TROPOSPHERIC OZONE IMPACT IN SELECTED FOREST ECOSYSTEMS OF THE WESTERN CARPATHIANS

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Abstract

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Monitoring of tropospheric ozone was realized in the chosen forest ecosystem of the Western Carpathians Mountains. The studies are carried out at 5 monitoring sites – Malé Karpaty Mts (Geldek), Malá Fatra Mts (Štefanová), Kozie chrbty Mts (Východná), Javorníky Mts (Turkov) and Turzovská vrchovina Mts (Riečky). The ozone measurement took place during vegetation period by two ways – by passive samplers (filters changed two times per month) and by Thermo Environmental Model 49 Ozone Analyzer installed at the locality of Východná. Measurements were carried out in the period of April–October in 1997–1999.

Key words: tropospheric ozone, monitoring, passive samplers, ozone concentration

Introduction

High concentrations of ozone, exceeding the phytotoxic level, and high levels of nitrogen and sulphur deposition may have disastrous consequences for the biodiversity and stability of the Carpathian ecosystems. Protection against the deleterious effects of air pollution should become an essential component of proper preservation policy in the Carpathian Mountains. It is necessary to establish a network of sites to monitor the air pollution systematically in the Carpathian arch to provide information on spatial and temporal distribution of ozone, sulphur dioxide and nitrogen dioxide concentrations. Results of the air pollution monitoring in conjunction with reliable and systematic forest health evaluation will provide the scientific basis for better understanding of causes of the continuing forest decline in the Carpathian Mountains.

Ozone is rising in troposphere (tropospheric ozone – ground ozone) and stratosphere (stratospheric ozone) by photochemical reactions induced by ultraviolet radiation. Of all atmosphere ozone, only 8–15% is contained in troposphere, while the rest is concentrated in lower part of stratosphere, first of all in ozonosphere. Maximum of ozone concentration is reached in heights of 20 up to 25 km.

Growth of ozone concentration observed since the late 1980s was recorded to be about 1μg.m^{-3} per year. It was linked to rising ozone precursor emission (NO_x, VOC, CO) originated in traffic, energy and other industry. In 1990s, tropospheric ozone concentration in Europe was stagnated more-less (Závodský, 2002).

Tropospheric ozone, for which episode-like occurrence is typical, exceeds critical concentration level for vegetation all around the Slovak Republic. Nowadays it is considered to be a main forest ecosystem stress factor and according to the Economic Commission for Europe (ECfE) it is a ground for 5–10% reduction of agricultural plant production (Závodský, 1998).

It is common, that public does not distinguish risks linked to tropospheric and stratospheric changes. High tropospheric ozone concentration, i.e. photochemical smog occurring during hot summer weather and low wind speed (the highest concentrations are recorded afternoon) can damage mucous membranes, aggravate respiration and lead to physical and mental performance.

The aim of this contribution is to evaluate measured ground ozone concentration during individual vegetation period months at Kozie chrbty Mts – Východná site (by ozone analyzer tool and passive samplers) and at the sites of Malé Karpaty Mts, Malá Fatra Mts, Turzovská vrchovina highland and Javorníky Mts (by passive samplers) and to find their impact on vegetation (forest stands, agricultural crops), eventually on human health.

Another aim was to determine ozone correlation to some meteorological parameters (temperature, cloudiness, moisture, precipitation). As those parameters were not measured for the Východná site, we used data from Tatranská Polianka meteorological station.

Material and methods

The ozone measurement was carried out in the period of vegetation season by two ways – by passive samplers (filters changed two times per month) and by Thermo Environmental Model 49 Ozone Analyzer device installed at the locality of Východná. Direct ozone concentration research took place at following sites: Malá Fatra Mts (Štefanová – Vrátna dolina), Malé Karpaty Mts (Geldek – Častá), Kozie chrbty Mts (Východná), Javorníky Mts (Turkov) and Turzovská vrchovina highlands (Riečky) (Fig. 1, Table 1). Measurements took place during April–October in the period of 1997–1999.

Ozone concentration measured by ozone analyzer device was recorded once per 10 minutes (10 minutes average ozone concentration) to the datalogger of Cambele CR 10 type. Passive samplers were located as follows: Malé Karpaty Mts – the edge of the beech stand, Malá Fatra Mts – abandoned pasture with young spruce trees, Javorníky Mts, Turzovská vrchovina highland and Kozie chrbty Mts – the edge of the spruce stand. The samplers were fixed on trunks at the height of 2–3 m (Fig. 2).

To analyze ozone concentration, passive samplers produced by Ogawa & Co, USA were used. The samplers contain two non-transparent thread filters. Nitrite ion is a main component of filter surface film, which is oxidized by ozone to nitrate ion. After sampling, the filters are extracted by distillated water and nitrate ions are analyzed using chromatography (Dionex Ion Chromatograph Model DX100) in the laboratory of the Institute of Botany of the Polish Academy of Sciences, Krakow. The concentrations of the nitrates were used to evaluate ozone concentration (Koutrakis et al., 1993).

