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AIR QUALITY MONITORING AT Mt. KRVAVEC: AEROSOL BLACK CARBON AND OZONE

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Abstract. We report on one-year continuous measurements of aerosol black carbon (BC) at the EMEP/GAW regional air quality station on Mt. Krvavec in Slovenia, where ozone concentration has been monitored routinely since 1991. The results show several characteristic BC and O_3 concentration patterns. At times we observe a negative correlation: high BC and low ozone can be attributed to the mixing of fresh polluted air up to the temperature inversion layer or to the local pollution sources, while low BC and high ozone can be due to down-welling from the free troposphere. At other times we observe a positive correlation between these two species, as a result of the transport of polluted air from regional sources, in the absence of strong temperature inversions.

INTRODUCTION

Ecosystems in the Alps are affected by the elevated ozone concentrations, often detected especially in the summer season. The data from ozone monitoring in southeastern part of the Alps are in general agreement with the results obtained at other Alpine measuring sites [1]. It was also found that upper troposphere ozone levels has increased in the Northern Hemisphere which could also contribute to the global warming [2]. BC as main constituent of soot and well known tracer of anthropogenic activity is also of increasing interest for atmospheric science community due to its physical and chemical

characteristics and influences on the environment [3]. BC is usually emitted as a unimodal aerosol with mass size distributions peaking at modal diameters about 0.1 µm aerodynamic equivalent diameter, while in the course of dynamic processes it can also be found in the upper submicron size range [4]. It is known that under certain conditions, the presence of soot particles can affect the ozone and NO_x concentrations due to heterogeneous destruction of ozone molecules on particles [5,6]. Our recent investigations of vertical profiles of air pollution have shown that BC concentrations are decreasing with the increasing height. Above the Ljubljana basin at the height of about 2000 m a.s.l. the BC concentration found was about 50-200 ng m^{-3} while at ground level (300 m a.s.l.) it was up to two orders of magnitude higher [7].

The main reason for studying the temporal behavior of ozone and BC concentrations at the Mt. Krvavec is the lack of such measurements at elevated sites in Central Europe. In the present work we report on the concentration patterns of BC and ozone at the Mt. Krvavec air quality measuring station. Some interesting short episodes were selected and analyzed in detail.

EXPERIMENTAL

Sampling site description

Continuous measurements of BC and ozone were performed at EMEP (The Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe)/WMO-GAW (Word Meteorological Organization - Global Atmospheric Watch) regional air quality monitoring station Mt. Krvavec managed by the Hydrometeorological Institute of Slovenia (HIS). The site is situated about 30 km north of Ljubljana at an elevation of 1740 m a.s.l. on the ridge of the south-eastern Alps close to the tree line where grassland already prevails. Beside the capital of Slovenia with population of about 300,000, some small and mostly scattered emission sources like smaller towns, several villages and main traffic lines are situated in the basin, which may impact on the air quality at the Mt. Krvavec site. Perhaps most important in this aspect are meteorological phenomena, with frequent and strong temperature inversions in the basin during much of the year, and frequent ground radiation fog especially in winter

season [8]. The measuring site is above the cold surface layer of air which forms in Ljubljana basin. Sometimes, not very often, the inversion layer at the hight of 2- 3 km a.s.l. (caused by subsidance in a stable anticyclone) sinks bellow the hight of the measuring site, and during such events the site is often in the cloud.

The station is being slowly upgraded since 1991, when ground based ozone measurements started. In October 1996 the National Institute of Chemistry (NIC) has installed an Aethalometer in order to measure aerosol black carbon at this elevated and regionally representative site. The equipment was installed inside the television transmitter tower. The air flow through the central sampling system, consisting of the 9 m long glass tube of 5 cm inner diameter (with the air inlet pointed down) and a fan at the end of the tube, was between 15-20 m^3 h^{-1}, depending on the outside wind intensity. The residence time of the air sample within the inlet system was between 2-3 seconds which is short enough to prevent ozone losses during the sampling. Sampling tubes of PE (Aethalometer) and PTFE (Ozone Analyzer) were attached to this main air inlet tube.

Black carbon measurements

BC was measured by an Aethalometer Model AE-23T, produced at NIC in cooperation with MageeSci Company. For calculation of BC concentration the empirical light absorption constant 19 cm^2 μg^{-1} was used. Reinforced quartz fiber tape was used for collection of samples. Flow rate was 11 l min^{-1}, the sampling time base was 10 minutes. In order to make the comparison of measurements easier the averaging time scale of 30 minutes is used in this presentation.

