9 *Modeling the Ozone Weekend Effect in Very Complex Terrains: a Case Study in the Northeastern Iberian Peninsula*

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9.1 Introduction

Tropospheric ozone results from 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 U.S. and Europe (Altshuler *et al.*, 1995; Bronnimann 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 is 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 hypotheses have been set for this area (CARB, 2003):

(1) *NO_x reduction*. Marr and Harley (2002a) analyzed the day-of-week behavior of O_3, NO_x and VOCs 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 nonmethane 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% and 14% lower than those of weekdays.

(2) *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.

(3) *Carryover near the ground* and (4) *carryover aloft.* Increased VOCs and NO_x emissions from traffic on weekend's 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).

(5) *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.

(6) *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 determining the causes of the ozone weekend effect. These inventories must reveal in sufficient detail the quantity, the timing, and the location of VOCs 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.

9.2 Methods

The weekend effect reported here corresponds to the pollution event in the Western Mediterranean Basin from that took place on 13-16 August, 2000 (see further description in Section 2.1). Two non-labor days (13 August and 15 August, 2000) and two working days (14 August and 16 August, 2000) are considered in order simulate with MM5-EMICAT2000-CMAQ the O_3 weekend effect in the domain of the northeastern Iberian Peninsula and for its assessment.

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 VOCs (Yarwood *et al.*, 2003) because of the unavailability of VOCs measurements in the area.

Those data were also utilized to indicate the performance of models results. 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 during daytime. In addition, the US Environmental Protection Agency guidelines (US EPA, 1991) indicated in Chapter 5 were considered in this work: 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 upon a 120 $\mu g\ m^{-3}$ threshold.

9.3 Results and Discussion

9.3.1 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. A cut-off value of 120 $\mu g\ m^{-3}$ is used to exclude observation-predictions pairs (Hogrefe *et al.*, 2001). Table 9.1 collects the results of both the discrete and categorical statistical analysis.

Table 9.1. Statistics of model performance for 1-hr O_3 during the episode of 13-16 August , 2000.

	EPA Goal	August 13, 2000	August 14, 2000	August 15, 2000	August 16, 2000
			Discrete evaluation		
Observed peak ($\mu g\ m^{-3}$)		157	177	189	171
Modeled peak ($\mu g\ m^{-3}$)		189	170	167	180
UPA (%)	<±20	14.4	-3.8	-11.7	5.2
MNBE (%)	<±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

The model results achieve the US 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, 2000. That suggests a slight tendency towards underprediction; however, US EPA goals of ±15% are met. 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, 2000 until 16 August, 2000 (16.8% to 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-hr averages during daytime) 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 can be greatly influenced by the overwhelming number of non-exceedances, to circumvent this inflation the critical success index and the probability of detection are 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).

9.3.2 Weekday/Weekend Emissions within EMICAT2000

Existing gridded inventories used as inputs to air quality models typically assume weekday patterns and lack of accurate estimates of emissions on weekends (Marr and Harley, 2002b). We used EMICAT2000 inventory emission model (Parra, 2004), which 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 for 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. Figure 9.1 shows some samples of hourly traffic profiles both for weekdays and weekends for highways and roads stretches in the northeastern Iberian Peninsula.

