Ozone Concentrations at the Bulgarian Govedartsi Ecosystem Site in Early Summer of 1994 and 1995[1]

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Abstract

Ozone measurements are presented from the Bulgarian Govedartsi ecosystem study site, Ovnarsko No. 3. The site is located on the south slope of the Govedartsi Valley in the northwestern part of the Rila Mountain area. The Rila is the highest mountain in the Balkan peninsula and is representative of rural conditions in that part of Europe. The experimental site, Ovnarsko, is situated at 1,600 m above sea level and about 10 km west of the village of Govedartsi. There are no anthropogenic sources for ozone precursors for at least 30 km in all directions. Ozone concentrations within the Govedartsi Valley are strongly influenced by thermally driven local winds from late spring to summer that occur during high pressure synoptic weather conditions. In these cases a thin stable cold layer of downslope wind is experienced during the night, separating surface air from the higher boundary layer air. This helps the reduction of ozone concentrations from dry deposition measured at the Ovnarsko site. During the 1994 and 1995 measurement periods no high ozone concentration episodes were detected. This may be because of either an absence of significant anthropogenic sources of ozone precursors in this part of the Balkan peninsula or to the shielding of the Valley during high pressure conditions. In general, ozone concentrations at Ovnarsko were below 35 ppb.

Introduction

In September 1991, an air-pollution study was launched at the Govedartsi in the highest mountain range in the Balkans. The site—designated as Ovnarsko No. 3—is located on the south side of the Govedartsi Valley on the northwestern part of the Rila Mountains (Zeller 1991). The Valley is bordered on the south and west by high ridges (~2,600 m), and on the north by a lower and more fractional ridge (highest point ~1,800 m). The Valley opens to the northeast with a narrow mountain pass, through which the Iskar river flows toward the Samokov area. The experimental site Ovnarsko is situated at 1,600 m above sea level and about 10 km west of the village of Govedartsi, which is on the less steep part of the northern slope of Rila Mountain. The terrain is higher in the western part and lower in the central part of Govedartsi Valley (*fig.1*). The greater part of Rila mountain lies to the south of the Valley area.

There are no anthropogenic sources for ozone precursors for at least 50 km in the south direction and for about 30 km in the west direction where the mountain ridge is a high obstacle for west-to-east transport of air pollutants. Weekly average measurements of SO_4^{2-}, NO_3^-, and some metals taken in 1991 (Zeller and others 1992) and 1992 demonstrated increasing air pollutant concentrations after each well-marked western air outbreak (strong winds accompanied by rain during cyclonic synoptic weather). However, during high-pressure weather systems (low wind and clear sky), decreased SO_4^{2-} and NO_3^- concentrations were observed. Under the latter weather conditions mountain-valley gradient wind flows predominate, allowing local natural sources of trace gases to determine the measured air quality. During such periods the Govedartsi Valley is probably screened from anthropogenic air pollutants from outside. In these cases the mountain ridges, surrounding the Valley, are mostly above the height of the planetary boundary layer causing the measured wind speeds at the experimental site to be low and wind directions to follow a diel cycle of mountain-valley circulation.

This paper presents data that the Ovnarsko experimental site is not impacted by ozone or its precursors of anthropogenic origin under high-pressure weather. This phenomenon is associated with so called episodes of high ozone concentrations

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in rural areas in other regions of the world (Cox and others 1975, Logan 1985). Many studies (Attmannspacher and others 1984, Guicherit and van Dop 1977, Mueller 1994, Prior and others 1981, Vukovich and others 1977) relate the high ozone levels to the presence of warm and slowly moving synoptic-scale high pressure systems, which was not observed at the Ovnarsko site.

