrocław	17.5±10.4	31.4±21.5	-14.0 (-80%)	0.000[a]
Łódź	12.2±5.9	16.8±8.3	-4.6 (-37%)	0.002[a]
Kraków	47.9±32.0	76.1±64.5	-28.2 (-59%)	0.049[a]
Poznań	18.0±11.0	30.7±39.3	-12.8 (-71%)	0.026[a]
Warszawa	14.7±8.8	20.5±11.8	-5.8 (-39%)	0.011[a]

Tables 2 and 3 present weekend – weekly minimum differences of O_3 and NO_x during the entire analyzed period (2015-2017) and additionally, for individual seasons for the years 2015-2017. The statistical significance of differences at each site was determined using non-parametric U-Mann-Whitney test ($p<0.05$ and $p<0.1$). This test does not require to meet the assumptions about the homogeneity of variance, equal number of cases in compared groups or existence of normal distribution.

The average O_3 concentration differences of the weekend and the weekly minimum (averaged for all stations) were about 14% over the period 2015-2017 and ranged between 11% in Łódź and 16% in Wrocław. The differences for individual seasons were equal to 13% during Spring, 6% during Summer, 20% during Autumn and 22% during Winter. The highest differences noted during Winter and Autumn oscillated within 16% in Poznań and 29% in Wrocław and within 12% in Łódź to 27% in Warszawa respectively. The lowest differences were noted definitely in the Summer ranging from 3% in Łódź and Kraków to 12% in Poznań.

Analyzing the existence of OWE during the entire analyzed period 2015-2017 it can be stated that concentration of O_3 at the weekends were significantly higher than those on Wednesday, Thursday and Friday (depending on the station) in all cities at the level $p<0.05$. Analyzing values of differences in particular seasons point out at the large discrepancy depending on the station which was observed. During spring season concentration of O_3 at the weekends was significantly higher ($p<0.05$) at all stations except Poznań. Opposite situation was noted in the summer, when only in Poznań concentration of O_3 at the weekends was significantly higher compared to the day of weekly minimum. During autumn significantly higher O_3 concentration at the weekends was noted at all stations, with significance level $p<0.05$ at Poznań and Warszawa stations and $p<0.1$ at Wrocław, Łódź and Kraków. During winter significantly higher concentration of O_3 on weekends was noted at all stations except Poznań, while the ozone weekend effect at the significance level $p<0.05$ was noted at 3 of 5 stations (Wrocław, Łódź, Kraków). Presented results clearly indicate that the ozone weekend effect was present in vast majority of cases. It is crucial that ozone weekend effect was confirmed by a significant part of the year (spring, autumn, winter). The differences of O_3 concentrations during winter and spring seasons presented the highest values (>5ppb). As listed in Table 2, NO_x concentration at the weekends was significantly lower ($p<0.05$) than those on the day of weekly minimum in almost all cases with the exception of Poznań during spring and autumn and Kraków during autumn season (where the differences were significantly lower at the level $p<0.1$).

3.6. Weekend/Weekday Concentration of O_x

The occurrence of OWE phenomenon is determined by number of factors and it changes spatially and temporally. The California Air Resources Board depicted main causes of OWE in cities [26]. Among the several hypotheses (including e.g.: reduction and delay of NO_x emission, carryover of O_3 precursors near the ground and carryover aloft, increased UV radiation, increased weekend emission, decreased O_3 titration), 2 of these are crucial in determining the cause of this phenomenon. First of them "NO_x reduction" based on the non-linear and complex series of reactions including VOC and NO_x leading to the O_3 formation. The second hypothesis "ozone quenching" is based on the process of O_3 titration by NO [2]. The dependency between NO, NO_2 and O_3 related with reactions 1-3 ($NO_2+h\nu \rightarrow NO+O$, $O+O_2+M \rightarrow O_3+M$, $O_3+NO \rightarrow NO_2+O_2$) represent a closed system of two groups of components: NO_x ($NO+NO_2$) and O_x (in this study defined as a sum of NO_2 and O_3). O_x is an indicator of the real photochemical ozone production meaning its promotion and inhibition [2, 3, 27]. Moreover representing total oxidative potential is not affected by basic chemical reactions eg. titration of O_3 by NO and photodissociation of NO_2. The comparison of differences between O_x concentrations at the weekend and on weekdays is a good indicator of possible cause of the OWE in a given area. According to Sadanaga [2] if the differences are not significantly higher during the weekend compared to weekdays, then the main cause of the phenomenon of OWE is ozone quenching hypothesis. Analysis of Table 4 reveals that differences of O_x at all stations were negligible (the values ranged between 0,02 ppb and 2,33 ppb of relative values) and in all cases statistically insignificant, so that the phenomenon of OWE analyzed in this study can be explained by the process of ozone titration by nitrogen oxides.

