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OZONE CONCENTRATION AT GROUND LEVEL DEPENDING ON THE CONTENT OF NO_x AND METEOROLOGICAL CONDITIONS

STĘŻENIE OZONU PRZY POWIERZCHNI ZIEMI W ZALEŻNOŚCI OD ZAWARTOŚCI NO_x I WARUNKÓW METEOROLOGICZNYCH

Abstract: This study analyzed the temporal variation of tropospheric ozone (O_3) in Poznan (midwestern Poland) on the basis of data collected from a State Environmental Monitoring air quality assessment station. The aim was to investigate the distribution and variation of O_3 levels and to assess the relationship with nitrogen oxides (NO_x) and meteorological conditions. These relationships were assessed by multiple regression analysis and cluster analysis. The O_3 levels showed a high annual, seasonal and daily volatility, and were significantly influenced by meteorological conditions and NO_x levels. High O_3 levels were accompanied by above-average levels of radiation (*Rad*), air temperature (T_a) and wind speed (W_s), together with below-average values of NO_x and humidity (R_h). Atmospheric pressure (P_h) had an ambiguous effect on O_3 levels.

Keywords: air quality, atmospheric gaseous pollutants, meteorological conditions, temporal variation

Introduction

Tropospheric ozone (O_3) is a secondary pollution produced not only by lightning but mainly by complex photochemical reactions occurring in the polluted air, for example with nitrogen oxides (NO_x) [1, 2]. In urban areas, these reactions are mainly based on the oxidation of nitrogen compounds derived from anthropogenic sources, mainly road transport [3-5]. At ground level, ozone is one of the major components of the 'photochemical smog' observed mainly in summer in large cities and industrial areas around the world [6, 7].

Similar to other regions of Central Europe, elevated concentrations of O_3 in Poland are due to natural sources or natural phenomena unrelated to human activity, to the influx of air

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pollution from other areas (including other countries), and to photochemical transformations resulting from intensive solar radiation and adverse weather conditions [8-10].

Meteorological factors are very significant for the gathering, scattering, flowing and transport of gaseous pollutants, including ozone [11-15]. O_3 can be transported over long distances and its maximum levels are recorded leeward of ozone emission precursors [16]. In urban areas air flow may be disrupted and so the levels recorded at a given station may not reflect the movement of air masses in a larger spatial scale. O_3 flows into Poland with air masses often coming from southern and south-western Europe [17-19]; apart from the wind, other meteorological conditions also significantly influence O_3 levels, especially solar radiation, temperature and humidity [20]. O_3 concentration also depends on other factors, such as terrain, altitude and geographic location [21].

O_3 has a significant effect on plants and animals, including humans [22-25]. Its elevated concentrations can cause dysfunction of the respiratory system: coughing, a limited ability to breathe deeply and absorb oxygen, deterioration of asthma symptoms and pneumonia. Other symptoms include eye irritation, headaches, and even depression among the elderly [26-29]. In plants, O_3 pollution causes damage to the surface of the lamina, a reduction of biomass production by increasing the dry matter content in leaves as an internal reaction to the presence of ozone, and also damage to the cell membrane, mitochondria and chloroplasts due to the inhibition of photosynthesis [22, 30, 31]. Finally, the strong oxidizing properties of O_3 cause the destruction of various other materials, most notably rubber and textiles [32], hence the importance of research on the distribution and variation of tropospheric O_3 levels in urban areas, their relation to the levels of nitrogen oxides and meteorological conditions. Therefore, the aim of this paper was to determine the distribution and the variation of the tropospheric O_3 levels in the Poznan conurbation (midwestern Poland), in relation to the NO_x levels and the evolution of meteorological conditions.

Material and methods

The location of the measurement station and measurement conditions

Data was collected from a State Environmental Monitoring (PMS) station located in the north-western part of Poznan, a major Polish city with an area of 262 km^2 and a population of about 550 thousand permanent residents (Fig. 1).

Fig. 1. Location of the State Environmental Monitoring (PMS) Station

At the end of 2012, there were 554 registered vehicles per 1,000 inhabitants in the city [33]. The measurement station is located in the Botanical Garden (λ = 16°52'38"E, ϕ = 52°25'13"N, *Hs* = 84 m above sea level) in close proximity to residential and recreational areas. The measurement site was arranged so that the air flow around the inlet sampling probe and weather sensors was not limited by any obstacles. In addition, the arrangement of the sampling site was designed to prevent the suction of air discharged from the measuring instrument and poorly mixed air from the inside of the casing of the instrument.

The O_3 and NO_x measuring instrument, and sensors used for the measurement of most meteorological elements, were located at a height of 3 m above the ground, with sensors to measure wind speeds at a height of 10-11 m above ground level.

Material

The study was based on the results of hourly measurements of tropospheric O_3 and nitrogen oxides NO_x, collected in consecutive years from 2005-2012. O_3 levels were measured using O342M analyzer (infrared absorption), and NO_x levels by AC32M analyzer (chemiluminescence in UV). Meteorological data were collected at the same time as the hourly measurements: total solar radiation (*Rad*), air temperature (T_a), relative humidity (R_h), atmospheric pressure (P_h), and wind speed (W_s).

