Aerosol and Air Quality Research, 14: 1862–1874, 2014

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2014.02.0026

Weekend-Weekday Effect Assessment for O_3, NO_x, CO and PM_{10} in Andalusia, Spain (2003–2008)

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ABSTRACT

Day-of-week variations in O_3, NO_x, CO and PM_{10} were analysed in the southwestern region of Europe (specifically Andalusia, Spain) using hourly concentrations collected at 43 stations (representing five typologies) over 6 years (2003–2008). This area has air pollution problems, and the study of the weekend effect is used as a tool to plan future strategies for emissions reductions. Maximum daily 8 h averages for O_3, daily 90th percentiles for NO, NO_2 and PM_{10} and mean daily values for CO were calculated and used to assess the weekend effect by applying three different metrics: weekly evolution, weekend-weekday differences and average daily difference between weekends minus workdays. Based on daily parameters and weekend-weekday differences, all the measured air pollutants exhibited clearly reduced concentrations (oscillating between 25 to 85%) on weekends, mainly at urban and suburban stations, with the exception of O_3 (less than 10 µg/m^3). This decrease on weekend days was mostly observed for NO, NO_2 and PM_{10} at urban stations, while differences at industrial and rural stations were low or null. CO showed a low reduction. Using the daily cycle of differences (weekend minus workdays) as a reference, positive deviations were observed at night and negative differences were observed during the daytime for NO, NO_2 and PM_{10} at urban traffic, urban background and suburban background sites. A reduction in morning rush hour traffic during the weekends was reflected in the data from urban stations, which showed a decrease of up to 50, 15 and 12 µg/m^3 for NO, NO_2 and PM_{10}, respectively. An opposite daily behaviour was found for ozone, which showed an increase at urban area sites of up to 15 µg/m^3 in the early morning.

Keywords: Weekend effect; Air pollution; O_3; NO_x; CO; PM_{10}; Weekly/Daily cycles.

INTRODUCTION

The concentrations of primary pollutants show weekly patterns; this temporal variation reflects day-to-day variations in the activities that generate anthropogenic emissions. In urban areas, the decrease in human activity on weekends produces lower emissions, and hence lower concentrations, of NO_x (NO and NO_2), CO, PM_{10} and VOCs than when compared with regular work days. These reductions could cause an opposite effect on ozone concentrations in urban environments, resulting in higher values on weekend days. However, in other regions, such as in suburban or rural areas with high biogenic VOC emissions, minimum ozone concentrations occur on the weekend (Heuss *et al.*, 2003; Qin *et al.*, 2004).

Heuss *et al.* (2003) presents several potential causes of weekday/weekend ozone differences, which have also been analysed in different studies: 1) Decrease in ozone titration with NO due to the reduction in NO_x on weekend days (Altshuler *et al.*, 1995; Wennberg and Dabdub, 2008); 2) Increase in weekend emissions of different origins compared with weekday emissions, which can lead to ozone formation; 3) Reduction in aerosols and a resulting increase in UV sunlight and ozone formation (Marr and Harley, 2002; Qin *et al.*, 2004); 4) NO_x timing, as weekend traffic is lower than on weekdays for several hours following sunrise. Nevertheless, the level of traffic at midday on weekdays is similar to that on weekends (Fujita *et al.*, 2003). During this time, the different pattern of NO_x emissions causes more effective ozone production; 5) Carryover in the lower layers. The increase in traffic on Friday and Saturday nights and the resulting ozone accumulation on the surface

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layer due to the major atmospheric stability may lead to elevated ozone formation after sunrise on next day; 6) Carryover aloft. Large amounts of ozone and other pollutants accumulate in the upper reservoir layers during the night and mix down the following day, which may exert a major influence on surface ozone on weekends when compared with weekdays.

The weekly pattern of air pollutants is of general interest, and studies have been carried out in North America (Blanchard and Tanenbaum, 2003; Pun *et al.*, 2003; Murphy *et al.*, 2007; Koo *et al.*, 2012), Europe (Brönnimann and Neu, 1997; Pont and Fontan, 2001; Jenkin *et al.*, 2002 Paschalidou and Kassomenos, 2004), Mexico (Stephens *et al.*, 2008), Japan (Sadanaga *et al.*, 2012), India (Debaje and Kakade, 2006; Pudasainee *et al.*, 2010; Srimuruganandam and Nagendra, 2011) and Egypt (Khoder *et al.*, 2009). Some of these studies analysed the influence of meteorological parameters, such as temperature and radiation, on the occurrence of the weekend effect (Brönnimann and Neu, 1997). In addition, the evolution of this phenomenon over a long time period has been assessed (Fujita *et al.*, 2003; Stephens *et al.*, 2008), and chemical transport models have been used to simulate different emission scenarios to better understand the changes in the magnitude and occurrence of weekend effects in urban areas and downwind regions (Jimenez *et al.*, 2005).

The Mediterranean Basin experiences frequent photochemical air pollution episodes caused by the topography, meteorological conditions and emissions (Millan *et al.*, 2002; Kalabokas and Repapis, 2004; Gangoiti *et al.*, 2006; Adame *et al.*, 2010). In this area, the weekend effect has been scarcely studied. The weekly variation has been only treated as a part of more general studies (Riga-Karandinos *et al.*, 2005; Felipe-Sotelo *et al.*, 2006) or analysed in a delimited period of time and area (Jimenez *et al.*, 2005; Schipa *et al.*, 2009).

In this region, the south of Spain has experienced air pollution problems related to ozone, PM_{10} and NO_x in recent years. This large area combines three factors that play a key role in the occurrence of air pollution events: high levels of temperature and solar radiation, complex topography and significant emissions of both biogenic and anthropogenic origin. An analysis of weekday/weekend (NO, CO, PM_{10} and O_3) differences would complement previous studies and increase in the understanding of pollutant behaviour in the area (Adame *et al.*, 2010; Sorribas *et al.*, 2011; Notario *et al.*, 2013).

The goal of this work is to assess the weekend effect for O_3, NO, NO_2, CO and PM_{10} in the southern Iberian Peninsula (Andalusia region) based on the analysis of hourly values from 43 monitoring stations from 2003 to 2008. This is the first time that 6 years of data and this many stations have been used to improve the temporal and spatial validity and representativeness of the results for the whole region. These results can be used to predict the response of pollutants to changes in emissions and the relationship between primary emissions (NO, CO, PM_{10}) and the production and transport of secondary pollutants (O_3). Consequently, this work will be useful in the design of air quality programs and in the identification of the most effective air pollution control strategies in the region.

MATERIALS AND METHODS

Study Area

The study area is Andalusia, located in the south of the Iberian Peninsula (Fig. 1(a)). This area covers 87000 km^2 and is divided into 8 provinces with approximately 7 million inhabitants. The Seville, Granada and Malaga metropolitan areas contain the majority of the area's population. In contrast, Andalusia also contains several important natural protected areas, including Doñana National Park (in the west) and Sierra Nevada National Park (in the east).

The Andalusia Government inventory of 2007 (www.juntadeandalucia.es/medioambiente), showed that CO emissions were 484007 tons/year, with 27% attributed to traffic, 10% to industrial activity and 60% to other activities. The annual emissions of non-methane volatile organic compounds (NMVOC) were 442372 tons/year with 48% attributed to biogenic sources and 11% to industrial activities. A total of 211544 tons/year of NO_x was emitted, with traffic and industrial activities as the main sources, at 36% and 34%, respectively. PM_{10} emissions were reported to be 29894 tons/year, with traffic recognised as the most significant source, accounting for 34.6% of the emissions. Therefore, the main sources of air pollutants in this region were traffic, industrial activities and biogenic emissions.