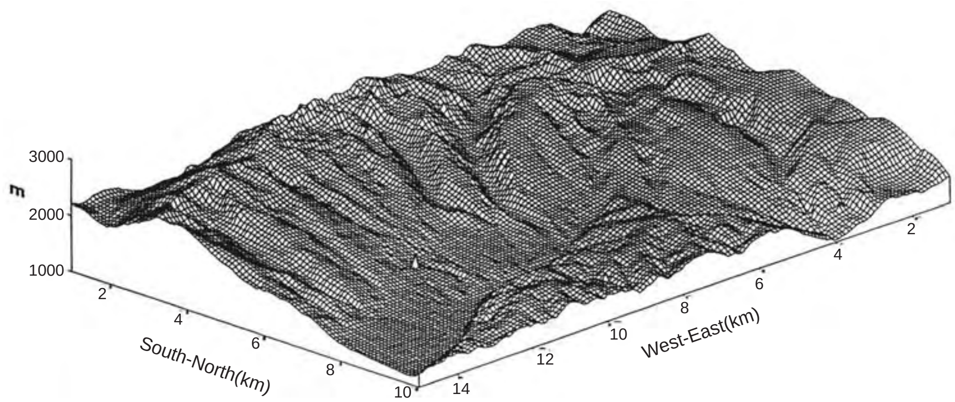


Figure 1 — The Govedartsi Valley from the northeast on a 100 m grid. The x axis, west-east, is 15 km and the y axis, south-north, is 10 km.

Data and Instrumentation

The reason for monitoring ozone at the Ovnarsko site was to determine the extent to which upwind anthropogenic sources influenced Govedartsi Valley ozone concentrations and whether the Ovnarsko site was representative as a background station for this part of Europe. The site location allows for separating synoptic from mesoscale meteorological wind regimes, isolating source regions for measured air pollutants. Because of difficult site access during winter and limited technical support after late summer, ozone concentrations were only measured from late spring to summer: May 28 to July 9, 1994 (Julian Days 148 to 190) and June 12 to July 30, 1995 (Julian Days 163 to 212). Wind speed and direction, air temperature and humidity at 5 m height, total solar radiation, wetness, precipitation, soil temperature and soil heat flux were measured through autumn. Hourly mean and standard deviations of the measured quantities were recorded with a Campbell Scientific 21x data logger (*table 1*).[5] Ozone was sampled through a teflon filter at 2 m height. The ozone instrument was calibrated in the United States before shipment to Bulgaria. It appeared to function normally; however, a post calibration was not made. Because of the inherent stability of the ultraviolet adsorption technique, the ozone concentrations were within ±5 ppb. The teflon filter used to remove foreign objects in the sample air was changed approximately every 15 days.

***Table 1** — Parameters measured hourly at the Ovnarsko site.*

Sensor	Parameter	Units
Teco 49	O_3	ppb
Metone	Wind speed	m s^{-1}
Metone	Wind direction	degree
Eppley	Solar radiation	watt m^{-2}
MRI Inc.	Precipitation	mm
Metone	Temperature	°C
Metone	Relative humidity	pct
Rad. energy	Soil heat flux	watt m^{-2}
thermocouple	Soil temperature	°C
thermocouple	Soil temp Gradient	°C
Campbell Sc.	Leaf wetness	wet/dry

[5] Mention of trade names or products is for information only and does not imply endorsement by the U.S. Department of Agriculture.

Results and Discussion

A difference in diurnal ozone concentration cycle patterns was observed after sorting the data by meteorological phenomena. Air laden with ozone and ozone precursors is frequently transported from urban areas to cleaner mountain and rural areas during periods with high atmospheric pressure and low wind speeds (Cox and others 1975, Vukovich and others 1977, Wolff and others 1977). The days with such weather are categorized: “days with clear skies and local winds” for this paper. On the other hand, cyclonic weather conditions with strong winds, and turbulent boundary layer air cause intense vertical mixing and potential dilution of polluted air. In the Govedartsi Valley, however, this same vertical mixing appears to cause downward ozone transport from higher ozone-laden layers of the troposphere. In remote areas higher mean ozone concentrations are often experienced under these more turbulent conditions when air, transported from distant upwind sources, is mixed downward (Zeller and others 1977). For Ovnarsko the data were separated into the two types of weather by using wind speed and direction and solar radiation as the main criteria. Precipitation, air, and soil temperatures were used as additional criteria when necessary.

