

SURFACE OZONE CONCENTRATIONS OVER THE SNOW COVER

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The goal of the following article is to examine the influence of the snow cover on the surface ozone concentration with emphasis on snow height changes.

Surface ozone is one of the most monitored pollutants, e.g. by the European EMEP project. There is a great number of articles concerning with negative effect of high ozone concentration on agricultural plant and wood productivity. Those studies are focused on the surface ozone concentrations during vegetation period and therefore winter concentration often stays neglected.

Fewer scientific articles are focused on surface ozone measurements over the snow cover. Most of them are taking place over stable snow cover in the polar regions, such as Antarctica and Greenland. Just a few articles are engaged in the surface ozone measurements over periodical and episodic snow cover. Some articles pointed out to the composition of the air trapped in snow and ice cover. Surface ozone and snow cover measurements from subalpine station in Stará Lesná (808 m above sea level) and alpine station in Skalnaté pleso (1778 m a.s.l.) were used in order to analyse the influence of the snow cover presence on surface ozone concentrations.

Measured locations are typical for high surface ozone concentration during the spring and mostly summer months as a consequence of intense photochemical activity in the atmosphere. The smallest concentration occurs in the autumn and than we observe slow consecutive increase during the winter period. Annual variations are mostly caused by changing photochemical activity, the presence of ozone precursors and its transfer through atmosphere. Concentrations of surface ozone during the days with and without snow cover were analysed for different temperature intervals (-1;1), (-2;2) and (-3;3)°C as well as for cyclonal and anticyclonal situations separately. Higher concentrations of surface ozone were registered mostly during the periods with snow cover in comparison to the periods without the snow cover in Skalnaté Pleso while in Stará Lesná this fact was not clearly expressed.

No influence of the snow cover height on the surface ozone concentrations was recognized.

Keywords: surface ozone concentrations, snow cover

INTRODUCTION

Surface ozone is one of the secondary pollutants whose concentration trends stay ambiguous despite of the constant decrease of its precursors during last decades. Mountain areas are more affected by higher surface ozone concentrations than urban and rural environment. Mountain stations in middle latitudes achieve minimum values of mean daily surface ozone concentrations during winter periods. It is attributed to the low winter solar radiation and therefore photochemical reactions are less intense. The presence of snow cover might be additional determining parameter. Wang's paper (Wang et al. 2011) pointed out that NO_x oxides, ozone precursors, are trapped in interstitial spaces of snowpacks. Constant release of NO_x from the snowpack strongly influence surface ozone concentration in ambient atmosphere. Measurements in Summit, Greenland showed that interstitial NO_x concentrations are higher than in the ambient air (Wang et al. 2011). NO_x and other gases being released from snowpack during photochemically intense periods are supposed to be the main source of ozone in the boundary layer of the area. The factors influencing NO_x release beyond photochemical activity are the following: air temperature, ion content (takes place in influencing chemical reactions and diffusion processes) and microbial activity. After the release NO_x reacts with chemical compounds, e. g. hydroxyl radical forming nitric acid HNO₃. Nitric acid is later transported back to the snowpack by the means of dry or wet deposition and a circle initiated by the photochemical radiation is closed (Davis et al. 2008). Surface ozone concentration is dependant on UV radiation intensity because according (Wang et al. 2011) it increases following NO_x release from snowpack. Apart from ozone precursors, ozone itself is strongly depleted within the snowpack and its

concentration is decreasing with the snow depth. Mechanisms of the ozone depletion within a snowpack are not clearly understood yet. It is expected that both light and dark phases (with or without solar radiation) take place in those processes (Albert et al. 2002). Chemical processes in the snow pack are strongly influenced by the mass transport and transport of chemical species. For dry snow we distinguish two main causes of transport: diffusion and advection. The former is driven by temperature gradient among snowpack and the later is driven by air pressure conditions and turbulence. Both of them affect transport of heat and chemical species transport among snowpack (Albert et al. 2002).