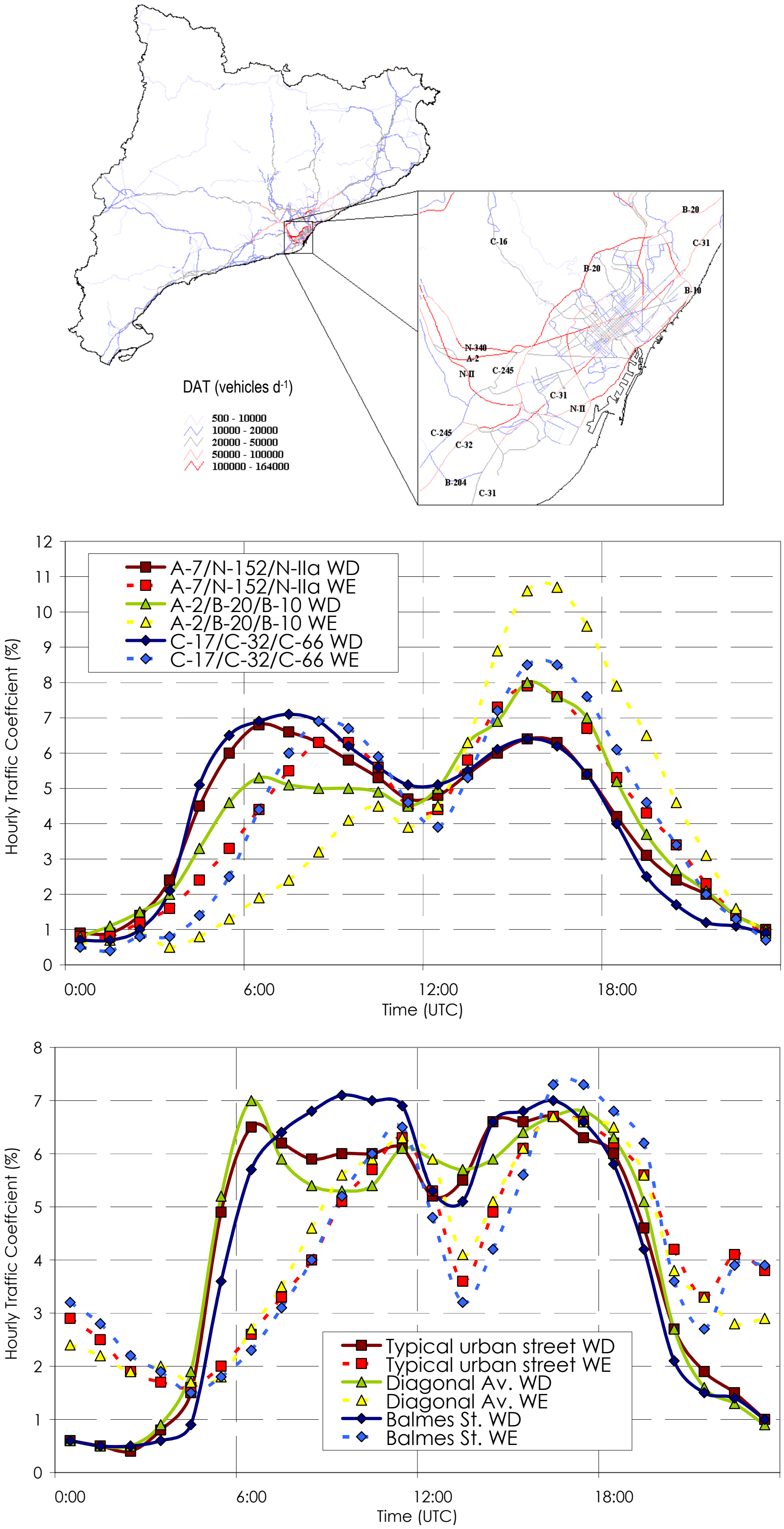


Figure 9.1. Map of roadways (up) in the northeastern Iberian Peninsula; weekday/weekend traffic profiles for (center) main roadways; and (down) streets in Barcelona (weekdays, solid, weekends, dashed).

Weekday profiles have higher percents about 0700UTC and 1700UTC. There are drops at midday and the lower percentages are present during night time and first hours of early morning. Weekend profiles have similar shapes, but the higher values during the morning are displaced to 0900UTC and the maximum values in afternoon are higher in relation to weekday. Figure 9.1 also indicates weekday/weekend urban traffic profiles of Barcelona city. Weekend profiles have important traffic percentages during night time 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 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.

Figure 9.2 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.

9.3.3 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, 2000 (non-labor days) and 14-16 August, 2000 (weekdays). A significant weekend increase in ozone weekend concentrations is observed in urban areas of the domain (Barcelona and Tarragona, mainly), where 1-hr peaks increase in over 30 $\mu g\ m^{-3}$ (Figure 9.3a). 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 9.2).

