Ground level ozone at the meteorological observatory Stará Lesná

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Abstract: Ozone data obtained at monitoring station Stará Lesná represent the special regional time series in the Slovak Republic. Mean hourly ozone concentrations measured by UV photometers at Stará Lesná during the 1992-2003 period were used. Average value 62.9 μg m^{-3} of ground level ozone concentration at Stará Lesná was observed. Maximal annual mean (71.8 μg m^{-3}), the highest number of exceedences (221) of the ambient air quality standard 110 μg m^{-3} (8 h) and maximal daily average (150 μg m^{-3}) of ground level ozone concentration was recorded in 1996. The primary spring maximum at Stará Lesná is connected with convenient photochemical conditions (decrease of relative humidity, increase of air temperature, positive changes in sunshine duration and UV radiation) and the abundance of pollution components as NO_2 and NO_3.

Key words: ground level ozone concentration, annual and daily course, air pollution over rural area, meteorological and radiation effects

1. Introduction

The formation, transport, and impact of tropospheric ozone along with other photo-oxidants is a major environmental problem due to high emissions of ozone precursors. Although major progress has been achieved within the last decade, there are still significant uncertainties in our understanding of the chemical behavior of the polluted atmosphere. Since 1987, more than 30 field research programs have been organized and implemented in

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North America and Europe to investigate tropospheric ozone and its precursors *(Solomon et al., 2000)*. Conclusions of Tropospheric Ozone Research (TOR-2) show that ozone peak values have been decreasing significantly over the last 10 years while background ozone and low ozone values in polluted areas have increased in Europe. Case studies have documented the variety of processes of vertical uplifting of boundary layer air into the free troposphere. In particular, warm conveyor belts have been shown to be an efficient mechanism for uplifting pollutants into the European free troposphere *(Lindskog et al., 2003)*. Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP project) represents European model evaluation studies. Based on the participation of the Slovak Republic, the regional ozone monitoring station was included to EMEP measuring network in 1991.

The purpose of this paper is to evaluate the variability of ground level ozone concentrations recorded at regional ozone monitoring station Stará Lesná during time period 1992–2003 and to provide the analysis of the relationship with the corresponding meteorological, radiation, and pollutant components.

2. Materials and methods

Experimental data obtained at Meteorological Observatory Stará Lesná from 1992-2003 were used. Mean hourly values of ozone concentration measured by ozone analyzers Thermo Environmental Instrument 49C, or Cranox, both based on UV absorption principle, have been evaluated. The national secondary ozone calibration standard was installed in Slovakia in 1993. Intercomparisons with the Czech primary ozone standard are regularly organized. Various gaps in the ozone data during considered time period occurred. Absent data fluctuated in the range from 0.6% in 2002 to 30.6% in 1993. They were completed in accordance with interpolation methods utilized in meteorology *(Nosek, 1972)*.

Measurements and recording of meteorological and radiation parameters are realized at Meteorological Observatory Stará Lesná (H = 810 m a.s.l., $\varphi = 49°09'$N, $\lambda = 20°17'$E) by central measurement data system ESM 200. The air temperature and relative air humidity are measured on thermometer screen at 2 m level above the surface. For air temperature the Kroneis

Tab. 1. Measurement programme of selected pollutants obtained at EMEP ozone monitoring station at Stará Lesná

Component	Unit	Sampling	Measurement period	Analysis methods
O_3	$\mu g\ m^{-3}$	UV-monitor	1 h	UV-absorption
NO_2	$\mu g\ N\ m^{-3}$	Absorbing solution NaOH and guajacol, 0.5 m^3/day	24 h	Spectrophotometric, Griess method
NO_3	$\mu g\ N\ m^{-3}$	Whatman 40 filter, 6-8 m^3/day	24 h	Ion chromatography/ Capillary electrophoresis
HNO_3	$\mu g\ N\ m^{-3}$	KOH-impregnated Whatman 41 filter, 6-8 m^3/day	24 h	Ion chromatography/ Capillary electrophoresis

NTC sensor, YSI 44212 (air temperature) and Vaisala MHP35D type relative air humidity were used. The Campbell-Stokes heliograph with green tape measures the sunshine duration and the tape evaluation is performed in tenths of the hour. Both global and diffuse radiations are measured by Sonntag pyranometer with galvanic thermels. Eppley UV-radiometer measures the global ultraviolet radiation on horizontal surface; model TUVR for wavelength range 290-385 nm. This instrument was recalibrated at the National Radiation Centre Hradec Králové according to the laboratory standard NBS with quartz-halogen lamp EPI-1755 1000 W. The 10-minute scanning interval of the local time is used for each sensor. These momentary data are stored in the central measurement station. The hourly averages, each calculated from 6 momentary values, are loaded on magnetic medium *(Ostrožlík and Smolen, 1998)*. Measurement data set submitted of precise control along with other parameters as characteristics of radiation fluxes, atmospheric pressure, and soil temperature are published in the yearbook of result of meteorological measurements *(Ostrožlík, 2002)*.

Measurement programme and analysis methods of selected pollutants obtained at EMEP ozone monitoring station at Stará Lesná include Tab. 1 (www.emep.int).

Methods of mathematical statistics *(Anděl, 1985; Montgomery and Runger, 1999; Nosek, 1972)* were used for evaluation of described experimental data with focus on comparison and relationship analysis.

