Assessment on the Ozone Air Pollution in a Medium Metropolitan Area: Seville (Spain)

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1. Introduction

Problems caused by the air pollution which are generated mainly in metropolitan areas and industrial complexes, become in the major challenges for the current society. The air pollution has its origin in the chemical species emission into the atmosphere which may be harmful for human health (Lin, et al., 2008; Doherty et al., 2009), vegetation and ecosystems (Cape, 2008). The pollutants in the atmosphere can be classified in primary, directly emitted to the atmosphere, or secondary, formed in the atmosphere from chemical or photochemical reactions.

Nowadays, the main air pollution problems are originated by secondary chemical species, as particles and surface ozone (Kumar et al., 2010; Lefohn et al., 2010). In Europe, there are several Directives to protect air quality, as the Directive 2008 which defines the new threshold for different pollutants.

Generally, the highest concentrations of secondary species are registered in areas far away from the emissions sources, as suburban and rural areas. Nevertheless, there are urban areas that due to both meteorological and emissions conditions can suffer high levels of secondary substances (Papanastasiou and Melas, 2009; Alvim-Ferraz et al., 2006).

In many countries there are air quality networks which measure concentrations both primary (NO, CO, SO_2) and secondary pollutants and provide air quality information in real-time. However, in spite of the elevated economic cost of these networks, it is usual that the collected data are only used to determinate if a pollutant exceed the legal threshold according to the current Directive. Nevertheless, with the information obtained in the air quality networks is possible to carry out studies in order to improve the understanding of the atmospheric pollution and to help in the definition of plans and control strategies to the air quality.

The work presented in this chapter is linked with a secondary pollutant, surface ozone, using data from an air quality network in a sensible region suitable to photochemical pollution problems. The study has been carried out in the Seville metropolitan area (low

Guadalquivir valley) and it is focused on the identification and analysis of ozone events. The events or episodes are defined such as situations with elevated ozone concentrations, exceeding the European Directive threshold, which are produced frequently in this region and affect to one millions inhabitants.
The aim of this paper can be double. To provide information of the ozone events in the metropolitan area with highest population in the southwest of Europe. In addition, to present a methodology which could be applied in other regions with air quality networks.
The first section of the chapter has been devoted to present a general vision of the photochemical air pollution. The second, Material and methods, shows the main features of the studied area, monitoring stations and dataset used in this work. The section 3 exposes the results obtained. The results section starts with a meteorological overview of this area. Following, seasonal and daily variation on ozone and NO_x are presented. In order to know the ozone events, criteria to extract of episodes has been applied and from the days selected as episodes have been analysed its features. In addition, a comparative analysis of days with and without events has been carried out. The phases of an event have been defined; and a specific episode has been studied with detail. Finally, conclusions have been included in the last section.

2. Materials and methods

In this section are presented the main characteristics of the study area as well as the monitoring stations and database used in this work

2.1 Description area

The Seville metropolitan area is located in the low Guadalquivir valley (south of Spain), about 100 km away from the gulf of Cadiz (Fig. 1). This metropolitan area has a population

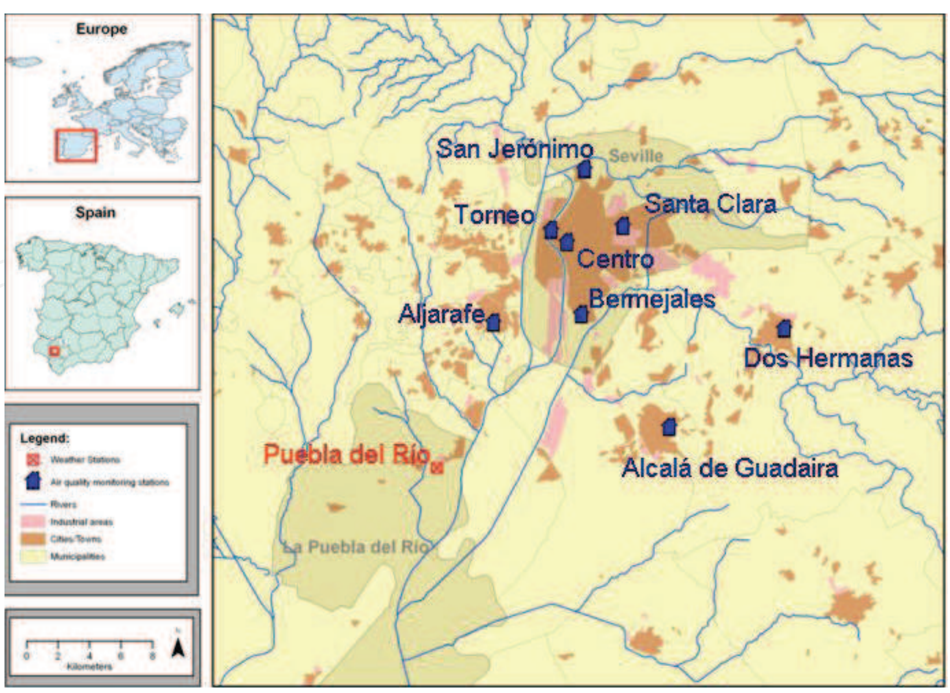


Fig. 1. Seville metropolitan area location in Europe. Air quality stations and meteorological tower used in this work.

of more than a million inhabitants, being the biggest urban zone of Andalusia. This region enjoys a Mediterranean climate with temperature between 4 and 15 ºC in winter and autumn, while summer temperature is ranging from 18 to 35 ºC.
According to the Andalusia government annual emission report 2003 (Junta de Andalusia, 2003), based on data taken in the year 2002 in Seville, the NO_x emission was about 26 500 tons per year, whose 59 % is attributed to traffic emissions. Meanwhile, the emission of non-methane volatile organic compounds (NMVOC) was 63 403 tons per year, with main contributions coming from the use of solvents 25% and traffic 13%. Seville metropolitan area shows the busiest road of the south of the Iberian Peninsula.

