Assessment of ozone variations and meteorological influences in a tourist and health resort area on the island of Mali Lošinj (Croatia)

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Abstract
The purpose of this study was to investigate ozone, variations, and its correlation with meteorological parameters at a remote location on the Mali Lošinj Island, which has been a tourist and health resort area in the northern Adriatic. The measured data are discussed in relation to the EU guidelines (Directive 2002/3/EC; Directive 2008/50/EC). In order to characterize ambient air with respect to ozone vegetation injury and photochemical pollution, we calculated accumulated dose over a threshold of 40 parts per billion index and two photochemical pollution indicators. The influence of local meteorological parameters on the measured ozone volume fractions was also investigated. We used the multivariate technique principal component analysis to trace correlations between measured ozone concentration and meteorological parameters.

Keywords: AOT40 index, Frequency analysis, Mali Lošinj, Mediterranean, Ozone, PCA, Photochemical pollution indicators, Vegetation injury

Introduction
In Croatia, heliomarinotherapy is practiced on the island of Lošinj located in the south of the Kvarner Bay (Northern Adriatic Coast). Although the main indication for heliomarinotherapy is psoriasis, this therapeutic option has also been used for treating atopic dermatitis and vitiligo; theoretically, it could be adapted to treat the pruritus from renal failure and human immunodeficiency virus (Stasić et al. 2004; Even-Paz and Efron 2003; Moosa and Esterhyse 2010). The therapeutic efficiency of heliomarinotherapy may be influenced by various climatic and meteorological factors, seasonal variations of tropospheric ozone, as well as by their mutual dependences on meteorological factors (Even-Paz and Efron 2003). Despite of its great influence on human activities and health, ozone in this part of Northern Adriatic is not
sufficiently researched and analyzed, especially concerning the meteorological basis of its 24-hourly variations.

At ground level in the atmospheric boundary layer, ozone is an important oxidant. It is formed in air by photochemical reactions of precursor pollutants such as NO\textsubscript{x} and volatile organic compounds (VOCs). In the Mediterranean, the summer months are of highest interest due to favorable meteorological conditions, high insolation, as well as anthropogenic and biogenic ozone precursors concentrations that favor photochemical ozone production (Dueñas et al. 2002; Paoletti 2009; Kalabokas et al. 2007, 2008; Sánchez et al. 2008; Schürmann et al. 2009; Notario et al. 2012).

Exposure to pollutants, in particular to ozone and particulate matter, leads to adverse health effects such as asthma, bronchitis, heart attack, and other cardiopulmonary problems and even premature death (Kunst et al. 1999; Stedman 2004; Chen et al. 2010). The target value for the protection of human health is 120 \(\mu\text{g/m}^3\) (8-h running averages) that may not be exceeded on more than 25 days per calendar year averaged over 3 years, which is in use in European countries. (Directive 2002/3/E; Directive 2008/50/EC).

Among many environmental effects, ozone also affects vegetation. The damage considered significant here includes growth changes, yield losses, visible injury, and reduced seed production and quality (Bytnerowicz et al. 2007; Ashmore 2005; Cape 2008; Wittig et al. 2009). Risks for agricultural and horticultural crops and forests are currently evaluated in Europe with the exposure index accumulated dose over a threshold of 40 parts per billion (ppb) (AOT40), i.e., the sum of the difference between hourly concentrations greater than 80 \(\mu\text{g/m}^3\) (=40 ppb) and 80 \(\mu\text{g/m}^3\) over a given period during daylight hours (Directive 2002/3/EC; Directive 2008/50/EC; Ferretti et al. 2007). An AOT40 of 20,000 (\(\mu\text{g/m}^3\times\text{hours}\) for daylight hours (from 08:00 to 20:00 CET), accumulated over a 6-month growing season (April to September), was proposed as a critical level to protect forest trees. For the protection of vegetation, the critical value for AOT40, accumulated over a 3-month growing season (May–July), is 18,000 (\(\mu\text{g/m}^3\times\text{hours}\) averaged over 5 years with a long-term objective of 6,000 (\(\mu\text{g/m}^3\times\text{hours}\) (Directive 2002/3/EC; Directive 2008/50/EC). Under this perspective, the knowledge about AOT40 values is important for assessment of risk of forest and vegetation injuries due to ozone exposure.