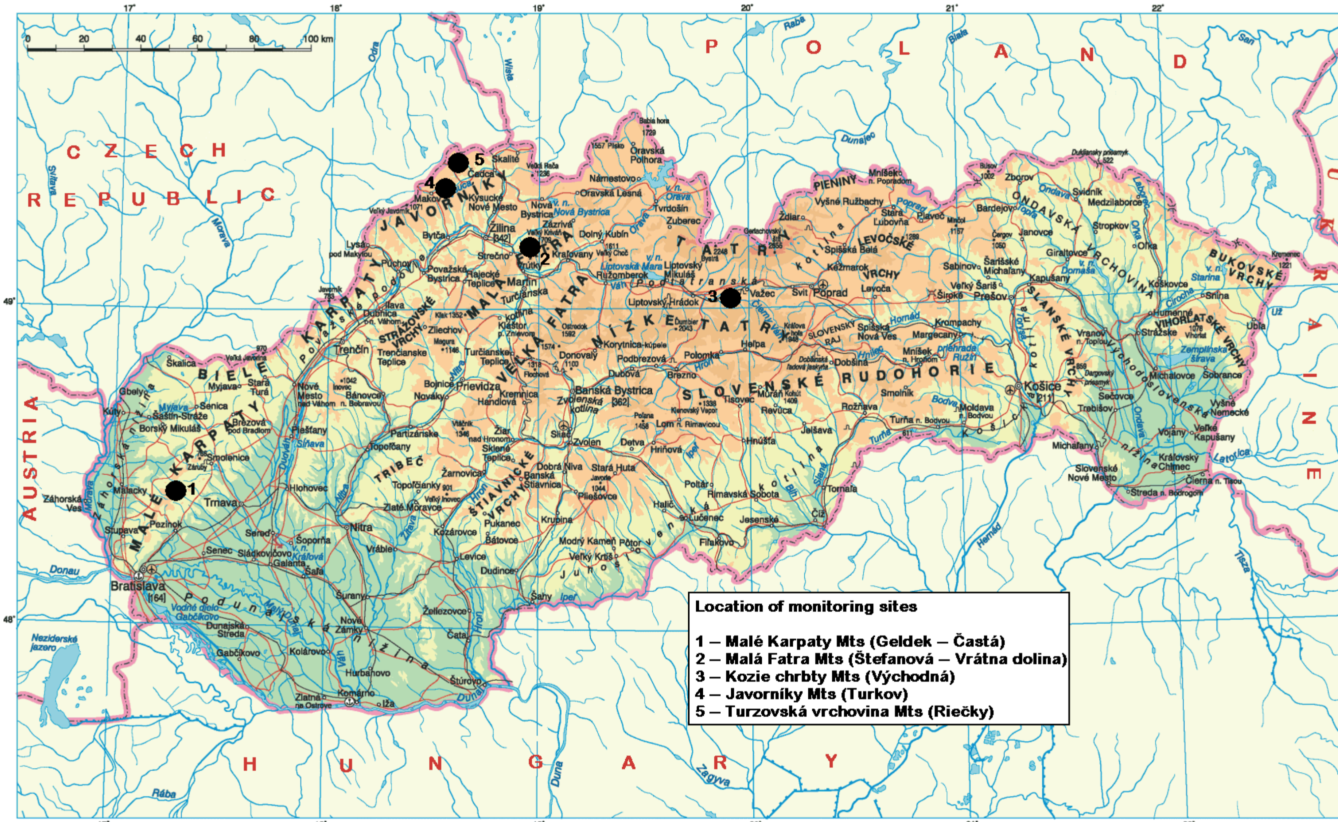

Fig. 1. Location of monitoring sites.

T a b l e 1. Location of ozone monitoring sites using passive samplers.

Locality	Latitude	Longitude	Elevation (m a.s.l)	Exposi-tion	Slope (°)
Malé Karpaty Mts – Geldek	48°25'54"	17°17'56"	670	S	0–5
Malá Fatra Mts – Štefanová	49°13'54"	19°04'21"	730	NWW	5–10
Kozie chrbty Mts – Východná	49°02'53"	19°54'19"	775	NW	25
Javorníky Mts – Turkov	49°22'48"	18°36'21"	560	W	30
Turzovská vrchovina Mts – Riečky	49°26'36"	18°36'19"	605	W	25

Fig. 2. Affixing, exposition of passive sampler, Malé Karpaty Mts – Geldek.

Limits of tropospheric ozone (ground ozone)

Concerning human health and vegetation protection, competent institutes suggested many sets of values, critical levels or immission limits for tropospheric ozone evaluation. By comparing of obtained ozone concentrations with critical values or immission limits, risk regions can be identified. Table 2 shows recommended immission limits according to the EÚ 92/72/EEC directive valid to 2001, while Table 3 contains target values for ground ozone according to the Regulation of MoE SR No. 705/2002, which has to be reach in 2010 in compliance with EU legislation.

T a b l e 2. Immission limits for ground ozone (valid until 2001).

Immission limits for ground ozone according to the directive 92/72/EEC		
immission limits	O_3 concentration [μg.m^{-3}]	average of period
for human health protection	110	8h*
for vegetation protection	200	1h
	65	24h
for population informing	180	1h
for population warning	360 (240**)	1h

Notes: * 8-h average is calculated as a slide average 4 times per day on the base of the values in time intervals: 0^{00}– 9^{00} h; 8^{00}–17^{00} h; 16^{00}–1^{00} h and 12^{00}–21^{00} h
** Modified value following new EU regulation for ozone

T a b l e 3. Target and threshold concentration values for ground ozone.

Target or threshold values	O_3 concentration [μg.m^{-3}]	Average of period
target value for human health protection	120*	8 h
target value for vegetation protection AOT40**	18 000 [μg.m^{-3}.h]	1st May–31st July
informational threshold for population warning	180	1 h
alarm threshold for population warning	240	1 h

Notes: * maximal day 8 h average of 120 μg.m^{-3} is not allowed to be exceeded more than 25 within calendar year, in the 3 year average
** AOT 40 expressed in μg.m^{-3}.h means sum of all differences between hour concentrations of ground ozone higher than 80 μg.m^{-3} (= 40 ppb) and 80 μg.m^{-3} in the time since 8,00 h to 20,00 h of Central European time since May 1 to July 31 and in average of 5 years

To evaluate 0_3 impacts on human health in Slovakia, there is same immission limit as in EU – 110 μg.m^{-3} (8h average) since 1996. Until 1996 less strict limit – 160 μg.m^{-3} (8-h average) was valid. To evaluate ozone impact for longer period, limit of 50 μg.m^{-3} was used commonly recommended by ECfE and calculated as ozone concentration average within 9^{00}–16^{00} h during the vegetation period (April–September).

Ozone concentration is determined either chemically or using UV photometric technology. Average natural ozone concentrations are about 20 μg.m^{-3}. In the areas of polluted air the concentrations exceeding 160 μg.m^{-3} occur in summer time, what was the limit for 8 h until 1996 (Závodský, 2002).

