Available online at www.sciencedirect.com

SCIENCE DIRECT®

Atmospheric Environment 39 (2005) 429–444

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Modeling the ozone weekend effect in very complex terrains: a case study in the Northeastern Iberian Peninsula

Pedro Jiménez, René Parra, Santiago Gassó, José M. Baldasano*

Laboratory of Environmental Modeling, Universitat Politècnica de Catalunya (UPC), Avda. Diagonal 647 10.23, 08028 Barcelona, Spain

Received 22 August 2004; accepted 24 September 2004

Abstract

Ambient ozone (O_3) concentrations tend to be higher on weekends than on weekdays in urban areas, a phenomenon known as the weekend effect. Nevertheless, its downwind influence could be diverse. The MM5-CMAQ model has been used to assess the causes of weekday/weekend O_3 differences in the north-eastern Iberian Peninsula during an episode of photochemical pollution covering the whole Western Mediterranean Basin (13–16 August 2000). Emissions were estimated with EMICAT2000 model. The key differences between weekday and weekend on-road vehicle emissions are in magnitude and timing. On-road traffic accounts for ~57% of the anthropogenic NO_x and VOC emissions in the modeling domain, and are principally located along the coast and mainly in the Barcelona Geographical Area. The drop of heavy-duty tracks traffic on weekends involves a 22% reduction of NO_x emissions and just a slight change in VOC emissions. Changes in the timing of emissions are directly related to differences in weekday/weekend traffic profiles, being emissions shifted 1–2 h later on weekends. The response of both ambient and simulated O_3 concentrations to day-of-week differences in emissions varies by location. The combination of VOC-sensitive regimes and NO_x-titration in urban areas as Barcelona, in addition to the different magnitude and timing of emissions (decreasing NO_x/VOC ratios on weekend mornings) causes the raise of O_3 on weekends (+54%). In non-urban regimes, principally associated to NO_x-sensitive chemistry, a lower concentration of O_3 is observed in non-labor days (decreases of –10% in downwind areas). Rural locations, dominated by medium-long range transport, depict similar O_3 concentrations. Both discrete and categorical model evaluations are shown in order to test the accuracy of the model for representing weekdays/weekends differences within the air basin. This work helps identifying the major causes of the weekend effect in the considered domain, as the changing in mass and time of precursors emissions, and may be a useful tool to reduce ambient O_3 levels.

Keywords: Ozone; Weekend effect; Air quality modeling; Photochemistry; Very complex areas

1. Introduction

Tropospheric ozone results form the photochemical interaction of NO_x and VOCs under the presence of sunlight. The ozone weekend effect refers to a tendency in some areas for ozone concentrations to be higher on weekends compared to weekdays, despite emissions of VOCs and NO_x are typically lower on weekends due to a different anthropogenic activity. This phenomenon was first reported in the United States in the 1970s (Cleveland et al., 1974; Lebron, 1975) and has been since reported mainly in the US and Europe (Altshuler et al.,

*Corresponding author. Tel: +34 934011744; fax: +34 93340255.

E-mail address: jose.baldasano@upc.es (J.M. Baldasano).

1352-2310/$ - see front matter
doi:10.1016/j.atmosenv.2004.09.065

1995; Brönnimann and Neu, 1997; Jenkin et al., 2002; Pun et al., 2003; Qin et al., 2004a; among others). Higher weekend ozone tends to be found in urban centers, while lower weekend ozone is found in downwind areas. Altshuler et al. (1995) and Blanchard and Fairley (2001) have suggested that the weekend effect is related to whether ozone formation in VOC- or NO_x-sensitive, with higher weekend ozone occurring in VOC-sensitive areas. However, a major problem for the study of NO_x-VOC sensitivity on ozone formation has been the inability to gain evidence based on direct measurements rather than theoretical calculations (Sillman, 1999). Despite there is a high uncertainty in the causes of the weekend effect, the California Air Resources Board has widely studied this problem in California, and six hypothesis have been set for this area (CARB, 2003):

NO_x reduction: Marr and Harley (2002a) analyzed the day-of-week behavior of O_3, NO_x and VOC for two decades of data from sites throughout California. They concluded that the pattern of higher O_3 on weekends has become more widespread between 1980 and 1999 but the pattern for precursors remained fairly constant over the same time period. This study reported that NO_x is significantly lower on weekends at 85 out of 93 sites. Blanchard and Tanenbaum (2003) found that in the South Coast Air Basin of California, the mean Sunday NO_x and non-methane hydrocarbon concentrations were 25–41% and 16–30% lower, respectively, than on weekdays. Qin et al. (2004b) indicated that concentrations of NO_x, CO, NMOC and PM_{10} and the light scatter in at weekend were about 37%, 18%, 15%, 14% lower than those of weekdays.

NO_x timing: Traffic studies (Chinkin et al., 2003; Fujita et al., 2003b) indicate that NO_x emissions on weekends are substantially lower than on weekdays for several hours following sunrise. However, the traffic near midday is similar on weekdays and weekends. The NO_x timing hypothesis is that the timing of NO_x emitted on weekends causes the midday emissions to produce O_3 more efficiently compared with the NO_x emitted on weekdays. Marr and Harley (2002b) indicated that NO_x emissions from heavy-duty truck activity reduced during all hours on weekend days and that car and light-truck activity is shifted in time because of the greatly reduced morning commute on weekend days. Yarwood et al. (2003) found out that the mass reduction effect was much larger than the timing effect and concluded that weekend ozone is relatively insensitive to changes in the timing of motor vehicle emissions.

Carryover near the ground and carryover aloft: Increased VOC and NO_x emissions from traffic on weekends nights may carry over near ground level and lead to greater O_3 formation after sunrise on the following day. Fujita et al. (2003a) concurred that pollutant carryover near the ground is at most a small factor because differences in precursor concentrations during the carryover period have only a small effect on precursor concentrations and ratios during the O_3 accumulation period. In addition, the reservoir of pollutants that carries over above the nocturnal boundary layer may exert a greater influence on surface O_3 concentrations on weekends than on weekdays. The hypothesis suggests that morning concentrations of NO_x titrate O_3 and quench radicals (Heuss et al., 2003).

Increased weekend emissions: Higher weekends O_3 levels may be caused by increased emissions from activities that occur more often on weekends that on weekdays, such as recreational and maintenance activities. CARB (2003) has concluded that, in the case of California, the increased weekend emissions hypothesis is not plausible because air quality data from the extensive monitoring network show that ambient levels of precursors are lower on weekends compared with weekdays for all daylight hours.

Increased sunlight caused by decreased soot emissions: Because soot absorbs UV sunlight and prevents it from initiating O_3 formation, the lower levels of soot on weekends results in increased UV sunlight and hence O_3 formation by influencing meteorological variables. While the soot and sunlight hypothesis is plausible as a factor that would increase O_3 on weekends, Blier and Winer (1999) indicated that measured solar radiation is not significantly higher on weekends than on weekdays.

In addition to these hypotheses, two recent studies suggest some additional chemistry may need to be added to the existing mechanisms in order to explain a possible weekend effect. Tanaka et al. (2003) suggest the possibility that chlorine (Cl) chemistry plays a role in areas with Cl sources. The other study (Knipping and Dabdub, 2002) is a proximate modeling exercise that suggests surface-mediated renoxification may play a role. In neither case, however, does there appear to be a weekday/weekend difference that would explain the variations in weekend effect.

Emission inventories for each day of week are needed to help determine the causes of the ozone weekend effect. These inventories must reveal in sufficient detail the quantity, the timing, and the location of VOC and NO_x emissions for weekdays and weekends (CARB, 2003). In this work, a day-specific hourly emissions inventory is used for stationary, area and on-road sources in order to help assessing the ozone weekend effect for the photochemical pollution episode of 13–16 August 2000, observed in a very complex terrain as the Northeastern Iberian Peninsula. In this area, ambient O_3 data indicates concentrations up to 189 $\mu g\,m^{-3}$ on weekends and 177 $\mu g\,m^{-3}$ during weekdays, exceeding the European Information Threshold of 180 $\mu g\,m^{-3}$. The hypothesis of changing mass and timing of emissions, ozone quenching and carryover are analyzed, discarding the hypothesis that have been proved not to have importance on weekend effect, such as increased emissions or increased sunlight on weekends. An evaluation of the performance of the model is also considered, comparing results with air quality stations data and analyzing the up-to-date hypothesis about the ozone weekend effect.

