

SURFACE OZONE VARIABILITY IN THE CONTEXT OF LAND COVER CHANGE



S. BIČÁROVÁ<sup>1</sup>, D. BILČÍK<sup>1</sup>, J. MAČUTEK<sup>1</sup>, R. JANÍK<sup>2</sup>, D. KELLEROVÁ<sup>2</sup>



<sup>1</sup>Geophysical Institute (GPI) and <sup>2</sup>Institute of Forest Ecology (IFE) of the Slovak Academy of Sciences (SAS), Slovakia

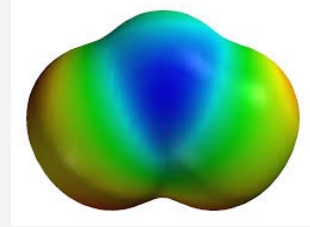


Abstract:

Extreme wind event in November 2004 caused spacious destruction of slope forests in the Tatra National Park, Slovakia. Surface ozone (O<sub>3</sub>) is a minor but not negligible compound of the ambient air. Control strategies for reduction of O<sub>3</sub> precursor emissions have been applied in Europe during last two decades. In spite of these reductions air quality indices suggest that highland sites are more vulnerable to health and environmental risk than lowlands where the most of emissions from road transport and industry are produced . Both anthropogenic emissions and biogenic precursors (BVOC) from forest vegetation play relevant role in the tropospheric photochemistry, especially in mountainous and rural locations. The purpose of this work is to describe the variability of O<sub>3</sub> before and after windstorm in 2004 with different amount of local BVOC precursors from forest vegetation.

Conclusions:

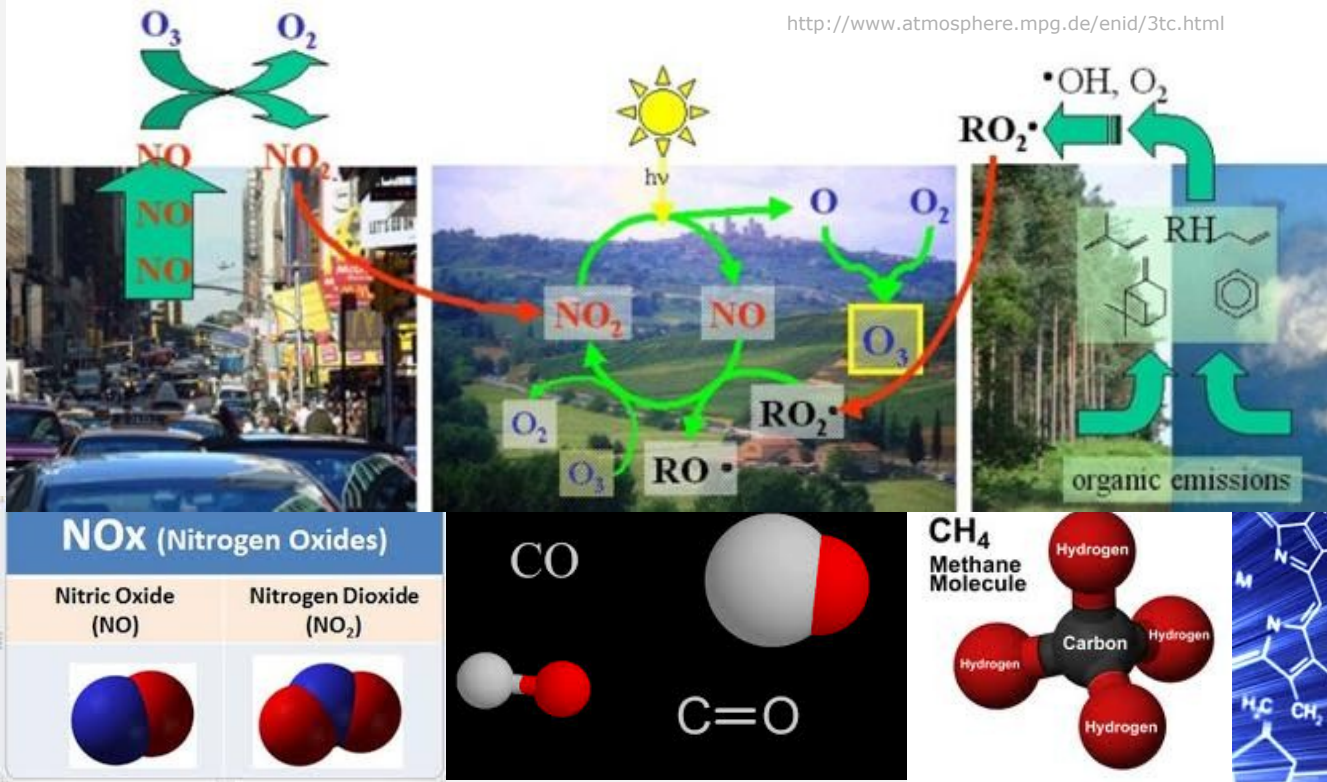
In the past decade, the High Tatras were affected by several natural disasters (strong windstorms, forest fires, flooding, insect invasions, etc.) as well as by an extensive construction of tourist centres and development of ski resorts. These events contributed to several visible landscape changes in the area including large deforestation of uphill slopes. Spacious destruction of forested area caused reduction of natural emissions from forest vegetation that play important role in surface ozone chemistry. Analysis of long-term O<sub>3</sub> series data for foothill station Stará Lesná suggest association between BVOC and O<sub>3</sub> concentrations in the context of land cover changes. Both, decrease of daylight and increase of nightly O<sub>3</sub> concentrations for selected time period is linked to changes of BVOC after windstorm in 2004. Further research is needed to take account of climate factor as well as effect of long-range transport.



