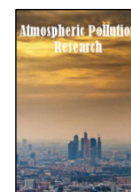


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Surface ozone variations at a rural area in the northeast of the Iberian Peninsula

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ABSTRACT

The aim of this paper is to study the levels and variability of surface ozone in the lower Ebre Valley and to estimate whether this surface ozone has its origin in local photochemical processes or in long-range transport. Surface ozone data series of twelve years (1994–2005) have been used from a rural area (Ebre Observatory) together with three years (2003–2005) data of nitrogen dioxide (NO₂). Ozone trends over the whole seasonal period, weekly and daily variations and exceedances of the legal threshold have been investigated. Furthermore, a representative ozone event has been studied in detail. Using ozone data from the twelve-year period resulted in a positive trend with an increase of 2.18 μg m⁻³ year⁻¹ and 0.64 μg m⁻³ year⁻¹ in summer and winter, respectively. The seasonal evolution of ozone gives a minimum value in winter and a maximum higher than 75 μg m⁻³ associated with the minimum values of NO₂. Ozone–NO₂ variation shows a weak ozone increase on weekdays and a small decrease in NO₂ concentrations at the weekends. Hence, a weekend effect is not observed. Ozone and NO₂ concentrations show a diurnal pattern with NO₂ peaks both in the early morning and in the evening, and maximum ozone concentrations, higher than 90–100 μg m⁻³, from 12:00 to 18:00 UTC in the warmer seasons. The threshold for the protection of human health has been exceeded from March to September each year, with a mean of 33 times per year. An event with high ozone levels originated by transport processes from the Mediterranean area was also analysed. The results suggest that high ozone could be caused mainly by transport mechanisms, and the Ebre valley could be considered to be a natural communication channel between the western Mediterranean basin and the Atlantic Ocean.

Keywords: Ozone, nitrogen oxides, ozone trends, seasonal–weekly–daily variations, ozone episode

doi: 10.5094/APR.2013.013



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Article History:

Received: 13 August 2012

Revised: 06 February 2013

Accepted: 06 February 2013

1. Introduction

Surface ozone is a secondary pollutant produced through a series of photochemical reactions that involve precursors such as nitrogen oxides and non-methane hydrocarbons—mainly, other volatile organic compounds (VOCs), and CO. In many areas around the world, photochemical pollution is characterised by medium to high ozone levels and is an important environmental problem (Baldasano et al., 2003; Shan et al., 2009; Roberts–Semple et al., 2012) with well-known effects on human health, vegetation and forests (Galizia and Kinney 1999; Paoletti, 2006).

Europe is a region significantly affected by ozone pollution due to the existence of important precursor sources (industrial and traffic emissions) as well as its weather conditions (Menut et al., 2005; Lasry et al., 2007; Tripathi et al., 2012). The Mediterranean countries of Europe are the ones most affected by ozone pollution due to several factors: high levels of solar radiation and temperatures, meteorological conditions governed by mesoscale processes, and emissions of anthropogenic and biogenic ozone precursors which favour photochemical ozone production (Augustin et al., 2006). Therefore, elevated ozone concentrations are common at different sites of the western Mediterranean basin (Viras, 2002; Gangoiti et al., 2006; Sanchez et al., 2007; Khoder, 2009). In this region, the ozone cycle shows a behaviour which differs significantly from one station to another, depending on

their topographic location (coast, valley, etc.), atmospheric circulations (land–sea breeze, valley breeze, synoptic flows) or chemical processes (Millan et al., 2002).

In the Iberian Peninsula, several studies related to surface ozone and its precursors have been carried out in recent years (Duenas et al., 2004; Garcia et al., 2005; Adame et al., 2008; Adame et al., 2010; Pires et al., 2012). In the northeast, the studies have mainly been carried out in Catalonia and Valencia (Figure 1). In Catalonia, the Barcelona metropolitan area and the industrial area of Tarragona are the most studied zones (Toll and Baldasano, 2000; Jimenez et al., 2005; Filella and Penuelas, 2006; Castell et al., 2008). These studies have focused mainly on the transport processes of ozone precursors emitted in coastal areas, which are transported inland by land–sea breeze mechanisms, leading to the consequent formation and accumulation of ozone in rural areas (Ribas and Penuelas, 2004; Ribas and Penuelas, 2006). On the other hand, the Valencia region, located in the east of the Iberian Peninsula, also offers favourable conditions (high levels of solar radiation and temperature, frequent mesoscale processes, intense biogenic and anthropogenic ozone precursor emissions, etc.) for the formation of photochemical pollutants. For this reason, ozone dynamics as well as the influence of ozone on the vegetation and crops of this region have been widely studied (Martin et al., 1991; Millan et al., 2002; Sanz et al., 2007). Nevertheless, there are rural zones in the north–east of the Iberian Peninsula which present

photochemical pollution problems. They have not been studied in detail or have merely been included as part of general studies (Felipe-Sotelo et al., 2006). These areas, which contain protected natural areas, crops and population, are also affected by medium to high ozone concentrations.

The aim of this paper is to study the levels and variability of ozone concentrations and to analyse the ozone trends in a rural area located in the lower Ebre Valley. From these results we aim to estimate if this surface ozone has its origin in local photochemical processes or in long-range transport. In addition, this study could contribute to the general knowledge of photochemical air pollution in the western Mediterranean basin. To perform this work we have

used the hourly concentration data recorded during a twelve-year period at the Ebre Observatory.

2. Method

2.1. Study area description

The measurement site is the Ebre Observatory (40.8 N, 0.5 E) located in the south of Catalonia, at the lower end of the Ebre valley, 15 km from the Mediterranean Sea coastline (Figure 1). The final stretch of the river flows in a NW–SE direction with mountains reaching 400 m above sea level (asl) on the eastern side and 1 400 m asl on the western side.

