Analyses of ozone in urban and rural sites in Málaga (Spain)

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Abstract

Ozone concentrations were measured at two (urban and a rural) sites near the city of Málaga (Spain). The aim of this study was to determine the daily, monthly and seasonal variation patterns of ozone concentrations at both sites and to study the possible regional influences. The daily variations mostly have the usual features with the afternoon maximum and the night minimum being more pronounced in the urban area. The average monthly concentrations throughout the year start to increase in March reaching their maximum values in July for the urban site. However, in the rural area, the monthly variations are smaller reaching their maximum value in June. The hourly evolution of the ozone concentrations in both sampling sites is well defined in spring and summer and not so well defined in autumn and winter. Taking into account the four seasons, the rural concentrations are higher than the urban ones. Summer is the season when there are similar concentrations at both sampling sites. Average hourly summer afternoon ozone for the hours 12:00–20:00 LST exceeded the 110 µg m⁻³ European Union guidelines for human health for 8 h ozone exposure at the urban and rural sites.

Keywords: Urban ozone; Rural ozone; Daily variation; Monthly variation; Seasonal variation; Málaga

1. Introduction

Ozone is an important chemical constituent of the atmosphere. Increasing tropospheric ozone (O₃) concentrations observed in the past decades in several regions of the Northern Hemisphere (Logan, 1994; Guicherit and Roemer, 2000) also constitute a potentially important climate forcing which needs to be assessed thoroughly. Tropospheric ozone is a trace gas which plays a key role in the oxidising capacity of the atmosphere. Ozone also exerts a significant influence on the radiation budget of the atmosphere owing to its properties as a greenhouse gas. Major ozone sources and sinks in the troposphere are the air mass exchange between the stratosphere and troposphere, in situ photochemical production or destruction and surface dry deposition. Taking into account that ozone precursors are also anthropogenically emitted, tropospheric background ozone levels have been modified during the last century. Direct measurements show that surface ozone has increased over industrialised continents in Northern mid-latitudes, such as Europe (Logan, 1994) and North America (Oltmans et al., 1998). A marked ozone increase throughout the 1970s and 1980s was followed in Europe by a decline in the increasing trend since the mid-1980s.

Surface ozone is mainly monitored in industrialised and relatively highly-populated continental regions because of its potential impact on human health and vegetation. High surface ozone concentrations photochemically produced from anthropogenic ozone

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precursors have been extensively described in continental regions surrounding the North Atlantic, i.e., Eastern United States (Trainer et al., 1993; Ryan et al., 1998), Western Europe (De Muer et al., 1997) and Western Mediterranean (Sanz and Millán, 1998).

The selection of an adequate model in a given area demands carrying out preliminary analyses to describe the most outstanding features of the ozone at a local scale. In the Mediterranean basin, the orographic conditions determine the recirculation of air around the coasts that creates an accumulation of atmospheric pollutants. This leads to chronic relatively high levels of ozone, a situation that European directives about air quality do not consider properly. This point is particularly interesting in our study area where measurements of this pollutant are very scarce. Few systematic ozone measurements have been carried out around the Mediterranean basin. Experimental work on atmospheric oxidants, in particular ozone, was found to be concentrated in and around a few cities within the Mediterranean; thus, e.g. in Greece (Kalabokas et al., 2000; Kouvarakis et al., 2000), in Croatia (Butkovic et al., 1990; Klasinc and Cvitas, 1996), in Italy (Cieslik and Labatut, 1997), in France (Pont and Fontan, 2000), in Spain (Sanz and Millán, 1998) and in Egypt (Gusten et al., 1994). With the exception of the long-term background measurements of Kalabokas et al. (2000) and Kouvarakis et al. (2000) all other measurements were either sporadic for short periods of a few weeks only or in a polluted environment.