2.2 Monitoring stations and dataset

This work has been performed with surface ozone concentrations and its precursors (NO and NO_2) collected in eight air quality stations sited in the Seville metropolitan area and belong to the Survey and Air Quality Control Network of the Environmental Department, Regional Government of Andalusia. Five stations are in the urban hull of Seville town: Santa Clara, San Jerónimo, Bermejales, Centro and Torneo, while the other three are in the metropolitan area: Aljarafe (west of the city), Dos Hermanas (southwest) and Alcalá de Guadaira (east), between 20-25 km from city centre (Fig. 1). The period used to perform this work has been from 2003 to 2006.
Moreover, meteorological parameters recorded in a meteorological station located in the south of Seville area has also been used, Puebla del Río. This meteorological station belongs to the Network of Climate Information of Andalusia.
Ozone and NO_x data have been taken each 10 or 15 minutes from which the average hourly values have been calculated. Ozone measurements were taken with ultraviolet absorption-based instruments while NO_x data have been measured by chemiluminescence. Both types of instruments have been tested and calibrated periodically. They undergo weekly maintenance of operational parameters and manifold; changing air filters and span calibration every two weeks. Meanwhile, monthly and annual maintenance are done according to the manufacture guidance (e.g. tubing and electrovalves).

3. Results

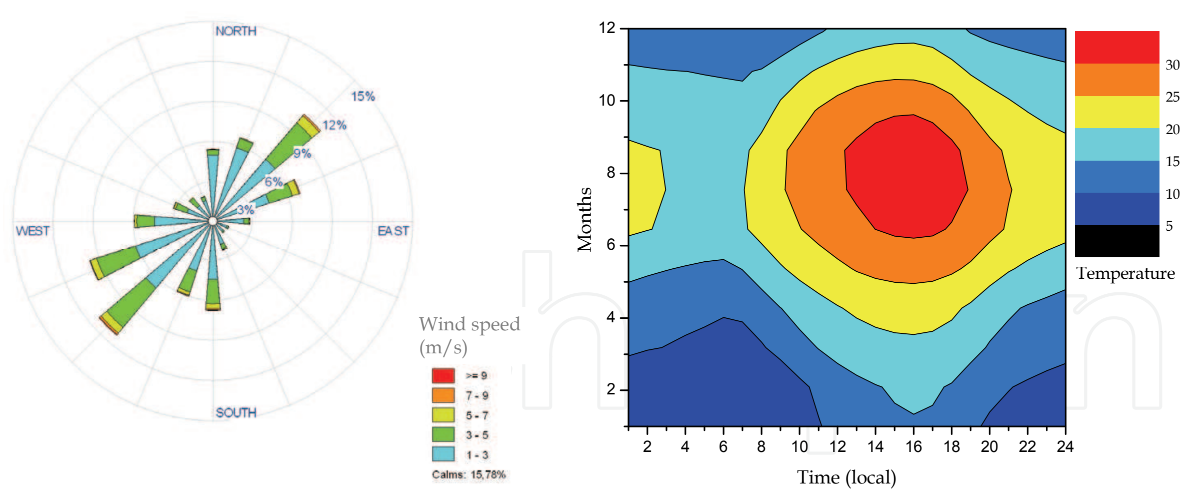
3.1 Meteorological overview

Photochemical pollution is conditioned by several factors: emissions, orograpy and meteorology, among others. The meteorology is an aspect to be considered in all the air quality studies. The levels and behaviour of the air pollutants will be defined by the meteorological scenarios and the values of the meteorological parameters. Several meteorological variables affect to the photochemical air pollution but perhaps with major intensity are necessary to study two variables: temperature and wind. Temperature is a parameter that can influence aspects such as the photochemical reaction velocity or the atmospheric stability. On the other hand, wind (speed and direction) point out the atmospheric ability to disperse or accumulate chemical species (depending of wind speed) as well as the origin the air masses (wind direction). In order to investigate the wind regime and the temperature evolution in this area, in the Fig. 2 are presented the annual wind rose and the daily and monthly temperature evolution measured in the mentioned meteorological station of Puebla del Río.

During the nights of November to February the temperature can vary between 5 and 10 ºC. Nevertheless, in spring and summer months the nocturnal values can reach values ranging between 15 and 25 ºC. In the diurnal period and in the autumn and winter months the temperature in Seville area vary from 15 to 20º C. In spring and summer these values are increase from 25 º C to levels higher than 30 ºC.

Wind regime in this area is characterised by two main flows from SW and NE which coincide with the Guadalquivir valley axis. Therefore, the valley acts as a natural channel for the travel of air masses. In winter months winds usually come from the first quadrant, with preferential synoptic origin, due to air masses originated in the north of Europe and the north Atlantic. In spring and autumn there is a meteorological scenario characterized by both the synoptic and mesoscale, with wind blowing from the first and third quadrant along the valley axis. The air masses coming from north cause the NE-ENE wind. Meanwhile, Atlantic air masses are quite frequent during these months; these air masses are channelling towards the Guadalquivir valley originating wind mainly from the SW. Moreover, these months show anticyclonic situation with clear sky, high solar radiation and high mean temperatures, and also an increase in earth's surface temperature. All these follow a daily evolution of a typical mesoscale pattern. These local scenarios show diurnal and nocturnal regimes with winds from the third and first quadrants respectively, according to the valley axis and perpendicular to the gulf of Cadiz coast line.

In summer months, the daily wind evolution reveals that mesoscale processes predominate over most of the days. During the day the main directions are SSW-SW, both directions coming from the third quadrant towards the valley and perpendicular to the cost line, which is coincident with the sea breeze. For the nocturnal period most frequent directions are from NE, wind speed records show lower values than for diurnal period since these directions mainly correspond to land breeze, which are weaker than sea breeze.



a) b)

Fig. 2. a) Annual wind rose. b) Daily and monthly temperature evolution. Puebla del Río (2003-2006).

3.2 Seasonal and daily variation on ozone and NO_x

In this section are presented both seasonal and daily cycles of surface ozone and NO_x. These pollutants show a marked seasonal evolution in the study area. As expected at mid-latitudes, NO_x present the maximum monthly values in winter and autumn and lower in

summer months. Opposite seasonal behaviour is found for surface ozone. Fig. 3 shows the monthly evolution of the three species in Torneo and Aljarafe stations as representative urban and suburban environments. The photochemical activity is more intense in the warm season, hence, ozone formation and transport processes are more effectives. In addition, there is a higher elimination of NO by these photochemical mechanisms and low levels of NO_x are found in the lower layers of the troposphere in these months.
The NO_2 monthly values are higher than NO, with the exception of January and December months in some stations such as Torneo, Bermejales and San Jerónimo. These facts could be attributed the high NO emissions and the unfavourable conditions to photochemical activity (low solar radiation and temperature levels) and favourable conditions (vertical atmospheric stability) to accumulate chemical species such as NO in the lower layers.