Andalusia generally has a typical Mediterranean climate, although due to its complex topography, the microclimates are highly variable. Andalusia's coastline is open to the Atlantic Ocean, from Portugal to the Gibraltar straight. By way of its topography, Andalusia is divided into three different areas: the Guadalquivir Valley, the Sierra Morena Mountains and the Beticas Mountains. The Guadalquivir valley begins in the Cadiz Gulf and extends almost 300 km inland, with a southwest-northeast axis. It is bounded to the north by the Sierra Morena and to the south by the Beticas Mountains. This last mountain system covers the centre of Andalusia and contains numerous valleys and high mountains, including Mulhacen (3481 m), the highest peak on the Iberian Peninsula.

Experimental Data

The Survey and Air Quality Control Network of the Environmental Department, Regional Government of Andalusia measures the concentrations of O_3, NO, NO_2, CO and PM_{10} in Andalusia. Ozone measurements are based on the absorption of ultraviolet radiation by ozone at 254 nm. NO_x (NO and NO_2) data are measured by a chemiluminescence-based analyser. This method measures NO directly, and NO_2 is measured indirectly after conversion to NO. Concentrations of CO are obtained by non-dispersive infrared spectroscopy. The beta attenuation method was used to determine the PM_{10} in ambient air. In addition, maintenance and calibration operations were routinely performed to guarantee the correct functioning of the instruments. All measurements of air pollutants are expressed in µg/m^3.

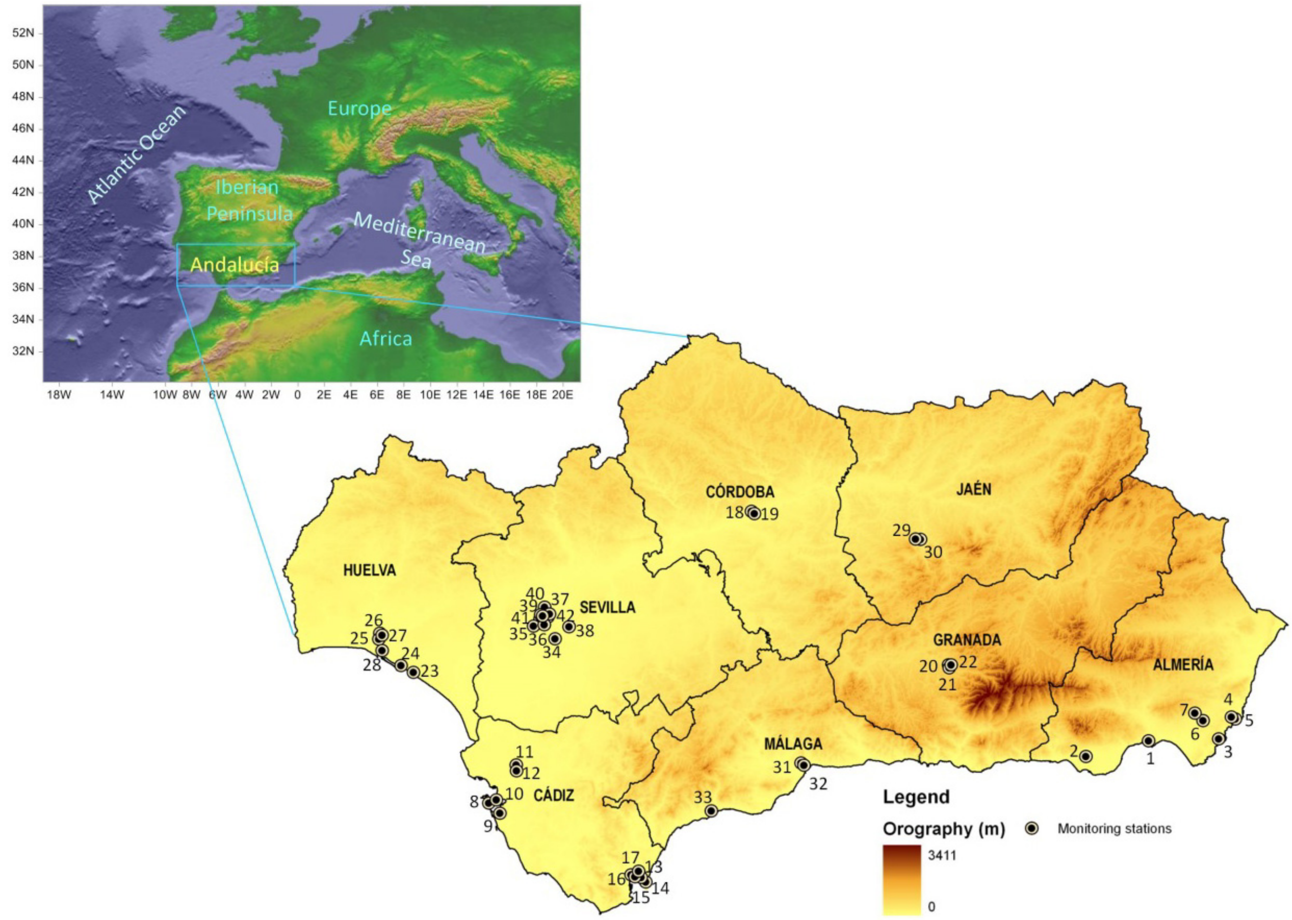

Fig. 1. South-western (Andalusia) Spain in Europe (a), orography and location of the air quality stations in Andalusia (b).

Concentrations were recorded at the air quality stations every 10 min, and the quality criteria of 85% was applied to calculate hourly values. Data from 43 monitoring stations were used for this study (Table 1, Fig. 1). According to Directive 2008, the monitoring stations are classified considering the macro-scale (urban, suburban and rural) and micro-scale (traffic, background and industrial) characteristics of the sampling sites. The combination of the two scales gives five station type classifications: urban traffic (UT), urban background (UB), suburban background (SB), suburban industrial (SI) and rural background (RB). Urban traffic stations are characterised by high traffic intensity and are located mainly in the centre of the cities. Urban background sites are stations where the pollution level is influenced by the integrated contribution from all sources upwind of the station and are located in the surroundings of the city centre. Suburban background sites are close to urban areas but not inside them and are located in mainly residential zones. Suburban industrial sites receive high contributions from industrial sources and are generally located in suburban areas. Finally, rural background sites are located where their measurements will not be influenced by agglomerations or industrial sites in the vicinity. According to these classifications, this study used 6 urban traffic, 14 urban background, 8 suburban background, 12 suburban industrial and 3 rural background sites (Table 1). This mosaic of monitoring stations ensures the representativeness of the results obtained in this work.

Assessment of the Weekend/Weekday Phenomena

There is not a unique methodology to analyse the "weekend effect". To determine its occurrence, typically one reference parameter is defined, and the parameter's evolution on weekdays and weekends as well as the differences between them are used to determine the "weekend effect". Depending on the pollutant considered, different parameters are used and different methods can be applied to assess the "weekend effect".