Surface ozone (O<sub>3</sub>)

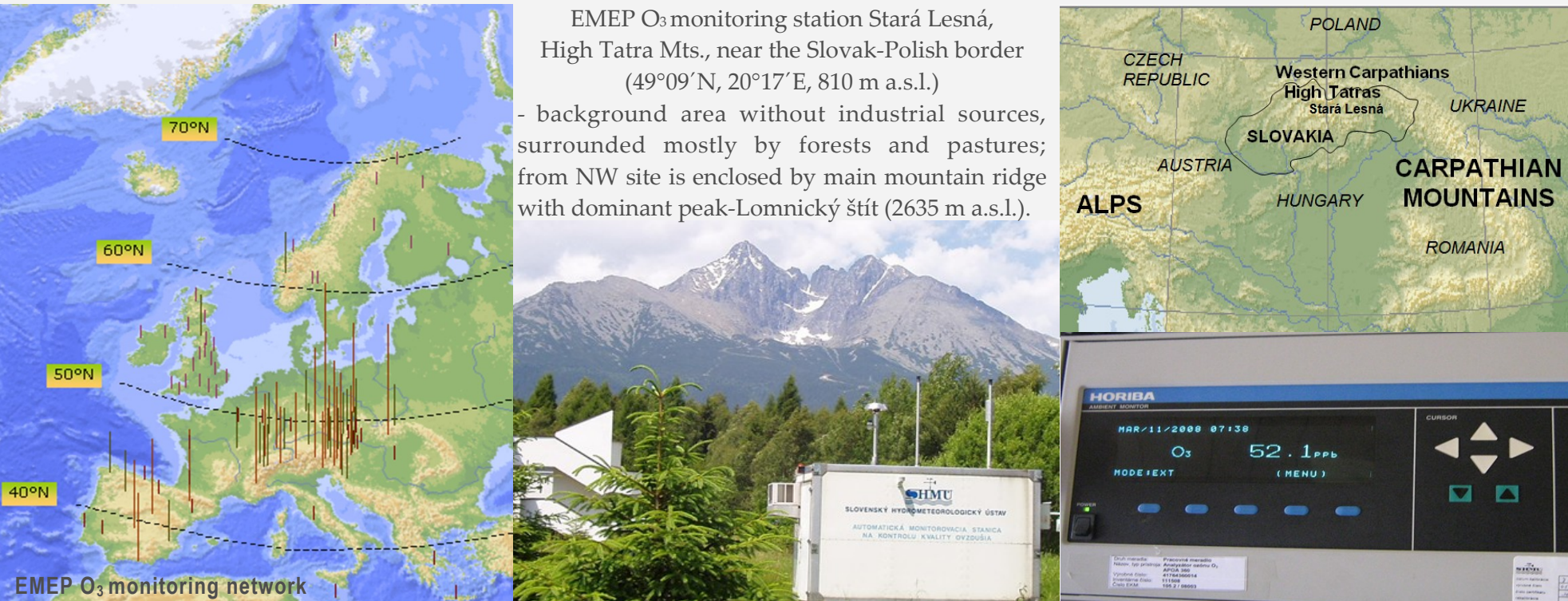
- minor component of ambient air and key marker of secondary air pollution
- secondary pollutants are formed in the troposphere due to transformation of primary emissions from variety of anthropogenic and natural source

