TROPOSPHERIC OZONE AT THE SLOVAK MOUNTAIN STATIONS IN 2003-2004

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Abstract: The continuous surface ozone monitoring in Slovakia started in 1992 when the Slovak Hydrometeorological Institute (SHMI) established a real time air pollution monitoring system of the Slovak Republic. Data from seven mountain stations have been analysed. Five of them are located in the High Tatras region. The station altitudes are from 694 to 2635 m. Annual averages of ozone concentrations and other statistical characteristics have been calculated. The annual averages range from 33,3 to 56,9 ppb in 2003 and from 30,9 to 49 ppb in 2004. These values represent interannual decrease from 4,6 to 16,2 %. The highest yearly averages are in both cases at peak mountain station Lomnický štít, the lowest at background EMEP station Stará Lesná. The mean daily and annual courses of surface ozone concentrations at these stations are presented in this paper. The shape of course curves and occurrence of maxima and minima on individual stations are described in detail. Also vertical profiles of the daily ozone averages for individual years and months are presented in the paper. Profiles from eight 3-hour intervals during the day have been calculated too.
Key words: surface ozone, mountain stations, annual course, daily course, vertical profile

Introduction

Over the last three decades some regional problems of air pollution have occurred in the atmosphere over Europe. The elevated emissions of sulfur and nitrogen and their long-range transport result into ecosystem acidification. This problem of acid deposition reached the zenith in the last decade. The problem has not been solved so far, but after passing the UN ECE Convention on long-range transboundary air pollution important progress has been made. Conversely, the photochemical oxidants and especially surface ozone have become major regional atmospheric pollutants throughout Europe.

The most of atmospheric ozone is present in the stratosphere (more than 90 %). In the troposphere there is only less than 10 %. The maximal ozone concentrations are in the layer in altitudes between 20 and 25 km. From this layer ozone penetrates the tropopause and the troposphere and then reaches the surface where it is destructed. This mechanism prevailed in the past when the stratosphere was the main source of ozone in the troposphere. At present the significant source of ozone is its photochemical production in the troposphere.

In the mid 1940s the episodes with the high concentrations of surface ozone occur for the first time in Los Angeles. This phenomenon was later named as the photochemical smog and it was thought to be a local problem of the air pollution only. But nowadays this problem obtains more than regional character. The measurements show that areas with the high concentrations of ozone can reach the horizontal dimensions about hundreds of kilometers during the episodes of the photochemical smog.

The photochemical smog affects a large part of Europe every year. European episodes of the high concentrations of surface ozone (90-200 ppb) are mostly connected with stagnant anticyclones. They usually last several days. The typical weather during episodes is a clear sky, a high intensity of solar radiation and a high temperature.

The present high surface ozone concentrations are caused by the elevated tropospheric ozone production. Photochemical processes produce ozone in the troposphere from nitrogen oxides (NO_X), volatile organic compounds (VOC) and carbon monoxide (CO). Natural processes in soils and vegetation emit these compounds. But the large emissions of these gases have the origin in combustion as well, especially by motor vehicles and industrial processes.

Ozone is a harmful air pollutant. The high concentrations of surface ozone have injurious effects on the health of humans, animals and vegetation. Therefore the tropospheric ozone is an internationally important pollutant. For these reasons national governments of Europe, taking into account obligations resulting from UN ECE Convention on long-range transboundary air pollution, support surface ozone monitoring programmes as well as are implementing measures to control the emissions of ozone precursors.

Summer in the year 2003 was extraordinarily photochemically active, extremely hot and dry (Faško et al., 2003). This fact was demonstrated by record number of exceedances of ozone imission limits and increasing of average concentrations at all Slovak stations. Therefore considerable attention was devoted to this year, for example we can recall paper by Hrouzková et al. (2004) and Bičárová et al. (2005).

Data

The continuous surface ozone monitoring in Slovakia started in 1992 when the Slovak Hydrometeorological Institute (SHMI) established a real time air pollution monitoring system of the Slovak Republic. The ozone analyzers Thermoelectron, MLU and Horriba are used. They operate on the principle of UV absorption. Their detection limit is 1 ppb. The national secondary ozone calibration standard was installed in Slovakia in 1994. Intercomparisons with the Czech primary ozone standard are regularly organized.

Quality of the ozone data was not adequate especially in first years of measurements. On some stations the various gaps in the ozone data as to duration occurred due to breakdowns of the analyzers, pumps and problems with air-conditioning. This disadvantageous state was caused by budgetary troubles of the Slovak Hydrometeorological Institute.