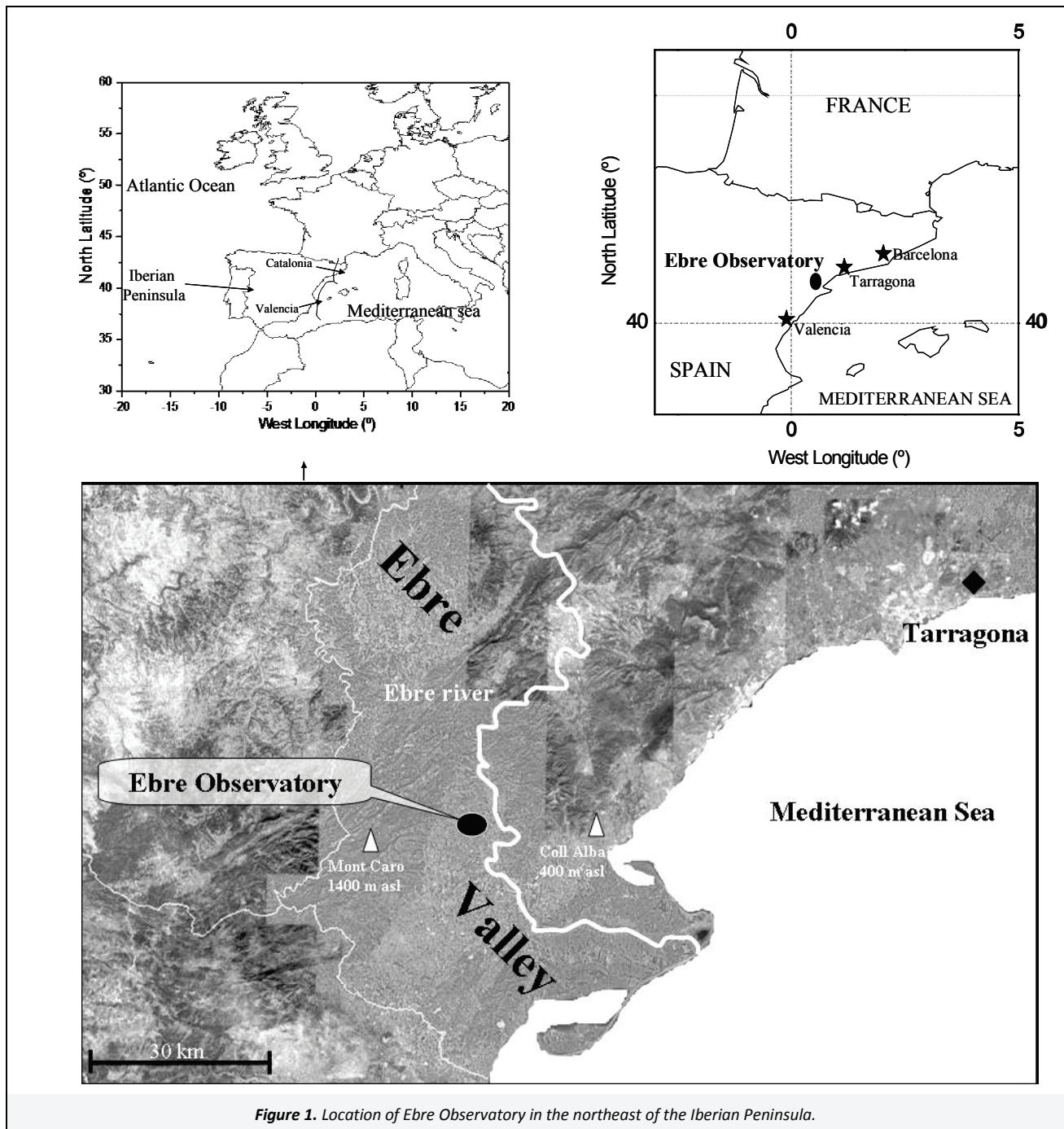


Figure 1. Location of Ebre Observatory in the northeast of the Iberian Peninsula.

The wind regime offers two prevailing directions. The N–NW direction is predominant in the winter months, while SE winds are predominant in summertime. These wind directions are controlled by the channelling effect of the valley. Therefore, orography has a strong bearing on the atmospheric surface dynamics in the winter period. The wind speed is high with gusts exceeding 27 m s^{-1} recorded almost every year. However, on summer days the wind speed ranges between 2 and 10 m s^{-1} and on windy days the strongest gust rarely exceeds 21 m s^{-1} . The climate in this region is typically Mediterranean, characterised by hot and dry summers. The monthly mean temperatures vary from 25°C recorded in July and August (the annual maximum), to a yearly minimum of 9°C in January. The average relative humidity during summer months is approximately 60%. Autumn is the season with most rainfall, with a monthly maximum of 82 mm in October. The study area is a rural environment, surrounded by forests and agricultural zones, with a population of around 40 000 inhabitants and very few industrial activities. Hence, the anthropogenic emissions of ozone precursors are mainly linked to traffic activity. The major ozone precursor emissions could be attributed to the vegetation and forests (Penuelas et al., 1999). The amount of NMVOCs emitted by vegetation in Catalonia during 2000 was estimated as $46.9 \text{ kt year}^{-1}$ with monoterpenes being the most abundant species (24.7 kt), followed by other biogenic volatile organic compounds (e.g. alcohols, aldehydes and acetone) (16.3 kt), and isoprene (5.9 kt) (Parra et al., 2004). This is of the same magnitude as on-road traffic emissions and one third of the total anthropogenic sources. In a general, this area in Catalonia has been identified as a zone of moderate industrial/urban influence and medium–high ozone levels (Felipe–Sotelo et al., 2006).

Potential sources of ozone precursors are found to the north and south of the Ebre valley. In the north, we find the metropolitan area of Barcelona (located 225 km from the Ebre Observatory) with emissions mainly from traffic and industry, and Tarragona (located 85 km north) with emissions from both the oil industry installations and traffic. Valencia, sited 150 km to the south, displays both industrial and urban emission sources.

2.2. Instrumentation and database

Ozone measurements have been conducted regularly since 1994 thanks to the collaboration between the Ebre Observatory and the Spanish National Meteorology Service (currently known as the Agencia Estatal de Meteorología, AEMET)—which performed the maintenance and calibrations of the instrumentation. Data were recorded with a MCV automatic ozone analyser from 1994 until 2000, when it was replaced with an UV photometric O_3 analyzer, Model 49C (Thermo Environmental Instruments Inc.). Both instruments work on the principle that ozone molecules absorb ultraviolet radiation at a wavelength of 254 nm. The instruments are periodically calibrated (approximately every six months). To collect NO_2 data, we used an analyser based on the chemiluminescence method which carries out simultaneous measurements of NO and NO_2 . While NO is measured directly, NO_2 is measured indirectly after conversion to NO. Both instruments show a detection threshold of 1 ppb with a precision of ± 2 –5%. The calibrations and maintenance operations mentioned for ozone have also been carried out on the NO_2 analyser.

Our study has been carried out with hourly ozone values recorded over twelve years from 1994 to 2005. To support this investigation, NO_2 data collected from 2003 to 2005 as well as

meteorological data (atmospheric pressure, wind speed and direction, relative humidity and temperature) have been used.

3. Results

3.1. Trends and ozone seasonal variation

Several studies revealed that, in general, surface ozone in the northern hemisphere has increased over the past three decades with an average increment of approximately 0.5 – $2\% \text{ yr}^{-1}$ at northern mid–latitudes (Vingarzan, 2004). Carslaw (2005) reported an average increase in ozone concentrations of $0.5 \mu\text{g m}^{-3} \text{ year}^{-1}$ over the period 1990–2001 and Derwent et al. (2007) an average increase of $0.62 \mu\text{g m}^{-3} \text{ year}^{-1}$ over the period from April 1987 to March 2007.

In this work, trends in the annual average ozone concentrations have been studied using the daily mean and the daily maximum 8 h average for each season (Figure 2). Winter has been considered as consisting of December, January and February; spring as March, April and May; summer as June, July and August and autumn as September, October and November.