Cumulative effect of exposition of agricultural crops, forest stands and other ecosystems to concentration exceeding a particular threshold value is characterized by the so-called index of exposition (AOT40) expressed as ppb.h. According to the expert of ECfE, actually proposed ozone concentration threshold is 40 ppb. Critical AOT 40 value of 3000 ppb.h (6000 μg.m^{-3}h) corresponds to decrease of agricultural crop production by about 5% (Závodský, 2002).

AOT40 value is calculated for day hours with global radiation > 50 W.m^{-2} during the period of May–July. For Europe forest protection, preliminary critical threshold of 10 000 ppb.h (20 000 µg.m^{-3}h) was proposed.

Also in this case, accumulation was calculated for day values, but within 6 months (April–September). This critical value was the same for both broadleaved and coniferous trees. For natural vegetation was recommended to use same AOT40 value as for agricultural crops. Nowadays, target value of exposition index for vegetation protection of 18 000 µg.m^{-3}.h is in force (Regulation of the MoE SR No. 705/2002 on air quality). This value is linked to concentrations calculated as average within 5 years. In the case there is no 5-year measurements, the AOT40 can be determined within shorter period either.

Results and discussion

Results of ozone monitoring at Východná site by ozone analyzer

Compare to other sites of similar character, immediate ozone concentration measured by ozone analyzer was different (e.g. Polish sites – Szdzuj, 1999).
30 min average ozone concentration was falling to zero in the early morning (period of 3.00 – 5.00 h), while it was very high during the day (12.00–15.00 h). The reason probably lies in the localization of the device as it was in the vicinity of fish ponds resulting in higher air moisture, which causes decrease of ozone concentration (Fig. 3).

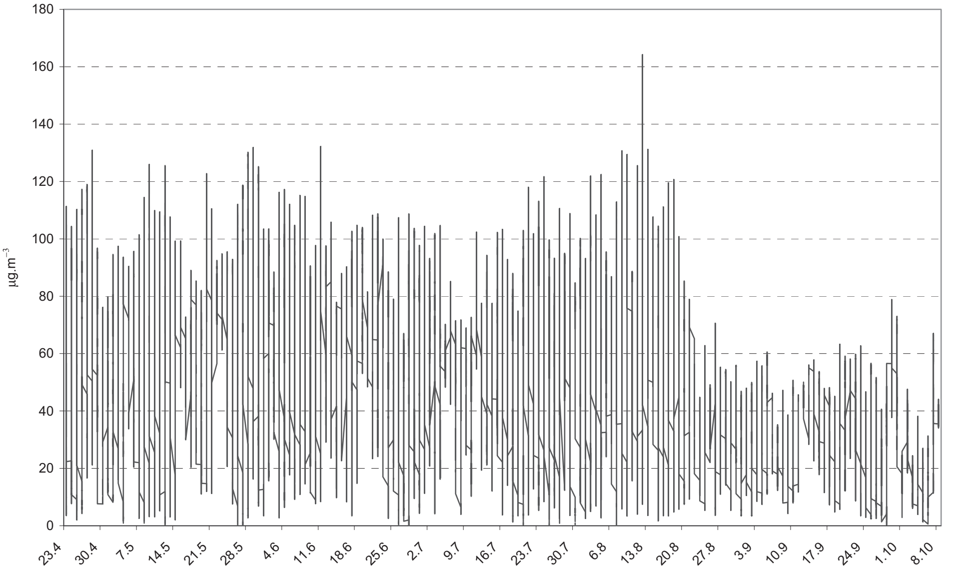

Fig. 3. 30 min. ozone concentration, Východná, 1998.

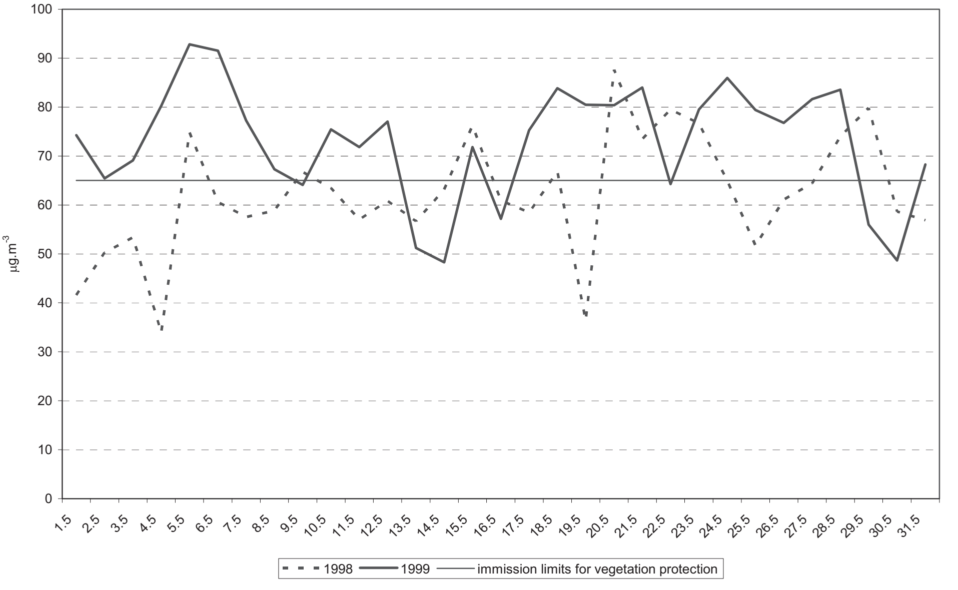

Fig. 4. 24 h ozone concentration, Východná, May.

Original immission limit for vegetation protection of 65 µg.m^{-3} (24 h average) valid in given time was most frequently exceeded in May, when in 1999 it reached 77% of records (Fig. 4). As the figure shows, the limits were not exceeded only within 7 day. The number of threshold exceeding in June were more-less same (31% in 1997, 33% in 1998 and 36% in 1999), only monthly progress was different. 1999 was in other months affected by increased exceeding of limits compare to other observed years.

