HIGH OZONE EPISODE AT ZAVIŽAN, CROATIA DURING 17–19 JULY 1998

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Abstract: We investigated an unusual elevated-ozone episode that took place at a high altitude measuring site Zavižan (44.817°N, 14.983°E, 1594 m a.s.l.). The episode was characterized by three consecutive peaks. The first one was the highest (over 120 ppbv), and it occurred at the late night on 17 July. Following two (both about 110 ppbv) appeared approximately 18 and 36 hours after the first peak, respectively. The night-time maximum and the departure from the usual diurnal variation of ozone concentration during investigated episode point to the non-local pollution sources, rather than to local photochemical production. Thus, recorded ozone peaks might arise due to the long-range transport of photo-oxidants; 2) stratospheric ozone intrusion; or 3) they might be result of both (1) and (2). In order to inspect which of above processes is responsible for the increased ozone concentrations we applied the unified EMEP model, which among others, simulates atmospheric transport and deposition of photo-oxidants, and, a mesoscale numerical weather prediction model WRF-ARW V2.2. Additionally, the larger scale atmospheric conditions were examined based on the ECMWF ERA-40 reanalysis fields. Results suggest that the stratospheric ozone intrusion played an important role in the occurrence of investigated episode.

Key words: *ozone episode, stratospheric ozone intrusion, long range transport, EMEP model*

1. INTRODUCTION

Tropospheric ozone (O_3) is a secondary pollutant. Thus it is formed from precursors through numerous photochemical reactions. The major anthropogenic precursors are volatile organic compounds (VOC), nitrogen oxides (NO_x) and carbon monoxide (CO) (e.g. Hidy, 2000; Trainer et al., 2000). Far from the local pollution sources, enhanced ozone concentrations may arise due to advection of boundary-layer O_3 or its precursors from polluted areas or due to stratospheric intrusion.

Investigations of ambient ozone in Croatia during a warm part of the year (Cvitaš et al., 2006; Kovač and Cvitaš, 2007; Cvitaš et al., 2007) show that ozone fractions at high-altitude background locations with clear air conditions are higher than those measured at lower altitudes and at urban/suburban locations.

The recent study of Cvitaš et al. (2007) called our attention to an episode of unusually high ozone levels at a mountain site which clearly originated elsewhere, rather in local photochemical production. As pointed out by Chevalier et al. (2007), the site's altitude (1594 m a.s.l.) does not necessary suggest the free-tropospheric ozone regime, since mountains generally affect the airflow for various reasons such as, roughness, synoptical lifting, thermal circulation etc. Thus, they also influence pollutant concentrations (e.g. Klaić et al., 2003; Bešlić et al., 2007).

Here we inspect which of possible mechanisms (namely, long-range transport of ozone and its precursors, or, stratospheric ozone intrusion) is responsible for the above episode. The peculiarity of this event is the occurrence of the multiple smooth peaks, which are untypical for the stratospheric intrusions. Yet, it will be shown that stratospheric ozone played an important role in investigated episode.

2. OZONE EPISODE

Ozone measurements were performed in the vicinity of the highest Croatian meteorological station Zavižan (44.817°N, 14.983°E, 1594 m a.s.l.) (Fig. 1). The data were acquired with a Dasibi 1008 AH instrument based on UV absorption and converted to hourly average volume fractions. (For more details refer to Cvitaš et al., 2007).

As of the night of 15/16 July, ozone volume fraction at the measuring site started to rise from about 55 ppb (at 00 LST 16 July) to about 122 ppb (at 02 LST on 18 July). This first peak was followed by a fall down to about 80 ppb (12 LST, 18 July) and another two prominent peaks: one of about 124 ppb (18 LST, 18 July) and the other of about 115 ppb (at 12 LST on 19 July). After the third maximum, the volume fraction gradually decreased. Thus, during the second part of 20 July, hourly volume fractions again attained usual values. The above pattern differs from a typical diurnal variation of a photo-smog episode, since the time difference between the two consecutive peaks is less than 24 hours. On the other hand, peaks also differ from the typical patterns of stratospheric intrusions, which are generally sharp. Here, all three peaks are much smoother - i.e. ozone volume fractions remain extremely high for several consecutive hours.

Figure 1. The measuring site at Zavižan: as seen from a distance (left) and a closer view (right). (Source: Meteorological and Hydrological Service of Croatia.)

