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Boundary layer ozone in Osijek, eastern Croatia

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Results of the first ozone monitoring in ambient air in eastern Slavonia are reported for the growth season in 2002 (April through September). The monitoring site at the northern boundary of the city was chosen to distinguish two types of air masses: one from the rural and marshy region to the north and the other urban and suburban from the south. The measured hourly average ozone volume fractions varied between 0 and 80 ppb, the average being 35 ppb. The low value indicated that the air is well mixed. No significant differences were found between air masses from the north and from the south. Thus, no significant photochemical pollution problems are expected for the city Osijek.

Keywords: air quality, ozone, tropospheric ozone

1. Introduction

Ozone is a natural constituent of the Earth's atmosphere. In the stratosphere it is formed by photochemically induced reactions from oxygen. It forms a layer of significantly higher volume fractions at altitudes between 15 and 35 km and is responsible for two important effects: (i) prevention of harmful UV radiation to reach living organisms on Earth's surface and (ii) heating of the air and changing the gradient of temperature with altitude (Wayne, 2000; Grewe, 2007).

In going from the stratosphere toward the surface of the Earth ozone fractions become significantly lower and reach values of 30 ppb in the unpolluted planetary boundary layer. However, there are locations where the volume fractions significantly exceed this average value. This is usually caused by local production from primary pollutants such as nitrogen oxides and hydrocarbons initiated by absorption of solar radiation in the visible and near UV region. Such elevated volume fractions of ozone in ambient air have a negative effect on some materials, on plant, animal and human health (Cvitaš et al., 2005; Vingarzan, 2004).

2. Experimental

Ozone volume fractions have been measured and analyzed for the first time in the region of Eastern Slavonia. The monitoring site was located at the northern boundary of Osijek close to the river Drava approximately 50 m above the ground (Figure 1).

Osijek is the largest urban centre in eastern Croatia at 45.32°N, 18.44°E and an altitude of 90 m above sea level. The measurements took place during the growth season (April through September) 2002 using a commercial instrument Dasibi 1008AH based on UV absorption photometry which has been regularly checked and calibrated. The data have been recorded every 3 minutes and stored in a data logger for further processing on a computer. The meteorological data were obtained from the Meteorological Service of Croatia, who monitored the meteorological parameters at Klisa ca. 20 km to the southeast of the monitoring site.

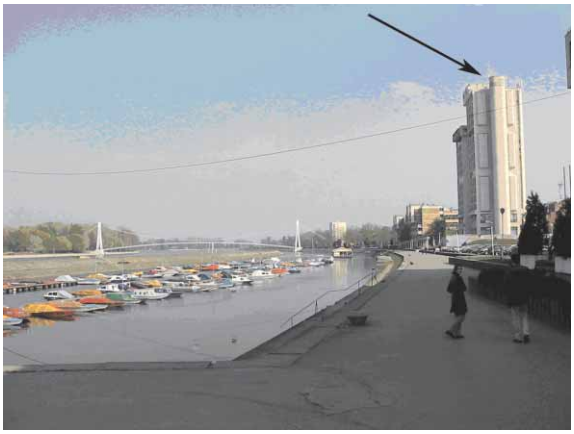

Figure 1. View of the monitoring site (from west to east) where the instrument was placed near the roof of Hotel Osijek, as indicated by the arrow.

3. Results and discussion

The data were converted to hourly average ozone volume fractions and analyzed in relation to meteorological data: wind direction and wind speed.

The average diurnal variation of ozone volume fractions for the April through September period of 2002 is shown in Figure 2 in the form a 'box and whiskers' plot. The distribution of values resembles a typical behaviour for a suburban or smaller urban site (Cvitaš et al., 1997; Oltmans et al., 2006; Cvitaš et al., 2006). The maximum values exceeded the limit of an hourly average

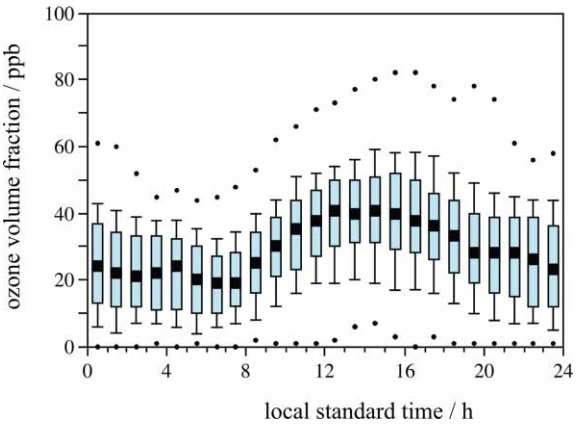

Figure 2. Diurnal distribution of ozone volume fractions for the April to September period of 2002. The black squares represent the medians for each hour of the day over the whole period, the box edges the 1st and 3rd quartile, the bars the 10th and 90th percentile and the dots the minimum and maximum values.

of 80 ppb on two instances only. The daily maximum values were measured in the early afternoon hours indicating that the source of primary pollutants is not far from the monitoring site. On the other hand they are very low for an urban site indicating that the air seems to be very well mixed with that of the surrounding region. Indeed, Osijek lies in a plane allowing winds from all directions and the wind rose resembles a circle closely.

It is important to note that conclusions reached on the basis of single-spot measurements during one season only are rather vague and can be used only for rough estimation of the state of atmospheric pollution in a location. Nonetheless, the data indicate that the city of Osijek did not suffer any significant photochemical pollution during 2002. In other locations in Croatia and the Mediterranean region significantly higher values were measured (Butković et al., 1999).

