

Ozone measurements at the mountain station Zavižan (Croatia) for 1997–2000

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Analysis of ozone concentrations measured at Zavižan, Croatia's highest altitude meteorological station (1594 m a.s.l.), during the spring and summer months of 1997–2000 shows that the actual new Croatian Air Quality standards are severely exceeded. Implication of this and similar findings from other elevated sites call for additional consideration of ozone behaviour at high altitudes in defining ozone standards.

Keywords: ozone, air quality standards, tropospheric ozone

1. Introduction

Ozone measurements from Croatia's highest altitude mountain lodge (built in 1927 and rebuilt in 1952) and meteorological station (founded in 1953) at Zavižan (44.817°N, 14.983°E, 1594 m a.s.l.) for 1997–2000 are reported and analyzed. The weather at Zavižan (Figure 1) is very harsh due to prolonged winter conditions and heavy storms which often cause malfunction and breakdown of sensitive electronic instrumentation. The station is regularly inaccessible via road between October and May. Results of ozone measurements and research within the EUROTRAC and EUROTRAC–2 projects, subprojects TOR (Tropospheric Ozone Research) 1988–1996 and TOR2 from 1998–2002 using a network of stations over Europe showed that the measured ozone data greatly depend both on season and location (Audiffren et al., 2003; Klasinc, 1994). In particular spring-time and high-altitude results proved to be highly interesting. Ozone is a secondary pollutant, i.e. it is not emitted directly into the atmosphere from a source, but is formed from precursors via numerous reactions induced by solar radiation. Thus, for the concern of rising ozone concentrations during the 20th century recent research showed that the cure is not as simple and easy achievable just by reducing some anthropogenic emission to the atmosphere. Actually, it seems that at the moment we have no measures to prevent the rise of ambient ozone concentrations during this century either.

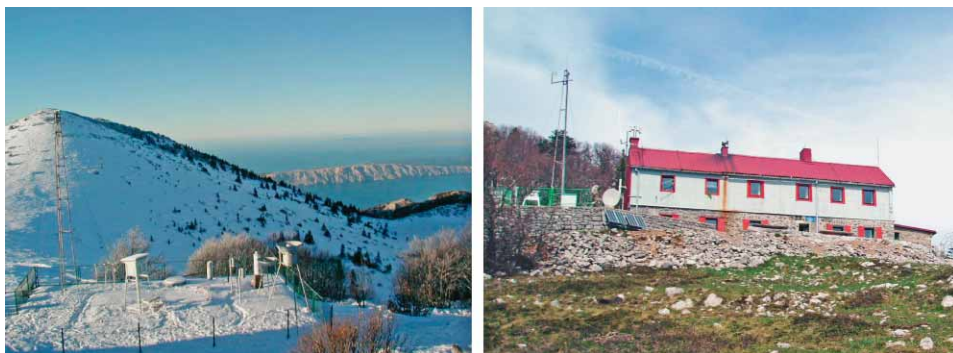


Figure 1. The meteorological station at Zavižan in winter looking westward (left, from www.crometeo.hr) and spring (right).

In October 2006 the Clean Air Scientific Advisory Committee of the American Environmental Protection Agency (EPA) wrote (C&N News, 2006) that there is no justification for retaining the current air quality standard at 0.08 ppm (8-hour average) because adverse health effects can be expected during longer exposures at significantly lower ozone volume fractions as documented by numerous scientific literature. However, the experience from thousands of ozone monitoring stations in the USA indicates that a simple reduction from 0.080 to 0.060 ppm without a careful analysis of how often and why such limits are exceeded would be overhasty. Therefore, the search for an optimal solution for the future standard has been prolonged until March 2008 (C&N News, 2007). One of the irritating monitoring results is that high altitude locations with, by all means, clean air conditions may exhibit rather, even hazardously high ozone fractions, probably caused by intrusions from the stratosphere but also by long-range transport from polluted areas. Namely, once all 'ozone-consuming' constituents are removed from an air package its ozone fraction becomes stable or even rises. Results from Zavižan, a station not included in the TOR network (Cvitaš and Kley, 1994), attracted our interest after we had found that ozone monitoring data at stations Puntijarka north of Zagreb at 980 m and Krvavec in Slovenia at 1700 m above sea level have significantly higher average values than those at lower altitudes (Cvitaš et al., 2006) during summer. At that time Zavižan was one of the EMEP high-altitude stations (Kovač et al., 2003) not yet equipped with ozone monitoring instruments and it became interesting to see whether the first ozone monitoring results would confirm the typical behaviour observed at other high-altitude stations.