For ozone, the daily maximum 8 h average is typically used and is a policy-relevant quantity (Qin *et al.*, 2004; Murphy *et al.*, 2007). This methodology has been successfully proven in a variety of photochemical environments when used to determine the weekday-weekend differences (Heuss *et al.*, 2003). Regarding NO, NO_2, CO and PM_{10}, the weekend effect has been analysed using different statistical approaches such as daily mean, daily maximum or the average over a specific time interval (Stephens *et al.*, 2008).

In this work, the weekend effect was analysed by defining the following parameters: for ozone, we used the daily maximum 8 h average; for NO, NO_2 and PM_{10}, we used the daily 90^{th} percentile value, which allows the identification of the time interval that is more affected by

Table 1. Air quality monitoring station name (province), type (UT: urban traffic, UB: urban background, SB: suburban background, SI: suburban industrial and RB: rural background) and measurement period (percentage of available data in %) collected for every pollutant. Province: Alm: Almería, Cad: Cádiz, Cor: Córdoba, Gra: Granada, Hue: Huelva, Jae: Jaen, Mal: Málaga and Sev: Seville. XX: No data.

Station (Prov)	Type	O_3	NO	NO_2	CO	PM_{10}
1. Mediterráneo (Alm)	UT	04–08 (97)	03–08 (97)	03–08 (97)	05–08 (82)	03–08 (96)
2. El Ejido (Alm)	UB	04–08 (85)	04–08 (87)	04–08 (87)	03–08 (96)	03–08 (97)
3. Rodalquilar (Alm)	SI	06–08 (94)	06–08 (85)	06–08 (85)	XX	06–08 (80)
4. La Joya (Alm)	SI	07–08 (80)	07–08 (80)	07–08 (80)	07–08 (80)	XX
5. Agua Amarga (Alm)	RB	04–08 (91)	04–08 (83)	04–08 (83)	XX	03–08 (96)
6.Campohermoso(Alm)	SI	04–08 (95)	04–08 (86)	04–08 (86)	XX	03–08 (80)
7. Nijar (Alm)	RB	04–08 (97)	04–08 (86)	04–08 (86)	XX	03–08(84)
8. Avda.Marconi (Cad)	UT	03–08 (98)	03–08 (92)	03–08 (92)	03–08 (98)	03–08 (93)
9. Río San Pedro (Cad)	UB	03–08(98)	03–08 (95)	03–08 (95)	XX	03–08 (93)
10. San Fernando (Cad)	SB	03–08 (95)	03–08 (92)	03–08 (92)	03–08 (97)	03–08 (82)
11. Jerez Chapín (Cad)	UB	04–08 (81)	03–08 (90)	03–08 (90)	04–08 (98)	04–08 (80)
12. Cartuja (Cad)	SI	03–08 (95)	03–08 (93)	03–08 (93)	03–08 (97)	03–08 (90)
13. Campamento (Cad)	SI	03–08 (94)	03–08 (82)	03–08 (82)	06–08 (85)	XX
14. La Línea (Cad)	SI	03–08 (94)	03–08 (91)	03–08 (91)	XX	03–08 (80)
15. Guadarranque(Cad)	SI	06, 08 (82)	06, 08 (81)	06, 08 (81)	06–08 (81)	XX
16. Cortijillos (Cad)	SI	03–08 (83)	03, 06–08 (91)	03, 06–08 (91)	04–08 (97)	XX
17. Carteya (Cad)	SI	03–08 (90)	03–08 (90)	03–08 (90)	XX	03–08 (90)
18. Lepanto (Cor)	UB	05–08 (80)	05–08 (98)	05–08 (98)	05–08 (81)	05–08 (95)
19. Asomadilla (Cor)	SB	05–08 (85)	05–08 (80)	05–08 (80)	05–07 (94)	05–08 (84)
20. C. Cartuja (Gra)	SB	06–08 (90)	05–08 (92)	05–08 (92)	06–08 (95)	06–08 (82)
21. Universitarios(Gra)	UB	XX	05–08 (81)	05–08 (81)	03–08 (98)	05–08 (83)
22. Granada-N(Gra)	UT	03–08 (96)	03–08 (89)	03–08 (89)	03–08 (98)	03–08 (93)
23. El Arenosillo (Hue)	RB	03–08 (92)	07–08 (81)	07–08 (81)	XX	XX
24. Mazagón (Hue)	RB	05–08 (94)	05–08 (83)	05–08 (83)	05–08 (93)	05–08 (85)
25. M. Titán (Hue)	SI	XX	03–08 (98)	03–08 (98)	03–08 (84)	03–08 (95)
26. El Carmen (Hue)	UB	03–08 (90)	03–08 (83)	03–08 (83)	XX	03–08 (85)
27. La Orden (Hue)	UB	03–08 (92)	03–08 (94)	03–08 (94)	XX	03–08 (94)
28. La Rábida (Hue)	SI	03–08 (89)	03–08 (85)	03–08 (85)	04–08 (82)	05–08 (81)
29. R. Valle (Jae)	UB	04–08 (80)	04–08 (81)	04–08 (81)	03–08 (94)	03–08 (91)
30. Fuentezuelas (Jae)	SB	06–08 (93)	06–08 (85)	06–08 (85)	XX	XX
31. Carranque (Mal)	UB	05–08 (85)	05–08 (84)	05–08 (84)	05–08 (85)	05– 08 (80)
32. El Atabal (Mal)	SB	04–08 (88)	04–08 (83)	04–08 (83)	04–08 (86)	04–08 (81)
33. Marbella (Mal)	SB	03–08 (89)	03–08 (84)	03–08 (84)	03–08 (97)	03–08 (91)
34. A. Guadaira (Sev)	UB	03–08 (87)	03–08 (97)	03–08 (97)	03–08 (98)	03–08 (97)
35. Aljarafe (Sev)	SB	03–08 (98)	03–08 (90)	03–08 (90)	XX	03–08 (84)
36. Bermejales (Sev)	UB	03–08 (95)	03–08 (94)	03–08 (94)	03–08 (95)	03–08 (85)
37. Centro (Sev)	UB	03–08 (89)	03–08 (86)	03–08 (86)	03–08 (98)	XX
38. D. Hermanas (Sev)	UB	03–08 (92)	05–08 (93)	05–08 (93)	04–08 (98)	XX
39. Principes (Sev)	UT	XX	03–08 (99)	03–08 (99)	03–08 (93)	XX
40. Ranilla (Sev)	UT	XX	03–08 (87)	03–08 (87)	04–08 (93)	XX
41. San Jeronimo (Sev)	UB	03–08 (93)	03–08 (81)	03–08 (81)	XX	03–06 (81)
42. Santa clara (Sev)	SB	03–08 (92)	03–08 (96)	03–08 (96)	03–08 (83)	03–08 (89)
43. Torneo (Sev)	UT	03–08 (93)	03–08 (95)	03–08 (95)	03–08 (84)	03–08 (92)

traffic and industrial emissions and the association of the type of station and the occurrence of early morning or late evening peaks; and finally, for CO, we used the mean daily value. The results are shown in section 3.3. Using the average daily difference between weekends minus workdays, the weekend effect can be evaluated as well as its impact at specific times; the results are stated in section 3.4.

RESULTS AND DISCUSSION

Meteorology Overview

This section provides a general overview of the main meteorological characteristics in the region during the sampling period (2003–2008). Fig. 2 shows the mean sea level pressure and surface temperature during the period corresponding to the warm (May to September) and cold (October to April) seasons (maps obtained from reanalysis data of NOAA Earth System Research Laboratory, http://www.esrl.noaa.gov/psd/cgi-bin/data/composites).