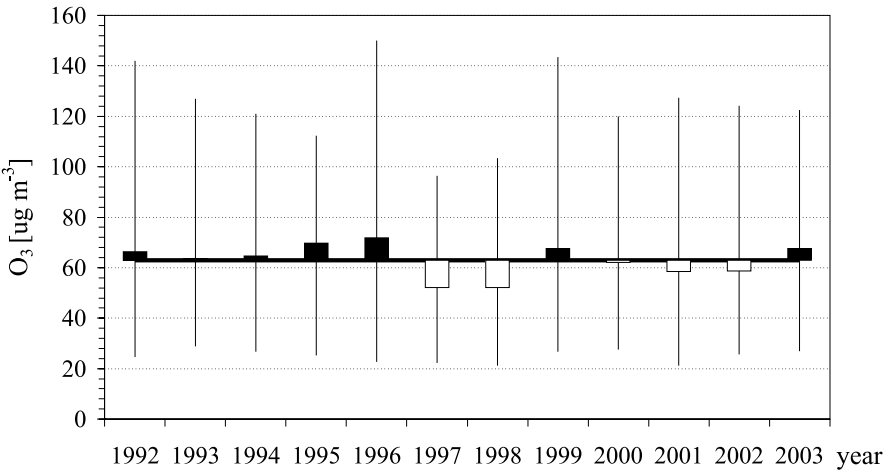

Fig. 1. Differences between the annual means of ground level ozone concentrations [μg m^{-3}] and long-term mean, maximal and minimal daily concentrations O_3 ozone at Stará Lesná from 1992-2003.

3. Results and discussion

Some selected characteristics of ground level ozone at Stará Lesná during the 1992-2003 period are graphically interpreted in Fig. 1. The analysis shows, that mean annual ozone concentration - 62.9 μg m^{-3} - is practically unchanged in comparison with results published by *Hrouzková et al. (2002)*. In 1990s also no significant trends of yearly means ground level ozone concentration over Slovakia were observed *(Závodský, 2001)*. Ozone level at Stará Lesná exceeds the level of urban areas roughly 20 μg m^{-3}, and on the other hand, mean annual ozone concentrations at the level 90 μg m^{-3} were recorded at higher situated regional stations as Chopok, Kojšovská hoľa *(Hrouzková et al., 2002)*. Obtained results correspond to those of EMEP study, where typical European spatial distribution of ground level ozone is 40 μg m^{-3} in Scandinavia, while in Mediterranean it is 100 μg m^{-3}. Slovakia is situated in the range 40–80 μg m^{-3} *(Vestreng, 2001)*.

According to Fig. 1 and Tab. 2 we can see the highest annual ozone concentrations (71.8 μg m^{-3}) in year 1996. Interesting is also the highest mean daily concentration O_3 (150 μg m^{-3}) on 23. April, 1996, as well as frequency

Tab. 2. Statistical evaluation of ground-level ozone concentration [μg m^{-3}] at Stará Lesná during the 1992-2003 period

	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
Annual mean O_3 [μg m^{-3}]	66.3	63.6	64.6	69.8	71.8	52.2	52.1	67.6	62.1	58.6	58.7	67.5
Standard deviation	28.1	23.1	26.1	26.4	32.1	20.2	22.4	33.2	26.7	28.9	26.5	28.5
Frequency of excess over the ambient air quality standard												
110 μg m^{-3} (8 h)	84	51	60	88	221	2	7	182	60	71	39	119
180 μg m^{-3} (1 h)	7	0	0	0	0	0	0	2	0	0	0	0
360 μg m^{-3} (1 h)	0	0	0	0	0	0	0	0	0	0	0	0
Maximum hourly O_3 concentration [μg m^{-3}]	204	160	174	164	180	130	132	226	171	164	143	166
Date	7.8.	3.5.	29.7.	21.7.	29.6.	5.5.	1.4.	11.3.	3.8.	4.4.	2.7.	23.8.
Maximum daily O_3 concentration [μg m^{-3}]	142	127	121	112	150	96	103	144	120	127	124	122
Date	10.8.	3.5.	30.7.	22.7.	23.4.	25.4.	28.4.	1.4.	20.8.	15.6.	2.7.	28.3.

of excess over the ambient air quality standard 110 μg m^{-3} (8 hourly mean) for health protection (221 times). On the other side the years 1997 and 1998 are characterized by low concentration levels (52.2 or 52.1 μg m^{-3}). Population information threshold level (180 μg m^{-3}) was achieved more often in 1992 (7 times) than in 1999 (twice). The highest mean hourly concentration recorded ever (11. March, 1999) was 226 μg m^{-3}. The warning level 360 μg m^{-3} was not overstepped during the whole considered period.

Annual course of ground level ozone at Stará Lesná (Fig. 2) shows 2 maxima in spring (March, April) and late summer (August) (line 1). It corresponds to results published by *Kremler (2002)*. As assumed in year 1996 with the highest annual ozone concentrations (line 2), daily ozone values are higher than long-term average almost during the whole year. The exceptions are months from September till December. On the other side, during the year 1998 with lowest annual ozone concentrations (line 3), daily ozone levels are always less than the long-term average.

Daily course of hourly ozone concentrations is characterized by the minimum (50 μg m^{-3}) in the early morning hours (4-6 h UTC at 5-7 h local time). The concentration is rising steadily, reaches its peak 80 μg m^{-3} in the afternoon (at 15 h local time), and it gradually starts to decrease. After this it shows the sequence of low night and morning ozone values. Similar results are provided by *Kremler (2002)*.

Fig. 2. Annual course of the ground level ozone concentrations [μg m^{-3}] modified by 31-day simple moving average at Stará Lesná: 1 – years 1992-2003, 2 – year 1996, 3 – year 1998.

The comparison of daily ozone course of years 1992-2003 and 1996, 1998 is illustrated in Fig. 3. Differences show higher ozone level in 1996 than in the 1992-2003 period not just for afternoon maximum, but also in morning, evening and night hours. In the year of lowest ozone concentrations (1998) all daily values were lower than the long-term average.