Ozone measurements

Ozone was measured by UV Photometric Ozone Analyzer, Thermo Environmental Instruments, Model 49C. Zero and span checks were carried out at the station automatically each day. Half hour data were transmitted every half hour via modem and radio line to HIS in Ljubljana, where routine checking of the measurements was performed on a daily basis. Accuracy of the measurements on site was determined by the portable ozone calibrator (TEI, Model 49C PS), being calibrated yearly against a NIST

UV Photometer, SRP #17 at the Czech Hydrometeorological Institute in Prague, Czech Republic. The latter is traceable to the GAW designated primary standard, i.e. NIST UV Photometer, SRP #15 at EMPA, Dübendorf, Switzerland.

RESULTS AND DISCUSSION

The average monthly concentrations, 50- and 95- percentile values of BC and ozone are presented in Table 1. In winter season, concentrations of ozone were lower than in summer (e.g. November - December: about 80 µg m^{-3}, June-July: about 110 µg m^{-3}). In general, ozone concentrations at elevated sites like Mt.Krvavec are higher than at the bottom of the valley, e.g. in Ljubljana [9].

Table 1. Average monthly concentrations, 50- and 95- percentile values of BC and ozone for the period October 1996 - July 1997.

	O_3			BC		
	Average (µg m^{-3})	50-percent. (µg m^{-3})	95-percent. (µg m^{-3})	Average (ng m^{-3})	50-percent. (ng m^{-3})	95-percent. (ng m^{-3})
Oct 1996	86	87	104	335	218	975
Nov 1996	77	77	95	173	137	465
Dec 1996	80	82	98	144	92	341
Jan 1997	86	86	103			
Feb 1997	93	95	114			
Mar 1997	96	98	115	447	361	1075
Apr 1997	113	106	157	347	257	908
May 1997	123	120	163	353	275	863
Jun 1997	113	114	135	355	281	737
Jul 1997	110	108	145	451	345	905

It is well known that in summer time the meteorological conditions (high temperature, low wind speed, higher global solar radiation) and gaseous precursors (NO_x, VOCs) are very often favorable for photochemical formation of ozone. On the other hand, even more pronounced differences were found with BC (e.g. about 150 ng m^{-3} in December and about 450 ng m^{-3} in July). Higher average concentrations of aerosol particles during summer than during winter season were observed also on other high altitude Alpine

stations, the effect being attributed to the extension of the planetary boundary layer containing polluted air up to the highest Alpine peaks [10]. Unfortunately, due to technical problem with the Aethalometer BC data from Mt. Krvavec are missing for the period of January-February 1997.

Diurnal variations of BC and ozone for two winter months November-December 1996 and two summer months June-July 1997 are shown on the Figures 1 and 2.

