

Ozone Measurement on mount Srd near Dubrovnik, Croatia

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Results and analysis of ozone monitoring at station Srd (46.25° N, 17.45° E, 412 m a.s.l.) near Dubrovnik from 1998 – 2005 are reported. It is confirmed that this is an unpolluted place despite of high summer solar radiation which could contribute to the photochemical air pollution formation. There is no significant trend in ozone levels found during this time and the overall average ozone fraction is found to be 46 ppb for the summer periods.

Keywords: ozone measurements, photochemical air pollution, Dubrovnik

1. Introduction

The oxidation capacity of boundary layers of the Earth atmosphere is increasing over the past hundred years (Volz and Kley, 1988; Lisac and Grubišić 1991; Cvitaš et al., 2005) and there is no way to slow it down in the near future. Photochemical pollution (beside the greenhouse effect and particle (aerosol) pollution) is one of the greatest atmospheric environmental problems today.

It is well known that anthropogenic activities through fossil fuel combustion (and consequent emissions of NO₂ and VOC (volatile organic compounds)) are changing the microconstituent content of the atmosphere causing side effects (Crutzen, 1998).

Photochemical pollution is highly dependent on regional characteristics although it also depends on long distance transport of pollutants and their precursors. The state of pollution and its effect on the environment is much better investigated in central and western Europe than in Croatia where such investigations are needed due to different climate and emission conditions.

At the Ruder Bošković Institute we have 30 years of experience in monitoring and investigation of air quality (predominantly of photochemical origin) in Croatia and abroad. Our team participated in the EUREKA environmental project EUROTRAC (environmental project on the transport and chemical

transformation of pollutants in the troposphere over Europe) on tropospheric ozone research (subproject TOR and TOR-2) from 1988 till 2002 (Cvitaš and Kley, 1994).

Within this project the measurements at Srđ started in the summer of 1998 and represent the first investigation of this type for the southern Adriatic region in Croatia.

2. Experimental

Monitoring equipment has been placed inside a van located near the summit of mount Srđ (Fig. 1a) (46.25° N, 17.45° E) above Dubrovnik from 1998 – 2005. Mount Srđ rises steeply to a height of 412 m a.s.l. On its top there is a ruin of an impressive 19th century Austrian military fortress, part of which was renovated into a TV-transmitter facility accompanied with a 150 m high antenna tower. The fortress and studio buildings with a height of approximately 10 m and length of 200 m effectively screen the plateau behind from every direct effect from the city of Dubrovnik on the southern foothills of the mountain (Fig. 1b and c).

The monitoring site was chosen to be at the plateau to measure preferably the remote and long range atmospheric characteristics. Actually, the distribution of wind directions measured there exclusively corresponds to the directions parallel with the mentioned buildings (Fig.3). The only exception was 2005 when the ozone monitor was placed within the studio building (Fig 1b and c) with the aim of sample collection oriented toward the city.

Ozone has been monitored with a commercial instrument DASIBI 1008AH based on UV absorption photometry which has been regularly checked and calibrated. Wind speed and direction was measured with an AMES KVT-60A anemometer.

3. Results and discussion

After careful check and selection of data, coverage for the whole period of measurement is very low mainly due to frequent instrumental malfunction. The best consecutive data coverage is obtained for the months of June. This is also the most interesting time for a year-to-year comparison because of intense solar irradiation, the main prerequisite for photochemical pollution.

Obtained ozone data are summarized in Table 1.

Local wind direction measurements which have been performed during the years 1998 and 1999 (wind rose is shown on Fig. 2) confirm the hypothesis that the buildings (Fig. 1) effectively screen the plateau behind from direct influence from the city. Wind measurements were discontinued after they had been found not to represent the state within broader area. The mentioned displacement of the instruments in 2005 to the nearby studio building on the



a)



b)



c)

Figure 1. a) View of the monitoring van situated on the summit plateau of Mount Srd from 1998 to 2004. (open to the air from the countryside to the North-East), b) view from the studio buildings where the instruments were placed in 2005 (open to the air from the sea side) and c) satellite picture of Dubrovnik showing the monitoring site with respect to the city.

top of the hill aimed to see such influence did not result in any significant increase of measured ozone concentration and its diurnal variation. Namely, it was expected that data from the new location may be affected by the city of

Table 1. Data coverage during the period of measurements, yearly and June mean values, pollution index (daily max/min ratio)⁶ and the number of hours exceeding the hourly average of 80 ppb (AOT80 values).

