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...
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]. \( \text{O}_3 \) 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. \( \text{O}_3 \) 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 \( \text{O}_3 \) levels, especially solar radiation, temperature and humidity [20]. \( \text{O}_3 \) concentration also depends on other factors, such as terrain, altitude and geographic location [21].

\( \text{O}_3 \) 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, \( \text{O}_3 \) 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 \( \text{O}_3 \) 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 \( \text{O}_3 \) 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 \( \text{O}_3 \) levels in the Poznan conurbation (midwestern Poland), in relation to the \( \text{NO}_x \) 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](image-url)
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 (\(\lambda = 16^\circ52'38''E, \phi = 52^\circ25'13''N, H_s = 84\) 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:

\[
MABE = \frac{1}{n} \sum_{i=1}^{n} |y_i - x_i|
\]

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 O₃ levels, we established four clusters of meteorological values and air NOₓ levels, occurring at diverse O₃ 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:

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

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

**Results**

In the analyzed period 2005-2012, the O₃ concentration curve course was almost inversely proportional to the NOₓ concentration curve (Fig. 2a).

Long-term average for O₃ ($\bar{x} = 42.72 \mu g \cdot m^{-3}$) was only about 0.8 $\mu g \cdot m^{-3}$ lower than the average NOₓ ($\bar{x} = 43.57 \mu g \cdot m^{-3}$), but between individual years it ranged from
38.3 µg · m⁻³ in 2009 to 46.5 µg · m⁻³ in 2006. Tropospheric O₃ had a distinctly lower temporal variation over a year than NOₓ (Fig. 2b). Minimum O₃ 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 NOₓ minima which ranged from 0.4 to 8.3 µg · m⁻³.

Maximum O₃ concentrations were approximately 2-3 times lower than maximums for NOₓ and reached from 87.7 µg · m⁻³ in 2012 to 121.1 µg · m⁻³ in 2006. Over the years, O₃ level percentiles Q₃₀, Q₆₀ and Q₉₀ were in the following ranges: 26.6-33.6, 45.1-53.0, 63.5-82.0 µg · m⁻³, with NOₓ 22.8-28.4, 34.9-42.8, 73.7-97.2 µg · m⁻³. Over the years 2005-2012, the highest seasonal average O₃ 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 NOₓ 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 O₃ 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 NOₓ 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).
On average, the greatest tropospheric $O_3$ concentrations, above 80.0 µg · 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 µg · 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 µg · 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. 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

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 O₃ and NOₓ, 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 O₃ between the years 2006 and 2009 could be observed in the afternoon (12-15 h) and evening (19-20 h), while NOₓ levels in the evening (19-22 h), which was confirmed statistically. Distributions of the 24 h structure of O₃ and NOₓ levels confirm their different evolution in individual years (Fig. 5).

In 2006 the highest concentration of O₃ was recorded in the period May-July between the hours of 12:00 and 17:00 (> 100 µg · m⁻³), while in 2009 - in the period of April-May and August, between the hours of 13:00 and 17:00 (> 80 µg · m⁻³), which is slightly different than in the entire multi-year period (Fig. 3c). The concentration of NOₓ in 2006 ranged from < 20 µg · m⁻³ in the period May-August - at 10:00-17:00 to > 120 µg · m⁻³ in October - at about 18:00. In 2009, the distribution and range of recorded values of NOₓ were similar to the distribution in 2006; however, the highest concentration amounting to > 140 µg · 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 O₃ were in the first three frequency ranges: 0-20, 20-40 and 40-60 µg · m⁻³, in the next two classes, approximately 15% in 60-80 µg · m⁻³ and about 7% in 80-100 µg · m⁻³. Immission of O₃ in the range >100 µg · m⁻³ occurred only in about 5% measurements (Fig 6a).

