"Physics of Auroral Phenomena", Proc. XXX Annual Seminar, Apatity, pp. 211 - 214, 2007

Polar Geophysical Institute

ON OZONE CONTENT IN THE EUROPEAN MOUNTAIN REGIONS

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Abstract. The analysis of ozone data from 60 stations located in mountainous area of the Alps, the Pyrenees, the Carpathians, the Pennines, the Balkans, the Khibiny and the Scandinavian mountains is presented. The selected stations are located at different altitudes between 500 and 3500 m a.s.l.
In winter the data suggest a fairly uniform ozone distribution in the Europe Mountains at altitudes above 500 m. The differences between ozone values at same level in all mountain systems are little. The mean monthly ozone concentrations in high- and moderate latitudes depended on altitude. The summer ozone levels in central Europe are higher than in North Europe because of photochemical ozone production. However the intensity of photochemical ozone production in the layer above the boundary layer is not enough as the diurnal variations are feebly marked at altitudes above 1.5-2.0 km. The increased ozone concentrations in the free atmosphere over the mountain regions in late spring and summer are most likely caused by accumulation of photochemical produced ozone. Also the upward transport through convection and turbulent mixing of ozone from the boundary layer contribute the ozone budget in the free atmosphere.
The period of the maximal ozone in the mountain regions of Central and Southern Europe is shifted on the late spring and summer months while ozone concentrations in the North European Mountain have a spring maximum.

Introduction

The mountain measurements have a great significance in the studies of tropospheric ozone as ozone concentrations are close to that in the free atmosphere at corresponding level. The mean ozone profiles according to data of surface mountain stations are almost similar to the mean vertical profile given by ozone sounding. Besides, the mountain ozone measurements have a better time resolution than the infrequent ozone sounding.
In this paper the seasonal and diurnal variations of tropospheric ozone and its vertical distribution in mountain regions of Europe will be analyzed.

Description of data

The data of World Data Centre for Greenhouse Gases (WDCGG) and EMEP (http://emep.int) for ozone monitoring stations located in the Alps (31 stations), in the Pyrenees and mountains of the central Spain (9), in the Carpathians (10), in Greece (1), in the Pennines mountains (1), in the Scandinavian mountains (4), in Spitsbergen (1) and Khibiny (1) were analyzed for this study.
In addition, the published results of ozone measurements at Swedish station Areskunan [*Bazhanov V., Rodhe,* 1997], the Kislovodsk mountain observatory [*Senik*, 2005] were used.

Analysis and discussion

The seasonal cycles of ozone concentrations at a mountain station in the Europe are shown in Figures 1 and 2.
The ozone concentrations in the northern Europe and the Arctic have a pronounced maximum in spring. As well known, the spring maximum is caused by the ozone transport from the stratosphere.
The diurnal ozone variations at northern mountain stations are feebly defined or absent (Fig.2). The midday and night ozone concentrations are almost identical even in summer. Thus ozone concentrations in the high-latitude troposphere do not depend on the solar radiation. At the same time it is well known that the solar ultraviolet radiation is the requisite condition for the photochemical ozone production.
The mountaintop ozone concentration always exceeds that at the surface stations, and this concentration is predictable by meteorological analysis [*Demin et al*, 2006]. This fact indicates that the ozone source locates above the boundary layer. This ozone-enriched air may reach the surface and/or remain in the middle troposphere depending on the turbulent mixing.
In winter the data suggest a fairly uniform ozone distribution in the Europe. The winter ozone concentrations in the mountain regions of the Central and Southern Europe are almost similar to observed values in the Scandinavian mountains at the same level. However the ozone maximum is shifted on late spring and summer (Fig. 1) and ozone concentrations are vastly more. The spring increase of ozone is annual observed at all sites and corresponds to the spring tropospheric maximum as in the case with the northern sites. The broad summer ozone maximum is caused

by the photochemical ozone production in the lower troposphere. A similar seasonal course is detected on ozonesonde measurements in the free atmosphere over the Central and Southern Europe.