- tropospheric O<sub>3</sub> is produced by photochemical oxidation of primary emissions including carbon monoxide (CO), methane (CH<sub>4</sub>) and non-methane hydrocarbons (NM VOC) in the presence of nitrogen oxides (NO<sub>x</sub>) - projection of air quality (Stocker et al., 2013) estimates that globally, warming decreases background surface ozone; high CH<sub>4</sub> levels can offset this decrease, raising background surface ozone by year 2100 on average by about 8 ppb (25% of current levels) relative to scenarios with small CH<sub>4</sub> changes



- Air quality is associated with presence of airborne surface pollutants, such as O<sub>3</sub>, CO, NO<sub>x</sub> and aerosols (solid or liquid particulate matter). Exposure to such pollutants exacerbates respiratory and cardiovascular diseases, harms plants and damages buildings. There is strong evidence that tropospheric O<sub>3</sub> also has a detrimental impact on vegetation physiology, and therefore on its CO<sub>2</sub> uptake.

Monitoring of O<sub>3</sub> at EMEP station Stará Lesná, Slovakia, High Tatras



Long-term series of O<sub>3</sub> data (1992-2013)

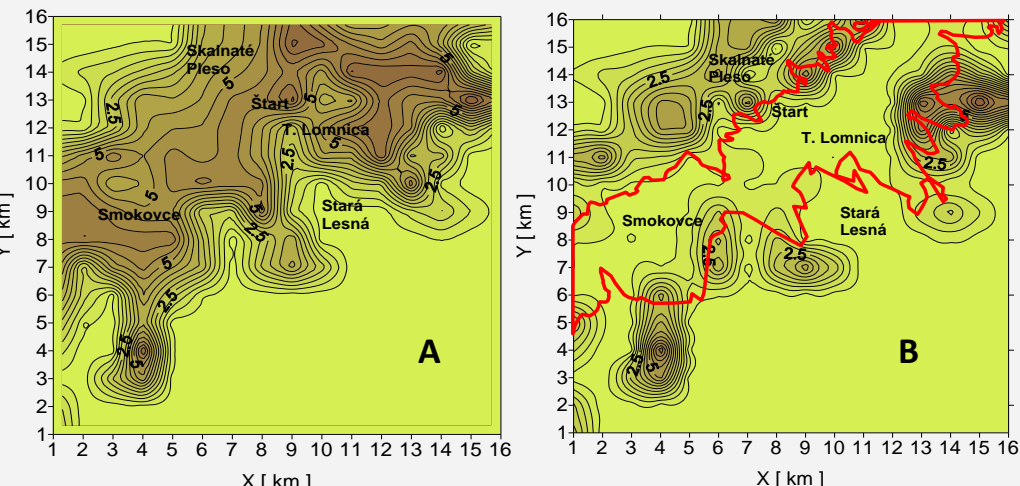
Measurement of O<sub>3</sub> concentration is provided by Slovak Hydrometeorological Institute (SHMI) that is national partner in EMEP project since end of year 1991. Continuously operating air monitoring station measures O<sub>3</sub> concentration by analyzer Horiba APOA360 and mean hourly O<sub>3</sub> are registered in EMEP database under code SK04 ([www.emep.int](http://www.emep.int)). Automatic O<sub>3</sub> analyser is regularly calibrated and data are validated in data centre of SHMI.