EMEP background station Chopok was until the year 1998 the only station measuring surface ozone concentrations in higher altitudes. Measurements at Kojšovská hoľa started in 1999, Štrbské Pleso in 2000 and Lomnický štít in 2002. Besides these stations in this study was used data from 2 lower located stations in the High Tatras region (Stará Lesná and Poprad Gánovce) and also from the station Solisko.

Measured ozone data in the electronic database of SHMI are in $\mu g.m^{-3}$. At first all mean 1-hour ozone concentrations had to be converted into ppb. Then were calculated average monthly and yearly values for individual hours, 3-hour intervals of the day and the whole day. On the base of these values daily and annual course of concentrations and vertical profiles at Slovak mountain stations were constructed.

Results and discussion

Calculated monthly and yearly averages of the surface ozone concentration for the years 2003 and 2004 at 6 Slovak mountain stations are in table 1 and 2. The mean values range from 33,3 to 56,9 ppb in 2003 and from 30,9 to 49 ppb in 2004. These values represent interannual decrease from 4,6 to 16,2 %. The highest yearly averages are in both cases at peak mountain station Lomnický štít, the lowest at background EMEP station Stará Lesná. The monthly means range from 21,2 to 67,6 ppb (2003) and from 17,6 to 56,8 ppb. Decrease of all commemorated characteristics in the year 2004 is particularly due to interannual change of meteorological conditions (photochemically very active summer in 2003).

Table 1 The mean surface ozone concentration in ppb for individual months and the whole year 2003 at Slovak mountain stations (maximal monthly averages in the yearly course are red, minimal blue)

Station	Alt. [m]	1	2	3	4	5	6	7	8	9	10	11	12	Year
Lomnický štít	2635	56,1	59,1	67,6	65,0	60,2	61,4	60,2	62,2	54,1	47,1	44,8	44,5	56,9
Chopok	2008	42,5	47,8	58,6	59,7	57,7	59,8	55,1	59,9	44,7				54,3
Štrbské Pleso	1354	30,4	37,9	47,1	47,2	50,4	52,8	47,3	57,1	45,3	33,5	33,3	36,7	43,2
Kojšovská hoľa	1248	31,5	40,2	51,5	51,4	56,5	57,3	54,7	60,3	48,1	33,3	33,1	36,0	45,5
Stará Lesná	808	24,5	36,6	42,8	43,9	32,3	35,1	37,2	41,1	36,4	23,6	22,3	25,9	33,3
Poprad Gánovce	694	23,4	31,1	39,5	42,3	41,2	40,9	39,1	44,6	33,6	26,2	21,2	23,3	33,8

Table 2 The mean surface ozone concentration in ppb for individual months and the whole year 2004 at Slovak mountain stations (maximal monthly averages in the yearly course are red, minimal blue)

Station	Alt. [m]	1	2	3	4	5	6	7	8	9	10	11	12	Year
Lomnický štít	2635	42,2	45,7	50,9	52,6	54,9	53,7	54,4	52,5	49,1	45,6	40,1	46,6	49,0
Chopok	2008	28,8	42,3	38,6	56,8	54,6	52,6	52,3	52,4	45,7	42,4	37,0	42,4	45,5
Štrbské Pleso	1354	33,1	39,3	42,6	48,1	43,1	42,6	37,5	39,8	35,1	33,4	28,8	35,2	38,2
Kojšovská hoľa	1248	32,1	39,5	45,5	52,7	51,1	48,6	50,1	50,3	43,4	39,0	31,5	32,2	43,0
Stará Lesná	808	26,5	34,6	37,9	41,4	37,8	32,8	31,8	34,2	27,5	23,2	23,3	20,4	30,9
Poprad Gánovce	694	24,8	34,6	37,8	38,4	40,8	36,4	34,1	35,5	29,1	26,0		17,6	32,3