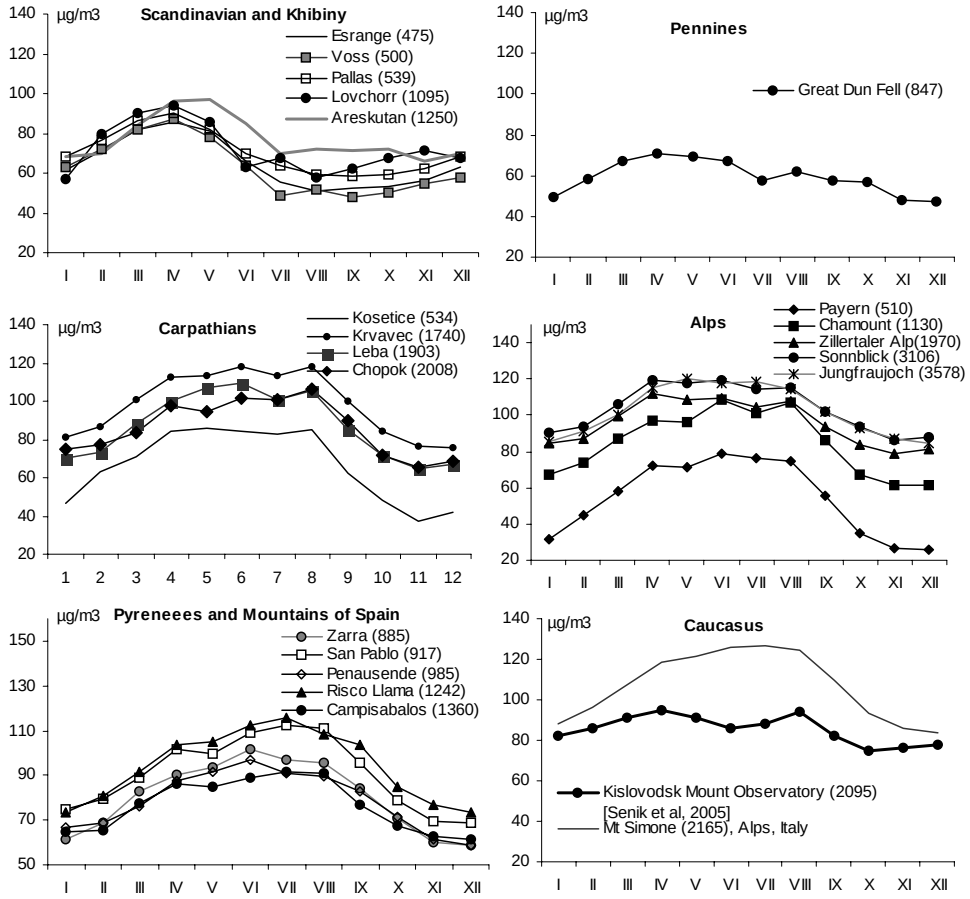

Fig. 1 Examples of seasonal cycles in ozone concentration in the European Mountain region

