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# Long-term Ozone Data Analysis

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Various approaches to the analysis of 10-year continuous ozone monitoring from the EUROTRAC-TOR network station Puntijarka near Zagreb are reported. The site has a rural character (45.90° N; 15.97° E, 980 m a.s.l.) and is representative of the lower troposphere of a wider region. Mean hourly ozone volume fractions measured from 1990–1999, autocorrelation plots for all data and for data for summer periods (May–Sep.), box and whiskers representations of diurnal variations during winter (Nov.–March) and summer periods, mean monthly values and 12-month moving averages, and the Fourier transform of the complete set of 94,248 hourly mean ozone volume fractions are discussed. The data show no increase, or possibly a slight decrease, of the ozone volume fraction toward the end of the decade.

*Key words:* long term ozone data, Fourier analysis, trend analysis.

## INTRODUCTION

Ozone in the troposphere is considered a pollutant causing plant damage, material damage, adverse health effects, visibility reduction, greenhouse effect and overall increase of the oxidation capacity of the atmosphere.[1] It has been reported that in the past one hundred years the ozone concentration near the ground has more than doubled and is still rising.[2–4] Long-term measurements are therefore underway to assess this trend. Ozone concen-

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trations monitored at any tropospheric site are influenced by the i) chemistry, *i.e.* the composition of air and insolation, ii) topography, especially altitude, type of terrain, vegetation, *etc*., and iii) meteorological parameters, in particular temperature, wind speed and direction, seasonal variation, and clouds.

Consequently, assessment of all factors influencing the ozone concentration at a particular site requires a complete knowledge of these factors not only for the site but also for its surroundings; this is achieved through measuring campaigns, which involve simultaneous use of a ground station, aircraft (and balloons) and satellite observation over a short period of time. Less demanding, but also very useful is the monitoring of ozone and selected species important for ozone formation and destruction, together with meteorological parameters within a network of fixed stations. Such data give clues about the regional dependence, daily, monthly and seasonal variations as well as about the trends of ozone concentration. Experimentally and financially, ozone concentrations are the easiest to monitor, and such data collected over longer periods of time at representative sites are often the only parameters available for comparative analysis. The aim of this paper is to describe various approaches to the analysis of such »ozone-only-measurements« and show the kind of information that they can yield.

The wind rose and the average wind speed as a function of wind direction for 1981 to 1991 show that long-range effects at higher wind speeds can be expected from the west while the local effect comes from the urban center in the south.[5] However, simultaneous measurements at 180 m a.s.l. at the Ruđer Bošković Institute in the northern part of Zagreb, at 580 m a.s.l. on the mountain and at Puntijarka station show that even under the high photosmog conditions above Zagreb the Puntijarka station remains above the mixing layer and is largely unaffected by the city.[6] The station has been chosen as representative of the area also because of its very low photochemical pollution index.[7]

## EXPERIMENTAL

Ozone was monitored with commercial Dasibi and Environment monitors, which were regularly checked and calibrated against primary ozone standard instruments. Collected data refer to average hourly ozone volume fractions measured during the ten-year period, from January 1,1990 to December 31, 1999, at the EUROTRACTOR network[8] station Puntijarka. The station is located about 10 km to the north of the city of Zagreb on the ridge of Mount Medvednica (45.90° N; 15.97° E, 980 m a.s.l.). There is an agricultural area with no significant industry to the north of the mountain. Meteorological parameters have been measured at Puntijarka since 1959, and the station is also part of the EMEP network.[9]

## RESULTS AND DISCUSSION

The mean hourly ozone volume fractions for the period 1990–1999 are shown in Figure 1(a) (top). The missing data due to the war situation in Croatia, malfunction of the instrumentation and damage by lightning have been adjusted by taking the average of the corresponding values (same hour and day) for the preceding and following years. The adjusted data set is shown in Figure 1(a) (bottom). The corresponding monthly average ozone volume fractions for the original and adjusted data are given in Figure 1(b) (top and bottom, respectively). The average diurnal variation of ozone volume fraction for the months January through December for Puntijarka, compared to that measured in Zagreb at the Ruđer Bošković Institute, exhibits negligible diurnal variation, especially during the winter months; this is also demonstrated by the autocorrelation plot of average hourly ozone volume fractions at Puntijarka for 1990–1999 in comparison to that for summer periods (May 1–Sep. 30) only.[10]

All this indicates that probably most of the ozone measured at Puntijarka, which is considerable during the summer months, is produced elsewhere and arrives to the station by transport.