2. Results and discussion

Ozone was monitored at Zavižan during four years 1997 through 2000 mainly during the growth season (1 April to 30 September). The data have been acquired with a Dasibi 1008 AH instrument based on UV absorption and

Table 1. Ozone measurement periods at Zavižan from 1997 to 2000 and corresponding violations of the Croatian Air Quality standards.

Year	Monitoring period / total time (data coverage) ^a	No. of days (No. of hours) with $\bar{\varphi}_{8h} > 60$ ppb	No. of days with $\bar{\varphi}_d > 55$ ppb
1997	11 Jun. – 25 Aug. / 1801 h (98.7 %)	61 (1148)	66
1998	9 Jul – 2 Aug / 586 h (97.7 %)	13 (202)	12
	13 Aug. – 8 Oct. / 1287 h (94.1 %)		
1999	15 Mar. – 8 Apr. / 533 h (92.5 %)	7 (84)	7
2000	16 Feb – 9 Apr. / 1113 h (85.9 %)	27 (193)	23
	5 May – 8 Jun. / 813 h (96.8 %)		
	29 Jul. – 22 Aug. / 595 h (99.2 %)		

^a total time refers to the number of validated hourly average values; data coverage refers to the percentage in which the total time covers the monitoring period.

^b a maximum of 25 days allowed with 8-hour average volume fractions $\bar{\varphi}_{8h} > 60$ ppb.

^c a maximum of 7 days allowed with daily average volume fractions $\bar{\varphi}_d > 55$ ppb.

converted to hourly average volume fractions prior to analysis. The instrument was regularly calibrated against the Dasibi 1008 PC model, or the Environics Series 100 model. The periods of time for which ozone data were collected, the number of validated hourly average ozone data collected (total time) with the percentage of the total hours covered within the monitoring period (data coverage), the number of 8-hour running averages during the period that exceeded 60 ppb and the number of days when this limit was exceeded and finally the number of days when the daily average ozone fraction exceeded 55 ppb are given in Table 1. Both values represent the limits defined by the Croatian air quality directive (Vlada RH, 2005): 60 ppb represents the tolerated limit for an 8-hour moving average, which should not be exceeded on more than 25 days in a year, and 55 ppb represents the daily average which should not be exceeded on more than 7 days in a year. Owing to difficult weather conditions and insufficient support the data coverage for the whole seasons April through September (183 days) is rather poor amounting to 41, 44, 4, and 37% for the years 1997 to 2000, respectively. Ignoring the data for 1999 due to insufficient coverage, the measured ambient air ozone fractions were found to be significantly higher than at low altitudes (below 500 m). The observed behaviour was found to be similar to that at other high altitude stations Kravac (1700 m) (Gomišček, 1994) and Puntijarka (980 m) (Klasinc, 1994; Scheel et al., 1997), but not at the lower altitude mount Srđ (420 m) near Dubrovnik

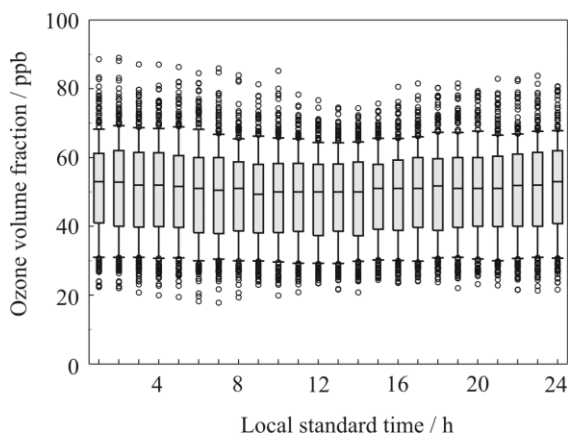


Figure 2. A box and whiskers plot of the Zavřizan ozone data for the period 1997–2000 (excluding the days 17 to 19 July 1998).