Málaga, with a population of around 540,000 is the major coastal city in the Andalusian region situated in the south-east of the Iberian Peninsula on the Mediterranean coast and surrounded by mountains to the north (Fig. 1). This city, like most large European cities, faces air pollution problems. The main reason is the high population density associated with the intense emission load constrained by the local topography. Another factor is the high level of solar irradiation leading to the formation of photochemical pollutants, ozone being the most characteristic and most abundant. In Central and Northern Europe there are many rural air pollution stations, providing a satisfactory picture of the spatial distribution of surface ozone concentrations, but there are few systematic measurements for the Mediterranean basin and the Eastern European continent.

In this study, statistical characteristics of ground level ozone are analysed according to the field monitoring data in two areas, urban and rural. The study deals with the characteristics of seasonal, monthly and daily mean ozone levels under different climatic conditions at an urban site and a rural site of Málaga (Spain). Reasons for the observed spatial and temporal variations of ozone levels are discussed. In addition, the data

![Fig. 1. The location of sampling points (US: urban site; RS: rural site).](image-url)

2. Data collection

Ozone levels were continuously monitored using Dasibi Environmental Corporation instrumentation (Dasibi 1008-RS), an ozone monitor based on the absorption of ultraviolet radiation by O₃ at 254 nm as the principle of measurement. This instrument has a limit of detection of 1 ppbv. The analyser has an internal ozone generator and is completely automated by means of the ACR-STACK-ON interface 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 continuously operating every day (for 24 h). The interval of each measurement was 2 min and data have been averaged into hourly periods. Air samples were collected through teflon inlet tubes. The height of the air intake was 2 m above the ground. The measured ozone concentration was represented in units of ppbv with a resolution of 1 ppbv and recorded on a strip chart and later 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 periodically compared with the standard ozone calibrator.

Measurements were carried out at two (urban and rural) sites in Málaga (see Fig. 1). The urban site (4°28′8″W; 36°43′40″N) was located on the Faculty of Sciences building, University of Málaga, in the northeastern part of the city. The sampling point was located approximately 5 km from the coast line, near the airport and surrounded by roads with dense traffic. The climate in Málaga is moderate, between temperate and warm and it has a low rainfall (550 mm yr⁻¹). The orographic features play an important role in the interpretation and understanding of ozone behaviour. Due to the influence of the local orography there are prevailing SE and NW winds. The SE and NW winds occur as a result of the sea-land and land-sea breezes, respectively. The rural site (4°3′20″W; 36°42′31″N) was located at the La Mayora experimental station in the village of Algarrobo. This site was 45 km from Málaga and approximately 2 km from the coast line. Although the area has recently experienced a demographic increase, it has always been characterised as an agricultural area largely dedicated to crops being cultivated under plastic. The experimental station covers 51 ha with almost 20,000 m² of greenhouses. The subtropical climate of this coastal area favours the production of vegetable crops under plastic greenhouses (tomato, melon, watermelon, etc.) and subtropical fruit trees (avocado, custard apple, mango, etc.). These species have a high productive potential and an enormous social and economical importance in this part of the country.

3. Results and discussion

3.1. Temporal variation of ozone at the urban site

The ozone concentration levels at the urban area have been analysed statistically based on several different scales such as hourly, monthly and seasonal from November 1996 until November 1997.

The box and whisker plots in Fig. 2 summarise the hourly ozone data from the urban site. At this site, ozone levels tend to follow the solar radiation intensity, resulting in higher ozone concentrations during the daylight period. In these 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 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.

An examination of the box and whisker plots in Fig. 2 shows numerous anomalous data (outliers), ranging between 5 and 30 µg m⁻³ which mainly correspond to the autumn and winter months and high values ranging between 160 and 190 µg m⁻³ mainly in the summer months. The median value in the middle of the day is higher that the mean value. This suggests that there is a bigger percentage of data with high values, showing the influence of unusually low data on the arithmetic mean value. The interquartile range is especially high at night time. All the atypical values are included in the two intervals that are of greatest interest in the evolution of the daily ozone concentration. The first interval is formed by the group from 6:00 to 8:00 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 followed by ozone near the ground in an urban area.