The presence of ozone in lower atmosphere is the output of dynamic photochemical balance of ozone formation and destruction, while many factors are involved in this process. Almost all chemical reactions are initiated in the atmosphere due to solar radiation. UV radiation and the air temperature mostly drive photooxidant formation. Increase of ozone concentrations depends on air temperature (when 20–30°C and total ozone is 300 Dobson units) around 2 ppb on 1°C *(Závodský, 2001)*. Dependence was confirmed with recorded data in Czech and Slovak Republics.

Relationships between mean and maximum daily ozone concentrations on one side, and between climatic characteristics on the other one, were subject of studies done by *Kremler (2001)* using correlations and regression analysis. Most important correlations were found between mean daily temperature and daily relative humidity. Analysis has shown on the ozone

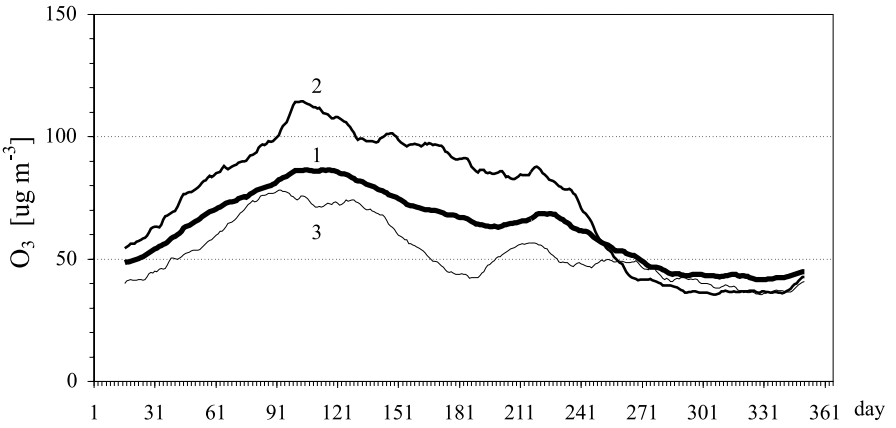

Fig. 3. Daily course of ground level ozone concentrations [μg m^{-3}] at Stará Lesná: 1 – years 1992-2003, 2 – year 1996, 3 – year 1998.

Tab. 3. Mean annual values of the selected meteorological and radiation elements and air pollution components in 1996 and in 1998 at the Meteorological Observatory Stará Lesná

	1996	1998	Δ (1996-1998)
Climatic parameters – average			
Air temperature T [°C]	4.5	5.5	-1.0
Relative humidity R [%]	78	79	-1.0
Sunshine and radiation parameters – annual sum			
Sunshine duration [h]	1682.5	1796.5	-114
Global radiation Q [J cm^{-2}]	332704	344299	-11595
Global ultraviolet radiation UV [J cm^{-2}]	(8899)	(9862)	(-963)
Pollutants concentrations – annual mean			
NO_2 [µg N m^{-3}]	2.99	1.86	1.13
NO_3 [µg N m^{-3}]	0.37	0.28	0.09
HNO_3 [µg N m^{-3}]	0.10	0.08	0.02
O_3 [µg m^{-3}]	71.8	52.1	19.7

- humidity dependence, that ozone levels increase, when relative humidity decreases. Nitrogen oxides (NO_x= NO + NO_2) play the key role in the formation of tropospheric oxidants. However, NO_x itself does not lead to O_3 production. Ozone production overcomes its destruction in the presence of air pollutants such as CO, CH_4 and NMHC and $NO_x > 20$ ppt *(Závodský et al., 2001)*.

Together with ozone concentrations at Stará Lesná the meteorological characteristics: air temperature, relative humidity, sunshine duration, solar radiation, UV radiation and concentrations of precursors NO_2, NO_3 and HNO_3 were studied. Tab. 3 shows the mean annual values of these elements for years 1996 and 1998.

According to air temperature and solar radiation the year 1998 was photochemically favorable for O_3 formation. In year 1996 higher ozone concentrations were induced due to higher levels of precursors, mostly NO_2. Opposite to year 1998 (mean O_3 value 52.1 μg m^{-3}), more ground level ozone was photooxidated in year 1996 (mean O_3 value 71.8 μg m^{-3}) with less favor temperature and radiation conditions, but with higher concentrations of pollutant precursors. Ozone culmination is observed in spring (March, April), when relative air humidity decreases, and we can see in Fig. 4, that ozone maximum is connected with air humidity minimum.

Long-term relative air humidity measurements in the High Tatras up to 1400 m a.s.l. show minimum of relative air humidity in May and maximum in December *(Murínová and Wiszniewski, 1974)*. Low relative humidity values come from abrupt change in air temperature, mostly by warming up during sunny spring days. Annual course of air temperature at Stará Lesná shows important rising in March – April for both years 1996 and 1998. It is clear from Fig. 5, when looking at mean monthly amplitudes of air temperatures. They obviously come from negative to positive values.

High ground level ozone concentrations have occurred under stable meteorological conditions, characterized by high air temperature, low wind speed, longer sunshine duration and higher concentration of local or regional pollution and/or precursors (*Brönniman, 1999; Pottier et al., 1997)*. Comparing the length of sunshine duration, the sum at Stará Lesná the year 1998 was 114 hours longer than in 1996 (Tab. 3).