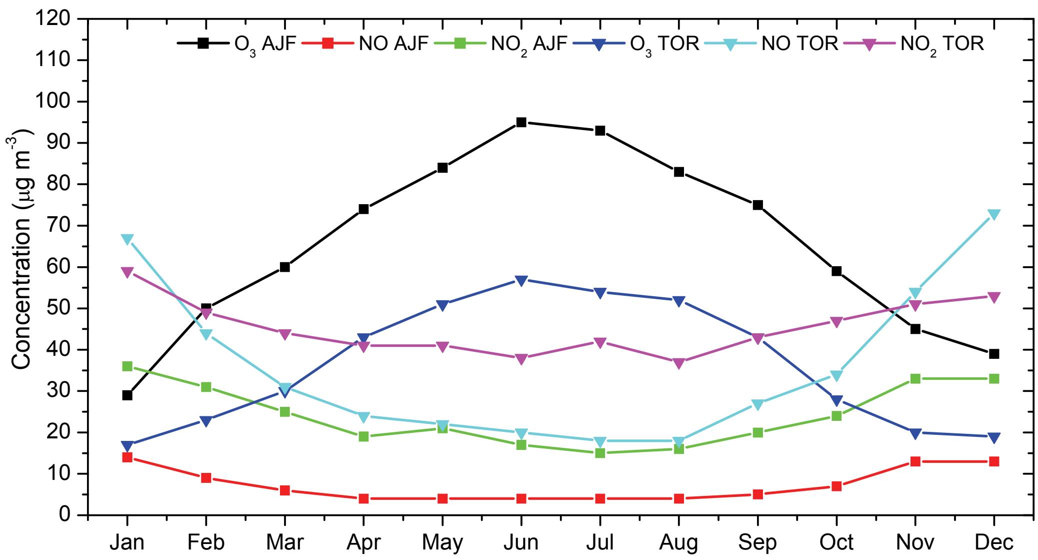


Fig. 3. Monthly evolution of O_3, NO and NO_2 in Aljarafe (AJF) and Torneo (TOR). 2003-2006.

The monthly cycle of NO and NO_2 is different according to the monitoring stations. In Bermejales and Tornero stations is obtained annual amplitude (difference between monthly maximum and minimum) for NO of 55 µg/m^3. In these stations NO_2 cycle presents a lower range with values of 21 and 32 µg/m^3 in Bermejales and Torneo respectively. These sites are strongly affected by the traffic emissions with elevated NO emissions which are accumulated in the surface layers under stability conditions. The formation of NO_2 from NO is similar in these stations in summer and winter time, i.e. elevated NO concentrations does not produce high NO_2 levels.
On the other hand, in stations located in the surrounding, the NO monthly cycle is weak with amplitudes between 10 and 14 µg/m^3, values measured in Alcalá de Guadaira and Aljarafe. In these same stations of NO_2 cycle amplitude is higher with values of 21 and 32 µg/m^3. These results could be associated to these stations are less affected by the traffic emissions that the sited in the city centre.
Fig. 4 shows the average daily evolution of O_3, NO and NO_2 registered during the study period in the eight air quality stations. A daily cycle is obtained in the three atmospheric species considered. This behaviour has its origin mainly in the traffic emissions, solar radiation levels and human behaviour patterns. These cycles are similar to find in other urban and suburban areas (Minoura, 1999; Mazzeo et al., 2005).

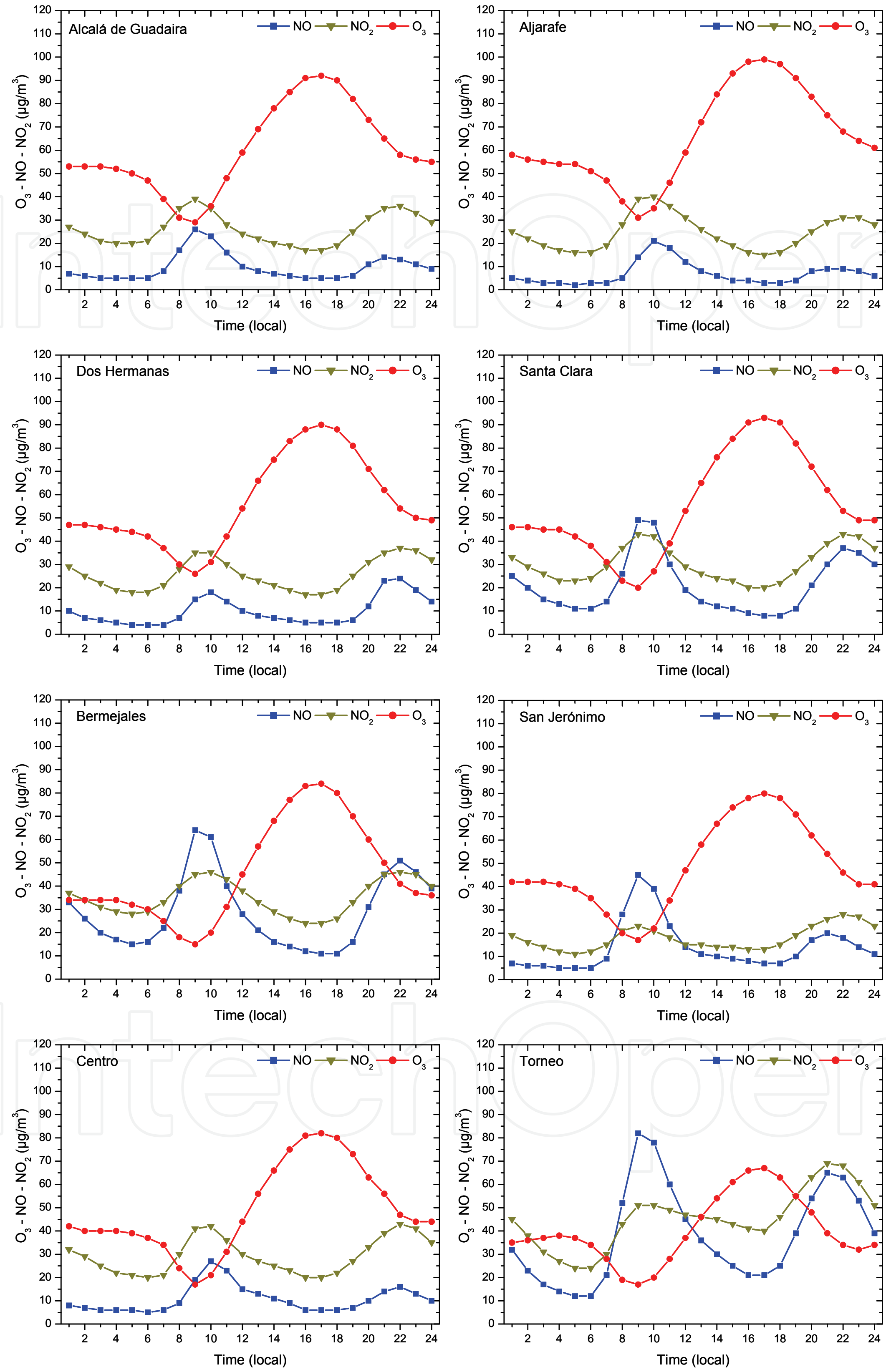


Fig. 4. Annual daily average evolution of O_3, NO and NO_2 in the eight air quality stations of Seville metropolitan area.