Fig. 6. Incidence [%] of hourly measurements of O₃ (a, c) and NOₓ (b, d) in 2005-2012 and the years 2006 and 2009, in intervals from 0-20 to more than 200 µg · m⁻³.
Frequency of NO\textsubscript{x} intervals differed from the distribution of tropospheric O\textsubscript{3} (Fig. 6b). Most often, with a frequency of approximately 35%, NO\textsubscript{x} immission measurements fell within the first two ranges of 0-20 $\mu$g $\cdot$ m\textsuperscript{-3} and 20-40 $\mu$g $\cdot$ m\textsuperscript{-3}, and then 15% in 40-60 $\mu$g $\cdot$ m\textsuperscript{-3}, 7% in 60-80 $\mu$g $\cdot$ m\textsuperscript{-3}, 4% in 80-100 $\mu$g $\cdot$ m\textsuperscript{-3}, and about 6% measurements were > 100 $\mu$g $\cdot$ m\textsuperscript{-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\textsubscript{3} immission and about 84% in 2006, and 80% in 2009 for NO\textsubscript{x} immission.

The frequency intervals > 100 $\mu$g $\cdot$ m\textsuperscript{-3} for NO\textsubscript{x} were most frequent in 2009 (8.3%), while for O\textsubscript{3} in 2006 (7.6%). High concentrations of O\textsubscript{3}, in the range from 100 to 180 $\mu$g $\cdot$ m\textsuperscript{-3}, were most often recorded between 10:00 and 17:00, and NO\textsubscript{x} - at 5:00-8.00 and 18:00-22:00 hours (Fig. 7ab).

![Graphs](image-url)

**Fig. 7.** Incidence [%] of O\textsubscript{3} and NO\textsubscript{x} measurements in 2005-2012 in intervals from 100-120 to 160-180 $\mu$g $\cdot$ m\textsuperscript{-3} (a, b), and ≤ 100 and > 100 $\mu$g $\cdot$ m\textsuperscript{-3} (c), and also ≤ 10 and > 10 $\mu$g $\cdot$ m\textsuperscript{-3} (d)

The study also evaluated changes in the share of results of measurements of O\textsubscript{3} and NO\textsubscript{x} levels in the consecutive hours of the day, also including the ranges of > 10 $\mu$g $\cdot$ m\textsuperscript{-3} ≤ 10 $\mu$g $\cdot$ m\textsuperscript{-3}, > 100 $\mu$g $\cdot$ m\textsuperscript{-3} and ≤ 100 $\mu$g $\cdot$ m\textsuperscript{-3} (Fig. 7cd). Shares of measurements showing O\textsubscript{3} levels ≤ 100 $\mu$g $\cdot$ m\textsuperscript{-3} ranged on average from 85 to 100%, and were least frequent in the afternoon, while > 100 $\mu$g $\cdot$ m\textsuperscript{-3} - from 0.1 to 14.5%, and were least frequent at night (Fig. 7c).

The share of O\textsubscript{3} measurements ≤ 10 $\mu$g $\cdot$ m\textsuperscript{-3} ranged from less than 5% at 11:00-14:00 - to about 25% at about 5:00 and 21:00, while > 10 $\mu$g $\cdot$ m\textsuperscript{-3} - from about 74 to 95% (Fig. 7d). Participation of NO\textsubscript{x} immission measurements in the range of > 10 $\mu$g $\cdot$ m\textsuperscript{-3}
≤ 10 µg · m⁻³, > 100 µg · m⁻³ and ≤ 100 µg · m⁻³ was almost inversely proportional to the distribution of O₃ results. The share of immission measurements of both air pollutants in the ranges ≤ 10 µg · m⁻³ and > 10 µg · m⁻³ was similar, but only at night, ie 24:00-3:00 h.

Daily O₃ levels can be significantly correlated with meteorological elements and the content of NOₓ in the years 2005 to 2012 (Table 1). A significant negative correlation existed between the concentrations of O₃ and NOₓ 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 O₃ was also negatively influenced by two meteorological elements; \( R_h \) and \( P_h \). \( R_h \) index significantly influenced O₃ 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 O₃ level in the fall-winter months (October, November, and January), and positively in May and July.