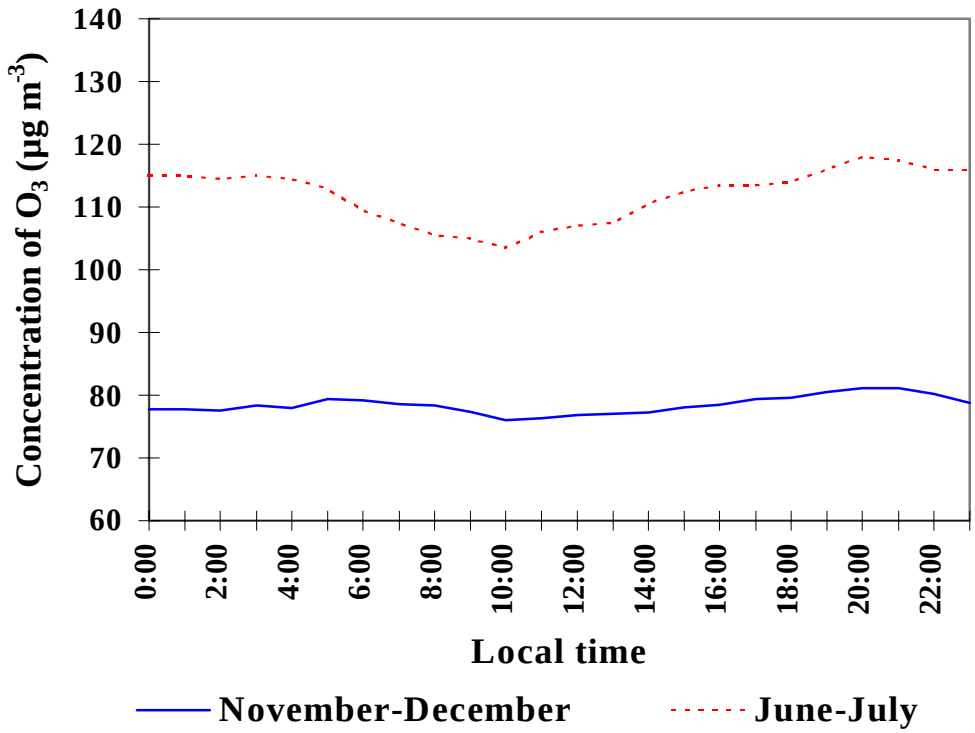

Fig. 1. Diurnal variation of ozone for November - December 1996 and June-July 1997 periods.

It is clearly seen that in winter time there were very slight changes of ozone concentration. In the summer time the curve is also pretty smooth; a slight decrease of ozone occurs during the nights and early mornings due to dry deposition, in the morning often the up-slope winds start bringing ozone formation precursors from the basin, while photochemical reactions increase ozone levels in the afternoon. Such behavior is typical for mountain locations [1]. However, the amplitude of the diurnal ozone variation on Krvavec is not pronounced which could be explained by insignificant contribution of

ozone removal effects, i.e. dry deposition and photochemical titration of ozone with NO. In addition, the ozone levels measured at Mt. Krvavec are comparable to those observed at the high altitude stations above 2000 m a.s.l. in Europe [11-13]. From the ozone concentration pattern it may be assumed that the station is predominantly well above the boundary layer, closer to the lower free troposphere conditions.

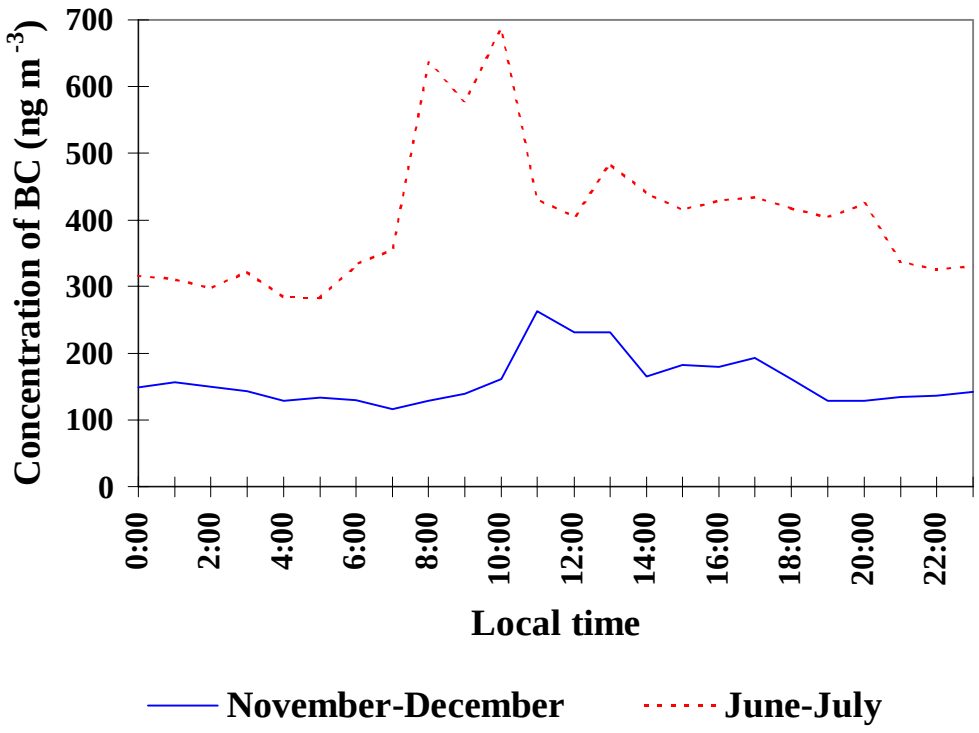

Fig. 2. Diurnal variation of BC for November - December 1996 and June-July 1997 periods.

The diurnal pattern of BC concentration in winter months shows a slight increase in the late morning, then gradually drops again in the afternoon and remains almost constant during the night. More pronounced increase was observed in the summer period. The concentration peak in the morning (few hours after the sunrise) is related to early developing up-slope winds and ground level temperature inversion break occurring much earlier in the summer than in the winter season. Differences between winter and summer diurnal BC variations can also be explained by the fact that in the winter the measuring site was most of the time above the temperature inversion layers which reduces the

influence of the polluted air from the valley. In the summer time up-slope winds and convective mixing bring polluted air from the basin to the higher levels, leading to a substantial increase of BC at the measuring site by more than a factor of two. This effect coincides very often with the breaking of the weak morning temperature inversions. The opposite situation (down-slope winds due to surface cooling) occurred in the late afternoons and during the nights, when BC dropped again.