2. Methods

2.1. Modeling case

Modeling was conducted for the photochemical pollution event in the Western Mediterranean Basin from that took place on 13–16 August 2000, after a 48-h spin-up in order to minimize the influence of initial conditions. Two non-labor days (13 and 15 August) and two working days (14 and 16 August) are considered in order to evaluate the O_3 weekend effect in the North-eastern Iberian Peninsula. Values over the European threshold of 90 ppb (180 $\mu g\, m^{-3}$) for ground-level O_3 are attained. The domain of study (Fig. 1) covers a squared area of $272 \times 272\, km^2$ centered in Catalonia, located in the Northeastern Iberian Peninsula. The complex configuration of the zone comes conditioned by the presence of the Pyrenees mountain range (with altitudes over 3000 m), the influence of the Mediterranean Sea

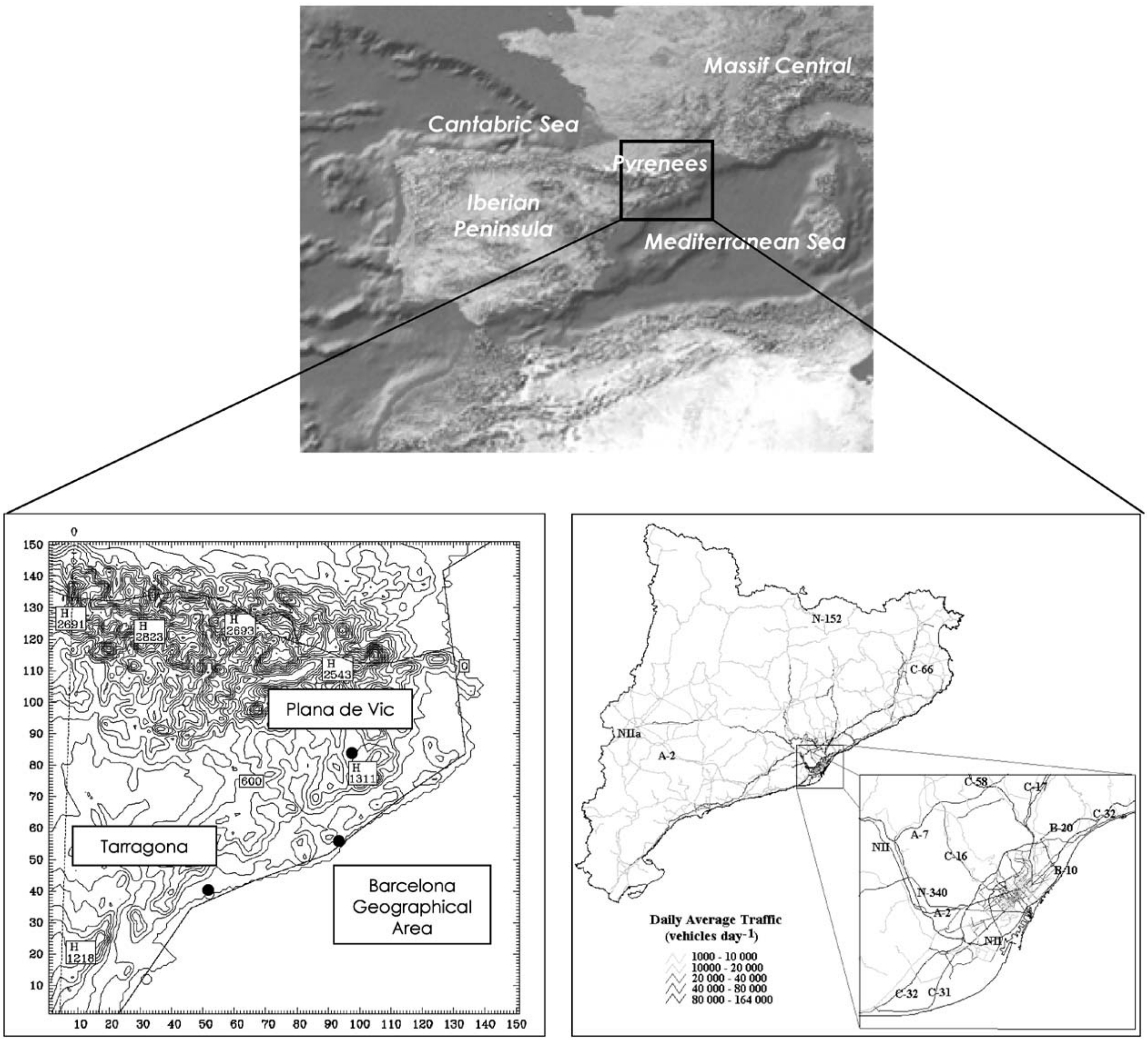

Fig. 1. Geography of the areas where main O_3 problems in the Northeastern Iberian Peninsula are located: Barcelona Geographical Area (urban, upwind), Plana de Vic (downwind) and Tarragona (upwind, industrial); and main important on-road traffic roads and highways.

and the large valley canalization of Ebro River. That produces a sharp gradient in the characteristics of the Northeastern Iberian Peninsula. The very complex orography of the area difficult the application both meteorological, emission and chemical transport models; and it induces an extremely complicated structure of the flow because of the development of α- and β-mesoscale phenomena that interact with synoptic flows. The characteristics of the breezes have important effects in the dispersion of pollutants emitted. In addition, the flow can be even more complex because of the non-homogeneity of the terrain, the land-use and the types of vegetation. In these situations, the structure of the flow is extremely complicated because of the superposition of circulations of different scale, and forces to the application of multiscale-nested models with very high horizontal and vertical resolution.

The weekend effects results reported here correspond to the episode of 13–16 August 2000, which corresponds to a typical summertime low pressure gradient with high levels of photochemical pollutants over the Iberian Peninsula. This situation is related to a decrease in air quality. The day was characterized by a weak synoptic forcing (Fig. 2), so that mesoscale phenomena, induced by the particular geography of the region would be dominant. This situation is associated with weak winds in the lower troposphere and high maximum temperatures. A high sea level pressure and almost non-existent surface pressure gradients over the domain characterize this day, with slow northwesterlies aloft.

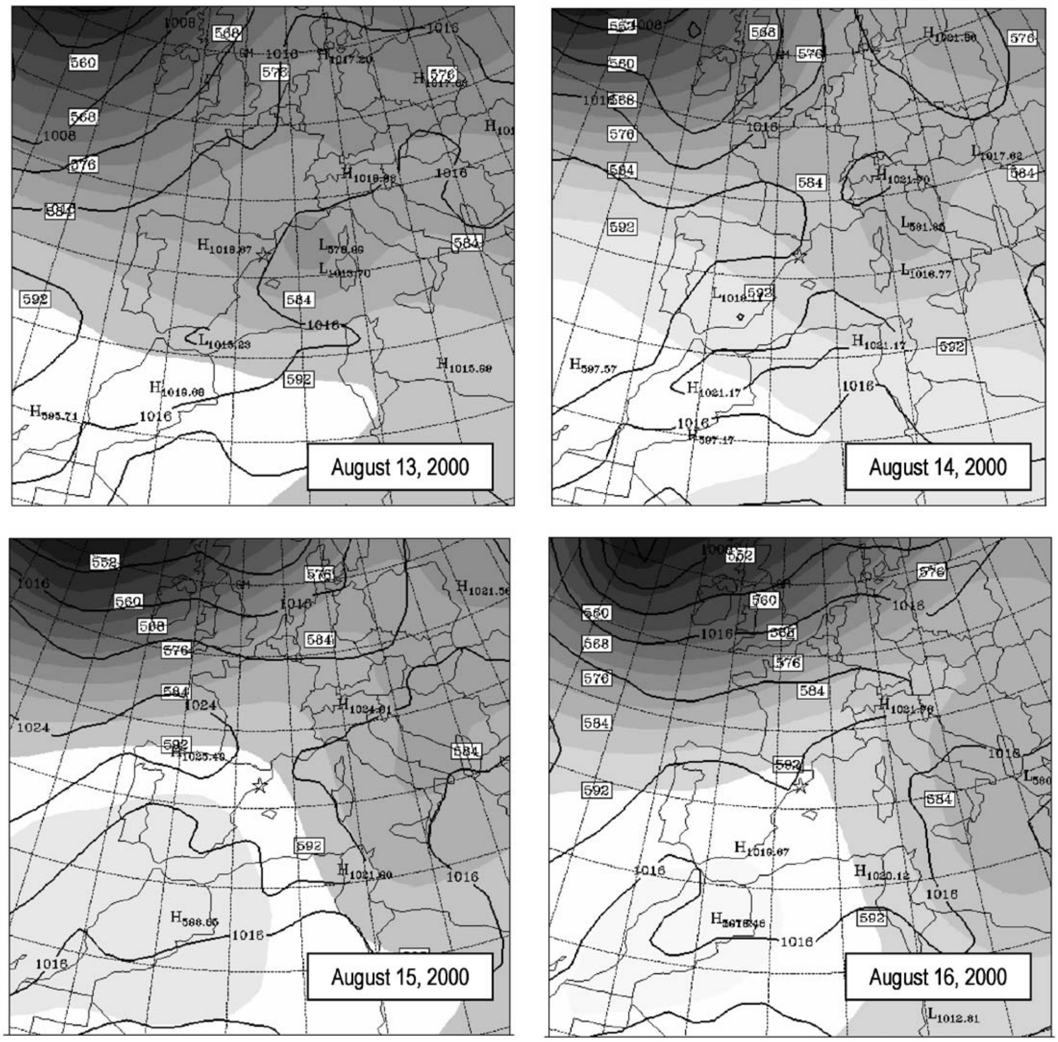

Fig. 2. Synoptic situation of 13 August–16 August 2000 (shaded map: 0000UTC 500 hPa analysis, contour map: 0000UTC surface analysis).

The meteorological situation of the episode (low pressure gradient with a weak anticyclone over the Mediterranean) strongly limits air mass inflows in the area. Under this weak synoptic forcing, strong insolation promotes the development of prevailing mesoscale flows associated with the local orography (mountain and valley breezes), while the difference of temperature between the sea and the land enhances the development of sea-land breezes (Barros et al., 2003). Meteorological conditions are indeed very similar for the 4 days covered in this episode, both on the synoptic and the meso- and local scale. The situation presented in this study is representative of an episode of photochemical pollution in the Western Mediterranean Basin, since the occurrence of regional re-circulations at low levels represents 45% of the yearly flow transport patterns over the area of study, and over 70% of summer transport patterns (Jorba et al., 2004) and these situations are associated with local-regional episodes of air pollution in the Northeastern Iberian Peninsula that result in high levels of ozone and an increase of particulate matter within the boundary layer during summer.