To evaluate longer-term ozone impact on vegetation, according to the "Draft Manual for Mapping Critical Levels/Loads, 1990", limit of 50 µg.m^{-3} was used (not in force nowadays), which had been recommended by ECfE and calculated as average of day hours (9^{00} 16^{00} h) during vegetation period (April–September). The length of vegetation period is different as it depends on regions. A main vegetation period is since the beginning of May to the beginning of September (i.e. 4–4.5 months), while a normal vegetation period starts in the beginning of April and ends by the end of September (i.e. 6 months). We sampled also in October, as we tried to include also the time, when some grassy species are in bloom, so we took into consideration period of April–October.

It should be mentioned, that in the time of monitoring, when the limit was valid, the most of values exceeded it. Vegetation was in this 3-year period under effect of high concentration of tropospheric ozone. Fig. 5 shows the result of this. It is a picture of spruce needle damage at the Východná site. Impact of ozone on vegetation can be immediate and permanent.

Fig. 5. Example of spruce needle damage (*Picea abies*) driven by ozone.

Actual target value for vegetation protection is 18 000 $\mu g.m^{-3}.h$ (average of 5 years). In this case we determined AOT40 for shorter period (3 years). We found, that the limit of 18 000 $\mu g.m^{-3}.h$ was not exceeded (11 345 $\mu g.m^{-3}.h$ in 1997, 10 236 $\mu g.m^{-3}.h$ in 1998 and 13 695 $\mu g.m^{-3}.h$. in 1999). So, the average for observed period is 11 758 $\mu g.m^{-3}.h$. For comparison purposes, AOT40s from close localities where the ozone monitoring have been running since 1992 is as follows: Štrbské Pleso 17 057 $\mu g.m^{-3}.h$, Stará Lesná 15 870 $\mu g.m^{-3}.h$ (period of 1999–2002) (The report on air quality and contribution of individual sources to its pollution in SR, 2002).

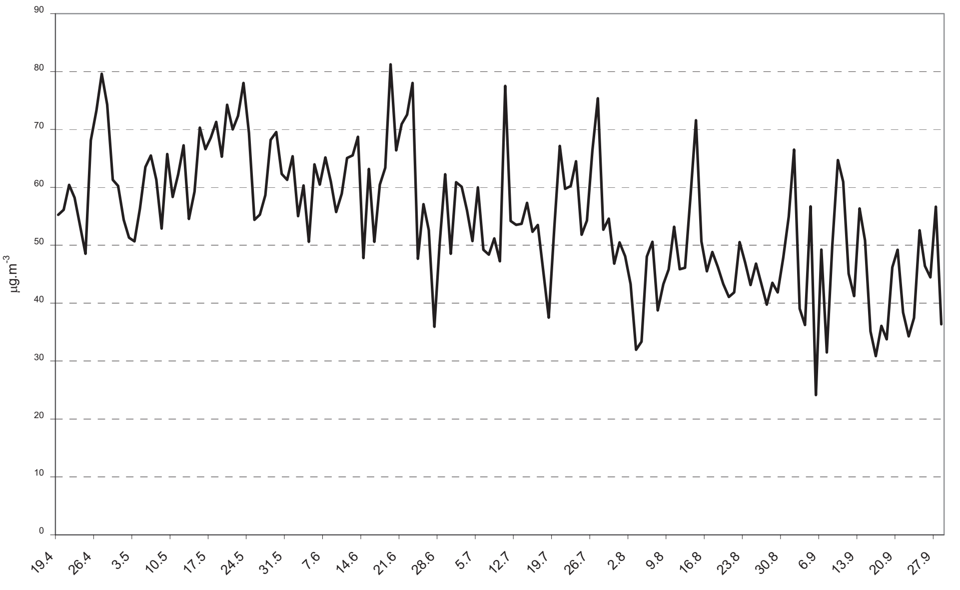

Fig. 6. Daily ozone concentrations, Východná, 1997.

The target value for human health protection is 120 $\mu g.m^{-3}$. This value was not exceeded, but the limit valid until 2001 (110 $\mu g.m^{-3}$) was exceeded most frequently in 1999, as much as 15 times. According to the calculations, the most critical days, concerning both human health and vegetation protection, were 24.5.–28.5.1999, when values of at least one measurement exceeded 110 $\mu g.m^{-3}$ (especially in periods of 8–17 h and 12–21 h)

Maximal day ozone concentration during first year (Fig. 6) was 81.23 $\mu g.m^{-3}$ (19.6.) while minimal 24.14 $\mu g.m^{-3}$ (5.9.). Compare to 1997, higher day concentrations were recorded in 1998 (Fig. 7) – maximum 87.64 $\mu g.m^{-3}$ (20.5.) and minimum 10.19 $\mu g.m^{-3}$ (5.10.). Ozone concentration progress in 1999 (Fig. 8) resembles previous year except for much higher September and October values. Maximum was 91.52 $\mu g.m^{-3}$ (6.5.) and minimum 29.71 $\mu g.m^{-3}$ (13.10.).

Monthly average values (Fig. 9) ranged from 31.45 $\mu g.m^{-3}$ (September 1998) through 57.22 $\mu g.m^{-3}$ (July 1997) up to 72.99 $\mu g.m^{-3}$ (May 1999).

On the base of mentioned information on ozone concentration at the Východná site, we can state the need to study relation of ozone concentration to some meteorological parameters (moisture, temperature, precipitation etc.).