In general, two main periods are observed, the first one being from 1995 to 1999 with an ozone decrease in the annual average calculated using both the daily mean and the daily maximum 8 h in all the seasons and, hence, there is a negative trend. Nevertheless, in the following years from 2000 to 2005 there is an ozone increase which means a positive trend. On the other hand, using the whole period and the annual averages, the trend has been calculated with the linear regression line for each season, giving a positive slope in all the cases (Figure 2). The linear trend shows an increase during the winter months between 0.64 , using mean daily values, and $0.68 \mu\text{g m}^{-3} \text{ year}^{-1}$, using daily maximum 8 h values. In spring, it varies between 0.42 and $1.88 \mu\text{g m}^{-3} \text{ year}^{-1}$, while in summer the highest increase is obtained with a ratio of 0.53 to $2.18 \mu\text{g m}^{-3} \text{ year}^{-1}$. On the contrary, the autumn months have the lowest trend increase. The values found are similar to those obtained in other works referenced above. The explanations to these trends could be associated to several reasons such as changes in the meteorological conditions, change in ozone precursor emissions from petroleum and natural gas which several modelling studies indicate that these emissions can produce regional scale ozone enhancements (Reidmiller et al., 2009) and the control of the domestic emissions (Cooper et al., 2012). Future works will be required to determine the causes.

The ozone annual maximum was recorded between May and July (most often in July) with very similar levels measured throughout the studied period. No inter–annual differences were found. The annual minimum was always observed in November and December, with very similar levels from year to year.

The seasonal evolution of ozone and NO_2 in the Mediterranean area has been documented in different studies (Monks, 2000; Millan et al., 2002). Figure 3 shows ozone, NO_2 , temperature and relative humidity monthly averages. In the area of our study, monthly minimum ozone values are recorded in the winter period (mainly in January and December) with values higher than $40 \mu\text{g m}^{-3}$. These values are similar or even higher than the ones measured at other sites in the western Mediterranean (Ribas and Penuelas, 2004). At this time of the year, the low temperatures ($10 \pm 2^\circ\text{C}$ in January and December), high relative humidity ($70 \pm 6\%$ in December), lower solar radiation, and structure of the

atmospheric boundary layer (Helmig et al., 2008) are not suitable for the formation of photochemical ozone. Moreover, during these months, the highest levels of NO_2 , ranging between 8 and $13 \mu\text{g m}^{-3}$, are recorded, due to the lower boundary layer height will raise the NO_x concentrations levels.

In spring and summer, ozone levels could be higher due to the transport of air masses bringing ozone from other sites or due to photochemical formation in situ. This formation is favoured by the high levels of temperature and solar radiation, mixing processes and emission levels of ozone precursors. Moreover, the formation of residual layers at heights and low horizontal dispersion under anticyclonic conditions bring air masses with ozone from other regions. At the Ebre Observatory the maximum was recorded in July with a value of $82 \pm 10 \mu\text{g m}^{-3}$ associated with the monthly maximum of temperature ($25 \pm 1^\circ\text{C}$), and the minimum of relative humidity ($62 \pm 2\%$) and NO_2 ($5 \pm 2 \mu\text{g m}^{-3}$). Despite the fact that the maximum occurs in July (a difference of $7 \mu\text{g m}^{-3}$ with respect to the previous months), ozone levels remain higher than $75 \mu\text{g m}^{-3}$ from April to June which is similar to the results found in other rural areas of Spain (Duenas et al., 2004; Garcia et al., 2005). In August, a decrease in the ozone levels associated with an increase in NO_2 concentrations and relative humidity as well as the decrease in temperature is recorded.

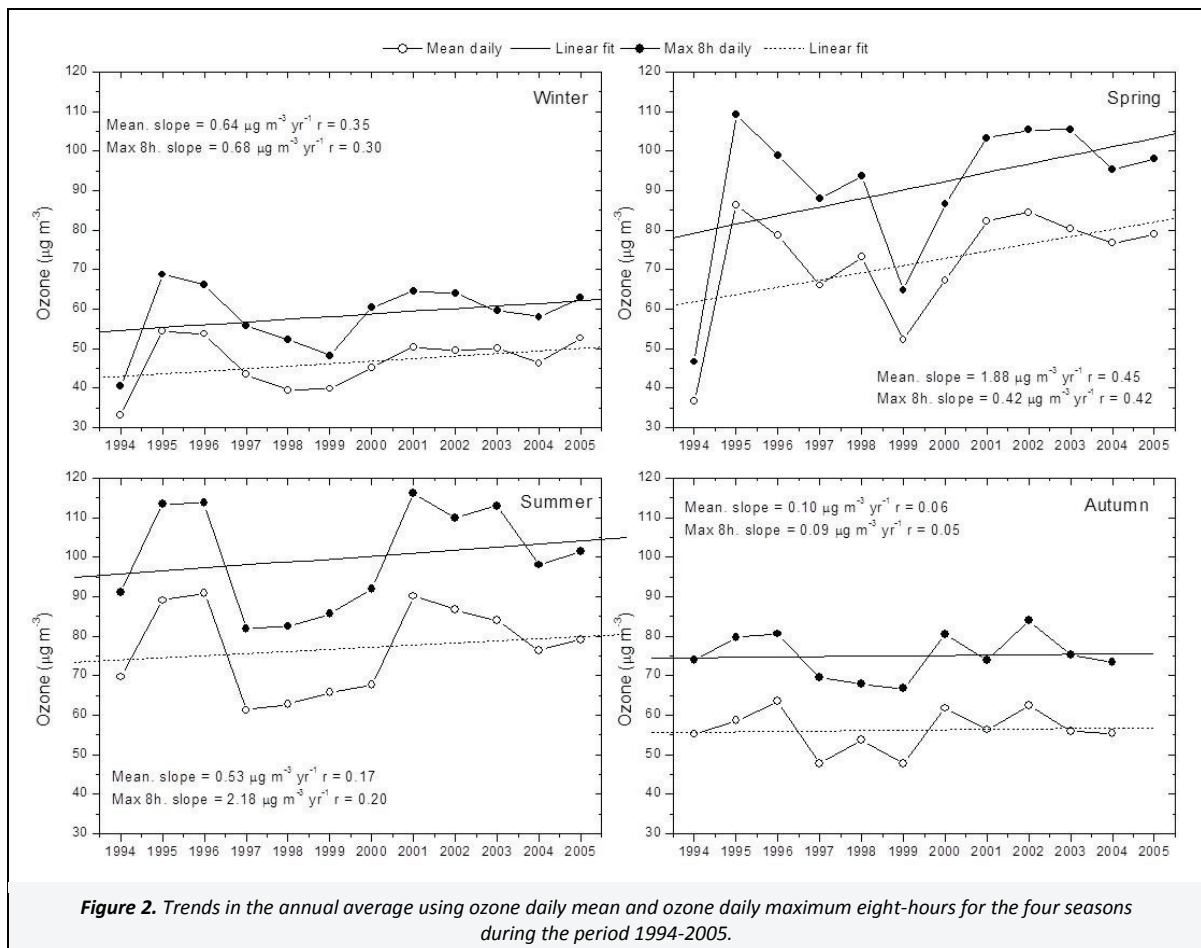
The seasonal cycle is very different from that observed in polluted urban–suburban areas with a marked peak in summer months (Adame et al., 2008). Therefore, this seasonal behaviour and the monthly levels recorded are closer to reflecting a rural character rather than an urban–suburban one.

