Introduction

The generation and development of ground-level ozone is a very complex process. Tropospheric ozone is generated in a system of photo-chemical reactions in the presence of ozone precursors, consisting of nitrogen oxides (NOx) and volatile organic compounds (VOCs), acting namely during warm periods (April-September). Ozone precursors originate from anthropogenic and natural sources. The dominating anthropogenic O3 precursor sources in Europe (accounting for 39% from the total emissions amount) are: car transport, energy production, combustion of solid fuels, utilization of solvents, and pollution from certain key industrial branches. The natural precursor sources are forests, with beech stands participating by ca 10% in biogenic VOC creation [1]. Tropospheric ozone is transported both vertically and horizontally. The ozone production and transport are mostly influenced by a range of meteorological factors: air temperature, solar radiation, rainfall amount, and air circulation [2-4]. The impact of warming is strongly aggravated [5, 6] connected with global climate change. The ozone concentrations rise with altitude [7-9], and they generally reach higher values in rural areas than in urban agglomerations [1, 10, 11].

Spatial and Temporal Variations in O3 Concentrations in Western Carpathian Rural Mountain Environments

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Abstract

O3 concentrations were monitored between 2006 and 2012 in rural environments in the Štiavnické and Kremnické mountains (the western Carpathian region). There were no spatial differences between the two sites. On the other hand, distinct temporal variations were noticed especially during 2006-08 and 2009-12, with O3 levels ranging between 36-77 and 42-84 µg·m⁻³ in the Štiavnickés and Kremnickés, respectively. Higher O3 levels correlated with the increases in ambient temperatures and were recorded simultaneously. The maximum mean annual O3 levels were recorded in 2008, representing 144 µg·m⁻³ and 116 µg·m⁻³ in both ranges in 2012. The standard deviations as well as standard errors were low in both localities, with the variability lower in the Kremnickés. The minimum annual O3 levels were observed in 2010, falling to 20.0 µg·m⁻³ at both sites. The seasonal maxima were recorded in summer. The ozone values at both sites were more influenced by temperature than by rainfall. The situation of the ground level ozone formation in the studied localities has not been levelled off so far; its developmental trend is not explicit. The occurrence of extreme ozone events is evident, and the associated environmental is serious.

Keywords: ground-level ozone, rural environment, air temperature, western Carpathian region

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is transported horizontally (especially from the southern situated areas) and, mixed and fused with hillside circulation, determines the local ozone concentration levels. Our research was aimed at ozone concentration history in two rural localities in central Slovakia with different pollution loads in the past. We also assessed the impact of select factors contributing to ozone generation. We recorded spatial patterns, temporal variability (seasonal and inter-annual differences) in the ozone levels, and episodes of exceeding the threshold values. We focussed on:

1. Determining if there is a significant difference in ground ozone levels between the localities as differed by their former pollution levels (the Štiavnické locality was exposed to strong emission load in the second half of the past century; the Kremnické locality was outside the pollution impact).
2. Quantifying, by regression analysis, the extent to which select climatic variables (mean air temperature and rainfall total) influenced ground-level ozone formation.
3. Specifying the trends in changes in O₃ concentrations at the two sites.

Materials and Methods

Study Areas

The Štiavnické and Kremnické are two mountain units of the Slovenské stredohorie in the western Carpathians. They are built of volcanic rocks. Their basins are under strong impact of intensive agriculture, industry, and land urbanization.

These mountain ranges are situated in the steppe zone dominated by the third, oak-beech forest vegetation tier. The experimental sites (ES) situated in Štiavnické is north-to-northwest facing. Both plots are equally remote from local and urban pollution sources, but they differ by their distance from the key pollution source. The Štiavnické plot is in close proximity (1,750 m) to a huge industrial pollution source (aluminium plant), whereas the Kremnické plot is 18 km away from this plant. Both plots are situated in open areas outside forest stands [12]. Plot descriptions are in Table 1.

The main substances contaminating the Štiavnické Mountains originated from local sources (aluminium plant, energy plants, local waste dumping site, highway system), and they represented fluorne, sulphur and nitrogen oxides, arsenic, cadmium, ozone, solid particles, and more. For many years, this locality was one of the most polluted in Slovakia. Toward the end of the past century, the emission load manifested a considerable fall, primarily due to modernizing the production processes and due to new environmental legislation in force.