3. SYNOPTIC CONDITIONS

Upper-level diagnostic charts of European Meteorological Bulletin and European Centre for Medium-Range Weather Forecasts (ECMWF) 40 Years Re – Analysis (ERA-40) database for the period 15 – 20 July 1998 (not shown here) exhibit synoptic features favourable for the occurrence of the tropopause fold, and consequent, stratosphere-troposphere exchange processes. Specifically, as of 16 July, a jet-stream is found at 300 hPa isobaric surfaces over the Atlantic south of the Island, whit a wide exit, diffluent region spreading over the central parts of Europe. In time, the jet-stream strengthens and moves eastward.

Simultaneously, geopotential fields at 700 and 850 hPa surfaces suggest western/north-western airflow over the Western Europe. Thus, prior to the arrival to greater Zavižan area, the lower-tropospheric air passed over the France, southern and central Germany and/or northern Italy. Such advection lasted until 20 July when synoptic conditions changed and the lower-tropospheric airflow turned to south-western.

4. MODELS

The EMEP model

The Unified EMEP model simulates atmospheric transport and deposition of acidifying and eutrophying compounds (sulphur and nitrogen), as well as photo-oxidants and particulate matter over Europe (Simpson et al, 2003; Tarrasón et al., 2003). The model domain covers Europe and the Atlantic Ocean with the grid size 50×50 km^2 while in the vertical there are a 20 terrain following layers reaching up to 100 hPa. The model uses 3-hourly meteorological input from a numerical weather prediction model. Currently, a considerable effort is expended in downscaling of the EMEP modelling system to national scales. Thus, there are two such ongoing joint projects: one for the UK domain (EMEP4UK, Tarrasón, personal communication, 6-7 November 2006), and the other for Croatia (EMEP4HR, Jeričević et al., 2007).

Here we applied two model versions. First one is the standard EMEP model with vertical diffusion coefficient given by O'Brien (1970). Additionally, in the modified version we employed linear exponential function for $K(z)$ (Grisogono and Oerlemans, 2002).

The WRF model

Mesoscale atmospheric conditions were simulated by the Eulerian nonhydrostatic Weather Research and Forecasting (WRF) modelling system – Advanced Research WRF (ARW) (Skamarock et al., 2007) version 2.2. The equations are formulated using a terrain-following hydrostatic-pressure vertical coordinate (Laprise, 1992), where the top of the model is set at a constant pressure surface. Until now, the model has been used in a variety of areas including storm prediction and research, air-quality modelling, wildfire, hurricane, tropical storm prediction and regional climate and weather prediction.

In the present study three domains, namely 2160 x 2160 km^2, 900 x 900 km^2 and 300 x 300 km^2 where selected with a two-way nesting option. Corresponding horizontal resolutions and integration time steps were 27 km, 9 km and 3 km, and 108 s, 36 s and 12 s, respectively. The model top was set to 50 hPa. Vertically, 75 layers were employed with an uneven spacing which gradually enlarged from the bottom to the top of the domain. Simulation covered a time interval from 15 July 1998 at 00 UTC to 20 July 1998 at 12 UTC.

5. RESULTS AND DISCUSSION

Results obtained by the EMEP model suggest the transport of ozone and/or its precursors from Western Europe, particularly from France, Germany and northern Italy (Fig. 2, right). The same is also in accordance with diagnostic synoptic charts for lower troposphere. However, since during 17 – 19 July the measured ozone volume fractions (Section 2) were at least twice as the modelled (Fig. 2, left), it is obvious that substantial portion of ozone should originate from reasons other than the long-range and regional transport of boundary-layer pollutants.

Moreover, results obtained by WRF model corroborate the occurrence of the deep stratospheric intrusion which is always accompanied with potential vorticity anomalies (Fig. 3) and sinking motions (not shown here). Thus, we may conclude that elevated ozone levels arose due to both boundary-layer pollutant transport and ozone of stratospheric origin.