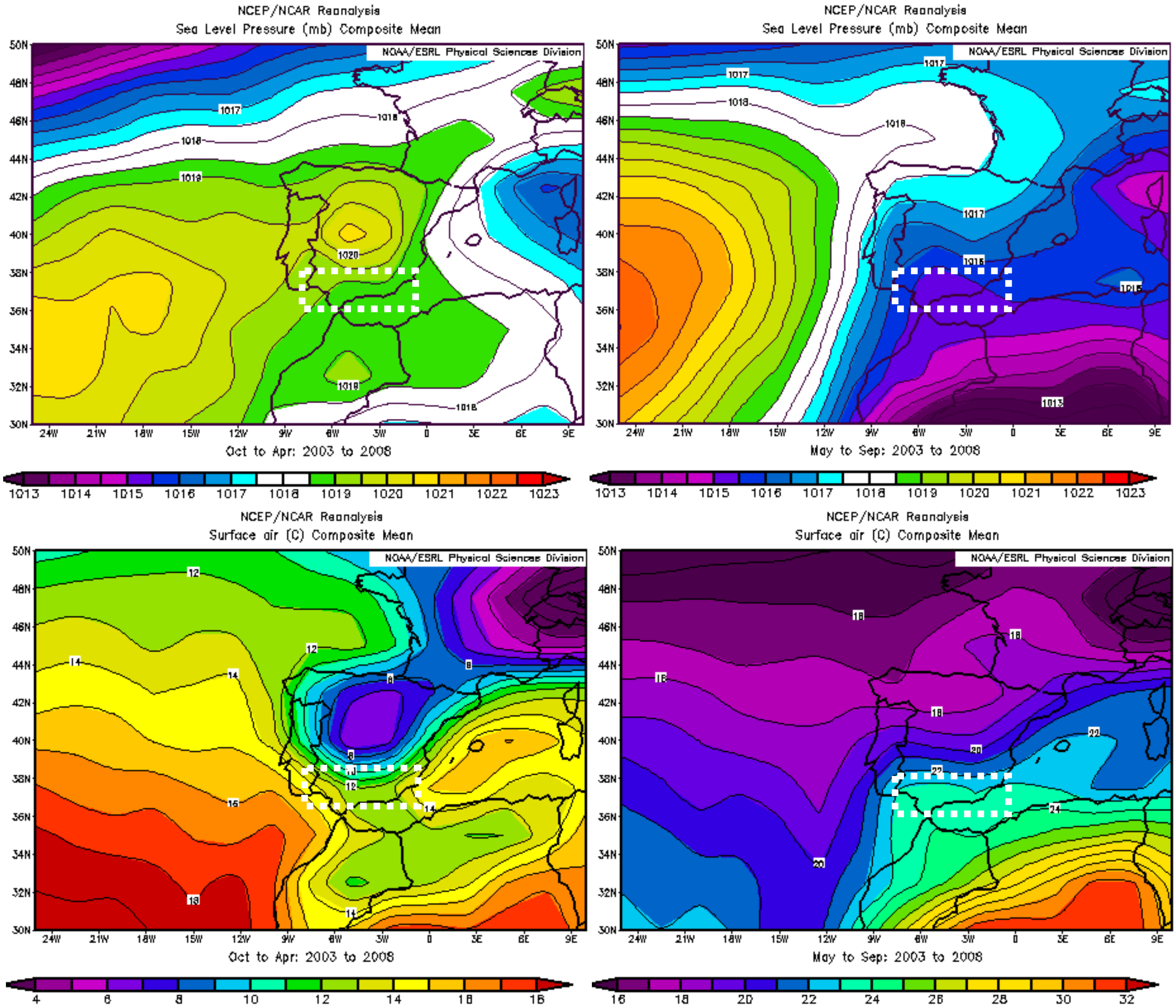

Fig. 2. Average fields (2003–2008) of mean sea level pressure (top) and surface temperature (bottom) in cold (October–April) and warm (May–September) seasons.

During the cold season Atlantic high pressure systems dominate, while low pressures are found in northern latitudes and in the western Mediterranean area. In the warm season, the low pressures in northern Africa and the Atlantic anticyclone resulted in lower atmospheric winds in the South of Spain. Both configurations agree with the definition of the main synoptic configuration over the Iberian Peninsula performed by Martin-Vide (2005). Associated with these atmospheric configurations, a large variety of air masses influenced this region, such as maritime air from the Atlantic Ocean and the Mediterranean Sea and continental air from the European continent or the Saharan desert (Toledano *et al.*, 2008; Hernandez-Ceballos, 2013). Due to the weak isobaric gradient that caused the predominance of anticyclonic conditions, from March to October there were frequent mesoscale processes, manifested as sea-land breezes in the Guadalquivir valley (Adame *et al.*, 2010, Hernández-Ceballos *et al.*, 2013).

In general, the Guadalquivir valley determines the surface wind behaviour in the western area, channelling the air masses along its southwest-northeast axis and allowing maritime air masses into inland areas far away from the coast. In addition, the Gibraltar Straight influences the wind regime in the region's southern area (Cadiz and Malaga provinces), channelling the winds along the west-east axis. Along the Malaga and Almeria coasts, mesoscale processes develop in the warm season but with less extension than in the Guadalquivir valley due to the proximity of the Beticas Mountains to the coastline. In this sense, the winds in the Beticas Mountains are not defined, as they are strongly influenced by the topography and the channelling effects of valleys.

The average temperature in Andalusia presented a marked and defined monthly cycle with maximum mean values in July and August between 25 and 27°C. Some areas of the Guadalquivir valley, such as Cordoba and Seville, registered the highest temperatures of the Iberian Peninsula, with daily maximums higher than 40°C. The coldest months were December and January, with mean values oscillating between 9 and 13°C. The lowest values were measured in Granada province, which has frequent snow-cover in wintertime.

The relative humidity (not shown) values were high in the provinces located along the coastline (Huelva, Málaga, Almeria and Cadiz), with an annual curve characterised by maximums in December and minimums in July and August. The western provinces (Seville, Huelva, Cadiz and Málaga) presented higher rainfall values than the eastern provinces (Almeria and Granada), which can be attributed to the arrival of maritime air masses from the Atlantic Ocean. The rainfall maximum was in December and January. Finally, the annual mean of sun hours exceeded 2800 in all provinces, with a maximum of 2998 hours in Huelva.

Mean Values and Average Daily Evolution

To highlight the air pollution problems in this region, this section presents a general overview of O_3, NO, NO_2, CO and PM_{10} concentrations at each type of sampling station during the reference period. We performed the analysis by grouping the types of station (Table 2).

Ozone concentrations varied between 51 µg/m^3 at urban traffic and 72 µg/m^3 at rural background stations, which are farther away from emission sources. The ozone levels at suburban background and suburban industrial sites were similar. Maximum levels of NO and NO_2 were observed at urban, traffic and background stations, and NO_x levels decreased at stations far away from city emissions. The differences between traffic stations and rural areas were 23 µg/m^3 for NO and 28 µg/m^3 for NO_2. Industrial areas showed lower values for NO and NO_2 when compared to those measured in urban and suburban areas, indicating that the contribution from traffic emissions was larger than that from industrial sources, which confirms the data given in section 2.1.