The ES in the Kremnické Mountains is close (cca 10 km) to the Zvolenská kotlina basin with three stationary energy plants, an industrial park, a highway system, and a big railway crossing. All these subjects can aggravate airborne-pollution on the plot due to meteorological conditions. Our research was carried out in spring and summer, and the meteorological conditions for pollution dissipation in the basin were favourable [13]. This research plot is outside the impact of long-range pollution transport. The input of other airborne polluting substances to the Kremnické region is discussed in [14, 15].

O₃ Monitoring

The local study of environmental contamination with airborne ozone is performed by passive sampling methods [16, 17]. Passive sampling is joined by measurements carried out in the frame of the European Monitoring and Evaluation Programme network, which monitors ozone amounts deposited on solid surfaces from free atmosphere. In localities that are exposed to airborne pollution but not easy to access physically, ground level ozone concentrations are assessed by the manual sorption-accumulation Werner’s method [16]. Werner’s method is based on the selective reaction of an indigo layer applied on a filter paper with atmospheric ozone. The papers are exposed in the field for 7-10 days, during growing seasons (April-September). Passive ozone collectors are placed on each face of two parallel, of 1.5 m above the surface. The exposed papers are extracted with ethanol in the laboratory. The reaction between indigo and ozone results in the creation of izatine, which is indicated by yellowing of the test papers. The content of izatine is determined using spectrophotometry at a wavelength of 408 nm. The final value of the extinction is proportional to the izatine content and, as follows, also to the ozone content. The measured extinction values reflect the ozone totals according to the calibration curve. Ozone concentrations are given in standard units of ppb or in µg·m⁻³ converted per day. From the daily values, we calculated the monthly and annual characteristics. The equipment used to expose the indigo papers consists of a roofed stand and a perforated cylinder (a passive sampler) into which we placed the extracted papers prepared in the laboratory. The detail description is in [18].
Meteorological Data

The temperature and wind flow data were supplied by the Slovak Hydrometeorological Institute (SHMI), stations Sliač (φ = 48º38’33” N, λ = 19º08’31”E) located at 313 m a.s.l. and Žiar nad Hronom (φ = 48º35’10”N, λ = 18º51’8”E) 275 m a.s.l.

The rainfall was assessed based on the amounts collected into closed vessels after each noteworthy rainfall episode.

Data Analysis

The statistical parameters of measure and position were calculated and processed with the aid of the software package Statistica v7. The normality of distribution of the basic set was tested by the Shapiro-Wilkov W test. The significance of differences between the study plots was evaluated by Student’s t-test for independent variables. The influence of temperature and of rainfall sum on free ozone concentrations was evaluated using Excel. The results were also verified by testing methods provided by Statgraphics software.

Results and Discussion

The results obtained in this study revealed that the concentrations of ground-level ozone of the two ES were different. Both plots are situated in rural areas, at very similar altitudes, but they strongly differ by air-pollutant-induced loads to which they were exposed in the past. The measurements were carried out during growing seasons, from April to September. The ozone levels measured in this period are generally higher. The mean annual ground-level ozone values on the ES in the Kremnické Mountains ranged from 42 to 84 µg·m⁻³, while the corresponding values on the ES Štiavnické Mountains were from 36 to 77 µg·m⁻³ (Table 2).

In 2009 and 2010 we measured relatively low mean annual ozone concentrations on the two sites (Fig. 1).

Table 2. Descriptive statistics of ground-level ozone in the Štiavnické and Kremnické mountains, 2006-12.