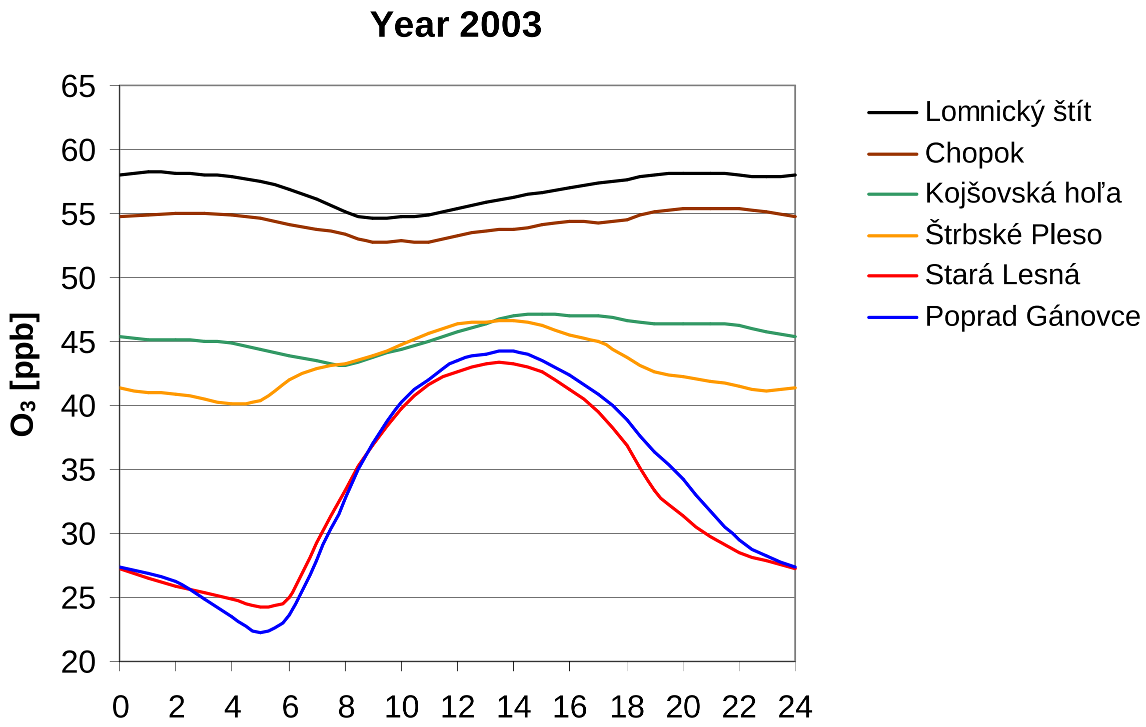
In figure 1 there are daily courses of the surface ozone concentrations at mountain stations in both years. We can demonstrate an impact of vertical ozone transport in atmospheric boundary layer and lower free troposphere by these curves. The highest levels of concentrations are at stations Lomnický štít and Chopok, high concentrations are also at Kojšovská hoľa and Štrbské Pleso. Lower values, but more substantial daily course one can observe at stations Stará Lesná and Poprad Gánovce, which are located in lower altitudes.

In the morning time ozone concentrations at highest stations are decreasing (typical mountain daily course, it is partly valid for Kojšovská hoľa too) and at lower station are increasing. This fact manifests vertical turbulent transport of ozone in the direction of ozone concentration gradient (from above to the bottom). It is sure that the whole increase at lower stations is not caused only by this transport. In the afternoon the maximal values at Stará Lesná and Poprad Gánovce are approaching to the concentrations at Štrbské Pleso and Kojšovská hoľa.

In January the daily ozone courses at Slovak stations have small amplitudes in general (figure 2 at the top). At 4 higher mountain stations we cannot talk about the daily course, because concentrations almost do not change. The levels of concentrations vary significantly at individual mountain stations in different altitudes. The concentration gradient is quite high, but turbulent transfer does not occur.

The daily courses are more expressive in April (figure 2 at the bottom). Course curves of mountains stations are getting closer. Daily maxima at Stará Lesná and Poprad Gánovce are higher than maximum at Štrbské Pleso.

The daily courses are very substantial from May to August (see figure 3). Curves at Lomnický štít, Chopok and Kojšovská hoľa are very close during the whole day, although stations are in diverse altitudes (1400 m difference). Significant vertical turbulent transport of zone occurs from the morning to noon. Ozone concentrations equalize at around 1 – 2 p. m. at all stations in the whole elevation profile. Summer curve of the daily course at Štrbské Pleso is attractive, because its shape is not typical for high mountain station (with morning time decrease of concentrations).