By calculating all the 8-hourly moving average ozone volume fractions it was found that the value of 60 ppb was exceeded only on a single day (18 May) for a total of 16 hours, whereas the Croatian Directive on Ozone (Vlada RH, 2005) allows this value to be exceeded for 25 days in year. The daily average of 55 ppb was also exceeded on that same day while the Directive allows 7 such days per year.

In order to see how the distribution of measured ozone volume fractions depends on the wind direction, we plotted the average value for each direction and obtained the plot in Figure 3.a. No particular direction could be associated with pronounced unusually high or low values. The lowest average value (20 ppb) is associated with the southwesterly wind and the highest (40 ppb) with the south-easterly wind. A better insight is obtained by plotting the relative

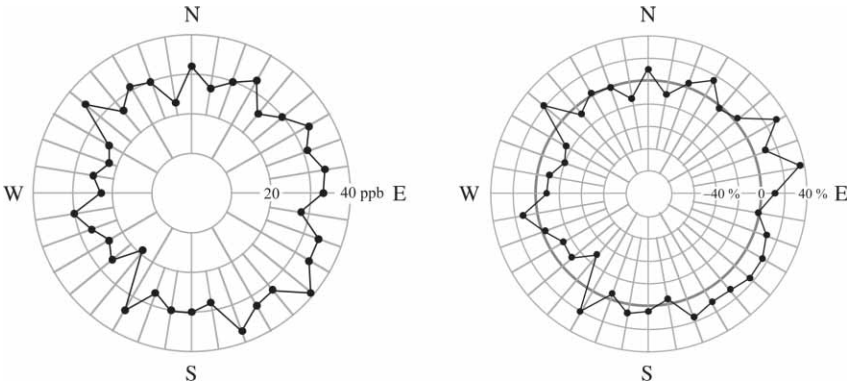

Figure 3. a) Polar diagram correlation ozone volume fractions and wind direction, b) Relative deviations from average ozone volume fractions.

deviations from the average value for each hour of the day as a function of the wind direction as given in Figure 3.b. We calculated the average diurnal behaviour for the whole season obtaining average volume fractions for each hour of the day. Then the deviations from these average values have been calculated and divided by the average to obtain the relative deviations for each hour. These values grouped for each of the 36 directions of the wind are plotted in a polar diagram in Figure 3.b. In this way the possible diurnal behaviour in wind direction is eliminated and positive and negative deviations for indivi-

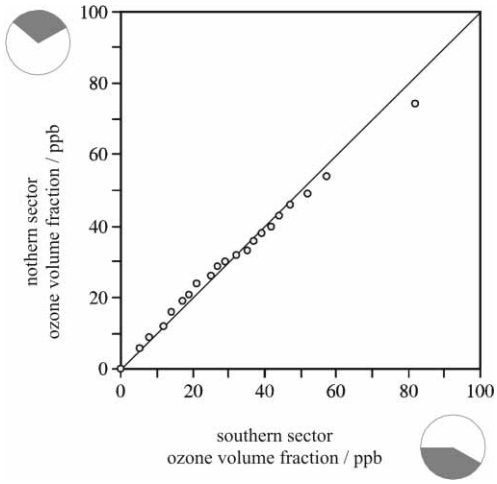

Figure 4. Comparison of ozone fraction distributions for two wind sectors: the northern bringing air from an agricultural and marshy region against the southern bringing air from the city centre and its industrial part.

dual wind directions can be identified. The plot indicates that positive deviations *i.e.* above average values are observed when the wind blows from the east and negative deviations are mainly associated with a westerly wind. However, the differences are small, never exceeding 40% of the average.

Osijek is situated to the south of the river Drava and the monitoring site on the river bank (Figure 1) is suitable to distinguish whether northerly winds bringing air from the agricultural and marshy region of Baranja have a significantly different effect on observed ozone volume fractions as compared to winds from the south bringing air masses *via* the city centre and industrial sections. We compared the two wind sectors, indicated by the grey shading of the small circles, by a quantile-quantile plot as shown in Figure 4. Surprisingly no difference in behaviour was found. It remains to be proven that the emissions of primary hydrocarbon pollutants in Baranja to the north and in the city and its southern parts are similar.

4. Conclusion

The results of the first ambient air ozone monitoring in eastern Slavonia are reported for the growth season (April through September) of 2002. The monitoring site at the northern boundary of the city was chosen to distinguish two types of air masses: rural and marshy from the north and urban and suburban from the south. The measured hourly average ozone volume fractions varied between 0 and 80 ppb, the average being 35 ppb. The low value indicates that the air is well mixed. No significant differences were found between air masses from the north and from the south. Thus, no significant photochemical pollution problems are expected for the city Osijek.

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SAŽETAK

Ozon u graničnom sloju u Osijeku, istočna Hrvatska

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Prikazani su rezultati prvih mjerenja volumnog udjela ozona u Istočnoj Slavoniji tijekom sezone rasta (1. travnja do 30. rujna) 2002. godine. Mjerno mjesto na sjevernoj strani grada Osijeka uz rijeku Dravu na visini od oko 50 m iznad tla odabrano je da se mogu razlikovati dva tipa zračnih masa: ruralno-močvarne sa sjevera i gradsko-predgradske s juga. Izmjereni satni proscjeci udjela ozona u zraku verirali su od 0 do 80 dijelova u milijardu, a srednja je vrijednost iznosila 35 ppb. Niske vrijednosti ukazuju na dobru izmješanost zraka. Usporedbom vrijednosti uz vjetar iz sjevernog odnosno južnog sektora nisu nađene bitne razlike pa se tako ne očekuju problemi fotokemijskog onečišćenja zraka u gradu Osijeku.

Ključne riječi: kvaliteta zraka, ozon, troposferski ozon

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