Methods

The evolution of O_3 and NO_x levels was examined hourly, monthly, seasonally (spring: March 1-May 31, summer: June 1-August 31, fall: September 1-November 30, winter: December 1-February 28/29) and annually. On the basis of hourly data there were established statistical indicators of O_3 and NO_x: mean ($\bar{x}$), minimum (*Min*), maximum (*Max*) and percentiles ($Q30$, $Q60$, $Q90$). We also calculated the incidence of the analyzed gaseous pollutants in the time intervals in both a multi-year period (2005-2012), as well as in the selected years 2006 and 2009, namely the years with the greatest difference between O_3 and NO_x levels. Daily data (calculated from at least 21 hourly measurements from a given day) were used to capture the relationship between the tropospheric O_3 and NO_x levels and meteorological elements: *Rad*, T_a, R_h, P_h and W_s.

The relationships between the analyzed variables were confirmed by a Pearson correlation coefficient (r) at $P \leq 0.01$. Daily data was used to construct the multiple regression equations used to extract a group of significant independent variables to determine the size of the O_3 concentration, and also to assess the effects of weather and NO_x levels on O_3 levels [10, 14]. Due to the relatively large set of independent variables, the linear multiple regression model used a stepwise elimination of variables with statistically insignificant effect.

Regression equations were calculated based on the coefficient of determination (R^2), *F*-Snedecor test and mean absolute bias error (*MABE*). *MABE* was calculated according to the formula:

$$MABE = \frac{1}{n} \sum_{i=1}^{n} \left| y_i - x_i \right| \tag{1}$$

where y_i is the actual value of O_3 level, and x_i - O_3 concentrations predicted by the multiple regression equations.

In addition, to obtain the strictest dependence describing the impact of independent variables on O_3 levels, we established four clusters of meteorological values and air NO_x levels, occurring at diverse O_3 levels, including high and low [18]. All measurements of analyzed variables were divided into clusters by using non-hierarchical k-means method in which a Euclidean distance was used. To determine the optimal number of clusters, we used a v-fold cross-validation. The significance of differences between clusters was estimated using an analysis of variance, using Fisher's test at $P \leq 0.01$.

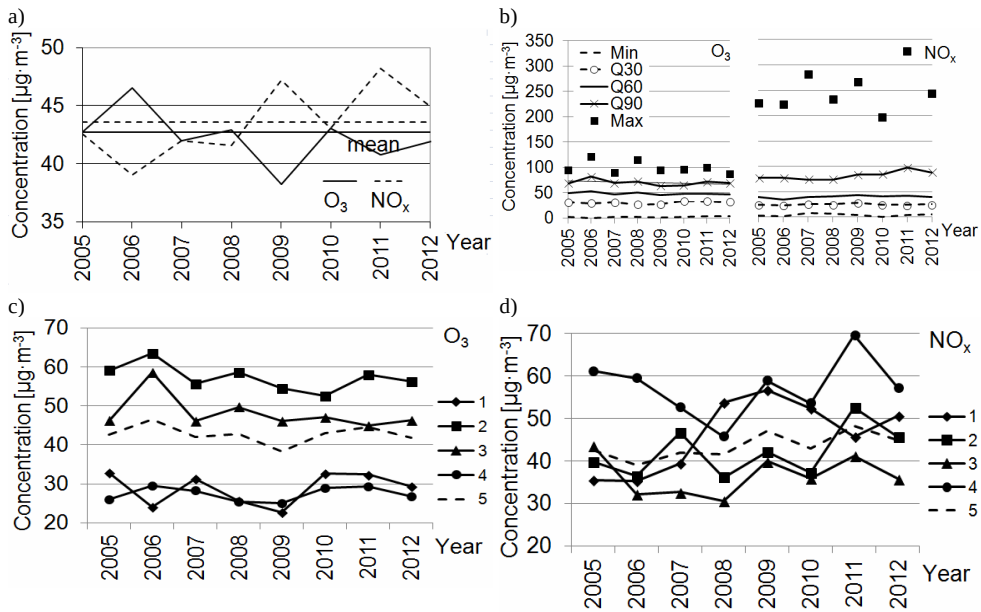
Before starting the analysis of regression and clusters in order to allow comparison of the variables (regardless of their original distribution and units in which they were measured), they were subjected to standardization according to the following formula:

$$z = \frac{y_i - \bar{y}}{S} \tag{2}$$

where: y_i - non-standardized variable, $\bar{y}$ - arithmetic mean, S - standard deviation.

Results

In the analyzed period 2005-2012, the O_3 concentration curve course was almost inversely proportional to the NO_x concentration curve (Fig. 2a).