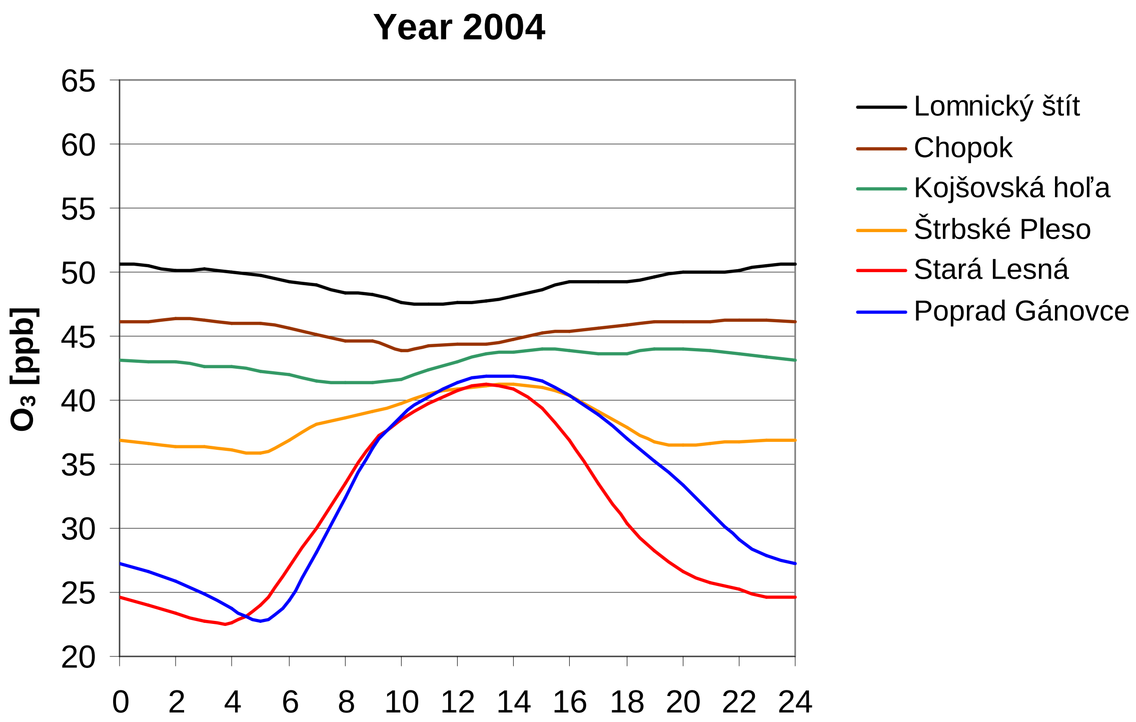


Figure 1 The daily course of surface ozone concentrations at Slovak mountain station in the years 2003 and 2004