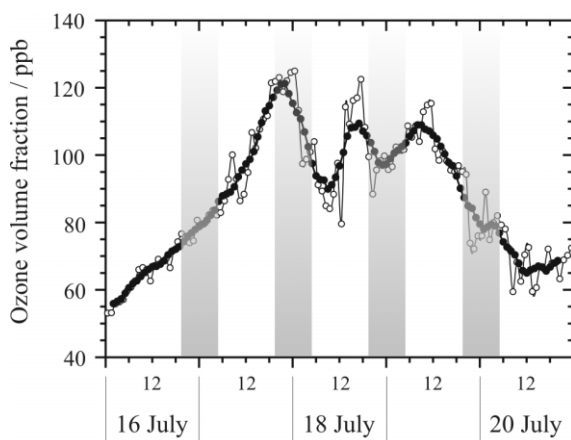


Figure 3. Hourly average (black circles) and 8-hour moving average (white circles) ozone volume fractions at Zavřizan for the 5-day period of 16 to 20 July 1998 showing the high-ozone episode from 17 to 19 July 1998. The grey bars denote night-time.

(Cvitař et al., 2006). The main difference in behaviour is seen in the diurnal variation of ozone fractions: in urban and suburban sites, but also in rural sites, the diurnal variation is prominent, roughly following the variation of sunlight, whereas at elevated sites it is hardly noticeable, ozone fractions being almost constant throughout the day.

The hourly ozone data for all days (except those for 17 to 19 July 1998) are presented as a box and whiskers plot in Figure 2. The central line represents the median, the box height covers the 25th to 75th percentile range, the

whiskers the 10th to 90th percentile and all the remaining hourly values are shown as circles. It is indicative that there is actually a minimum of ozone levels close to noontime whereas maximum values appeared at times without sunlight – both indicating that ozone at the Zavižan site is not produced locally, but rather due to transport of its precursors and ozone itself.

During the days 17 to 19 July 1998 a high-ozone episode took place at Zavižan. It started from low (below 60 ppb) values in the night of 15/16 July steadily rising all day on 16 July right to late night on 17 July reaching values of over 120 ppb followed by a fall and subsequent rise on 18 and again on 19 July as shown in Figure 3. The three maxima resemble a typical diurnal variation during a photo-smog episode, however the time difference is 18 and less hours rather than 24. After the three atypical days the ozone fractions kept steadily falling from noon on 19 July to return to »normal« approximately constant values of 60 ppb on 20 July. The night-time maximum and off-diurnal variation indicate clearly that the high values are not the result of local photochemical

Table 2. Wind direction and force on the Beaufort scale for 4 days in July 1998.

Hour	16 July 1998		17 July 1998		18 July 1998		19 July 1998	
	Direction	Force*	Direction	Force*	Direction	Force*	Direction	Force
4	E	5	WNW	2	C	0	S	1
5	E	5	C	0	C	0	SW	2
6	E	5	NW	1	C	0	WSW	1
7	E	5	C	0	C	0	WSW	1
8	E	5	C	0	C	0	C	0
9	E	5	C	0	C	0	S	2
10	E	3	C	0	C	0	WSW	1
11	E	2	WNW	1	W	1	WSW	1
12	E	2	C	0	W	1	WSW	2
13	SSE	2	WNW	1	W	1	WSW	2
14	C	0	WNW	1	W	1	WSW	1
15	C	0	WNW	1	W	1	WSW	1
16	C	0	WNW	1	W	1	WSW	2
17	C	0	C	0	C	0	WSW	2
18	C	0	C	0	C	0	WSW	1
19	W	1	C	0	SW	1	C	0
20	W	1	C	0	SW	1	C	0
21	W	1	C	0	C	0	C	0

* in accordance with the Beaufort scale (0–12)

production, but rather of transport. Unfortunately, there are no continuous data on wind speed and direction, for the time of monitoring: only 18 observations per day at every hour from 4:00 to 21:00 hours in terms of 16 wind directions and Beaufort wind force scale (0 – 12) as given in Table 2. Thus, no detailed correlation of ozone fractions and wind data could be made.

On the other hand, we learned from earlier meteorological analyses (J. Miller, WMO, personal communication) that out of 732 clustered back-trajectories arriving at Zavižan at 1600 m in 1988, 65% came from the NW originating at north Greenland (11%), eastern Canada (17%), western Canada (7%) and south Greenland (30%). However, 20% of air masses did come slowly from the west *i.e.* across the Adriatic from Northern Italy and southern to western France, and only 15% even slower from SE Europe (Romania and Bulgaria). Thus, it is safe to say that most air masses arrive at Zavižan from NW. It follows from the hourly observations of wind direction and wind force mentioned above (Table 2) that the excessive-ozone episode took place during nearly calm (C) to light breeze conditions from WNW, W and WSW on July 17, 18 and 19, respectively. The unusually high levels of ozone measured at Zavižan far from any source of ozone precursors indicate clearly that the ozone is not produced locally. The maximum observed on 17 July close to midnight also proves that its origin has to be found elsewhere rather than in photochemical production. It must obviously involve transport of ozone itself and of its precursors.