Meteorology

The hourly and 24-hour mean wind direction and 24-hour wind speed sums for the 1994 and 1995 measurement periods were obtained through summation of mean values for each hour (*fig.2a,b*). There are two distinct meteorological regimes affecting wind flow as measured at Ovnarsko: locally generated winds and synoptic winds. During local wind days regional synoptic pressure gradients are weak and local mountain-valley circulation predominates. On such days the wind direction follows

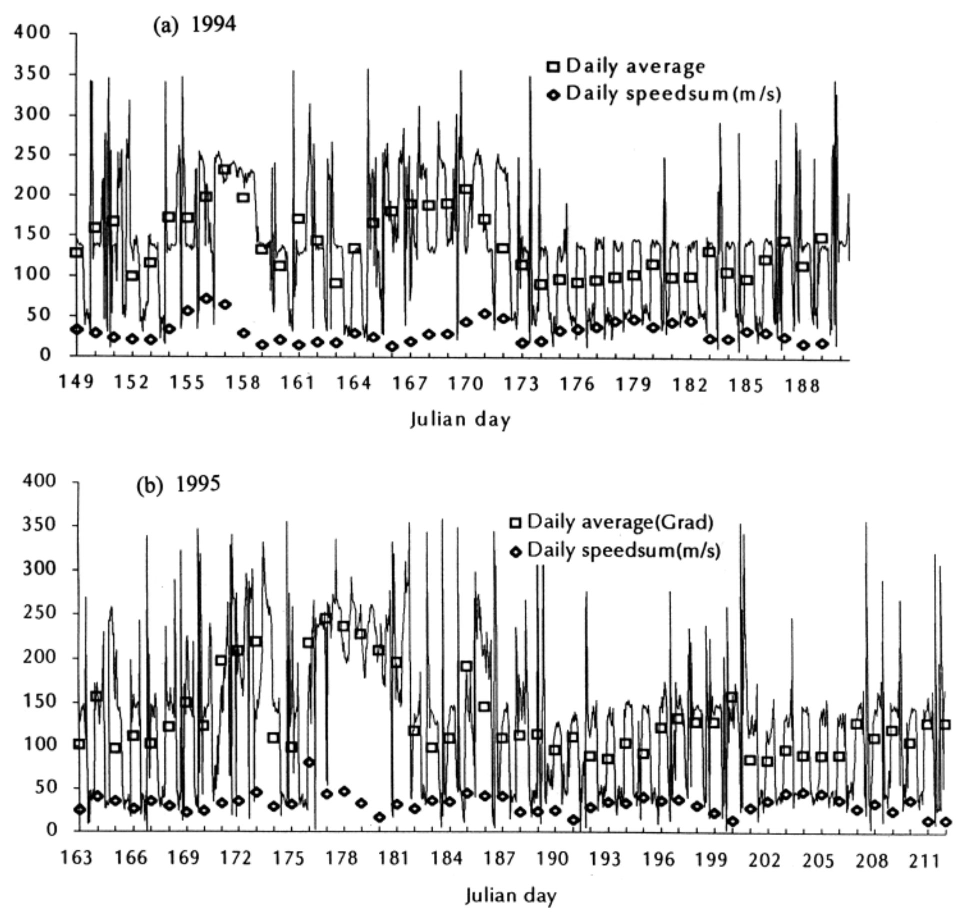
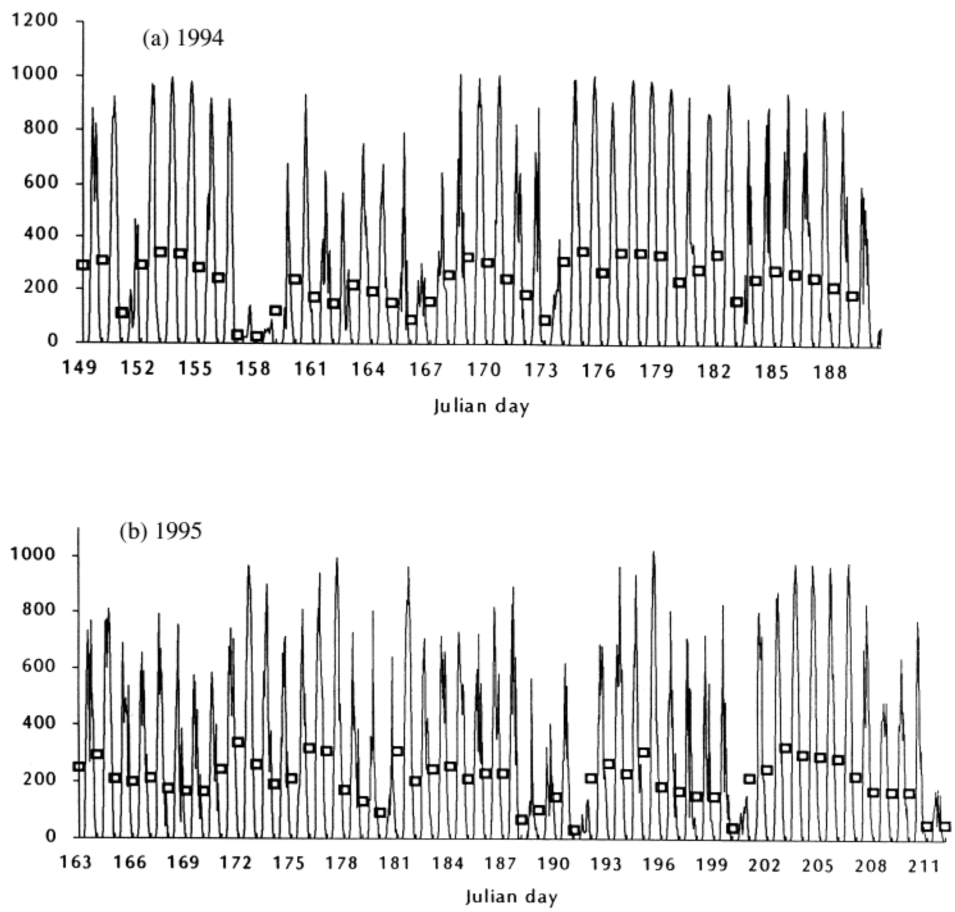


