Nocturnal ground level ozone at the rural station Stará Lesná, Slovakia

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Abstract: Study of ground level ozone (O_3) behaviour in the nocturnal boundary layer is important from the point of view of O_3 progress after sunrise. Data of the EMEP database obtained by O_3 measurement at rural station Stará Lesná for time period 1992–2005 are used for the investigation of the seasonal variation and relationship between nocturnal and peak daylight O_3 concentration. Seasonal variability of nocturnal O_3 values (22–04 h UTC) ranges between $40\,\mu g\,m^{-3}$ for the autumn-winter and $80\,\mu g\,m^{-3}$ for the spring months. On the other hand, hourly course of O_3 concentration indicates the substantive night O_3 depletion during the spring-summer season, particularly in May. Results of analysis show relevant linear relationship for seasonal O_3 variables: (y) - negative difference between nocturnal and daily O_3 value, (x) - positive difference between daylight peak and daily O_3 values. It is assumed that lower daylight O_3 peak is linked with higher nighttime O_3 concentration, and vice versa. The increase of nocturnal O_3 level demonstrates also the simulation considering 15% reduction of peak daylight O_3 values. Furthermore, the simulation documents minimally the affect of O_3 peak reduction on the mean daily O_3 values. The achieved results suggest that the decrease of the highest O_3 concentrations as a consequence of anthropogenic emissions reduction can be compensated by increase of nocturnal O_3 values with marginal impact on the mean O_3 values. The growth of nocturnal O_3 values due to lower daylight O_3 peak in the spring-summer season, as well as slight removal by surface deposition and long-lasting persistence of air pollution during winter can enrich the background O_3 level. Further investigation will be needed to explain the nocturnal O_3 contribution to background O_3 concentration.

Key words: ground level ozone, nocturnal and daylight O_3 concentrations, rural site, background ozone, seasonal variation

1. Introduction

Complex chemistry and synergistic interaction between anthropogenic and biogenic emissions *(Tao et al., 2003)* upon varying meteorological conditions play an important role in sensitive ground level ozone (O_3) balance.

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Photochemical ozone is processed in the presence of sunlight during the day. On the other hand, specific night chemistry *(Dentener and Crutzen, 1993)*, horizontal advection, vertical mixing through local and mesoscale wind systems *(Eliasson et al., 2003)*, and dry deposition at the surface *(Güsten et al., 1998)* have substantial impact on nocturnal O_3 concentration. All these processes that control O_3 level in the night make the base for further O_3 evolution after sunrise.

Typical diurnal O_3 cycle with a mid-afternoon peak and nighttime minimum is observed at rural sites located in the middle latitude and altitude zones of Europe (*Oyle et al., 2002; Kremler, 2002*). Measurements of Slovak O_3 monitoring network show more O_3 abundance at rural than urban locations in the night while daylight O_3 peak is higher in urban sites than in remote localities *(Bičárová et al., 2005)*. Although the daily and seasonal O_3 variability is analysed in many papers (*Nelson et al., 1984; Brönimann et al., 2000; Garcia et al., 2005*) there are not included straight conclusions concerning to the relationship between night and daylight O_3 values arising from long-time measurement.

Studies that investigate O_3 behaviour in nocturnal boundary layer explain unusual occurrence of secondary O_3 maxima *(Eliasson et al., 2003; Reitebuch et al., 2000; Salmond and McKendry, 2002*) and removal mechanism with respect to NO chemistry, surface deposition, wind system (*Banta et al., 1997; Broder and Gygax, 1985; Güsten et al., 1998*) or secondary trace species (*Hastie et al., 1992; Jenkin and Clemitshaw, 2000*). The night O_3 reduction by NO is effective at urban sites. Titration of locally generated NO by boundary layer O_3 forms the nighttime NO_2 plumes that are subsequently transported into remote area (*Gafney et al., 2002*). In the suburbs and further downwind of large cities, where local NO_X emissions are lower, the formation generally dominates over depletion and elevated O_3 levels are found *(Louka et al., 2003)*. It is probably one of the reasons why mean seasonal O_3 values at remote sites are higher than around areas of industrial emission sources *(Bičárová et al., 2005; Duenas et al., 2004* and *Coyle et al., 2002)*.

Nocturnal O_3 values represent O_3 behaviour without photochemical activity and are often used to study background conditions. There is some indication that background ozone levels over the midlatitudes of the Northern Hemisphere rise over the past three decades (*Vingazan, 2004; Solberg and*

Lindskog, 2005; Derwent et al., 2007). Background concentration (*EPA, 2005*) includes contributions from photochemical interactions involving natural emissions of VOCs, NO_X, and CO; the long-range transport of O_3 and its precursors; and stratospheric-tropospheric exchange (STE). Environmental conditions at Stará Lesná correspond to EPA criteria for monitoring of O_3 background concentration. Monitoring station surrounded by meadow and forest is situated under the High Tatra Mts. that forms orographic barrier, especially for the north components of general atmospheric circulation. The prevailing wind from S and SSW directions (*Ostrožlík, 2007a*) moves polluted air from southwestern Europe therefore influence of long-range transport to O_3 concentration is not negligible at Stará Lesná *(Bičárová and Fleischer, 2007)*.