1 - winter, 2 - spring, 3 - summer, 4 - fall, 5 - year

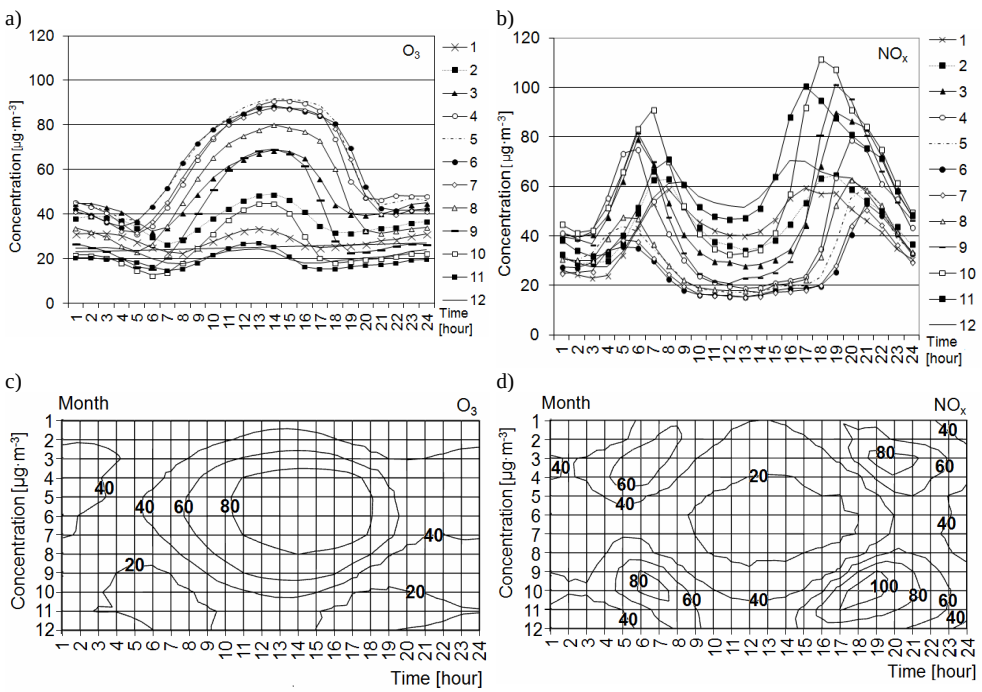
Fig. 2. Variation of O_3 and NO_x levels in 2005-2012: a) mean, b) extreme values (*Min*, *Max*) and percentiles (*Q*30, *Q*60, *Q*90), c), d) average seasonal and annual

Long-term average for O_3 ($\bar{x}$ = 42.72 µg · m^{-3}) was only about 0.8 µg · m^{-3} lower than the average NO_x ($\bar{x}$ = 43.57 µg · m^{-3}), but between individual years it ranged from

38.3 µg · m^{-3} in 2009 to 46.5 µg · m^{-3} in 2006. Tropospheric O_3 had a distinctly lower temporal variation over a year than NO_x (Fig. 2b). Minimum O_3 levels ranged from 0.1 µg · m^{-3} in 2006 to 4.0 µg · m^{-3} in 2012, in all the years it was less than NO_x minima which ranged from 0.4 to 8.3 µg · m^{-3}.

Maximum O_3 concentrations were approximately 2-3 times lower than maximums for NO_x and reached from 87.7 µg · m^{-3} in 2012 to 121.1 µg · m^{-3} in 2006. Over the years, O_3 level percentiles *Q*30, *Q*60 and *Q*90 were in the following ranges: 26.6-33.6, 45.1-53.0, 63.5-82.0 µg · m^{-3}, with NO_x 22.8-28.4, 34.9-42.8, 73.7-97.2 µg · m^{-3}. Over the years 2005-2012, the highest seasonal average O_3 level was recorded in spring, then in summer, and the lowest - in the fall or winter (Fig. 2c). Such distinct seasonality was not observed in the case of NO_x levels (Fig. 2d).

Changes in the concentration of the analyzed pollutants during 24 h not only depended on the time of day, but also on the month (Fig. 3ab). In the years 2005-2012, the largest amplitude of daily O_3 concentrations occurred in April (59.7 µg · m^{-3}), and then in the summer months, in August (57.0 µg · m^{-3}) and July (55.8 µg · m^{-3}), while the lowest - in December (7.1 µg · m^{-3}) and January (11.0 µg · m^{-3}). In the case of NO_x the greatest differences between the 24 h maxima and minima were recorded in September (80.6 µg · m^{-3}) and October (79.2 µg · m^{-3}), and then in March (62.0 µg · m^{-3}) and April (60.1 µg · m^{-3}); the lowest were observed in July (35.5 µg · m^{-3}) and February (35.8 µg · m^{-3}).



1 , 2, 3… 12 - consecutive months of the year

Fig. 3. Variation of air pollutants by hour and months in the period 2005-2012: a), c) O_3, b), d) NO_x

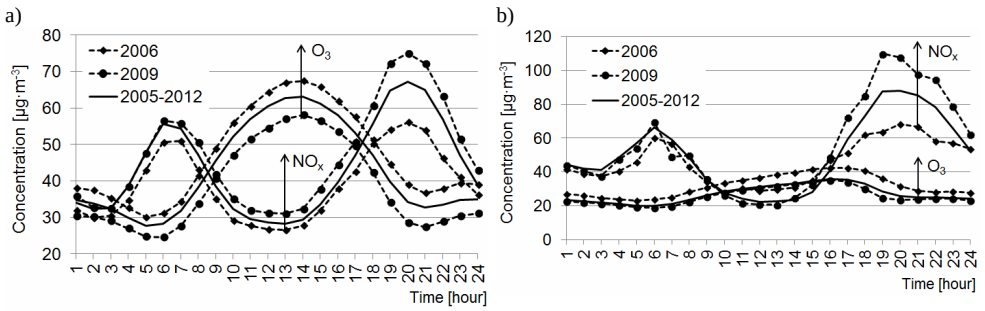


Fig. 4. Dynamics of changes in concentrations of O_3 and NO_x by hours in 2006 and 2009 and a multi-year period 2005-2012: a) mean, b) standard deviation

On average, the greatest tropospheric O_3 concentrations, above 80.0 $\mu g \cdot m^{-3}$, occurred over five consecutive months, from April to August, between the hours of 11:00 and 17:00, while the lowest, less than 20 $\mu g \cdot m^{-3}$, were observed, among others, in the period November-December between the hours of 6:00 and 9:00 and 15:00 and 20:00 (Fig. 3c). Temporal distribution of NO_x concentration during 24 h was different between months; the highest levels, above 100.0 $\mu g \cdot m^{-3}$, were recorded most often in the period October-November at 17:00-19:00 hours (Fig. 3d), and the lowest when O_3 immission in the air was the highest.