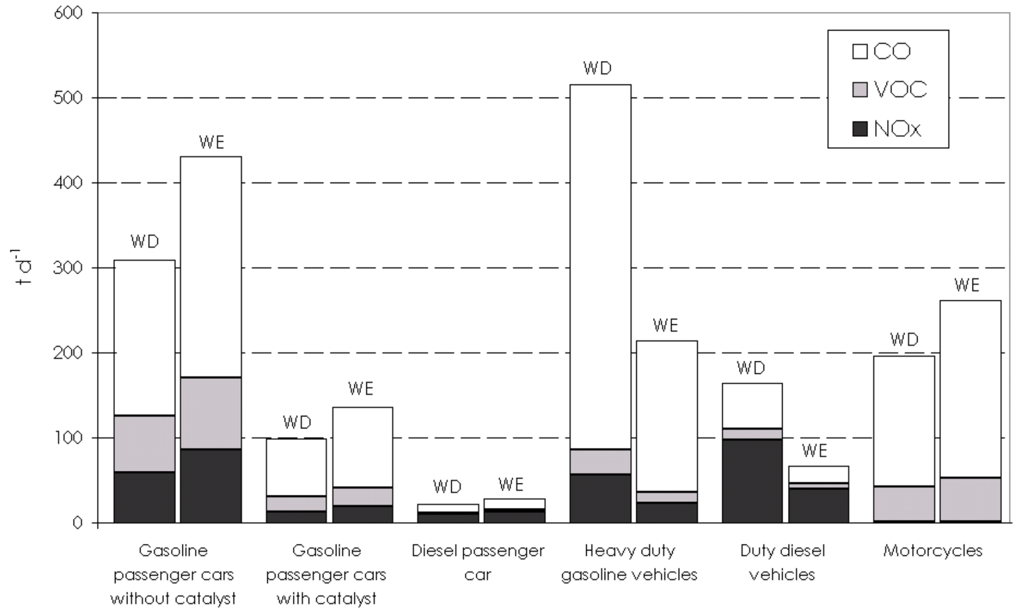


Figure 9.2. Emission of primary pollutants according to the type of vehicle for weekdays (WD, left) and weekends (WE, right) in August, 2000 for the area of the northeastern Iberian Peninsula. The 60% reduction of heavy-duty gasoline vehicles on weekends has an important impact on NO_x level; VOCs emissions and their reductions do not show a great weekday/weekend difference.

This behavior is also stated for average daily values (Figure 9.3b), where both simulations and observations provide growths around 14 μg 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 μg m^{-3} (-10%) on weekends are detected in peak-O_3 values in Vic for both measurement and simulations (Figure 9.3 and Table 9.2); and this reduction is also observed for daily-average levels, but this effect is less pronounced in simulations (~6%). Rural-background air quality stations don't 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 useful test of the model system and weekend emission changes (Yarwood *et al.*, 2003). Figure 9.4 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-hr peaks and average day levels.

