Assessment of ozone variations and meteorological effects in an urban area in the Mediterranean Coast

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Abstract

Ozone concentrations are valuable indicators of possible health and environmental impacts. However, they are also used to monitor changes and trends in the sources of both ozone and its precursors. For this purpose, the influence of meteorological variables is a confusing factor. This study presents an analysis of a year of ozone concentrations measured in a coastal Spanish city. Firstly, the aim of this study was to perceive the daily, monthly and seasonal variation patterns of ozone concentrations. Diurnal cycles are presented by season and the fit of the data to a normal distribution is tested. In order to assess ozone behaviour under temperate weather conditions, local meteorological variables (wind direction and speed, temperature, relative humidity, pressure and rainfall) were monitored together with ozone concentrations. The main relationships we could observe in these analyses were then used to obtain a regression equation linking diurnal ozone concentrations in summer with meteorological parameters.

Keywords: Urban ozone; Coastal Mediterranean site; Meteorological parameters

1. Introduction

Increased tropospheric ozone concentrations are currently a matter of large concern. Since the beginning of this century, it is obvious that background ozone concentrations have more than doubled (Volz and Kley, 1988; Staehelin and Smith, 1991; Rydley, 1991; Staehelin et al., 1994). The assessment of ozone levels is extremely important since ozone is a key element to control the chemical composition of the troposphere and climate as it is also a greenhouse gas. The presence of ozone in the troposphere is understood to arise from two basic processes: (i) tropospheric/stratospheric exchange that causes the transport of stratospheric air, rich in ozone, into the Troposphere; and (ii) production of ozone from photochemical reactions occurring within the Troposphere. The production of ozone in the Troposphere is accomplished through a complex series of reactions referred to as the ‘photochemical smog mechanism’. Urban air pollution in many cities is currently an issue of great concern to the general public maintaining a high profile on the political agenda. The reality of numerous situations in which the near-surface...
ozone concentration exceeds the adopted threshold values, has attracted considerable public attention due to the well-known harmful impact on biosphere, human health, animal populations, agriculture productivity and forestry (Zierock and Bartaire, 1988; Lippmann, 1991; Schenone and Lorenzini, 1992; Brauer and Brook, 1997). Despite the concern, little is known about the mechanisms of chemical transformation and transportation of air pollutants within the complex geometry of an urban environment.

Although ozone chemistry has been extensively investigated in many chamber experiments and in photochemical modelling studies, there are still significant difficulties in predicting accurately ambient ozone levels, as well as its spatial distribution, behaviour and associated trends. It is believed that there are more parameters than just precursor concentrations that lead to ozone formation/destruction processes in the air.

To track and predict ozone, one must create an understanding of not only ozone itself but also the conditions that contribute to its formation. It is necessary to apply models that describe and understand the complex relationships between ozone concentrations and the many variables that cause or hinder ozone production. Some other factors, such as regional transport of ozone and its precursors, can affect ozone levels. Ozone concentrations are strongly linked to meteorological conditions. In addition, favourable meteorological conditions (clear skies, warm temperatures and soft winds) have a great influence on ozone concentrations (Vecchi and Valli, 1999). Land–sea breezes also influence ozone concentrations at coastal sites. In Europe, the highest ozone concentrations take place in summer under stable high-pressure systems with clear skies. During these episodes, ozone levels well above the international guidelines (WHO, 1987; UN-ECE, 1988) have been observed in large areas and ozone concentrations of 100–150 ppb may last for several days. The situation in the Mediterranean area is as follows (Millán et al., 1991, 1996). The ozone threshold of the European Union directive for damages to human health (120 µg m$^{-3}$, 8 h average) exceeded systematically for at least 4 months of the year, and the one for the information to the population (180 µg m$^{-3}$, hourly average) can also be exceeded frequently from April to August. The one for the vegetation (65 µg m$^{-3}$ as a 24-h average) was exceeded systematically for more than 6 months of the year. Several experts have recognised that abatement strategies are required to decrease the ozone surface levels observed (Bultges et al., 1988; Heck, 1989). Nevertheless, all of them agree that such measurements can only be proposed after improving the current state of the art in the main parameters involved in the formation of photochemical oxidants. This is particularly important in Spain, where the experimental evidence of oxidants and precursors is very limited (Zurita and Castro, 1983; Millán et al., 1991; Sánchez and Sanz, 1994).

Urban ozone formation is a complex phenomenon since this pollutant is not emitted into the atmosphere directly but it is produced thanks to the interaction of meteorology, NO, and VOCs (Finlayson-Pitts and Pitts, 1986; Saunders et al., 1991). Therefore, several surveys have tried to assess the impact of meteorological factors taking into consideration ozone levels in order to detect changes in ozone precursor emissions (Korsog and Wolff, 1991; Smith and Shively, 1995; Bloomfield et al., 1996; Cox and Chu, 1996; Dapeng et al., 1996; Pryor, 1998; Gardner and Dorling, 2000).