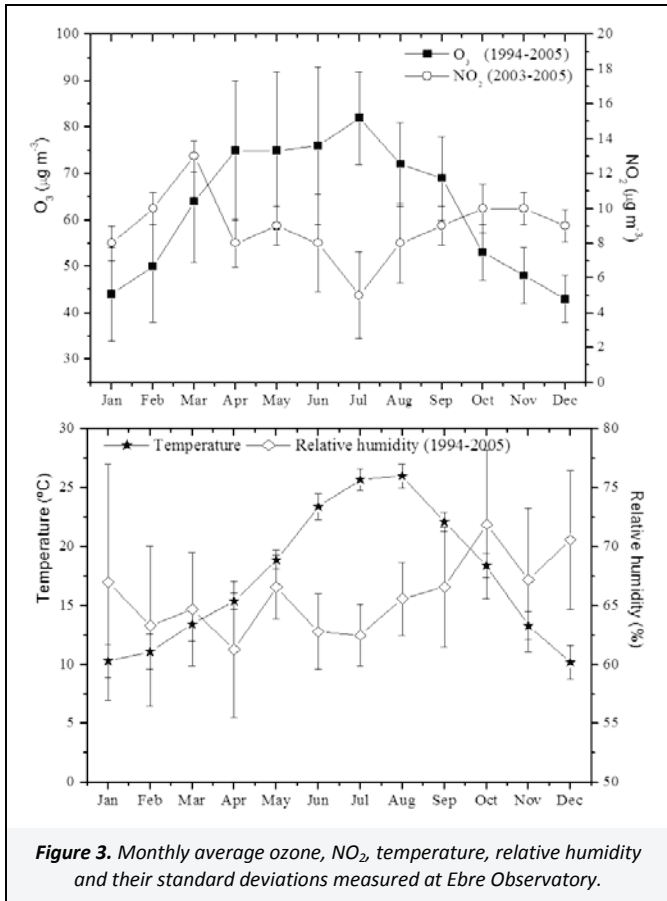
3.2. Diurnal variation

A good way of unravelling the ozone dynamics is to examine its diurnal pattern since the different processes of formation and destruction as well as transport is reflected by the diurnal variations. Figure 4 shows the seasonal variation of daily ozone and NO_2 as well as temperature and relative humidity, with the aim of studying the daily behaviour dependent on the season.

At night, the ozone concentration remains constant in winter ($\sim 45 \mu\text{g m}^{-3}$), with a slight increase in autumn (~ 50 to $45 \mu\text{g m}^{-3}$) and spring (~ 60 to $55 \mu\text{g m}^{-3}$), and a more abrupt one in summer (~ 65 to $55 \mu\text{g m}^{-3}$). Nocturnal NO_2 levels display similar concentrations (7 to $10 \mu\text{g m}^{-3}$) in all seasons. Temperature and relative humidity recorded in the nocturnal period show differences according to the season, with a major cooling in winter and a higher relative humidity, and the opposite variation in summer months. The lower nocturnal ozone levels are associated with *in situ* destruction of ozone by the well-known reaction between ozone and NO and deposition mechanisms.

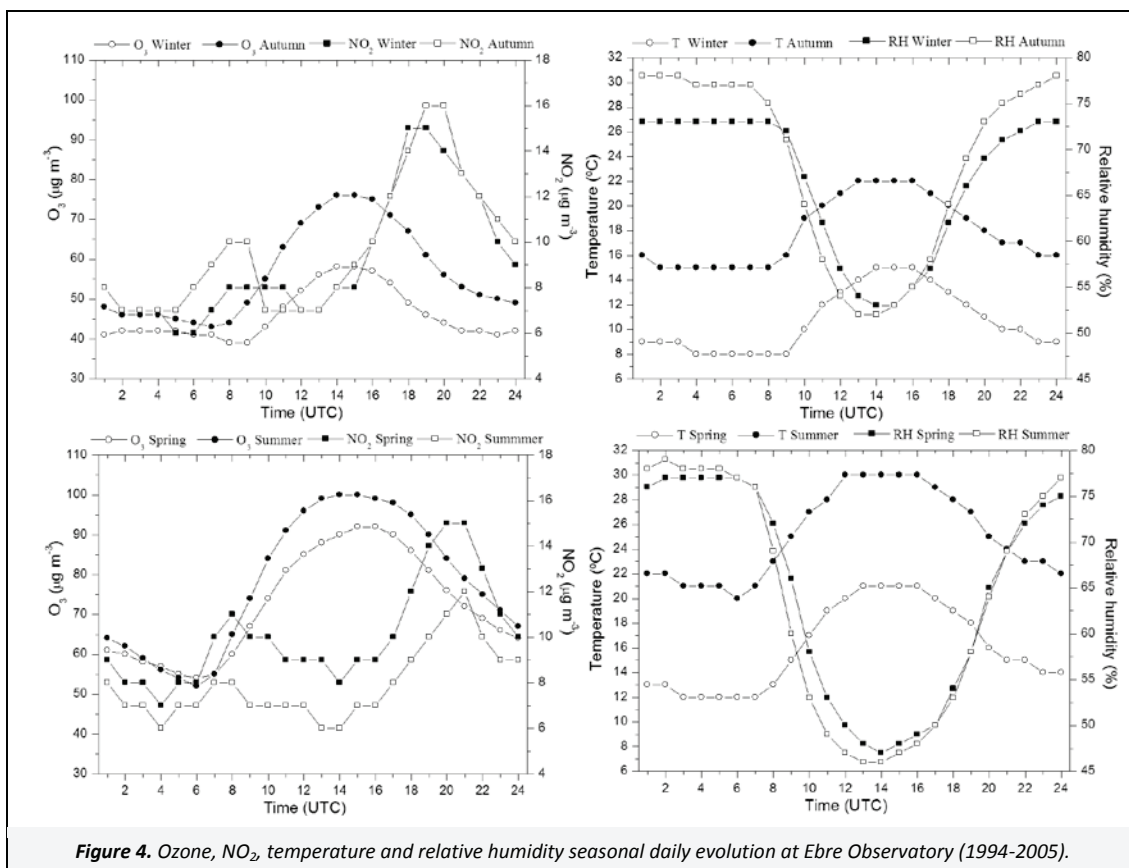
From 6:00 UTC onwards the NO_2 levels show a slight increase, with a maximum between 8 and $11 \mu\text{g m}^{-3}$ at 8:00–9:00 UTC which indicates that the fresh emissions are of low intensity. Moreover, in urban and suburban polluted areas, where the NO_x levels are high, a decrease in ozone concentrations with respect to nocturnal levels is recorded, due to the destruction by NO. However, in the study area this decrease is not observed. This could reflect the fact that the NO_x levels are not very high, given that traffic emissions are negligible, and are insufficient to remove the ozone accumulated during the night.





The ozone increase after sunrise could be attributed to the vertical transport from upper layers which are favoured at noon by the convective activity in the continental boundary layer activated by solar radiation (Millan et al., 2000; Monks et al., 2000). On the other hand, it is also possible to observe ozone with its origin in the local photochemical production in the mixing layer; although with the NO₂ levels observed, the photochemical activity is not very intense.