In this paper, O_3 data collected at rural station Stará Lesná in Slovakia during the time period of 1992–2005 are examined to investigate the relationship between the nocturnal and daylight peak O_3 concentrations. Detailed analysis of diurnal and seasonal O_3 variation can provide more information about O_3 behaviour at rural background locations.

2. Materials and methods

Location Stará Lesná (H = 810 m a.s.l., $\varphi = 49°09'$ N, $\lambda = 20°17'$ E) is situated in the High Tatra Mts. region on the northeastern part of Slovakia (Fig. 1). There is the Meteorological Observatory of the Geophysical Institute SAS (MO GPI SAS) that provides measurements of meteorological and radiation parameters since 1989. Data set is published in the yearbook of result of meteorological measurements (*Ostrožlík, 2007b*). According to cooperation between GPI SAS and Slovak Hydrometeorological Institute (SHMI), O_3 monitoring is carried out in frame of project EMEP (Cooperative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe). In this study, mean hourly O_3 concentrations for Stará Lesná and period 1992–2005 obtained from EMEP measurement online database (`http://www.nilu.no/projects/ccc/emepdata.html`) have been examined by statistical methods *(Anděl, 1985; Montgomery and Runger, 1999)*. Current O_3 measurement at Stará Lesná is performed by equipment APOA-360 developed by Horiba. It is an automatic O_3 analyser using ultra-violet-absorption method (NDUV) based on

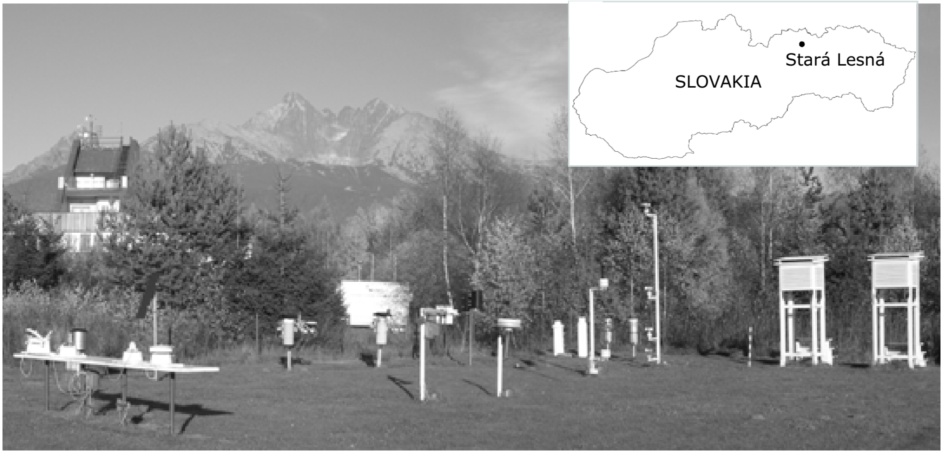

Fig. 1. Meteorological Observatory GPI SAS (http://gpi.savba.sk/) and EMEP http://www.emep.int/) O_3 monitoring station of SHMI (http://www.shmu.sk/) at Stará Lesná.

the principle that ozone absorbs ultra-violet rays in the area of 254 nm. Measurements are taken from continuous, alternate injections of the sample gas and the reference gas into the measurement cell, controlled by a long-life solenoid valve. The cross flow modulation method is characteristically zero drift-free. A comparative calculation circuit automatically compensates all fluctuations in the mercury-vapor light source and in the detector (Fig. 2).

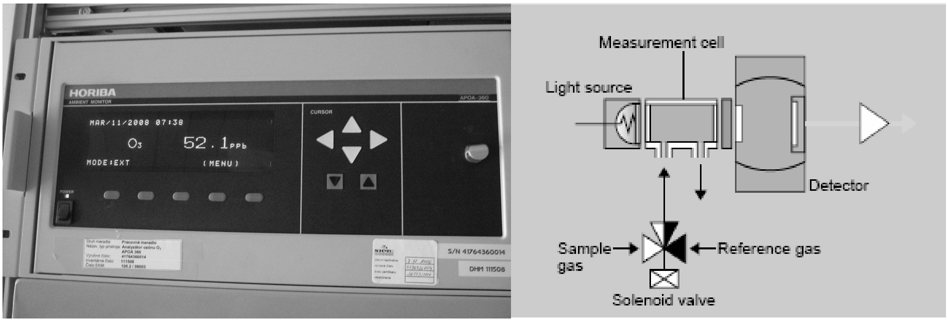

Fig. 2. Horiba APOA-360 O_3 analyser and ultra-violet absorption method (NDUV), http://www.horiba.com using for O_3 measurement at EMEP station Stará Lesná.