<table>
<thead>
<tr>
<th>Year</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Štiavnické vrchy Mts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>70.8</td>
<td>68.7</td>
<td>39.3</td>
<td>49.7</td>
<td>35.8</td>
<td>65.5</td>
<td>76.7</td>
</tr>
<tr>
<td>Minimum</td>
<td>58.0</td>
<td>42.0</td>
<td>28.0</td>
<td>32.0</td>
<td>20.0</td>
<td>36.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Maximum</td>
<td>96.0</td>
<td>86.0</td>
<td>54.0</td>
<td>64.0</td>
<td>61.0</td>
<td>106.0</td>
<td>116.0</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>13.0</td>
<td>16.9</td>
<td>10.9</td>
<td>13.4</td>
<td>14.5</td>
<td>24.7</td>
<td>32.1</td>
</tr>
<tr>
<td>Std. Error</td>
<td>5.3</td>
<td>6.9</td>
<td>4.5</td>
<td>5.5</td>
<td>5.9</td>
<td>10.1</td>
<td>13.1</td>
</tr>
<tr>
<td>Coeff. of Variation</td>
<td>18.4</td>
<td>24.6</td>
<td>27.7</td>
<td>26.9</td>
<td>40.2</td>
<td>37.7</td>
<td>41.9</td>
</tr>
<tr>
<td>Kremnické vrchy Mts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>58.8</td>
<td>75.0</td>
<td>73.3</td>
<td>41.7</td>
<td>44.5</td>
<td>84.0</td>
<td>64.7</td>
</tr>
<tr>
<td>Minimum</td>
<td>46.0</td>
<td>48.0</td>
<td>42.0</td>
<td>22.0</td>
<td>20.0</td>
<td>34.0</td>
<td>49.0</td>
</tr>
<tr>
<td>Maximum</td>
<td>74.0</td>
<td>96.0</td>
<td>144.0</td>
<td>80.0</td>
<td>77.0</td>
<td>106.0</td>
<td>80.0</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>9.6</td>
<td>15.9</td>
<td>35.9</td>
<td>23.2</td>
<td>19.2</td>
<td>27.8</td>
<td>12.5</td>
</tr>
<tr>
<td>Std. Error</td>
<td>3.9</td>
<td>6.5</td>
<td>14.7</td>
<td>9.5</td>
<td>7.8</td>
<td>11.3</td>
<td>5.1</td>
</tr>
<tr>
<td>Coeff. of Variation</td>
<td>16.3</td>
<td>21.3</td>
<td>49.0</td>
<td>55.6</td>
<td>43.2</td>
<td>33.1</td>
<td>19.3</td>
</tr>
</tbody>
</table>

Std. Dev. – Standard deviation

Fig. 1. Trend of annual mean ozone concentrations at rural experimental sites in the Štiavnické and Kremnické mountains (µg·m⁻³).
The value recorded in 2010 in the Štiavnické Mountains was 36 µg·m⁻³ and in the Kremnické it was 45 µg·m⁻³. Similarly, the average value for Slovakia was also lower than usual at 59 µg·m⁻³ [13]. The average O₃ concentration recorded for rural sites in Europe is 60 µg·m⁻³ [1]. This evidently corresponds well to the overall situation and events contributing to ozone formation. In terms of mean annual ozone concentrations, the Slovak Hydrometeorological Institute [9, 20], calls 2009 and 2010 photo-chemically less active, compared to the very active 2003. In 2009 and 2010, a reduction in ozone precursors released into the atmosphere in Slovakia was recorded, too. The highest mean annual ozone concentration on our study plots was 84 µg·m⁻³ and it was recorded in 2011 on the ES in the Kremnické Mountains. In this year, and also in the following year (2012), very high values were also obtained for the whole of Slovakia: representing 61 and 63 µg·m⁻³, respectively, and reaching up to 93 a 96 µg·m⁻³ on Chopok (2,046 m a.s.l.) in the Low Tatra Mountains. The 2011 and 2012 growing seasons were very warm and dry, similar to 2003.

There were no confirmed significant differences in the measured ground-level ozone amounts between the two sites (Table 3). On the other hand, the time-based difference between 2006-08 and 2009-12 in the Štiavnické Mountains was statistically very significant, at the 99.9% level. No similar inter-annual differences were found for the ES in the Kremnické.

Seasonal variations in ground-level ozone concentrations in higher altitudinal zones in Central Europe usually manifest peaks in April and in August [13, 21]. According to our research results, this may not be true for medium altitudes. The average monthly levels measured in April (2006-12) were 65 µg·m⁻³ on both sites. The levels measured in August were the lowest, representing 47 µg·m⁻³ and 52 µg·m⁻³ in the Štiavnické and Kremnické mountains, respectively. On the other hand, the highest monthly average level over the study period was 73 µg·m⁻³, and this value was recorded in the Kremnické in September. The concentrations on the ES there were generally higher than in the Štiavnické, except for May (Fig. 2). The results show that the former spring O₃ concentration peak connected with ozone transport from higher atmospheric layers had been expanded over the whole summer period, due to photochemical production of ozone in the boundary atmospheric layer [22].