As there was no possibility to perform own meteorological measurements at the localization of ozone analyzer device, we used data from the Slovak Hydrometeorological Institute (SHMI) stations placed as close as possible – Tatranská Polianka and Poprad Gánovce. Both

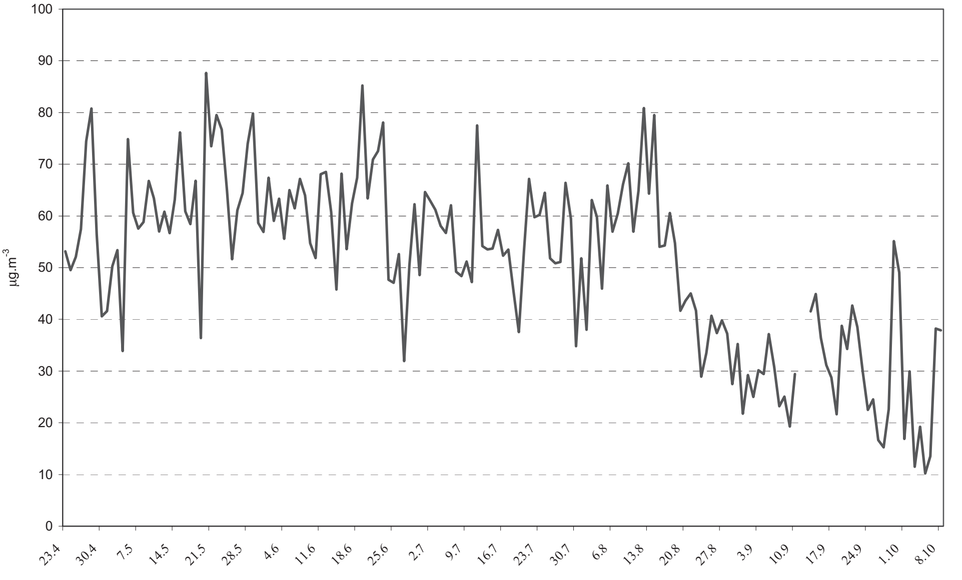

Fig. 7. Daily ozone concentrations, Východná, 1998.

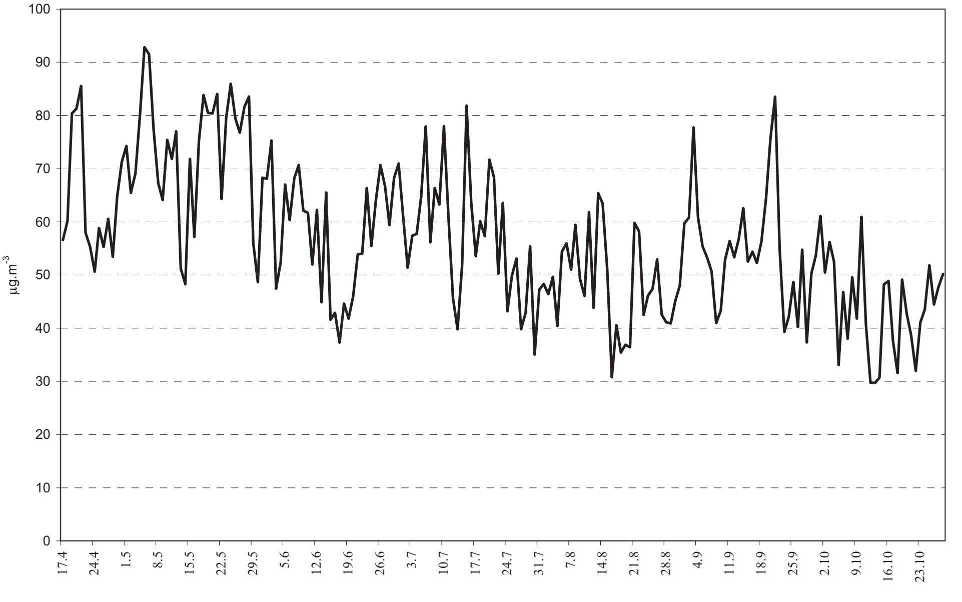

Fig. 8. Daily ozone concentration, Východná, 1999.

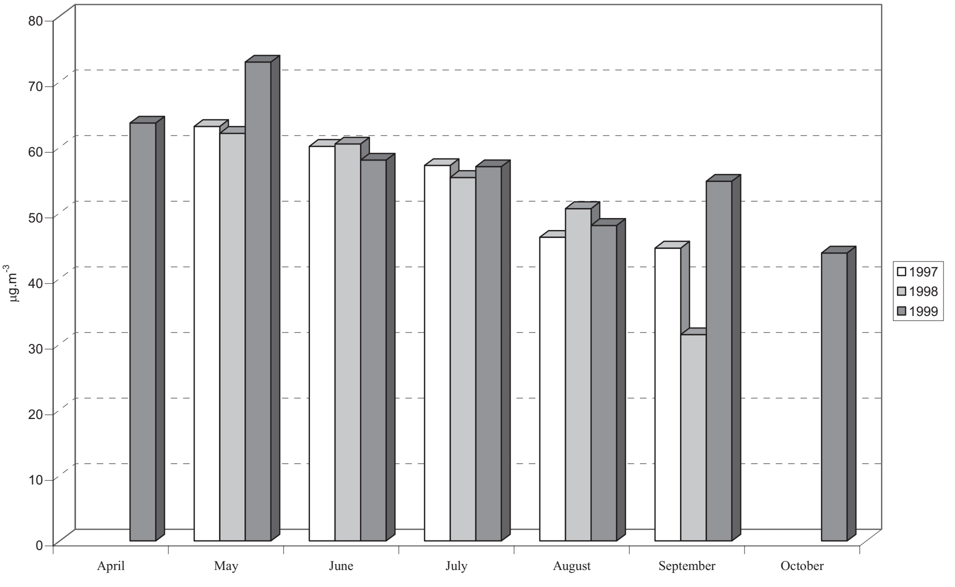

Fig. 9. Monthly ozone concentration, Východná, measured by Ozone Analyzer.

localities are relatively distanced; therefore these data cannot exactly reflect state around ozone analyzer location. However, progress of weather at the locality is similar; therefore these data can be used to evaluate the relations between climatic conditions and ozone.

Correlating ozone and meteorological parameters from Tatranská Polianka station we found, that the strongest relation of ozone concentration is to moisture (Figs 10, 11) and precipitation (Fig. 12), best illustration yields July values of 1998 – Fig. 13. During nice and sunny days, average moisture was somewhere in the region of 49.8% and ozone concentration was 82.18 $\mu g.m^{-3}$. On the other hand, when average moisture was somewhere in the region of 80%, that ozone concentration was 62.88 $\mu g.m^{-3}$. Temperature was another studied parameter. During summer, as the temperature is getting higher, ozone concentration is increasing either.