The highest CO concentrations were observed in traffic and industrial stations, which reflect the direct impact of these emission sources on the air quality in these areas. The urban and suburban background stations showed similar CO values, while rural stations presented the lowest CO concentrations but with an elevated background level close to 200 µg/m^3. For PM_{10}, the highest level (the same value as the European Directive threshold) was measured at traffic stations, and the lowest concentrations were measured at rural stations.

Table 2. Mean daily and standard deviation (in µg/m^3) for O_3, NO, NO_2, CO and PM_{10} according to the station type. UT: urban traffic, UB: urban background, SB: suburban background, SI: suburban industrial and RB: rural background.

Station type	O_3	NO	NO_2	CO	PM_{10}
UT	51 ± 11	26 ± 8	39 ± 9	664 ± 166	40 ± 8
UB	56 ± 6	13 ± 5	25 ± 7	496 ± 86	34 ± 5
SB	66 ± 8	10 ± 3	23 ± 5	498 ± 190	35 ± 5
SI	65 ± 7	8 ± 3	17 ± 6	548 ± 283	35 ± 7
RB	72 ± 8	3 ± 1	11 ± 2	193	23 ± 2

To further characterise the pollutant behaviour in this area, Fig. 3 shows the mean diurnal cycles of O_3, NO, NO_2, CO and PM_{10} for each type of station over the entire study period.

For urban traffic and urban and suburban background stations, the daily patterns of each pollutant were similar although with different concentration. NO, NO_2, CO and PM_{10} increased during the morning rush hours, and the levels were associated with the impact of traffic emissions and the transition period from stable to unstable atmospheric conditions, with a primary peak at 9:00 LT. In the following hours, the concentrations decreased, which could be attributed to the decrease in the intensity of emissions and the rapid growth of the convective boundary layer. At the same time that NO, NO_2, CO and PM_{10} levels started to increase in the morning hours, surface ozone decreased due to titration reactions with NO and the rupture of the nocturnal inversion layer. The daily minimum for ozone agreed with the first maximum of the rest of pollutants. Ozone concentrations continued to increase during the morning due to photochemical reactions and/or horizontal and vertical transport processes and reached a daily maximum at 17:00 LT. The highest maximum value was observed at suburban stations due to intense ozone production. The decrease in ozone values was followed by a reduction in temperature and solar radiation, formation of an inversion layer in the lower atmosphere and an increase in the urban fresh emissions of NO, NO_2, CO and PM_{10}, with a new peak at 22:00 LT.

The early nocturnal peak of NO was lower than the peak observed in the morning rush hours, with a reduction of 50% in the levels for suburban stations. This result could be related to the rapid oxidation of NO to NO_2 with the intervention of O_3 around 20:00–22:00 LT. Due to the high ozone levels in the late evening, the urban atmosphere had a strong oxidative capacity. The NO_2 evening peak was very similar to the observed morning peak. One exception was the suburban background station where the evening maximum was lower than that of the morning.

The maximum peak of PM_{10} in the late evening was higher than the peak in the morning, and the differences increased at stations far from the city centre. For example, at urban traffic stations, the difference was 5 µg/m^3, while the morning and evening differences at the suburban background stations were 9 µg/m^3.

CO showed a similar behaviour, with higher values in the late evening than in the morning. However, the spatial behaviour was opposite of PM_{10}, with a decrease in the peaks far from the city centre. At urban traffic stations, the difference between the peaks was 67 µg/m^3, while at urban and suburban stations, the differences were 31 and 13 µg/m^3, respectively.

In contrast, the suburban industrial stations presented a different daily behaviour. NO, NO_2 and CO showed similar concentrations throughout the day. In industrial areas, NO concentrations ranged between 6 and 8 µg/m^3, NO_2 between 14 and 20 µg/m and CO between 480 and 530 µg/m^3. From 7:00–8:00 LT, concentrations of NO, NO_2 and CO showed a slight increase that could be attributed to traffic

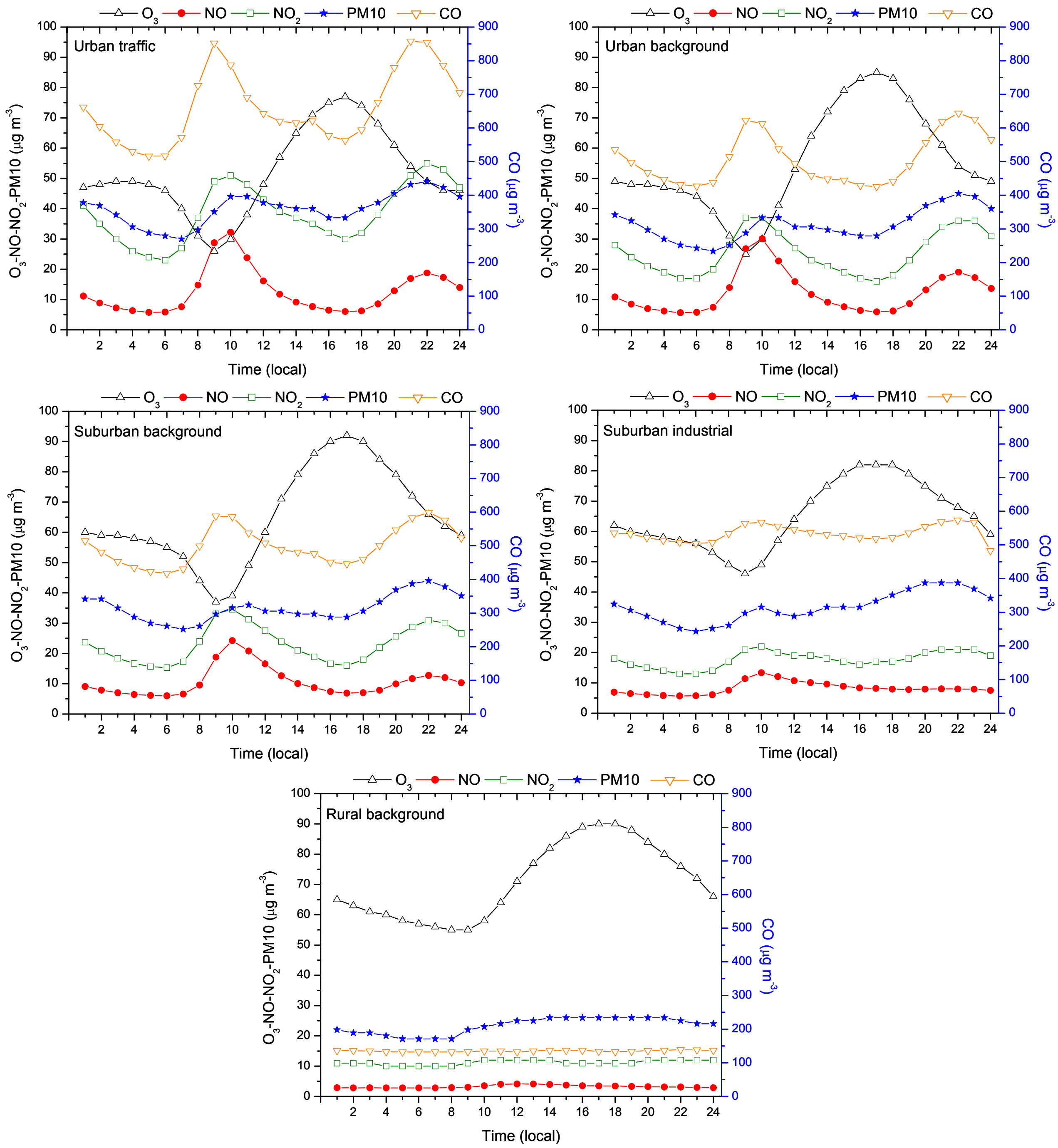

Fig. 3. Average daily concentrations of O_3, NO, NO_2, CO and PM_{10} as a function of the station type in the Andalusia region during the period from 2003 to 2008.

emissions due to start of factory shifts. The daily evolution of PM_{10} at industrial stations showed an increase in the concentrations from 10:00 LT to the end of the day, which could be related to the direct impact of emissions or to transport from other regions.

