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*Original Scientific Article*

# Assessment of Variations of $O_3$ Concentrations in *Kopački Rit* Nature Park, Eastern Croatia

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*Abstract.* Result of the first ozone monitoring in ambient air Nature Park of Kopački Rit (Eastern Croatia) are reported for the growth season in 2008. The measured hourly concentrations of ozone in the air do not exceed the limit value of 110 μg $m^{-3}$ statutory regulation by Croatian legalization for the protection of human health. There were only 13 days exceeding of the target value of 120 μg $m^{-3}$ (8-h averages) as established in the European Union guidelines on ozone pollution in ambient air. In contrast to the measured AOT40 whose value does not exceed the critical level of 18 000 (μg $m^{-3}$) · h for vegetation injury, an estimated AOT40 value was somewhat higher. The relationships between $O_3$ and meteorological variables were investigated by a principal component analysis (PCA). Fourier analysis methods applied to ozone concentrations data showed that the most important variations in the $O_3$ data are represented by usual daily cycles. (doi: 10.5562/cca2147)

*Keywords:* ozone, meteorology, principal component analysis, Fourier analysis, Nature Park

## INTRODUCTION

Kopački Rit Nature Park is part of the geographic entity of Baranja located between the Drava and Danube rivers. Kopački Rit is one of the largest natural marshlands in Europe, covering an area of almost 240 $km^2$. Preservation of Kopački Rit as one of the few natural marshlands in Europe remaining intact is of great importance. This was recognized by UNESCO who nominated it for the World Heritage List.[1,2] Due to the constant changes in water levels in Kopački Rit, there are mixed woodlands with black and white poplar, oak, white willow, and hornbeam trees. Most of the space however, is occupied by swamp and aquatic vegetation.

Ozone concentrations in ambient air have been monitored at various locations in Croatia, but the only nature reserve studied in this way so far is Medvednica, a mountainous region adjacent to the large urban centre of the city of Zagreb to the north.[3]

Ozone is not emitted directly to the atmosphere, but is formed in reactions between oxides of nitrogen ($NO_x$) and volatile organic compounds (VOC), these reactions being driven by absorbed solar radiation. There are natural sources of $NO_x$, such as its production by lightning and direct emission from soils, and of BVOCs (biogenic volatile organic compounds. Air pollutants can enter a plant along with air in the course of the normal respiration of the plant, and once in the leaf of the plant, pollutants destroy chlorophyll and disrupt photosynthesis.[4]

Ozone is a phytotoxic pollutant and agent of climate change and is still considered the most important pollutant in the air for plants because an increase in background ozone concentrations over 40 ppb by a few ppb can lead to severe damage symptoms such as flecks, bleaching, bleached spotting or growth suppression.[5–8] Although emissions of ozone precursors fell during the most recent period in Europe, ozone is still an air pollutant of major concern for plants because of meteorological variability and the increasingly growing long-distance transport of pollution.[9] Various factors play a crucial role in the production and destruction of ozone. Ozone concentrations monitored at the tropospheric site are influenced by chemistry, type of terrain, vegetation and weather conditions. Meteorological conditions such as solar radiation, cloudiness, precipitation, temperature, relative humidity, wind speed and direction can strongly affect the efficiency of photochemical processes, leading to $O_3$ formation and destruction.[10–13]

The present study focuses on a marshy plain and the possible atmospheric interaction with the city of Osijek 20 km to the southeast. It is an interesting ex-

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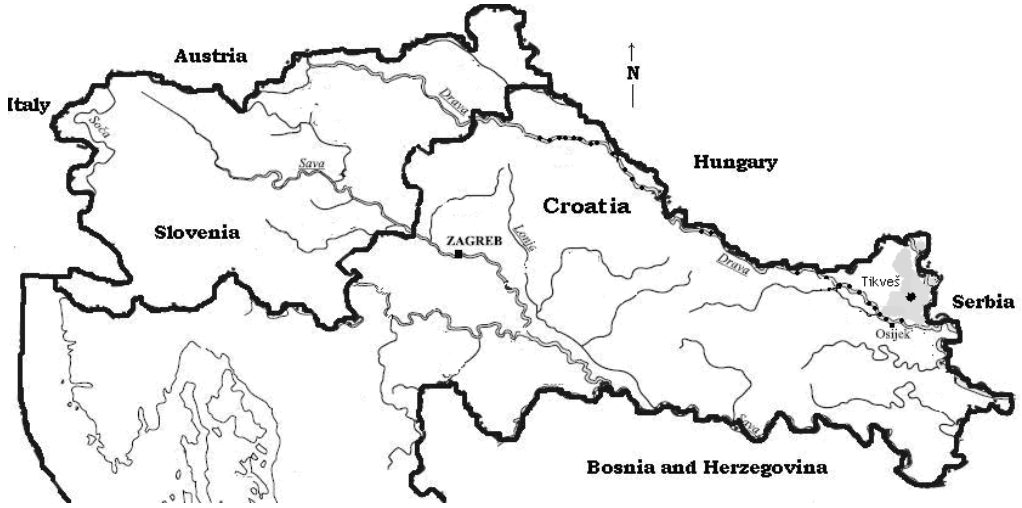