Fig. 6 compares annual ozone concentration with monthly sum of sunshine duration in 1996 and 1998. The course of the curves indicates some

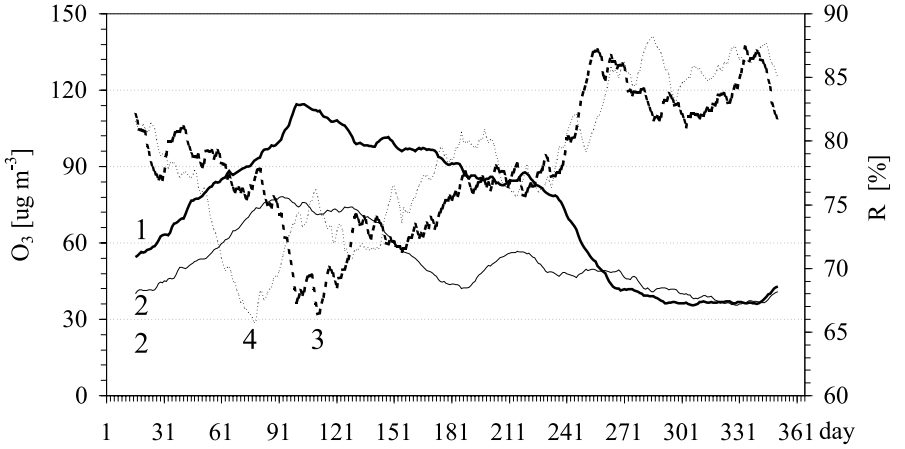

Fig. 4. Annual course of ground level ozone [μg m^{-3}] and annual course of relative air humidity R [%] modified by 31-day moving average at Stará Lesná: 1 – O_3 in 1996, 2 – O_3 in 1998, 3 – R in 1996, 4 – R in 1998.

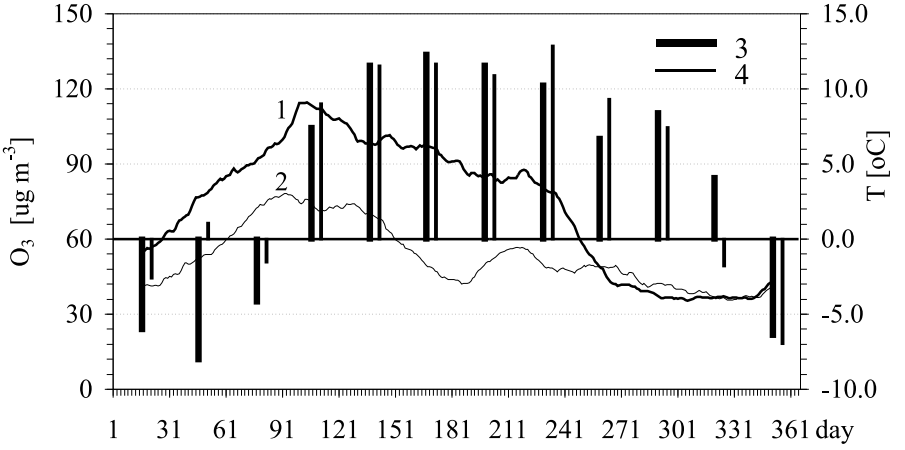

Fig. 5. Annual course of ground level ozone [μg m^{-3}] modified by 31-day moving average and mean monthly amplitude of air temperature T [°C] at Stará Lesná: 1 – O_3 in 1996, 2 – O_3 in 1998, 3 – T in 1996, 4 – T in 1998.

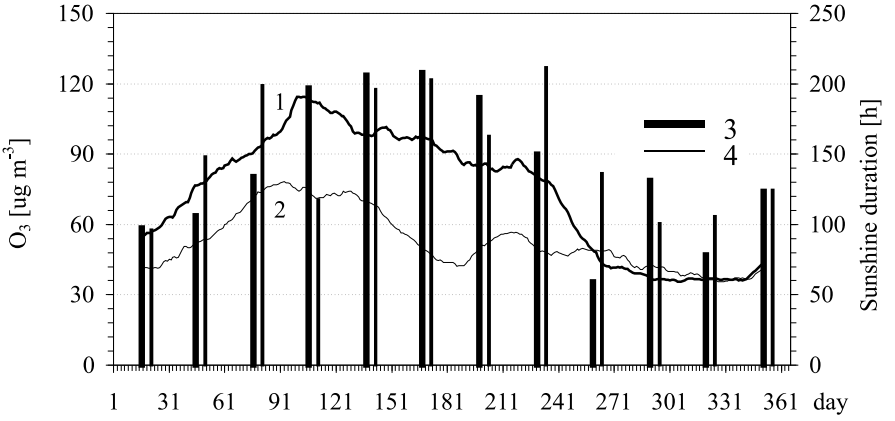

Fig. 6. Annual course of ground level ozone [μg m^{-3}] modified by 31-day moving average and monthly sum of sunshine duration [h] at Stará Lesná: 1 – O_3 in 1996, 2 – O_3 in 1998, 3 – sunshine duration in 1996, 4 – sunshine duration in 1998.