Another approach for the assessment of ambient air quality through the monitoring of ozone is by calculating photochemical pollution indicators (Kovač-Andrić et al. 2010; Klasinc et al. 2011). These indicators use as a basic parameter the average of the daily maximum to minimum ratio of hourly ozone concentrations over a period of time corrected by taking into account either daily average of ozone and its maximum or the time a limit value has been exceeded.

Meteorology plays an important role in the formation and transport of ozone. Changes in weather conditions, i.e., light winds, high temperatures, and strong sunlight (clear sky), can affect the formation and increase in ozone volume fraction in the boundary layer. Principal component analysis (PCA) was used to identify the important factors influencing ozone concentrations, for examination of outliers, and clustering of days. Summer months are of particular interest because the arrival of a large number of tourists and an associated increase in traffic (Božić et al. 2006), which causes a substantial increase in pollution. The influence of meteorological variables on the ozone concentrations during this period is particularly wind direction.

**Experimental**

The town of Mali Lošinj is situated in the southern part of the island of Lošinj, in the northern Adriatic, and it is a small maritime, commercial, and tourist center. The climate is
Mediterranean, with average summer temperatures of 24 °C and winter of 11.7 °C. With over 2,600 h of sunshine per year, or an average of about 7 h a day, Mali Lošinj is one of the sunniest places in Croatia.

Measurements of ozone concentration were carried out during the spring, summer, and autumn months of 2005 at Mali Lošinj (44.53° N 14.46° E, 43 m a.s.l.) (see Fig. 1). The monitoring station was located away from major pollution sources. The closest emission sources are Pula (air distance 63 km), Zadar (air distance 79 km), and the highly industrialized town of Rijeka (air distance 85 km). There are no significant pollution sources on the island itself except increased traffic during the tourist season. The monitoring period was from April 27th 2005 to October 19th 2005. We achieved 100 % coverage of data for the vegetation growing season (May–July) and 85.2 % coverage of data for the 6-month growing season (April–September) as we started the measuring campaign at the end of April. Ozone has been monitored with a commercial UV photometer Ansyco O341M (Environnement S.A.). The equipment has regularly maintained and calibrated.

Meteorological data were obtained from the Meteorological and Hydrological Service of Croatia. Monitored meteorological parameters were solar radiation time (Sun, expressed in hours), temperature (t expressed in degrees Celsius), relative humidity (Rh, expressed in percent), cloudiness (Clo, expressed in percent), visibility (Vis, expressed in kilometers), wind speed (WS, expressed in kilometres per hour), precipitation (Pr, expressed in millimeter), and pressure (p, expressed in hectopascal).

**Results and discussion**

Based on the 1-min values obtained from the instrument, we calculated hourly mean values, diurnal distribution of ozone volume fractions, and the eight hours running averages. Variation of ozone in relation with meteorological parameters has been analyzed, and photochemical pollution indicators and an AOT40 exposure index were also calculated. The PCA method has also been used to investigate relationships between ozone volume fractions and meteorological variables.
**Daily and seasonal ozone variations and frequency analysis**