The ozone maximum is achieved around 15:00 UTC in winter with monthly mean temperatures oscillating between 15 and 22 °C. Nevertheless, in spring and summer months there is not a clear peak of ozone, although its concentrations remain between 90 and 100 µg m⁻³ for 6 hours (12:00 to 18:00 UTC). In the warmer seasons, the monthly temperature varies from 21 to 30 °C and the monthly relative humidity in central hours is about 47% which indicates that the ambient air is dry and warm, suitable for the mixing processes. These concentrations are similar or even higher than those recorded at other locations of the Mediterranean Basin (Kalabokas et al., 2000; Riga-Karandinos and Saitanis, 2005) and in rural areas of the Iberian Peninsula (Duenas et al., 2004; Ribas and Penuelas, 2004). In polluted urban and suburban areas strongly affected by ozone precursor emissions, an increasing trend of ozone is seen during the morning with a clear peak at noon or in the afternoon (Filella and Penuelas, 2006). Nevertheless, the ozone daily behaviour and low NO₂ values recorded at the Ebre Observatory could indicate that ozone concentrations recorded during these hours may originate mainly in horizontal or vertical transport or, and with minor intensity, via local formation. Another possible explanation could be the combination of high biogenic VOC emission levels with lower values of NO_x yielding medium-high ozone levels.



From evening until midnight the intensity of solar radiation and temperature decreases, while relative humidity increases. Under these conditions, photochemical reactions are inhibited and ozone depletion is principally driven by the removal via deposition. In addition, at approximately 17:00 UTC NO₂ concentrations begin to increase with a peak at 21:00 UTC, which is very probably caused by local traffic emissions and the formation of the nocturnal boundary layer (Pournazeri et al., 2012). This nocturnal peak with values between 12 and 16 µg m⁻³ is higher than the one measured during the morning. However, NO₂ levels measured are very low compared to urban and suburban areas. In addition, in other rural Mediterranean areas NO₂ concentrations are measured around 30 or 40 µg m⁻³ with the same or even lower ozone concentrations (Riga-Karandinos and Saitanis, 2005).

3.3. Weekdays–weekend daily differences of ozone and NO₂

Differences in ozone and NO_x levels according to the day of the week, with higher ozone levels and lower NO_x values at weekends than on weekdays, are observed mainly at monitoring sites with an influence from urban emissions. This behaviour is caused by weekly changes in emissions from human activities. This emission–concentration relationship at urban, suburban and rural sites is not well elucidated as can be seen in contradictory reports (Jenkin et al., 2002; Fujita et al., 2003; Stephens et al., 2008).

In regions where weekday and weekend ozone values are approximately the same, the processes of background or long-range transport dominate, while sites dominated by regional or local anthropogenic ozone production present weekday–weekend differences (Heuss et al., 2003). At clean background sites, we would expect to record the same ozone levels on weekdays and at the weekend. However, polluted sites characterised by high ozone level precursors could also present similar ozone concentrations on workdays and non-working days because of a variety of different factors, mainly of meteorological character, which are more influential than the change in traffic emission patterns.

Therefore, an analysis of ozone–NO₂ differences on weekdays and at weekends is an information source worth investigating to see whether ozone has its origin in local photochemical production or in transport processes. Weekdays are taken as Monday to Friday while weekends are Saturday and Sunday.

In order to analyse the weekend effect in the studied area, ozone and NO₂ daily evolution have been calculated on weekdays and at weekends and in all four seasons, as well as the daily average difference between weekend and weekdays (weekend minus weekdays). The results obtained are shown in Figure 5.

In winter and autumn, the average daily difference of ozone shows positive values throughout the day, with concentrations higher at the weekends than on weekdays, although there is a maximum close to 5 µg m⁻³ at 9:00 UTC. During the night, the differences are negative but with a value of 1 µg m⁻³. The NO₂ mean daily differences in autumn and winter are negative, with NO₂ being higher on weekdays than at the weekend. Nevertheless, during 75% of the day the differences are lower than 2 µg m⁻³ and the maximum difference has been found at 19:00 UTC with a value of 4 µg m⁻³.

Regarding spring and summer, ozone levels offer positive differences all day, and the maximum difference was found at 9:00 UTC with values of 7 and 5 µg m⁻³ in spring and summer

respectively. Although in the early hours of the night in summer, NO₂ shows positive values close to 1–2 µg m⁻³, the rest of the day, in both spring and summer, the NO₂ differences are always negative. The highest differences are found at 8:00 UTC and 21:00 UTC with maximum values of 5 µg m⁻³. According to the criteria used by Blanchard and Fairley (2001), the ozone weekend effect is statistically significant if the ozone difference exceeds 10 µg m⁻³. Sadanaga et al. (2008) found negative NO₂ differences in suburban stations higher than 16 µg m⁻³ and positive differences in ozone levels higher than 2 µg m⁻³. On the other hand, Fujita et al. (2003) divided the intensity of the ozone weekend effect into three types, according to the value of ozone peak difference: no weekend effect (concentration difference of peak O₃ ≤ 10 µg m⁻³), moderate weekend effect (10 µg m⁻³ < concentration difference of peak O₃ ≤ 30 µg m⁻³), and intensive weekend effect (concentration difference of peak O₃ > 30 µg m⁻³).

Applying these criteria and comparing with the results obtained at other sites, the studied area does not present a weekend effect. In addition, taking the low NO₂ levels and the medium–high ozone concentrations measured, together with the weak influence of traffic emissions (the NO₂ daily evolution displays peaks of low concentration which could be attributed to the traffic) too weak to produce a weekend effect, it could be suggested that ozone behaviour is governed mainly by transport mechanisms of ozone air masses with their origin at different sites and with less intensity on local photochemical production.