Figure 2 a, b — Wind direction for each hour (line), mean wind direction (squares), and velocity for each day (diamonds) for the two measurement periods in 1994 (a) and 1995 (b).

a typical diurnal cycle: southeast at night (mountain catabatic winds) and northeast during the day (upslope winds). On days influenced by synoptic weather the diurnal cycle of mean wind direction does not follow a predictable course but varies from south to west demonstrating the effect of upwind regional air intruding into the Govedartsi Valley. The strongest of these winds are from southwest and west during such days and tending to return to southeast at night demonstrating the surface layer decoupling from upper synoptic winds on most but not all synoptic nights.

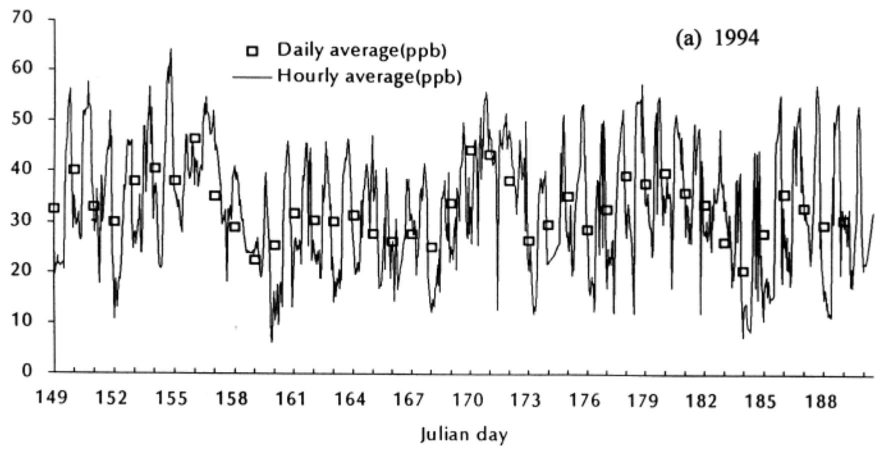
The total solar radiation was calculated for each hour in addition to the daily mean (*fig. 3a,b*). Days with high solar radiation (indicating few or no clouds) are typically days when local winds occur ("days with clear skies and local winds") and vice versa: lower solar radiation (cloudy days) are the days with stronger westerly winds. The 1994 study days determined as "days with clear skies and local winds" are: Julian days 152-154 and 174-182, 12 days out of the 42-day measurement session. For 1995 the study days are the Julian days 163, 183, 184, 194, 195 and 202-207—11 days out of the 50-day measurement session.

Figure 3 a, b — Total solar radiation (watts/m²) for each hour (line) and daily mean values (squares) for the two measurement periods in 1994 (a) and 1995 (b).



Ozone Concentration

Hourly and daily mean ozone concentrations from the 1994 and 1995 measurement periods were plotted (*fig. 4a,b*). These values, adjusted to mean sea level, rarely exceeded 35 ppb during the day and drop to 15 to 20 ppb at night. This diurnal swing in concentration is similar to summertime results taken in a spruce-fir forest in Snowy Range, Wyoming above 3,000 m elevation at 3 m above ground level but below canopy height (Wooldridge and others 1994, 1995). Ozone concentrations taken at 30 m above ground (13 m above canopy height) at the same Wyoming site only vary 2 to 3 ppb from day to night (Zeller 1995). At Ovnarsko, higher nighttime ozone concentrations were measured during the synoptic wind days when air from Central or Southern Europe apparently entered the Valley (e.g., Julian days 156 and 170 from 1994 and days 176 and 186 in 1995). There were no high ozone concentration episodes during either classification period in 1994 and 1995. With the exception of Julian days 154 in 1995 and 195 in 1996, periods when outer air masses penetrated into the Valley (i.e., days without clear skies and local winds) tended to be associated with similar daily maximum ozone concentration; however, the nighttime minimums on such days were much higher, causing larger daily averages. These data suggest that strong exchange of air within the whole boundary layer during these periods enhanced vertical ozone transport, advected from distant upwind sources, and maintained an above ridge-height ozone source preventing the Valley from experiencing lower nighttime ozone concentrations. The lower nighttime minimums during days with clear skies and local winds were from ozone deposition to surfaces and the lack of a transport mechanism to vertically transport the upper ozone to maintain higher surface concentrations. This explains the strong influence of the local winds (mountain-valley circulation) on the diurnal cycle of ozone concentrations in the Govedartsi ecosystem.