Millán et al. (1997) generally described the re-circulations processes occurring along the Western Mediterranean Basin under similar synoptic situations to those observed in this episode. During the day the sea breezes transport coastal pollutants inland, while at the leading edge of the breeze front, breezes combine with upslope winds to inject a fraction of these pollutants in their return flows aloft at heights ranging from 2 to 3 km. Once in those upper layers, pollutants move back toward the sea (Baldasano et al., 1994), the air at the middle troposphere is forced to go down by the subsidence over the east coast, once in low levels the air masses re-circulate over the sea with a possible later return to the seaboard. Pérez et al. (2004) confirmed this behavior when analyzing the characteristic re-circulations produced along the east coast of the Iberian Peninsula for 14 August 2000.

The main emissions sources in the Northeastern Iberian Peninsula are located on the coast, being the most important emitting source the Barcelona Geographical Area. The peculiar topography of the zone is the principal driving mechanism that contributes to the dispersion of pollutants in the given domain. Maximum O_3 levels in Catalonia are measured downwind Barcelona and Alcover, downwind the industrial zone of Tarragona.

2.2. Models

MM5 numerical weather prediction model (MMMD/NCAR, 2001) provided the meteorology dynamical parameters. MM5 physical options used for the simulations were: Mellor-Yamada scheme as used in the Eta model for the PBL parameterization; Anthes-Kuo and Kain-Fritsch cumulus scheme; Dudhia simple ice moisture scheme; the cloud-radiation scheme; and the five-layer soil model. Initialization and boundary conditions for the mesoscale model were introduced with analysis data of the European Center of Medium-range Weather Forecasts global model (ECMWF). Data were available at a 1-degree resolution (100-km approximately at the working latitude) at the standard pressure levels every 6 h.

The high resolution (1-h and 1 km^2) EMICAT2000 emission model has been applied in the Northeastern Iberian Peninsula. This emission model includes the emissions from vegetation, on-road traffic, industries and emissions by fossil fuel consumption and domestic-commercial solvent use. Biogenic emissions were estimated using a methodology that takes into account local vegetation data (land-use distribution and biomass factors) and meteorological conditions (surface air temperature and solar radiation) together with emission factors for native Mediterranean species and cultures (Parra et al., 2004). On-road traffic emission includes the hot exhaust, cold exhaust and evaporative emissions using the methodology and emission factors of the European model EMEP/CORINAIR–COPERTIII (Ntziachristos and Samaras, 2000) as basis, and differencing the vehicle park composition between weekdays and weekends (Parra and Baldasano, 2004). Industrial emissions include real records of some chimneys connected to the emission control net of the Environmental Department of the Catalonia Government (Spain), and the estimated emissions from power stations (conventional and cogeneration units), cement factories, refineries, olefins plants, chemical industries and incinerators.

The chemical transport model used to compute the concentrations of photochemical pollutants was Models-3/CMAQ (Byun and Ching, 1999). The initial and boundary conditions were derived from a one-way nested simulation covering a domain of $1392 \times 1104\,km^2$ centered in the Iberian Peninsula, which used EMEP emissions corresponding to year 2000. However, as commented before, the limitation in air mass inflows in the domain due to the meteorological conditions of the episode minimizes the influence of boundary conditions on ozone maximum concentrations. The impact of modifying boundary ozone or precursors on a 50% in ground-level ozone keeps under a factor of 0.2 during the whole period of simulations for most sites in the Northeastern Iberian Peninsula, since boundaries of the domain selected are far enough from relevant sites not to have a significant influence. A 48-h spin-up was performed in order to minimize the effects of initial conditions (Berge et al., 2001). The chemical mechanism selected for simulations was CBM-IV (Gery et al., 1989), including aerosols and heterogeneous chemistry. NO_x and VOC specification of EMICAT2000 emissions, as required by CBM-IV, could be found in Parra (2004). The algorithm chosen for the resolution of tropospheric chemistry was the Modified Euler Backward Iterative (MEBI) method (Huang and Chang, 2001). Horizontal resolution considered was 2 km, and 16-sigma vertical layers cover the troposphere.

2.3. Air quality data

Air quality stations hourly data averaged over the domain of study were used in order to report weekend/weekday differences. Hourly measures of ground-level O_3, NO_x and CO was provided by 48 air quality surface stations in Northeastern Spain which belong to the Environmental Department of the Catalonia Government (Spain). CO was used as a surrogate for VOC because of the unavailability of VOCs measurements in the area (Yarwood et al., 2003).

Those data were also utilized to indicate the performance of models results. Despite a surface measurement represents a value only at a given horizontal location and height, while the concentration predicted by the model represents a volume-averaged value, ground-level O_3 results were statistically evaluated by comparing the first-layer simulations results and the values measured in the air quality stations of the domain under study. The analysis of the results will consist in a statistical comparison of both discrete and categorical parameters. The European Directive 2002/3/EC relating to ozone in ambient air establishes an uncertainty of 50% as the quality objective for modeling assessment methods. This uncertainty is defined as the maximum error of the measured and calculated concentration levels. In addition, the US Environmental Protection Agency has developed guidelines (US EPA, 1991) for a minimum set of statistical measures to be used for these evaluations where monitoring data are sufficiently dense. Those statistical figures, considered in this work, are the mean normalized bias error (MNBE), the mean normalized gross error for concentrations above a prescribed threshold (MNGE), and the unpaired peak prediction accuracy (UPA). Categorical statistics, as derived from Kang et al. (2003), have also been used to evaluate the different vertical and horizontal resolution, including parameters as the model accuracy (A), bias (B), probability of detection (POD), critical success index (CSI) and false alarm rates (FAR). These criteria based also upon a 120 $\mu g\,m^{-3}$ threshold.

3. Results and discussion

3.1. Model evaluation

Ground-level O_3 simulation results were compared to the measurements from 48 surface stations in the Northeastern Iberian Peninsula, located in both urban and rural areas. Observation-prediction pairs are often excluded from the analysis if the observed concentration is below a certain cut-off; the cut-off levels vary from study to study but often a level of 120 $\mu g\,m^{-3}$ is used (Hogrefe et al., 2001), which is the criterion applied in this work. Table 1 collects the results of both the discrete and categorical statistical analysis. Although there is no criterion set forth for a satisfactory model performance, US EPA (1991) suggested values of $\pm$10–15% for MNBE, $\pm$15–20% for the UPA and +30–35% for the MNGE to be met by modeling simulations of O_3 have been considered for regulatory applications. The model results achieve the EPA goals for a discrete evaluation on all episode days. The O_3 bias is negative on each day, ranging from −2.1% on the first day of simulation until −14.3% on 15 August. That suggests a slight tendency

Table 1
Statistical measures of model performance for 1-h O_3 during the episode of 13–16 August 2000

	EPA goal	13 August 2000	14 August 2000	15 August 2000	16 August 2000
Discrete evaluation					
Observed peak ($\mu g\,m^{-3}$)		157	177	189	171
Modeled peak ($\mu g\,m^{-3}$)		189	170	167	180
UPA (%)	$<\pm 20$	14.4	−3.8	−11.7	5.2
MNBE (%)	$<\pm 15$	−2.1	−11.0	−14.3	−5.6
MNGE (%)	<35	16.8	19.8	21.7	26.7
Categorical evaluation					
A (%)		91.1	92.2	90.0	89.7
B (%)		0.7	0.1	0.1	0.4
POD (%)		22.1	6.9	9.6	11.5
CSI (%)		15.0	6.7	9.2	9.1
FAR (%)		67.9	33.3	31.3	69.6

towards underprediction; however, EPA goals of ±15%. This negative bias may suggest that the O_3-production chemistry may not be sufficiently reactive. The modeled episode peak (189 $\mu g\,m^{-3}$) is well-captured by the model. Peak accuracy is overestimated on the first and last day of simulations (14.4% and 5.2%, respectively) and underestimated on the central days of the episode (−3.8% and −11.7%). The mean normalized error increases from 13 August until 16 August (16.8–26.7%), mainly to deviations in meteorological predictions that enlarge with the time of simulation (Jiménez et al., 2004). The objective set in the Directive 2002/3/EC (deviation of 50% for the 1-h averages) is also achieved for the whole period of study.

Respect to categorical forecasting, statistical parameters indicate that the accuracy (percent of forecasts that correctly predict an exceedance or non-exceedance) is around 90% for every day of simulation, decreasing the performance by the end of the episode. Since this metric van be greatly influenced by the overwhelming number of non-exceedances, to circumvent this inflation the critical success index and the probability of detection is used. Both parameters perform similarly during the episode, yielding more accurate values (22% for 13 August 2000 –weekend– vs. 7% for 14 August 2000 –weekday–) when ozone peaks are higher (and when exceedances of the 120 $\mu g\,m^{-3}$ threshold taken as reference are more frequent). The value of bias ($B<1$ for all simulations) indicates that exceedances are generally underpredicted, which corresponds with the value of MNBE obtained for discrete evaluations. Last, the fifth categorical parameter, the false alarm rate, indicated the number of times that the model predicted an exceedance that did not occur. This metric is high for the first and last day of the simulations (around 68%), since of the possible initialization influence during the first moments of simulation, that can be high for the sum of reservoir species for O_3 (Berge et al., 2001); and the errors attributable to the meteorology, that accumulate over the period and perturb through the forecasts, as commented before. Nevertheless, values shown here agree with (or slightly improve) the results found by (Kang et al., 2003).

3.2. Weekday/weekend emissions within EMICAT2000

Existing gridded inventories used as input to air quality models typically lack of accurate estimates of emissions on weekends (Marr and Harley, 2002b). We use EMICAT2000 inventory emission model (Parra, 2004) that takes into account main weekday/weekend differences on ozone precursors emissions profiles due mainly to variations in on-road traffic emissions. EMICAT2000 considers different emissions of VOCs associated to the domestic and commercial use of solvents between Saturdays and Sundays.