3.4. Exceedances of the thresholds established in the European Ozone Directive

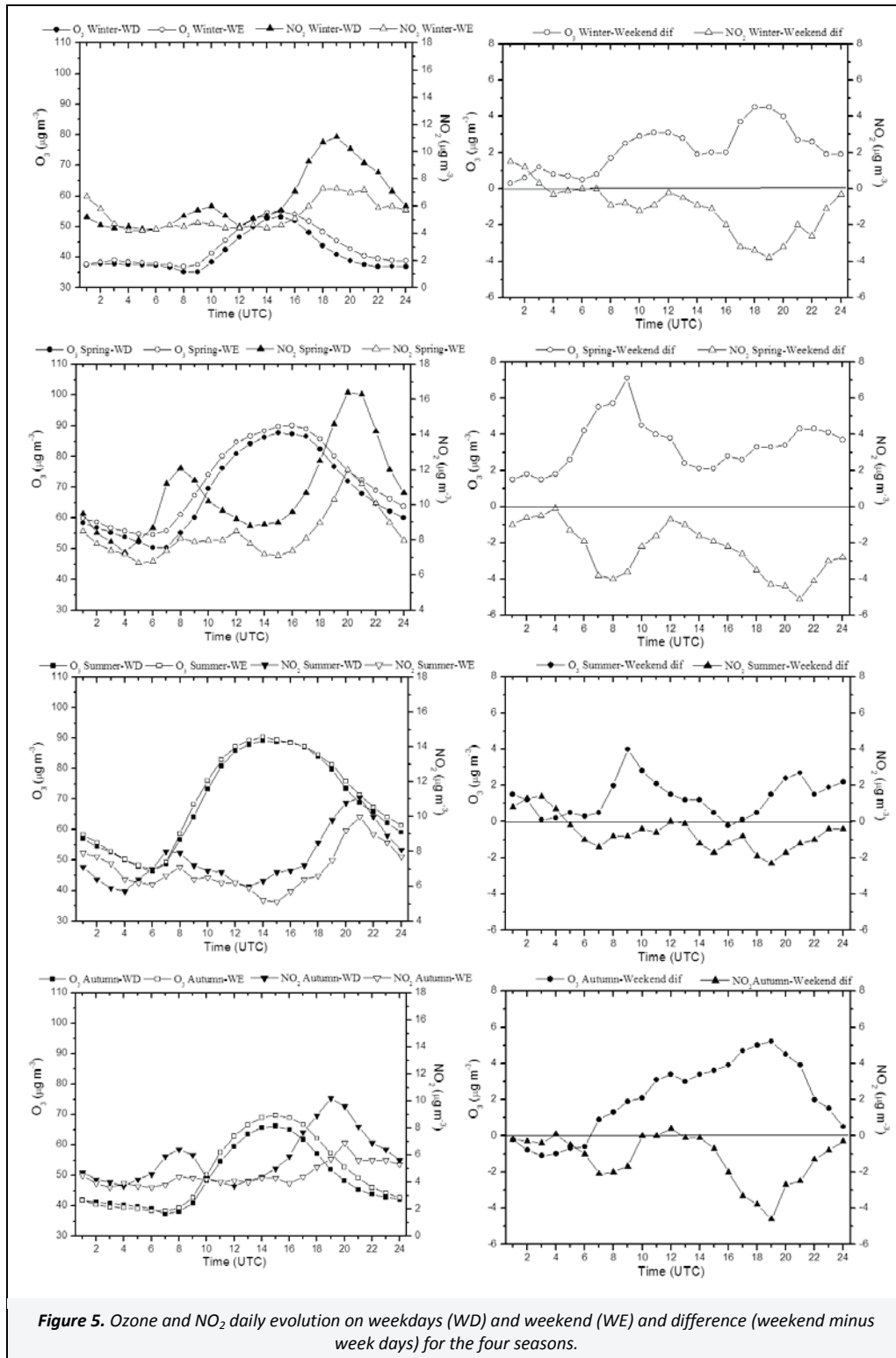
The European Directive 2002/3/CE on ozone in ambient air (ED, 2002) and Directive 2008/50/EC on ambient air quality (ED, 2008) and cleaner air for Europe define ozone target values and long-term objectives. The target values for 2010 with regard to ozone ambient air concentrations are: 120 µg m⁻³ as the maximum daily eight-hour average which must not be exceeded on more than 25 days per calendar year averaged over 3 years. This value is also a long-term objective for the protection of human health. This directive also includes 180 µg m⁻³ for a 1 h average as the information threshold and 240 µg m⁻³ for the 1 h average as the alert threshold. The alert threshold was not reached during the studied period. However, the information threshold was reached on 5 July 1994 with a value of 189 µg m⁻³ at 21:00 UTC which is the historical maximum. The occurrence of this maximum at this time may indicate a possible origin in transport processes. The target for human health protection was exceeded between March and September (Figure 6), and more frequently in June and July. Figure 6 shows the monthly averages of daily mean, daily maximum 8 h (calculated with 8 h values) and daily maximum (calculated with hourly values) for days exceeding the threshold for human health protection. In this area a typical day exceeding this threshold presents a daily mean of ~98 µg m⁻³, a daily maximum 8 h of ~130 µg m⁻³ and a daily maximum of ~141 µg m⁻³ as an hourly average.

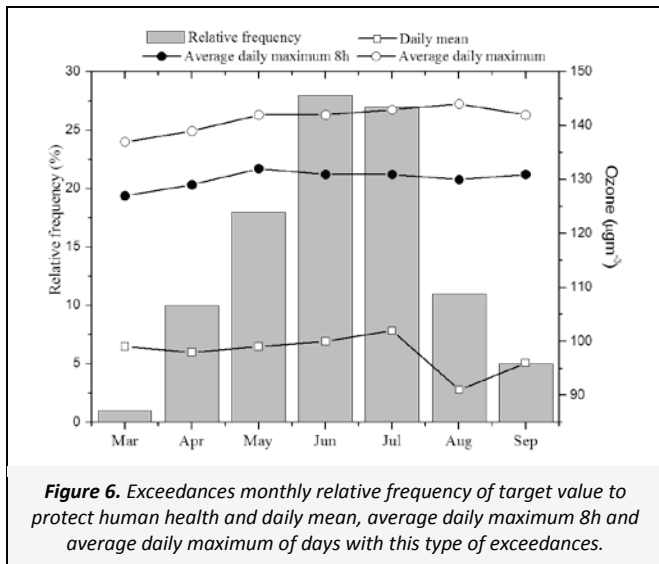
The number of cases exceeding this threshold shows differences from one year to another, since it is strongly affected by the weather conditions of each year. The mean number of exceedances per year is 33, and the maximum numbers of cases were observed in 1995 and 2003 with 47 and 43 days respectively, while the minimum was in 1998 with 11 days. The threshold of 65 µg m⁻³ as a 24 h average was defined to protect the vegetation in the ozone Directive 1992 but is not used currently. However, this

threshold has been calculated in order to compare with other studies. This threshold was exceeded in each month, but mainly in the spring–summer seasons with a mean of 163 days per year in the period 1994–2005 and a maximum of 261 and 234 days in 2005 and 2002 respectively. These values are higher than those obtained at other rural sites in the Iberian Peninsula (Duenas et al., 2004).

In the ozone Directive 2002 a new level, based on the parameter AOT40, was established. This was called “accumulated dose over a threshold of 40 ppb” and ratified in the Directive 2008.

This threshold is calculated as the sum of the differences between the hourly mean ozone concentration (in ppb) and 40 ppb for each hour when the concentration exceeds 40 ppb, accumulated during daylight hours along a defined time interval (either a 3– or 6–month). The critical daytime AOT40 value for trees over 6 months is $20\,000\ \mu\text{g m}^{-3}\text{ h}$ ($10\,000\ \text{ppb h}$), calculated from April to September, whereas the AOT40 to protect the vegetation is $6\,000\ \mu\text{g m}^{-3}\text{ h}$, calculated from May to July.