The work reported in this paper is an investigation into the importance of meteorology in determining surface ozone concentrations, and deals with the use of linear regression method for predicting ozone concentrations as a function of meteorological parameters. The study focuses on the impact of meteorological parameters on ozone variability at an urban Mediterranean coastal station in the city of Málaga (with a population of approx. 540 000). From November 1996 to November 1997, a sampling campaign was carried out to measure ozone concentrations under typical temperate weather conditions. The campaign was aimed at studying ozone concentrations and the influence of the most relevant meteorological variables on an average coastal Spanish city where precursor emissions are mainly due to traffic exhaust.
2. Measurements

Ozone levels were continuously monitored using Dasibi Environmental Corporation instrumentation (Dasibi 1008-RS), an ozone monitor based on the absorption of ultraviolet radiation by means of $O_3$ at 254 nm. This instrument has a detection limit of 1 ppbv. The analyser has an internal ozone generator and is completely automated thanks to the ACR-STACK-ON interface that has been incorporated into the Dasibi 1008-RS. During the sampling period, the ozone zero was checked every week and a fixed ozone concentration produced by the ozone internal generator was measured. The instrument was operative 24 h a day. There was a 2-min interval between measurements and data were collected every hour. Air samples were collected through Teflon inlet tubes. The height of air intake was 2 m above the ground. The measured ozone concentration was represented in ppbv units, with a resolution of 1 ppbv. It was recorded on a strip chart and then with a digital data logger. The instrument was calibrated in the factory by using a stabilised ozone source scaled by a long-path UV absorption instrument and it was periodically compared with the standard ozone calibrator.

The site where the measurements were carried out (4° 28’ 8” W; 36° 43’ 40” N) was located at the Faculty of Sciences, University of Málaga, in the north-west of the city (see Fig. 1). Málaga is the major coastal city of Andalucia region, South Spain. The urban sampling point was located approximately 5 km away from the coastline, near the airport and surrounded by roads with traffic exhaust. This Spanish city on the Mediterranean is distinguished by its mild, temperate and warm climate with low rainfall and approximately 320 days of sun a year. The coast is backed by a series of mountains that have to be crossed to reach the inland valleys. Orography plays an important role in the interpretation and understanding of ozone behaviour. As Málaga is located on the coast, its ambient air is influenced by both continental and maritime air masses. Due to the influence of the
local orography, SE and NW winds prevail (Ortega and Sánchez, 1976) and these winds can be observed in the sea–land and land–sea breezes, respectively.

3. Results and discussion

3.1. Daily ozone cycle

In general, ozone variation over the diurnal scale can provide insight to the interplay of emissions, chemical and physical processes that operate on a diurnal cycle. Ozone levels tend to follow the solar radiation intensity, resulting in higher ozone concentrations during the daylight period. In these diurnal cycles, the increase in ozone levels during daylight is attributed to the combined effects of photochemical production of the ozone in the mixing layer and the transport from upper layers (US EPA, 1996), which is favoured at noon by the convective activity in the continental boundary layer. Both mechanisms are activated by solar radiation. The lower nocturnal ozone levels are attributed to in situ destruction of ozone by the well-known reaction between O₃ and NO.

In this section, we describe the daily ozone evolution on an hourly basis. The Box and Whiskers plot in Fig. 2 shows a graphical summary of data distribution for the period of measurements at this coastal site. The vertical box encloses the middle 50%. The median is the horizontal line inside the box and the cross represents the mean value. Vertical lines, called whiskers, extend from each end of the box. Values that fall beyond the whiskers are plotted as individual points. Far outside points (outliers) are distinguished by a special character (a point with a + through it). Outliers are points more than three interquartile ranges below the lower quartile or above the upper quartile.

An examination of the Box and Whiskers plot in Fig. 2 shows numerous anomalous data (outliers), corresponding the inferior ones to values reached in the autumn and winter months, whereas the high anomalous values mainly correspond to summer months. The median value in the middle of the day is higher than the mean value. The interquartile range is especially high at nighttime. All the atypical values are included in both the intervals that are of highest interest in the evolution of the daily ozone concentration. The first interval is formed by that group from 06.00 to 08.00 h and the second group includes the hours in the middle of the day, from 11.00 to 17.00 h. The diagram displays the normal behaviour that follows the ozone near the ground in an urban area. Three main stages stand out:

1. A minimum value appears in the early hours of the morning. This minimum is not very pronounced in this coastal site and it is approximately 07.00 h. From then on, the ozone concentration begins to increase associated with processes of rupture of the night inversion layer on one hand and photochemical reactions with nitrogen oxides on the other.
2. Coinciding with the beginning of the solar radiation an increase is observed in the ozone concentration values reaching its maximum at 15.00 h in full agreement with the maximum solar radiation.
3. The solar radiation starts to decrease from 16.00 h and, therefore, the descent of the ozone concentration begins. The lowest concentration levels are reached at this third stage. Once the night inversion layer is formed no great changes occur in the ozone concentrations during these hours.