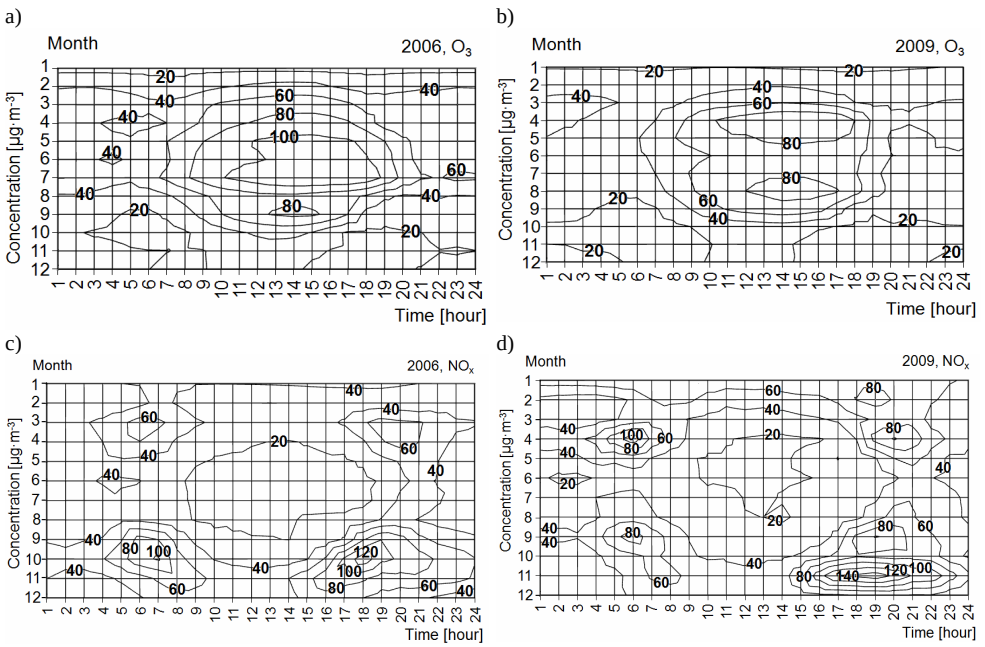


Fig. 5. Daily structure of the concentrations of O_3 and NO_x, by month in the years: a), c) 2006, b), d) 2009

Dynamics of changes in O_3 and NO_x, described by the means and standard deviations for consecutive hours over 24 h, were similar in 2006 and 2009, as well as in the entire period 2005-2012, although concentrations were different (Fig. 4ab). The biggest difference in tropospheric O_3 between the years 2006 and 2009 could be observed in the afternoon (12-15 h) and evening (19-20 h), while NO_x levels in the evening (19-22 h), which was confirmed statistically. Distributions of the 24 h structure of O_3 and NO_x levels confirm their different evolution in individual years (Fig. 5).

In 2006 the highest concentration of O_3 was recorded in the period May-July between the hours of 12:00 and 17:00 (> 100 $\mu g \cdot m^{-3}$), while in 2009 - in the period of April-May and August, between the hours of 13:00 and 17:00 (> 80 $\mu g \cdot m^{-3}$), which is slightly different than in the entire multi-year period (Fig. 3c). The concentration of NO_x in 2006 ranged from < 20 $\mu g \cdot m^{-3}$ in the period May-August - at 10:00-17:00 to > 120 $\mu g \cdot m^{-3}$ in October - at about 18:00. In 2009, the distribution and range of recorded values of NO_x were similar to the distribution in 2006; however, the highest concentration amounting to > 140 $\mu g \cdot m^{-3}$ was recorded in November between 17:00 and 19:00 h.

In the years 2005-2012 about 73% of one-hour measurements of tropospheric O_3 were in the first three frequency ranges: 0-20, 20-40 and 40-60 $\mu g \cdot m^{-3}$, in the next two classes, approximately 15% in 60-80 $\mu g \cdot m^{-3}$ and about 7% in 80-100 $\mu g \cdot m^{-3}$. Immission of O_3 in the range >100 $\mu g \cdot m^{-3}$ occurred only in about 5% measurements (Fig 6a).