The linear trend in the mean monthly concentrations did not manifest a final tendency. On the ES in the Štiavnické this trend looked to be moderately decreasing. This fact may be assigned to the high inter-annual variability of the concentrations in the growing season. The mean concentration in the 2009 growing season was 50 µg·m⁻³, in 2010 it was 36 µg·m⁻³, and in 2011 it was 77 µg·m⁻³. This relatively big variation range corresponded to the meteorological conditions during measuring. We may deduce it based on assessment of the influence of select climatic variables (high average day temperature, low rainfall amount) on the deposited ozone concentration (Table 3). The literature approves that the accelerated ozone production is closely associated with meteorological conditions and with altitude [7, 23]. Recently, an important influence of climatic factors has been recognized, especially in connection with actual climate warming. The results of correlation analysis (Table 3) and the values of correlation coefficients show that ground-level ozone formation was more affected by temperature than by precipitation. The mean temperature range over the growing season in the Kremnickés was from 16.0ºC measured in 2006 to 17.1ºC recorded in 2012.

In the Štiavnické the temperature mean for the 2006 growing season was 16.3ºC and in 2012 it was 17.6ºC (Table 4). The air temperature in the growing season in this region is clearly higher than the long-term mean of 14.8ºC for 1961-90 as reported from Sliač meteorological station. These data are evident; on the other hand, forest and landscape ecosystems are very complex. Thus, the time and seasonal trends cannot be assessed easily. This requires a much longer time series than the series obtained to this date [24].

![Fig. 2. Seasonal variations in average monthly O3 concentrations at rural sites in 2006 and 2012.](image-url)
Almost over the entire study period there occurred episodes with high daily values, considerably exceeding the allowable limit of 65 µg·m⁻³ (up to 144 µg·m⁻³). In 2007 we measured from 74 to 96 µg·m⁻³ on both plots. The mean annual ozone concentration measured in Slovakia in this year was 62 µg·m⁻³ – the second highest in history [25] (and also there was high photochemical activity).

The highest concentrations of O₃ (142 and 144 µg·m⁻³) were recorded during April 2008 in the Štiavnické and Kremnické mountains, respectively. Other very high levels were recorded in 2012 in the Kremnickés in May and in June: 116 µg·m⁻³. This was due to high tropospheric ozone concentrations over the European continent, in the accumulation layer encompassing from 800 to 1,500 m above the ground [26]. A warning fact is that in the Kremnickés levels exceeding the daily limit of 65 µg·m⁻³ were recorded in each study year. On the other hand, on the ES in the Štiavnickés this threshold was exceed only in 2009 and 2010 (Fig. 3). The ozone concentrations and airborne pollution were assessed based on the limit value of 65 µg·m⁻³ (32.5 ppb·day⁻¹) established by the EU in 1992 as 24 hours mean daily concentration [27], indicating initiation of chronic damage to vegetation. Our ozone concentrations have been converted to daily values, thus they could be compared with the 24-hour limit.

High ozone concentrations have been reported recently from Italy [28], Spain [5], and all of Europe [8], including the Czech Republic with 38-39 ppb (corresponding to 80 µg·m⁻³) attained in several localities in several years [29]. Extreme ozone episodes are regarded as more dangerous for vegetation than long-term exposure to lower concentrations [30]. Extreme ozone concentrations may result in visible damage to vegetation even after a few hours.

The rise in O₃ concentration and worsened air quality can be assigned to some extent to the local sources emitting VOC and NOₓ. The dominating local O₃ precursor source in Europe is car traffic, accounting for 39% from the total pollutants emitted [31]. Both localities inspected are in close proximity to busy motorways, so it is reasonable to suppose that this factor has an impact on O₃ concentrations on these plots.

### Conclusions

Significant differences in ground-level ozone concentrations between the sites differing by their loads with airborne-substances have not been confirmed. The analysis of the actual concentration values revealed that these values remain rather high, show in differences primarily between the time distribution patterns. The variability between the sites seems equalized, also due to the fact that they are situated in comparable altitudes. A serious risk factor is extreme values occurring evidently on both plots. The occurrence of such levels, mainly connected with the current climate change, meaning, among anthers, higher temperature and less rainfall, may induce significant changes in the environment.
Regression analysis confirmed that ozone concentrations increased with increasing mean air temperature. Trends in the ground level ozone concentration history in the Štiavnické demonstrate a moderate decrease. For the Kremnické, no definite developmental trend was possible to identify, because the variability of the levels measured was high.

The overall condition concerning the formation and distribution of ground-level ozone has not been levelled off yet.

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