3.2. Monthly ozone concentrations and study of the distribution type

Once the daily pattern of ozone concentrations at this site has been established, we studied the monthly evolution of these data.
The yearly course of the monthly concentrations are shown in a Box and Whiskers plot in Fig. 3. Comparison of the monthly values indicates that ozone concentration starts to increase slowly from January to July. In this month the highest value is reached and the ozone value starts to decrease until December, dropping to a minimum during November. This behaviour is similar to the one observed at different sampling points at latitudes similar to Málaga (Serrano et al., 1985; Sánchez et al., 1991; Danalatos and Glavas, 1996; Lalas et al., 1983; Vecchi and Valli, 1999). The variable weather conditions, often occurring during autumn and spring and appearing less frequently in summer, in Málaga, may be the reason for the observed scattering of the monthly values. The month that shows the lowest range is December with 82 μg m⁻³, July being the one that shows the highest values for this statistic, exceeding the value of 170 μg m⁻³. The lower bar of the box for each month remains practically constant with values of approximately 10 μg m⁻³. On the other hand, it can be seen that the values of the higher upright bar of the block show a great fluctuation. In July, that value is the highest at over 180 μg m⁻³ while in November this value is under 90 μg m⁻³.

It is important to know whether the experimental data can be fitted to some type of theoretical distribution. The fit of the monthly values of ozone concentration to a normal distribution was carried out by the Kolmogorov–Smirnov test (K–S) with a Lilliefors significance level. The null hypothesis in the K–S test rejects a normal distribution if the value of significance level is lower than 0.05. As it is lower than 0.05 in all cases, the null hypothesis is rejected, and in consequence we can affirm that normality does not exist in the distribution of the ozone concentrations, with a 95% confidence level, for each of the mentioned months, according to the K–S value. The main trend to normal distribution is observed in May, June, July and August.

As the data are not normally distributed, the non-parametric test of Kruskall–Wallis was used with the aim of finding out whether the median of the different months are statistically the same (Göndar, 1998). It was found that significant differences exist between the medians of each month with a confidence level of 95%.

### 3.3 Seasonal ozone data grouping and behaviour of the concentrations

Since there are differences among the ozone concentration values for each of the mentioned months, a multiple range test with a 95% confidence level was carried out by the Bonferroni method with the aim of finding out which months form homogeneous groups (Göndar, 1998). Taking into account the results of this test, we made seasonal grouping of the data into 4 groups: winter months (December, January and February) spring...
months (March, April and May) summer months (June, July and August) and autumn months (September, October and November), September is the only one which does not clearly adjust to this classification showing a behaviour more similar to a month in spring than its corresponding place in autumn. This is due to its condition of transition between seasons.

The results of hourly evolution of ozone concentrations for each season are represented in diagrams of Box and Whisker (see Figs. 4–7). These diagrams clearly display the diurnal pattern of ozone near the ground in an urban area with the three main stages previously observed in the daily cycle of ozone values. These three stages are reproduced in all seasons becoming intense in summer. This intensification is basically produced by strong and persistent inversions at night as well as during the day because of the increase in the solar radiation. In addition, the sunny and dry weather, coupled with the subsidence of air, provides conditions favourable for photochemical formation of ozone (Rhoads et al., 1997; Cárdenas et al., 1998).

In Fig. 5, six atypical values can be observed in the behaviour followed by the ozone concentration throughout the spring. They are mainly high values that coincide with unseasonably warm weather and days close to summer. Comparing to the plot for winter season (Fig. 4) the increase of the maximum values stands out as well as a major incidence in the minimum of the early hours of the morning that starts an hour earlier with respect to the spring season at approximately 05.00 h reaching the absolute minimum value at 07.00 h. The behaviour in the interval between 13.00 and 16.00 h is different from that observed in winter since there is not so much difference between the average and the median, with both presenting very similar values. During the last interval, between
20.00 and 23.00 h, a slight increase of the ozone concentration is characterised and established between 50 and 60 µg m⁻³ during the whole night.

In Fig. 6, the hourly evolution of the ozone concentration can be seen throughout the summer period. The summer months represent the group of greater interest in the study of the behaviour of photochemical origin (Zurita and Castro, 1983; Buhr et al., 1995; Dapeng et al., 1996; Danalatos and Glavas, 1996) due to the favourable meteorological conditions that are produced in this season, such as strong sunshine that provokes the start of chemical reactions with the precursors and the scarce atmospheric diffusion that favours the accumulation of ozone in the layers close to the ground. According to Fig. 6, in the set interval between 00.00 and 06.00 h, the ozone level begins to decrease from 04:00 h reaching its minimum value at 06:00 h. At approximately 18.00 h, a continuous decrease of concentration begins, reaching its minimum at 20.00 h. This decrease is due to the suspension of the production of ozone after dusk and its continual destruction by NO and other lost processes. The large number of hours in which the average concentration is 100 µg m⁻³ is to be emphasised, precisely in the interval corresponding to the hours around midday. It can be seen that the average value is approximately 62 µg m⁻³ in this urban area for the four seasons, though high ozone episodes occurred during spring and summer. It is clear that this coastal site is highly visited in those months being an important tourist destination in Europe. Then, urban ozone in spring and summer can be severely impacted by anthropogenic emissions.