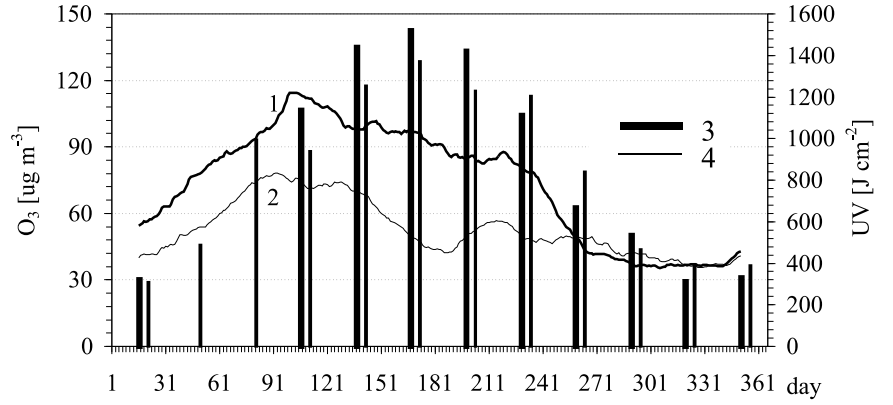

Fig. 7. Annual course of ground level ozone [μg m^{-3}] modified by 31-day moving average and monthly sum of UV (290–385 nm) radiation [J cm^{-2}] at Stará Lesná: 1 – O_3 in 1996, 2 – O_3 in 1998, 3 – UV in 1996, 4 – UV in 1998.

differences, e.g. in April 1996, when ground ozone reached its maximum, the sunshine sum was 200 hours. In 1998 it was one third less, 134 hours. Conversely, in August 1998 sunshine duration was by more than 200 hours, and 1996 it was 50 hours less.

Insolation refers to the incident solar radiation that reaches the Earth from the Sun. Main part of insolation is visible radiation (400–700 nm), another important components are UV (<400 nm) and infrared radiation (>700 nm). Ultraviolet (UV) radiation makes up a very small part of the total energy content of insolation, roughly 8%–9%. The ultraviolet spectrum has been subdivided into three regions: UVC (100–280 nm), UVB (280–315 nm) and UVA (315–400 nm). Wavelengths below ∼290 nm represent less than 1% from global solar radiation. Solar radiation with wavelengths in the range 200–300 nm is effectively absorbed in the stratosphere by the ozone layer (Hartley absorption band). Reductions in stratospheric ozone allow more solar ultraviolet radiation to reach the lower atmosphere and surface. The amount of solar UV radiation measured at the Earth's surface depends upon a number of factors, which include solar zenith angle (time of day, season and geographical latitude), stratospheric ozone, atmospheric pollutants, weather, ground reflectance and altitude. Photochemical processes in atmosphere are strongly dependent on absorbing capacity of photons, especially those in energetically important UV wavelengths. Annual sum of global UV (290-385 nm) radiation at Stará Lesná are included in Tab. 3. Results in brackets are not reliable because measurements during February and March 1998 failed. The monthly sums of global UV radiation at Stará Lesná are shown in Fig. 7.

From the course of the curves in Fig. 7 a simple annual course of UV radiation with minimum in winter and maximum in June can be seen. When comparing UV radiation and ozone courses, UV peak is shifted almost 3 months. Global UV radiation from April to July was more intensive in 1996 than in 1998. Based on mentioned facts one can expect that favorable UV radiation for photochemical reactions increases from April to June.

UV-B radiation (280–315 nm) has enough energy for photolyse atmospheric trace gases, such as ozone (O_3), nitrogen dioxide (NO_2), hydrogen peroxide (H_2O_2), formaldehyde (HCHO) and nitric acid (HNO_3) *(Graedel and Crutzen, 1993)*. Selected reactions significantly participating in O_3 chemistry are presented in Tab. 4. Key role is played by photodisociation of

NO_2 (R1), which is a source of oxygen atoms $O(^3P)$ and consequently also of ozone (R2). Nitrogen dioxide absorbs solar radiation from the entire visible and UV spectrum. In wavelength interval 380–600 nm excited molecules are created, and below <430 nm its photodisotiation takes place. Ozone generated from NO_2 might be consumed by NO oxidation (R3), under low air pollution content, so the final ozone production might be zero - called as zero reaction sequence *(Závodský et al., 2001).*

Annual course of daily average NO_2 concentrations at Stará Lesná during 1996 and 1998 is presented in Fig. 8. More than twice higher NO_2 concentrations are recorded in the 1996 (year with the highest O_3 concentrations) in comparison with year 1998. Especially high NO_2 concentrations occurred in February – May. During following months daily averages of NO_2 went down steeply and minimum was achieved in July. During 1998 such differences in diurnal average NO_2 concentrations have not been recorded. Higher values were in February August and December. Daily averages of NO_2 are typical with very high variability allowing us to state rather generally: annual course of NO_2 concentration has its peak at the end of winter and spring months and minimum values occur in summer.

Prevailing part of NO_2 is formed in polluted atmosphere by NO oxidation. Notation NO_x is often used to describe a sum of NO + NO_2. Among anthropogenic activities producing NO prime role is played by emissions from energy, especially fuel sources and transport. Period of higher NO_2 concentrations at Stará Lesná is more or less identical with heating season. That's why one can expect the origin of NO_2 from these sources. On the other hand there is some discrepancy between mentioned status and registered amount of NO_x pollution. According to Register of Emissions and Air Pollution Sources of the Slovak Republic the emission of NO_2 was approximately the same in 1996 and 1998 *(Marečková et al., 2001).* Significant decline of NO_x, CO, NMVOC emission during last 15 years in Slovakia confirms data published by *Spišáková et al. (2003).* The amount of NO_x from in-land sources has been stable and parallel annual average of NO_2 almost doubled in 1996, when compared to 1998 at Stará Lesná. An explanation might be the influence from another sources, e.g. long distance pollution. Regional character of Stará Lesná observatory supports this possibility.