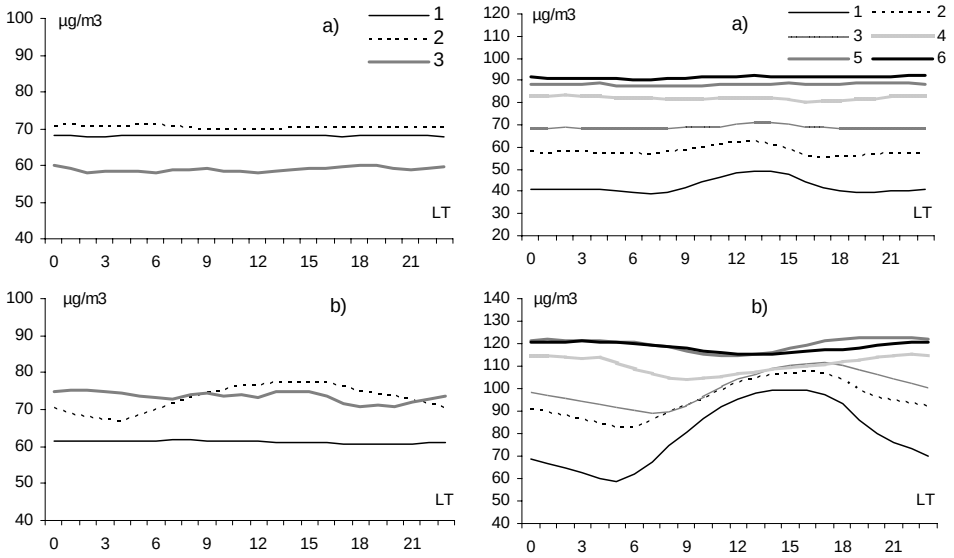

Fig. 2. Examples of diurnal cycles in ozone concentration in the mountain sites of the Northern Europe in January (a) and June (b): 1—Zeppelinfjel (Spitsbergen, 474 m), 2—Pallas-Sammaltunturi (Finland, 565 m), Lovchorr (Khibiny, 1095 m, only 2004 and 2005).

Fig. 3. Examples of diurnal cycles in ozone concentration in the Alps Mountains in January (a) and June (b): 1— 500-750 m (8 stations), 2—750-1000 m (6 stations), 3— 1-1.5 km (9 stations), 4—1.5 -2 km (2 stations), 5—2-3 km (3 stations), 6— > 3 km (2 stations).

The month of summer peak ozone concentration is not constant and depended on a year [*Zanis et al*, 2007]. It is the evidence of the photochemical ozone production as this phenomenon usually occurs only under anticyclonic conditions coinciding with increased sunlight, high temperatures and low wind speed, i.e. it is depended on meteorological conditions, other than on a season. Thus, the large variability of ozone in summer is likely a consequence of photochemical production from anthropogenic precursors [*Chevalier A. et al*, 2007].

Surface ozone concentrations depend on complex combinations of chemical processes and meteorological influences. However the significant diurnal course of ozone concentration is the reliable evidence of local (in-situ) photochemical processes. The diurnal maximum is reached in the afternoon (around 1300 LT). After this time, the ozone concentration decreases slowly through the evening and night. The midday ozone concentrations in the conditions of photochemical processes are many times higher than night ones.

At the same time the diurnal ozone variations in the Alps, Carpathians and Caucasus show very little diurnal variation at altitudes above 1.5-2.0 km (fig.3). This fact is the evidence that the mean rate of local ozone production in the free atmosphere is small. In a number of cases the mountain ozone concentrations shows a small minimum in morning and midday hours as opposed to local photochemical formation (fig.3). This minimum is caused by diurnal courses of dry deposition velocity of ozone [*Zaveri et al*, 1995] and by the arrival of polluted air out on boundary layer with the mountain valley wind. The photochemical ozone production in the boundary layer and the following turbulent mixing cause a equalization of the vertical ozone profile within the mixed layer, so that the ozone concentrations in lower troposphere are close. For this reason there are not any indisputable evidences that the ozone increase in the afternoon hours by 2-5 ppb is caused only by local photochemical ozone production.

The absence of ozone diurnal course suggests that main photochemical ozone sources occur in the boundary layer. In that case the long and intensive ozone anomalies at background sites are prefixed to the ozone anomalies at the upper levels of the mountain regions. The photochemical ozone production occurs mainly in the layer below 1.5 km.

All wide-spread ozone episodes observed in North and Central Europe from 1994 occurred in spring and summer with dry, sunny weather conditions in stagnant air, were ozone precursors, such as nitrogen oxides, carbon monoxide and volatile organic compounds, accumulate. The slow-moving high-pressure systems with a pronounced high elevation (1-3 km) inversion and weak winds lead to accumulation of ozone from one day to the next [*National Research Council,* 1992]. On the first/second days of the episodes, the exceedences can be mostly attributed to local/regional photochemical formation, whereas, on the following days, long-range transport plays a major role in the cross-border redistribution of ozone concentrations. [*Tropospheric Ozone in EU,* 1998]. The background ozone lifts to the upper level of the mixed layer. Thus the ozone accumulates there and forms the field of increased concentration as the lifetime of ozone in the free atmosphere is increased. The circulation of the troposphere causes the movement of this field of increased ozone concentrations. For examples, the highest ozone concentrations were recorded at Mt Simone not only in connection with air masses coming from continental Europe and the Po basin boundary layer, but also in air masses coming from the middle troposphere (above 3000 m a.s.l.) [*Cristofanellia P. et al*, 2007]. This fact suggests the presence of ozone-rich atmospheric layers over Europe. This could be due to the large extension of the mixing layer, which favored the transport of high concentrations of ozone and its precursors to altitudes that would usually be in the free troposphere. The photochemical ozone production in the immediate free troposphere contributes insignificantly to the ozone budget in the mountain regions.