On-road traffic emission module is built with a digital map of all the highways and most important roads and streets (daily average traffic > 3000), including the hot and cold exhaust emissions, and evaporative emissions, and includes monthly, daily and hourly traffic profiles; differencing the vehicle park composition and traffic profiles between weekdays and weekends. Fig. 3a shows some samples of hourly traffic profiles both for weekdays and weekends for highways and roads stretches in the Northeastern Iberian Peninsula. Weekday profiles have higher percents about 0700 UTC and 1700 UTC. There are drops at mid-day and the lower percentages are present during nighttime and first hours of early morning. Weekend profiles have similar shapes, but the higher values during the morning are displaced to 0900 UTC and the maximum values in afternoon are higher in relation to weekday. Fig. 3b also indicates weekday/weekend urban traffic profiles of Barcelona city. Weekend profiles have important traffic percentages during nighttime and first hours of early morning. On weekends, there is an average 60% reduction of heavy-duty traffic in the Northeastern Iberian Peninsula. Moreover, heavy-duty vehicles average 22% and 14% of traffic fleet

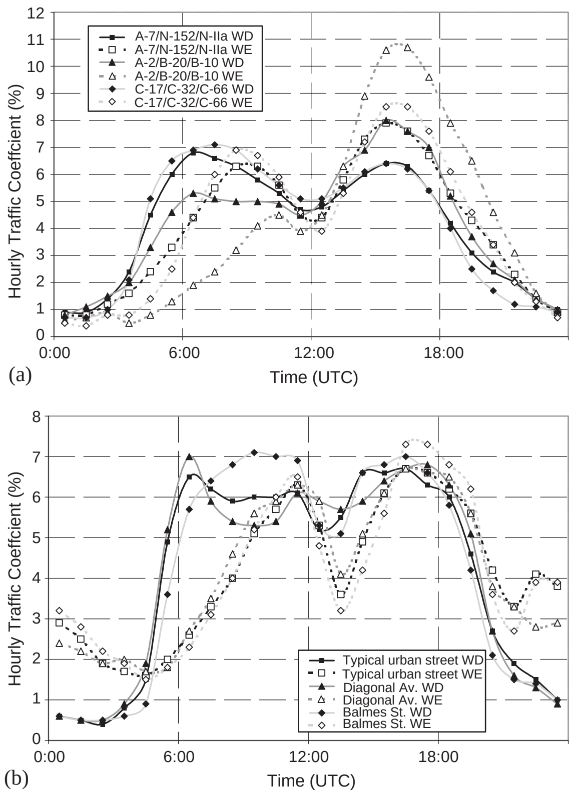

Fig. 3. Weekday/weekend traffic profiles for (a) main roadways in the Northeastern Iberian Peninsula; and (b) streets in the city of Barcelona (WD, weekdays, solid, black pointers; WE, weekends, dashed, white pointers).

on highways and roads, respectively. EMICAT2000 uses this and other information related with mileage distance traveled into the two vehicle park composition each one defined for weekday and weekend. The different behavior of gasoline and diesel-vehicles traffic is important in order to understand the contribution of fleet and mileage driven on ozone precursors emission. NO_x were emitted mainly by heavy-duty diesel vehicles (37%), gasoline passenger cars without catalyst (30%) and heavy-duty gasoline cars (20%). Therefore, the 60% reduction of heavy-duty vehicles on weekends has an important impact on NO_x levels. VOCs were emitted mainly by gasoline passenger cars without catalyst (38%), motorcycles (30%) and heavy-duty gasoline cars (14%), and therefore diesel vehicles are not important contributors to VOCs emissions and their reductions are not so important. Fig. 4 shows the structure of the emission of primary pollutants according to the type of vehicle for weekdays and weekends in August 2000. Heavy-duty gasoline vehicles and motorcycles contribute with low mileage driven percents (5% and 6%, respectively), but their emission factors are high, providing important contributions of primary pollutants (31% and 18%). Gasoline vehicles mean 71% of the fleet, but they emit 57% of NO_x and 92% of VOCs.

3.3. Evidence of the ozone weekend effect

An analysis of ozone weekday/weekend differences was prepared by averaging concentrations in the whole domain of the Northeastern Iberian Peninsula for 13–15 August (non-labor days) and 14–16 (weekdays). A significant weekend increase in ozone weekend concentrations is observed in urban areas of the domain (Barcelona and Tarragona, mainly), where 1-h peaks increase in over $30\,\mu g\,m^{-3}$ (Fig. 5a). In the case of Barcelona city, simulations yield differences over $50\,\mu g\,m^{-3}$ (increment of +66% on weekends). This value is supported by observations, where increments from $81\,\mu g\,m^{-3}$ (weekdays) until $125\,\mu g\,m^{-3}$ (weekends) are measured in air quality stations in the area (increment of +54% on weekends) (Table 2). This behavior is also stated for average daily values (Fig. 5b), where both simulations and observations provide growths around $14\,\mu g\,m^{-3}$ (+21%) for ozone weekend effect. On the other side, areas downwind the city of Barcelona exhibit the inverse trend in the weekend effect. O_3 reductions of about $20\,\mu g\,m^{-3}$ (−10%) on weekends are detected in peak-O_3 values in Vic for both measurement and simulations (Fig. 5 and Table 2); and this reduction is also observed for daily average levels, but this effect is less pronounced in simulations (≈6%). Rural-background air quality stations do not imply a significant weekend effect since pollutants in these areas are consequence of short-medium range transport.

Several factors likely contribute to the lower weekend O_3 in downwind areas, including the upwind shift in O_3 peaks caused by reduced NO_x inhibition, and reduced O_3 production in the downwind areas in response to lower anthropogenic emissions. These effects can also be described in terms of the upwind areas being VOC-sensitive and the downwind areas being NO_x-sensitive (Jiménez and Baldasano, 2004). Therefore, the response of predicted ozone concentrations to day-of-week differences highly depends on the location in very complex terrains.

Comparing the spatial patterns in modeled and observed weekday/weekend O_3 differences provides a

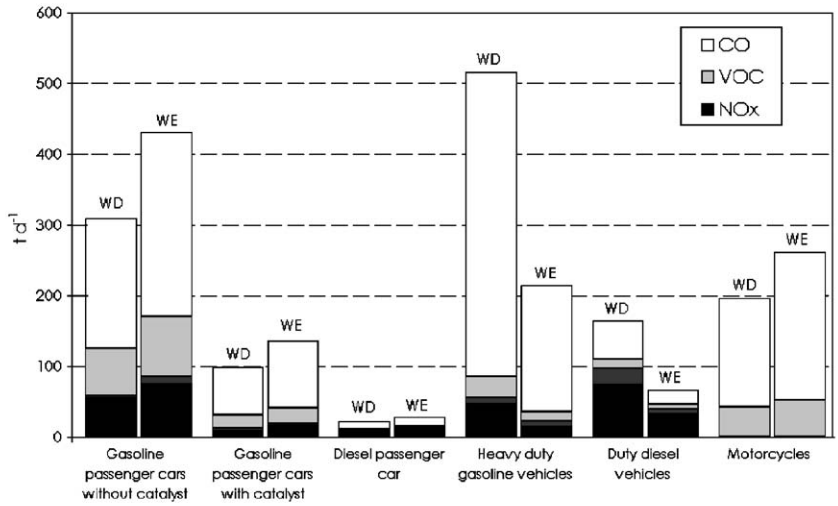

Fig. 4. Emission of primary pollutants according to the type of vehicle for weekdays (WD, left) and weekends (WE, right) in August 2000 for the area of the Northeastern Iberian Peninsula. The 60% reduction of heavy-duty vehicles on weekends has an important impact on NO_x level; VOCs emissions and their reductions are not as important and do not show a great weekday/weekend difference.