Equipment measures O_3 concentration in accordance with the secondary national ozone calibration standard of SMHI. Intercomparisons with the Czech primary ozone standard are regularly organized. Hourly data are collected in central SHMI database and after validation are published at EMEP measurement data online page. O_3 measurement at Stará Lesná since 1992 represents the longest time series of the O_3 background concentration in Slovakia.

3. Results and discussion

3.1. Seasonal O_3 variation and background O_3 concentration

The variation in the mean daily O_3 concentration (0–23 h UTC) between different months of the year at Stará Lesná for the period 1992–2005 (Table 1) shows the highest values about $87\,\mu g\,m^{-3}$ in April and $70\,\mu g\,m^{-3}$ in August. During autumn months O_3 content declines and minimum level of $45\,\mu g\,m^{-3}$ is achieved in November and December. At the beginning of the year, O_3 concentration gradually rises from $50\,\mu g\,m^{-3}$ in January to $87\,\mu g\,m^{-3}$ in April. Fig. 3 presents seasonal differences of nocturnal (22–04 h UTC) O_3 values between the winter-spring and summer-autumn period. Primary spring O_3 maximum in April is associated with nocturnal O_3 values in range from 60 to $80\,\mu g\,m^{-3}$ while night O_3 values slightly overlap the level of $40\,\mu g\,m^{-3}$ during the secondary summer O_3 maximum in August.

Seasonal variation at rural sites shows specific distinctions that reflect the influence of local meteorology, topography, geographical position and O_3 precursor sources. For example, in Central and Alpine Europe the variation is characterised by a broad summer maximum with high monthly means from May to August. Springtime maximum in April and May followed by a gradual decline to a minimum in November-December is found for sites in England, the Netherlands and the southern parts of Scandinavia and Finland. A spring maximum followed by a minimum in the summer is generally found in Ireland, Scotland and the northern parts of Scandinavia and Finland *(Fjæraa and Hjellbrekke, 2007)*. Observations at a rural area of the upper Spanish plateau indicate the temperature-dependent main monthly O_3 maximum around $80\,\mu g\,m^{-3}$ in June-July and O_3 concentration

Table 1. Descriptive statistics of O_3 data [$\mu g\,m^{-3}$]: arithmetic mean of daily O_3 values μ_d (0-23) for individual months (I–XII) and standard deviation σ_d (0-23); arithmetic mean of hourly O_3 values μ_h (I-XII) and standard deviation σ_h (I–XII) at Stará Lesná for time period between 1992–2005

O_3 [$\mu g\,m^{-3}$] Months / h UTC	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	μ_d (0 - 23)	σ_d (0 - 23)
I	47	47	47	47	47	47	46	45	46	48	53	57	59	61	62	59	53	49	48	47	48	47	47	47	50	5.4
II	59	59	59	59	59	57	56	55	58	64	69	73	76	78	79	78	75	68	63	61	60	59	59	59	64	8.2
III	70	70	70	70	70	65	64	67	72	78	83	88	91	93	94	93	91	86	79	75	73	71	70	70	77	10.5
IV	79	79	79	79	79	68	71	80	87	94	99	102	104	105	106	105	104	101	93	86	82	80	79	79	87	13.7
V	70	70	70	70	70	58	67	78	86	93	98	100	101	101	102	101	100	97	90	81	75	70	70	70	81	16.7
VI	58	58	58	58	58	49	59	69	78	85	89	91	92	92	92	92	90	87	81	72	64	59	58	58	71	17.7
VII	54	54	54	54	54	44	53	65	73	81	86	88	88	89	89	89	86	82	75	66	60	56	54	54	67	17.4
VIII	57	57	57	57	57	45	51	63	73	84	91	95	95	96	95	95	92	86	75	66	62	59	57	57	70	19.1
IX	47	47	47	47	47	40	43	51	59	66	73	76	78	79	80	78	74	65	55	49	48	47	47	47	57	14.6
X	41	41	41	41	41	38	37	40	47	52	57	62	65	67	66	64	56	48	44	43	43	41	41	41	48	10.4
XI	41	41	41	41	41	41	39	39	42	46	50	53	55	57	56	52	46	44	42	42	41	41	41	41	45	5.7
XII	42	42	42	42	42	44	43	42	42	45	49	52	54	55	54	49	44	42	42	42	42	42	42	42	45	4.5
μ_h(I-XII)	53	52	51	51	50	50	52	58	64	70	75	78	80	81	81	80	76	71	66	61	58	56	55	54	-	-
σ_h(I-XII)	11	11	10	10	10	10	11	15	17	18	19	18	18	18	18	19	21	21	19	16	14	13	12	12	-	-

in range between $50-60\,\mu g\,m^{-3}$ in autumn and winter (*Garcia et al., 2005*). Monthly O_3 mean varies from $80\,\mu g\,m^{-3}$ in the winter to $140\,\mu g\,m^{-3}$ in the summer at Mt. Cimone (2165 m a.s.l.), a site representative of Northern Mediterranean free troposphere. At this place, the yearly principal O_3 max-