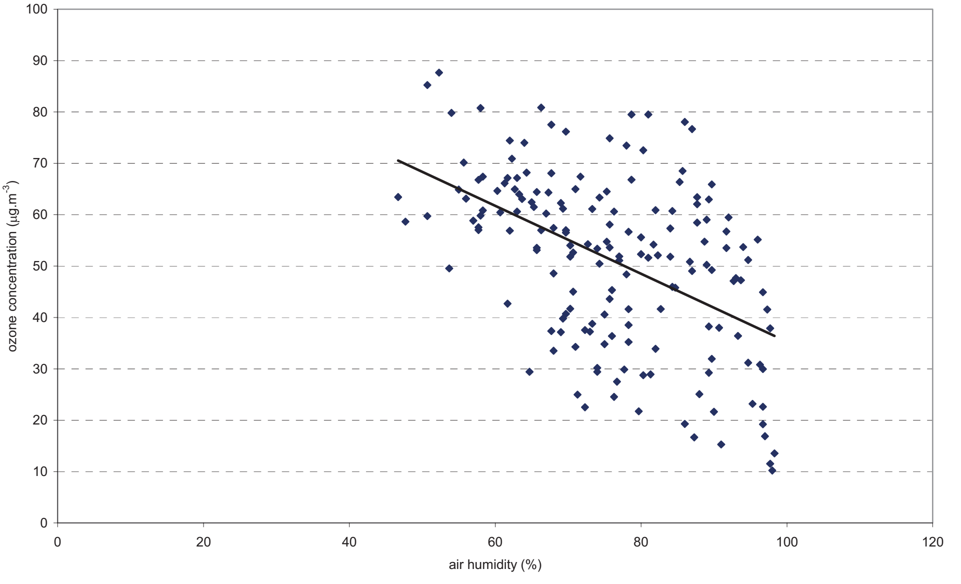

Fig. 10. Correlation of ozone concentration – moisture, 1998.

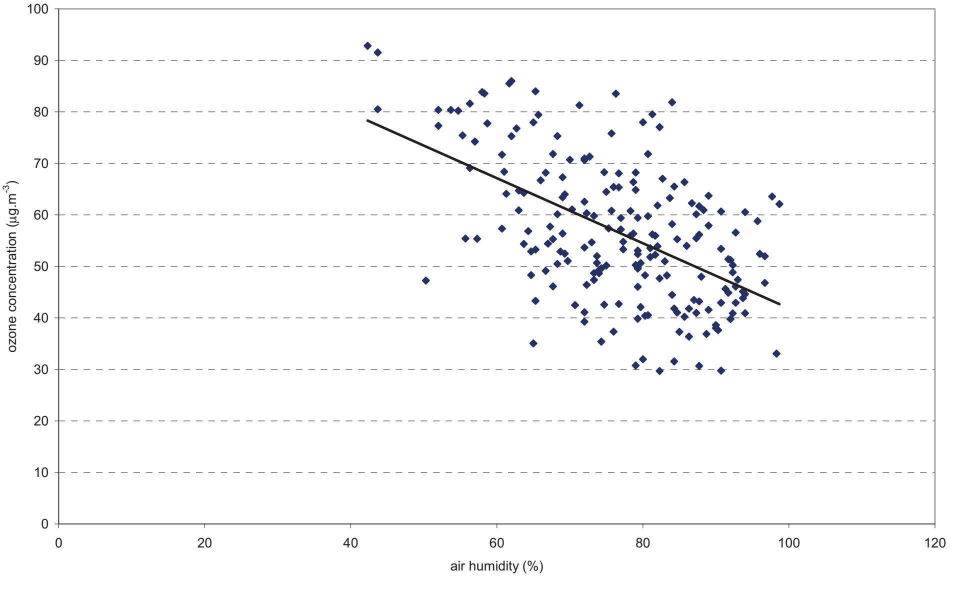

Fig. 11. Correlation of ozone concentration – moisture, 1999.

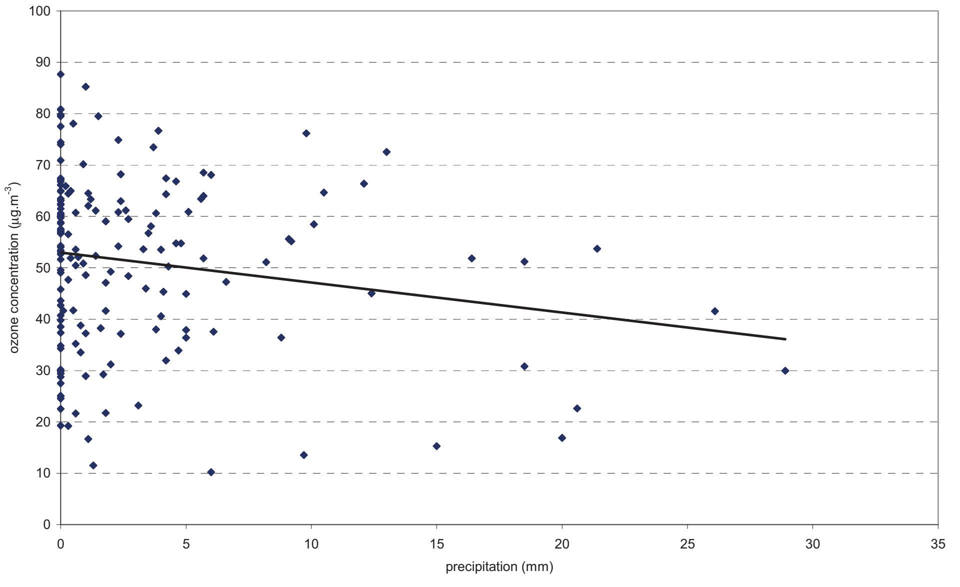

Fig. 12. Correlation of ozone concentration – precipitation, 1998.