Figure 3 shows the concentrations of both species in November 1996. The first half of this month was more dry (9 mm of rain) and the average temperatures were relatively high, while after the 16th a period of cooling and strong south to south-western winds began. The average temperature 4.5 °C during first 16 days dropped to -4 °C during the rest of the month. In this period frequent local precipitation totaling 155 mm also occurred.

On November 16 and 17 the precipitation was the most abundant with daily amounts of 46 and 25 mm respectively. A sudden drop of BC concentration due to scavenging process and dilution of polluted air reflects this weather change.Ozone concentrations in November were low due to low photochemical activity. The weather change in the second part of the month did not have any significant effect on its values.

Figures 4 and 5 show cumulative frequency distributions of ozone and BC for November 1996. The absence of half-hour ozone concentrations below 30 $\mu g/m^3$ means that there was no influence of the local air pollution sources causing ozone chemical titration with freshly emitted NO.

We can see that ozone cumulative frequency distribution is curved in the low concentration range while it is very close to log-normal in the higher range of concentrations. Similar frequency distribution pattern for ozone is reported also for other rural sites in Europe [14]. In the case of BC the concentration range is much broader (more than two orders of magnitude) and almost straight line indicates a log-normal distribution. The high BC concentrations indicate that the site was occasionally exposed to the polluted air originated either from the valley or from the local man-made activities at the surrounding ski resort area.