At these industrial stations, the daily ozone evolution showed nightly values and a minimum in the early morning, which was higher than those observed at urban and suburban stations. The NO levels in industrial areas were lower, and therefore, the removal of ozone through reaction with NO to produce NO_2 would be of minor importance. During the daylight hours, the ozone levels and the maximum concentrations were similar to those at the urban background stations, although the levels of precursors (NO, NO_2, CO) were lower.

Finally, rural background stations showed almost constant values of NO, NO_2, CO and PM_{10} during the day. The concentrations observed at the rural stations were 2–4 µg/m for NO, 10–12 µg/m^3 for NO_2, 133–140 µg/m^3 for CO and 19–24 µg/m^3 for PM_{10}. For ozone, the daily pattern showed a defined evolution.

The ozone concentrations reached daily maximum concentrations between 16:00 to 19:00 LT, with values higher than 88 µg/m^3. The origin of these levels could be *in situ* photochemical production. However, the low levels of ozone precursors (NO, NO_2, CO) suggest that the main origin of ozone measured at these monitoring stations was transport combined with ozone formation during transport from urban-industrial areas to rural environments.

To evaluate the impact of pollution in the region and to determine if this region has air pollution problems, the observations were compared with the European directive thresholds. During the study period, the ozone alert (240 µg/m^3 as 1 h average) and information (180 µg/m^3 as 1 h average) thresholds were exceeded at the Seville, Huelva and Cordoba stations. These exceedances were linked with the meteorological conditions and air mass transport along the Guadalquivir valley. The health protection threshold (120 µg/m^3 as daily maximum 8 h average) was exceeded at numerous air quality stations in the region. These exceedances occurred between March and October, i.e., the warm season. Suburban and rural stations in western Andalusia, influenced by the Guadalquivir valley, presented the largest threshold exceedances.

The PM_{10} threshold for human health (50 µg/m^3 as 1 h average) was frequently exceeded at industrial and urban stations. The Saharan outbreaks, mostly observed in summer months, increase the number of PM_{10} exceedances in whole region. NO concentrations reached maximum daily values higher 200 µg/m at stations with an elevated influence of traffic emissions, such as the urban stations of Seville and Granada, and mainly during the cold season from November to February. The NO_2 levels increased in the last years at numerous sites in Andalusia due to the increase in the volume of traffic, especially in the metropolitan areas. The CO concentrations were elevated in both urban and industrial areas. Hourly observations at stations such as Granada-Norte, Torneo, Marconi or M. Titan were frequently higher than 800 µg/m^3. These results indicate the existence of air pollution problems in this region and the necessity to conduct further studies to better understand the situation.

Concentrations on Workdays and Weekends and Weekly Trends

This section presents the concentrations measured during workdays (Monday to Friday) and weekends (Saturday and Sunday), as well as the evolution of each pollutant during each day of the week. In section 2.3, we defined the parameters used to evaluate the weekend effect; Table 2 shows the average (and standard deviation) results of each parameter during work and weekend days for the five pollutants and for each of the station type. The weekend effect is calculated by the difference of weekend minus weekdays.

The results for O_3 differences were similar at all sites, with differences varying between 1.8 and 2.1 µg/m^3, increasing only ~2–2.5%. Similar ozone increases to measure in other Mediterranean regions (Rigas-Karandino *et al.*, 2005; Schipa *et al.*, 2009) but lower than obtained in big urban areas (Stephens *et al.*, 2008) According to these results, in the case of ozone, there was no weekend effect, independent of type of station (similar criteria applied in Qin *et al.* 2004).

For NO, NO_2, CO and PM_{10}, the values fell on weekends compared to weekdays. The daily 90th percentile for NO was between 27 and 85% lower on weekends, except at rural stations. The largest reduction was found at the suburban background and urban traffic sites. This is due to the decrease in human activity during the weekend in these areas, as people remain at home or travel to rural areas, resulting in less traffic in the cities. Similar results were found for NO_2 but with a smaller decrease in the values, around 9–17%. At industrial stations, the reduction was lower than in urban and suburban areas. At rural stations, the observed decrease was below 1 µg/m^3. Therefore, for NO, the weekend effect was observed except in rural environments.

Regarding CO, the reduction was 4–9% in sites within the city or nearby, while in industrial and rural environments, a weekend effect was not observed because the differences were lower than 1%. For PM_{10}, the reduction at urban stations was marked, reaching percentages between 21 and 48%. At suburban background and industrial sites, the reduction was lower, while rural sites registered an increase of 5% in the 90th percentile of PM_{10}.

Fig. 4 displays the weekly trends of each parameter to assess the weekend effect at each type of station. For NO at urban sites, the concentrations peaked on Thursday and Friday, with values 26 µg/m^3 higher than the period from Monday to Wednesday. At suburban and rural stations, similar values were found on work days. A clear decrease in NO was observed on the weekends at urban and suburban sites, but not in rural environments. This decrease was more marked in urban stations affected by traffic. For NO_2, on workdays, the values were quite similar across urban, suburban and rural stations. Decreases in NO_2 concentrations were observed on weekend days, oscillating between 7 and 17 µg/m^3 at urban and suburban stations, while the rural sites were not affected.

Although ozone concentrations varied according to station type, from Thursday to Saturday, the values were similar (variation of 1–2 µg/m^3). An increase was observed on Sunday and Monday (lower than 10 µg/m^3), being higher at those stations with lower absolute ozone levels. From Tuesday to Friday, the ozone decrease was similar. At rural and industrial stations, the increase on weekends was 2 µg/m^3 or null. These results can be explained by the delayed impact of the weekend decrease in primary emissions affecting ozone on Sunday and Monday, but not immediately.

CO concentrations remained at similar values during the week, with variations lower than 6% for all station types, with the exception of urban traffic sites. At urban traffic sites, a CO decrease of approximately 12% was observed. The weekly variation exhibited by the 90th percentile for PM_{10} depended on the station type. A clear weekend effect was observed at urban traffic stations, with a decrease of more than 30 µg/m^3 compared with workdays. The urban background, suburban background and suburban industrial sites exhibited a decrease on weekends but of concentrations lower than 10 µg/m^3. Finally, rural stations did not exhibit this decrease and even registered a slight increase on Saturdays.