MATERIALS AND METHODS

In this paper, we investigated the relation between the changes of snow cover height and the surface ozone concentrations. Measurements from Skalnaté pleso (1788 meters above sea level) and Stará Lesná (808 m a. s. l.) were at disposal. Both stations are located on the south slope of the High Tatra Mts. Surface ozone measurements at Stará Lesná station (SL) were carried out within the international EMEP monitoring program since 1992 till 2013. SL terminated its manual measurements as the climatological station in 2013. The data from Skalnaté pleso were available from 2000 till 2015. Ozone data were obtained by ozone analyzers Horiba APOA360, Thermo Environmental Instrument 49C or Cranox. All instruments were based on UV absorption principle. Calibrations were provided by the national secondary ozone calibration standard installed in 1993 in Bratislava. Both stations operated during measured period as climatological stations. Data for snow cover height were measured manually by the snow stake.

RESULTS

The data were processed into graph visual. Figure 1 represents the dependence of surface ozone concentrations on interdiurnal snow cover height change for measurements at Skalnaté pleso station. X-axis represents interdiurnal change of snow cover height (Δ SCH or Δ VSP). Positive values denote interdiurnal increase of snow cover, negative values denote decrease. We divided the data into three categories. All data (AL), the data from anticyclonal situations (AC) and the data from cyclonal situations (CY). The analysis was also based on temperature intervals. The first category includes mean daily air temperature interval from -1°C to 1°C . The second interval includes temperatures between $(-2; 2)$ and the third between $(-3; 3)^{\circ}\text{C}$. The index from 1 to 3 next to the synoptic situation symbol represent the actual temperature interval. Those intervals represent the data close to 0°C and they should be the

intervals with natural appearance of the conditions with and also without snow cover. Those data comes from cold period of the year. Finally, we distinguished the data to two categories. The former contains the situations with snow cover. Those data are represented in figures by light blue color. The data from periods when ground was not completely covered by snow were excluded. The later category “without snow” contains the data coming from days without the snow cover. Those data are represented in figures 1 to 4 with light brown color against light blue background. This data is lined up in just one line through the middle of the figure. It is obvious, because during periods without snow cover the change of snow cover height stays zero and data are distinguished only by the different values of surface ozone concentrations ($c\text{O}_3$) or interdiurnal surface ozone concentrations changes ($\Delta c\text{O}_3$). Positive values of $\Delta c\text{O}_3$ represent the interdiurnal increase of surface ozone concentration.

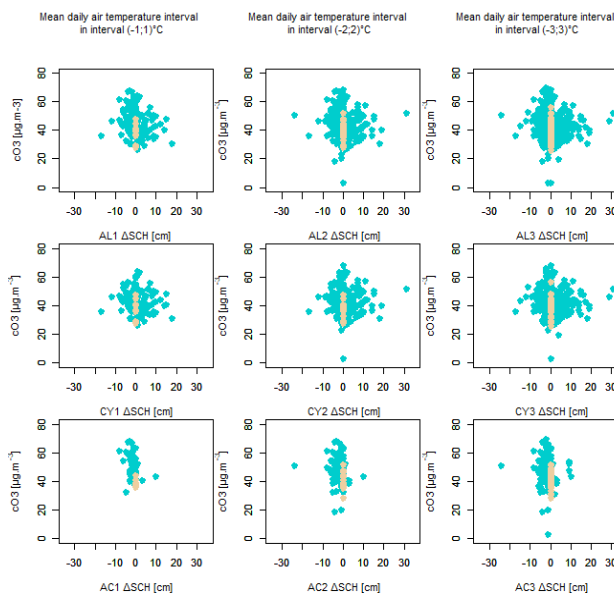


Figure 1. The dependency of surface ozone concentration from snow cover height change during all synoptic, cyclonal and anticyclonal situations in regime with and without snow at the Skalnaté pleso station