**Figure 1.** Location of the monitoring site (●) and area of Kopački Rit Nature Park (gray area).

ample of the mutual influence of urban and rural (wetland) areas and site monitoring is suitable to distinguish whether winds bringing air from the agricultural and marshy region of Baranja have a significantly different influence on the measured ozone volume fractions as compared to winds from the south bringing air masses *via* the city of Osijek.

The studied area is mainly uninhabited, and there are no significant human activities within the marshland of Kopački Rit which could affect the atmospheric conditions, thus a background of clean air is expected to be present there.

However, the marshland by itself could be a major natural source of VOC's in the air and hence may contribute to the formation of tropospheric ozone which has a significant role in forest injuries.[14]

This paper discusses the results of ozone monitoring conducted at the rural site of Tikveš, located in Kopački Rit Nature Park, in the growth season (27$^{th}$ May to 30$^{th}$ September) 2008. The aim of this study was to investigate the background condition because of the lack of anthropogenic activities in this area. Diurnal and seasonal variation of ozone has been analysed and accumulated ozone time or accumulated exposure to ozone above a threshold (AOT) were also calculated. In order to examine the influence of meteorological variables on $O_3$ concentrations, principal components analysis (PCA) models were developed together for both, ozone and meteorological parameters. We used the power of chemometrics i.e. principal component analysis technique (PCA) to identify the main relationships between the ozone concentration and observed meteorological parameters. A major advantage of the PCA is that if the first few components account for a substantial portion of the total variation in the data, then we can interpret the results of the PCA by a visualization of the principal component scores and loadings.[15–18]

As there is no available data about ozone concentrations as well as the influence of meteorology on ozone levels from the rural area west of the Danube up to Medvednica, which is approximately one third of the territory of the Republic of Croatia, it is very important to obtain results from this important part of Croatia to complete the monitoring situation over the entire area of Europe.

## EXPERIMENTAL

### Measurements

The district of Kopački Rit Nature Park is located on the part of the Croatian Republic mostly in the low areas between the Drava and Danube rivers (Figure 1). Geographically, Kopački Rit extends between 45.53° and 45.78° northern latitude and 18.75° and 18.98° eastern longitude. The altitude in Baranja does not exceed 250 m, and the whole area of the Nature Park lies between 78 m (bottom lakes) and 86 m in altitude.

The monitoring site was located near Tikveš. The village of Tikveš (with a population of approximately 29) lies in the centre of the northern part of the Nature Park (45.67° N; 18.85° E), at an altitude of 82 m above sea level. The measurements took place during the growth season (27$^{th}$ May to 30$^{th}$ September 2008) by using a commercial instrument Environment S.A. based on UV absorption photometry which has been regularly checked and calibrated. The data were recorded every minute and stored in a data logger for further processing on a computer. Meteorological data were obtained from the Meteorological and Hydrological Service of Croatia who monitored the meteorological parameter at airport Klisa (it is nearest meteorological station is approx. 20 km south of the monitoring site). In this work, we used experimental data which were measured for the first time at the rural site of Tikveš.

The data were converted to hourly average ozone volume fractions and analyzed in relation to meteorological parameters: duration of sunshine (Sun, expressed in h), temperature (*T*, expressed in °C), relative humidity (RH, expressed in %), cloudiness (Clo, expressed in %), precipitation (Pr expressed in mm/min), wind speed (WS expressed in m/s), visibility (Vis, expressed in km) and wind direction (expressed in degrees).

## Methods

*Principal Component Analysis (PCA)*

Multivariate methods such as PCA are frequently used for handling monitoring data. One of the reasons for the use of PCA in environmetrics resides in the enormous amount of data produced by measurement techniques. In adition, PCA allows us to observe the sources of variation in complex data, it can be used for classification of data, finding similarities and outliers and can explain the association between samples (objects) and variables.The purpose of PCA is to find simple underlying principal components (PCs) and to attribute characteristic features to them.