The corresponding diagram of autumn (Fig. 7) shows a quite similar type of behaviour of ozone concentrations to the ones in winter. The only difference is a slight increase in the interval of central maximum values.

3.4. Meteorological effects

Meteorology plays an important role in ozone formation and transport. As a result, substantial variations in meteorological conditions (in all time scales) can exert such a large impact on ozone concentrations that they mask long-term trends in ozone that could reasonably be traced to changes in precursor emissions such as NOₓ, and VOCs. On the other hand, as found in many studies, certain meteorological conditions are required for the formation and accumulation of high concentrations of O₃ (Colbeck and Mackenzie, 1995 and references therein). These conditions often include a well-defined boundary layer, subsidence inversion, light winds, high temperatures and high solar radiation.

Under this assumption, we have carried out a survey to assess the behaviour of ozone concentration in surface air with several meteorological variables available. The analysis focuses on studying dependencies of ozone concentration levels and different meteorological parameters in a Mediterranean urban coastal station. Our aim was to identify the variables with the higher impact on ozone concentrations under temperate weather conditions. Meteorological data from the Meteorological Institute were collected by the meteorological station located 1 km away from the sampling site (see Fig. 1). We have used average hourly values from meteorological data. The selected variables were as follows: temperature (T, expressed in °C), pressure (P, expressed in mb), relative humidity (H, expressed in %), wind direction (D, expressed in sexagesimal degrees), wind speed (v, expressed in m/s), and rainfall (r, expressed in mm).

In order to find the meteorological factors influencing ozone concentration and to assess them in order of importance, a regression analysis was carried out with the STATGRAPHICS-PLUS software. First of all, we carried out a simple regression on ozone concentrations and some meteorological factors available. This study was carried out taking into consideration: (1) all data; and (2) data for summer period. In Table 2, Pearson and Spearman correlation coefficients (Bunzl, 1993) between ozone concentration and these meteorological parameters are summarised. Looking at the coefficients, it can be seen that temperature, wind speed and relative humidity are the most important meteorological factors influencing the variation in ozone levels at our coastal site. The correlation with pressure and rainfall is not very significant. The importance of tempera-
Table 2
Correlation studies between ozone concentrations and the main meteorological variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>O_3 (all data)</th>
<th>O_3 (summer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wind speed</td>
<td>p (P) 0.456 (&lt;0.01)</td>
<td>p (P) 0.557 (&lt;0.01)</td>
</tr>
<tr>
<td></td>
<td>r (P) 0.502 (&lt;0.01)</td>
<td>r (P) 0.533 (&lt;0.01)</td>
</tr>
<tr>
<td>Temperature</td>
<td>p (P) 0.434 (&lt;0.01)</td>
<td>p (P) 0.560 (&lt;0.01)</td>
</tr>
<tr>
<td></td>
<td>r (P) 0.446 (&lt;0.01)</td>
<td>r (P) 0.552 (&lt;0.01)</td>
</tr>
<tr>
<td>Humidity</td>
<td>p (P) -0.509 (&lt;0.01)</td>
<td>p (P) -0.525 (&lt;0.01)</td>
</tr>
<tr>
<td></td>
<td>r (P) -0.516 (&lt;0.01)</td>
<td>r (P) -0.502 (&lt;0.01)</td>
</tr>
<tr>
<td>Rainfall</td>
<td>p (P) -0.092 (&lt;0.01)</td>
<td>p (P) -0.040 (&lt;0.01)</td>
</tr>
<tr>
<td></td>
<td>r (P) -0.026 (&gt;0.01)</td>
<td>r (P) -0.034 (&gt;0.01)</td>
</tr>
<tr>
<td>Pressure</td>
<td>p (P) -0.024 (&gt;0.01)</td>
<td>p (P) -0.009 (&gt;0.01)</td>
</tr>
<tr>
<td></td>
<td>r (P) 0.006 (&gt;0.01)</td>
<td>r (P) -0.008 (&gt;0.01)</td>
</tr>
</tbody>
</table>

Values of Spearman (p) and Pearson (r) coefficients are given together with the associated correlation probabilities (P).

...and wind speed is discussed in the following sections. Relative humidity is also important because this variable may play a role in the overall reactivity of the system, either by affecting chain termination reactions or in the production of wet aerosols, which in turn affect the ultraviolet actinic flux. Furthermore, humidity is considered to be a restrictive factor in the disposition of NO_2 because high percentages of humidity favour the reaction of the NO_2 with particles of NaCl, very common in coastal places (Vera et al., 1997). There is a negative correlation between these data and relative humidity.