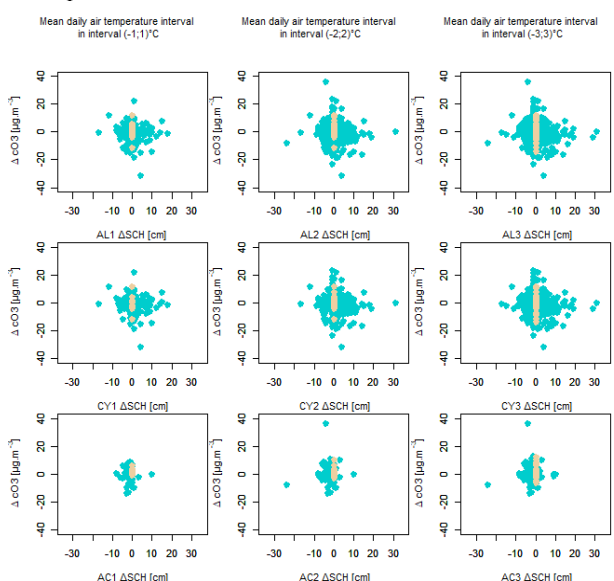


Figure 2. The dependency of surface ozone concentration change from snow cover height change during all synoptic, cyclonal and anticyclonal situations in regime with and without snow at the Skalnaté pleso station

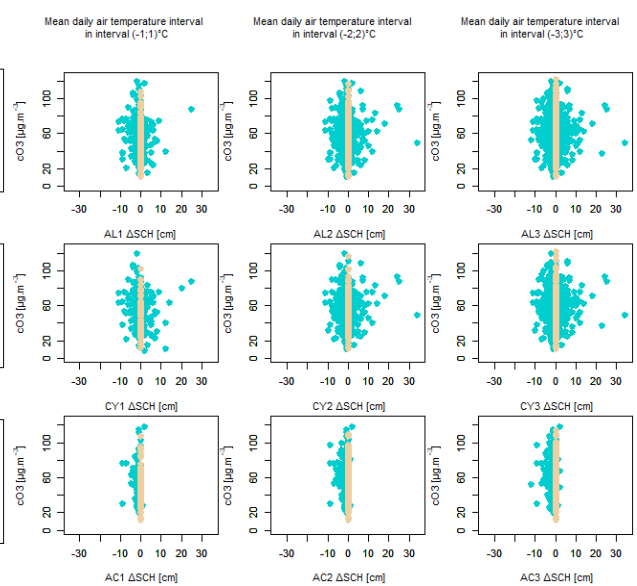


Figure 3. The dependency of surface ozone concentration from snow cover height change during all synoptic, cyclonal and anticyclonal situations in regime with and without snow at the Stará Lesná station

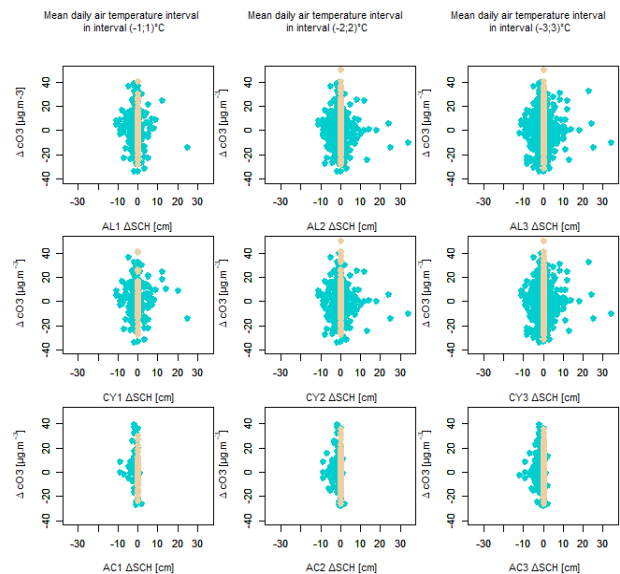


Figure 4. The dependency of surface ozone concentration change from snow cover height change during all synoptic, cyclonal and anticyclonal situations in regime with and without snow at the Stará Lesná station