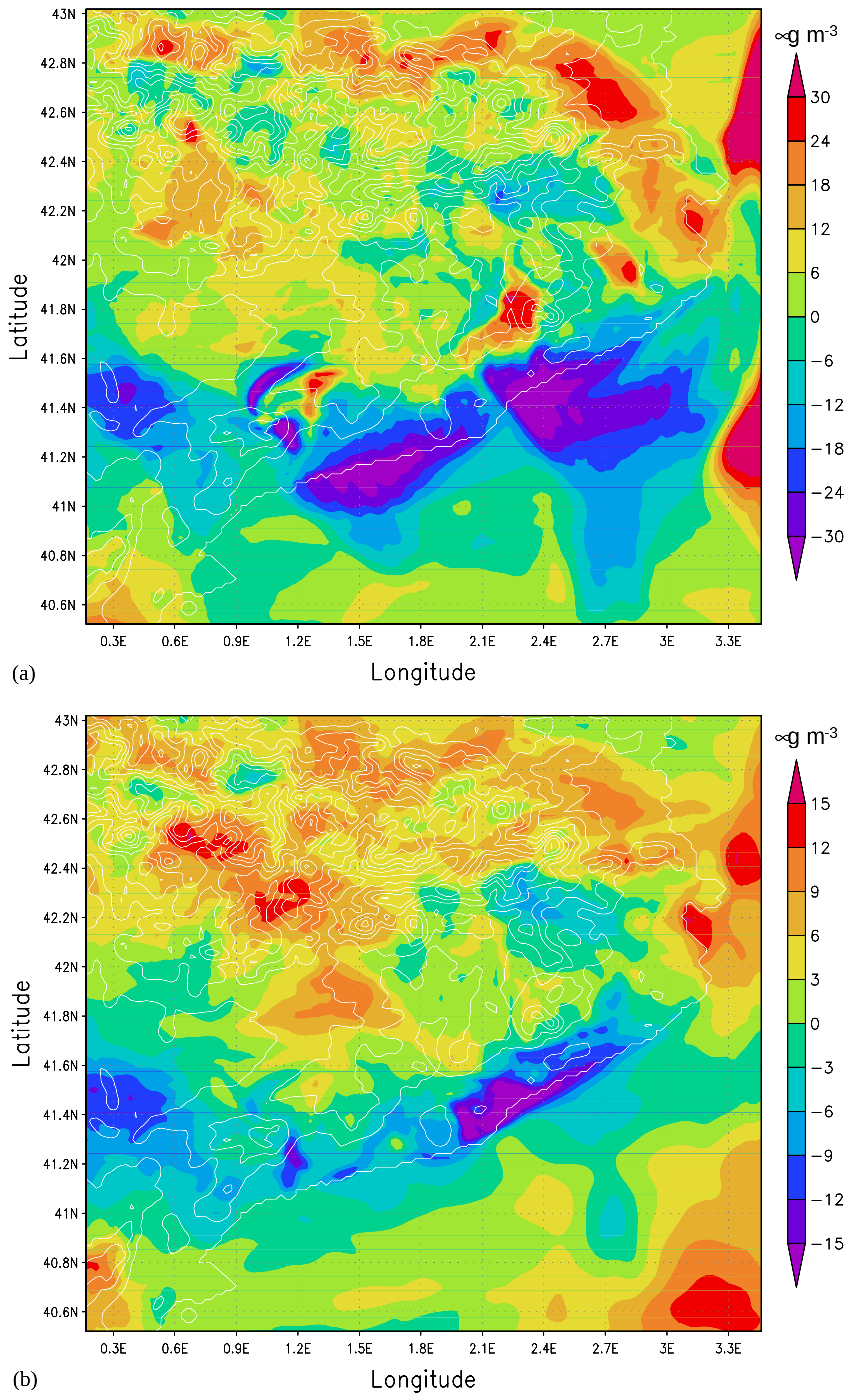

Fig. 5. Differences in weekday/weekend ozone ($\mu g\,m^{-3}$) for (a) 1-h daily maximum concentration; and (b) average daily values. Higher weekend values are observed in upwind areas (violet) whereas a reverse weekend effect is observed downwind (red).

useful test of the model system and weekend emission changes (Yarwood et al., 2003). Fig. 6 compares modeled and observed weekday/weekend O_3 differences at six sites spanning the Northeastern Iberian Peninsula from the city of Barcelona (upwind) to northeast (downwind) for the episode considered, both for maximum 1-h peaks and average day levels. The largest weekend/weekday differences for ambient data and

Table 2
Summary of measured and simulated values for ozone and its precursors in upwind and downwind areas of the domain for the episode of 13–16 August 2000. Percentual difference in maximum 1-h peaks and average values are also depicted

		Barcelona city (upwind)						Plana de Vic (downwind)					
		O_3 ($\mu g\,m^{-3}$)		NO_x ($\mu g\,m^{-3}$)		CO (ppb)		O_3 ($\mu g\,m^{-3}$)		NO_x ($\mu g\,m^{-3}$)		CO (ppb)	
		Measured	Simulated	Measured	Simulated	Measured	Simulated	Measured	Simulated	Measured	Simulated	Measured	Simulated
WD	Max	81	80	220	224	1350	1198	174	170	67	71	500	518
	Avg	45	50	89	97	485	584	81	84	35	43	237	354
WE	Max	125	133	149	87	950	726	156	149	43	49	300	495
	Avg	57	64	68	58	305	472	73	79	24	27	242	341
Difference	Max	+53.7%	+66.1%	−32.3%	−61.1%	−29.6%	−39.4%	−10.1%	−12.3%	−35.8%	−31.8%	−40.0%	−4.41%
	Avg	+21.8%	+21.4%	−23.0%	−40.7%	−37.1%	−19.1%	−11.7%	−6.2%	−32.8%	−38.5%	−2.0%	−3.9%

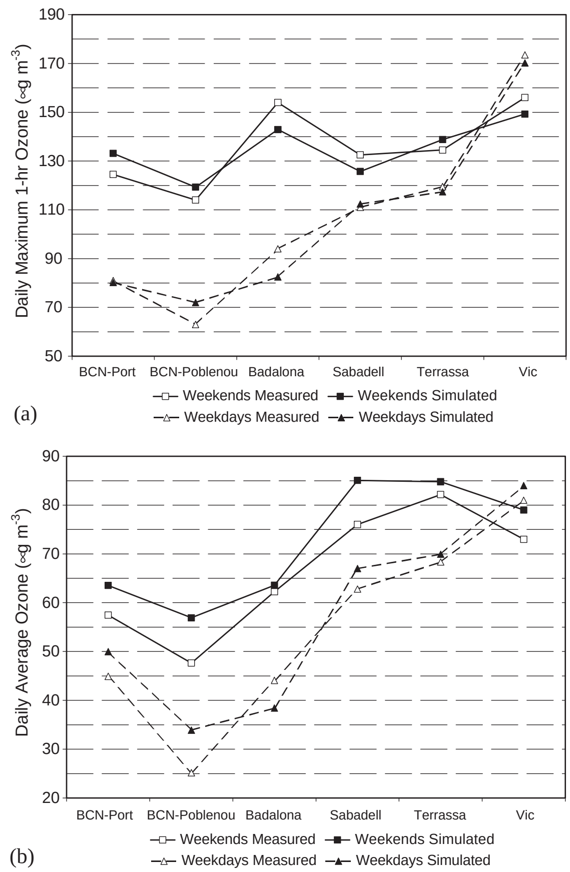

Fig. 6. Measured (white) and simulated (black) weekday (dashed line)/weekend (solid line) ozone ($\mu g\,m^{-3}$) at six sites spanning from upwind to downwind areas. The (a) daily maximum 1-h concentrations and (b) average concentrations show the decrease of ozone weekend effect in downwind areas departing from Barcelona city.

model results are found in the city of Barcelona and at the mid-basin (Badalona and Sabadell stations). Nevertheless, smallest O_3 increases are observed downwind, where the air mass has an elevated photochemical age and becomes NO_x-limited. In the case of Vic station, both average and peak levels indicate an inverse behavior to nearest downwind areas, being weekday levels more elevated than those corresponding to weekends.

3.4. Mass and timing of emissions

Reduction of heavy-duty traffic and hourly variations imply different profiles precursors O_3 emissions on weekend. On weekday NO_x, VOCs and CO emissions were 236, 172 and 898 t day^{-1}, respectively. On weekends, emissions were 184 t day^{-1} for NO_x, 179 t day^{-1} for VOCs and 780 t day^{-1} for CO (Table 3).

Table 3
Total emissions of ozone precursors for weekdays and weekends in the Northeastern Iberian Peninsula for August 2000 (t day^{-1})

	Weekday			Weekend		
	NO_x	VOC	CO	NO_x	VOC	CO
Vegetation	—	341.1	—	—	368.1	—
On-road traffic	235.7	171.7	897.6	183.8	179.3	780.3
Industrial activities	105.9	61.8	20.3	104	61.9	20.2
Fossil fuels[a]	5.3	0.3	1.7	5.3	0.3	1.7
Solvents[a]	—	48.5	—	—	48.5	—
Total	346.9	623.4	919.6	293.1	658.1	802.2

[a]Due to their use in the residential and commercial sectors.

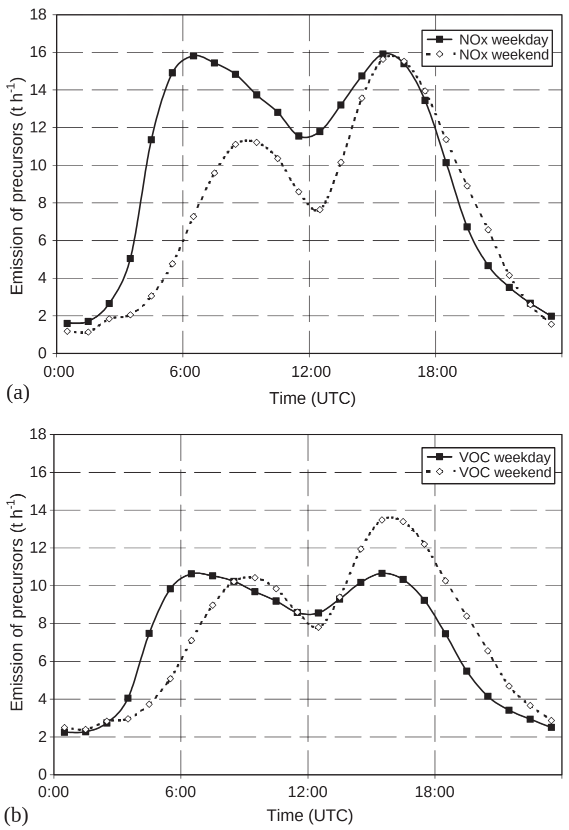

Fig. 7. Hourly emission of (a) NO_x and (b) VOCs (both in t h^{-1}) on weekday (solid, squares) and weekend (dashed, diamonds) of August in the Northeastern Iberian Peninsula. At weekday, NO_x peaks occur about 0700UTC and 1700UTC, but at weekend first peak is lower and displaced to the right (around 0900-1000UTC). For VOCs, similar timing as in the case of NO_x is observed, but first peaks have equivalent magnitudes and the later peak is higher on weekends.

At weekend, traffic from heavy-duty vehicles during all hours undergoes a substantial reduction (60% in average), and also variations of on-road traffic. They both imply differences in emission profiles. Total NO_x emission on weekends is 22% lower than weekdays. The evolution of ozone precursors emissions during weekday and weekend of August shows a bimodal profile for both NO_x and VOC (Fig. 7). At weekday, NO_x peaks occur about 0700UTC and 1700UTC, but at weekend first peak is lower and displaced to the right (around 0900–1000UTC). Therefore, the timing of NO_x emitted on weekends causes the midday emissions to produce O_3 more efficiently compared with the NO_x emitted on weekdays. NO_x-reduction, in combination with the NO_x-timing, contribute to the ozone weekend effect.