3.4.1. Influence of temperature

The relationship between ozone concentration and temperature can be explained on theoretical grounds. Temperature plays an enhancing role in the propagation rate of the radical chain, and has an opposite effect on the termination rate of these chains (Ruiz-Suárez et al., 1995). The evolution of ozone concentration with temperature can be seen in Fig. 8, where it can be observed that the evolution of both variables is similar. This behaviour remains unaltered until July and an increase in the temperature can be observed in August that does not depend on an increase in ozone concentration. A similar situation can be observed in May.

In order to quantitatively assess the influence of temperature on monthly ozone concentration, we have carried out a simple regression analysis assessing different functional, linear, multiplicative, exponential and reciprocal dependencies between hourly concentration data and the hourly temperature. The best adjustments were obtained by means of the linear regression. These are shown in Table 3, where N is the number of data, r is the correlation coefficient and N.S. means that the correlation is not significant for a confidence level of 90%. In Table 3, we can observe that there is a significant correlation between both variables for the February–October period. The lowest value for the correlation coefficient is obtained in October 1997, with a significance level of 90%; for remaining months, in which there is a significant correlation, the significance level is higher than 99%. The best results were obtained for summer months. The most representative statistical parameters of hourly temperature values for this Mediterranean coastal site have been included in Table 3 in which the average, maximum and minimum values are shown as well as the variation range and coefficient for every month. The coefficient of temperature variation is below 25% for all months with a minimum value of 13.7% in September. The average thermal range is 16.1 °C. This value is low as compared with continental areas, mainly due to sea dimming acting as a heat regulator and softening temperature changes.

This relationship between temperature and ozone concentration has been mentioned by several authors (Serrano et al., 1985; Sánchez et al., 1991; Buhr et al., 1995; Bloomfield et al., 1996). Some studies were focused on the evolution of ozone concentration and Pearson...
Table 3

<table>
<thead>
<tr>
<th></th>
<th>O$_3$ (summer, daytime, SE)</th>
<th>O$_3$ (summer, daytime, NW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(N=217)</td>
<td>(N=105)</td>
</tr>
<tr>
<td>Wind speed</td>
<td>$p$ ($P$)</td>
<td>0.491 ($&lt;0.01$)</td>
</tr>
<tr>
<td></td>
<td>$r$ ($P$)</td>
<td>0.551 ($&lt;0.01$)</td>
</tr>
<tr>
<td>Temperature</td>
<td>$p$ ($P$)</td>
<td>0.412 ($&lt;0.01$)</td>
</tr>
<tr>
<td></td>
<td>$r$ ($P$)</td>
<td>0.459 ($&lt;0.01$)</td>
</tr>
<tr>
<td>Humidity</td>
<td>$p$ ($P$)</td>
<td>-0.397 ($&lt;0.01$)</td>
</tr>
<tr>
<td></td>
<td>$r$ ($P$)</td>
<td>-0.450 ($&lt;0.01$)</td>
</tr>
<tr>
<td>Rainfall</td>
<td>$p$ ($P$)</td>
<td>-0.113 ($&gt;0.01$)</td>
</tr>
<tr>
<td></td>
<td>$r$ ($P$)</td>
<td>-0.169 ($&lt;0.05$)</td>
</tr>
<tr>
<td>Pressure</td>
<td>$p$ ($P$)</td>
<td>0.289 ($&lt;0.01$)</td>
</tr>
<tr>
<td></td>
<td>$r$ ($P$)</td>
<td>0.286 ($&lt;0.01$)</td>
</tr>
</tbody>
</table>

Values of Spearman ($p$) and Pearson ($r$) coefficients are given together with the associated correlation probabilities ($P$).

concentration with the value of maximum daily temperature (Dapeng et al., 1996; Cox and Chu, 1996) whereas others consider diurnal and nocturnal intervals in the correlation between ozone and temperature. In Figs. 9 and 10, the charts of both intervals for monthly ozone concentrations have been included. Diurnal interval ranges between 07.00 and 19.00 h, being in this interval where ozone is photochemically produced. The nocturnal period ranges between 20.00 and 06.00 h.

In Fig. 9, we can observe that there is a closer relationship between ozone concentration and temperature in diurnal hours, being partly softened the anomalies observed in Fig. 8. However, the behaviour in nocturnal periods presents a poor correlation as compared with that mentioned before, specifically in August. Fig. 10 reflects such situation. In these figures, temperature on a monthly time-scale appear to lag ozone concentrations probably implying that rather solar radiation might be a more important parameter when predicting ozone values at our site. There is a strong and clear positive correlation between solar irradiance values and air temperatures and positive correlation between ozone and solar irradiance values is well known. This latter linkage is not always clear. Abdul-Wahab and Al-Alawi (2002) present the development of three models able to predict the tropospheric (surface or ground) ozone concentrations as a function of meteorological conditions. It was found that temperature played an important role while solar radiation had a lower effect than expected.