Table 1

<table>
<thead>
<tr>
<th>Month</th>
<th>NOₓ ( [\mu g \cdot m^{-3}] )</th>
<th>( T_a ) ( [^\circ C] )</th>
<th>( R_h ) [%]</th>
<th>( P_h ) [hPa]</th>
<th>( W_s ) [m · s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−0.48*</td>
<td>n.s.</td>
<td>−0.25*</td>
<td>−0.24*</td>
<td>0.75*</td>
</tr>
<tr>
<td>2</td>
<td>−0.53*</td>
<td>n.s.</td>
<td>−0.38*</td>
<td>n.s.</td>
<td>0.42*</td>
</tr>
<tr>
<td>3</td>
<td>−0.52*</td>
<td>n.s.</td>
<td>−0.33*</td>
<td>n.s.</td>
<td>0.34*</td>
</tr>
<tr>
<td>4</td>
<td>−0.48*</td>
<td>0.45*</td>
<td>0.32*</td>
<td>−0.53*</td>
<td>n.s.</td>
</tr>
<tr>
<td>5</td>
<td>−0.41*</td>
<td>0.57*</td>
<td>0.52*</td>
<td>−0.71*</td>
<td>0.20*</td>
</tr>
<tr>
<td>6</td>
<td>−0.20*</td>
<td>0.58*</td>
<td>0.58*</td>
<td>−0.66*</td>
<td>n.s.</td>
</tr>
<tr>
<td>7</td>
<td>−0.23*</td>
<td>0.57*</td>
<td>0.72*</td>
<td>−0.70*</td>
<td>0.26*</td>
</tr>
<tr>
<td>8</td>
<td>−0.22*</td>
<td>0.39*</td>
<td>0.54*</td>
<td>−0.45*</td>
<td>n.s.</td>
</tr>
<tr>
<td>9</td>
<td>−0.38*</td>
<td>0.45*</td>
<td>0.48*</td>
<td>−0.60*</td>
<td>n.s.</td>
</tr>
<tr>
<td>10</td>
<td>−0.46*</td>
<td>0.28*</td>
<td>n.s.</td>
<td>−0.40*</td>
<td>−0.20*</td>
</tr>
<tr>
<td>11</td>
<td>−0.60*</td>
<td>n.s.</td>
<td>n.s.</td>
<td>−0.28*</td>
<td>−0.28*</td>
</tr>
<tr>
<td>12</td>
<td>−0.63*</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>0.68*</td>
</tr>
</tbody>
</table>

* significant with \( P \leq 0.01 \), NOₓ - 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 O₃ level. \( Rad \) significantly determined the level of tropospheric O₃ 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 O₃, 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 O₃ immission; NOₓ, \( T_a \), \( R_h \) and \( W_s \) (Table 2). The greatest standardized multiple regression coefficients, ie the strongest effect on O₃, were shown for NOₓ 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.

NOₓ significantly determined the O₃ 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
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 µg · m$^{-3}$ in September to 9.1 µg · m$^{-3}$ in February.

Table 2

Combined effect of meteorological factors and NO$_x$ immission on daily O$_3$ concentration in 2005-2012

<table>
<thead>
<tr>
<th>Month</th>
<th>Standardized multiple regression coefficients</th>
<th>Statistical evaluation of the equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO$_x$</td>
<td>Rad</td>
</tr>
<tr>
<td></td>
<td>[µg · m$^{-3}$]</td>
<td>[h]</td>
</tr>
<tr>
<td>1</td>
<td>-0.24*</td>
<td>-0.11*</td>
</tr>
<tr>
<td>2</td>
<td>-0.37*</td>
<td>-0.34*</td>
</tr>
<tr>
<td>3</td>
<td>-0.51*</td>
<td>-0.46*</td>
</tr>
<tr>
<td>4</td>
<td>-0.52*</td>
<td>0.21*</td>
</tr>
<tr>
<td>5</td>
<td>-0.44*</td>
<td>0.19*</td>
</tr>
<tr>
<td>6</td>
<td>-0.31*</td>
<td>0.39*</td>
</tr>
<tr>
<td>7</td>
<td>-0.31*</td>
<td>0.48*</td>
</tr>
<tr>
<td>8</td>
<td>-0.41*</td>
<td>0.48*</td>
</tr>
<tr>
<td>9</td>
<td>-0.31*</td>
<td>0.26*</td>
</tr>
<tr>
<td>10</td>
<td>-0.21*</td>
<td>-0.40*</td>
</tr>
<tr>
<td>11</td>
<td>-0.22*</td>
<td>-0.13*</td>
</tr>
<tr>
<td>12</td>
<td>-0.37*</td>
<td></td>
</tr>
</tbody>
</table>

$R^2$ - determination coefficient, $F$ - Snedecor’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