This section describes the daily distribution of ozone volume fractions, seasonal cycles, and frequency analysis of ozone data for the monitoring period. The box and whiskers plot in Fig. 2 summarizes the hourly ozone volume fractions for the measuring period at Mali Lošinj. The daily range of variation during the spring and summer are more marked than in autumn, when the range is smaller. Concentrations decline from a peak in the spring to a minimum during the autumn, which is typical of a Northern Hemisphere rural site. During spring and summer periods are pronounced diurnal cycle with low levels of ozone in the early morning, minimum around 7 am local time, and peak concentrations in the afternoon, from 12 to 16 pm local time. This pattern is likely to be attributed almost exclusively to physical processes as the influence of chemistry in this nonindustrial and health resort area is expected to be minimal. The ozone levels tended to follow the daily cycles of temperature and solar radiation intensity, resulting in higher ozone levels during the daylight hours. The information (180 µg m⁻³) and alert (240 µg m⁻³) threshold value of the 98th percentile values for hourly averages as established in European Union legislation to protect human health were not exceeded once throughout the measurement period. Regarding the protection of human health, there were only 9.6 days exceeding the 60 ppb threshold versus the 25 days per calendar year as established in the EU Directive and also in Croatian law for ozone pollution in ambient air. Since higher concentrations of ozone are expected in spring and summer months, we do not expect that this value at Mali Lošinj might be exceeded if we take into account the entire year. For comparison, due to long warm summer, at some locations in the nearby Rijeka Bay, the number of days exceeding the running 8-h target value for human health protection in 2005 were considerably higher (as much as 130 days) (Alebić-Juretić 2011).

![Box and whiskers plot of the hourly ozone volume fractions for the period April 27 to October 19, 2005 at Mali Lošinj.](image)

It is well known that this coastal site is highly visited in summer months being an important medical and touristic destination, so ozone concentrations can be influenced by human activities. There is no known natural or meteorological mechanism that creates climate cycles
with weekly periodicity, but such cycles have been shown to exist in and around centers of urbanization and have been generally attributed to anthropogenic activities (Shuters and Balling Jr. 2006; Klasinc et al. 2008; Cvitaš et al. 2004; Kovač-Andrić et al. 2009; Gvozdić et al. 2011). To investigate the occurrence of possible ozone “weekend effect” at the site, we examined the weekly cycles of hourly averaged ozone concentrations. The timing of maximum and minimum ozone concentrations did not vary between weekend and weekdays. Maximum ozone concentrations were observed around 15–16 pm and minimum between 6 and 8 am both on weekend and weekdays. In Fig. 3, we observed differences of only 1–3 ppb in ozone volume fractions for weekdays and weekend days. Applying criteria by Blanchard and Fairley (Adame et al. 2008), which propose that the weekend effect is generally statistically significant if the ozone concentration difference exceeds 10 µg m⁻³ (≈5 ppb), we conclude that Mali Lošinj does not show a weekend effect, but it still indicates that the weekend values are higher, which somewhat expected at rural sites with some influence from traffic due to titration of ozone from NOₓ due to car exhausts (Kley et al. 1994).

![Fourier transformation of O₃ data](image)

**Fig. 3** The Fourier transformation of O₃ data and average hourly ozone volume fractions for weekdays and weekends for the measurement period at the site of Mali Lošinj. The number of hours corresponding to the statistically significant frequency peaks is denoted by an arrow.

Nevertheless, in order to investigate existence of possible significant periodicities in the time series of ozone data, we calculated their Fourier spectra for the whole measurement period. Fourier analysis confirms the existence of variation in ozone volume fractions periods such as usual daily cycle, but a statistically significant frequency peak for a 7-day cycle was not observed. The occurrence of the weekend effect is usually observed at highly polluted sites, where emission changes have an immediate and detectable influence on photochemistry. However, this phenomenon is often attenuated if there are other factors contributing to the ozone formation, for example, in coastal areas the influence of coastal breezes. Therefore, local atmospheric mechanisms may affect the ozone levels more strongly than possible changes in the emissions of precursors according to the weekday (Adame et al. 2008).
AOT40 index and photochemical pollution indicators

For the calculation of AOT40 values, we used hourly mean values above 40 ppb (80 µg/m$^3$) of 12 h daylight period (0800 to 2000 CET) between May–July and April–September. There were 1,472 h for the period of April–September and 1,008 h for the period May–July above the threshold of 40 ppb. We also calculated AOT40 estimate because there were no available data for all days for April 2005 (see Table 1). Total possible number of hours (the number of hours within the time period of AOT40 definition) for the period 1 April–30 September (0800 to 2000 CET) is 2,196 h.

**Table 1** Data coverage, AOT40 measured, and AOT40 estimate for the measurements at Mali Lošinj for the period April to September 2005.