Land cover changes



BVOC

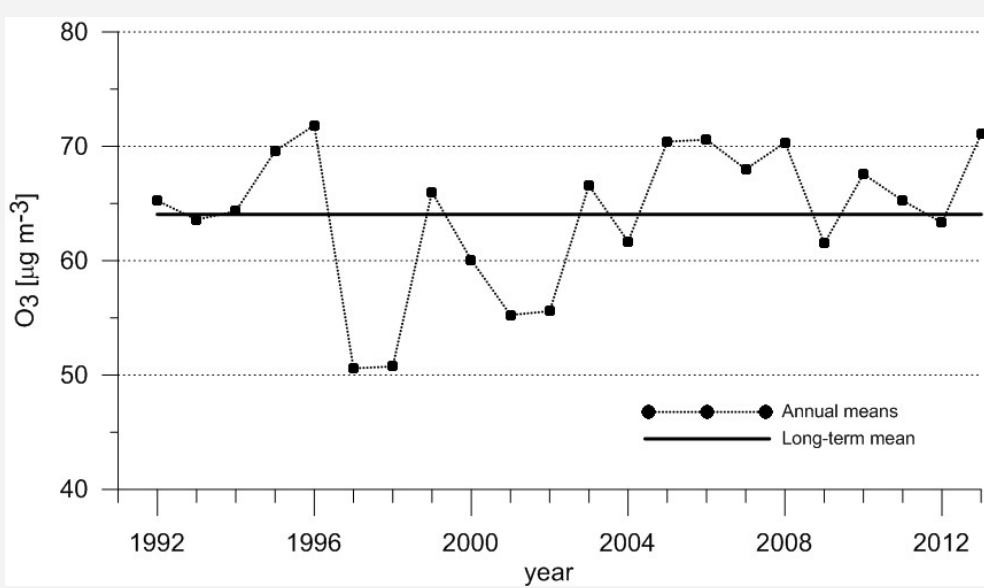
Forest vegetation is important natural source of Biogenic Volatile Organic Compounds (BVOC) such as isoprene and monoterpenes that play a significant role in the tropospheric photochemistry, especially in suburban and rural locations. Estimations of BVOC emissions for the High Tatras region before and after devastative windstorm using BEIS2 series of GLOBEIS model show decrease of BVOC emissions in range 53 – 59% that is adequate to 59% reduction of forest vegetation area (Bičárová and Fleischer, 2006).



Spatial distribution of total BVOC emissions (isoprene, total monoterpenes and other VOC) for the High Tatras model domain of periods: A – before windstorm, B – after windstorm (solid red line – border of damaged forest area).

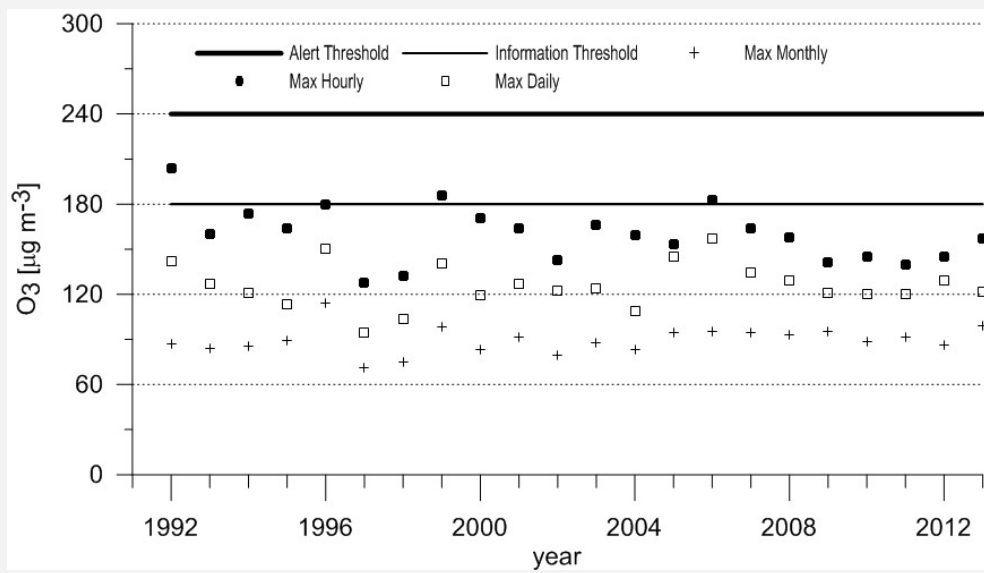
Variability of O<sub>3</sub> concentration at Stará Lesná for period 1992-2013