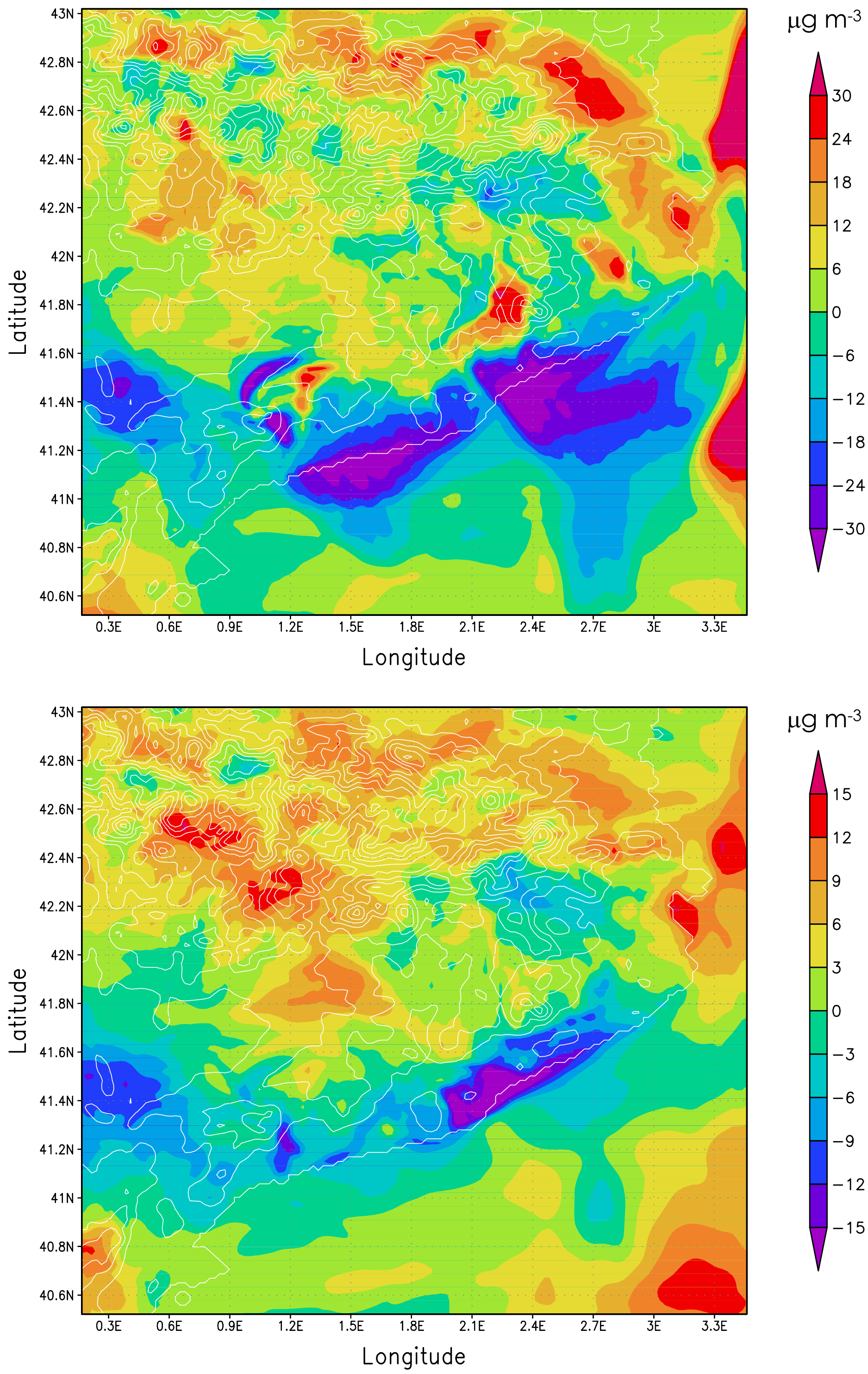


Figure 9.3. Differences in weekday / weekday ozone (μg m^{-3}) for (up) 1-hr daily maximum concentration; and (down) average daily values. Higher weekend values are observed in upwind areas (blue-violet) whereas a reverse weekend effect is observed downwind (red).

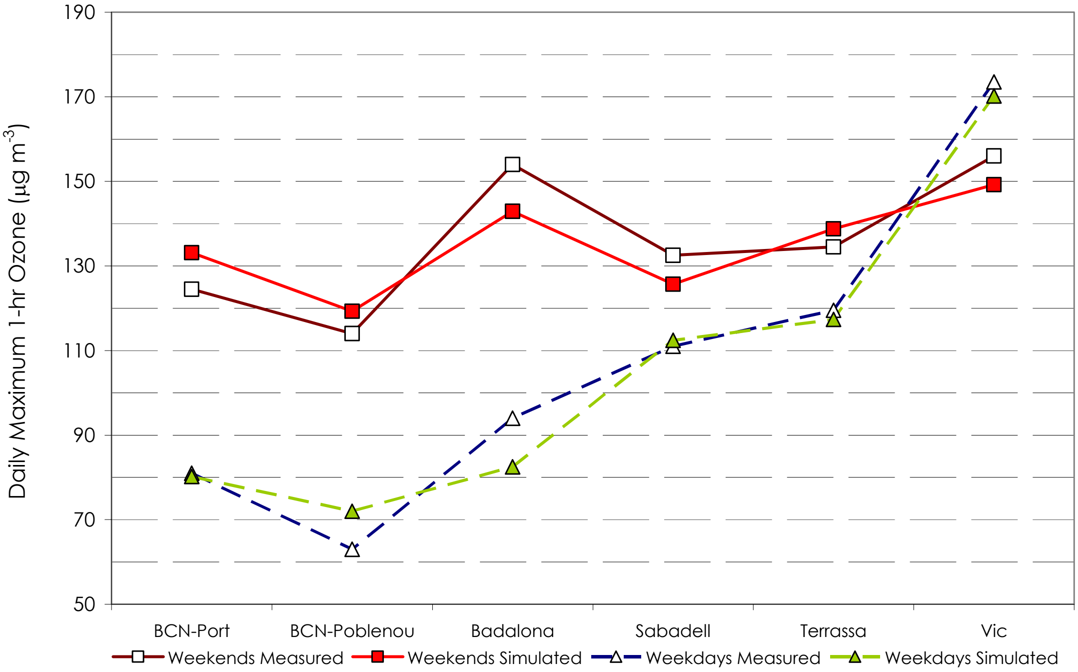
Table 9.2. Summary of measured and simulated values for ozone and its precursors in upwind and downwind areas of the domain for the episode of August 13-16, 2000. Percentual difference in maximum 1-hr peaks and average values are also depicted.