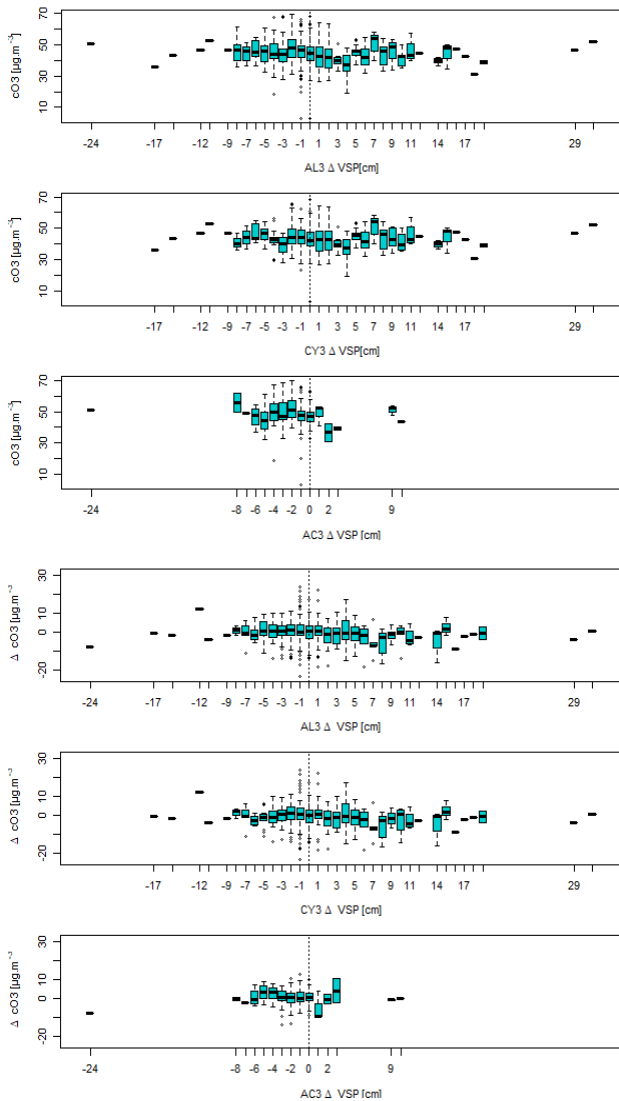


Figure 5. The boxplot of surface ozone concentration and concentration change from snow cover height change during all synoptic, cyclonal and anticyclonal situations in regime with snow cover at the Skalnaté pleso station