We have correlated the ozone concentration and temperature but taken into consideration diurnal and nocturnal periods separately. This survey is

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**Fig. 9.** Average monthly daytime values of ozone concentration and temperature.

**Fig. 10.** Average monthly night-time values of ozone concentration and temperature.
the coastal urban site. Monthly correlation between ozone concentration and temperature and monthly temperature values during the sampling period at Table 4

<table>
<thead>
<tr>
<th>Month</th>
<th>N</th>
<th>r</th>
<th>Equation</th>
<th>Temperature</th>
<th>Max.</th>
<th>Min.</th>
<th>Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nov 96</td>
<td>250</td>
<td>N.S.</td>
<td>–</td>
<td>16.2</td>
<td>23.3</td>
<td>5.4</td>
<td>18.2</td>
</tr>
<tr>
<td>Dec 96</td>
<td>417</td>
<td>N.S.</td>
<td>–</td>
<td>11.9</td>
<td>23.8</td>
<td>4.9</td>
<td>26.5</td>
</tr>
<tr>
<td>Jan 97</td>
<td>324</td>
<td>N.S.</td>
<td>–</td>
<td>11.3</td>
<td>19.2</td>
<td>6.7</td>
<td>25.1</td>
</tr>
<tr>
<td>Feb 97</td>
<td>296</td>
<td>0.566</td>
<td>(O_3 = (5.2 \pm 0.4)T + (-24.5 \pm 6.8))</td>
<td>14.9</td>
<td>24.7</td>
<td>7.7</td>
<td>23.2</td>
</tr>
<tr>
<td>Mar 97</td>
<td>324</td>
<td>0.586</td>
<td>(O_3 = (8.1 \pm 0.6)T + (-30.1 \pm 9.7))</td>
<td>14.7</td>
<td>21.7</td>
<td>7.9</td>
<td>19.4</td>
</tr>
<tr>
<td>Apr 97</td>
<td>443</td>
<td>0.617</td>
<td>(O_3 = (6.2 \pm 0.4)T + (-32.2 \pm 6.5))</td>
<td>16.9</td>
<td>24.2</td>
<td>9.3</td>
<td>17.9</td>
</tr>
<tr>
<td>May 97</td>
<td>274</td>
<td>0.586</td>
<td>(O_3 = (5.0 \pm 0.4)T + (-34.7 \pm 9.0))</td>
<td>20.6</td>
<td>28.6</td>
<td>15.4</td>
<td>15.8</td>
</tr>
<tr>
<td>Jun 97</td>
<td>326</td>
<td>0.630</td>
<td>(O_3 = (4.5 \pm 0.3)T + (-23.7 \pm 7.3))</td>
<td>22.3</td>
<td>34.5</td>
<td>15.2</td>
<td>16.6</td>
</tr>
<tr>
<td>Jul 97</td>
<td>639</td>
<td>0.615</td>
<td>(O_3 = (5.6 \pm 0.3)T + (-47.5 \pm 7.0))</td>
<td>24.1</td>
<td>32.6</td>
<td>15.1</td>
<td>15.2</td>
</tr>
<tr>
<td>Aug 97</td>
<td>306</td>
<td>0.727</td>
<td>(O_3 = (6.5 \pm 0.4)T + (-92.3 \pm 6.5))</td>
<td>26.0</td>
<td>33.9</td>
<td>19.0</td>
<td>14.2</td>
</tr>
<tr>
<td>Sep 97</td>
<td>687</td>
<td>0.657</td>
<td>(O_3 = (6.6 \pm 0.3)T + (-95.4 \pm 6.8))</td>
<td>23.4</td>
<td>32.9</td>
<td>15.7</td>
<td>13.7</td>
</tr>
<tr>
<td>Oct 97</td>
<td>335</td>
<td>0.433</td>
<td>(O_3 = (4.0 \pm 0.5)T + (-46.6 \pm 10.1))</td>
<td>22.0</td>
<td>31.0</td>
<td>14.3</td>
<td>14.8</td>
</tr>
</tbody>
</table>

only carried out for the summer period since it is the best season for the follow-up of the evolution of ozone concentration. Ozone formation is driven by photochemically initiated reactions and is correlated to air temperature, so that elevated ozone levels are typically found in high-pressure meteorological situations, with clear skies and high temperatures (Simpson et al., 1995). Results are shown in Table 4, highlighting the photochemical formation of ozone and its special incidence in diurnal hours, where temperature increase is higher. However, that cannot be applied to nocturnal hours. In diurnal hours, ozone concentration ranges between 40 and 95 \(\mu g \cdot m^{-3}\) (as minimum and maximum values, respectively). This range is reduced to 32–70 \(\mu g \cdot m^{-3}\) in nocturnal hours.