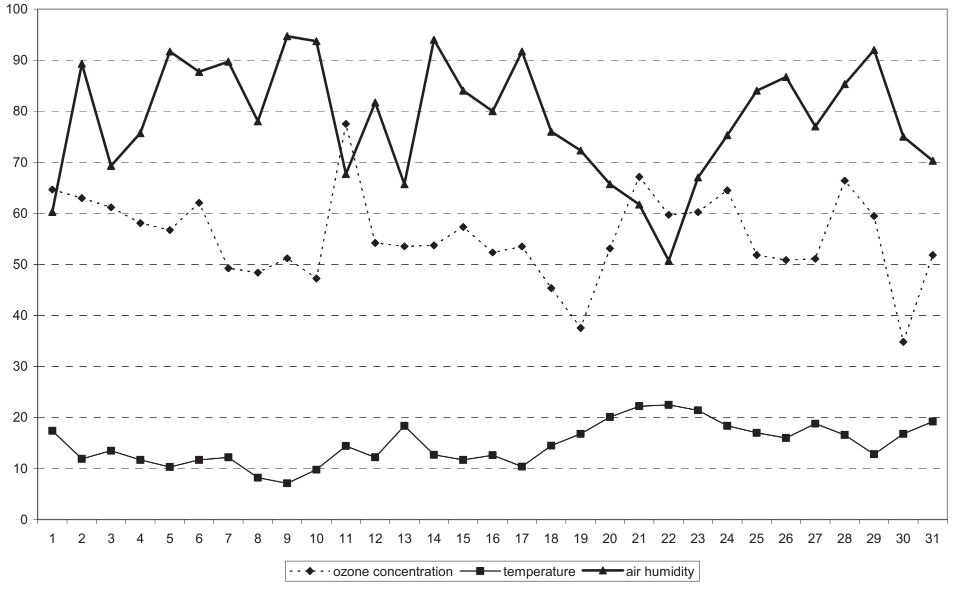

Fig. 13. Relation of ozone concentration to moisture and temperature, July 1998.

Results of ozone measurements by passive samplers

Ozone concentration recorded by passive samplers yields more-less same trend at individual sites. The half-month average values were in the range of 40–120 μg.m^{-3}, only at Malé Karpaty Mts and Malá Fatra Mts they reached 144.23 μg.m^{-3} and 179.08 μg.m^{-3} in May, 1998 (Fig. 14).
In the Malé Karpaty Mts, the highest monthly average values were recorded during of May – 110.88 μg.m^{-3} (1998), 121.24 μg.m^{-3} (1999) and August – 107.73 μg.m^{-3} (1998). The lowest monthly ozone concentration was recorded. The highest seasonal (May up to September) average of ozone concentration was recorded in 1998 reaching 96.26 μg.m^{-3}.

Concerning Malá Fatra Mts site, ozone concentration was on average lower in compare with the previous site. The highest monthly average values were recorded during of August – 114.79 μg.m^{-3} (1998) and May – 117.09 μg.m^{-3} (1999). The highest seasonal average of ozone concentration was recorded in 1998 (as by the previous site) and reaching 95.18 μg.m^{-3}.

The site of Kozie chrbty Mts – Východná yields the lowest monthly average values. The highest seasonal average value of all 3 years was in 1998 – 63.75 μg.m^{-3}. The highest monthly average values in individuals years were as follows: 71.1 μg.m^{-3} in June (1998) and 76.38 μg.m^{-3} in May (1999).

As for the Javorníky Mts (Turkov) site, the highest seasonal ozone concentration average was in 1998 – 79.02 μg.m^{-3}. The highest recorded monthly average value was in May – 90.88 μg.m^{-3} (1998) and in August – 89.1 μg.m^{-3} (1998).

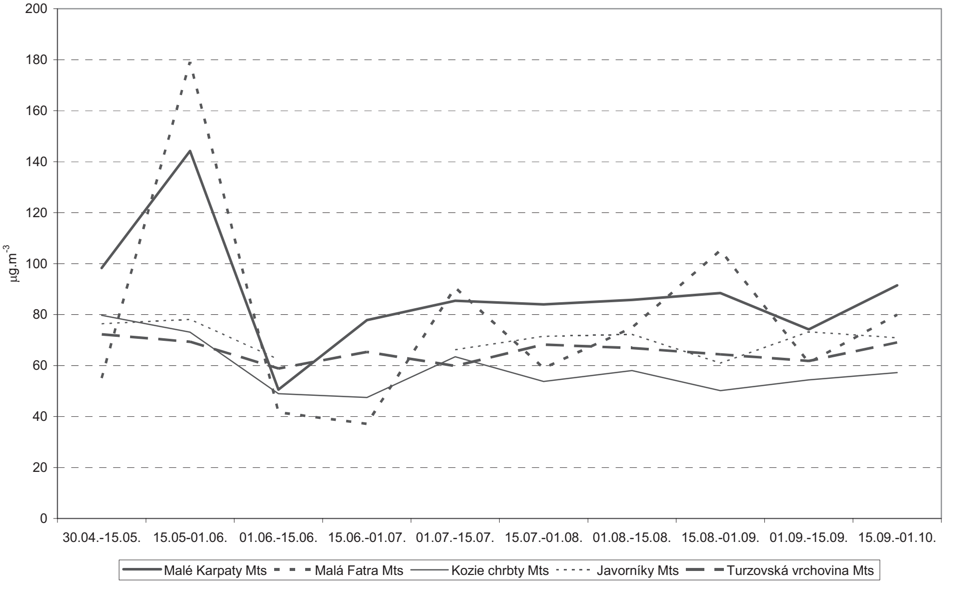

Fig. 14. Half month average ozone concentration, 1999.

Ozone concentrations from Turzovská vrchovina Mts (Riečky) site resemble previous site. The highest concentration was in 1998, when in August was monthly average value of 86.07 $\mu g.m^{-3}$. This year was reached also the highest seasonal average (71.75 $\mu g.m^{-3}$). In 1997, the highest monthly average concentration was 50.69 $\mu g.m^{-3}$ and in 1999 65.60 $\mu g.m^{-3}$.

Comparing ozone concentrations measured by ozone analyzer device and passive samplers at the Východná site we found, that in 1997, the values of monthly concentrations were balanced (Fig. 3). In 1998, the values measured by passive samplers were higher (except for May), the highest differences were recorded in August and September, it was ranged from 20.36 $\mu g.m^{-3}$ to 21.36 $\mu g.m^{-3}$ (Fig. 15). Differences in 1999 were not as distinct as in previous year (Table 4).