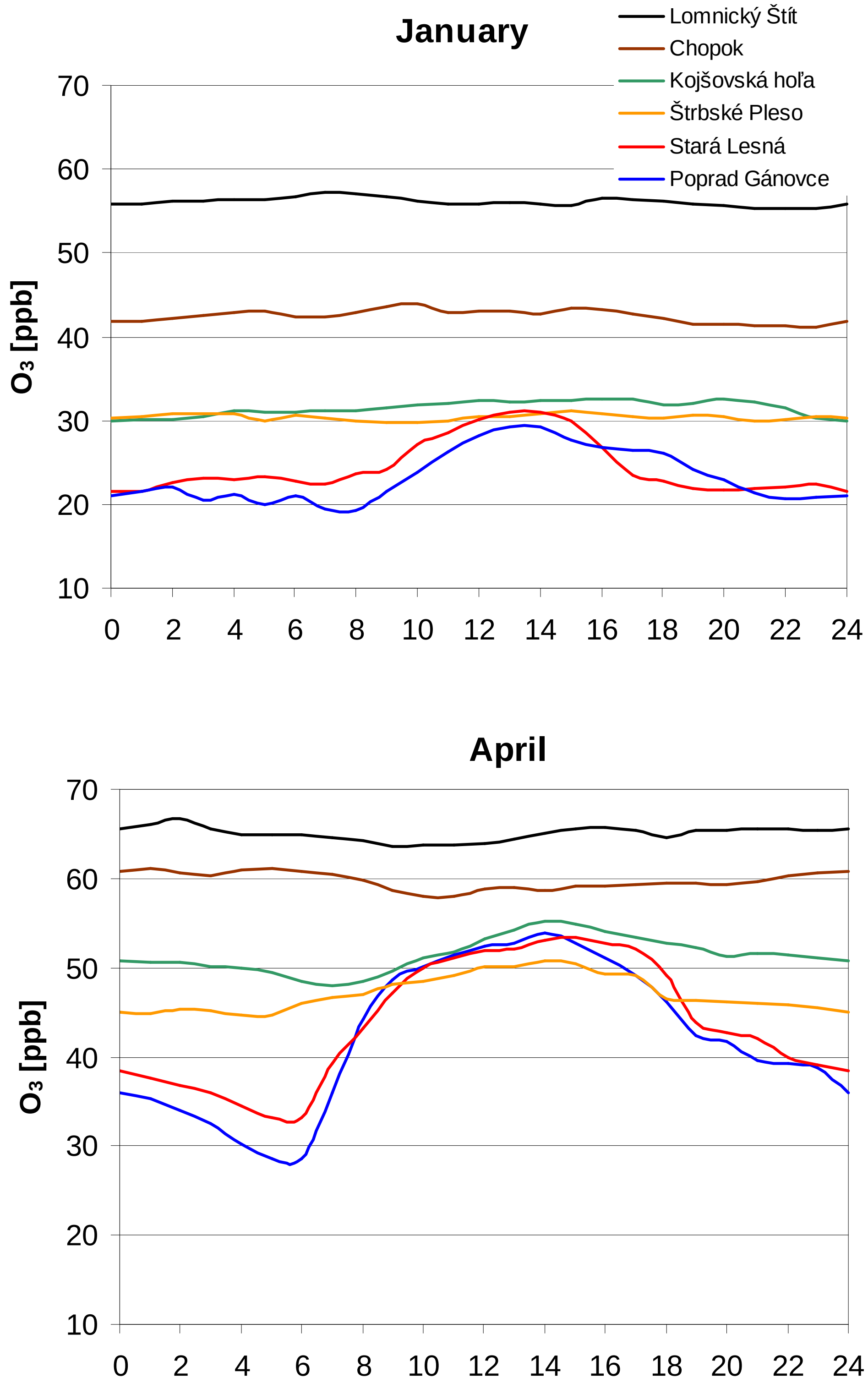


Figure 2 The daily course of surface ozone concentrations at Slovak mountain station in January and April 2003