<table>
<thead>
<tr>
<th>Growing season</th>
<th>Data coverage (%)</th>
<th>AOT40 measured (µg/m$^3$) × hours</th>
<th>AOT40 estimate (µg/m$^3$) × hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>May–July</td>
<td>100</td>
<td>26,100</td>
<td>–</td>
</tr>
<tr>
<td>April–September</td>
<td>85.2</td>
<td>32,067</td>
<td>37,637</td>
</tr>
</tbody>
</table>

In the period 1 May to 31 July, we have 100 % coverage of ozone data. For the period 1 April–30 September, we have missing data, and the hourly data coverage is 85.2 %. Thus, we calculated AOT40 estimate in regard to 100 % data coverage.

AOT40 estimate is calculated from the formula:

$$\text{AOT40 estimate} = \text{AOT40 measured} \times \frac{\text{total possible number of hours (⋆)}}{\text{number of measured hourly values}}$$

All the values for AOT40, measured and estimated, exceed the critical level of 20,000 (µg/m$^3$) × hours for the protection of forest and of 18,000 (µg/m$^3$) × hours for the protection of vegetation. Until today, in Croatia, there has not been any research related to the injury of forest trees on the island of Lošinj. Nevertheless, as pointed out by many authors in the literature, ozone plant injury is more closely related to dose (ozone flux through the stomata) than to external ozone exposure (Cieslik 2004; Mills et al. 2011; Baumgarten et al. 2009.) Thus, studies of damage on trees are needed to evaluate the condition of the trees and the impact of ozone on them. However, the AOT40 index indicates that there is a possibility of ozone injury on vegetation.

To characterize ambient air with respect to photochemical pollution, we also calculated two photochemical pollution indicators. These two parameters are the ozone volume fractions in excess of an hourly average of 80 ppb as the limit value for air quality. One gives an overall total volume fraction that crossed the limit for the entire period measured, and the second is the total number of hours in which he exceeded the limit of 80 ppb. If the index value $P_1 < 7$, measurement sites are considered clean due to photochemical pollution. Calculating the index $P_2$ gives a simple option of grouping the data into three classes: pure ($P_2 < 10$), medium clear ($10 < P_2 < 40$), and the contaminated area ($P_2 < 100$) (Kovač-Andrić et al. 2010; Klasinc et al. 2011). The photochemical pollution indicators for the period April–September were calculated from the formula $P_1 = R*M/A$ and $P_2 = R*(1 + 7*D/N_d)$, where $R$ is the average maximum to minimum ratio of hourly ozone data, $M$ is the average maximum value obtained as the average of daily maximum values, $A$ is the average of hourly mean values, $D$ is the number of hours ozone volume fractions exceeded the limit of 80 ppb, and $N_d$ is the number
of monitoring days per monitoring period, in our case 176 days. Thus, with indicator values below 2, $P_1 = 1.92$ and $P_2 = 1.72$, the location of Mali Lošinj can be considered as relatively clean area with negligible local photochemical pollution.

**PCA and influence of meteorology**

The relationship of ozone volume fractions with winds from different sectors was studied in order to investigate the possible transport of ozone from various directions. Since ozone is generated during daylight hours, the aim of this research was to perform PCA of diurnal mean ozone concentrations only for that period, and meteorological parameters are thus calculated as the mean values for that period. Figure 4 presents the correlation between the wind directions and ozone volume fractions. It is not surprising that higher ozone concentrations arrive with southwest air masses as there is a possibility of overseas transboundary transport of pollution coming from west Mediterranean area. This finding is also consistent with the results of Prtenjak et al. (2009) who reported higher ozone concentrations in the Rijeka Bay area advected from Gulf of Trieste. The Rijeka Bay has a unique topography where airborne pollutants are not easily ventilated out of the Bay under light wind conditions. O$_3$ originating from Gulf of Trieste is carried by the western sea breeze and then caught by the convergence zone above Istria (Prtenjak et al. 2009). However, climatological studies conducted along the Adriatic Coast from June to September showed that the strongest sea breezes ($5.5$ m s$^{-1}$) are observed in Mali Lošinj, which makes this area much more ventilated and thus more comfortable and healthy for humans than the coastal region. This finding is supported by the fact that average monthly ozone concentrations in Mali Lošinj region were lower in comparison with concentrations measured at several sites of the Rijeka Bay area, in the same period (Alebić-Juretić 2011).