In the night time the concentrations remain with similar levels or with a slight increase trend with NO concentrations are always lower than NO_2. At 6:00 has been observed an increase in the NO_x levels due to the start of human activity and therefore the emissions from the traffic. In addition, the ground begins to heat up by the solar radiation and as consequence the mixing processes are produced in the lower layers. Due to fresh emissions of NO in rush hours and to the mixing mechanism, the residual ozone down from upper layers and is eliminated by the reaction with NO to produce NO_2, observing a decrease on ozone levels. At 9:00 is reached a NO and NO_2 maximum and the daily ozone minimum.

The NO_x morning maximum shows two behaviours according to the station type, urban or suburban. In some stations the NO maximum is higher than NO_2 (urban monitoring sites) while in others the behaviour is opposite (suburban). In stations such as Torneo, Bermejales or Santa Clara, NO maximum is higher than NO_2 due to are stations strongly affected by traffic emissions and the NO emissions are more elevated that the NO_2 production by the oxidation of NO with O_3. However, in sites located in the periphery such as Aljarafe, Alcalá de Guadaira and Dos Hermanas the NO_2 are higher than NO. In these cases of traffic emissions are less intense and the conversion of NO to NO_2 is more relevant that the emissions.

Maximum concentrations of NO show clear differences between the stations located in the Seville city and the sites located in the periphery less affected by emissions. Nevertheless, NO_2 maximum are very similar, not showing elevated differences between stations sited in the city and in the periphery.

During the morning, increase the solar activity, mixed ability and photochemical mechanism; have as consequence that NO_x present a decrease trend and surface ozone an increase trend. At 17:00 occurs the ozone maximum in all the air quality stations. The maximum ozone level is different, with higher values in stations away from city centre, such as Aljarafe and Alcalá de Guadaira and low values in stations as Torneo.

In the evening, with the cease of solar activity and therefore of photochemical reactions, ozone concentrations start to decrease. At the same time, it is observed an increase of the NO_x levels caused by several factors: there is an increase of the human activity in the city and their surroundings, hence fresh NO_x are emitted by traffic; decrease of mixing processes and starts of atmospheric stability, therefore accumulation of species in the lower atmospheric layers.

At 22:00 is recorded a secondary NO_x maximum. In all the stations, to exception of Bermejales, NO_2 level registered to this time is higher than the NO level. However, if compared the morning and nocturnal NO_x maximums, are found differences according to the station and the chemical specie (NO or NO_2).

In the NO case, the nocturnal maximum always is lower than the morning maximum in all the stations. The percentage differences vary, thus are found differences of 20-25 % in stations as Torneo, Bermejales and San Jerónimo (sited in the city). Whereas, in stations such Aljarafe or Alcalá de Guadaira (in the periphery) these differences can reach values between 30 to 50%. Due to the NO levels recorded are a clear demonstration of the direct traffic emissions, it is possible to conclude that the traffic activity in this area is more intense during the morning that during the last hours of the day.

For NO_2 in urban stations, Torneo, Bermejales or San Jerónimo, the NO_2 maximum in the first hours of the night is higher than the registered during the morning, with percentage differences between 5 and 33 %. Nevertheless, in suburban stations (Aljarafe and Alcalá) the NO_2 nocturnal maximum is lower than the morning with differences between 9 and 20 %.

3.3 Identification, ocurrence and ozone events characteristics

To the identification of ozone events it is necessary to apply criteria to extract from ozone data series of days considered as events. Using previous works which looking for to know episode situations (Cristofanelli et al., 2006; Oh et al., 2006), have been used two parameters. The daily ozone maximum and the threshold established to protect the human health (Directive, 2008). This threshold has been defined with a value of 120 μg/m³ as the maximum daily 8h, using this criteria ensure that a day with ozone event has been an exceedance of this legal limit. The other parameter has been taken as a value of 160 μg/m³ as daily maximum, this concentration has been defined using the ozone data series levels. Therefore, a day defines as ozone event should satisfy simultaneously of two parameters.

Appling the mentioned criteria to the hourly ozone series of the eight stations, the days with ozone events have been extracted. The total of days with events has been classified in function of the month. The results are shown in the Fig. 5. Ozone events are registered between the period from May to October with a high frequency in June and July; both months sum the 60% of all the events.

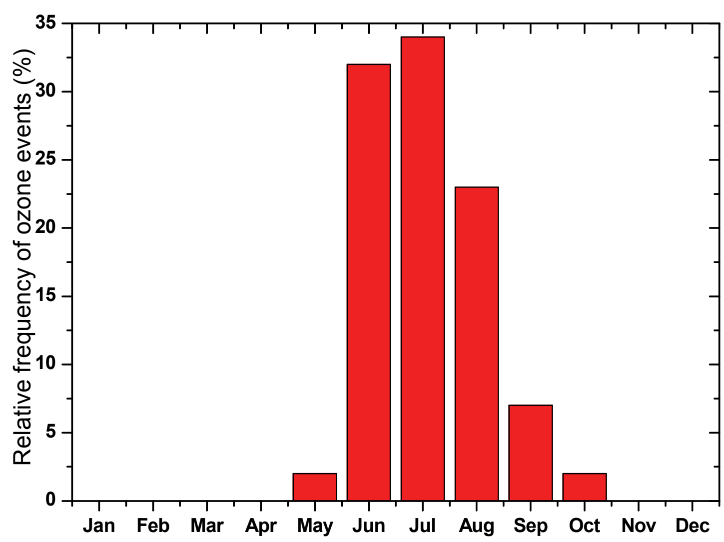


Fig. 5. Relative frequency of ozone events in Seville metropolitan area (2003-2006).