In general:

$$C_i = l_{1i} X_1 + l_{2i} X_2 + \ldots + l_{ni} X_n \quad (1)$$

where PCi is the *i*-th principal component and $l_{ji}$ is the loading of the observed variable *Xj*.

PCs are arranged in decreasing order according to the percentage of the variance they account for. The main goal is to obtain a small number of components that would explain most of the total variation in the data set. Interpretation of the data may be easier using the rotation procedure, thus, in this study principal components were subjected to raw varimax rotation. Before computations the data were mean (average) centered in order to avoid misclassifications arising from different orders of magnitude of observed variables.

More details on this method can be found elsewhere.[17]

*Fourier analysis*

Several expected (1-year, 24-hour) regularities in ozone concentrations were found to exist naturally. Although there is no known natural or meteorological mechanism that creates cycles with weekly periodicity, such cycles have been shown to exist in and around human centers of urbanization and have been generally attributed to anthropogenic causes.[18] Ozone concentrations data is time series data, therefore an ideal way of analyzing periodicity in the time series data is by Fourier analysis. In addition to noticeable cycles, the measured data may contain some less noticeable features (*e.g.* pertaining to a particular region) observable after applying Fourier analysis method. In this study the data obtained in the period of continuous ozone monitoring (no missing data) were analyzed by applying Fourier analysis in order to identify significant regularities as well as possible less noticeable ones in *t*-domain.[8,13,17]

## RESULTS

Measurements conducted in Kopački Rit have shown a great diversity in ozone concentrations during the monitored period. As seen in Figure 2, maximum daily average ozone volume fractions were recorded in May, minimum values were detected at the end of the growing period, in September. Average values for the growing season (May to September) fluctuated between 7.97 and 54.84 ppb with average values of about 30 ppb (≈ 60 μg $m^{-3}$). As shown in Figure 2, 24-h average values of $O_3$ were lower than 110 μg $m^{-3}$ which is the Croatian national ambient air quality standard (target value) for human health protection.[19]

The very useful presentation of the measurement data is obtained by plotting the median percentile values as a box as well as the minimum and maximum values as whiskers for each hour of the day. Such a graph gives a lot of statistical information for a given day and also points out higher values of ozone volume fractions happening on a very short time basis. The average diurnal variations of ozone concentrations are shown in Figure 3. in the form of a box- and- whiskers diagram.

The daily cycle of ozone is quite pronounced with the highest value of 85.1 ppb. The lowest ozone values (below 10 ppb) were measured in the early morning hours and a maximum value (above 80 ppb) in the early afternoon. Afterwards, $O_3$ volume fractions started to decrease. As shown in Figure 3, the $O_3$ concentrations values did not exceed the information and alert threshold values for hourly averages prescribed by the European Union legalization to protect human health.[20] In reactions with the ozone precursors $NO_x$ and VOC's are formed: aldehydes, peroxides peroxy acyl nitrates and