### 3.4.2. Influence of wind direction and speed

We have studied the influence of the wind direction and speed on ozone concentration. It is of interest to see how ozone changes under different wind patterns. It is known that there is a clear relationship between ambient air quality and wind speed and direction. These two are important factors for the dispersion of ozone precursors from local industrial/transport, and for ozone transport from the stratosphere. The sea/land breezes also play a significant role in the distribution of ozone and transport of ozone from the urban to the coastal and mountain areas. The sea breeze is a weak system, extending vertically to a height of less than 1 km with the wind speed less than 4 m s\(^{-1}\). The land breeze can transport the photochemically produced ozone and its precursors over the sea. The accumulated ozone on the sea can return to the land with the sea breeze. This kind of transport tends to contribute significantly to high-ozone episodes in clean coastal and mountain regions (Liu et al., 2002).

We will begin this analysis with an explanation of the most important characteristics of winds in Málaga. There are three types of winds in the area (known as levante, poniente and terral), together with a breeze regime that appears when the isobaric gradient is not so strong. Breeze, specifically sea breeze, plays a leading role in the distribution and transport of pollutants.

Levante wind (E–SE direction) brings humid air from the Mediterranean and it is constant and persistent. This wind goes through the valley of the Guadalhorce River and heads for the SE; when it is intense, it heads for the East. Poniente wind (W direction) is strong and gusty but not as persistent. When there is a strong N wind, it heads for the NW when it enters the banks of the Guadalhorce River, originating terral winds. Besides the above-mentioned winds, when they are not very strong, we should mention the sea–land and land–sea regime of breezes, a typical phenomenon of coastal cities. With the breeze regime, NW winds blow during the night and SE winds in the day. These local winds are not very intense and are largely limited.
According to the samples taken at 07.00, 13.00 and 18.00 h T.M.G., in Fig. 11 we have presented the frequency of wind directions, that were measured for 20 years (1964–1983) at the meteorological station of Málaga at the airport. The number in the centre of the circle indicates the percentage of calms. In this figure, we can observe a predominance of SE and NW winds due to the influence of local orography. By means of the software SPSS 9.0, we have created crosstabs for all the seasons analysing the influence of wind both in speed and in direction (Cañete, 2001). For the wind speed, we have considered the following intervals: calms (speed lower than 0.2 m/s); soft winds (speed between 0.2 and 2 m/s); moderate wind (speed between 2 and 4 m/s); and strong winds (speed higher than 4 m/s). Now, we summarise the information given in these crosstabs:

- In winter, NW winds prevail (32.2%), as well as W winds (16.1%). Also SE winds are outstanding (15.1% of the total figure).
- In spring, this behaviour is reversed, prevailing SE and S winds (50.5% of the total figure). NW winds ranges third with a contribution of 20.1%.
- In summer, a sort of balance is achieved between the two main components representing SE winds 23.3% and NW winds 25.8%. It is in this season when the sea–land and land–sea breeze phenomenon becomes obvious.
- Autumn is characterised by a large contribution of NW winds (31.3% of the total figure).

Likewise, from the information included in crosstabs, we have grouped ozone concentration by sectors of wind direction. In Figs. 12–15, values of ozone concentration in every sector and in every season are presented. From these figures, we can come to the following conclusions:

- In winter, the maximum ozone concentrations correspond to SE and N–NW winds, coinciding with the most frequent wind sectors. The minimum concentration has a close relationship with NE winds.
- The increase in ozone concentration in spring is more obvious in the second quadrant and the lowest levels appear in the NE sector.
In summer, a uniform distribution of ozone concentration can be observed in the different sectors. It is worth mentioning the N, S and SE sectors, where they clearly go beyond the 75 \( \mu g \ m^{-3} \) line.

- The autumn period is very similar to the winter season.

For primary pollutants, a rise in wind speed implies a rise in the transport of air masses, behaving like an agent diluting this type of pollution; however, the role played by this variable in secondary pollutants is much more complex. Fig. 16 reflects that in situations of moderate or strong winds, ozone concentration is maximum. In general, low wind speed episodes induce high \( NO_x \) and low ozone concentrations. On the contrary, higher wind speed events lead to lower \( NO \) and higher ozone concentrations (Dapeng et al., 1996; Dabdub et al., 1999; Rodríguez and Guerra, 2001).

Taking into consideration the chart of wind speed and ozone concentration for every sector, we study the incidence of wind on ozone concentration. Figs. 17 and 18 show the summer season behaviour and that of all data, respectively. In Fig. 17, N–NE winds never present a speed higher than 4 m/s. With these moderate winds, we reach the highest concentrations in the remaining sectors, whereas with soft winds, the highest value of ozone concentration is 60 \( \mu g \ m^{-3} \). No large differences can be found between its behaviour in summer and that in the remaining seasons.

3.5. Regression analysis to ozone concentration and meteorological parameters

As stated by different investigators, high ozone events occur mainly in summer. Ozone exceedances in Mediterranean cities are often very pronounced. On this basis, we studied the variability of ozone concentration in this season taking into consideration local meteorological conditions and only data collected in this period were selected for regression evaluation. The regression technique has been widely used to model ozone concentrations as a function of meteorological parameters such as temperature, wind speed, solar radiation, relative humidity and wind direction. It ratifies the capa-
bility of detecting ozone trends disguised by meteorological variations (Rao and Zurbenko, 1994).