The highest ozone concentrations are recorded between May to September since in this time have the favour meteorological conditions to the formation and transport of surface ozone. In the four-year period analysed, 2003 to 2006, have been identified 373 days with ozone events. Table 1 exposes these events days in function of the year and monitoring station. An annual variability has been obtained, thus, 2003 and 2004 are the years with highest number of ozone episodes. However, in 2005 and 2006 this number has decreased.

The causes to explain the existence of an ozone event number in a specific year are mainly determined by the meteorological conditions. In function of the meteorological scenarios that characterise the study area between May to October, will condition the atmospheric features in the lower atmosphere: temperature, solar radiation and humidity levels, mesoscale processes, mixing mechanism, Saharan intrusions, etc. According to the intensity and occurrence of these processes an ozone events number will occur this year.

Under episodic situations the maximum daily 8h ranging between 125 μg/m³ of Torneo and 156 μg/m³ of Aljarafe. The maximum daily average is close to 180 μg/m³ (information threshold defined in the Directive 2008) in several stations and even is exceeded in Aljarafe station. This result point out that in days with ozone events the daily maximum ozone is elevated and the absolute maximum exceed 200 μg/m³ in all the stations to exception of San Jeronimo.

On the other hand, the days with ozone events present a lower percentage of occurrence if is considered of whole period. Aljarafe has been the station with the highest number of events follows by Santa Clara, Bermejales, Dos Hermanas and Alcalá de Guadaira. These five stations sum the 75% of the events identified.

	2003	2004	2005	2006	Total
AJF	47	46	17	12	122
ALG	--	20	8	8	36
BER	14	20	5	8	47
CEN	4	11	9	6	30
DHN	9	25	2	3	39
SCL	17	26	18	18	79
SJE	9	1	7	0	17
TOR	0	3	0	0	3
Total	100	152	66	55	373

Table 1. Number of days with ozone events (exceedance of the threshold to protect of human health and daily maximum of 160 μg/m³) in the air quality stations for the period from 2003 to 2006.

3.4 Comparative analysis of days with and without events: daily evolution

Surface ozone series could be divided in days with ozone events and days without events. Since more than 75% of the ozone events have been identified in five stations, it has been considered to perform a comparative analysis using the ozone data from these stations.

The average daily ozone evolution, NO and NO_2, recorded in days with events has been compared with the days without events, during the period from May to October since is the period which have been identified the events. On the other hand, it is interesting to know the levels and variation that present the meteorological variables most influential in the ozone concentration such as temperature, relative humidity and wind speed. For this reason, the average daily evolution of these parameters has been studied both in days with and without events. The meteorological data has been obtained from Puebla del Río station. As a representative case in Fig. 6 is shown the results obtained for Santa Clara station.

In all the stations analysed the ozone concentrations are higher in days with events that in days without events. In the nocturnal time has been observed an ozone increase which varies between 5 to 30 μg/m³. In the diurnal period the differences found are not constant but an elevated photochemical activity produce higher differences. From the first hours in the morning, the differences show an increase trend, reaching maximum values in the noon. In episodic days the daily maximum ozone reaches values of 160 to 170 μg/m³ while in non

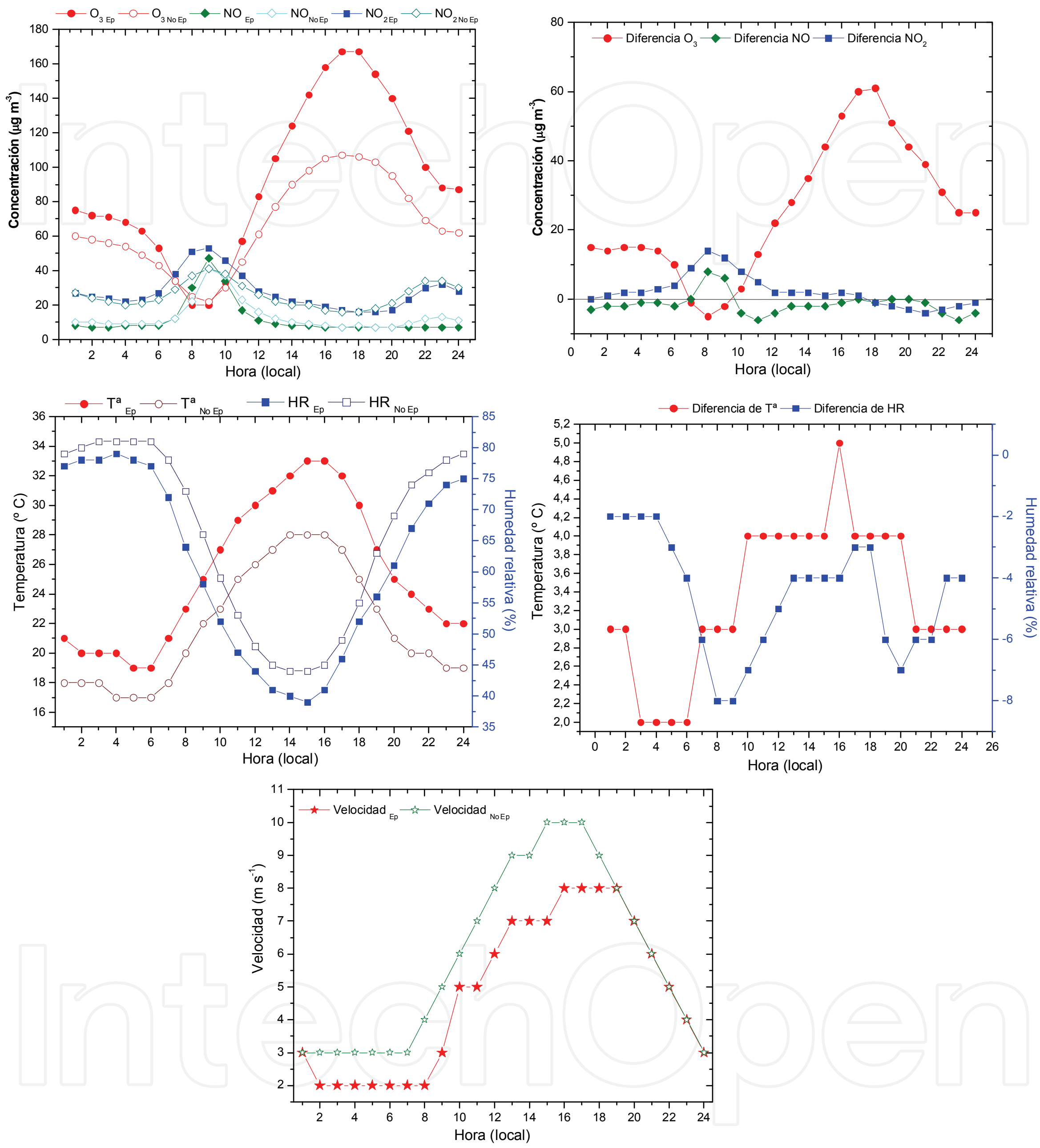


Fig. 6. Ozone, NO and NO_2 daily average evolution recorded in episodic and non episodic days as well as the difference between them in Santa Clara station. Temperature, relative humidity and wind speed daily average evolution collected in episodic and non episodic days and difference between them in Puebla del Río station. 2003-2006.

episodes days the daily maximum varies between 50 to 60 μg/m^3. Therefore, in days with ozone events there are an increase of 50 to 60 μg/m^3.