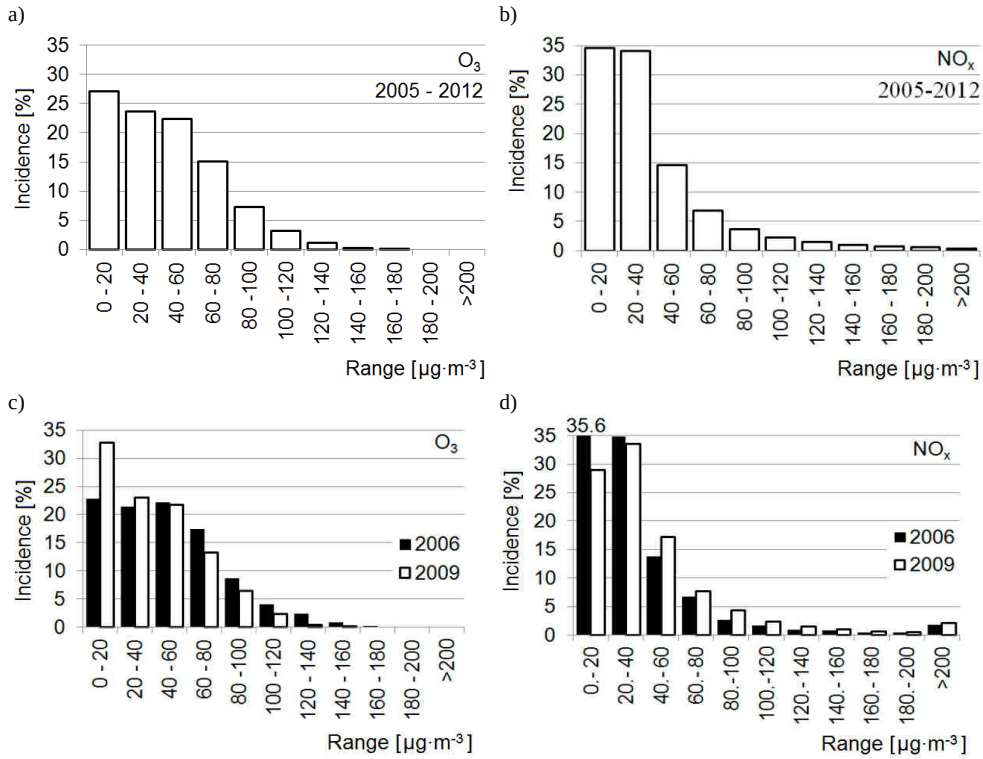


Fig. 6. Incidence [%] of hourly measurements of O_3 (a, c) and NO_x (b, d) in 2005-2012 and the years 2006 and 2009, in intervals from 0-20 to more than 200 $\mu g \cdot m^{-3}$

Frequency of NO_x intervals differed from the distribution of tropospheric O_3 (Fig. 6b). Most often, with a frequency of approximately 35%, NO_x immission measurements fell within the first two ranges of 0-20 µg · m^{-3} and 20-40 µg · m^{-3}, and then 15% in 40-60 µg · m^{-3}, 7% in 60-80 µg · m^{-3}, 4% in 80-100 µg · m^{-3}, and about 6% measurements were > 100 µg · m^{-3}. The frequency distribution of the results of both gaseous pollutants analyzed in 2006 and 2009 was similar to the distribution in the entire period 2005-2012 (Fig. 6). Most measurements fell within the first three frequency ranges, about 67% in 2006 and 78% in 2009 - in the case of O_3 immission and about 84% in 2006, and 80% in 2009 for NO_x immission.

The frequency intervals > 100 µg · m^{-3} for NO_x were most frequent in 2009 (8.3%), while for O_3 in 2006 (7.6%). High concentrations of O_3, in the range from 100 to 180 µg · m^{-3}, were most often recorded between 10:00 and 17:00, and NO_x - at 5:00-8.00 and 18:00-22:00 hours (Fig. 7ab).

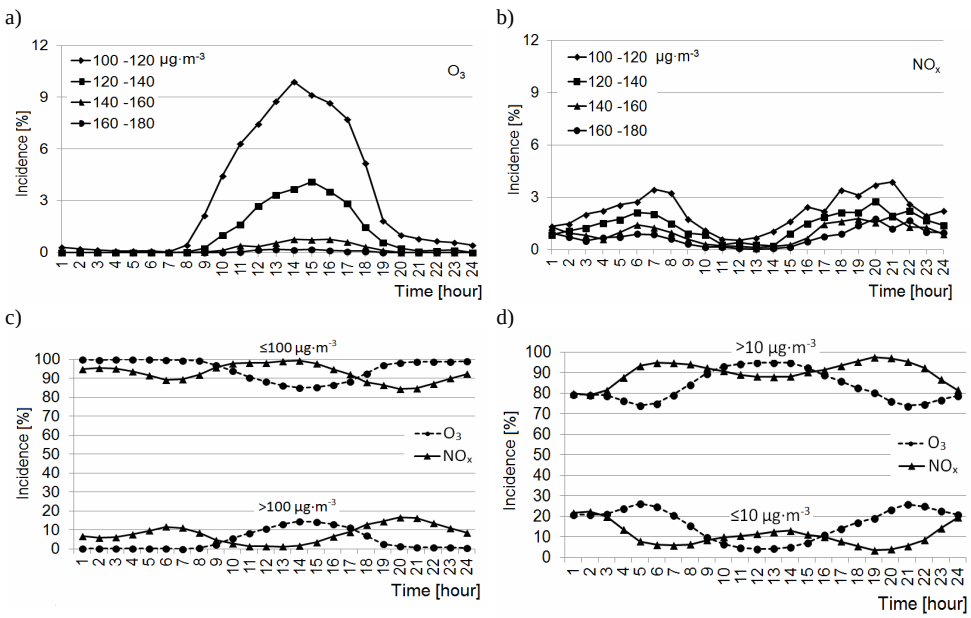


Fig. 7. Incidence [%] of O_3 and NO_x measurements in 2005-2012 in intervals from 100-120 to 160-180 µg · m^{-3} (a, b), and ≤ 100 and > 100 µg · m^{-3} (c), and also ≤ 10 and > 10 µg · m^{-3} (d)

The study also evaluated changes in the share of results of measurements of O_3 and NO_x levels in the consecutive hours of the day, also including the ranges of > 10 µg · m^{-3} ≤ 10 µg · m^{-3}, > 100 µg · m^{-3} and ≤ 100 µg · m^{-3} (Fig. 7cd). Shares of measurements showing O_3 levels ≤ 100 µg · m^{-3} ranged on average from 85 to 100%, and were least frequent in the afternoon, while > 100 µg · m^{-3} - from 0.1 to 14.5%, and were least frequent at night (Fig. 7c).