Year	Data coverage %	June data coverage %	Mean ozone volume fraction/ppb	June mean ozone volume fraction/ppb	June index max/min	AOT80 value
1998	8.6	0	34.1	–	–	0
1999	28.5	40.3	48.3	48.1	1.62	0
2000	45.1	59.2	48.9	57.8	1.37	47
2001	48.0	59.9	36.9	39.5	1.47	0
2002	36.0	44.3	28.1	48.2	1.43	0
2003	–	–	–	–	–	–
2004	35.0	21.9	39.5	49.4	1.47	0
2005	25.0	74.9	40.0	39.3	1.77	0

Dubrovnik and the busy Adriatic coastal road which passes below along the slopes of Srđ from Dubrovnik towards the airport and further to the south.

Consequently we can conclude that the city of Dubrovnik and the road below do not substantially contribute to photochemical air pollution at the Srđ plateau. This is interesting in view of the planned sport activities there (e.g. golf).

The maximum to minimum of the diurnal ozone concentrations ratios (Table 1, column 6), which were previously used for characterizing monitoring sites (Cvitaš et al., 1995), are used to assess the level of photochemical pollution. High values are representative for sites with significant local photochemical production as well as for ozone consumption. Index values below 2

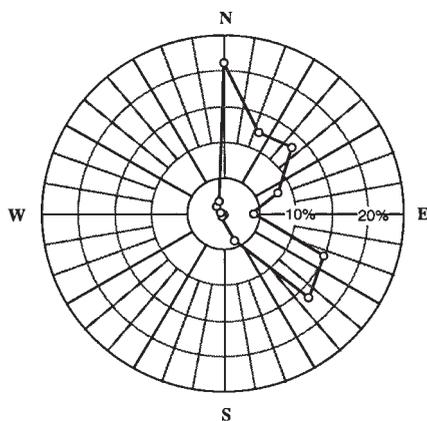


Figure 2. Wind rose for 1998 and 1999 at Srđ station.

which were found at Srđ for June are a reliable indication that this is a relatively clean area with negligible local photochemical production. Photochemical episodes exceeding the air quality standard for ozone given by an hourly average of 80 ppb are scarce as indicated by the sum of hourly volume fractions in excess of 80 ppb the so called accumulated ozone time (AOT80) (Wayne, 2000) in Table 1, column 7.

The average diurnal variation of ozone volume fractions depicted as a box and whiskers plot for Junes 1999 – 2005 is given in Figure 3. The diurnal behaviour is typical for an elevated site such as Mount Immitos above Athens (Cvitaš et al., 1988) or Puntijarka above Zagreb (Cvitaš et al., 1997). Mount Srđ is of about half the altitude of Mt Immitos and Medvednica (Puntijarka). The city of Dubrovnik has less than a tenth of the population of Athens and Zagreb and no industry.

It is interesting to note that the scattering of values around the median (Fig. 3) during night-time is greater than that during day-time. This indicates that the ozone at the monitoring site is not produced locally, but that its origin can be attributed to a displaced source requiring the air some 8 hours to reach Mt Srđ. Taking the average wind speed this would amount to 180 km.

Average summer (May to September, 1998 – 2005) ozone concentration at Srđ was 46 ppb which is lower than published summer values at around 50