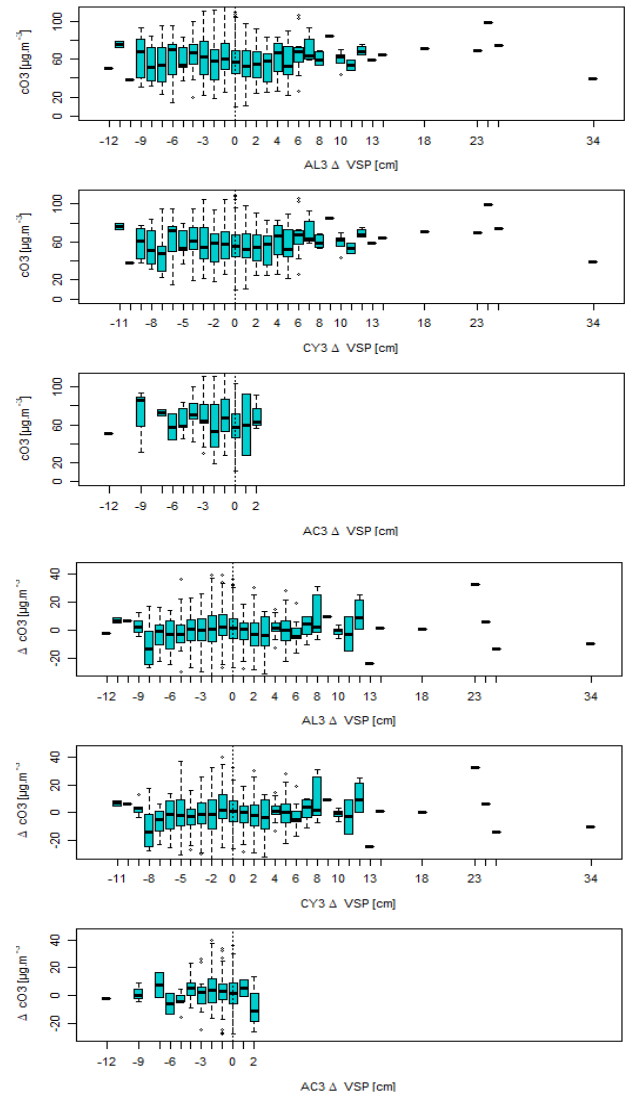


Figure 6. The boxplot of surface ozone concentration and concentration change from snow cover height change during all synoptic, cyclonal and anticyclonal situations in regime with snow cover at the Stará Lesná station

Figure 1 depicts measured concentrations of surface ozone on station Skalnaté pleso during mean air temperature in intervals (-1;1)°C, (-2;2)°C and (-3;3)°C from left to right for all synoptic (AL), cyclonal (CY) and anticyclonal (AC) situations. The data are shown in set of nine plots.

Figure 2 depicts interdiurnal surface ozone concentrations (y-axis) under the same conditions as the previous case. Following 18 plots on the right side (Fig. 3 and 4) illustrate similar measurements at Stará Lesná station. Obviously, data from AC situations are less regular than CY data. It is caused by meteorological conditions during AC situations which are unfavourable on atmospheric precipitation.

In figures 5 and 6 there are depicted boxplots for categories with snow cover for only one temperature interval (-3;3)°C at both stations. We can observe already mentioned anticyclonal irregularity in the data.

Table 1 contains the number of individual measurement which belong to selected categories.

Table 1. Number of selected values in individual categories

| | Synoptic situation | Temperature interval | | |
|-----------------|--------------------|----------------------|-----|-----|
| | | 1 | 2 | 3 |
| SP without snow | AL | 37 | 81 | 136 |
| | CY | 30 | 60 | 104 |
| | AC | 7 | 21 | 32 |
| SP with snow | AL | 252 | 507 | 742 |
| | CY | 176 | 333 | 490 |
| | AC | 76 | 174 | 252 |
| SL without snow | AL | 183 | 371 | 591 |
| | CY | 88 | 189 | 322 |
| | AC | 95 | 182 | 269 |
| SL with snow | AL | 278 | 552 | 809 |
| | CY | 206 | 400 | 594 |
| | AC | 72 | 152 | 215 |

CONCLUSION

During episodes with snow cover without the change of its height (lightblue line across zero x-value), we observe higher concentration than during episodes without snow cover at Skalnaté pleso station. Measurements of interdiurnal surface ozone concentration change had not prove any significant differences between examined subjects.

The difference between snow and without snow situations at Skalnaté pleso station indicate that during snow period higher surface ozone concentration are more frequent than during without snow situations. The effect could be caused by the difference in the number of measurements which fall into individual categories, as we see in *Table 1*.

The data from Stará Lesná station did not show significant differences of surface ozone concentrations between with and without snow cover situations during investigated period. On the other hand the datasets from this station showed greater dispersion of surface ozone concentration or interdiurnal changes than the data from Skalnaté pleso station.

Boxplots depict distribution of measured values for interdiurnal snow cover height. Naturally, mostly decrease of snow cover heights was observed during anticyclonal situation. Our set up allowed us to notice that negative snow cover height change (i. e. snow cover decrease) was accompanied with more extreme values, both high and low, of surface ozone concentration than we observed during periods with snow cover height increase.

Presented investigation indicated than in SP station located in mountain environment, there are higher concentrations of surface ozone during the periods with snow cover than during

the periods without it. Nevertheless, it looks that surface ozone concentrations depends rather on the complex of climatic parameters and simple analysis towards the snow cover has not shown closer and statistically significant relation to the respective concentrations.

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