The urban average monthly concentrations are shown in Fig. 3. A great dispersion is observed among the values measured in summer compared with the ones obtained in winter months. The month that shows the lowest range is December with 81 µg m$^{-3}$, July is the month with the greatest range exceeding 170 µg m$^{-3}$. The lower bar of the box for each month remains practically constant with values of around 10 µg m$^{-3}$. The values of the higher upright bar, in the block, show greater changes. In July the value obtained is the highest, over 180 µg m$^{-3}$, while in November this value is set under 90 µg m$^{-3}$. From the same figure, we can infer that ozone concentration starts to increase slowly from January to July. In July the highest value is reached and the ozone value starts to decrease. The lowest value is reached in November.

The fit of the monthly values of ozone concentration to a normal distribution was tested using the Kolmogorov–Smirnov test (K–S) with a Lilliefors significance level. The null hypothesis in the Kolmogorov–Smirnov 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 the ozone concentrations are not normally distributed, with a 95% confidence level for each of the mentioned months. 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 medians of the different months are statistically the same. This test showed that there were significant statistical differences between the mean values of the different months at 95% confidence level. Since there are differences among the monthly ozone concentration values, a multiple range test with a 95% confidence level was carried out by the Bonferroni method (Gondar Nores, 1998) with the aim of finding out which months form homogeneous groups and to carry out the seasonal ozone data grouping. Taking into account the results of this test, we put the data into four seasonal 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 conform 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.

According to this seasonal grouping, the results of the urban site for each season are represented in Fig. 4. These diagrams display the normal behaviour of 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 our case and it is around 7:00 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 solar activity an increase is observed in ozone concentration values reaching a maximum at 15:00 h in full agreement with the maximum activity for this time of year.

3. The solar activity starts to decrease after 16:00 h and therefore the ozone concentration declines. 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.

These three stages are reproduced in the other 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.

The behaviour followed by the ozone concentration throughout the spring can be observed in Fig. 4 where six a typical values can be seen. They are mainly high values that coincide with days close to summer. Comparing to the winter data, the increase in 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 previous season at about 5:00 h, reaching the absolute minimum value at 7:00 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, both presenting very similar values.
the last interval, between 20:00 and 23:00 h there is a slight increase in ozone concentration with levels between 50 and 60 µg m\(^{-3}\) during the whole night.

The summer months represent the group of greatest interest in the study of the behaviour of photochemical origin 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 limited atmospheric diffusion that favours the accumulation of ozone in the layers close to the ground. Most publications point out that photo-smog is a serious problem in the Mediterranean (Klabokas et al., 2000; Nolle et al., 2002). The general weather conditions in summer are relatively similar for all the Mediterranean countries and determined by high-pressure situations leading to strong solar radiation, high temperatures and generally low wind speeds. These conditions support the development of a number of mesoscale circulation systems that are connected in particular to sea-breeze phenomenon. It was observed that these circulation cells create very effective reservoirs for ozone and its precursors, which may lead to significant photosmog episodes with peak values in excess of 429 µg m\(^{-3}\) (Alper-Simann et al., 1997; Kassomenos et al., 1998; Pont and Fontan, 2000) in metropolitan and other Mediterranean coastal regions.

According to the box and whisker plot of ozone concentrations for summer (Fig. 4), in the set interval between 0:00 and 6:00 h the ozone level begins to decrease from 4:00 h reaching its minimum value at 6:00 h. At about 18:00 h, a continuous decrease in concentration begins, reaching its maximum 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 loss processes. The large number of hours when the average concentration is 100 µg m\(^{-3}\) should be noted precisely in the interval corresponding to the hours around midday.

The corresponding diagram for autumn shows a quite similar type of behaviour of ozone concentrations to the ones in winter. The only difference being a slight increase in the interval of central maximum values.

3.2. Temporal variation of ozone at the rural site

The ozone concentration levels at the rural site are analysed statistically based on several different scales such as hourly, monthly and seasonally from February 1998 until October 1999.