For VOCs, similar timing as in the case of NO_x is observed, but first peaks have equivalent magnitudes and the second peak on weekends is higher. Total VOCs emissions on weekends are slightly higher (4%) than weekdays. This strongly influences the NO_x/VOCs ratio, an indicator of the activity of the photochemical system. On weekdays, this ratio achieves 2.0–2.7, mainly in cells correspond to highways axis. Because influence of

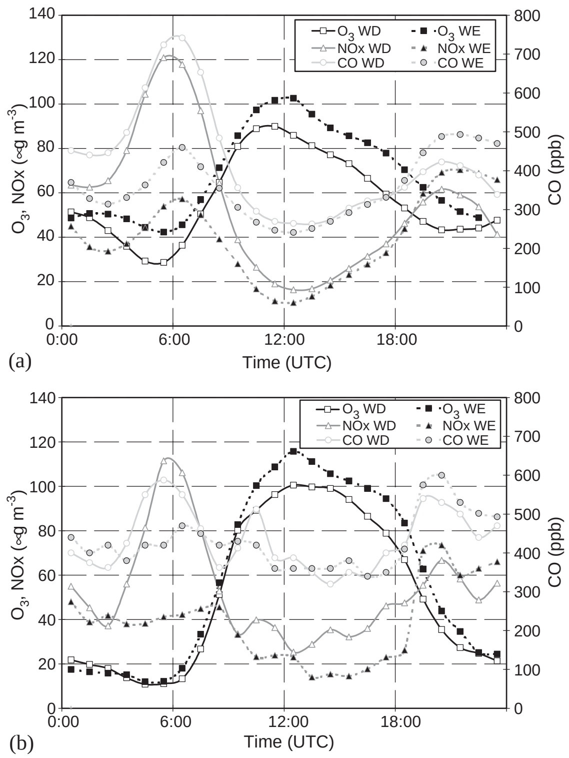

Fig. 8. Averaged hourly weekday (solid) and weekend (dashed) ozone (black, squares) and precursors (NO_x, triangles, dark gray; CO, circles, light gray) for the Northeastern Iberian Peninsula during the episode of 13–16 August 2000; (a) simulations; and (b) measurements.

circulation speed considered ($108\,km\,h^{-1}$) in EMICAT2000 model, high NO_x and low VOCs emissions are yielded. In addition, heavy-duty vehicle circulation in highways is higher on weekends, and therefore, higher NO_x emissions. In urban cells, NO_x/VOCs relation is lower. On weekends, lower NO_x emissions provide values for the considered ratio under 1.0. Values of

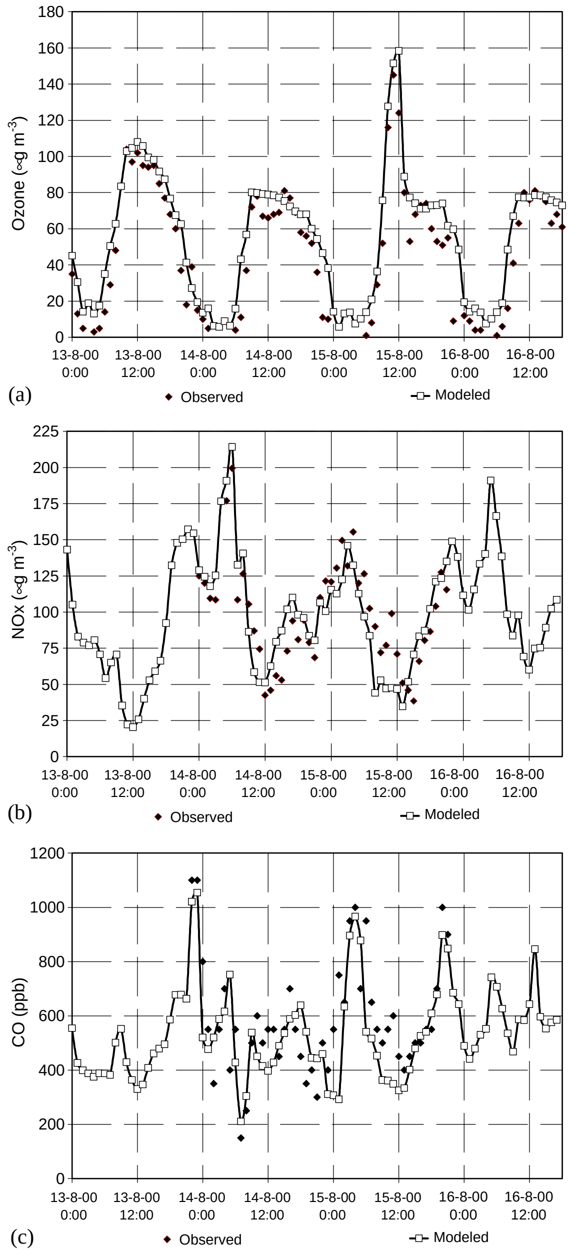

Fig. 9. Time series for (a) ozone; (b) NO_x and (c) CO both for observations (black diamonds) and simulations (solid line, white squares) in the area of Barcelona (upwind) for 13–16 August 2000.

NO_x/VOCs are 40% lower on weekends. The ratio NO_x/CO also plays an important role in tropospheric formation of ozone. This ratio varies from 0.27 on weekdays until 0.20 on weekends, making photochemistry more reactive. Furthermore, CO and PST reductions were 13% and 12%, respectively, on weekends. Emissions are mainly located on the Metropolitan Area of Barcelona and on the axis of highways following the coastline, precisely in front of the sea breeze.

The model simulations show that CO and NO_x ground-level concentrations on weekends are lower than on weekdays, as shown in (Fig. 8a) (–19% and –41%, respectively, for average values and –39% and –61% for 1-h peaks) but the higher proportional reduction of NO_x makes ozone-forming photochemistry more active on weekends compared to weekdays (lower NO_x/VOC ratios). These phenomena are also present in measured ambient concentrations of precursors (Fig. 8b). CO and NO_x are also significantly averagely reduced in a −37% and −23%, respectively (Table 2). The cause of this phenomenon is that reductions in traffic on weekends, according to the emission model, imply higher NO_x-than VOC-reductions. This important NO_x reductions in areas that are VOC-limited, as the city of Barcelona (Jiménez and Baldasano, 2004), increase O_3 formation on weekends (Fig. 9). Nevertheless, nighttime precursors concentrations are higher on weekends than on weekdays, and this phenomenon might contribute to the carryover effect, that will be analyzed later. This reduction of precursors is also observed downwind the emitting sources, as Vic. Nevertheless, if we take into account modeling results, ambient NO_x decreases on weekends are important in downwind areas (over −30% for peak and average values), but the influence of VOCs (represented by CO) is not as important (reductions of −4% for simulated maximum and average levels). Therefore, Vic constitutes an NO_x-limited domain whose O_3 weekend effect (exhibiting weekday values 10% over weekend levels) comes conditioned by the reduction of NO_x emissions in the area on weekends during this episode of photochemical pollution (Fig. 10).

3.5. *Ozone quenching*

Emissions of O_3 precursors are greater during the morning on weekdays than on weekends, as stated before. The higher values of NO in NO_x emissions destroys (quenches) more of the available ground-level ozone in pervasive emission areas as cities, according to the titration reaction in which NO and O_3 combines to produce NO_2 and oxygen ($NO+O_3 \rightarrow NO_2+O_2$). Thus, ozone is suppressed more and its formation is retarded more on weekdays compared to weekends, contributing to the weekend effect. Moreover, the NO_2 formed from the O_3 titration removes radicals by the reaction $NO_2+OH \rightarrow HNO_3$. If NO_x emissions are reduced, as

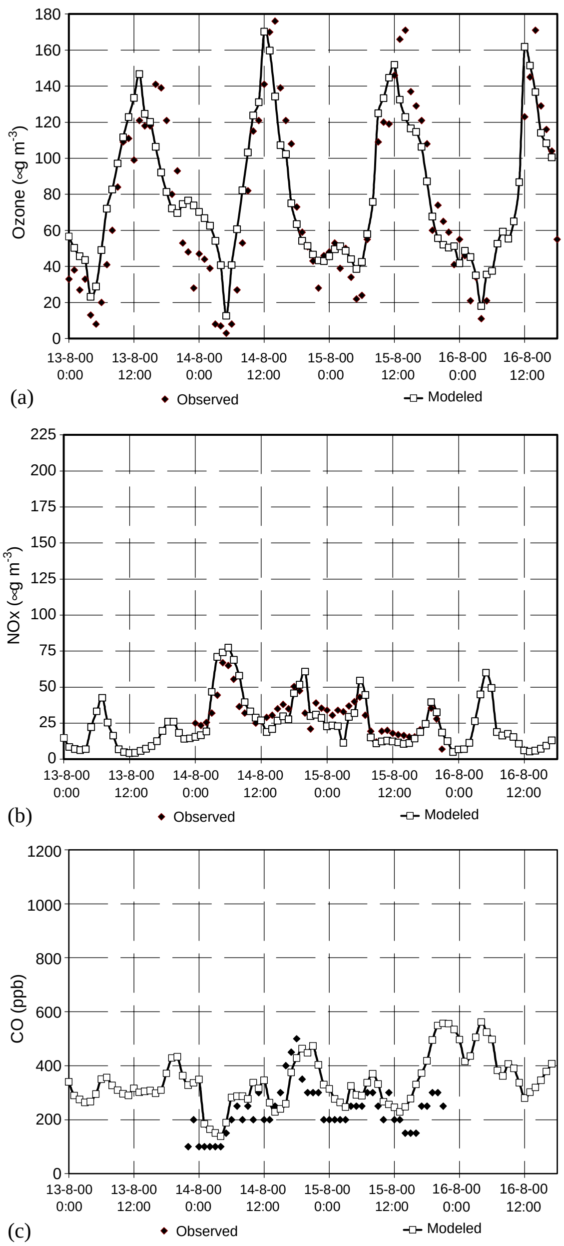

Fig. 10. Time series for (a) ozone; (b) NO_x and (c) CO both for observations (black diamonds) and simulations (solid line, white squares) in the area of Vic (downwind) for 13–16 August 2000.

occurs on weekends, the NO_2 concentration is lower, the radical concentration is higher and formation of new O_3 proceeds faster. As stated by Heuss et al. (2003), ozone at steady state depends on the rate of NO_2 photolysis and the ratio NO_2 to NO. In the absence of other processes that convert NO to NO_2, the photolysis of NO_2 is balanced by the aforementioned reaction of NO with O_3. When VOCs are present, they participate in chain-carrying reactions that convert NO to NO_2 without using up an O_3 molecule (Atkinson, 2000). Thus, the amount and kind of hydrocarbons determine the ratio of NO_2 to NO.