In Aljarafe and Alcalá de Guadaira stations of NO concentrations are very similar both episodic and non episodic days. This result could point out that the traffic emissions in these suburban stations are equally affected in both types of days. However, in stations affected by the traffic emissions and sited in the Seville urban area such as Bermejales and Santa Clara, have been observed an increase in the NO concentrations in days with events respect to days without events, in the period from 7:00 to 10:00. Accordingly, in these stations and under event conditions the NO maximum is of 70 μg/m^3 while in days without events reaches 50 μg/m^3. These results could be attributed to a low wind speed in days with events, therefore, an atmosphere less dispersive and favouring the accumulation of NO close to the ground.

The daily evolution of NO_2 states two different behaviours. In the first, NO_2 concentrations always are higher in events days. This pattern is obtained, for instance, in Bermejales station. The second pattern identified is characterised by NO_2 levels higher in events days but only in the time interval between 7:00 to 17:00 approximately. In this case, the highest differences are found in the early morning between 9:00 to 11:00. While in events days are detected NO_2 values of 50 to 55 μg/m^3 in not episodic days the NO_2 concentration was of 38 to 45 μg/m^3. NO_2 levels are similar from 11:00 to 17:00 both episodic and non episodic days.

The daily temperature evolution shows higher levels in episodic days. The events days present average nocturnal temperature between 19 and 21 ºC, with approximately 2 ºC higher that the registered in nights with non episodic days. In the diurnal time the difference found are higher, between 3 and 4 ºC. In some situations have been measured temperatures in days defined as events up 30 ºC in the period from 11:00 to 17:00 and daily maximums of 33 ºC. On the contrary, the relative humidity, in the nocturnal time, presents lower values than in non episodic days, approximately between 2 to 4 %. The values registered during the night in episode days are of 77 to 80 %. During the day the relative humidity decreases to 39 to 41 %, values 4 to 8 % lower than in days without ozone events.

It is well known that the photochemical activity is favour by high temperatures and low relative humidity. These conditions are generally associated with an atmosphere not dispersive, hence, with low level of wind speed. Analysing this variable, during the night of events days the wind speed is 1m/s lower than in days without events. These differences are higher during the day, for example, from 8:00 to 19:00 the differences found are of 2 to 3 m/s. From 20:00 the wind speed measurements are very similar in both cases.

3.5 Ozone events: study case

This section has been devoted to analysis of ozone events using O_3, NO and NO_2 as well as meteorological parameters in several episodic situations. The ozone event duration oscillates between 2 to 10 days with an average value of 3.5 days. The two longest episodes occurred from 29 July to 12 August 2003 and from 9 to 18 June 2004. During 2005 and 2006 years have not occurred long episodes. To present the main characteristics of the ozone events the episode of 2004 will be used.

In the occurrence of an ozone event have been identify three phases. In the first, the ozone concentrations are low. The meteorological conditions that govern this stage is a synoptic flow from S-SW with origin in an high centre pressure system located in the Atlantic Ocean and a low pressure system in the British isles. The SW of Iberian Peninsula under these synoptic conditions could register wind coming from W and NW. However, in summer months under these situations a thermal low is developed in the centre of Iberian Peninsula which produces a flow in the diurnal time from coastal area to inland using as natural channels of valleys (Millán et al., 2002). For these reasons, in Seville area (100 km far from coastal line) is measured wind coming from S-SW.

A similar condition to expose above was registered during 6 and 7 June 2004 which was the starts one long ozone events. In the initial stage the Iberian Peninsula was affected by anticyclonic conditions and a thermal low was developed in the centre of Iberian Peninsula, due to this configuration the wind blows from SW in the study area.

The second phase (central stage) of the event starts thank to the movement of the Atlantic high pressure system toward Europe continent. This new isobaric configuration provokes weak isobaric gradient over the Iberian Peninsula. These conditions favoured the development of mesoscale processes in coastal areas.

From the analysis of many ozone events occurred in Seville metropolitan area have been identified sea-land breeze conditions or a weak (low wind speed) synoptic flow from SW as the main meteorological scenarios in the central phase of the event. Due to the higher ozone concentrations are recorder under mesoscale processes, these will be analysed with detail. In this area, the nocturnal breeze coming from the first quadrant, higher frequency from NE sector, starts approximately between 3:00 to 5:00 and remain during the next 8 hours. At 11:00 to 12:00 cease the land breeze and begin the marine breeze with wind blowing from SW. The marine breeze present higher values of wind speed and remain during the next 12 to 14 hours.

In order to illustrate with detail the behaviour both chemical species and meteorological parameters of an ozone event, Figs. 7 and 8 show the specific case of June 2004. Under episodic conditions, from 00:00 to 3:00 the ozone measured in the air quality stations of Seville metropolitan area presents a decrease trend. Nevertheless, NO and NO_2 shows similar concentrations during this period. At this time, the temperature ranges between 15 to 17 ºC and the relative humidity is close to 80%.

From 3:00 to 5:00, the ground is sufficiently cold and starts the transition between the regimes of the breeze, ceases the marine regime and starts to blow from land. This transition is identified by a change in the wind direction and a decrease in the wind speed. Under these conditions has been observed that NO levels remain similar both urban and suburban station. However in some urban stations the NO_2 could present slight increase while in the suburban stations this increase has not been observed. On the other hand, surface ozone can state two behaviours, to remain with similar values or well increase with a rise of 20 to 40 $\mu g/m^3$. In the Fig. 7, this variation is observed in the nights 16 and 17 June 2004.