Fig. 5 shows the box and whisker diagram of the hourly evolution in ozone concentrations. There are a large number of outliers due to the decrease in the interquartile range with an average value of 26 µg m\(^{-3}\). Therefore the length of each of the bars is much shorter. A great similarity is observed between the average value and the median of each of the analysed hours in the same figure. The box presents almost symmetrical aspects. There is less fluctuation in the ozone concentration values throughout the day in the rural area than the urban one, so the minimum effect that appears in the
early hours of the morning is as minimised as the period of maximum concentrations at midday. These results are in agreement with the behaviour observed at other rural sampling sites (Vecchi and Valli, 1999; Nollet et al., 2002; Saitanis, 2003; So and Wang, 2003).

The monthly average concentrations are shown in Fig. 6. This figure shows the increase in the monthly average ozone concentration from February to April. Average levels are then more or less stable until August. A lower ozone concentration is presented in September whereas October reflects a higher average value than expected for that time of the year if the values obtained at the urban site are taken as reference. The average value of ozone concentration in November, December and January decreases to the lowest levels detected during the studied period. In January 1999 the lowest average value is 69.9 \( \mu \text{g m}^{-3} \) whereas the highest average value corresponds to an average concentration of 102 \( \mu \text{g m}^{-3} \) obtained in June 1999. March, May and July present average values of about 90 \( \mu \text{g m}^{-3} \) showing the little difference in ozone levels during spring and summer in this area. The range is 21 \( \mu \text{g m}^{-3} \) against 45 \( \mu \text{g m}^{-3} \) registered at the urban site.

The monthly evolution is similar to the one found by various authors in rural areas. With respect to the Mediterranean, reports of averages of ozone from two rural stations inland of the eastern Spanish coast (Sanz and Millán, 1998) look very similar to the observations made at this site. The existence of maximum peaks in June and April is generally associated to the vertical transport of air and/or tropospheric chemistry. Several papers have appeared recently showing that the spring maximum in ozone observed at the ground is due to tropospheric chemistry. The vertical transport from the upper troposphere is usually revealed by the increase in the activity of radionuclide \(^7\text{Be}\) of cosmogenic origin just like other investigators have stated (Cañete, 2000).

Analogously to the urban site, it was found that significant differences exist between the medians of each month with a confidence level of 95%. The Bonferroni method was used for the seasonal data grouping at the rural site.

In Fig. 7 the small difference that exists between the arithmetic mean and the median value during the whole winter can be observed. From 0:00 to 5:00 h no large variations in the ozone concentration can be seen, the average variations being less than 2 \( \mu \text{g m}^{-3} \) per hour. From 6:00 h on, a slight decrease is produced. The minimum value of 65 \( \mu \text{g m}^{-3} \) is reached at 8:00 h and from then on, the concentration increases about 5 \( \mu \text{g m}^{-3} \) per hour until 15:00 h when the maximum value of 94 \( \mu \text{g m}^{-3} \) is reached. The same behaviour occurs in the urban area. Once the maximum value is reached, the loss process starts until reaching an average value of 73 \( \mu \text{g m}^{-3} \) which is observed at 20:00 h and is maintained until the end of the day. Therefore the relative minimum value present at 20:00 h in the urban area does not appear at the rural site. Numerous anomalous values appear in spring. The minimum morning value appears at 7:00 h and increases every hour until reaching the maximum value, which represents around 26% with respect to the previous season. The maximum value is reached at 15:00 h, followed by a small decrease to return to the base concentration of around 80 \( \mu \text{g m}^{-3} \), with very little variation being observed at this level throughout the night.

In summer, the figure shows that the minimum value of the early hours (66 \( \mu \text{g m}^{-3} \)) in the morning is reached between 6:00 and 7:00 h. The maximum value measured between 14:00 and 15:00 h is 112 \( \mu \text{g m}^{-3} \), which means an increase of 46 \( \mu \text{g m}^{-3} \). This is the largest observed in all the seasons for the period considered. The interval of the maximum concentrations extends from 12:00 until 16:00 h, which is followed by a marked decrease than that observed in winter and spring. The daily average concentration is high with values above 100 \( \mu \text{g m}^{-3} \) from 11:00 until 19:00 h reaching a maximum value of 180 \( \mu \text{g m}^{-3} \) on 10th June 1998 at 15:00 h. In autumn, the figure is very similar to that of winter months, but with a major difference between the arithmetic mean and the median. The average concentration never goes over the
value of 100 µg m⁻³ for any hour, whereas the maximum value is of 142 µg m⁻³ and measured at 14:00 h on 3rd October 1998.