Nitrogen dioxide is a product of photochemical reactions in ground layer of atmosphere with the presence of CO, CH_4 and non-methane hydrocar-

Tab. 4. The scheme of important photochemical and chemical reactions exerted in ozone formation and decomposition processes

	Reaction scheme	Chemical process and photochemical reactions with effective wavelength interval
R1	$NO_2 + hv \rightarrow O(^3P) + NO$	Photolysis of NO_2, 290-420 nm
R2	$O(^3P) + O_2 + M \rightarrow O_3 + M$	Primary formation of O_3
R3	$NO + O_3 \rightarrow NO_2 + O_2$	Oxidation NO and O_3
R4	$O_3 + h.\nu\ (\lambda \leq 330\ nm) \rightarrow O(^1D) + O_2$	Photolysis of O_3, 290-320 nm
R5	$O(^1D) + H_2O \rightarrow OH + OH$	Formation of OH radicals due to photolysis of O_3
R6	$CO + OH + O_2 + M \rightarrow CO_2 + HO_2 + M$	Formation of HO_2 radicals due to oxidation CO
R7	$HO_2 + NO \rightarrow NO_2 + OH$	Oxidation NO and HO_2
R8	$O_3 + NO_2 \rightarrow NO_3 + O_2$	Oxidation NO_2 and O_3
R9	$O(^3P) + NO_2 + M \rightarrow NO_3 + M$	Oxidation NO_2 and $O(^3P)$
R10	$NO_3 + NO_2 \rightarrow N_2O_5$	N_2O_5 formation
R11	$N_2O_5 + H_2O \rightarrow HNO_3$	HNO_3 formation by hydrolysis
R12	$OH_2 + NO_2 \rightarrow HNO_3$	HNO_3 formation by oxidation
R13	$NO_3 \rightarrow NO + O_2$	Photolysis of NO_3, 585-635 nm
R14	$NO_3 \rightarrow NO_2 + O(^3P)$	Photolysis of NO_3, 400-635 nm

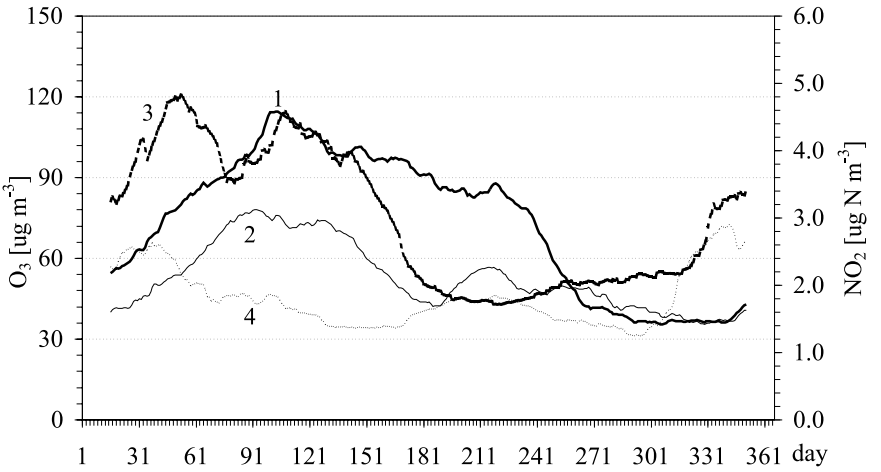

Fig. 8. Annual course of ground level ozone [μg m^{-3}] and mean annual course of NO_2 concentrations [μg N m^{-3}] modified by 31-day simply moving average at Stará Lesná: 1 – O_3 in 1996, 2 – O_3 in 1998, 3 – NO_2 in 1996, 4 – NO_2 in 1998.

bons. Hydroxyl radical (OH) is an important initialization factor for both NO_2 and O_3 formation. OH radicals are generated during reaction of oxygen atoms $O(^1D)$ with water vapour (R5). Atoms of oxygen $O(^1D)$ are in higher energetic state, when compared to the basic state $O(^3P)$, which occurs during photodisociation of O_3 by solar radiation with length of $\sim$ 300 nm (R4). Oxidative environment stimulates reaction of OH radical with CO or methane and hydroperoxyls radicals are created HO_2 (R6), respectively RO_2, oxidation of NO to NO_2 in polluted environment (R7). In a case of NO oxidation in reaction R(3) – O_3 is oxidant, in reaction (R7) as an oxidant serves more active HO_2 radicals and former O_3 stays unattached, which leads to positive O_3 balance *(Závodský et al., 2001)*. Besides photodissociation, NO_2 is removed from the atmosphere also by oxidation. NO_3 is formed during oxidation with ozone (R8) or during reaction with oxygen atoms (R9). Generated NO_3 reacts with NO_2 producing N_2O_5(R10). Under wet conditions HNO_3 is formed (R11). Next step in polluted environment is nitrate formation washed away by rain in final stage. Source of HNO_3 in gaseous form in atmosphere is reaction of OH radical with NO_2 (R12). Under day-light conditions photolytic destruction of NO_3 is very fast(R13, 14); it means that relatively stable NO_3 is formed mostly during nights (R8). During winter with low OH concentration and low sunshine radiation the reactions R(8-11) are the main source of NO_3 in the atmosphere *(Dentener and Crutzen, 1993)*. Mentioned NO_3 mechanism is detectable on diurnal average concentrations of NO_3 and HNO_3 in 1996 (Fig. 9 and 10). Reaction R8 might explain winter NO_3 elevation especially in January and February. NO_2 present in the atmosphere reacts with O_3 and generates NO_3. Elevated concentration of HNO_3 shows continuity of NO_3 deformation according to reactions R(10, 11).