Table 4. *Weekend – the lowest day of the week differences of O_x, where (together with standard deviation): We – mean O_3, NO_x concentration on weekend; Min – mean O_3, NO_x concentration on the lowest day of the week; We-Min – difference in ppb; p-value (U-Mann-Whitney test).*

	O_x [ppb]			
	We	**Min**	**We-Min**	**p**
2015-2017 Entire period				
Wrocław	35.4±9.2	35.4±9.7	0.1	0.964
Łódź	36.5±9.9	36.2±10.5	0.3	0.82
Kraków	34.6±8.2	36.1±8.9	-1.5	0.083
Poznań	33.7±8.7	33.2±8.6	0.4	0.725
Warszawa	33.7±9.3	33.7±9.7	0	0.919
2015-2017 Spring				
Wrocław	39.7±6.7	39.1±7.1	0.6	0.604
Łódź	41.4±7.2	40.9±6.7	0.5	0.544
Kraków	38.1±6.3	38.8±7.5	-0.7	0.453
Poznań	38.9±6.6	39.1±5.8	-0.1	0.804
Warszawa	39.3±6.9	40.3±6.2	-1	0.524
2015-2017 Summer				
Wrocław	42.2±8.1	43.2±7.7	-1	0.62
Łódź	43.5±9.2	44.3±9.0	-0.9	0.919
Kraków	40.4±7.9	42.5±6.6	-2	0.159
Poznań	38.6±9.0	37.4±8.6	1.2	0.747
Warszawa	39.9±7.5	39.9±8.6	0	0.996
2015-2017 Autumn				
Wrocław	29.1±8.4	29.6±9.9	-0.5	0.928
Łódź	30.1±8.1	30.8±9.8	-0.7	0.95
Kraków	28.0±5.4	30.3±7.5	-2.3	0.177
Poznań	28.4±6.7	26.5±5.8	1.8	0.287
Warszawa	27.1±7.6	25.6±7.3	1.5	0.386
2015-2017 Winter				
Wrocław	30.3±5.0	30.0±6.0	0.3	0.833
Łódź	30.8±6.6	29.3±7.9	1.4	0.474
Kraków	31.2±5.9	32.7±8.1	-1.6	0.287
Poznań	28.5±5.2	29.7±6.9	-1.2	0.503
Warszawa	27.9±5.7	28.3±5.9	-0.4	0.658

4. Conclusions

Day of the week variations of O_3 and NO, NO_2 and NO_x from five large cities in Poland from 2015-2017 were analyzed for 1) representing the background O_3 concentration in selected cities 2) analysis weekend/weekdays variation of O_3, NO_x and 3) investigation the phenomenon of OWE.

Analysis of selected individual locations reveals that relationship between O_3 and NO_x and consequently existence of OWE has significant site-to-site differences. The highest 3-year averaged ozone concentration values were noted in Łódź (26,9±11,9 ppb) simultaneously with the lowest NO_x level (12,3±7,3 ppb). The opposite situation was in Kraków where the lowest O_3 concentration values (18,3±9,8 ppb) and the highest NO_x concentration values (42,1±36,0 ppb) within the whole measuring period were noted. The diurnal variation of O_3 concentration shows peak values after midday (about 14:00), lower evening and night-time concentration and minimum in the early morning, just before the sunrise.

The maximum daily O_3 means concentration at all stations was revealed on Sunday whereas the minimum was noted on Wednesday, Thursday and Friday. The average value of difference between the weekend and the day of the ozone weekly minimum, during the whole analyzed period, ranged from 2,75 ppb (Kraków) to 4,03 ppb (Wrocław). The weekly pattern of NO_x is completely opposite to ozone with the maximum on Thursday and Friday and minimum on Sunday. The greatest number of exceeded target threshold (60 ppb and 90 ppb) was recorded on Sunday and the sum of exceeded amounts on Saturday and Sunday was up to 44% (Poznań) of total exceeded amounts for all the week. The analysis showed that all of the stations present higher O_3 concentration during the weekend compared to weekdays. The U-Mann-Whitney test results revealed that for most periods the OWE was confirmed with statistical significance, simultaneously with the reduction of NO_x emission up to 50% during the weekend.

The possible reasons of OWE presumably are connected with significantly greater (twice) emission of NO on weekdays mornings which delays accumulation of O_3 due to intensive titration of O_3 by NO. Inhibition phase of O_3 ends about 1,5 hour earlier at the weekends compared to weekdays, simultaneously the duration of accumulation of O_3 reaches significantly higher values at the weekends (04:50) than on weekdays (03:20). Moreover in all seasons of the year the O_x concentration at the weekend was not significantly higher at the weekends than on weekdays. This result suggests that the limited processes of O_3 titration by NO (ozone quenching hypothesis) is the main explanation of OWE in all the studied cities.

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