		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%

Table 9.3. Total emissions of ozone precursors for weekdays and weekends in the northeastern Iberian Peninsula for August 2000 ($t\ d^{-1}$).

	Weekday			Weekend		
	NO_x	VOCs	CO	NO_x	VOCs	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*	5.3	0.3	1.7	5.3	0.3	1.7
Solvents*	-	48.5	-	-	48.5	-
Total:	346.9	623.4	919.6	293.1	658.1	802.2

* Due to their use in the residential and commercial sectors



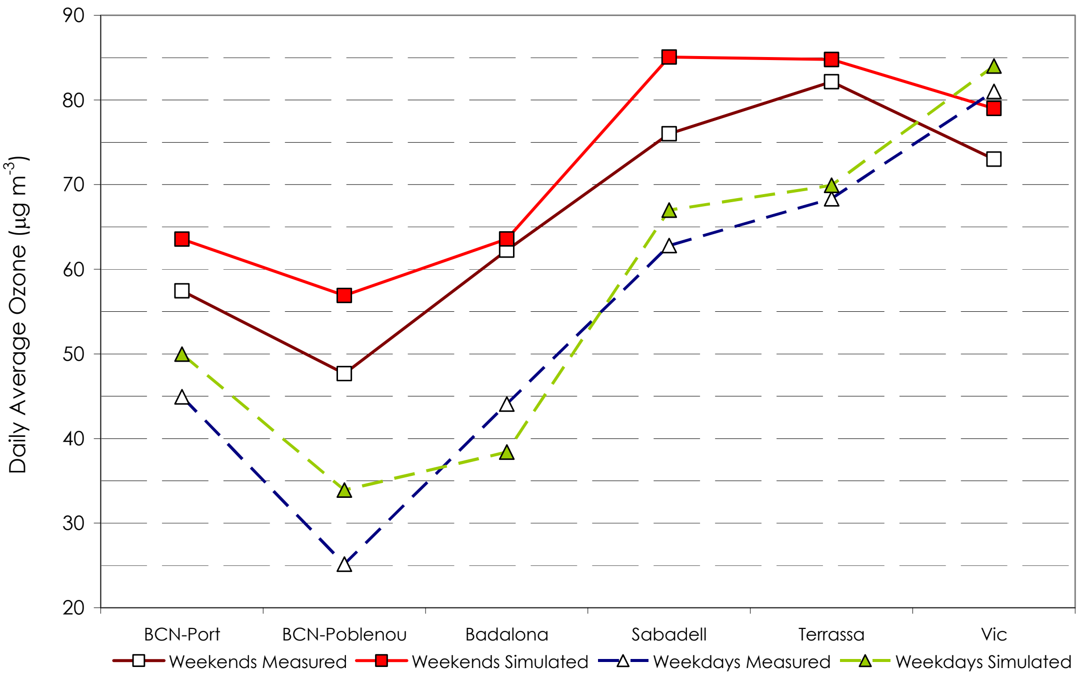


Figure 9.4. Measured (white) and simulated (color) weekday (dashed line)/weekend (solid line) ozone (µg m^{-3}) at six sites spanning from upwind to downwind areas. The (up) daily maximum 1-hr concentrations and (down) average concentrations show the decrease of ozone weekend effect in downwind areas departing from Barcelona city.

The observed and modeled maximum weekend/weekday differences 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.