Firstly, we carried out a simple regression (see Table 5) on diurnal values of ozone concentrations in summer and the meteorological factors available. Diurnal ozone data (and meteorological parameters) were re-grouped according to the prevailing wind categories (SE and NW winds). The importance of meteorological variables in relation to ozone concentrations during the summer were, in order of importance, temperature, wind speed and relative humidity. In addition, as coefficient values are concerned, it can be said that a high diurnal ozone concentration in summer for SE winds is present under high temperature and wind speed conditions. Finally, there is a strong negative correlation between ozone diurnal concentrations in summer for NW winds and relative

![Fig. 17. Ozone concentration with wind speed and direction in summer.](image1)

![Fig. 18. Ozone concentration with wind speed and direction for all the data.](image2)
humidity and also a good correlation with temperature and wind speed.

In order to determine the extent to which variations in ozone concentration might be due to the combination of these meteorological parameters, we carried out a multiple regression. Meteorological variables were obtained and arranged in a decreasing order, taking into account the linear coefficient. Columns in Tables 6 and 7 include the regression equations with the error coefficient of each independent variable, the $R^2$-squared value (the amount of the variance accounted for by the equation), the probability index ($P$) taking into account the number of data and the standard error of the estimate (S.E.) (the square root of the residual mean square).

In the validity analysis, each regression equation was taken into account, the relative error of the coefficient of each independent variable, the standard error of the estimate and the $R^2$-squared value.

Using these criteria, the following equations were chosen for diurnal ozone concentration in summer for SE winds and diurnal ozone concentration in summer for NW winds, respectively, taking into consideration the results of the stepwise backward regression method:

**SE winds,**
\[
O_3 = -(1300 \pm 500) + (15.3 \pm 1.5)v - (0.6 \pm 0.2)H + (2.7 \pm 0.9)T + (0.013 \pm 0.005)P
\]

**NW winds,**
\[
O_3 = -(130 \pm 20) - (1.74 \pm 0.17)H + (1.4 \pm 0.6)T
\]

These equations show the number of parameters that most interfere in the fluctuations of diurnal ozone concentration in summer for SE and NW wind directions. The contribution of meteorology on the ozone concentration variation was found to fall within the range 51–71% according to the main wind directions (see Tables 6 and 7).
Fig. 19. Ozone concentration experimentally observed vs. the values calculated by the regression equation for daytime values in summer with SE winds.

results of the first equation offer insights into the dependence of ozone on wind speed, relative humidity, temperature and pressure with SE winds. However, wind speed and relative humidity are less sensitive predictors with NW winds, based on the results of the second equation. Any remaining variability could be attributed to other causes such as chemical interaction between hydrocarbons and oxides of nitrogen. The resulting high values of correlation coefficients indicate that, in the absence of measured data, equations could be invoked to predict an estimate of ozone values according to few meteorological parameters and prevailing wind direction. Gardner (1996) used the neural network to investigate the importance of local meteorology in determining the surface ozone concentration.

Fig. 20. Ozone concentration experimentally observed vs. the values calculated by the regression equation for daytime values in summer with NW winds.
The data included hourly observations of temperature, humidity, irradiance, wind speed, direction and ozone concentrations for an entire year. Interestingly, Gardner’s model did not involve any chemical data as input to the model. The model showed that over a period of a year, 48% of the ozone variation can be attributed to changing meteorological conditions.

Finally, Figs. 19 and 20 show experimentally observed values vs. the values derived from the regression equations. The results clearly indicate a good agreement, particularly in the region of moderate to high values of ozone concentrations.

4. Summary and conclusions

This study emphasises the variability of ozone concentrations and examines ozone values from a climatological perspective. We discuss frequency distributions of ozone at a Mediterranean coastal site. In this work, a regression analysis to ozone and meteorological parameters has made it possible to analyse variations in ozone concentrations in this coastal site collecting data from an urban atmosphere. The regression evaluation was carried out using summer data, when ozone concentrations are the highest. In order to determine the extent to which variations in ozone concentration might be due to the combination of these meteorological parameters, we carried out a multiple regression. The resulting high values of correlation coefficients indicate that, in the absence of measured data, equations could be invoked to predict an estimate of ozone values according to few meteorological parameters and prevailing wind direction. Because of the length of the analysed time period, ozone concentrations in this urban site does not constitute a statistical significant trend but represents the change observed during this year of measurement under typical temperate weather conditions. The results presented here may be used to design studies that account for ozone trends under temperate climate. These coastal site measurements could provide useful background information for development of regional models within the Mediterranean area.

References


Brauer M, Brook JR. Ozone personal exposures and health effects for selected groups residing in the Fraser Valley. Atmos Environ 1997;31(14):2113–2121.