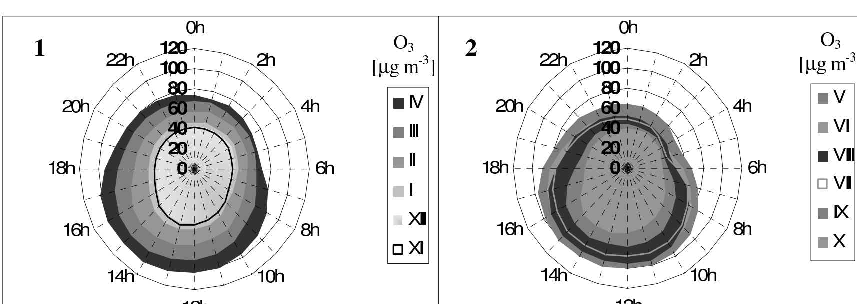

Fig. 3. Mean daily course of O_3 concentration [$\mu g\,m^{-3}$] in individual months of year: 1 – from November (O_3 minimum) to April (primary O_3 maximum); 2 – from May to August (secondary O_3 maximum) and then to October (decrease to O_3 minimum) at Stará Lesná (1992 – 2005).

imum is recorded in summer but under background conditions the highest O_3 level is achieved in spring (*Bonasoni et al., 2000*). It is in line with the O_3 behaviour at background sites in the Northern Hemisphere that is characterized by main spring maximum. Sites, which are affected to some extent by local ozone production, exhibit a broad summer maximum (*Vingarzan, 2004*). From this point of view, the primary O_3 maximum observed at Stará Lesná during early spring also documents that it is a background site with marginal influence of local pollution.

3.2. Nocturnal O_3 concentration

The seasonal changes of mean nocturnal O_3 values (Table 2) and mean daily O_3 values (Table 1) are nearly similar. Elevated O_3 concentration is characteristic for 24-hours periods as well as for night hours in April ($79\,\mu\mathrm{g\,m^{-3}}$) and August ($57\,\mu\mathrm{g\,m^{-3}}$). Low O_3 level is typical for both, the whole days and nights (about $40 - 50\,\mu\mathrm{g\,m^{-3}}$) at autumn months. Coef-

Table 2. Nocturnal (22–04 h UTC) O_3 concentration [$\mu\mathrm{g\,m^{-3}}$]: arithmetic mean (μ_n) standard deviation (σ_n) coefficients (a, b) of linear regression (y = ax + b), correlation coefficient (r), standard error of regression (S_{yx}) for different months of year (I–XII) at Stará Lesná (1992–2005)

O_3 [μg m^{-3}]										Coefficients and erorr of linear regression										
x	1	2	3	4	5	6	7	μ_n	σ_n	y = ax + b										
h UTC	22	23	0	1	2	3	4	(22 - 04)		a	b	r	y1	y2	y3	y4	y5	y6	y7	Syx
I	47	47	46	47	47	47	47	47	0.4	0.05	46.74	0.27	47	47	47	47	47	47	47	0.44
II	59	59	58	59	57	58	57	59	0.7	-0.23	58.90	-0.73	59	58	58	58	58	58	57	0.51
III	70	69	68	67	67	66	66	70	1.5	-0.68	70.43	-0.97	70	69	68	68	67	66	66	0.37
IV	78	77	74	72	72	71	69	79	3.2	-1.45	79.05	-0.99	78	76	75	73	72	70	69	0.51
V	68	67	65	63	61	59	57	70	3.8	-1.77	69.90	-0.99	68	66	65	63	61	59	58	0.31
VI	57	54	53	50	49	47	46	58	3.6	-1.67	57.60	-0.99	56	54	53	51	49	48	46	0.56
VII	53	51	49	48	48	46	44	54	3.1	-1.38	53.98	-0.97	53	51	50	48	47	46	44	0.77
VIII	56	54	52	50	49	48	47	57	3.2	-1.45	56.82	-0.98	55	54	52	51	50	48	47	0.61
IX	47	45	44	43	43	43	42	47	1.8	-0.77	46.89	-0.95	46	45	45	44	43	42	41	0.60
X	41	40	40	39	40	39	39	41	0.6	-0.27	40.79	-0.92	41	40	40	40	39	39	39	0.27
XI	41	41	42	42	41	41	41	41	0.3	-0.01	41.28	-0.05	41	41	41	41	41	41	41	0.32
XII	42	42	43	44	43	44	45	42	0.8	0.35	41.84	0.89	42	43	43	43	44	44	44	0.42