9.3.4 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 and VOCs emissions were 236 t d^{-1} and 172 t d^{-1}, respectively. On weekends NO_x and VOCs emissions were 184 t d^{-1} and 179 t d^{-1} (Table 9.3). 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 emissions on weekends are 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 (Figure 9.5). 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, contributes 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. Figure 9.6 depicts the distribution of the ratio NO_x (kg km^{-2} h^{-1})/VOCs (kg km^{-2} h^{-1}) ratio on weekdays and on weekends. In the former case, this ratio achieves 2.0-2.7. These cells correspond to highways axis; because influence of 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, NO_x emissions are also higher. 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 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 TSP 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 (Figure 9.7a) (–19% and –41%, respectively, for average values and –39% and –61% for 1-hr 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). This pattern is also present in measured ambient concentrations of precursors (Figure 9.7b). CO and NO_x are also significantly averagely reduced in a –37% and –23%, respectively (Table 9.2).

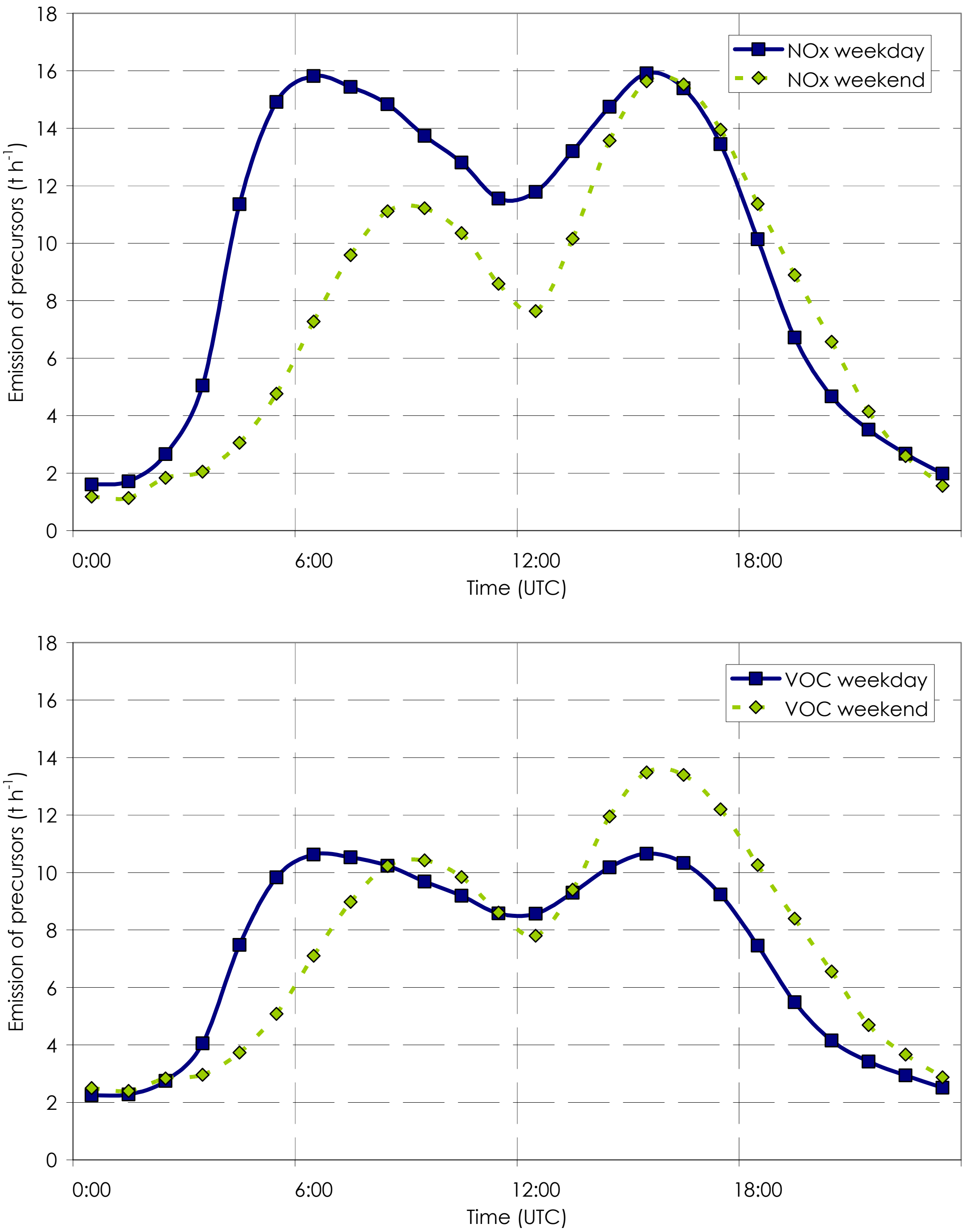


Figure 9.5. Hourly emission of (up) NO_x and (down) VOCs (both in t h^{-1}) on weekday (solid, squares) and weekend (dashed, diamonds) of August in the northeastern Iberian Peninsula. At weekday, NO_x peaks occur about 0700UTC and 1700 UTC, but at weekend first peak is lower and displaced to the right (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.