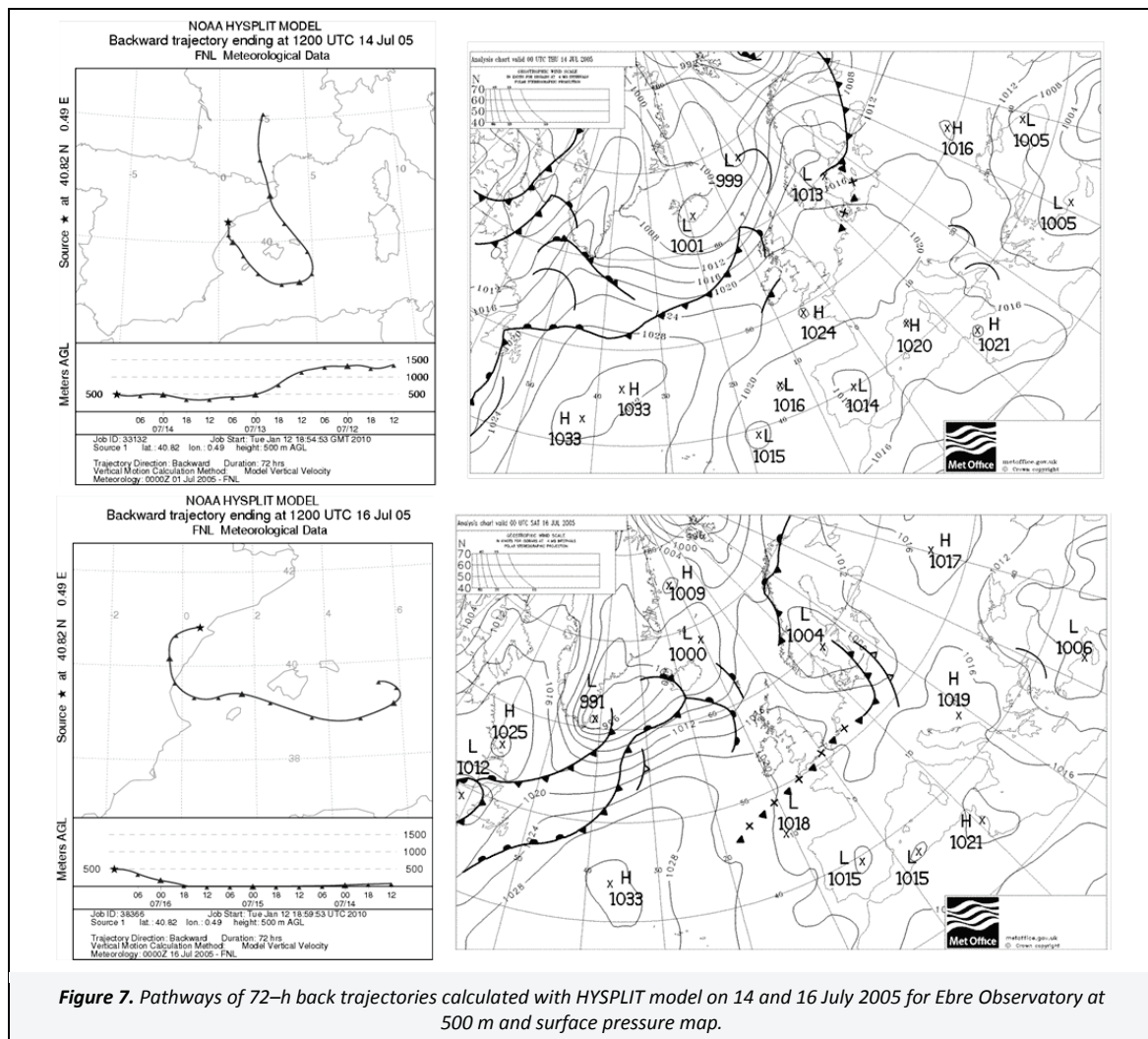
At the Ebre Observatory the mean value of AOT40 obtained from April to September was 19 780 $\mu\text{g m}^{-3}\text{ h}$. Therefore, this result exceeds the threshold by a factor of 3.2. With respect to AOT40, defined to protect trees, it was exceeded by a factor of 1.6 with a mean value of 31 929 $\mu\text{g m}^{-3}\text{ h}$. The high number of cases exceeding the thresholds to protect both human health and vegetation found in this region indicates that ozone concentrations

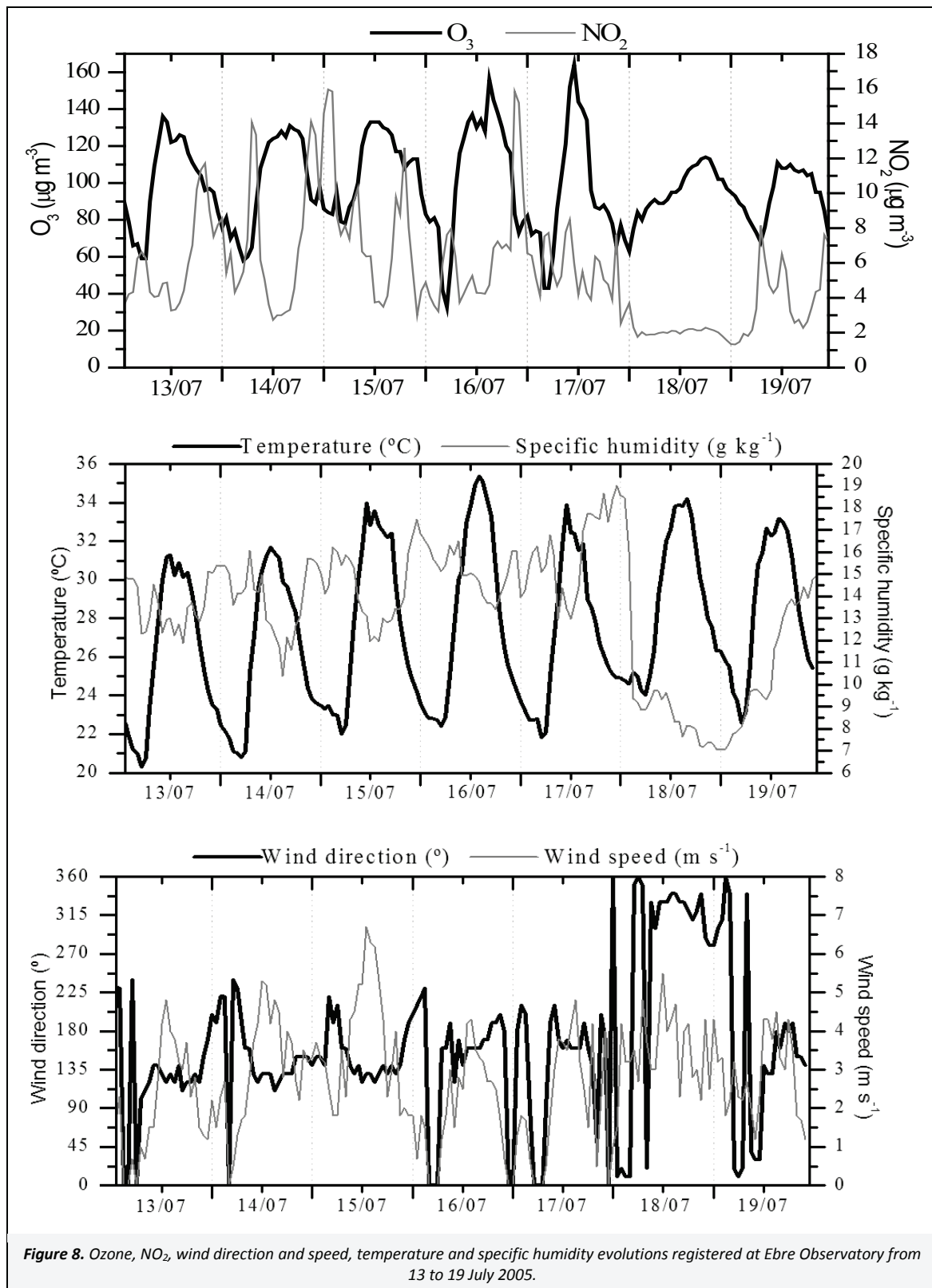
could be affecting human health in spring–summer seasons, and vegetation and forests at any time of the year.