ficients of linear regression (a in Table 2) suggest time dependence of O_3 concentrations during night hours, markedly in spring-summer season. Obvious decrease with slope –1.77 is observed in May. Intercept coefficients (b in Table 2) show typical nocturnal O_3 values under level of $60\,\mu g\,m^{-3}$ for nearly all months of the year except for spring months (III–V) when they increase to level of $70-80\,\mu g\,m^{-3}$. Interestingly, the nocturnal O_3 values are lower in summer months (VI–VIII) than in February (Fig. 4). Probably different amount and reactivity of O_3 depletion components as NO, VOC, secondary organic aerosol (SOA) in different environmental and meteorological conditions leads to seasonal changes of O_3 night values. Abundance of NO_2, NO_3 and HNO_3 during winter period at Stará Lesná (*Bičárová and Fleischer, 2004)* indicates loss of O_3 due to NO titration. Biogenic VOC associated with secondary organic aerosol (SOA) formation can influence the ozone balance, especially during summer. This suggestion is supported by findings of EMEP EC/OC campaign *(Yttri et al., 2007)* that show higher contribution of organic carbon (OC) than elemental carbon (EC) for summer than for winter at Stará Lesná. Under such circumstances it is assumed that night O_3 sink leading to HNO_3 formation dominates in winter while O_3 decrease in summer is influenced also by reactivity of added BVOC. Similar results are presented by *Geyer et al. (2001)* for rural site Lindenberg near Berlin.

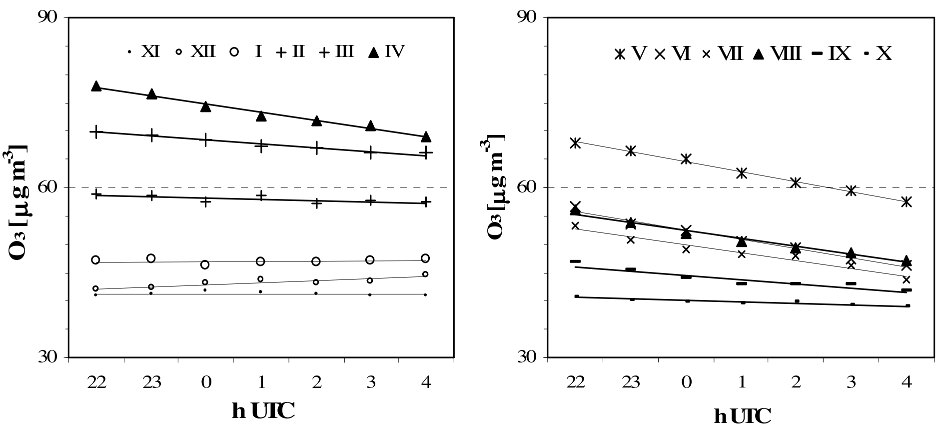

Fig. 4. Mean hourly nocturnal O_3 concentration [$\mu g\,m^{-3}$] and regression lines for the different months of year (I–XII) at Stará Lesná (1992–2005).

3.3. Relationship between low nocturnal and peak daylight O_3 concentration

As indicated above (Table 1, Table 2), O_3 measurements show seasonal variation of mean daily μ_d (0-23 h UTC) and mean nocturnal μ_n (22–04 h UTC) values. Table 3 includes seasonal O_3 peak values between 12 and 15 UTC. Arithmetic mean of O_3 peak values μ_p (12-15 h UTC) also copy inter-monthly variation typical for O_3 course at Stará Lesná. Regardless, differences between nocturnal and daily $\delta\,(\mu_n - \mu_d)$, as well as differences between daylight peak and mean daily $\delta\,(\mu_p - \mu_d)$ O_3 values exhibited distinct seasonal regime. Negative deviation of nocturnal O_3values $\delta\,(\mu_n - \mu_d)$ gradually declines from January ($-3\,\mu g\,m^{-3}$) to June ($-20\,\mu g\,m^{-3}$) and positive deviation of peak O_3 values $\delta\,(\mu_p - \mu_d)$ grows from January ($10\,\mu g\ m^{-3}$) to August ($25\,\mu g\ m^{-3}$). During next period from August to December, both negative and positive deviations approach to the minimal values $-2\,\mu g\,m^{-3}$ and $8\,\mu g\,m^{-3}$, respectively. July is a specific month because nocturnal deviation starts to be weaker and the rise of peak deviation slightly continues to achieve maximum in August. Probably wet and cloudy weather influences

Table 3. Arithmetic mean (μ_p), standard deviation (σ_p) of peak (12–15 h UTC) O_3 concentration [$\mu g\,m^{-3}$] and mean differences between: daily (μ_d) and nocturnal values $\delta\,(\mu_n - \mu_d)$; daily (μ_d) and peak values $\delta\,(\mu_p - \mu_d)$ for individual months (I–XII) at Stará Lesná (1992–2005)