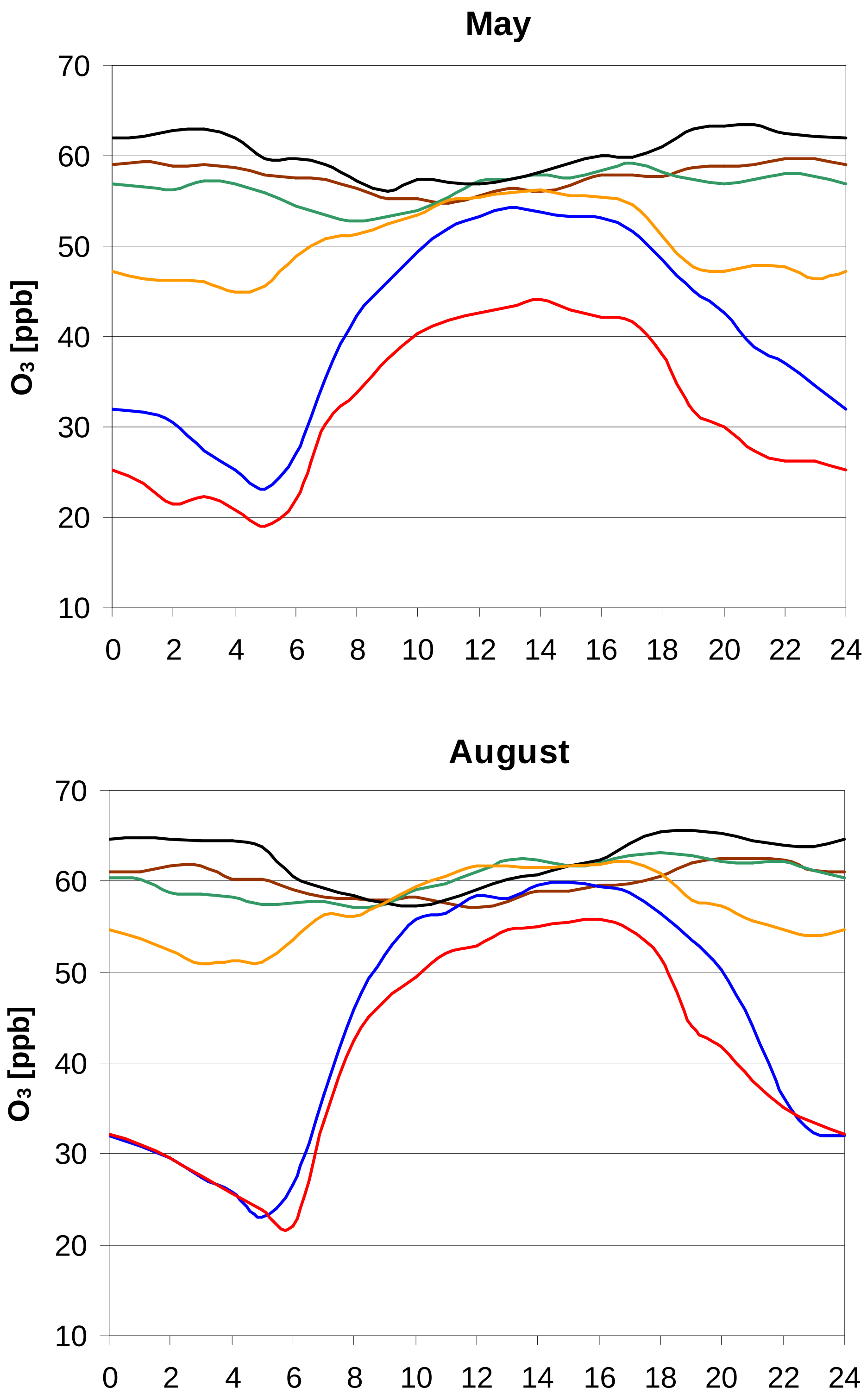


Figure 3 The daily course of surface ozone concentrations at Slovak mountain station in May and August 2003

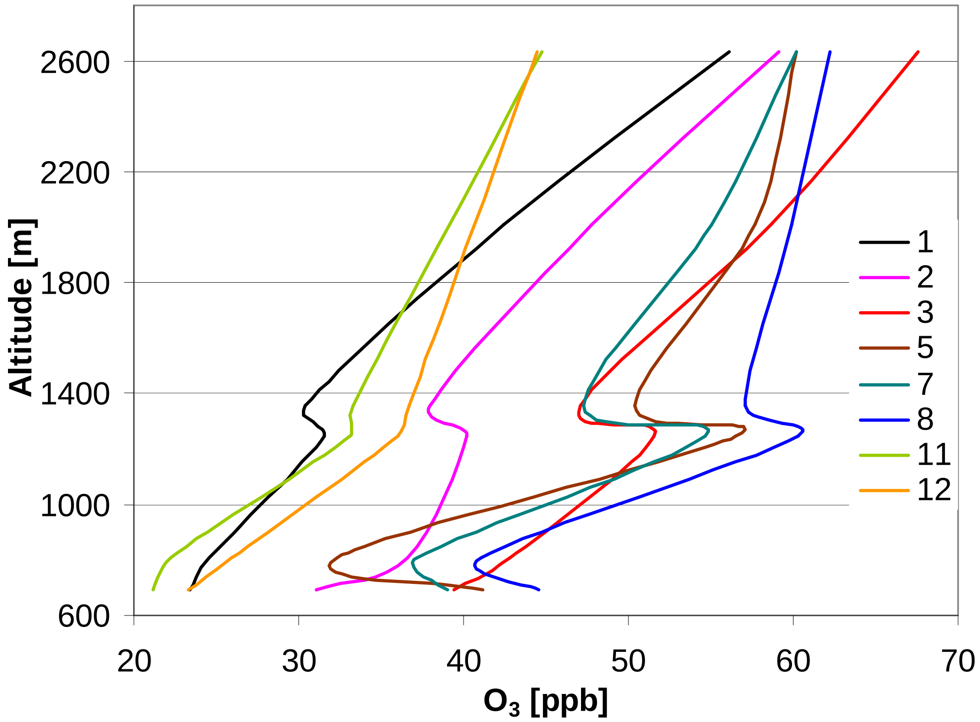


Figure 4 The vertical profiles of surface ozone concentrations at Slovak mountain station in selected months of the year 2003