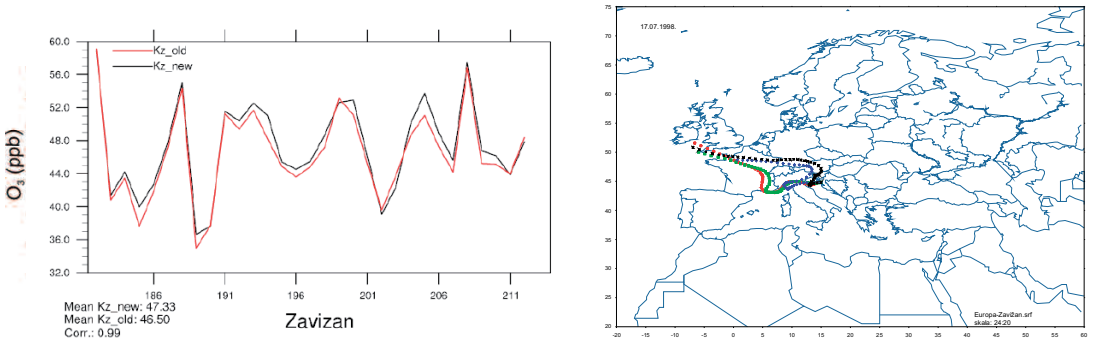

Figure 2. EMEP model results. Left: Standard (red) and modified (black) daily mean ozone volume fractions for Zavižan for July 1998. Right: 4-day backward 925 hPa trajectories arriving at Zavižan on 17 July 1998, at 00 (black), 06 (blue), 12 (green) and 18 (red) UTC. Parcel positions are given for every 2nd hour.

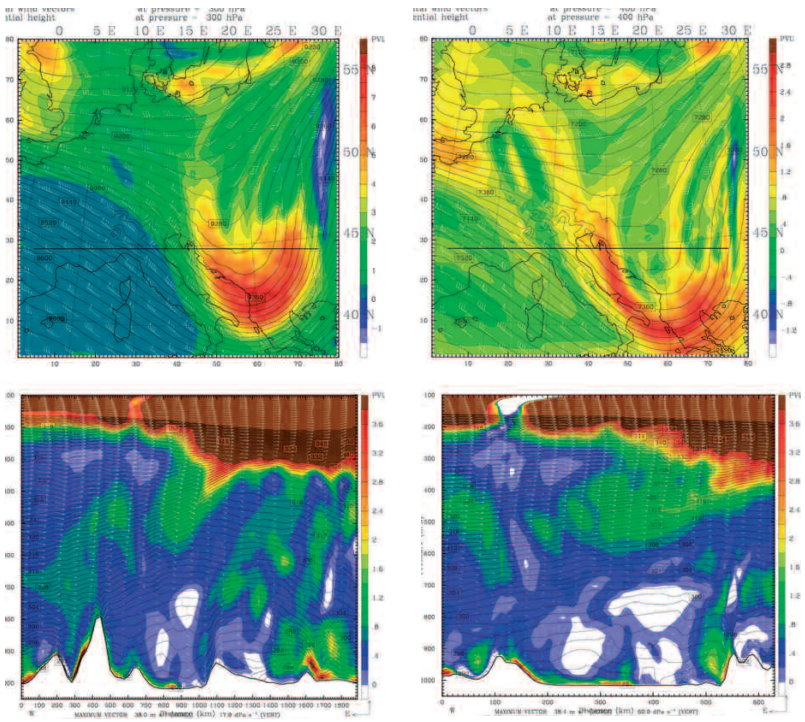

Figure 3. WRF model results for 16 July 1998 at 06 UTC. Top: potential vorticity (PVU, colour scale), horizontal wind (white barbs) and geopotential height (gpm, black lines) at 300 (left) and 400 hPa (right) isobaric surfaces for the largest domain. Thick black line shows the base of the W-E vertical cross-section through Zavižan. Bottom: vertical cross-sections of potential vorticity (PVU, colour scale), wind component in *xz* plane (white vectors) and potential temperature (K, black lines) for the largest and medium domains (left and right panels, respectively). Position of Zavižan is at *x* = 1107 km (left) and x = 558 km (right).

6. SUMMARY AND CONCLUSION

An unusual high-ozone summertime episode characterized by multiple smooth peaks was observed at the high-altitude measuring site far from pollution sources. The episode was analyzed by two models with different scopes, namely mesoscale numerical weather prediction (WRF) and the long-range transport of pollutants (EMEP) model. Results suggest that the episode was caused by both, the deep stratospheric ozone intrusion and the transport of boundary layer polluted air from France, southern Germany and northern Italy.

In future work, the possible role of the thermally induced up- and down-slope circulation in the episode pattern (e.g. Klaić et al., 2003) should be investigated.

Finally, the employment of two different vertical diffusion schemes in the EMEP model, one of O'Brien (1970) and the other of Grisogono and Oerlemans (2002), resulted in similar modelled ozone volume fractions.

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