O_3 [$\mu g\ m^{-3}$]										
x	1	2	3	4	μ_p	σ_p	μ_d	μ_n	$\delta(\mu_n - \mu_d)$	$\delta(\mu_p - \mu_d)$
h UTC	12	13	14	15	(12-15)		(0-23)	(22-04)		
I	59	61	62	59	60	1.4	50	47	-3	10
II	76	78	79	78	78	1.4	64	58	-6	14
III	91	93	94	93	93	1.3	77	68	-9	16
IV	104	105	106	105	105	0.9	87	73	-13	18
V	101	101	102	101	101	0.5	81	63	-18	21
VI	92	92	92	92	92	0.3	71	51	-20	21
VII	88	89	89	89	89	0.3	67	48	-19	22
VIII	95	96	95	95	95	0.5	70	51	-19	25
IX	78	79	80	78	79	0.7	57	44	-13	22
X	65	67	66	64	66	1.3	48	40	-8	18
XI	55	57	56	52	55	2.1	45	41	-3	10
XII	54	55	54	49	53	2.5	45	43	-2	8

O_3 behaviour in July. Meteorological observations (1992–2005) at Stará Lesná show substantially higher mean monthly amount of precipitation in July (138 mm) than in August (92 mm). Contrary, mean monthly sum of sunlight duration is 196 hours in July and 211 hours in August while mean monthly temperature (15.4 and 15.6) and relative humidity (about 76%) are comparable. Seasonal variation of differences and possible functional relationship between time (months) and difference values is illustrated in Fig. 5. Slope coefficients indicate that relatively moderate increase of peak O_3 values is linked to a sharp decrease of nocturnal O_3 values during winter-spring season. On the other hand, decline of peak O_3 values corresponds to the growth of nocturnal O_3 values for the summer-autumn season. Linear dependence has been found for O_3 differences: $y = \delta\,(\mu_\mathrm{n} - \mu_\mathrm{d})$ and $x = \delta\,(\mu_\mathrm{p} - \mu_\mathrm{d})$. Relationship expressed by equation $y = -1.148x + 8.535$ is characterized by the Pearson correlation coefficient $r = -0.931$ and standard error $S_{yx} = 2.619$. Analysis of variance (ANOVA) documents the significance of the tested regression equation (Table 4). P value less than

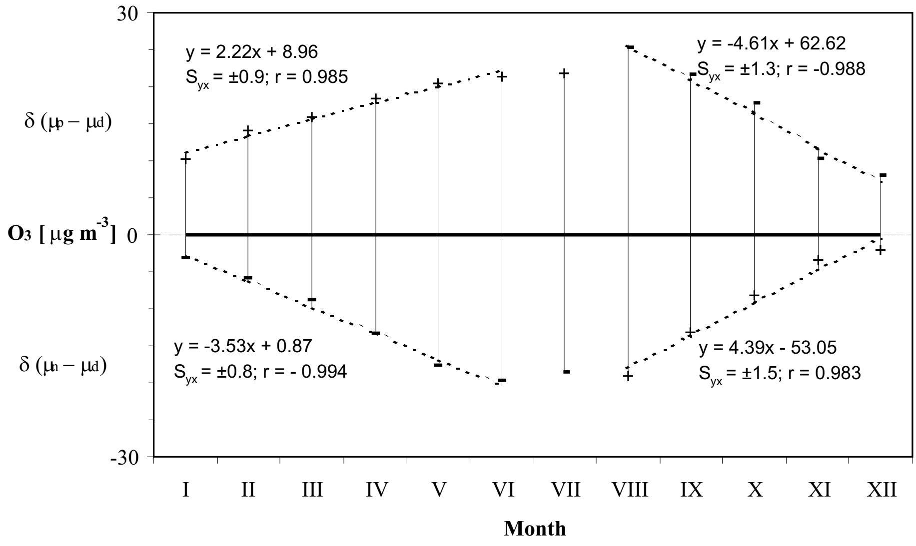

Fig. 5. Linear regression of mean differences between daily values and nocturnal $\delta\,(\mu_\mathrm{n} - \mu_\mathrm{d})$ and peak $\delta\,(\mu_\mathrm{p} - \mu_\mathrm{d})$ O_3 concentration [μg m^{-3}] in different months (I–XII) of year at Stará Lesná (1992–2005).

Table 4. Characteristics of linear regression between $y = \delta\,(\mu_n - \mu_d)$ and x: $\delta\,(\mu_p - \mu_d)$

Pearson Correlation		ANOVA		Regression Coefficients						
Coefficient of determination r^2	0.866	Sum of squares	444.337	Coefficient		Std Error	-95% C.l	+95% C.l.	t value	Probability
Correlation coefficient r	0.931	Degrees of freedom	1	Slope	-1.148	0.143	-1.466	-0.831	-8.049	0.000
Standard error of estimate	2.619	F value	64.791	Intercept	8.535	2.552	2.849	14.221	3.345	0.007
		Probability	0.000011							

0.00001 assumes high probability of the relationship between the dependent and independent variables. The construction of 95% confidence limits (Fig. 6) is based on the analysis of the regression coefficients (Table 4). Verification of presented linear equation by comparison between measured and fitted nocturnal O_3 data (Fig. 7) also demonstrates appropriate agreement.