The persistency of NO_2 in the atmosphere supports relatively unsuitable conditions for photolysis (short time sunshine radiation, low temperature, low UV radiation density), with adequately low O_3 concentrations in winter months. During March and April meteorological conditions for photolytic reactions and ozone formation dramatically improve (almost double sunshine duration, temperature increasing, higher density of UV radiation). Probably NO_3 reactions (R 8, 13, 14) are important forces for spring ozone maximum formation at Stará Lesná. This assumption is supported by comparison between annual course of concentrations NO_3 and O_3 (Fig. 9). Max-

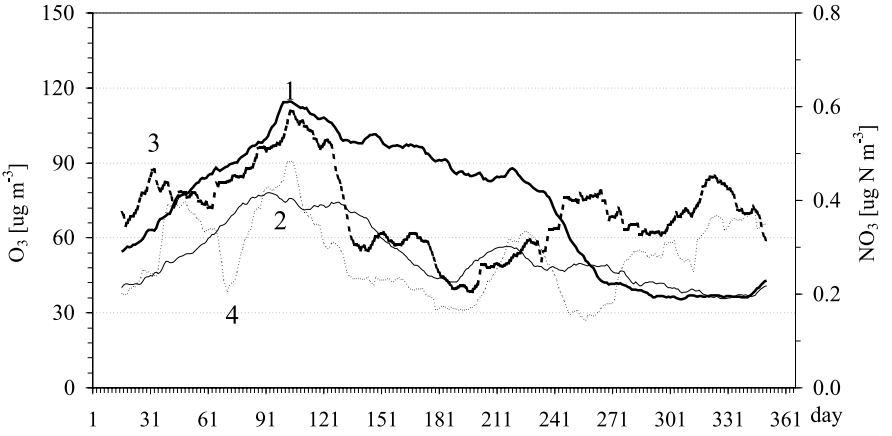

Fig. 9. Annual course of ground level ozone [μg m^{-3}] and mean annual course of NO_3 concentrations [μg N m^{-3}] modified by 31-day simply moving average at Stará Lesná: 1 – O_3 in 1996, 2 – O_3 in 1998, 3 – NO_3 in 1996, 4 – NO_3 in 1998.

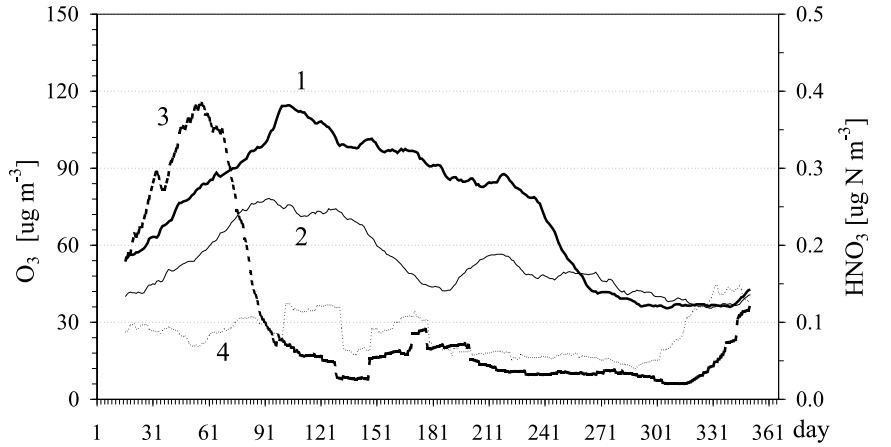

Fig. 10. Annual course of ground level ozone [μg m^{-3}] and mean annual course of HNO_3 concentrations [μg N m^{-3}] modified by 31-day simply moving average at Stará Lesná: 1 – O_3 in 1996, 2 – O_3 in 1998, 3 – HNO_3 in 1996, 4 – HNO_3 in 1998.

imum concentration O_3 occurs simultaneously with NO_3 peaks in April.

The presence of reactive hydrocarbons with a high potential for O_3 formation (POCP group) is highly important for local ozone situation. Gaseous hydrocarbon emissions grow during the summer from both anthropogenic and biogenic sources. According to *(Lubkert and Schopp, 1989)* hydrocarbon emission increases with temperature. Photolysis of O_3 controls the OH radicals production during daylight hours only. Reaction of O_3 with isoprene and terpenes can be an important source of HO_x in forested regions; these reactions are the dominant radical source in the late afternoon and in the night *(Paulson and Orlando, 1996)*. Relatively high yields of OH radicals from the gas-phase reaction of O_3 with a series of C_{10} terpenes have been measured. These OH radical yields are independent of water vapor concentration over the range $(0.34–2.7)\times10^{17}$ molecule cm^{-3} (5–40% relative humidity) *(Aschmann et al., 2002)*. Terpens are the main component of biogenic emissions from coniferous trees. As the vicinity of observatory at Stará Lesná is situated in forested region with dominancy of conifers one can expect that terpens might play an important role in photochemical cycle of formation and degradation of ozone, especially during summer. At the observatory at Stará Lesná, and at its vicinity, the data on volatile hydrocarbons are not yet measured.

4. Conclusion

The purpose of this paper is to evaluate the variability of ground level ozone concentrations recorded at regional ozone monitoring station Stará Lesná during the 1992–2003 period, and to provide the analysis of the relationship with the corresponding meteorological, radiation and pollutant components.

It was shown that the mean value of ground level ozone concentration at Stará Lesná is 62.9 μg m^{-3}. Maximal yearly mean (71.8 μg m^{-3}), the highest number of exceedances (221) of the ambient air quality standard 110 μg m^{-3} (8 h) and maximal daily average (150 μg m^{-3}) of ground level ozone concentration was recorded in 1996. Minimal yearly mean (52.1 μg m^{-3}) occurred in year 1998. Threshold level for information of population (180 μg m^{-3}) was achieved more often in 1992 (7 times) than in 1999 (twice). The highest

mean hourly concentration recorded ever (11. March, 1999) was 226 μg m^{-3}. The warning level 360 μg m^{-3} was not overstepped during the whole considered period.