The simplest explanation would be to attribute the high values to vertical transport *via* stratospheric intrusions. Indeed, such effects have been well known, especially at high altitudes. Occasionally stratospheric ozone was found to reach even ground level (Lisac et al., 1993; Klaić et al., 2003). However, such events are characterized by a sudden steep rise of ozone fractions well above 100 ppb and a subsequent drop to relatively normal conditions. The characteristic conditions favouring intrusions can be seen in synoptic charts. However, without having the necessary meteorological data, we can only conclude that the observed behaviour with clearly pronounced maxima on three consecutive days makes the stratospheric intrusion an unlikely cause. The appearance of maxima hints to a photochemical production, yet the time of day corresponding to the maxima shows that the production must have occurred at some distance from the monitoring site. The wind data for the three days 17, 18 and 19 July indicate that the wind was predominantly very weak and mainly from a westerly direction. Hence the photochemical production of ozone must have taken place over the Adriatic region after the relatively strong wind from the east had ceased on 16 July. The question on where did the precursors of ozone come from remains open and a detailed analysis of the motion of air masses in the region is needed.

The recently proposed air quality standards for ozone (Vlada RH, 2005) are based on relatively long-term averages such as daily averages or eight-hour averages as opposed to the old standards which were based on one- or

even half-hour average volume fractions or mass concentrations. Such a change is immediately reflected in the treatment of high and low altitude measurements. In polluted areas where ozone gets completely depleted during evening and night-time hours the long-term averages are usually lower than in mountainous regions. Indeed, by applying the new air quality standard to mountain stations an unexpected result is obtained: the eight-hour average exceeded the 60 ppb limit for 61 days out of 76 in 1997, 13 out of 80 in 1998 and 27 out of 67 in 2000. By scaling the numbers up to 183 monitoring days of the season representing full coverage the number of violations of standards would be 147 for 1997, 30 for 1998 and 74 for 2000 where the air quality standard requires less than 25 during the whole year. The message we are getting is obviously to avoid mountain air and to stay at low altitudes, preferably within cities, if we fear ozone induced damages to our health. The daily averages give an even worse picture. The value of 55 ppb was exceeded for 66 days out of 76 in 1997, 12 days out of 80 in 1998 and 23 days out of 67 in 2000 when only a maximum of 7 days are allowed in the whole year according to the directive (Vlada RH, 2005). Even in the short period of less than a month in 1999 for which we have data (15 March to 8 April) the daily average of 55 ppb was exceeded on 7 days.

3. Conclusion

The results of ambient ozone monitoring at the high altitude station Zavižan during the April to September season in the years 1997 to 2000 show that, in spite of poor data coverage, average ozone volume fractions are relatively high, that little diurnal variation is observed and that sometimes excessive-ozone episodes can be expected.

The recent Croatian air quality directive, most probably based on low altitude urban air data, is frequently violated. This obviously calls for reconsideration of the standard, or for restricting its validity to low altitude conditions.

Midday ozone peak volume fractions get destroyed in evening traffic-exhaust gases leading to lower average values. Modern instruments record ozone fractions sensitively and selectively, but products of ozone destruction are likely to represent at least as much a health hazard as ozone itself. The standards based solely on ozone cannot be expected to faithfully represent the air quality at high altitudes with hardly any primary pollutants as well as that in urban sites where many ozone decomposition products escaping monitoring also affect human well being.

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SAŽETAK

Mjerenja ozona na planinskoj postaji Zavižan (Hrvatska) tijekom 1997. – 2000.

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Analiza podataka o volumnom udjelu ozona na Zavižanu, najvišoj meteorološkoj postaji u Hrvatskoj (1594 m iznad mora) tijekom proljeća i ljeta 1997. do 2000. godine pokazuje da vrijednosti znatno prelaze granične vrijednosti za kvalitetu zraka važeće nove hrvatske Uredbe o ozonu. Dobiveni rezultati i mjerenja s drugih visinskih postaja ukazuju da potrebu razmatranja uvjeta i na visinskim postajama pri definiranju graničnih vrijednosti za kvalitetu zraka s obzirom na ozon.

Ključne riječi: ozon, norme za kvalitetu zraka, troposferski ozon

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