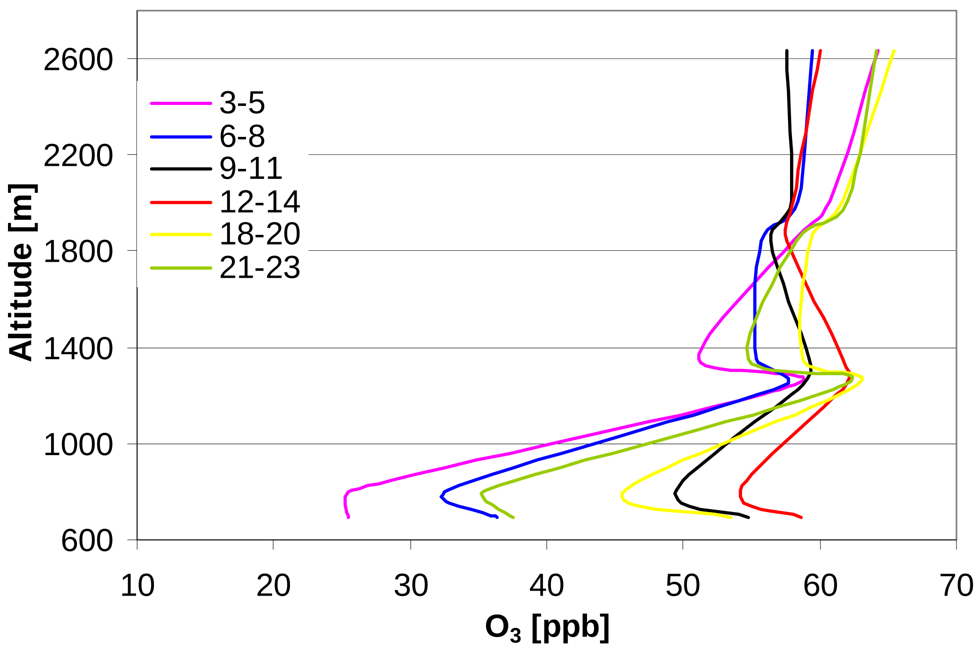


Figure 5 The vertical profiles of surface ozone concentrations at Slovak mountain station in selected 3-hour intervals of the day in August 2003

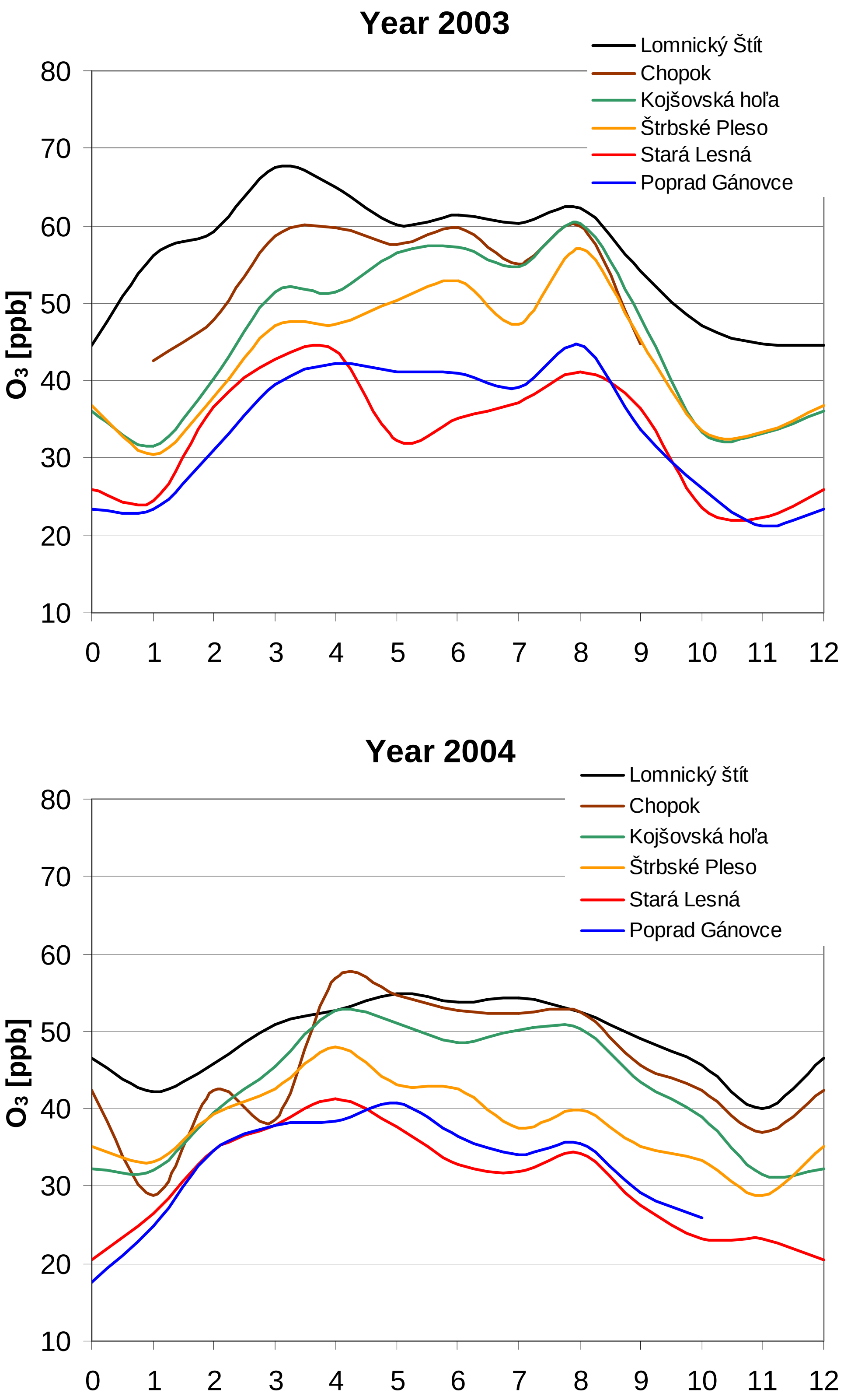


Figure 6 The annual course of surface ozone concentrations at Slovak mountain station in the years 2003 and 2004