Annual O<sub>3</sub> means



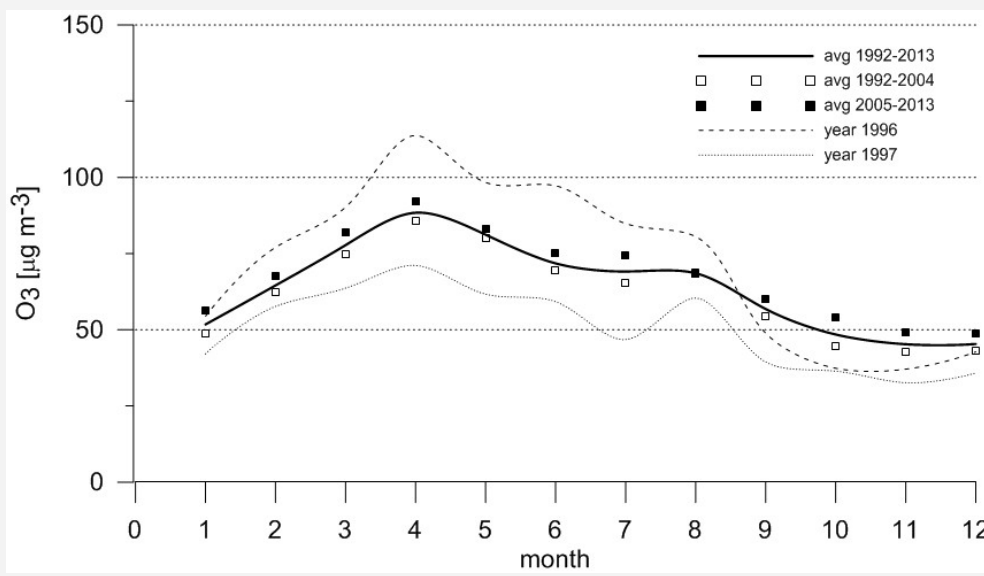
Multiple variable analysis of validated O<sub>3</sub> data shows that mean annual values fluctuate around long-term O<sub>3</sub> mean of 64.1 ±3.6 µg m<sup>-3</sup>. Change of annual means during period 1992-2013 is statistically not significant. However, mean values for period before (1992-2004) and after windstorm (2005-2013) increased from 62.5 to 67.6 µg m<sup>-3</sup>. Coefficients of variation document higher variability (22%) of annual means for period 1992-2004 than for period 2005-2013 (5%). It corresponds with wider range of mean values (50-72 µg m<sup>-3</sup>) until 2005 than for following years. During last 9 years mean values only above 60 µg m<sup>-3</sup> were occurred.