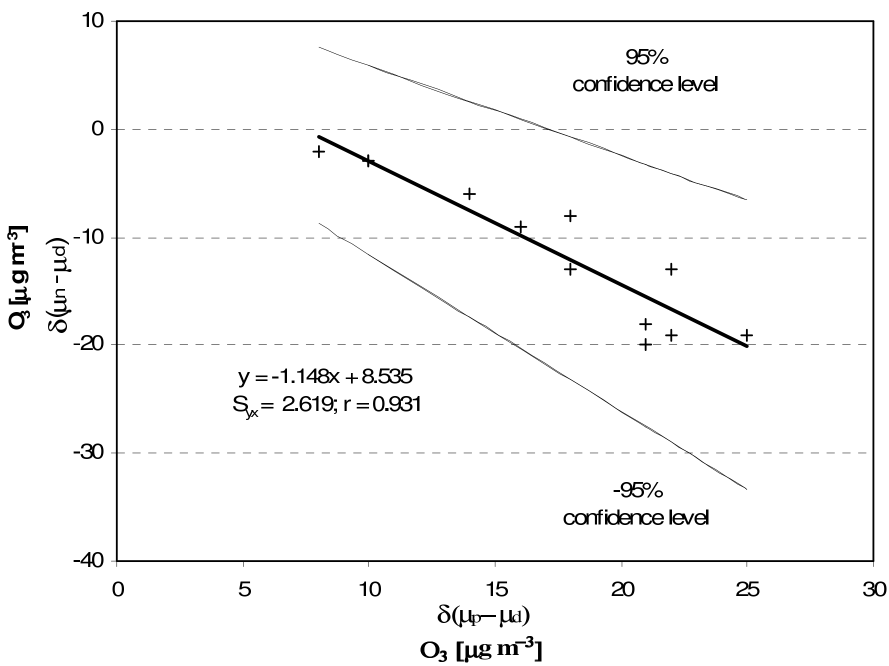

Fig. 6. Relationship between differences of peak $\delta\,(\mu_p - \mu_d)$ and nocturnal $\delta\,(\mu_n - \mu_d)$ O_3 concentration $[\mu g\,m^{-3}]$ at Stará Lesná (1992–2005).

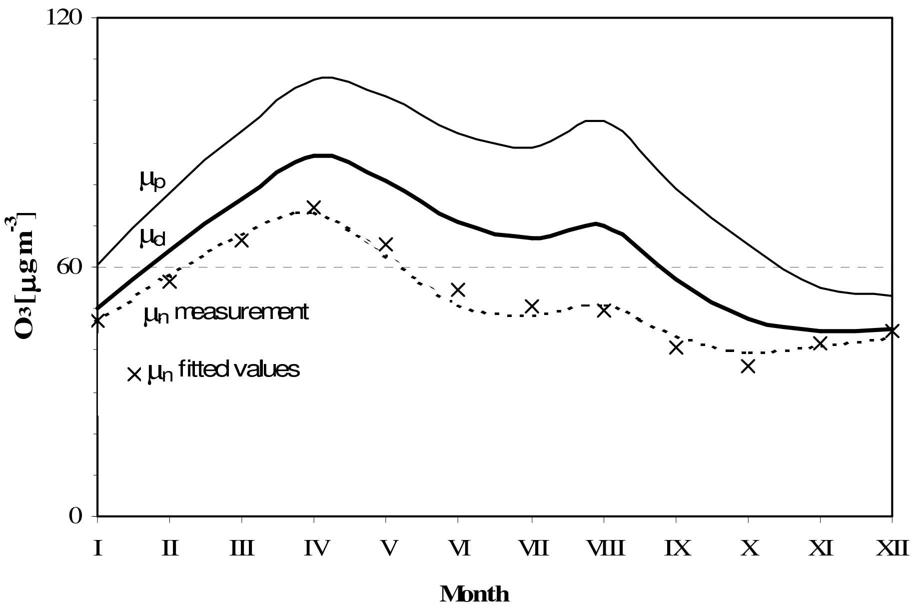

Fig. 7. Mean peak (μ_p), daily (μ_d) O_3 concentration [$\mu g\, m^{-3}$] and comparison between nocturnal (μ_n) values according to measurement and corresponding fitted values at Stará Lesná (1992–2005).

The obtained linear regression is useful for studying the response of peak O_3 values decrease to nocturnal and mean daily O_3 values. Simulation assuming the 15% reduction of peak O_3 values (Fig. 8) shows an increase of O_3 level at night, particularly in summer months (above level of $60\,\mu g\, m^{-3}$). Interestingly, nearly the same seasonal mean daily O_3 concentrations for both situations, with and without 15% peak O_3 reduction, have been achieved. Results of these simulations suggest that a decrease of the highest daylight O_3 concentrations as a consequence of anthropogenic emissions reduction can be compensated by an increase of nocturnal O_3 values without significant changes concerning seasonal mean daily O_3 values. This suggestion is supported by a finding that there is not clear trend in the measured exceedances of the threshold values for AOT40 in association with peak ozone reduction during the 1990s *(Solberg et al., 2004)*. Furthermore, the observed trends of annual O_3 avalues are in general not statistically significant in Europe over the period 1996–2002 *(EEA, 2005)*. Probably the nocturnal O_3