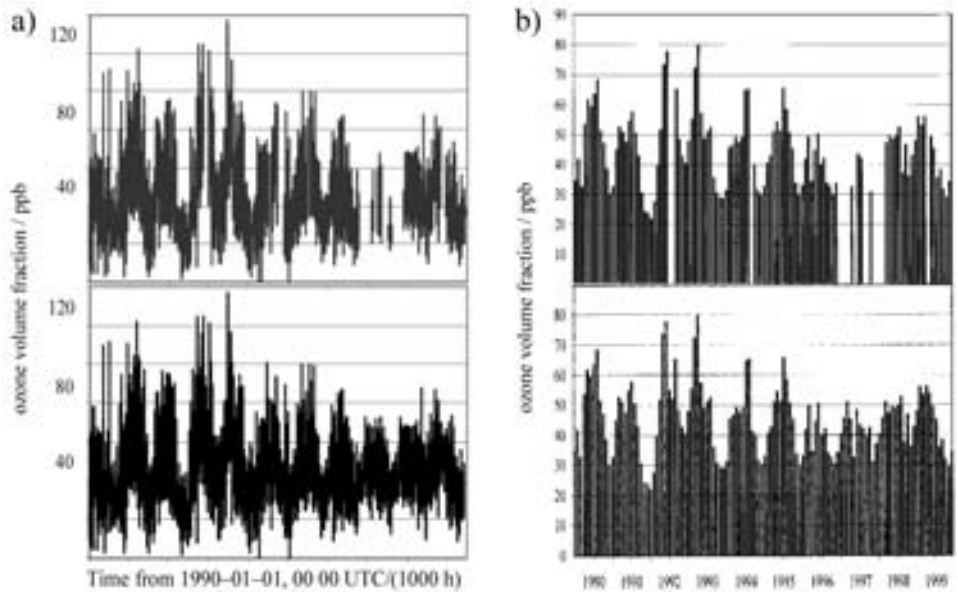


Figure 1. (a) Measured (top) and adjusted (bottom) data sets; (b) Corresponding average monthly ozone volume fractions.

Two important questions are supposed to be answered by measuring ozone at stations like Puntijarka: i) is there a trend in ozone concentration over the years, and ii) is there some not easily recognizable regularity in the data showing up in long-term measurements?

Concerning the trend, there is an indication at the Puntijarka station that the exponential rise observed for the boundary layer ozone in the last century in Europe was slowing down if not descending in the 1990's, after having reached a maximum in 1992/1993. The annual mean values, the moving averages for the 129 monthly means and the least squares statistical analysis of the years 1990–1999 confirm either no increase of ozone volume fraction or a slight decrease of 5 ppb per decade (Figure 2). A possible reason for this general trend could be the depletion of ozone in the lower stratosphere, resulting in its decreased input into the troposphere by diffu-

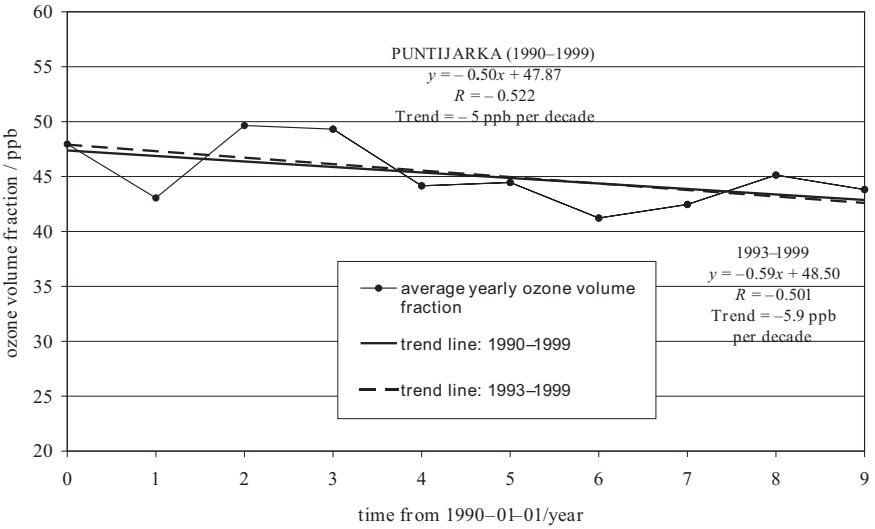


Figure 2. Average yearly ozone volume fractions and regression analysis for the Puntijarka station.

sion and intrusion, but more probably the dramatic changes in Croatian industry and transportation (considerable reduction of air traffic over Zagreb) during the last decade. Interestingly, there is a rather strong trend in monthly maxima and minima (Figure 1(b)) beginning with the year 1992 (*i.e.*, with the war in Croatia), which might be due to the smaller »titration effect«[4] because of a lower concentration of pollutants.

In order to answer the second question, we have converted the adjusted data set made up of a time series of 94,248 mean hourly ozone volume frac-

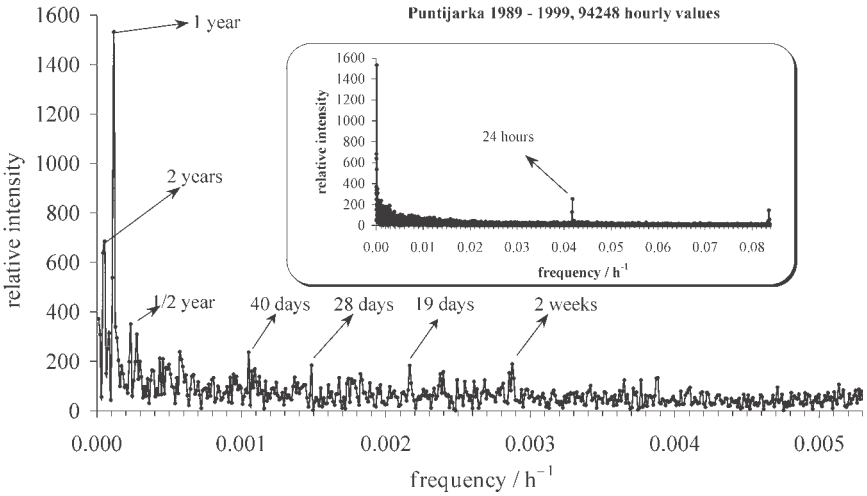


Figure 3. Fourier transform spectrum of the adjusted data set (Figure 1(a) bottom) of ozone volume fractions.