Maxima - hourly, daily and monthly



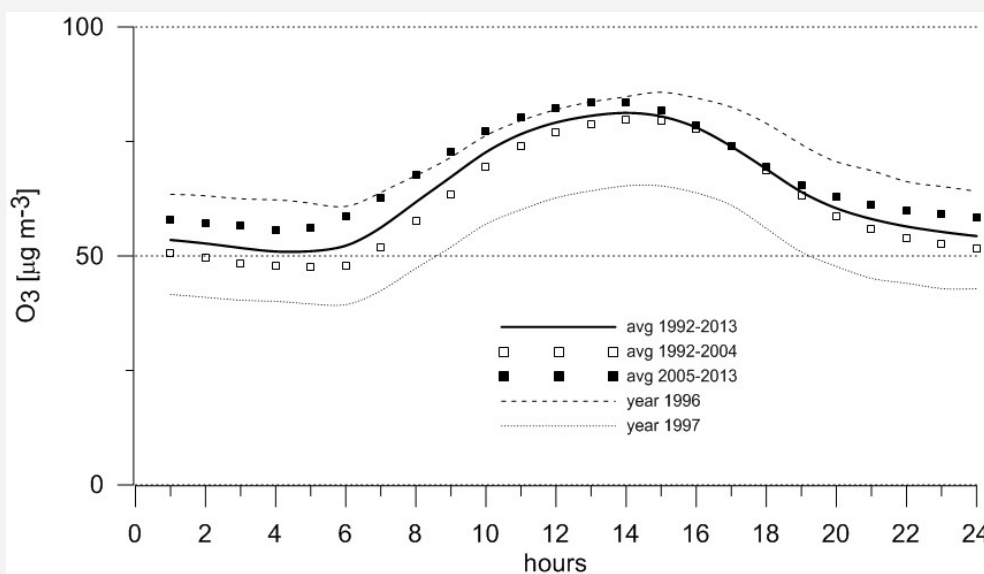
Maximal O<sub>3</sub> concentrations recorded Stará Lesná were close the information threshold of 180 µg m<sup>-3</sup>. Altogether, 9 exceedances of information threshold were occurred, frequently in 1992 (7 times) then once in 1999 and 2006. The alert threshold 240 mg m<sup>-3</sup> was not overstepped during the whole considered period. The highest mean hourly O<sub>3</sub> concentration of 204 µg m<sup>-3</sup> was in the afternoon in July 1992. Maxima of daily mean O<sub>3</sub> concentration ranged from 94 µg m<sup>-3</sup> to 157 µg m<sup>-3</sup> and maxima of monthly means varied from 71 µg m<sup>-3</sup> to 114 µg m<sup>-3</sup>. Different variability appears to be associated with differences in ozone daily pattern.

Seasonal changes



The course of monthly O<sub>3</sub> means at Stará Lesná shows primary maximum in spring (88 µg m<sup>-3</sup> in April) and secondary in summer (69 µg m<sup>-3</sup> in August). During autumn starts O<sub>3</sub> decrease that continues to winter minima (45 µg m<sup>-3</sup> in November-December). From January to March O<sub>3</sub> concentrations gradually rise until reaching primary spring maximum. Monthly means averaged over period after windstorm (avg 2005-2013) are slightly above long-term line and suggest moderate O<sub>3</sub> increase in comparison with period before windstorm (avg 1992-2001).