Annual course of ground level ozone at Stará Lesná is characterized by two maxima in spring (March, April) and late summer (August). The main spring maximum is connected with convenient photochemical conditions (decrease of relative humidity, increase of air temperature, positive changes in sunshine duration and UV radiation) and the abundance of pollution components such as NO_2 and NO_3. Terpens as biogenic source of gaseous hydrocarbon emissions might play an important role in photochemical cycle of formation and degradation of ozone, especially during summer. Daily course of hourly values of O_3 is characterized by the minimum (50 μg m^{-3}) in early morning hours (4–6 h UTC at 5–7 h local time). The concentration is rising steadily, reaches its peak 80 μg m^{-3} in early afternoon (at 15 h local time), and gradually starts to decrease.

Ozone concentration in atmosphere is a result of dynamic stability between ozone formation and decomposition processes. For this reason, the uniquely determined ozone production mechanism is very demanding. The only exact tool for explanation and probable quantification of this process are chemical models requiring rigorous emission inventory and sufficient amount of direct measurements especially in case of VOC. Unfortunately VOC are not measured yet at Stará Lesná observatory, and neither in its vicinity.

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References

Anděl J., 1985: Mathematical statistics. SNTL/ALFA. Praha, 346 p. (in Czech).

Aschmann S. M., Arey J., Atkinson R., 2002: OH radical formation from the gas-phase reactions of O_3 with a series of terpenes. Atm. Environ., **36**, 4347–4355.

Brönnimann S., 1999: Early Spring Ozone Episodes: Occurrence and Case study. Phys. Chem. Earth, **24/5** , 531–536.

Dentener F. J., Crutzen P. J., 1993: Reaction of N_2O_5 on tropospheric aerosols: impact on the global distributions of NO_X, O_3 and OH. J. Geophys. Res., **98**, 7149–7163.

Graedel T. E., Crutzen P. J., 1993: Atmospheric Change: An Earth System Perspective W. H. Freeman and Co., New York, 446 p.

Hrouzková E., Kremler M., Závodský D., 2002: Ground level ozone at the territory of Slovakia in 1992-2001. Acta Met. Univ. Comenianae, **31**, 19–38.

Kremler M., 2001: Surface ozone in Slovakia. In: Extrémy prostredia (počasia) - limitujúce faktory bioklimatologických procesov: 10.–12. september 2001, Račková dolina. CD nosič. ISBN 80-7137-910-7 (in Slovak).

Kremler M., 2002: Daily and annual course of surface ozone concentrations at Slovak monitoring stations. Meteorol. čas., **5**, 29–36.

Lindskog A., Beekmann M., Monks P., Roemer M., Schuepbach E., Solberg S., 2003: Tropospheric Ozone Research, Overview of Subproject TOR-2. In: Midgley P. M., Reuther M. (Eds.), Towards Cleaner Air for Europe - Science, Tools and Applications Part 2. Overviews from the Final Reports of the EUROTRAC-2 Subprojects, Margraf Verlag, Weikersheim, ISBN 3-8236-1391-X, 251–270.

Lubkert B., Schopp W., 1989: A model to calculate natural VOC emissions from forests in Europe. IIASA WP 89-082, Laxenburg, Austria, 55 p.

Marečková K., Pukančíková K., Mitošinková M., Kozakovič Ľ., Závodský D., Magulová K., 2001: Air Pollution in the Slovak republic 2000. Slovak Hydrometeorological Institute and Ministry of Environment of the Slovak republic, 150 p. (in Slovak).

Murínová G., Wiszniewski W., 1974: Relative air humidity. In: Klíma Tatier (Ed: M. Konček). Veda. Vydavateľstvo SAV, 855 p. (in Slovak).

Montgomery D. C., Runger G., 1999: Applied Statistics and Probability for Engineers. John Wiley & Sons, Inc., New York, ISBN 0-471-17027-5, 817 p.

Nosek M., 1972: Climatology methods. Academia. Praha, 433 p. (in Czech).

Ostrožlík M., Smolen F., 1998: Solar radiation receipt during the vegetation period in the mountains conditions. In: Atmosférická depozícia a ekofyziologické procesy v ekosystémoch. Poľana 12.–13. jún 1996. Technická univerzita vo Zvolene, 235–238 (in Slovak).

Ostrožlík M., 2002: Results of meteorological measurements at the observatories of the Geophysical Institute of the Slovak Academy of Sciences. Geophysical Institute of SAS, Bratislava, 33 p.

Paulson S. E., Orlando J. J., 1996: The reactions of ozone with alkenes: an important source of HO_x in the boundary layer. Geophys. Res. Letters, **23**, 3727–3730.

Pottier J. L., Pryor S. C., Banta R. M., 1997: Synoptic variability related to boundary layer and surface features observed during Pacific '93. Atm. Environ., **31**, 2163–2173.

Solomon P., Cowling E., Hidy G., Furiness, 2000: Comparison of scientific findings from major ozone field studies in North America and Europe. Atmospheric Environment **34**, 1885–1920.

Spišáková K., Sajtáková E., Závodský D., 2003: Emission of Air Pollutants in the Slovak Republic. Meteorol. čas., **6**, 11–16.

Vestreng V., 2001: Emission data reported to UNECE/EMEP: Evaluation of the spatial ditributions of emissions. EMEP/MSC-WNote 1/01 `http://www.emep.int/reports/DNMI_NOTE_1_2001.pdf`.

Závodský D., 2001: Expected trends of ground level ozone concentrations over Slovakia. Acta Met. Univ. Comenianae, **30**, 1–17.

Závodský D., Medveď M., Ďurec F., 2001: Atmospheric chemistry and modelling of air pollution. Univerzita Mateja Bela, Banská Bystrica, 126 p. (in Slovak).