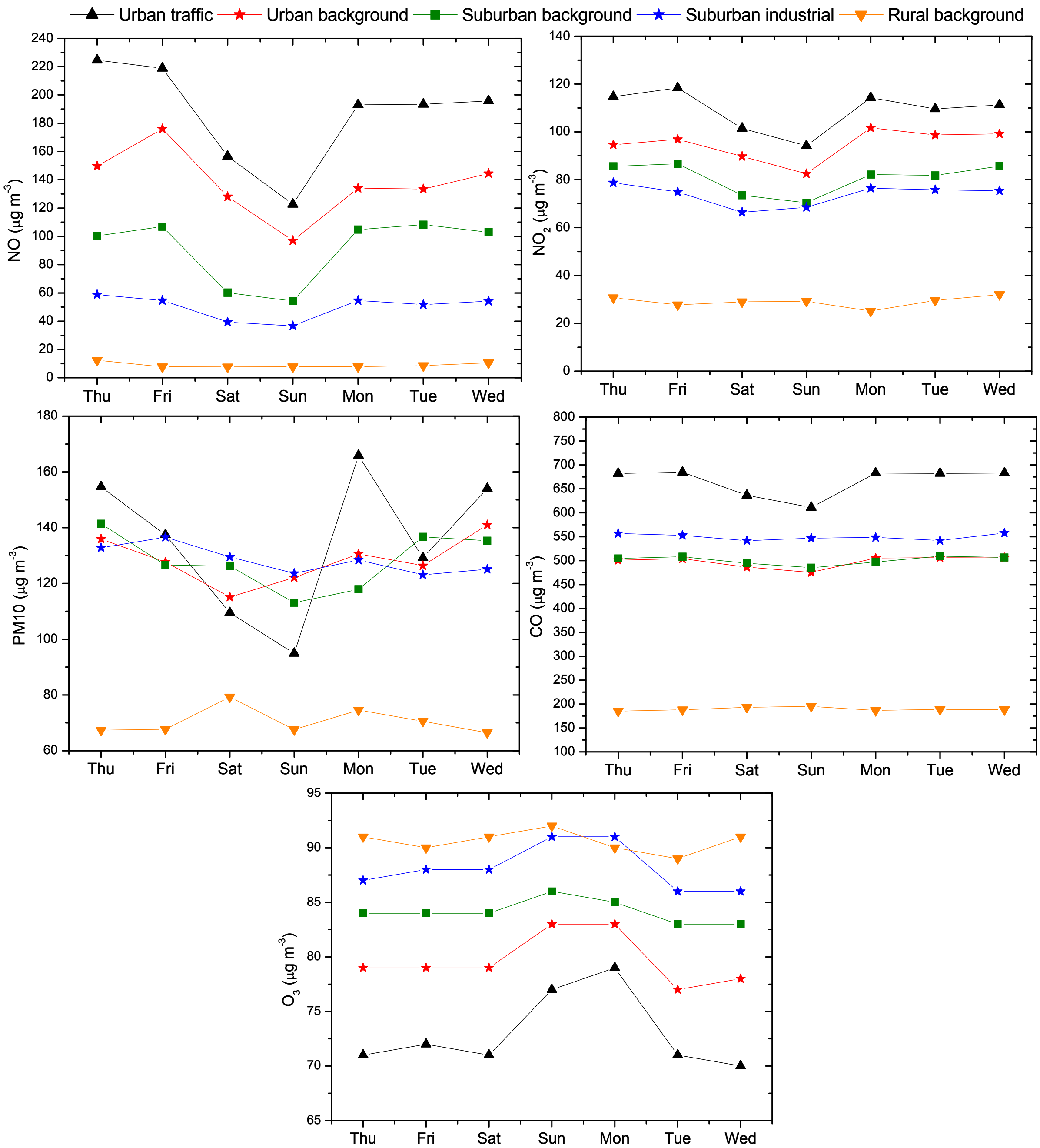

Fig. 4. Weekly patterns of maximum daily 8 hours mean for O_3, 90th percentile daily for NO, NO_2 and PM_{10}, and average daily for CO as a function of the station type.

Weekend Effect: Daily Differences Evolution

Fig. 5 shows the daily cycle of the concentration differences obtained for each pollutant by applying the formula of weekend days minus work days. This information can be used to determine the time of day with the largest differences between weekend days and working days. Ultimately, these differences allow the accurate determination of hourly influences on pollutant levels.

Regarding NO, NO_2 and PM_{10}, the daily cycle showed a similar behaviour, with positive differences during the night and negative differences during the daylight hours. The stations most affected were the urban traffic, urban background and suburban background sites, while the suburban industrial and rural sites were not affected.

The daily profiles showed that from midnight to 8:00 LT, the emissions of these three species were larger on weekend days than on work days. Therefore, traffic emissions generated by human activities were higher on weekend nights. At rural and industrial stations, this difference was not observed. The largest magnitude differences for NO-NO_2-PM_{10} were from 9:00 to 11:00 LT, with a peak at 9:00 LT. These results could be explained by the typical decrease in traffic emissions during the weekend days, especially in the early mornings of Saturday and Sunday. Therefore, a