The share of O_3 measurements ≤ 10 µg · m^{-3} ranged from less than 5% at 11:00-14:00 - to about 25% at about 5:00 and 21:00, while > 10 µg · m^{-3} - from about 74 to 95% (Fig. 7d). Participation of NO_x immission measurements in the range of > 10 µg · m^{-3}

$\leq 10\ \mu g \cdot m^{-3}$, $> 100\ \mu g \cdot m^{-3}$ and $\leq 100\ \mu g \cdot m^{-3}$ was almost inversely proportional to the distribution of O_3 results. The share of immission measurements of both air pollutants in the ranges $\leq 10\ \mu g \cdot m^{-3}$ and $> 10\ \mu g \cdot m^{-3}$ was similar, but only at night, *ie* 24:00-3:00 h.

Daily O_3 levels can be significantly correlated with meteorological elements and the content of NO_x in the years 2005 to 2012 (Table 1). A significant negative correlation existed between the concentrations of O_3 and NO_x in all months, with the strictest correlation ($r \geq 0.4$, $P \leq 0.01$) in the period from October to May. The immission of O_3 was also negatively influenced by two meteorological elements; R_h and P_h. R_h index significantly influenced O_3 throughout the year, except in December; it was the strongest in May ($r \geq 0.71$, $P \leq 0.01$) and July ($r \geq 0.70$, $P \leq 0.01$). P_h significantly negatively influenced the O_3 level in the fall-winter months (October, November, and January), and positively in May and July.

Table 1

Correlation coefficient for the linear relationship between daily levels of O_3 and meteorological factors and NO_x immission in 2005-2012

Month	Variable					
	NO_x	*Rad*	T_a	R_h	P_h	W_s
	[$\mu g \cdot m^{-3}$]	[h]	[°C]	[%]	[hPa]	[$m \cdot s^{-1}$]
1	–0.48*	n.s.	n.s.	–0.25*	–0.24*	0.75*
2	–0.53*	n.s.	n.s.	–0.38*	n.s.	0.42*
3	–0.52*	n.s.	n.s.	–0.33*	n.s.	0.34*
4	–0.48*	0.45*	0.32*	–0.53*	n.s.	n.s.
5	–0.41*	0.57*	0.52*	–0.71*	0.20*	n.s.
6	–0.20*	0.58*	0.58*	–0.66*	n.s.	n.s.
7	–0.23*	0.57*	0.72*	–0.70*	0.26*	n.s.
8	–0.22*	0.39*	0.54*	–0.45*	n.s.	n.s.
9	–0.38*	0.45*	0.48*	–0.60*	n.s.	0.32*
10	–0.46*	0.28*	n.s.	–0.40*	–0.20*	0.63*
11	–0.60*	n.s.	n.s.	–0.28*	–0.28*	0.81*
12	–0.63*	n.s.	n.s.	n.s.	n.s.	0.68*

* significant with $P \leq 0.01$, NO_x - nitrogen oxides, *Rad* - total solar radiation, T_a - air temperature, R_h - relative air humidity, P_h - atmospheric pressure, W_s - wind speed, n.s. - non significant, $P > 0.01$

Rad, T_a and W_s had a positively significant effect on the O_3 level. *Rad* significantly determined the level of tropospheric O_3 in the air from April and October, most strongly in the May-July period ($r \geq 0.57$, $P \leq 0.01$). A similar effect on O_3, in terms of strength, direction and period, was exerted by air temperature. Another meteorological factor, W_s, had a positive influence in fall-winter months, from September to March, the strongest in November ($r \geq 0.81$, $P \leq 0.01$).

Regression analysis showed that among the six variables, four had an effect on O_3 immission; NO_x, T_a, R_h and W_s (Table 2). The greatest standardized multiple regression coefficients, *ie* the strongest effect on O_3, were shown for NO_x from March to May, T_a - in July and August, R_h - in May, June and September, and W_s - in the period from October to January.

NO_x significantly determined the O_3 immission in all months, R_h - in the period January-November, T_a - in the period April-September, and W_s - in the periods January-March and September-December, therefore slightly different than shown by the

analysis of correlation. The impact of the entire group of variables on O_3, described by the determination coefficient, ranged from about 43% ($F = 53.2$, $P \leq 0.01$) in February to 75% ($F = 239.5$, $P \leq 0.01$) in May. The *MABE* calculated for individual regression equations ranged from 4.8 $\mu g \cdot m^{-3}$ in September to 9.1 $\mu g \cdot m^{-3}$ in February.