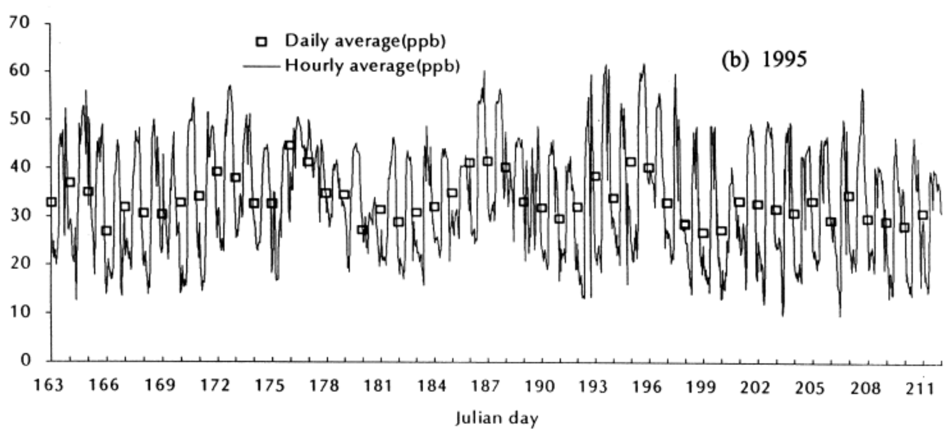


Figure 4 a, b — Hourly mean ozone concentration (line) and daily mean values (squares) for the two measurement periods in 1994 (a) and 1995 (b).

The existence of well-manifested thermally driven local wind system in the Valley around the Ovnarsko site gives us the opportunity to compare the influence of upslope and downslope winds on the diurnal variations of ozone concentration. The mean diurnal cycle of ozone concentration, temperature, wind speed, and direction (degree/10) was calculated for the chosen days with clear skies and local winds. The thermally driven mountain-valley circulation is clearly seen especially during the night when the cold downslope/down valley winds along the north-northwest slope are constantly east-southeast to east in direction from 22:00 local standard time until 8:00 LST. Northeast upslope winds begin after 8:00 LST until 20:00 to 21:00 LST. Diurnal ozone concentrations show a typical diurnal cycle for the clear skies days in rural areas (Bottenheim and others 1994, Meagher and others

1987, Prevot and others 1993): minimum values in the morning until upslope conditions take over, and maximum values in the afternoon. During a typical afternoon the east to northeast wind passes through the agrarian Govedartsi village 10 km E (upwind at this time) of Ovnarsko. There is little automobile traffic and few farm vehicles that are not horse-drawn. It is possible some anthropogenic ozone precursors come from Samokov, a larger city about 15 km farther east, however, in general there is a lack of so called high ozone concentration episodes, frequently experienced in the eastern part of the USA and in Western Europe under similar weather conditions (Aneja and Li 1992, Aneja and others 1994, Davies and others 1992, Mueller 1994, Trainer and others 1993).

In mountainous terrain, Brother and Gydax (1985) found an increase of ozone during the day caused by upslope air transport with photochemical ozone production. During the night ozone concentrations decreased on the slope due to dry deposition. In another case Prevot and others (1993) concluded that thermally driven winds defined the origin of air masses of the Reuss Valley in the summer during high pressure systems. During the night the thickness of the downslope wind layer experiencing efficient dry ozone deposition seemed to be very thin on the slopes. They found that ozone concentrations at 2 m height were significantly lower than those at 15 m height during the night similar to Wooldridge and others (1994, 1995). The nocturnal concentrations measured at Ovnarsko at the same 2 m height during downslope winds were rather low (*fig. 5a, b*) for a site at 1,600 m elevation. The low nighttime Ovnarsko ozone values may be a result of dry deposition of ozone to surfaces, including reactions with soil emitted NO (Brother and Gydax 1985) within the cold stable downslope flow. The downslope flow concentrated within a thin layer near the earth will not interact with the air mass above, where ozone concentration is most likely higher and not effected by dry deposition mechanisms. Mueller (1994) showed a clear tendency for diurnal ozone amplitudes to diminish at rural mountain sites as site elevation increases. For some mountain experimental sites a tendency for a reversed diurnal cycle of ozone