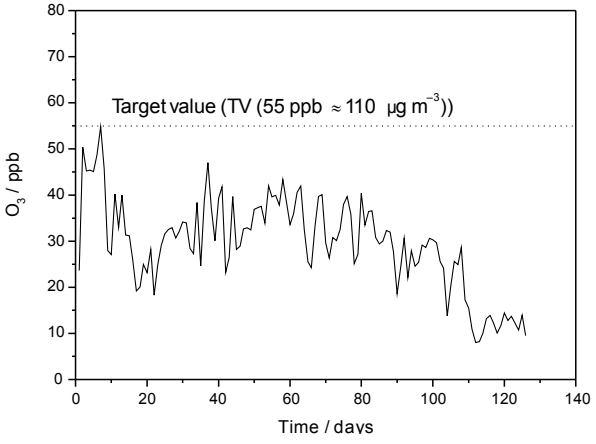


**Figure 2.** Daily mean ozone volume fractions for the May to September period of 2008.

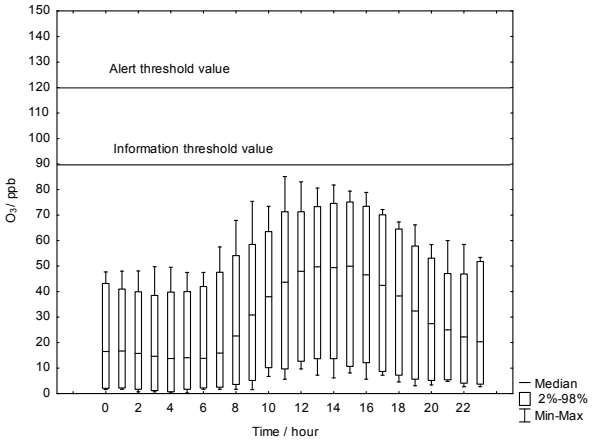


**Figure 3.** Box-and-whiskers plot of ozone volume fractions for measured period.

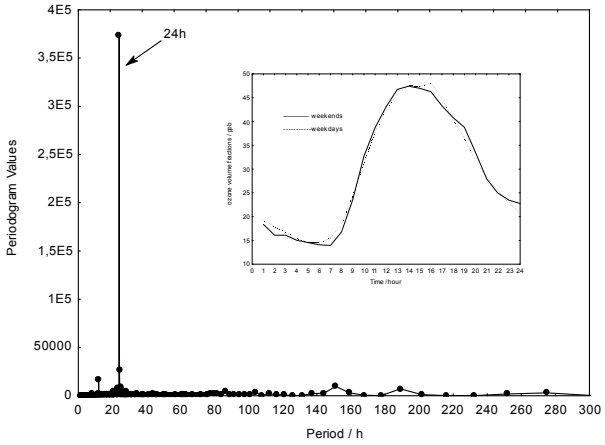


**Figure 5.** Fourie spectra for grow season 2008 and figure located within that displays average diurnal changes of $O_3$ by day of week.

other compounds which can have very harmful effects. Hydroxyl radical represents the most important reactant which is involved in the range of reactions which accompany the development of ozone in the troposphere. It is involved in the degradation of hydrocarbons and carbon monoxide. During this reaction with the hydroxyl radical and expending causes formation of either $RO_2^{\bullet}$ or $HO_2^{\bullet}$ radicals. However even lowest concentrations of $NO^{\cdot}$ radicals $HO_2^{\bullet}$ transform back to hydroxyl radicals. During this reaction $NO_2$ is formed, which is a precursor of ozone and ozone therefore formation increases with gusts concentrations of hydrocarbons.[21,22]

Figure 4 presents correlations between the wind and ozone concentrations. Although somewhat higher concentrations were recorded in the sector extending west to northwest, there were no significant differences in ozone concentrations as far as wind direction is concerned.

For the calculation of $AOT40_{measured}$ value for the protection of vegetation we used hourly mean values above 40 ppb (80 μg $m^{-3}$) of a 12 hour daylight period (8:00 to 20:00 CET) from 27$^{th}$ May to 30$^{th}$ July. In order to avoid underestimation of the AOT40 (due to missing data) the measured AOT40 calculated on the basis of the available measurements was weighted.[20] Thus, we calculated $AOT40_{estimate}$ because there were not available data for all of May 2008. In contrast the $AOT40_{measured}$ (11 450 μg $m^{-3}$ h), $AOT40_{estimate}$ value (22 900 μg $m^{-3}$ h), exceed the critical level of 18 000 μg $m^{-3}$·h for the protection of vegetation.[20]