4. Comparison of the ozone concentration in urban and rural areas

Fig. 8 shows the evolution of the hourly average of ozone concentrations in winter, spring, summer and autumn in urban and rural areas. From this figure the following can be deduced:

(1) The average ozone concentrations in all the four seasons are higher at the rural site than at the urban one. This can be attributed to the lower number of sinks in the rural area and/or to the arrival of precursors transported from mid and long distances (Hov and Schmidbauer, 1992; Saitanis, 2003).

(2) The daily cyclical behaviour is weaker at the rural area in particular regarding the minimum value in the early hours of the morning being a clear indicator of less development in the nocturnal inversion layer and/or lower sources of NO. The habitual loss processes of ozone at night, especially in the urban area, are fundamentally due to the cessation of the mixing of ozone in the middle layers after dusk and a loss of ozone by titration with NO associated with surface deposition as a consequence of the local emission of nitrogen oxides in the superficial layer (Hakola et al., 1991).

(3) For the midday hours, characterised by the photochemical formation of ozone, winter and autumn are the seasons that show the greatest difference between the urban and rural sites. This difference is smaller in spring, while in summer similar behaviour is observed in both study areas.

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, agricultural productivity and forestry. The ozone threshold of the European Union directive for damage to human health (120 µg m⁻³, 8 h average) is exceeded in the Mediterranean area systematically for at least 4 months of the year. The one for informing the population (180 µg m⁻³, hourly average) can also be exceeded frequently from April to August. The one for vegetation (65 µg m⁻³ as a 24-h average) is exceeded systematically for more than six months of the year.

Following the European Union guidelines, Table 1 exhibits the percentage of ozone data exceeding the thresholds at the urban and rural sites for the different seasons, both for the population and vegetation. It is remarkable that the 110 µg m⁻³, 8-h ozone standard for human health protection may often be exceeded at noon and during the afternoon (12:00–20:00) during the summer months at the two sites, especially at the urban site. Spain’s hourly population information threshold (180 µg m⁻³) is exceeded more often at the urban station.
than the rural one. Regarding the threshold for vegetation, ozone concentrations are frequently exceeded mainly during spring and summer months in the rural area. It is important to the agriculture in this area, and other Mediterranean countries, that ozone concentrations remain fairly high from autumn to spring, which is the actual growing season for plants in the region. There is evidence of ozone-induced adverse effects on crops in the Mediterranean. Biomonitoring and field observations have indicated that ozone injury is widespread on crops grown in the Mediterranean (Fumagalli et al., 2001). Due to the complexity of the phenomenon, further research is needed for the study of important parameters governing the formation and distribution of rural ozone in the boundary layer and the free troposphere in the southern part of the European continent.

5. Conclusions

The study of surface ozone levels recorded at two stations, in Málaga city and in La Mayora experimental station at a distance of 45 km from Málaga, showed that the surface ozone levels at the rural site are generally high when compared with the urban site. At these two stations there is a clear seasonal variation exhibiting a maximum in summer and a minimum in winter. In winter, spring and autumn, urban ozone concentrations are always lower at the urban station than at the rural station, while concentrations are similar during the summer months. The diurnal variation at the urban site is considerably larger than at the rural site which may be attributable to the different site characteristics influencing the nocturnal

![Fig. 8. Average hourly evolution of ozone concentrations in winter, spring, summer and autumn at the urban and rural sites.](image-url)
ozone destruction close to the ground. Ozone concentrations at the urban station vary from 184 to 5 μg m⁻³ and the values at the rural site vary from 189 to 11 μg m⁻³. Ozone standard for human health protection may be often exceeded at noon and afternoon during the summer months at the two sites, especially at the urban site. Spain’s hourly population information threshold is exceeded more often at the urban station. The thresholds for the vegetation are frequently exceeded at the rural site mainly during spring and summer months. All these results will provide a physical basis for accurately predicting ozone concentration in extensive future research.

References