tions by Fourier transform to a frequency series (Figure 3). The transformation reveals regularities over the investigated period of time in terms of frequencies, *i.e.* recurrent events. It is interesting to note that the same regularities were found also by the transformation of the original, not adjusted, data set. Some of them, *e.g.* the 1-year, 24-hour and 12-hour frequencies were expected. The biannual frequency is more surprising, but similar (»quasibiannual«) behavior has been observed before in meteorology and aeronomy (Antarctic »ozone hole«). Most surprising are the 4- and 2-week frequencies, which, of course, can have nothing to do with the lunar cycle but could be an indication of a bias in the data. Namely, Medvednica is a resort area and it is possible that the enhanced weekend traffic to the mountain is reflected in the increased ozone production. Since the Fourier transformation of limited data sets (spectra) can result in observation of artifacts, we are currently investigating the long-term ozone data series from other similar stations in Europe to look for clues to explaining the present findings. It is interesting to compare the Puntijarka station and the nearby TOR station Krvavec, Slovenia, at 46.3° N, 14.5° E and 980 m a.s.l., with other TOR stations in the winter and summer periods (Figure 4, see also Ref. 11). They fit well on the surface representing the mean summer ozone values recorded at TOR ground stations all over Europe but are outliers of the surface for the corresponding winter values. We explain this by the fact, that unlike the other stations, the elevated stations Puntijarka and Krvavec are within the free troposphere during the winter periods.

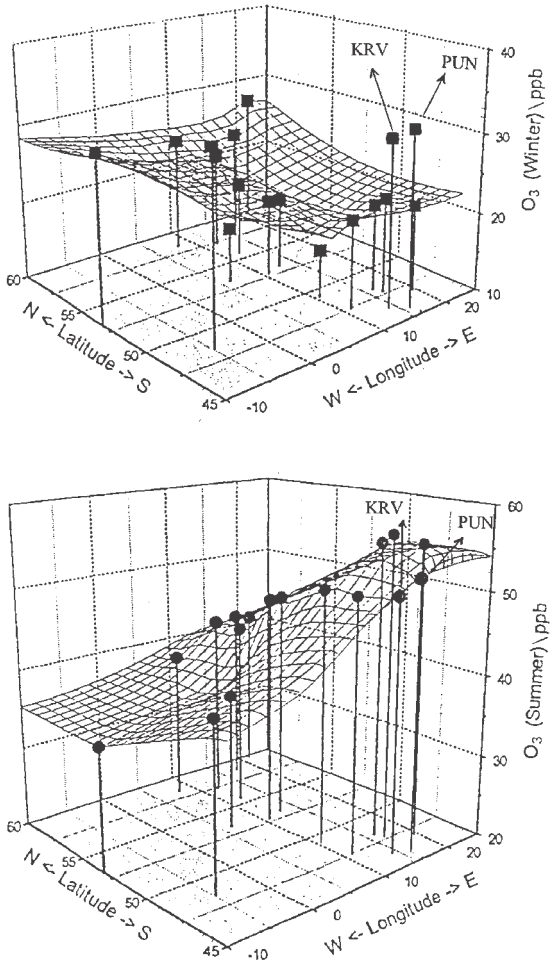


Figure 4. Comparison of the Puntijarka (PUN) and Krvavec (KRV) station data with the data for EUROTRAC/TOR low altitude stations[8] during winter (top) and summer (bottom) months.

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## SAŽETAK

### Analiza podataka dugoročnog mjerenja ozona

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Razmotreni su različiti pristupi analizi 10-godišnjih podataka kontinuiranog mjerenja ozona na postaji Puntijarka kraj Zagreba. Postaja Puntijarka, s koordinatama 45,90° S; 15,97° I, 980 m iznad morske razine, ima obilježja ruralne postaje i reprezentativna je za širu regiju. U radu su korišteni satni prosjeci volumnih udjela ozona, mjereni u razdoblju 1990–1999, autokorelacijski dijagrami za sve podatke i za ljetne periode (svibanj-rujan), tzv. »box and whiskers« prikazi dnevnih hodova ozona za zimska i ljetna razdoblja, mjesečni prosjeci i 12-mjesečni pomični prosjeci te primjena Fourierove transformacije na kompletni skup podataka. Podaci pokazuju stagnaciju ili slabo opadanje volumnih udjela ozona tijekom prošlog desetljeća.