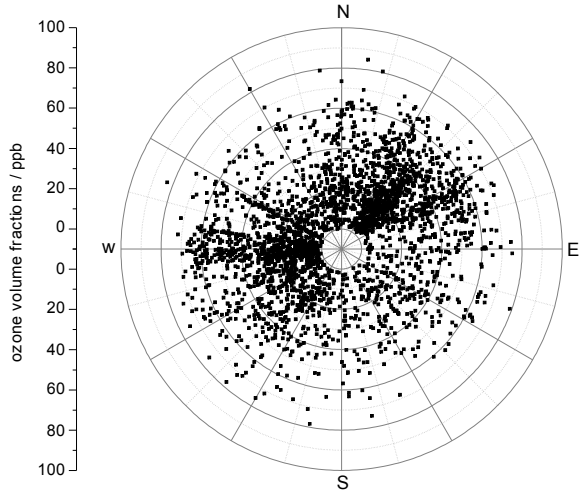


**Figure 4.** Wind rose (measured ozone concentrations at measured wind directions).

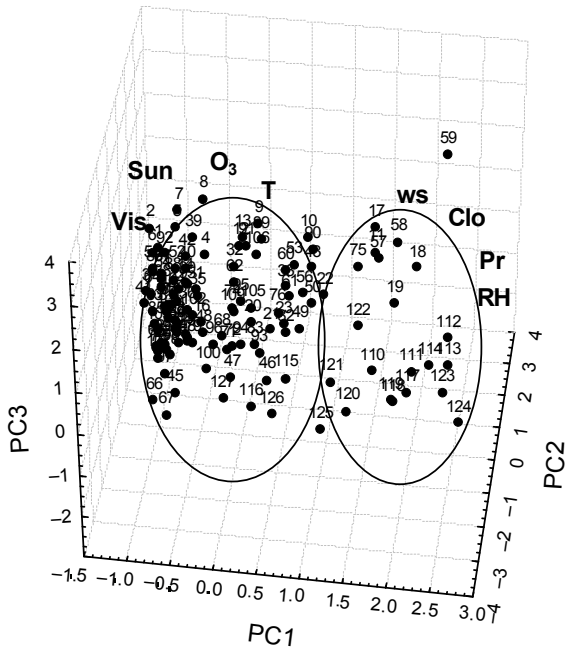


**Figure 6.** 3D plot of scores and loadings for ozone and meteorological parameters: visibility (Vis), Sun radiation (Sun), temperature (T), wind speed (ws), cloudy (Clo), precipitations (Pr), relative humidity (RH).

Ozone volume fractions data by its nature is time series data, therefore an ideal way of analyzing periodic data is by Fourier analysis. Time series of 3024 mean hourly ozone fractions in *t*-domain are transformed into frequency domain using a Fourier transform method and are expressed by a periodogram. It is clearly seen in Figure 5 that only semi-daily and daily cycles are observed. Simultaneously, the small figure located within Figure 5 shows the weekend effect *i.e* higher concentrations of $O_3$ during the weekend were not observed.

PCA, followed by varimax rotation yields the results given in Figure 6 for the loadings and scores (*i.e.* bi-plot). It provides an overview of interrelationships between monitored parameters and collected air samples. The model developed for both $O_3$ and meteorological variables showed that ozone concentrations are highly positively correlated with air temperature, sunshine duration time and visibility but negatively with relative humidity, precipitation, cloudiness and wind speed. The bi-plot can also be used for the determination of the contribution of the various sources of variances (PCs) on each day. For example, Figure 6 shows the 127 objects (days) plotted in a plane defined by three components. It is possible to see similarities and differences and then make a classification of the days into groups. Two main clusters of objects can be distinguished: a rather compact cluster in the left-hand portion of the figure contains the majority of cases. Since the variables that point toward certain objects are more important for those objects, it is obvious that these were the days with higher ozone concentrations, higher temperatures and longer sunshine duration, but lower relative humidity, wind speed, cloudiness and precipitation, which was expected. The thin cluster in the right portion of Figure 6. contains the days which are less frequent. It can clearly be seen in Figure 6 that these days (mostly mid-June and the second part of September) were characterized by a higher relative humidity, precipitation and wind speed but lower temperature, solar radiation time, and consequently, lower ozone concentrations.

## DISCUSSION

The ozone levels recorded in this study represent the background ozone in the marshland area of Kopački Rit Nature Park, which had never been investigated in this way, until now. This area is isolated from major pollution sources and nearby roads have little traffic. There are no significant human activities within the marshland of Kopački Rit which could affect the atmospheric conditions in the area. However, the marshland by itself could be a major natural source of biogenic volatile hydrocarbons whose emission into the air is most intensive at noon.

A strong diurnal profile is observed for Kopački Rit with the afternoon values being almost three times higher than the nocturnal ones. This difference of ozone between day and night is likely to be attributed almost to the physical processes because the influence of the chemistry during the night (anthropogenic influences are low) is not significant. In accordance with the Croatian Law on Air Quality values, the target value for the protection of human health of 110 μg $m^{-3}$ (24-h averages) was not exceeded, which means that the air could be considered clean with respect to ozone. Ozone concentrations did not exceed information (90 ppb ≈ 180 μg $m^{-3}$) and alert threshold (120 ppb ≈ 240 μg $m^{-3)}$ values for ozone as established in European Union legalization to protect human health.[20] Regarding the protection of human health there were only 13 days exceeding of the 60 ppb (120 μg $m^{-3}$) threshold versus the 25 days per calendar year as established in the European Union Directive on $O_3$ pollution in ambient air and also in Croatian law. Since higher concentrations of ozone are expected in the spring and summer months we do not expect that this value at Tikveš could be exceeded if we take into account the entire year. Measured daily values of the ozone have decreased over the period measured (Figure 2). This is expected, the proportion of winter ozone accumulates in the air and the spring portion of ozone in the air decreases. The behavior of ozone in the air during the year has its own periodicity, and takes turns and trends.[36]