Measured and simulated ground-level precursors (Table 2), indicate ambient levels of NO_x are substantially lower on weekends morning than on weekdays (around −40% both in upwind and downwind areas for average NO_x levels) and smaller reductions of VOCs levels at weekends (reductions of only −4% for average simulated CO levels and −2% for measured CO), and therefore the potential for ozone quenching importantly decreases since NO_x/VOC ratios are lower on weekends. The higher proportional presence of VOCs oxidizes NO to NO_2 and thus NO does not contribute to the ozone titration reaction. The ratio NO_x on weekends to NO_x on weekdays is low for corresponding daylight hours, particularly during the hours where ozone is likely to reaches its maximum levels. Furthermore, in the study case, both ambient data and simulation depict that the NO_2/NO relationship is higher for almost all daylight hours on weekends compared to weekdays in all upwind locations, so the amount of NO available for quenching ozone near the surface is smaller on weekends than on week days.

3.6. Carryover contribution to the weekend effect

Increased VOC and NO_x emissions from traffic on weekend nights may carry over near ground level and lead to greater O_3 formation after sunrise on the following day (surface carryover). In addition, the reservoir of pollutants that carries over above the nocturnal boundary layer may exert a greater influence

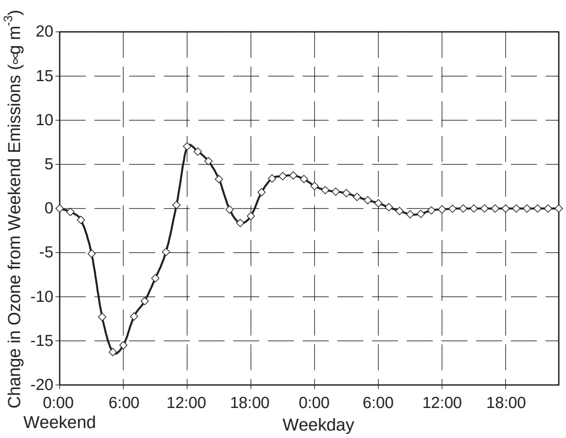

Fig. 11. Analysis of carryover impact from weekends to weekdays by changing weekend/weekday emissions. Differences measured in ground-level O_3 return to values under $2\,\mu g\,m^{-3}$ around 0200UTC of the following day due to pervasive early morning emissions.

on surface O_3 concentrations on weekends than on weekdays. Morning concentrations of NO_x titrate O_3 and quench radicals. However, the higher weekday concentrations of NO_x do more to reduce O_3 and radicals so that they have little effect on surface concentrations. On weekends, according to this hypothesis, carryover O_3 and radicals are not quenched as much and thereby cause higher surface O_3 concentrations (Heuss et al., 2003).

The importance of carryover because spatial/temporal source–receptor relationships was investigated by changing weekend emissions into weekday emissions for the whole period of study. Fig. 11 shows the change in O_3 relative to the base case (considering both weekend and weekday specific emissions) for the Northeastern Iberian Peninsula. As derived from simulations, pollutant carryover is a negligible factor because differences in precursor concentrations during the carryover period have only a small effect on precursor concentrations and ratios during the O_3 accumulation period. Results show that changing weekend emissions by weekday emissions leads to important decreases of O_3 on weekends nights and early morning due to higher titration of O_3 since of higher weekday emissions. Higher O_3 concentrations are depicted and noon in the case of considering weekend–weekday profiles instead of not considering weekend–weekday differences, since mass and timing of emissions have been changed. However, no differences are observed in the labor-days, and that implies that increases the O_3 effects are dominated by the same-day emission changes. Although total emissions of precursors on weekends nights are greater than total traffic on other nights, the small differences in ground-level O_3 levels measured overnight returned to values under $2\,\mu g\,m^{-3}$ around 0200 UTC. The additional nighttime emissions appear to be much lower than the additional fresh emissions from traffic that occurs in the morning. Therefore, ozone precursors that carryover does not appear to be a significant cause in the study case for Northeastern Iberian Peninsula ozone weekend effect.

4. Conclusions

Day-of-week emission inventories are needed to support air quality models that simulate the ozone weekend effect. Dynamic simulations should be used to compare and contrast the effects of periodic emission reductions on weekends to the effects of hypothetical strategic emission reductions. A day-specific hourly emissions inventory considering day-to-week variations in emissions is used for stationary, area and on-road sources has been developed in the framework of EMICAT2000 emission model. This emission model has been coupled with MM5-CMAQ to conduct a study of the weekend effect of ozone and its precursors with very high spatial resolution, as derived from the necessity of assessing the weekend effect of ozone and other pollutants observed with air quality stations in a complex terrain as the Northeastern Peninsula.

A significant weekend increase in ozone weekend concentrations is simulated in coastal urban areas of the domain where 1-h peaks increase in a +66% on weekends. This behavior is also stated by observations, since increments of +54% on weekends in ambient ozone are measured in air quality stations. This behavior is also stated for average daily values, where both simulations and observations provide growths around +21% for ozone weekend effect. On the other side, areas downwind the Barcelona Geographical Area reduce or even reverse the weekend effect, with O_3 reductions of about −10% on weekends at Vic. Rural-background air quality stations do not imply a significant weekend effect since pollution in these areas are consequence of short-medium range transport. Several factors likely contribute to the lower weekend O_3 in downwind areas, including the upwind shift in O_3 peaks caused by reduced NO_x inhibition, and reduced O_3 production in the downwind areas in response to lower anthropogenic emissions. These effects can also be described in terms of the upwind areas being VOC-sensitive and the downwind areas being NO_x-sensitive.

Respect to the behavior in the emission of precursors, reduction of heavy-duty traffic and hourly variations imply different profiles precursors O_3 emissions on weekends. On weekends, traffic from heavy-duty vehicles undergoes a substantial reduction. Total NO_x emission on weekends are 22% lower than weekdays, but total VOCs emissions on weekends are slightly higher (4%) than weekdays. Also, CO and PST reductions in emissions are 13% and 12%, respectively, on weekends. The shift of 1–2 h in peaks of precursors emissions at weekends causes the midday emissions to produce O_3 more efficiently compared with the NO_x emitted on weekdays. Model simulations and air quality stations measurements for precursors depict that CO and NO_x ground-level concentrations on weekends are lower than those corresponding to weekdays. The higher proportional reduction of NO_x makes ozone-forming photochemistry more active on weekends compared to weekdays (lower NO_x/VOC ratios).

Emissions of NO are greater during the morning on weekdays than on weekends, highly contributing to the ozone quenching effect. The potential for ozone quenching importantly decreases on weekends since NO_x/VOC ratios are lower (−40% on weekends). The higher proportional presence of VOCs on weekends oxidizes NO to NO_2 and thus NO does not contribute to the ozone titration reaction. The NO_2/NO relationship is found higher for almost all daylight hours on weekends compared to weekdays in all upwind locations, so the amount of NO available for quenching ozone near the surface is smaller on weekends than on weekdays.

The importance of carryover because of spatial/temporal source–receptor relationships has been analyzed, finding out that pollutant carryover is a negligible factor because differences in precursor concentrations during the carryover period would have only a small effect on precursor concentrations and ratios during the O_3 accumulation period. The small differences in ground-level O_3 levels measured overnight returned to values under $2\,\mu g\,m^{-3}$ around 0200 UTC. The additional nighttime emissions have a weaker influence of ozone than the pervasive additional fresh emissions from traffic that occurs in the morning, thus the weekend is primarily a same-day phenomenon for the study case.

An evaluation of the performance of the model has also been considered by comparing results with air quality stations data. The MM5-EMICAT2000-CMAQ modeling system with the CBM-IV performed very well in simulating the O_3 levels observed during the 13–16 August 2000, episode; it is noteworthy that simulations meet all the criteria established by US EPA and the European Directive 2002/3/EC for model evaluations. The fact that, moreover, this modeling system performed well in describing the weekday/weekend differences in ozone levels, which helps supporting the use of this air quality model for future scientific and air quality planning applications in very complex terrains, since this approach provides a novel contribution to the analysis of the weekend effect in Western Mediterranean Basin. Nonetheless, further additional studios under different meteorological conditions and emission scenarios are needed to more accurately account for weekend changes.

Acknowledgements

This work was developed under the research contract REN2003-09753-C02 of the Spanish Ministry of Science and Technology. The Spanish Ministry of Education and Science is also thanked for the FPU doctoral fellowship hold by P. Jiménez. The authors gratefully acknowledge O. Jorba for providing meteorological inputs and E. López for the implementation of EMICAT2000 into a GIS system. Air quality stations data and information for implementing industrial emissions were provided by the Environmental Department of the Catalonia Government (Spain).