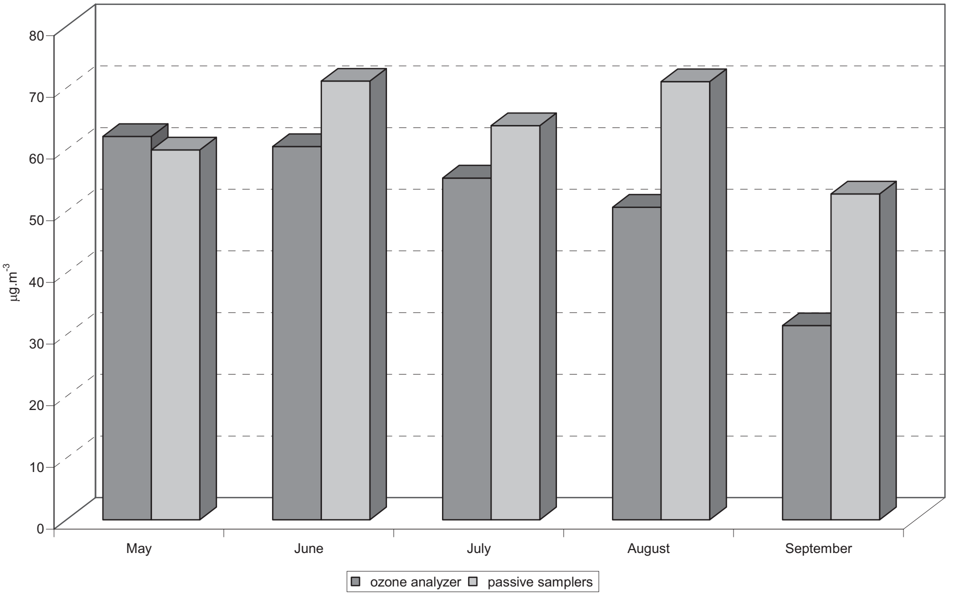

Fig. 15. Comparison of monthly ozone concentration, Východná, 1998.

Conclusion

Contemporary valid target and threshold concentration values for ground ozone were not reached nor exceeded at observed sites as actual limits are much more moderate and they do not reflect ground ozone negative impact on vegetation and population.

International limits set by EU and Economic Commission for Europe concerning vegetation and human health protection valid until 2001 were exceeded at sampled sites frequently.

T a b l e 4. Monthly average ozone concentration comparison during observed period at the Východná site.

Year	Month	Ozone analyzer (μg.m^{-3})	Passive samplers (μg.m^{-3})
1997	May	63.18	61.45
	June	60.15	63.97
	July	57.22	50.42
	August	46.29	45.11
	September	44.65	42.82
1998	May	62.13	59.95
	June	60.49	71.11
	July	55.40	63.89
	August	50.65	71.01
	September	31.45	52.81
1999	May	72.99	76.38
	June	58.06	48.20
	July	57.06	58.61
	August	48.10	54.09
	September	54.83	55.82

The highest values using ozone analyzer were recorded in May, which is also period of the most frequently exceeded limit (65 μg.m^{-3} within 24 hours) set for vegetation protection. Spring ozone concentration maximum reflects ozone transport from higher parts of atmosphere and is spread as a consequence of ozone photochemical production in border layer of atmosphere to all summer time.

At longer-term monitoring of ozone impact with the limit of 50 μg.m^{-3}, this was exceeded all the time, in some cases doubly. The plants exposed to such permanent stress are getting much more vulnerable and their damage is faster, as during vegetation period they are the most sensitive.

The most critical period of ozone concentration impact was the end of May, 1999. Recorded values exceeded limit of 110 μg.m^{-3}.

Reasons of these concentrations may be various. We found, that one of the reasons can lie in correlation to some meteorological parameters, e.g. moisture, precipitations and temperature. Under the effect of high moisture the ozone concentration descends. At the Východná site, the concentration has fallen to zero, what should not happen in those natural conditions. High moisture can play major role also in this case. High concentration can be caused also by anthropogenous emission growth and its precursors: hydrocarbons, NOx and CO.

The monitoring of ozone concentration by passive samplers showed that it renders similar trends at individual sites. Concentrations are in the range of 40–120 μg.m^{-3} and have more–less similar progress except for 1999, where ozone concentrations at the sites of Malé Karpaty and Malá Fatra reached high values in May.

It is important to note, the tropospheric ozone can be transported by air mass tens up to hundreds of km. Under the effect of some special climatic conditions it is possible, that ozone from e.g. Katowice can be respired in the region of Vysoké Tatry Mts or Nízke Tatry Mts. Tropospheric ozone is one of the factors supporting formation of acid atmospheric depositions.

Monitoring of tropospheric ozone, as significant air pollutants and stress factor, points to the fact, how the ozone effects negatively vegetation as well as human health. Its continual concentrations can cause respiration problems and decrease of physical performance to population, and affect photosynthesis processes.

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References

Koutrakis, P.J., Wolfson, J.M., Banyaviroch, A., Froelich, S.E., Hirano, K., Mulik, J.D., 1993: Measurement of ambient ozone using a nitrite-coaled filter. Anal. Chem., *65*: 210–214.

Mazúr, E., Lukniš, M., 1980: Geomorphological units (in Slovak). In Atlas SSSR, SAV.

Regulation of MoE SR No. 705/2002 on air quality.

Szdzuj, J., 1999: Attempt to determine a relationships between forest damage and air pollution level. Brenna case study (in Polish). Thesis, Uniwersytet Śląski, Katowice, 105 pp.

Závodský, D., 1998: Ground ozone (in Slovak). XXI. century, *1*, 2: 26–27.

Závodský, D., 2002: Atmospheric ozone (in Slovak.) In Správa o kvalite ovzdušia a podiele jednotlivých zdrojov na jeho znečisťovaní v Slovenskej republike 2001. SHMÚ, MŽP SR, 132 pp. 42 tab., 131 fig.