**Fig. 4** Average ozone volume fractions for different wind directions at Mali Lošinj for the monitoring period April to October 2005

A good understanding of the connection between meteorology and ozone concentrations is needed to evaluate the likely effects of climatic changes on ozone concentrations. PCA has
been successfully applied to identify the dominant relationships presented in measured data (Statheropoulos et al. 1998).

To investigate the influence of meteorological parameters on ozone volume fractions, a PCA model has been developed (Lengyel et al. 2004; Abdul-Wahab et al. 2005; Kovač-Andrić et al. 2009; Gvozdić et al. 2011). PCA, followed by varimax rotation, yields the results given in Fig. 5 for the loadings and scores (i.e., biplot). It provides an overview of interrelationships between monitored meteorological parameters and collected air samples. The model developed for both the ozone and meteorological variables showed that ozone is highly correlated with temperature, pressure, solar radiation time, and visibility. Ozone concentrations are highly influenced by temperature and sun radiation time, which reflects the importance of photochemistry for ozone formation. It is known that Mediterranean summers, connected with high pressure systems leading to subsidence, stability, clear skies, and high sun intensity, enhance photochemical processes and emissions of biogenic volatile organic compounds to the atmosphere (Kalabokas and Repapis 2004; Velchev et al. 2011).

Furthermore, analysis of these data for summer showed wind speed does not affect ozone formation, whereas relative humidity, cloud cover, and rainfall were strongly negatively correlated to \(O_3\). Higher relative humidity and wet weather are usually associated with lower ozone concentrations due to reduction of photochemical activities, but the main factor that decreases ozone concentration is reduction in radiation and temperature. Besides,
ambient humidity affects minimum temperature via absorption of long-wave radiation by the Earth that would otherwise, under dry conditions, be lost in space and via the release of the latent heat of condensation as the sensible temperature falls to dew point (Banja et al. 2012). The biplot can be used for the determination of the contribution of the various sources of variances (PCs) on each day. Figure 5 shows the objects (176 days) plotted in a plane defined by three components. Two main clusters of objects can be distinguished: A rather compact cluster in the right-hand portion of the figure contains the majority of days (mainly from end of April until September). Since the variables that point toward certain objects are more important for those objects, it is obvious that these were the hot, cloudless, sunny days with light winds, higher atmospheric pressure (stagnant anticyclonic conditions), and consequently higher ozone concentrations. Thin cluster in the left portion of Fig. 5 contains the days, which are less frequent. It can clearly be seen that these days (mostly the first part of October) and lower ozone concentrations were supported by mostly cyclonic conditions (i.e., substantial cloud cover, as well as rainy, windy weather). It has been proven that PCA can be a useful and effective tool for researching voluminous sets of data such as ozone and meteorological data. Its application helped to visualize two distinct clusters with different ozone concentrations as well as dominant relationships existing in measured data.

Conclusion

Although Mali Lošinj is during summer period under heavier traffic load, the values of the two photochemical pollution indicators indicate low photochemical pollution, which is a consequence of anthropogenic factors, not just the local emissions. The values of AOT40 cumulative index show that there is a possibility of ozone injury to vegetation, but in regard to the value for the protection of human health, ozone concentrations are below the limits given by the EU Directive and Croatian law. The results of PCA revealed underlying relationships among O₃ concentrations and meteorological data and showed that higher ozone concentrations are associated with slow-moving high pressure weather systems that result in sunny, moist, cloudless conditions and with typically light wind and air masses advected from Adriatic Sea. PCA proved to be a useful and effective tool for analysing voluminous sets of data such ozone and meteorological data. Specific factors that contribute to the relatively moderate O₃ levels observed in the area are certainly lack of industry and its remote location with effective ventilation conditions. Further permanent studies are certainly needed to determine anthropogenic influences and transport of pollution as well as ozone injury on vegetation.

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References


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