References

Altshuler, S.L., Arcado, T.D., Lawson, D.R., 1995. Weekday vs. weekend ambient ozone concentrations: discussion and hypotheses with focus on Northern California. Journal of the Air and Waste Management Association 45, 967–972.

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NO_x. Atmospheric Environment 34, 2063–2101.

Baldasano, J.M., Cremades, L., Soriano, C., 1994. Circulation of air pollutants over the Barcelona geographical area in summer. In: Proceedings of the 6th European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants, Varese (Italy). Report EUR 15609/1 EN: 474–479.

Barros, N., Toll, I., Soriano, C., Jiménez, P., Borrego, C., Baldasano, J.M., 2003. Urban photochemical pollution in the Iberian Peninsula: the Lisbon and Barcelona Airsheds. Journal of the Air and Waste Management Association 53, 347–359.

Berge, E., Huang, H-C., Chang, J., Liu, T.-H., 2001. A study of the importance of initial conditions for photochemical oxidant modeling. Journal of Geophysical Research 106, 1347–1363.

Blanchard, C.L., Fairley, D., 2001. Spatial mapping of VOC and NO_x-limitation of ozone formation in central California. Atmospheric Environment 35, 3861–3873.

Blanchard, C.L., Tanenbaum, S.J., 2003. Differences between weekday and weekend air pollutant levels in Southern California. Journal of the Air and Waste Management Association 53, 816–828.

Blier, W., Winer, A.M., 1999. Analysis of weekday/weekend differences in ambient air quality and meteorology in the South Coast air basin. Final Report No. 95-334. California Air Resources Board, Sacramento, CA, June.

Brönnimann, S., Neu, U., 1997. Weekend-weekday differences of near-surface ozone concentrations in Switzerland for different meteorological conditions. Atmospheric Environment 31, 1127–1135.

Byun, D.W., Ching, J.K.S. (Eds.), 1999. Science algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. EPA Report N. EPA-600/R-99/030, Office of Research and Development. US Environmental Protection Agency, Washington, DC.

CARB, 2003. The ozone weekend effect in California. Staff Report, The Planning and Technical Support Division, The Research Division, California Air Resources Board, Sacramento, CA, 30 May.

Chinkin, L.R., Coe, D.L., Funk, T.H., Hafner, H.R., Roberts, P.T., Ryan, P.A., Lawson, D.R., 2003. Weekday versus weekend activity patterns for ozone precursor emissions in California's South Coast Air Basin. Journal of the Air and Waste Management Association 53, 829–843.

Cleveland, W.S., Graedel, T.E., Kleiner, B., Warner, J.L., 1974. Sunday and workday variations in photochemical air pollutants in New Jersey and New York. Science 186, 1037–1038.

Fujita, E.M., Stockwell, W.R., Campbell, D.E., Keislar, R.E., Lawson, D.R., 2003a. Evolution of the magnitude and spatial extent of the weekend ozone effect in California's South Coast Air Basin, 1981–2000. Journal of the Air and Waste Management Association 53, 802–815.

Fujita, E.M., Campbell, D.E., Zielinska, B., Sagebiel, J.C., Bowen, J.L., Goliff, E.S., Stockwell, W.R., Lawson, D.R., 2003b. Diurnal and weekday variations in the source contributions of ozone precursors in California's South Coast Air Basin. Journal of the Air and Waste Management Association 53, 844–863.

Gery, M.W., Whitten, G.Z., Killus, J.P., Dodge, M.C., 1989. A photochemical kinetics mechanism for urban and regional scale computer modeling. Journal of Geophysical Research 94 (D10), 12,925–12,956.

Heuss, J.M., Kahlbaum, D.F., Wolff, G.T., 2003. Weekday/weekend ozone differences: what can we learn from them? Journal of the Air and Waste Management Association 53, 772–788.

Hogrefe, C., Rao, S.T., Kasibhatla, P., Hao, W., Sistla, G., Mathur, R., McHenry, J., 2001. Evaluating the performance of regional-scale photochemical modeling systems: Part II–ozone predictions. Atmospheric Environment 35, 4175–4188.

Huang, H.-C., Chang, J.S., 2001. On the performance of numerical solvers for a chemistry submodel in three-dimensional air quality models. Journal of Geophysical Research 106, 20,175–20,188.

Jenkin, M.E., Davies, T.J., Stedman, J.R., 2002. The origin and day-of-week dependence of photochemical ozone episodes in the UK. Atmospheric Envrionment 36, 999–1012.

Jiménez, P., Baldasano, J.M., 2004. Ozone response to precursor controls: the use of photochemical indicators to assess O_3–NO_x–VOC sensitivity in the Northeastern Iberian Peninsula. Journal of Geophysical Research 109, D20309.

Jiménez, P., Jorba, O., Baldasano, J.M., 2004. Influence of horizontal model grid resolution on tropospheric ozone levels. In: Suppan, P. (Ed.), Harmonisation 2004, Ninth International Conference on Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes, vol. 2. Garmish-Partenkircher, Germany, pp. 219–223.

Jorba, O., Pérez, C., Rocadenbosch, F., Baldasano, J.M., 2004. Cluster analysis of 4-day back trajectories arriving in the Barcelona Area (Spain) from 1997 to 2002. Journal of Applied Meteorology 43 (6), 887–901.

Kang, D., Eder, B.K., Schere, K.L., 2003. The evaluation of regional-scale air quality models as part of NOAA's air quality forecasting pilot program. In: 26th Nato International Technical Meeting on Air Pollution Modeling and its Application, Istanbul, Turkey, pp. 404–411.

Knipping, E.M., Dabdub, D., 2002. Modeling surface-mediated renoxification of the atmosphere via reaction of gaseous nitric oxide with deposited nitric acid. Atmospheric Environment 36, 5741–5748.

Lebron, F., 1975. A comparison of weekend-weekday ozone and hydrocarbon concentrations in the Baltimore–Washington metropolitan area. Atmospheric Environment 9, 861–863.

Marr, L.C., Harley, R.A., 2002a. Spectral analysis of weekday-weekend differences in ambient ozone, nitrogen oxide, and non-methane hydrocarbon time series in California. Atmospheric Environment 36, 2327–2335.

Marr, L.C., Harley, R.A., 2002b. Modeling the effect of weekday-weekend differences in motor vehicle emissions of photochemical air pollution in central California. Environmental Science and Technology 36, 4099–4106.

Millán, M., Salvador, R., Mantilla, E., Kallos, G., 1997. Photooxidant dynamics in the Mediterranean basin in summer: results from European research projects. Journal of Geophysical Research 102, 8811–8823.

MMMD/NCAR, 2001. PSU/NCAR Mesoscale Modeling System Tutorial Class Notes and User's Guide: MM5 Modeling System Version 3.

Ntziachristos, L., Samaras, Z., 2000. COPERTIII Computer programme to calculate emissions from road transport. Methodology and emission factors (Version 2.1), European Environment Agency, Technical Report No. 49.

Parra, R., 2004. Development of the EMICAT2000 model for the estimation of air pollutants emissions in Catalonia and its use in photochemical dispersion models. Ph.D. Thesis (in Spanish), Polytechnic University of Catalonia (Spain) available at: http://www.tdx.cesca.es/TDX-0803104-102139.

Parra, R., Baldasano, J.M., 2004. Modeling the on-road traffic emissions from Catalonia (Spain) for photochemical air pollution research. Weekday—weekend differences. In: 12th International Conference on Air Pollution (AP'2004), Rhodes (Greece).

Parra, R., Gassó, S., Baldasano, J.M., 2004. Estimating the biogenic emissions of non-methane volatile organic compounds from the North western Mediterranean vegetation of Catalonia, Spain. The Science of the Total Environment 329, 241–259.

Pérez, C., Sicard, M., Jorba, O., Comerón, A., Baldasano, J.M., 2004. Summertime re-circulations of air pollutants over the North-eastern Iberian coast observed from systematic EARLINET lidar measurements in Barcelona. Atmospheric Environment 38, 3983–4000.

Pun, B.K., Seigneur, C., White, W., 2003. Day-of-week behavior of atmospheric ozone in three US cities. Journal of the Air and Waste Management Association 53, 789–801.

Qin, Y., Tonnesen, G.S., Wang, Z., 2004a. One-hour and eight-hour average ozone in the California South Coast Air Basin: trends in peaks values and sensitivity to precursors. Atmospheric Environment 38, 2197–2207.

Qin, Y., Tonnesen, G.S., Wang, Z., 2004b. Weekend/weekday differences of ozone, NO_x, Co, VOCs, PM_{10} and the light scatter during ozone season in southern California. Atmospheric Environment 38, 3069–3087.

Sillman, S., 1999. The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. Atmospheric Environment 33, 1821–1845.

Tanaka, P.L., Reimer, D.D., Chang, S., Yarwood, G., McDonald-Butler, E.C., Apel, E.C., Orlando, J.J., Silva, P.J., Jiménez, J.L., Canagaratna, M.R., Neece, J.D., Mullins, C.B., Allen, D.T., 2003. Direct evidence for chlorine-enhanced urban ozone formation in Houston, Texas. Atmospheric Environment 37, 1393–1400.

US EPA, 1991. Guideline for Regulatory Application of the Urban Airshed Model. US EPA Report No. EPA-450/4-91-013, Office of Air and Radiation, Office of Air Quality Planning and Standards, Technical Support Division, Research Triangle Park, North Carolina, US.

Yarwood, G., Stoeckenius, T.E., Dunker, A.M., 2003. Modeling weekday/weekend ozone differences in the Los Angeles region for 1997. Journal of the Air and Waste Management Association 53, 864–875.