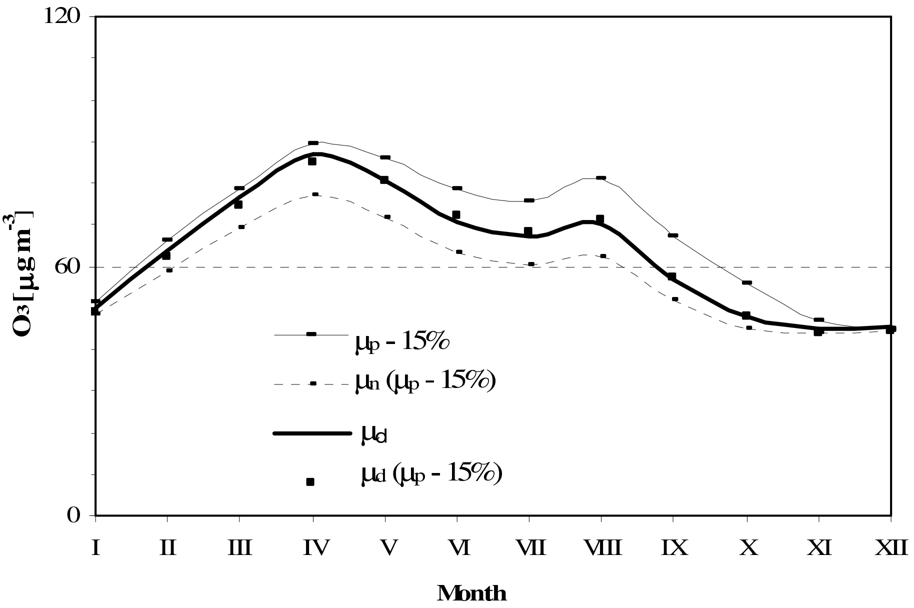

Fig. 8. Simulation of response of nocturnal (μ_n) and mean daily (μ_d) O_3 concentration [$\mu g\, m^{-3}$] to 15% decrease of peak values (μ_p) using linear relationship between differences of peak $\delta\,(\mu_p - \mu_d)$ and nocturnal $\delta\,(\mu_n - \mu_d)$ values at Stará Lesná (1992–2005).

concentration plays an important role in the mean daily, seasonal and annual O_3 trend characteristics. Both physical (surface deposition) and chemical (NO_x oxidation, VOC ozonolysis, OH_x production, SOA) processes determinated by meteorological conditions (wind system, heat capacity, vapour water content) leading to weakly removal and high persistence of ozone in the nightime boundary layer might contribute to an increase of the background ozone level at rural sites, particularly in the winter. Contrary, high daylight O_3 peak observed during recent years *(EEA, 2005)* linked with the stronger nighttime O_3 declination during the summer might be one of the reasons why trends of mean O_3 concentration are weaker in the summer than in the winter-spring season over the laste decade period (e.g. *Derwent et al., 2007; Oltmans et al., 2006; Vingarzan, 2004*). A more in-depth analysis is needed to study the effect of nocturnal O_3 behaviour on variation of seasonal O_3 background in atmospheric boundary layer.

4. Conclusions

A dynamical balance between nocturnal and daylight O_3 is characteristic for O_3 behaviour at rural station Stará Lesná. The night O_3 abundance rises from 40 $\mu g\,m^{-3}$ in the autumn-winter to the highest level of $70-80\,\mu g\,m^{-3}$ in the spring and then decreases to the level of about $50-60\,\mu g\,m^{-3}$ in the summer season. Together with the seasonal rise, the time-dependent O_3 decrease during night hours appears to be in the period from March to August, particularly in May. The investigation of seasonal night μ_n (22–04 h UTC), daylight peak O_3 values μ_p (12–15 h UTC) and daily μ_d (0–23 h UTC) shows relevant linear relationship between negative nocturnal $\delta\,(\mu_n-\mu_d)$ and positive peak daily $\delta\,(\mu_p-\mu_d)$ O_3 differences. Dependence $y=\delta\,(\mu_n-\mu_d)$ on $x=\delta\,(\mu_p-\mu_d)$ expressed as equation $y=-1.148x+8.535$ is described by the Pearson correlation coefficient $r=-0.931$, standard error $S_{yx}=2.619$ and probability with P value < 0.00001. The simulation of 15% daylight peak O_3 reduction using the obtained regression formula demonstrates an association of lower daylight with higher nocturnal O_3 concentrations. The achieved results suggest that the expected effect of the O_3 maxima decrease due to lower anthropogenic emissions can be offset by higher nocturnal O_3 contribution to mean daily O_3 value with the enrichment of the background O_3 level. Additional studies will be needed to better understand the role of nocturnal ozone behaviour in relation to the background O_3 concentration.

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