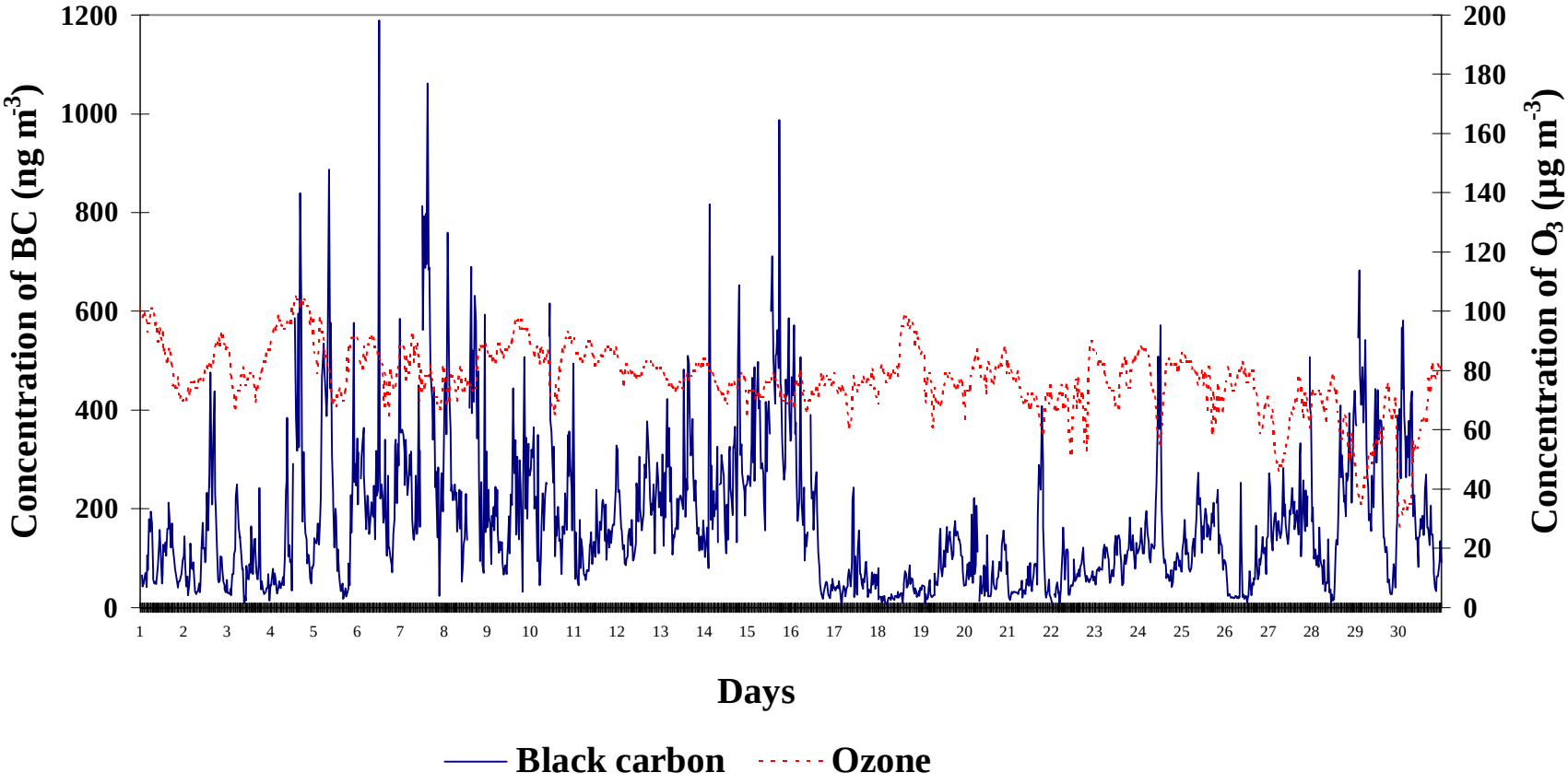

Fig. 3. Variation of ozone and aerosol black carbon concentration in November 1996.

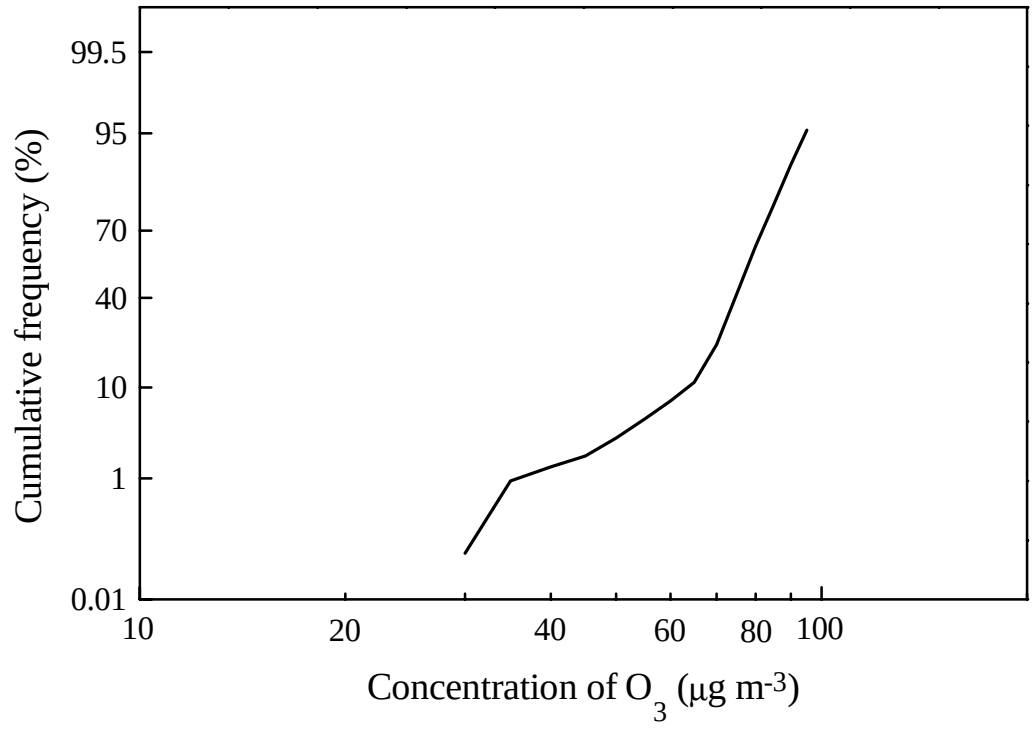

Fig. 4. Frequency distribution of 30-min ozone values for November 1996.