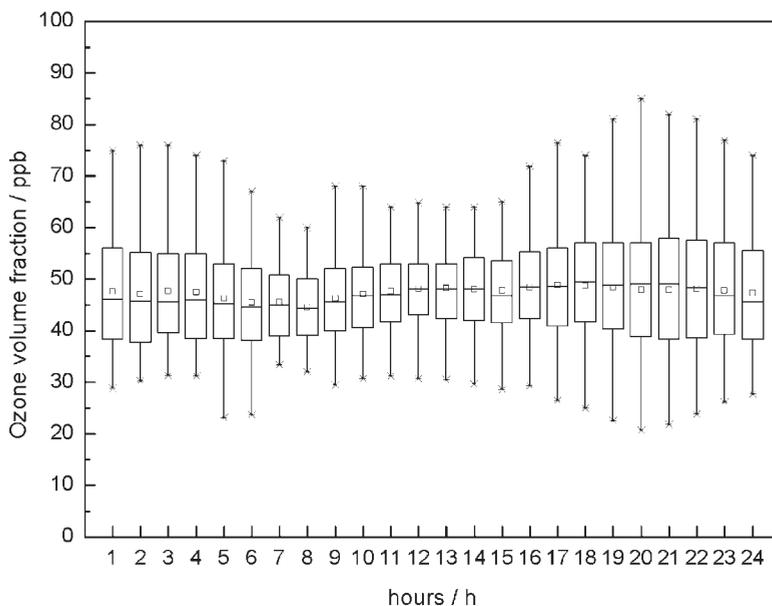


Figure 3. Box and whiskers plot of ozone volume fraction for the measurements in Junes from 1999 to 2005. The line denotes the median, small square the mean, the box edges the 1st and 3rd quartile, and the bars the 10th and 90th percentile.

ppb for Croatia elevated sites Puntijarka and Zavižan (Cvitaš et al., 1997; Scheel et al., 1997) and similar to that found on the island of Lošinj at Mali Lošinj 44 ppb.

The period of ozone measurements from 1998 to 2005 was too short for a statistical long-term trend analysis. The data for the June averages are listed in Table 1 and do not show any noticeable trend over the 8 years.

4. Conclusions

Ozone measurements at the location Srđ, near Dubrovnik show that this region is substantially free of photochemical pollution episodes in spite of intense solar radiation during the summer months. Ozone concentration values are comparable with other Croatian coastal locations and somewhat lower than found at two elevated Croatian locations Puntijarka and Zavižan.

References

- Crutzen, J. P. (1998): How the Atmosphere keeps itself clean and how this is affected by human activities, *Pure Appl. Chem.*, **70**, 1319–1326.
- Cvitaš, T., Kezele, N., Klasinc, L. and Lisac, I. (1995): Ozone Measurements in Croatia. *Pure Appl. Chem.*, **67**, 1450–1453.
- Cvitaš, T., Kezele, N. and Klasinc, L. (1997): Boundary Layer Ozone in Croatia, *J. Atmos. Chem.*, **28**, 125–134.
- Cvitaš, T., Kezele, N., Klasinc, L., McGlynn, S. P. and Pryor, W. A. (2005): New Directions: How dangerous is ozone?, *Atmos. Environ.*, **39**, 4607–4608.
- Cvitaš, T. and Kley, D., eds. (1994): *The TOR network. A description of TOR measurement stations*, Garmisch-Partenkirchen, EUROTRAC.
- Güsten, H., Heinrich, G., Cvitaš, T., Klasinc, L., Ruščić, B., Lalas, P. D. and Petrakis, M. (1988): Photochemical formation and transport of ozone in Athens, Greece, *Atmos. Environ.*, **22**, 1855–1861.
- Lisac, I. and Grubisic, V. (1991): An analysis of surface ozone data measured at the end of the 19th-century in Zagreb, Yugoslavia, *Atmos. Environ. A*, **25**, 481–486.
- Scheel, H. E., Areskoug, H., Geiss, H., Gomišček, B., Granby, K., Haszpra, L., Klasinc, L., Kley, D., Laurila, T., Lindskog, A., Roemer, M., Schmitt, R., Simmonds, P., Solberg, S. and Toupance, G. (1997): On the Spatial Distribution and Seasonal Variation of Lower-Troposphere Ozone over Europe, *J. Atmos. Chem.*, **28**, 1–3, 11–28
- Volz, A. and Kley, D. (1988): Ozone Measurements in the 19th Century: An Evaluation of the Montsouris Series, *Nature*, **332**, 240–242.
- Wayne, R. P. (2000): *Chemistry of the atmospheres*, 3rd edn., Oxford University Press, Oxford, pp. 422–439.

SAŽETAK

Mjerenja ozona na brdu Srđ blizu Dubrovnika, Hrvatska

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Prikazani su rezultati i analiza mjerenja ozona na postaji Srđ (46.25° N, 17.45° E, 412 m a.s.l.) blizu Dubrovnika u razdoblju od 1998 do 2005. Potvrđen je neonečišćeni karakter ove lokacije unatoč jakom Sunčevom zračenju ljeti. Mjerenja nisu dala naznake trenda u koncentracijama ozona, a prosječna vrijednost udjela ozona u ljetnom periodu je bila 46 ppb.

Ključne riječi: mjerenja ozona, fotokemijsko onečišćenje zraka, Dubrovnik

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