Table 2

Combined effect of meteorological factors and NO_x immission on daily O_3 concentration in 2005-2012

Month	Standardized multiple regression coefficients						Statistical evaluation of the equation			
	NO_x	*Rad*	T_a	R_h	P_h	W_s	R^2	*F*	*MABE*	$\bar{x}$
	[$\mu g \cdot m^{-3}$]	[h]	[°C]	[%]	[hPa]	[$m \cdot s^{-1}$]	[%]		[$\mu g \cdot m^{-3}$]	[$\mu g \cdot m^{-3}$]
1	–0.24*			–0.11*		0.64*	63.7	134.6	7.2	28.5
2	–0.37*			–0.34*		0.24*	43.1	53.2	9.1	37.0
3	–0.51*			–0.46*		0.22*	48.3	75.3	8.0	48.8
4	–0.52*		0.21*	–0.46*			61.4	120.2	6.6	60.3
5	–0.44*		0.19*	–0.66*			74.9	239.5	6.1	63.1
6	–0.31*		0.39*	–0.55*			68.7	151.9	6.6	61.3
7	–0.31*		0.48*	–0.46*			74.5	234.9	6.5	58.8
8	–0.41*		0.48*	–0.42*			53.3	89.3	6.3	48.8
9	–0.31*		0.26*	–0.51*		0.23*	62.2	94.1	4.8	36.8
10	–0.21*			–0.40*		0.47*	55.3	89.0	5.4	25.1
11	–0.22*			–0.13*		0.66*	64.7	119.2	5.7	19.4
12	–0.37*					0.49*	56.1	146.5	6.5	21.5

R^2 - determination coefficient, *F* - Snedocor's test, *MABE* - mean absolute bias error, $\bar{x}$ - average. Other explanations, see Table 1

The greatest difference between *MABE* and the O_3 long-term average was determined for four months, from April to July, which may testify to a better fit of regression lines to empirical data than for other analyzed months.

Table 3

Statistical characteristics of clusters describing the O_3 level

Variable	*SS*	Df_{SS}	*SSE*	Df_{SSE}	Fisher's test	*P*
O_3 [$\mu g \cdot m^{-3}$]	165.37	3	79.26	248	166.90	0.01
NO_x [$\mu g \cdot m^{-3}$]	145.43	3	97.56	248	119.24	0.01
T_a [°C]	115.39	3	125.93	248	73.30	0.01
R_h [%]	156.66	3	85.74	248	146.17	0.01

SS - sum square error of between-group variation, Df_{SS} - number of degrees of freedom for sum square error *SS*, *SSE* - sum square error of within-group variation, Df_{SSE} - number of degrees of freedom for sum square error *SSE*, *P* - level of probability. Other explanation, see Table 1

In addition, based on the cluster analysis for the strictest dependence between O_3 in May and the analyzed group of variables, there were established four clusters (Table 3). All variables included in the analysis were significant at $P \leq 0.01$, we also confirmed a significant difference between the determined clusters (Table 4).

Among 248 observations (8 years x 31 days), cluster 1 included 30 observations, cluster 2 - 106 observations, cluster 3 - 78 observations and cluster 4 - 34 observations. Cluster 4 included the highest levels of tropospheric O_3 (90.8 ± 11.7 $\mu g \cdot m^{-3}$), which was accompanied by below-average NO_x (19.3 ± 8.2 $\mu g \cdot m^{-3}$) and air humidity levels

(48.6 ± 8.6%), and above-average air temperature (15.2 ± 3.1ºC). Daily maximum O_3 levels ranged, depending on the cluster, from 63.5 $\mu g \cdot m^{-3}$ in cluster 1 to 121.8 $\mu g \cdot m^{-3}$ in cluster 4.

Table 4

Statistical characteristics of NO_x and meteorological factors in May for each isolated cluster describing O_3 level (clusters 1, 2, 3, 4 and Σ 1-4)

Month	Cluster number	Number of observations	O_3 concentration [$\mu g \cdot m^{-3}$] $\bar{x} \pm S$, *Max*	Independent describing the O_3 level variable		
				NOx [$\mu g \cdot m^{-3}$]	T_a [ºC]	R_h [%]
				$\bar{x} \pm S$, *Max*		
May	1	30	48.6 ± 11.0, 63.5	66.5 ± 16.7, 111.5	12.1 ± 4.1, 19.9	68.8 ± 11.0, 98.0
	2	106	53.3 ± 9.3, 75.6	26.6 ± 9.9, 47.0	10.2 ± 2.5, 15.8	83.5 ± 9.7, 98.0
	3	78	71.2 ± 7.8, 86.9	29.7 ± 10.3, 50.5	17.4 ± 3.9, 26.6	62.0 ± 7.9, 83.4
	4	34	90.8 ± 11.7, 121.8	19.3 ± 8.2, 41.4	15.2 ± 3.1, 21.9	48.6 ± 8.6, 70.3
	Σ 1-4	248	63.1 ± 16.6, 121.8	31.4 ± 17.3, 111.5	13.4 ± 4.6, 26.6	70.7 ± 15.5, 98.0

$\bar{x}$ - average, S - standard deviation, *Max* - maximum absolute. Other explanations, see Table 1 and 2

Discussion

Distribution of O_3 levels in Poznan, similar to other regions in the world, show a clear annual, seasonal and daily variation [2, 8]. Annual O_3 levels in 2005-2012 were higher than, for example, in Obinsk in Russia [14], and lower than in other regions of Poland, *ie* in the south-east, in Carpathians [34], or the north-west - in Widuchowa [11] and Szczecin [35].