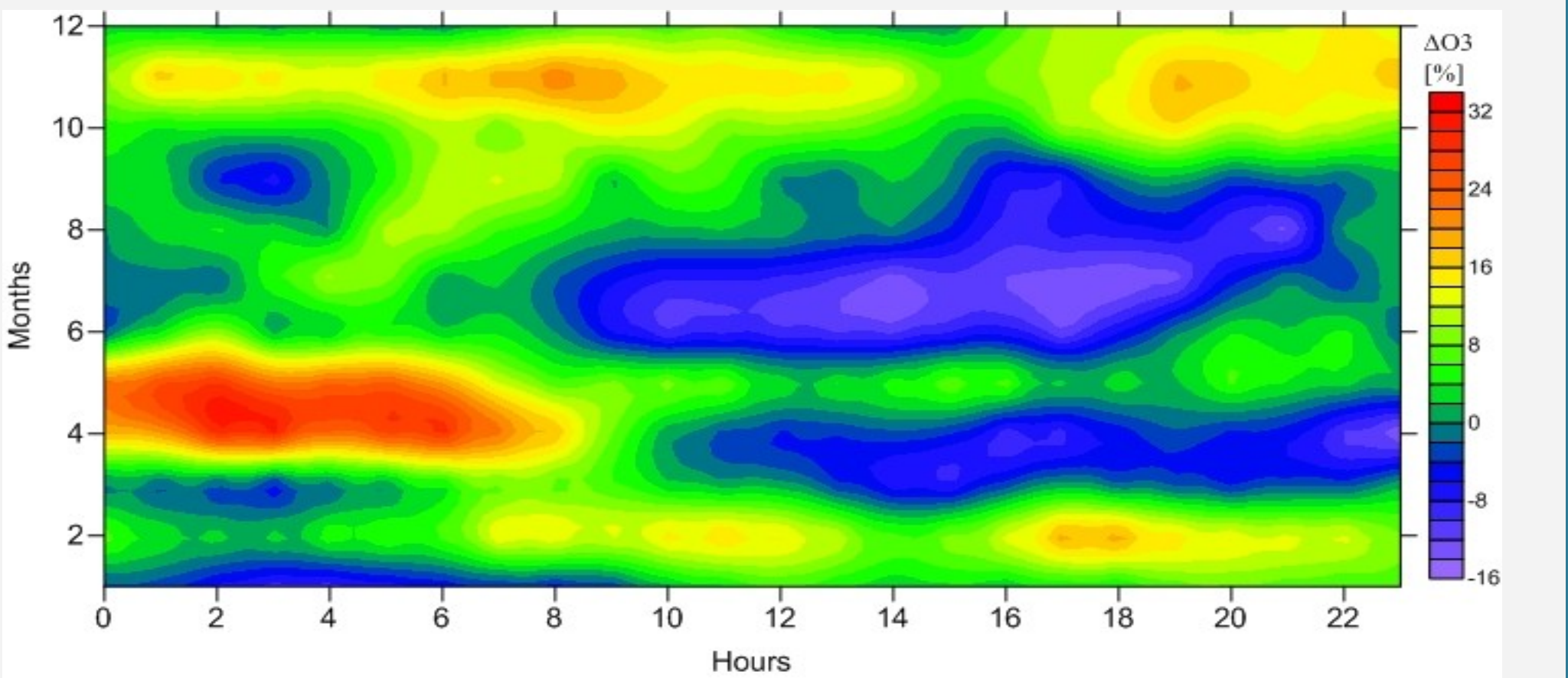
Daily course



Daily course of hourly O<sub>3</sub> concentrations averaged for long-time period 1992-2013 is characterized by the minimum (51 µg m<sup>-3</sup>) in the early morning hours (4-5 h UTC at 5-6 h local time). The concentration is rising steadily reaches its peak 81 µg m<sup>-3</sup> in the afternoon (14 h UTC) and it gradually starts to decrease. After this it shows the sequence of low night and morning ozone values. Daily course after windstorm (avg 2005-2013) shows moderately high values in comparison with long-term average, especially for night hours.

Changes of O<sub>3</sub> after windstorm in 2004

- Hourly O<sub>3</sub> data averaged over period before (O<sub>3\_avg1</sub>) and after (O<sub>3\_avg2</sub>) windstorm in 2004 were used.
- Temporal distribution of relative differences [%] between O<sub>3\_avg1</sub> and O<sub>3\_avg2</sub> shows changes in O<sub>3</sub> concentrations, especially for night (increase) and daylight (decrease) hours.
- Marked, more than 30% increase for night and early morning hours (0-7h) from April to May after 2004.
- Approximately 10-20% increase for late autumn and winter seasons (Oct-Feb).
- Decrease until -16% in spring and summer seasons indicate lower photochemical O<sub>3</sub> production during daylight hours may be associated with absence of BVOC for reactive radicals activation.
- Statistical analysis suggests significant relationship between O<sub>3\_avg1</sub> and O<sub>3\_avg2</sub> for selected time range from 0 to 7 hours in May
- It is assumed that reduced BVOC sources resulted to decrease of O<sub>3</sub> daylight concentrations in summer due to lower production of reactive OH, HO<sub>2</sub> radicals. In contrast, deficit of BVOC may cause significant increase of O<sub>3</sub> night concentrations in spring due to lower O<sub>3</sub> depletion via ozonolysis.



**Acknowledgement** This research was supported by the Grant Agency of the Slovak Republic under the projects VEGA No. 2/0053/14, No. 2/0089/14, and by the Slovak Research and Development Agency under the contract No. APVV-0429-12. The authors are grateful to the Slovak Hydrometeorological Institute for providing of EMEP data.