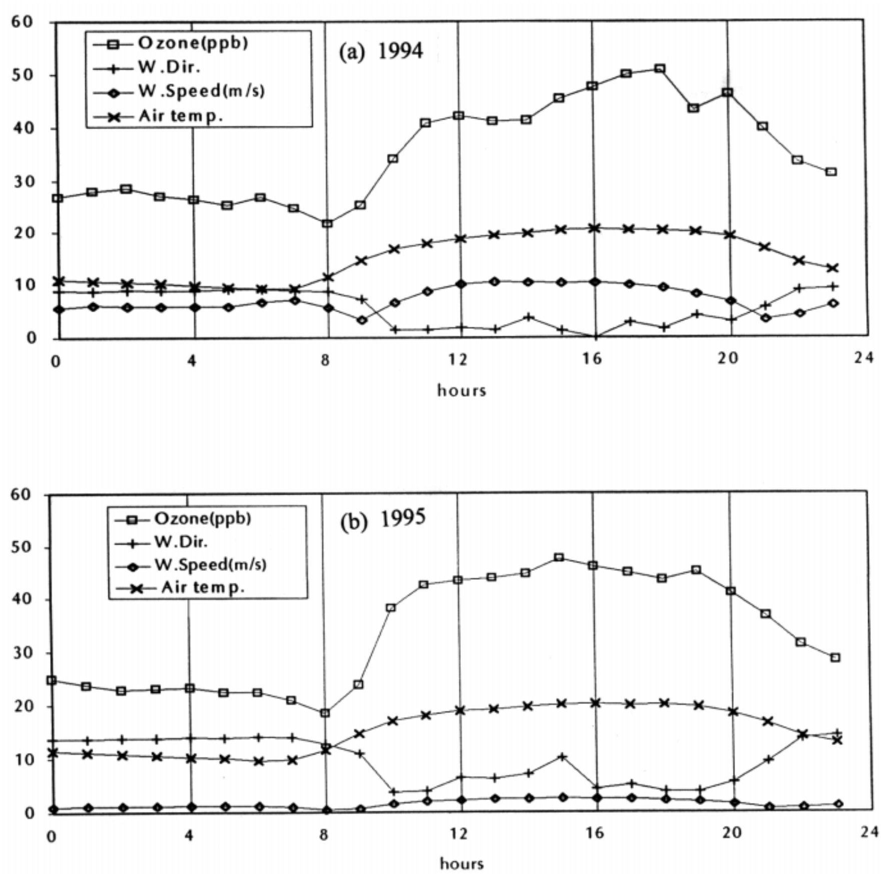


Figure 5 a, b — Mean diurnal cycle of ozone concentration (squares: parts per billion), wind speed (diamonds: m/s), wind direction (+: degree x 10^{-1}), and air temperature (x: °C) for the two measurement periods in 1994 (a) and 1995 (b).

concentration has been detected when maximum values are measured during the night (Aneja and Li 1992). This is not the case for sites under the influence of a mountain-valley circulation.

Apparently ozone concentrations are lower in this rural part of Bulgaria compared to more populated areas. For instance, within southeast Sofia during the end of the summer 1-m height, 10-day daily mean ozone concentrations were between 40 and 50 ppb, with maximum values reaching 70 to 80 ppb. These Sofia values are similar to those in metropolitan Denver, Colorado (Zeller 1995). Ozone values found in forested areas of Poland are predominantly above 60 ppb and often exceed 80 ppb (Bytnerowicz and others 1993), unlike the Ovnarsko results.

Conclusion

Ozone concentrations within the Govedartsi Valley are strongly influenced by thermally driven local winds from late spring to summer during high pressure systems. In these cases, a thin stable cold layer of downslope wind is experienced during the night, which separates surface air from the higher boundary layer air causing reduction of ozone concentrations from dry deposition measured at the Ovnarsko site. During the two measurement periods, no high ozone concentration episodes were detected. This condition may be a result of the absence of significant anthropogenic sources of ozone and its precursors in this part of the Balkan peninsula or from the shielding of the Valley during high pressure conditions where the surrounding mountain ridges are above the boundary layer height and the air in the valley flows as thermally-driven local circulation.

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