<table>
<thead>
<tr>
<th>Variable</th>
<th>SS</th>
<th>$Df_{SS}$</th>
<th>SSE</th>
<th>$Df_{SSE}$</th>
<th>Fisher’s test</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$ [µg · m$^{-3}$]</td>
<td>165.37</td>
<td>3</td>
<td>79.26</td>
<td>248</td>
<td>166.90</td>
<td>0.01</td>
</tr>
<tr>
<td>NO$_x$ [µg · m$^{-3}$]</td>
<td>145.43</td>
<td>3</td>
<td>97.56</td>
<td>248</td>
<td>119.24</td>
<td>0.01</td>
</tr>
<tr>
<td>$T_a$ [$^\circ$C]</td>
<td>115.39</td>
<td>3</td>
<td>125.93</td>
<td>248</td>
<td>73.30</td>
<td>0.01</td>
</tr>
<tr>
<td>$R_h$ [%]</td>
<td>156.66</td>
<td>3</td>
<td>85.74</td>
<td>248</td>
<td>146.17</td>
<td>0.01</td>
</tr>
</tbody>
</table>

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 µg · m$^{-3}$), which was accompanied by below-average NO$_x$ (19.3 ± 8.2 µg · m$^{-3}$) and air humidity levels.
Ozone concentration at ground level depending on the content of NOx …

(48.6 ± 8.6%), and above-average air temperature (15.2 ± 3.1°C). Daily maximum O3 levels ranged, depending on the cluster, from 63.5 µg · m⁻³ in cluster 1 to 121.8 µg · m⁻³ in cluster 4.

Table 4
Statistical characteristics of NOx and meteorological factors in May for each isolated cluster describing O3 level (clusters 1, 2, 3, 4 and Σ 1-4)

<table>
<thead>
<tr>
<th>Month</th>
<th>Cluster number</th>
<th>Number of observations</th>
<th>O3 concentration [µg · m⁻³]</th>
<th>Independent describing the O3 level variable</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\bar{x} \pm S$, $Max$</td>
<td>$\bar{x} \pm S$, $Max$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NOx [µg · m⁻³]</td>
<td>$T_a$ [°C]</td>
</tr>
<tr>
<td>May</td>
<td>1</td>
<td>30</td>
<td>48.6 ± 11.0, 63.5</td>
<td>66.5 ± 16.7, 111.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>106</td>
<td>53.3 ± 9.3, 75.6</td>
<td>26.6 ± 9.9, 47.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>78</td>
<td>71.2 ± 7.8, 86.9</td>
<td>29.7 ± 10.3, 50.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>34</td>
<td>90.8 ± 11.7, 121.8</td>
<td>19.3 ± 8.2, 41.4</td>
</tr>
<tr>
<td>Σ 1-4</td>
<td></td>
<td>248</td>
<td>63.1 ± 16.6, 121.8</td>
<td>31.4 ± 17.3, 111.5</td>
</tr>
</tbody>
</table>

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

**Discussion**

Distribution of O3 levels in Poznan, similar to other regions in the world, show a clear annual, seasonal and daily variation [2, 8]. Annual O3 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 O3 is usually found on the leeward edges of conurbations [19, 30]. In the years 2005-2012 the highest level of O3 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 O3, 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 O3 temporal variation was lower than NOx, similar to Munir et al [4] and Adame et al [37]. In the years 2005-2012 percentiles $Q30$, $Q60$ and $Q90$ of O3 levels were lower than in Saudi Arabia [4], which can be attributed to differences in climate.

In Poznan, NOx had a different temporal distribution than O3 - 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 O3 and NOx ranged from 0 to 40 µg · m⁻³, which was different than Nidzgorska-Lencewicz [35] showed for Szczecin, Poland. A large variation in tropospheric O3, 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 O3 and NOx, similar to our paper, was shown by Silman [1], Im et al [36] and Yasuyuki et al [38], according to which NOx had a large significance for the production of harmful tropospheric O3. In this paper we show significant correlations between O3 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 µg · 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 µg · m$^{-3}$ in 2010 to 327.7 µg · m$^{-3}$ in 2011.

The high O$_3$ ranges ≥ 100 µg · 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 $W_s$.

**References**


Ozone concentration at ground level depending on the content of NOx ...


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

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