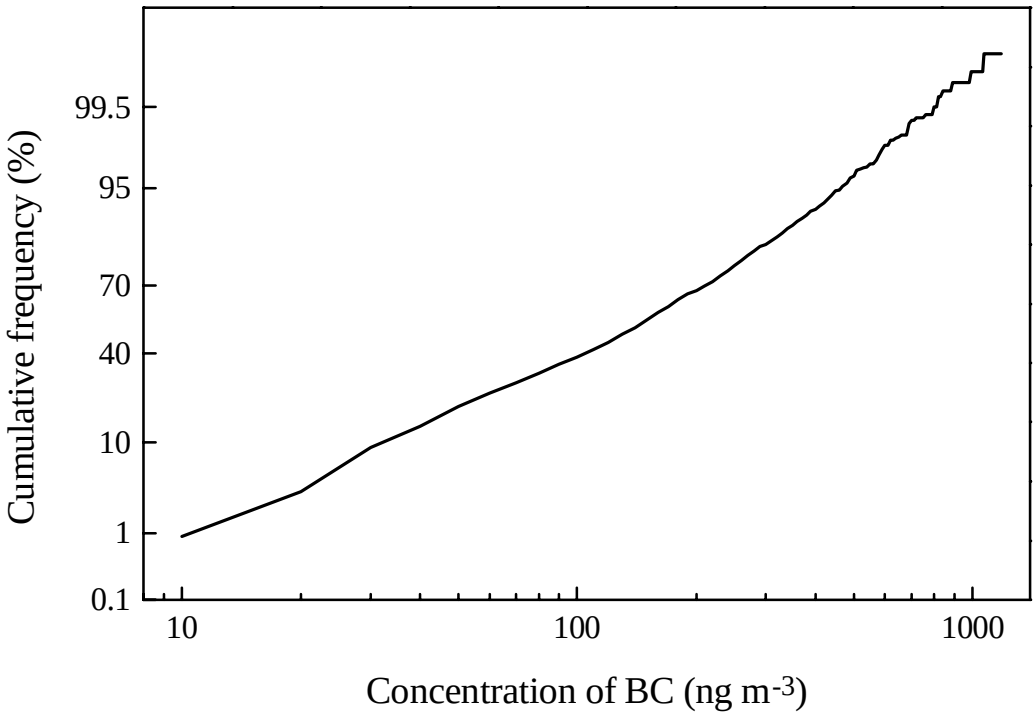

Fig. 5. Frequency distribution of 30-min BC values for November 1996.

Some interesting episodes of positive and negative correlation between O_3 and BC were found. The following selected examples represent three different types of correlation.

24-hr episode 16 October 1996 (Fig. 6)

Over the north Mediterranean See the secondary cyclone developed on the cold front which was slowly moving toward east. The south-west wind was bringing a wet and relatively warm air mass. It started to rain in the morning at the passage of the cold front, locally even thunderstorms developed and precipitation was quite intense. After the passage of the cold front the air was well mixed, but in the lower troposphere the south-west wind was still blowing. After midnight an increase of ozone concentration was recorded, which then stabilized to normal level after mid day. This slight increase could be due to mixing with ozone rich air from free troposphere. In this period BC concentration dropped due to the same air mixing process and also due to the scavenging because of the rain.

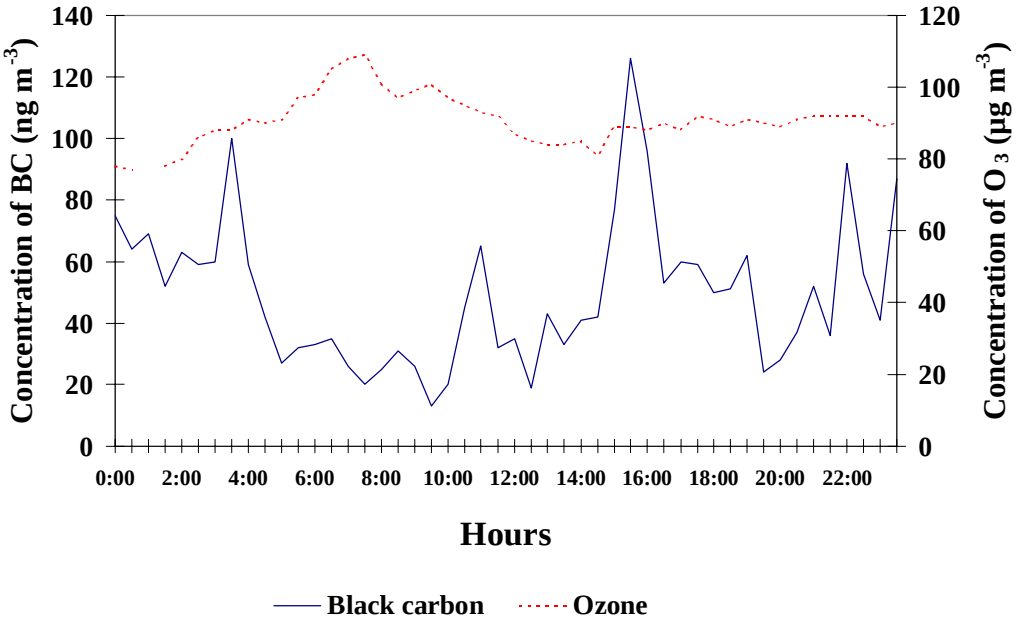

Fig. 6. 24-hr variations of ozone and BC at Mt.Krvavec on 16 October 1996.