This increase in the nocturnal ozone can have two origins. The transition between the two breeze regimes is associated to a decrease in the wind speed, as has been mentioned before, therefore atmospheric stagnation conditions can lead to an increase in the ozone levels. On the other hand, the ozone has been transported during the previous hours from third to first quadrant, with the change in the breeze regime, the air masses follow the same pathway but in opposite sense, recirculation processes. This behaviour has been also measured and documented in others areas (Eliasson et al., 2003).

From 6:00, under nocturnal regime of breeze (blowing from NE), there is an increase of NO levels due to the fresh emissions from the traffic. In breeze periods the increase in the NO levels at this time is relevant, and more pronounced in urban stations close to traffic sources, such as Torneo and Bermejales. Under land breeze the wind speed is low or even calms, then an atmosphere non dispersive which favours the processes of NO accumulation close

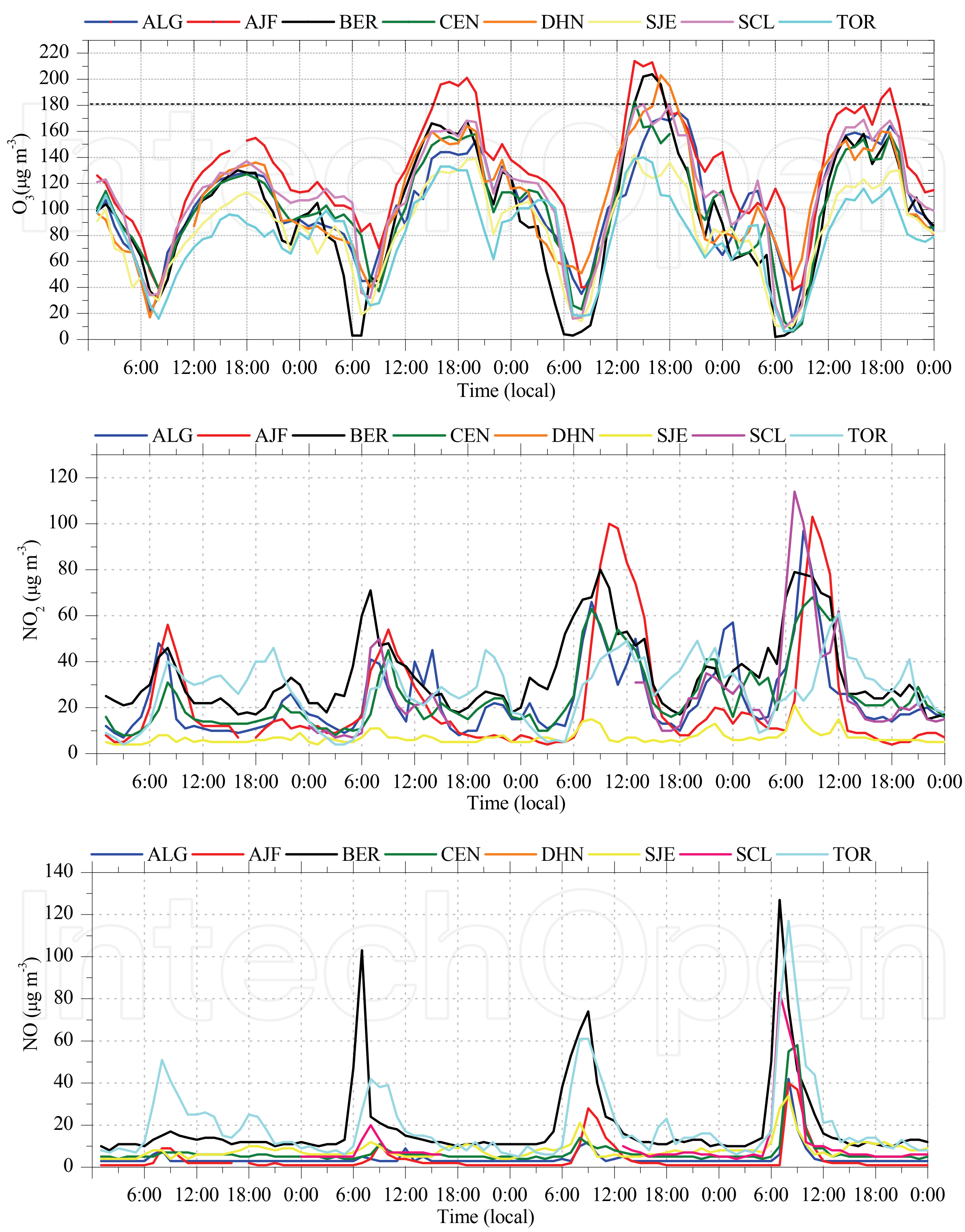


Fig. 7. Hourly ozone, NO and NO_2 evolution in Seville stations from 15 to 18 June 2004.