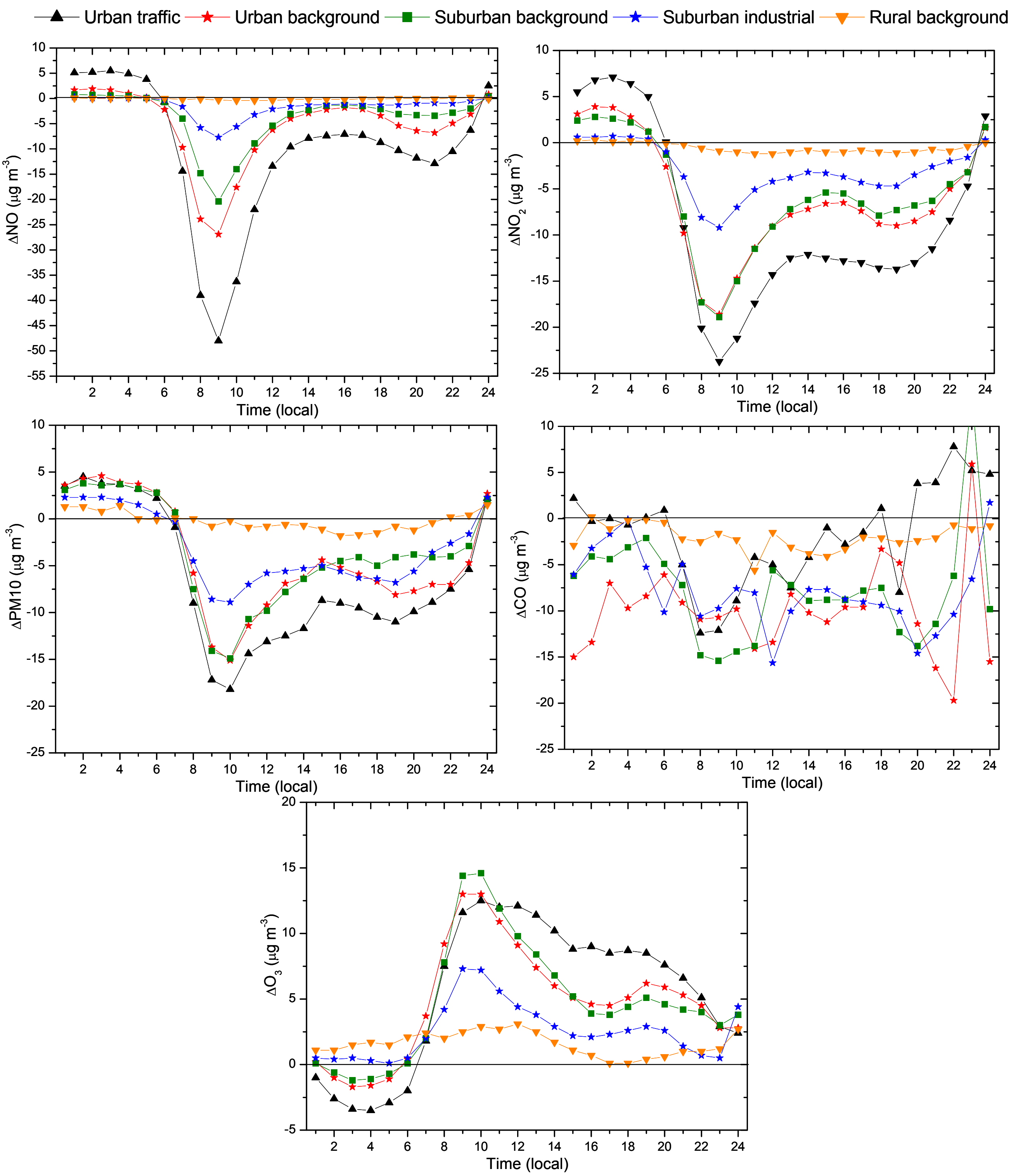

Fig. 5. Daily cycle of the differences (weekend minus work days) for O_3, NO, NO_2, PM_{10} and CO as a function of the station type.

reduction in traffic emissions could cause a reduction at the mentioned three station types of ~20–50 μg/m^3 for NO, more than 15 μg/m^3 for NO_2 and more than 12 μg/m^3 for PM_{10}, while at industrial sites, this reduction was ~5–10 μg/m^3 for NO, NO_2 and PM_{10}. The reduction observed in NO_x is similar or even higher than in other urban-suburban areas (Sadanaga *et al.*, 2008).

From noon to 20:00 LT, a weekend effect was observed, but its impact depended on air pollutant and station type. From 21:00 LT to midnight, the effect decreased; hence, the traffic emissions were very similar on both weekend and work days.

For CO, the results showed negatives values and did not depict a similar daily pattern. Instead, its daily evolution depended on the station type. Moreover, general trends or difference peaks in the early morning were not detected. The reduction in peak CO was 10–15 µg/m^3, a low concentration given the absolute CO levels observed, i.e., around 10%.

For surface ozone, as shown in Fig. 5, there was an opposite pattern from that observed for NO-NO_2-PM_{10}. This behaviour has been also obtained in other regions with similar features (Schipa *et al.*, 2009). During weekend nights, the ozone concentrations were higher than on work days, although the differences did not exceed 5 µg/m^3, with the exception of suburban industrial and rural stations, which presented positive differences or differences near zero.

The lower ozone levels were due to higher NO and NO_2 concentrations because ozone is removed by the reaction with NO. The opposite effect was observed during day time, as lower NO concentrations and therefore higher ozone levels were observed because of the decreased atmospheric ability to eliminate ozone. The highest ozone increase was associated with the highest decrease in NO_x, occurring between 7:00 to 11:00 LT. During this time period, urban traffic, urban background and suburban background sites were the most affected, with an increase in ozone of 12–15 µg/m^3. However, these stations showed the lowest absolute levels (Fig. 3); therefore, this increase in the ozone levels did not produce an increase in the number of threshold exceedances defined in the European Directives (section 3.2). It is well known that suburban and rural stations have more exceedances in Europe. These results demonstrate that an ozone increase of 5 µg/m^3 at rural stations could be associated with the weekend effect, and the occurrence of exceedances attributed to the weekend effect would be scarce or null. There are other factors that influence ozone levels more than the weekend effect, such as atmospheric transport processes and development of the atmospheric boundary layer, among others.

Finally, from noon to 22:00 LT, the three stations most affected by the weekend effect showed increases in ozone oscillating between 5 and 10 µg/m^3, while positive increases lower than 5 µg/m^3 were observed at suburban industrial and rural background sites.

CONCLUSIONS

The weekend effect for O_3, NO_x, CO and PM_{10} has been evaluated in Andalusia (South of Spain) in the period 2003–2008. Hourly air quality data, with a percentage of valid data higher than 80%, has been used. The analysis of the concentrations and European Directives threshold exceedances highlights the existence of air pollution problems in the area studied. The mean diurnal cycles for O_3, NO, NO_2, CO and PM_{10} were evaluated according to the five stations types. In urban traffic, urban and suburban background stations, air pollutants showed similar daily patterns, though with different absolute levels, and were modulated by the direct influence of urban emissions. Suburban industrial stations exhibited different behaviours when compared with urban sites, due to industrial emissions or aged air pollutants transported from other regions. Rural background stations showed almost constant concentrations for NO, NO_2, CO and PM_{10}, while ozone had a strong daily cycle as well as the highest values among the station types.

Three daily parameters were applied to evaluate the weekend effect: maximum daily 8 h averages for ozone, daily 90th percentile for NO, NO_2 and PM_{10} and mean daily for CO. According to these parameters, the weekend effect was not observed for ozone, with a reduction of only ~2.5%. However, NO, NO_2, CO and PM_{10} showed the weekend effect, mainly in urban and suburban stations, with variations oscillating between 25 and 85%; these results were not observed in rural environments.

The weekly trends showed a significant variation for NO and NO_2, with a decrease on weekends at urban and suburban stations affected by urban emissions, while little variation was observed in rural areas. An ozone increase was observed, less than 10 µg/m^3, at those stations with the lowest levels (most affected by traffic emissions), while at rural stations, a null effect on ozone was observed. CO weekly variations showed a reduction on weekends between 6 and 12%. The decrease in PM_{10} on weekends varied amongst station types, at urban traffic sites, reductions of 30 µg/m^3 were observed, while at industrial or rural sites, the difference was less than 10 µg/m^3. Therefore, a large weekend effect was found for NO, NO_2 and PM_{10} mostly at urban stations, although the effect was reduced at areas farther from emission sources. While for ozone, no weekend effect was observed.

The daily cycle of the differences observed in concentrations measured using the difference between weekend and workdays was also analysed. For NO, NO_2 and PM_{10}, positive differences were found at night, and negative differences were observed in the daylight period, mostly at urban traffic, urban background and suburban background sites. These findings suggest more human activity on weekend nights than on workdays. At urban stations, from 9:00 to 11:00 LT, a reduction in the traffic emissions produced a decrease of ~20–50 µg/m^3 for NO, > 15 µg/m^3 for NO_2 and > 12 µg/m^3 for PM_{10}, while at industrial sites, this reduction was ~5–10 µg/m^3 for NO, NO_2 and PM_{10}. CO showed negative differences throughout the day; however, the reduction on weekend days was low.

The daily weekend differences in ozone exhibited an opposite pattern than that observed for NO-NO_2-PM_{10}. On weekend nights, the ozone values were higher than on workdays, but the concentrations were less than 5 µg/m^3 at urban and suburban stations and null at rural stations. Positive differences were observed in the daytime, mainly during the morning rush hours, even though the ozone increase did not exceed 15 µg/m^3. In addition, the highest positive differences were observed in urban areas with the lowest ozone levels.

ACKNOWLEDGMENTS

The authors wish to thank the Survey and Air Quality Control Network belonging to the Environmental Department of the Regional Government of Andalusia (Spain) for access to its database. The authors also acknowledge the

NOAA/ESRL Physical Sciences Division for providing the meteorological data used to plot the meteorological maps.

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Received for review, February 7, 2014
Accepted, May 31, 2014