48-hr episode 11-12 March 1997 (Fig. 7)

A strong anticyclone extended over most of the central and southern Europe. On the second day the anticyclone started to weaken slowly due to advection of warmer air and at the end of the considered period the typical subsidential temperature inversion below the measuring site built up. At 7 LST (6 UTC) on 11th March a shallow ground temperature inversion up to the 400 m a.s.l. formed, while isothermy prevailed form 400 to 700 m. During the morning the temperature inversion dissipated and the lower troposphere mixed up, also the wind at the bottom of the basin increased. In the evening due to intensive radiative cooling the ground temperature inversion built up again, but also the warmer air advection in the level between 1200 and 3000 m straightened the temperature inversion so that the temperature inversion at 7 LST on the 12th March reached the height of 1700 m a.s.l. Compared to the previous day, breaking of temperature inversion and mixing of the lower troposphere occurred later in the afternoon. On a larger synoptic scale these variations can be explained with the moving of the center of the high pressure field. A sudden drop of ozone and increase of BC in the late afternoon in both days at about 18 LST could be first of all attributed to the above mentioned mixing. Low BC during the night is related to the temperature inversion layer formation.

48-hr episode 11-12 April 1997 (Fig. 8)

On 11th April at 7 LST the strong temperature inversion was recorded in the layer between 950 and 1200 m a.s.l. In the evening cold front passed over and the wind turned from west to north-east. The temperature inversion dissipated and the cold air advection started. Afternoon peaks of ozone and BC on 11th April are result of raising of the polluted air from the basin while a substantial drop of both species during the next day is due to the passage of cold front. Photochemical pollution with peak ozone hourly concentration of 167 $\mu g\ m^{-3}$ was observed in Ljubljana in the afternoon on 11th April as well.

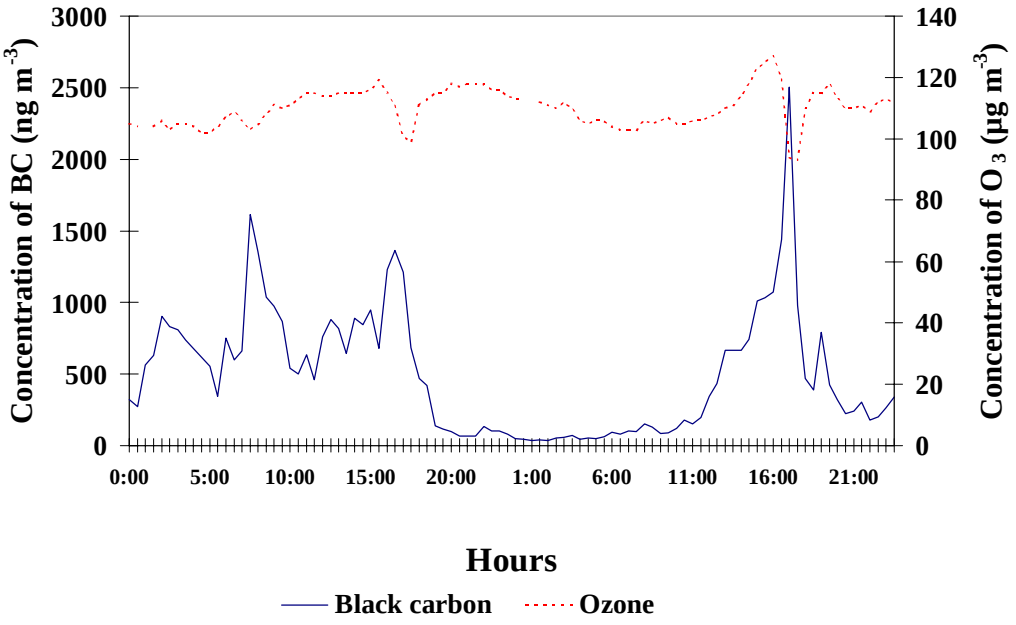

Fig. 7. 48-hr variations of ozone and BC at Mt.Krvavec on 11-12 March 1997.