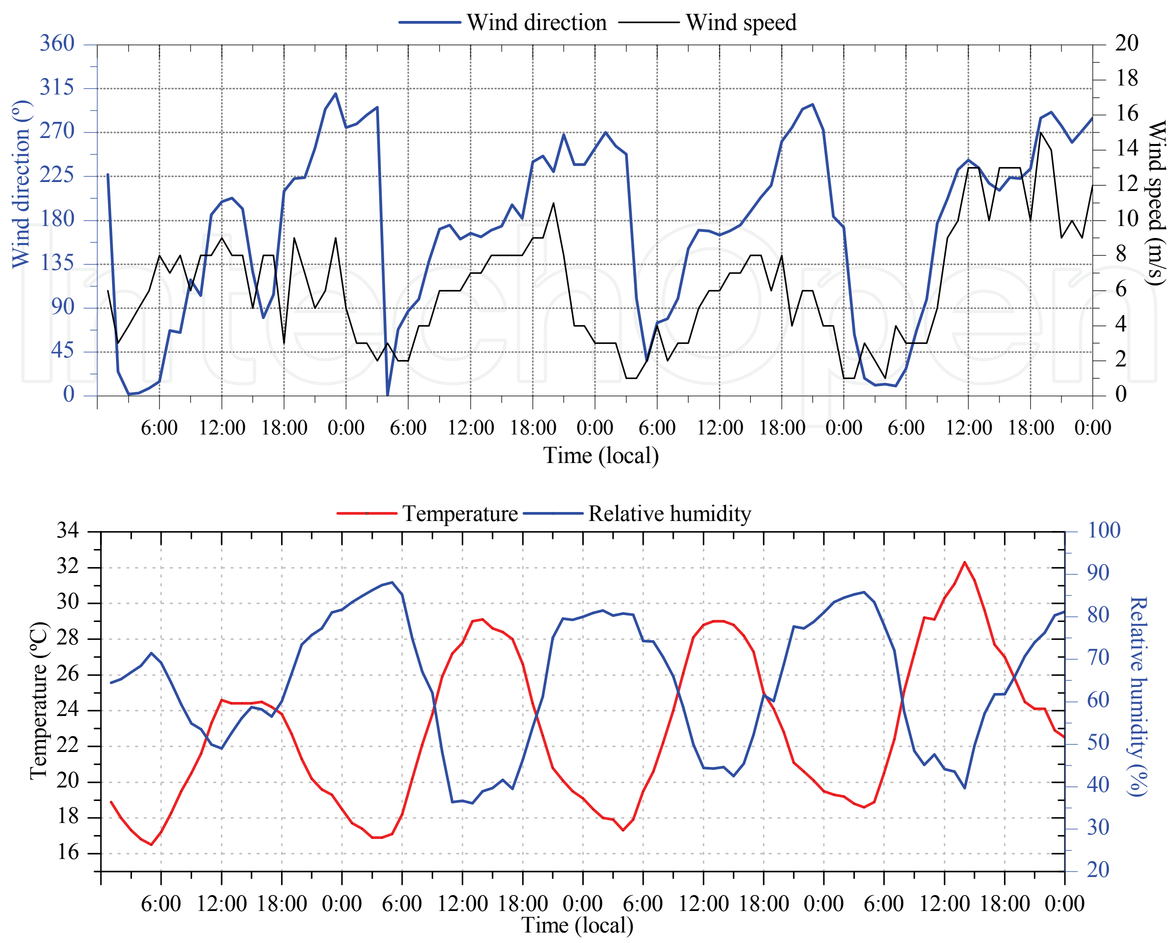


Fig. 8. Hourly wind (direction and speed), temperature and relative humidity evolution at Puebla del Río from 15 to 18 June 2004.

to the ground. NO_2 in these early hours also increase due to the oxidation processes with NO. The suburban stations are the sites with the higher NO_2 increases.

At this time, ozone levels starts to increase which could be associated to several processes. The onset of the solar activity helps to begin the photochemical reactions; hence, ozone can have its origin in this first local photochemical formation. Solar radiation leads to the broken of stable nocturnal boundary layer and the formation of the mixing layer. Mixing mechanisms can be brought from uppers layers both residual ozone and NO_2.

From 10:00 to 12:00 starts to blow wind from S-SW. In this period the increase of the ozone could be caused by horizontal (air masses with ozone from SW) and vertical transport (mixing processes). In addition, NO_2 also starts to increase. In suburban stations as Aljarafe and Alcalá NO values exceed the 40 $\mu g/m^3$. Fig. 7 shows the NO_2 levels reached in these stations 17 and 18 June 2004, probably caused by the transports processes before commented.

In the afternoon the ozone continues to increase and NO_2 values to decrease. Thank to fresh emissions from the traffic in the first hours of the night, ozone starts to decrease and NO_2 to increase. However, NO concentrations remain constant due to NO emitted is converted to NO_2 thanks to the high ozone levels available to react with NO.

A change in the synoptic configuration, movement of the high pressure system and arrival of a low pressure system, provokes and higher isobaric gradient over the Iberian Peninsula.

Hence, unfavourable conditions to mesoscale developments. In the studied area is frequent that the events finish, third stage, with wind blowing from W-SW which has an effect of ventilation and cleaning of the atmosphere.

4. Conclusions

In this work has been evaluated the ozone, NO and NO_2 concentrations measured in eight air quality stations of Seville metropolitan area during the period from 2003 to 2006. Seasonal and daily variation of this three air pollutants have been studied. While higher values of NO and NO_2 have been measured in winter and autumn months, in summer months are recorder the highest ozone levels. The monthly cycles are different according to the stations considered. Urban stations, more influenced by traffic emissions, show higher NO and NO_2 levels and a higher seasonal range (difference between maximum and minimum monthly). NO_2 monthly values are, in general, higher than NO monthly levels. On the other hand, suburban station presents higher ozone concentration and a higher pronounced seasonal cycle.

A well define daily cycle has been found for the three species analysed. NO_x show two peaks in the morning and in the first hours of the night. In general the NO_2 concentrations are higher than the NO. Morning peak of NO is higher than the nocturnal peak. Nevertheless, in NO_2 the opposite behaviour is found. Ozone shows the daily peak in the afternoon with elevated levels in suburban stations.

A criterion has been applied to identify and extract of the days with ozone events from the historical series. A day with ozone event was considered if there is an exceedance of the threshold to protect the human health and exceeds its daily maximum in 160 $\mu g/m^3$. Ozone events occur between May to October with a high frequency in June and July.

A comparative analysis of days with and without events has been performed. The maximum of NO is higher in episode days in urban stations but not in suburban. NO_2 can be higher in events days in urban stations while in suburban in an specific time period. In days with events the ozone peaks could be increased between 50 to 60 $\mu g/m^3$. In the afternoon of days with events the temperature can be 3-4 ^oC higher than in non episodic days. The relative humidity 4 to 8% lower and the wind speed also 2-3 m/s lower.

Several periods with ozone events have been investigated with detail. During the studied period, 2003 to 2006, have been found long episodes (up to the week) but the average was of 3.5 days. In an event have been identified three phases. The meteorological conditions of each stage have been also defined. In the central phase, where the ozone concentrations are episodic, the surface atmospheric dynamic in this region is governed by the mesoscale processes or wind coming from SW with slow wind speed.

Once analysed and indentified the ozone events in this area, in order to improve the understanding of these processes, modelling tools are being applied. Specific ozone events are being simulated using meteorological mesoscale models. The aim is to know not only the surface behaviour both chemical and meteorological parameters but the profile of these substances. Thanks to use of meteorological model will be possible to carry out the atmospheric boundary layer characterisation of this area which will be essential to understanding the vertical transport and the formation of ozone residual layers.

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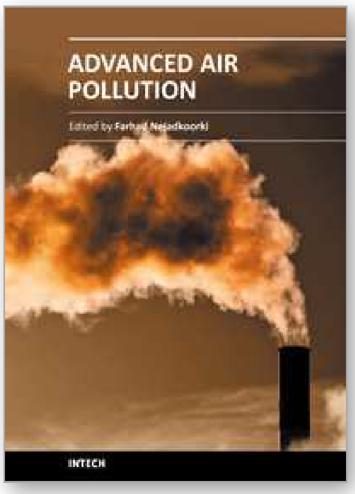

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