3.5. Case study: ozone event in July 2005

As mentioned in the previous Section, the higher ozone concentrations in this area are observed between March and September. The situations with medium–high ozone concentrations are useful to improve our understanding of both ozone dynamics and air quality. Several ozone events were analysed in this area using this ozone data set and similar features were found. In order to show a typical and representative ozone event, we selected an event from the summer period, July 2005, with cases of exceedances of human health protection limits. The evolution and meteorological conditions of this event are similar to others recorded at the Ebre Observatory.

Three days before the event, ozone concentrations showed a clear daily cycle with maximum values close to 130 $\mu\text{g m}^{-3}$ and minimums from 60 to 65 $\mu\text{g m}^{-3}$. The NO_2 showed maximum values between 12 and 14 $\mu\text{g m}^{-3}$. Synoptic meteorological conditions were characterised by two high pressure systems, one in the Atlantic and another in area of the Mediterranean which influenced the study area (Figure 7). Therefore, the wind, in the lower Ebre valley, was blowing mainly from SE, as shown in Figure 8.





In order to find out the pathways of the air masses arriving at the Ebre Observatory, the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model has been used to calculate back trajectories (Draxler et al., 2009). Trajectories were computed for a 72-h period which is considered sufficient to represent the synoptic air flows. The trajectory terminates at Ebre Observatory at 12:00 UTC and at an elevation of 500 m above ground level. Figure 7 shows the pathway of the air masses during the previous

days coming from the Mediterranean Sea. This result indicates that the ozone measured at the Ebre Observatory was to be found over the Mediterranean Sea 72 hours beforehand.

From 15th to 17th July there is a change in the synoptic configuration – the isobaric gradient over the Mediterranean is weaker and the high pressure system disappears. As a consequence, the Ebre Observatory recorded wind from the SE, as on

previous days, but this time the wind speed was lower. This decrease in wind speed is also associated with an increase in the maximum daily temperature, with maximum values higher than 32 °C. Air masses during these days show short pathways (Figure 7). These air masses probably bring ozone and ozone precursors from the Mediterranean Sea during these two days with a possible origin on the east coast of the Iberian Peninsula, given the trajectory followed by the air mass. This ozone and the ozone precursors contribution from these source areas result in a fast ozone rise in the early morning on the 16th and 17th, reaching a daily maximum higher than 150 $\mu\text{g m}^{-3}$. During these days the threshold for the protection of human health was exceeded.

The direction of the wind indicates that air mass transported ozone towards northwest along the Ebre valley. Due to the fact that ozone is a secondary pollutant, if (during the transport) we find biogenic VOC emissions then it will be likely that zones located inland in the valley could experience ozone concentrations similar to or higher than 150 $\mu\text{g m}^{-3}$. Therefore, this event shows an ozone transport from the Mediterranean to the north using the Ebre valley as a natural channel.

The event was finished by the evolution of a high pressure system located in the Atlantic Ocean which moved towards the European continent. This new configuration produced wind of a northern component in all the north of Iberian Peninsula, which is channelled along the Ebre valley reaching the Ebre Observatory on 18th July. The main changes in local meteorological conditions were: change in wind direction, increase in wind speed and a significant decrease in relative humidity (Figure 5). This change of scenario produces a ventilation effect and a decrease in ozone levels on 18th and 19th July of 40 to 50 $\mu\text{g m}^{-3}$ with respect to the previous days.

In previous investigations, carried out in other areas of the western Mediterranean basin and Iberian Peninsula, the arrival of ozone air masses to the Basque Country (northern Spain) from the western Mediterranean using the Ebre valley as a pathway (Gangoiti et al., 2006) has been documented. Moreover, emissions from western Mediterranean and southern France sources have been observed travelling up the Ebre valley to the northern coast of the Iberian Peninsula (Millan et al., 2000). Therefore, the results of this analysis support the previous works.

4. Discussions and Conclusions

Twelve years of ozone hourly data and three years of NO₂ hourly measurements have been used to determine the level, trend and variability of the ozone concentration in a rural area in the northeastern Iberian Peninsula. Annual trends, seasonal, weekly and daily variations, as well as cases exceeding the legal thresholds have been studied. A representative case study of an ozone enhancement event has been included. Using meteorological conditions and by computing back trajectory, the possible origin of the ozone has been estimated.

Using ozone annual averages, we computed trends from 1994 to 2005. We found positive trends, but the slope varies as a function of the season. Considering winter months, the trend is 0.68 $\mu\text{g m}^{-3} \text{ year}^{-1}$, while in summer months we obtained a value of 2.18 $\mu\text{g m}^{-3} \text{ year}^{-1}$. Ozone values offer a clear positive trend in this region, similar to that obtained at other locations.

Ozone concentrations show a seasonal evolution typical of rural environments with a minimum in November and December and monthly mean values higher than 75 $\mu\text{g m}^{-3}$ from April to June with a maximum in July, which is associated with a minimum of monthly NO₂ values. No year-to-year differences in the levels and occurrence of the annual maximum (observed from May to July) and minimum (November and December) have been found.

Ozone and NO₂ concentrations show a diurnal pattern with constant levels during the nocturnal time. From 6:00 UTC onwards, a weak increase in NO₂ levels is observed, while the ozone maximum is achieved at 15:00 UTC in winter and autumn months, and remains higher than 90–100 $\mu\text{g m}^{-3}$ from 12:00 to 18:00 UTC in warmer seasons. A second peak greater than that seen in the morning is observed for the NO₂ concentrations at 21:00 UTC. The weekly patterns of ozone and NO₂ were analysed using the daily evolution of ozone and NO₂ at weekends and on weekdays as well as their differences. Positive differences were found for ozone (weekend minus weekdays) and negative ones for NO₂. Nevertheless, the values of the differences are low and applying the criteria defined in the literature, we see that this region is not affected by the weekend effect and, hence, it could not be considered under the influence of urban emissions.

Concerning the exceedances of the threshold defined in the European Directives, both to protect human health and vegetation, we can see that in the studied region the information threshold has been exceeded once, while the threshold to protect human health is exceeded every year from March to September with a mean of 33 times per year. The levels to protect the vegetation and forest according to the AOT40 parameter were also exceeded by a factor 3.2 and 1.6 respectively.

The origin of the ozone measured at a certain place is the sum of the local photochemical activity and transport processes. Our results show positive trends, seasonal variations – with values higher than 75 $\mu\text{g m}^{-3}$ from April to September, no weekdays/weekend differences, daily variations with elevated ozone concentrations for six hours, low NO₂ levels, and an elevated number of threshold exceedances in a rural area with no important ozone precursor sources. Together with the pathways of air masses in situations with ozone events, this could point to long-range transport processes being dominant as opposed to local photochemical activity.

On the other hand, as a result of the analysis of ozone events, it is possible to suggest that the Ebre valley could be a natural communication channel between the western Mediterranean basin and the Atlantic Ocean through the north of Iberian Peninsula. For these reasons, studies are being carried out to investigate the ozone levels and behaviour of the air masses that arrive at this region and to determine where the ozone sources that affect this region are located. The study carried out in this rural area as well as future works mentioned may contribute to improve the knowledge of ozone dynamics in the western Mediterranean basin.

Acknowledgements

The authors thank the Spanish National Meteorology Service (the current Agencia Estatal de Meteorología–AEMET) for providing the ozone and NO₂ data.

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