In figure 4 we can see the vertical profiles of ozone concentrations at Slovak mountain station in selected months of the year 2003. The increase of concentrations with altitude is almost linear in winter months (the highest increase is in January). The increase is slowing down in April in altitudes above 2000 m. In summer the ozone concentrations increase rapidly in locations between 700 and 1350 m and slowly above 1350 m on the other hand (especially in August). During autumn the vertical profile of concentrations is approaching to winter profile.

Slightly lower values at station Štrbské Pleso in comparison with Kojšovská hoľa (situated in lower altitude) are surprising at first sight. As you can see in figure 6, where annual courses in the years 2003 and 2004 are presented, the difference between these two stations is smaller in winter and bigger in summer. This fact is due to location of the stations. At first ozone concentrations at Kojšovská hoľa are probably higher (because of southern position) than concentrations that would be at the station located in the High Tatras region with the same altitude. At second station Štrbské Pleso is situated near sanatorium Helios in the mouth of Mengusovská valley. Obviously there is higher ozone deposition (trees near the station) in comparison with other high mountain stations, which are located at the mountain peaks, and particularly ozone concentrations are influenced by local emissions nitrogen oxides from car transport and heating. Also this is supported by the daily course at the station, which differs from other high mountain station. The daily maximum at Štrbské Pleso occurs in the afternoon like at the stations in lower altitudes, but the amplitude is smaller.

The vertical profiles for selected 3-hour intervals during the day in August 2003 are presented in figure 5. Also data from the station Solisko (1840 m a.s.l.) are included in these profiles. Picture shows the curve approaching to vertical direction in the morning time and it's persisting in this direction in the afternoon. Some interesting findings emerge from this figure. Station Solisko measures slightly lower values than peak stations Chopok and Kojšovská hoľa. The difference can be probably assigned to higher ozone deposition at this slope station. The daily amplitude is similarly small. We have already talked about Štrbské Pleso. The next strangeness of the vertical profile is differences in concentrations between stations Stará Lesná and Poprad Gánovce (distance approximately 20 km, elevation difference 120 m). The values at these stations are equal in the night hours. Higher afternoon and evening concentrations at Gánovce can be explained only by local production. Gánovce are more exposed to local emissions of nitrogen oxides than Stará Lesná.

Figure 6 shows the annual courses of the surface ozone concentrations at mountain station in the years 2003 and 2004. The highest concentrations during the whole year 2003 are at station Lomnický štít. This documents the importance of the ozone transport from higher levels. Maximum in the annual course occur at this station in March (2003). It is in agreement with conclusion of the project EUROTRAC II about relevance of in situ ozone production in the free troposphere from January to March. In 2004 the maximum at Lomnický štít occurs in May, but this result is influenced by significant data gaps in March and April. In these months substantial gaps were also at Chopok.

Conclusions

The mean annual ozone concentrations at Slovak mountain stations range from 33,3 to 56,9 ppb in 2003 and from 30,9 to 49 ppb in 2004. They represent interannual decrease from 4,6 to 16,2 %. The highest yearly averages are in both cases at peak mountain station Lomnický štít, the lowest at background EMEP station Stará Lesná. Decrease of all commemorated characteristics in the year 2004 is particularly due to interannual change of meteorological conditions.

In the morning time ozone concentrations at highest stations are decreasing (typical mountain daily course) and at lower station are increasing. This fact manifests vertical turbulent transport of ozone in the direction of ozone concentration gradient (from above to the bottom). It is sure that the whole increase at lower stations is not caused only by this transport. In the afternoon the maximal values in the daily course at lower stations are approaching to the concentrations at stations in higher altitudes.

Maximum in the annual course occur at the highest peak station Lomnický štít in March (2003). It is in agreement with conclusion of the project EUROTRAC II about relevance of in situ ozone production in the free troposphere from January to March.

Location and altitude of the station have significant influence on levels of ozone concentrations and shape of the annual and daily course curves.

Acknowledgements: The Grant Agency of the Slovak Republic under the Project VEGA No. 1/1043/04 supported this study and SHMI data has been used. Author gratefully acknowledges the support.

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