This conclusion does not rule out the possibility of intensification of the photochemical ozone production in the free atmosphere in favorable meteorological and chemical conditions as only the question of the mean velocity is being discussed.

Since the 1960s/1970s there was a continuing debate about the role of vertical transport versus local photochemical formation with regard to the annual tropospheric ozone budget. The current consensus view is that in situ chemical production is the major contributor to the observed ozone levels in the ambient tropospheric air. Nevertheless, the contribution of ozone transport down from the free troposphere may not be negligible [*Davies and Schuepbach*, 1994].

Note that winter ozone concentrations in all European mountain regions are similar (Figs 1 and 4). The difference occurs only in spring and summer. This fact demonstrates clearly the important role of the photochemical processes of ozone production in the central and southern Europe in late spring and in summer. At the same time the dynamic processes have a dominant role in winter and in the Northern Europe and the Arctic.

The role of man-made pollution is conveniently illustrated by comparison of measurements in the Caucasus and the Alps. For example, the summer ozone concentrations in the Kislovodsk observatory are less by 10-25 ppb than at the Mount Simone [*Senik et al*, 2005] whereas their altitudes and latitudes are close (2095 and 2165 m asl, 47.3N, 42.7E and 44.3N, 10.7E, respectively). Most likely the difference is caused by less concentrations of an ozone precursor in the Caucasus region in comparison with the Central and East Europe regions. The winter ozone concentrations at the Kislovodsk observatory are close to ones at the Mount Simone (fig.1).

The observed cycles at the Spain mountain stations could be especially difficult to interpret. On the one hand the located in the Pyrenees Mountains at the North of Spain stations show the seasonal course which is similar to the Alps stations. At the same time the spring maximum is detected unexpectedly at the mountain stations located in coastal sites. The reason is that in Southern Europe and the Mediterranean Basin the observed O_3 cycles depend strongly on the topographic location of the observing station. [*Derwent R.G. and Davies T.J*., 1994]. As a result, no single station can be considered representative of regional processes, and much less of the whole situation [*Tropospheric Ozone in EU*, 1998].
In the papers [*Millána M.M et al*, 2004, *Donev E. et al.*, 1995] the important role of local mountain circulation in the ozone variations in the mountain regions was noted also.

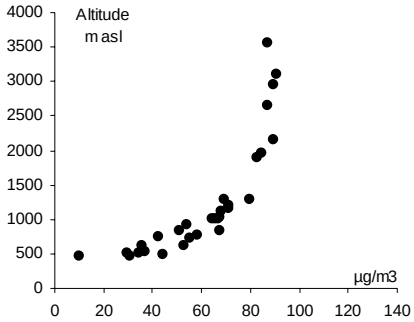

Fig. 4. Vertical distribution of monthly mean ozone concentrations in the Alps (December—January)

Conclusions

The analysis of ozone data from 60 stations located in mountainous sites in the Alps, the Pyrenees, the Carpathians, the Pennines, the Balkans, the Caucasus, the Khibiny and the Scandinavian mountains is present. The selected stations are located at different altitudes between 500 and 3500 m a.s.l.
The analysis shows, that the nature of ozone in northern, central and southern Europe is different. In the northern Europe (the Arctic) the dynamic processes have a dominant role in the tropospheric ozone variations. The photochemical processes in the boundary layer have a pronounced effect on ozone in the Central and Southern Europe and only in later spring and summer.
The diurnal ozone variations in the Alps are feebly defined at altitudes above 1.5-2.0 km. This suggests that the main photochemical ozone sources locate in the layer below 1.5 km. The broad late spring and summer ozone maximum is caused by accumulation of ozone in the free atmosphere 1.5-2 km. In winter the data suggest a fairly uniform ozone distribution in the Europe in the layer above 500 m. The winter ozone concentrations at high- and moderate latitudes are almost similar and depended on altitude.