Although new assessment methods were developed[23–25] the AOT concept, due to its simplicity is still useful as a preliminary tool for the prediction of the risk of plant injuries.[20,26]

The value of estimated AOT40 suggests that over the period May-July 2008 the target value for the protection of vegetation was exceeded. It should be taken into account that only one year is considered, thus our result should be viewed as a preliminary finding. The ozone plant injury is more closely related to dose (ozone flux through the stomata) than to external ozone exposure. Nevertheless, as pointed out, both standards have their limitations and an ideal ozone standard should be biologicallybased.[25] Certainly, studies of damage on vegetation are needed to evaluate the condition of the vegetation and the impact of ozone on them. Until today, there has not been any research related to plant injury by ozone for vegetation in the Kopački Rit area.

Ozone concentrations are highly variable in the lower atmosphere where meteorological conditions may greatly affect its level. By using the PCA technique we have tried to reveal underlying relationships between ozone concentrations and meteorological data. As can be seen in Figure 6 conditions of higher temperatures, sun radiation time, visibility and lower wind speed providing the necessary energy to ozone formation showed comparatively higher ozone concentrations. The

results of the PCA show that wind speed showed a negative correlation with ozone concentrations, which indicates an increase in its level with a decrease of wind speed. Conversely, lower ozone concentrations are supported by wet, cloudy, rainy, windy weather with high relative humidity. A similar pattern was observed by several studies conducted in these areas.[8,13,15,16] Ozone concentrations are highly influenced by temperature because of the temperature dependences of the number of reactions involved.[4] As is well known[27–29] the isoprene emission, like ozone, increases with ambient temperature and solar radiation, resulting in the highest emission at noon. The preliminary research conducted in Kopački Rit during the growing period in 2008 showed that daily periods of increased ozone concentrations coincide with the occurrence of maximum isoprene concentrations in accordance with the mechanisms of its being released from deciduous trees and wetland plants.[30,31] The analysis has shown that no difference in behavior was found and no pronounced wind direction, which is associated with significantly higher ozone concentrations. Although Kopački Rit Nature Park is tourist resort, bicycle and boat tourism in this area are the most common activities over a greater period of the year. With no significant local emission sources close to a measuring station it should not be surprising that there is no difference in the daily variation between weekends and weekdays and there was no 7-day periodicity which can be addressed to anthropogenic causes.[32,33] The measurements of ozone levels in the Reserve Park during growing period 2008 showed that daily median values (13–50 ppb) seem to be not much higher than those observed in an urban atmosphere of Eastern Croatia during 2002 (7–38 ppb) and 2007 (11–48 ppb).[8,13,35] Such small differences should not be surprising if one takes into account the results of recent studies that showed that in the nearby urban centre, the city of Osijek, where industry is not very active and precursor emissions are mainly due to traffic, no significant photochemical pollution problems were detected. As in previous studies[8,13,34] no significant influence of wind direction on ozone concentrations has been observed. South-westerly wind (which brings air masses from the city centre) does not have a significant effect on ozone concentrations compared to the rest of the wind directions (which bring air masses from the surrounding agricultural area of Baranja).

Although elevated $O_3$ concentrations during 2008 were measured mostly in rural Mediterranean areas, ozone levels during the growing season of 2008 were the lowest since the reporting of Europe-wide data commenced in 1997.[35] Therefore, categorization of air quality in the rural part of Croatia and especially in numerous Croatian nature reserves and national parks should be based on the whole year's measurements which will form the basis of future investigations.

## CONCLUSION

The results of the first ozone volume fractions measurements in the rural-marshy area of Kopački Rit Nature Park located in Eastern Croatia, during the growing season of 2008 showed that the ozone level is not alarming, thus no significant photochemical pollution problems were observed in this protected area. The results of the Fourier analysis showed that the most important variations in the $O_3$ data are represented by usual semi-daily and daily cycles, and that additional oscillations which can be considered to be markers of anthropogenic influences did not occur. Principal component analysis was applied to provide the relationships between ozone concentrations and some meteorological variables. Higher ozone concentrations occurred in stagnant air under dry and sunny weather conditions.

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