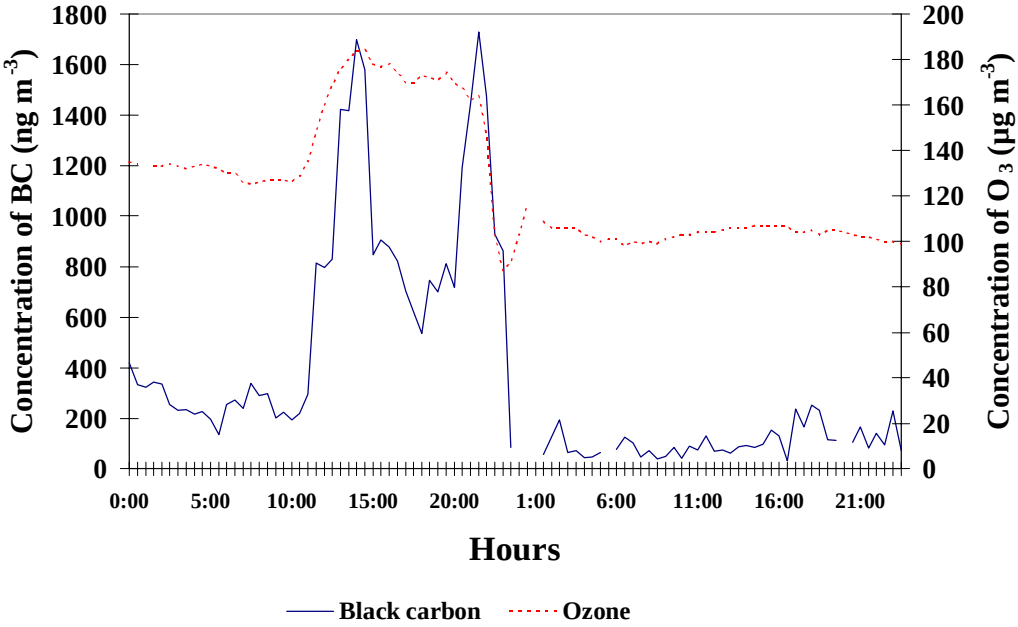

Fig. 8. 48-hr variations of ozone and BC at Mt.Krvavec on 11-12 April 1997.

CONCLUSIONS

In this paper the seasonal and short term concentration patterns of BC and ozone measured at Mt. Krvavec are discussed. In general, most of the time during the nights the site is exposed to the air of the lower free troposphere, while during the day convection mixing may bring also the polluted air masses from the valley. In the winter time the station is most of the time above the inversion layer and therefore polluted air from the basin can not reach the measuring site. For this reason the average BC concentrations are lower in the winter months. On the other hand the average O_3 concentrations at the elevated site of Mt. Krvavec are considerably higher than at the bottom of the valley because of the influence of the free tropospheric ozone. The main reason for higher average ozone levels during the summer time is the photochemical activity. The results presented in this work support the above general observations.

Diurnal variations of ozone show very slight changes in the summer time that appear due to photochemical activity and almost no changes in the winter. Diurnal BC pattern shows peak concentration which follows breaking of the temperature inversion and is more pronounced in summer.

The short term peak concentrations of BC and ozone show two patterns: negative and positive correlation which may be explained mainly by analysis of meteorology during the pollution or clean air episodes. Rapid increase of BC concentration coincides sometimes with the drop of ozone. This is explained by the reaction of ozone with NO in fresh polluted air masses originating either from the valley or more locally from the ski resort. On the other hand simultaneous high BC and ozone levels during the periods of photochemical activity reflect the effect of older polluted air masses (photochemical smog). High ozone and low BC concentrations episodes are related to the influence of the air coming from the free troposphere.

ACKNOWLEDGMENT

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Povzetek. V članku poročamo o enoletnih meritvah elementarnega ogljika v aerosolih (BC) in ozona na regionalni ekološki postaji EMEP/GAW na Krvavcu. Rezultati kažejo nekaj značilnih koncentracijskih profilov BC in ozona. Povišane koncentracije BC ob hkratnih nižjih koncentracijah ozona lahko pripišemo reakciji med ozonom in NO v onesnaženem zraku, ki je prispel iz smeri lokalnih izvorov, ali pa mešanju zraka v inverzijski plasti. Obraten pojav (nizek BC in višji ozon) je lahko posledica vdora zraka iz proste troposfere. V posameznih obdobjih brez temperaturne inverzije smo opazili pozitivno korelacijo (povišane vrednosti obeh merjenih komponent), kar pojasnjujemo s transportom starejših onesnaženih zračnih mas iz regionalnih izvorov.