Acknowledgments. This study was supported by RFBR, grants No 05-05-64271 and No 06-05- 64427

References

Bazhanov V., Rodhe Henning Tropospheric Ozone at the Swedish Mountain Site Åreskutan: Budget and Trends // J. Atmos. Chem.. Vol. 28. 1997. Number 1-3. 61-76

Chevalier A., Gheusi F., Delmas R., C. Ordóňez, C. Sarrat, R. Zbinden, Thouret V., Athier G., and J.-M. Cousin Influence of altitude on ozone levels and variability in the lower troposphere: a ground-based study for western Europe over the period 2001–2004 // Atmos. Chem. Phys. Discuss., 2007. 7. 1327–1356

Cristofanellia P., Bonasonia P., Carbonib G., Calzolaria F., Casarolab L., Zauli Sajanic S. and Santaguidad R. Anomalous high ozone concentrations recorded at a high mountain station in Italy in summer 2003 //Atmos. Environ. Vol. 41. 2007. 7. 1383-1394

Davies, T. D., and Schuepbach, E. Episodes of high ozone concentrations at the Earth's surface resulting from transport down from the upper troposphere/lower stratosphere: a review and case studies // Atmos. Environ., Vol. 28. 1994. 1. 53-68.

Demin V.I., Karpechko A.Yu., Beloglazov M.I., Kyroe У. On the role of turbulent mixing in formation of ground-level ozone concentration in the Kola Peninsula // Atmospheric and Oceanic Optics, Vol 19. 2006. No.5. 400-402 (in Russian)

Derwent R.G. and Davies T.J. Modelling the impact of NOx or hydrocarbon control on photochemical ozone in Europe. // Atmos. Eniron., 28. 1994. 2039-2052.

Donev E.; Zeller K.; Bojinov C. Ozone concentrations at the Bulgarian Govedartsi ecosystem site in early summer of 1994 and 1995 //Proceedings of the international symposium on air pollution and climate change effects on forest ecosystems. Gen. Tech. Rep. PSW-GTR-166. Albany, CA: U.S. Department of Agriculture, Forest Service, Pacific Southwest Research Station. 65-72

Millána M.M., Mantillaa E., Rosa Salvadora R., Carrataláa A., Maria José Sanza M.J., Alonsob L., Gangoitib G., and Navazob M. Ozone Cycles in the Western Mediterranean Basin: Interpretation of Monitoring Data in Complex Coastal Terrain // J. Appl. Met. V. 39. 2004. 487–508

National Research Council, (1992) Rethinking the ozone problem in urban and regional air pollution, National Academy Press, ISBN 0-309-04631-9. 500 p, Washington DC

Senik I.A., Yelansky N.F., Belikov I.V., Lisitsyna L.V., Galaktionov v.V., Kortunova Z.V Main patterns of the temporal variability of surface ozone in the region of the town Kislovodsk at 870 and 2070 m above sea level // Izvestiya. Atmospheric and Ocean Physics. 2005. Vol. 41. 67-79 (in Russian)

Tropospheric Ozone in EU. Topic report No 8/1998- The consolidated report // http://reports.eea.europa.eu/TOP08-98/en

Zanis P., Ganser A., Zellweger C., Henne S., Steinbacher M., and Staehelin J. Seasonal variability of measured ozone production efficiencies in the lower free troposphere of Central Europe // Atmos. Chem. Phys., 2007.7. 223–23

Zaveri R.A.; Saylor R.D.; Peters L.K.; McNider R.; Song A. A model investigation of summertime diurnal ozone behavior in rural mountainous locations //Atmos. Environ., Vol. 29. 9. 1995. 1043-1065