Contrary to other pollutants, whose highest levels are generally recorded in the centers of large cities, the highest immission of O_3 is usually found on the leeward edges of conurbations [19, 30]. In the years 2005-2012 the highest level of O_3 was observed in spring, then in summer. The lowest could be found in fall and winter, similar to other regions of Europe [36], but different than in Spain [37].

Tropospheric O_3, apart from monthly variation, also shows daily variation, which is confirmed by the results of many papers [14, 18, 20, 36, 37]. In this paper, we show that O_3 temporal variation was lower than NO_x, similar to Munir et al [4] and Adame et al [37]. In the years 2005-2012 percentiles $Q30$, $Q60$ and $Q90$ of O_3 levels were lower than in Saudi Arabia [4], which can be attributed to differences in climate.

In Poznan, NO_x had a different temporal distribution than O_3 - its highest levels were observed in the morning and afternoon; different than in the papers by Im et al [36] and Yasuyuki et al [38]. In the period 2005-2012 the greatest number of measurements of O_3 and NO_x ranged from 0 to 40 $\mu g \cdot m^{-3}$, which was different than Nidzgorska-Lencewicz [35] showed for Szczecin, Poland. A large variation in tropospheric O_3, a secondary pollutant, is associated mainly with the differences in weather conditions in Poland in consecutive years and the content of ozone precursors, *eg* nitrogen oxides [1, 7].

A significant negative correlation between the levels of O_3 and NO_x, similar to our paper, was shown by Silman [1], Im et al [36] and Yasuyuki et al [38], according to which NO_x had a large significance for the production of harmful tropospheric O_3. In this paper we show significant correlations between O_3 levels and meteorological conditions, positive with radiation, air temperature, wind velocity, while negative with air humidity, and negative or positive with atmospheric pressure, which is similar to the findings of Liu et al [10], Aref'ev et al [14], Stathopoulou et al [17], Adame et al [37], Puc and Bosiacka [39].

An increase in O_3 with an increased wind velocity can be associated with the sources of pollution situated at a certain distance from the PMS station. Apart from NO_x, in the group of meteorological factors, the strongest impact on O_3 air levels was exerted by T_a, R_h and W_s; meteorological conditions explain about 40% to even 70% of the variation [8, 10, 18]. The lack of confirmation of the significant effect of *Rad* in the group of meteorological factors on O_3 levels may be caused by the co-linearity of the independent variables, *ie* a strong correlation between *Rad* and R_h.

Conclusions

The O_3 levels in Poznan had a distinct annual, seasonal and daily variation. Among the 8 analyzed years (2005-2012), the highest average O_3 level (46.5 $\mu g \cdot m^{-3}$) was observed in 2006. It was always about two times higher in spring than in the autumn-winter season. In May-July, above-average daily O_3 levels were recorded mostly around noon and in the afternoon.

In the years 2005-2012, the evolution of NO_x levels was significantly different from O_3; the highest levels were observed in autumn or winter in early morning and in the evening. There was a significant negative correlation between O_3 and NO_x levels, the strongest in the period March-May. Maximum NO_x levels were as much as 2-3 times greater than O_3 levels, and ranged from 197.6 $\mu g \cdot m^{-3}$ in 2010 to 327.7 $\mu g \cdot m^{-3}$ in 2011.

The high O_3 ranges $\geq$ 100 $\mu g \cdot m^{-3}$ were most frequent between 12:00 and 17:00 h, while the same range of NO_x between 18:00 and 22:00 h. The distribution of O_3 depended not only on the content of NO_x in the air, but also on meteorological conditions, mainly T_a, R_h and W_s.

The greatest determination coefficient for the entire group of variables was calculated for the regression equation for two months: May (R^2 = 74.9%), and July (R^2 = 74.5%). Moreover, correlation analysis showed that the level of tropospheric O_3 was significantly influenced by *Rad* and P_h. These two factors were not taken into account due to the strong correlation between *Rad* and R_h and T_a, and between P_h and W_s.

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STĘŻENIE OZONU PRZY POWIERZCHNI ZIEMI W ZALEŻNOŚCI OD ZAWARTOŚCI NO_X I WARUNKÓW METEOROLOGICZNYCH

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Abstrakt: Analizę czasowej zmienności ozonu troposferycznego w Poznaniu (środkowo-zachodnia Polska) podjęto na podstawie danych zebranych ze stacji oceny jakości powietrza Państwowego Monitoringu Środowiska. Celem pracy było poznanie rozkładu i zmienności stężenia O_3 oraz ocena zależności między rozpatrywanym zanieczyszczeniem a zawartością NO_x i przebiegiem warunków meteorologicznych. Do oceny zależności między rozpatrywanymi zmiennymi posłużyły analiza regresji wielokrotnej i analiza skupień. Stężenie O_3 odznaczało się dużą zmiennością roczną, sezonową i dobową. Warunki meteorologiczne i zawartość NO_x istotnie determinowały wielkość stężenia O_3. Dużym stężeniom analizowanego zanieczyszczenia sprzyjały głównie ponadprzeciętne wartości: Rad, T_a i W_s oraz poniżej przeciętne wartości NO_x i R_h. Niejednoznaczny wpływ na wartość stężenia O_3 miało P_h.

Słowa kluczowe: jakość powietrza, zanieczyszczenia gazowe atmosfery, warunki meteorologiczne, zmienność czasowa