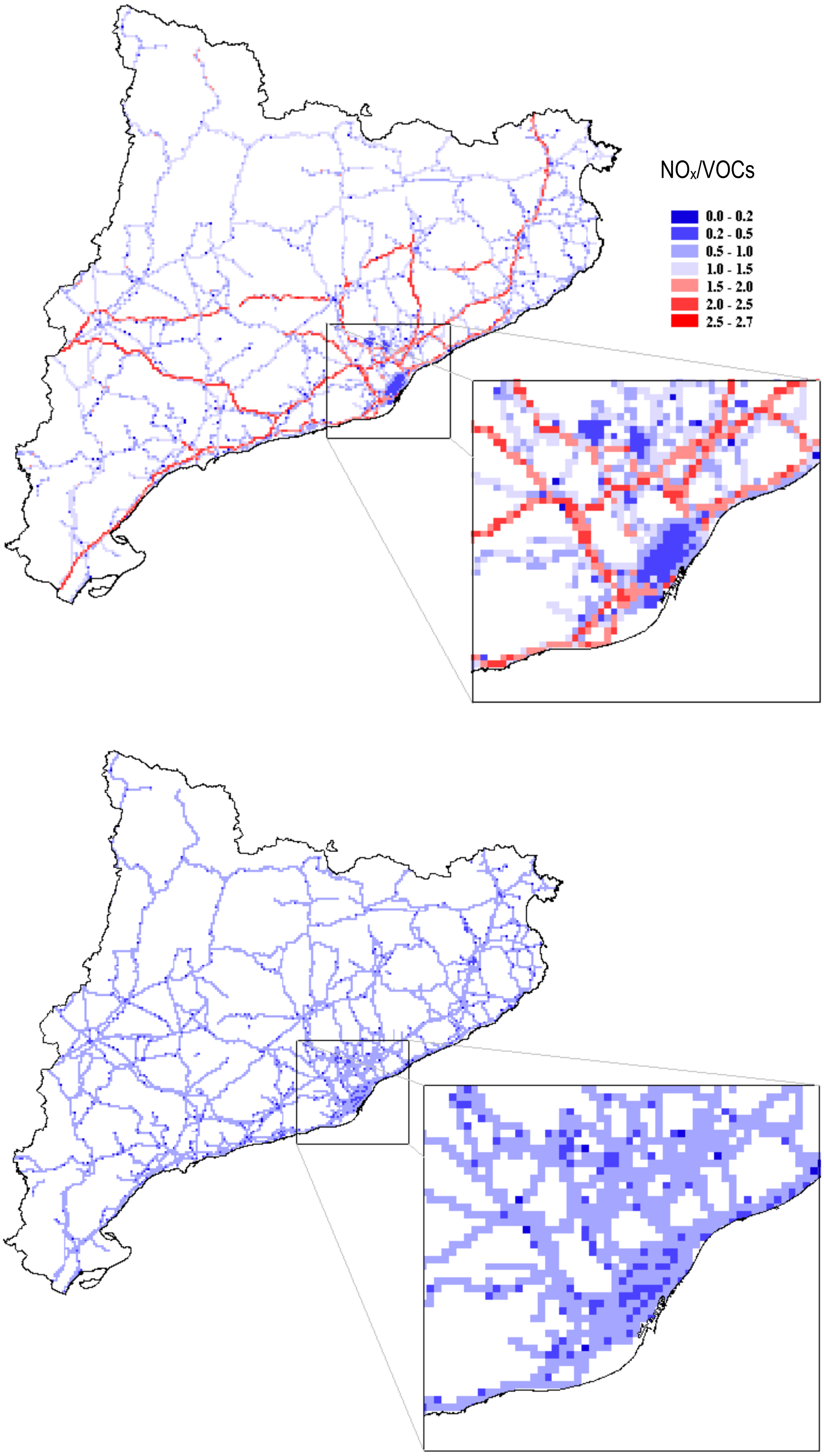
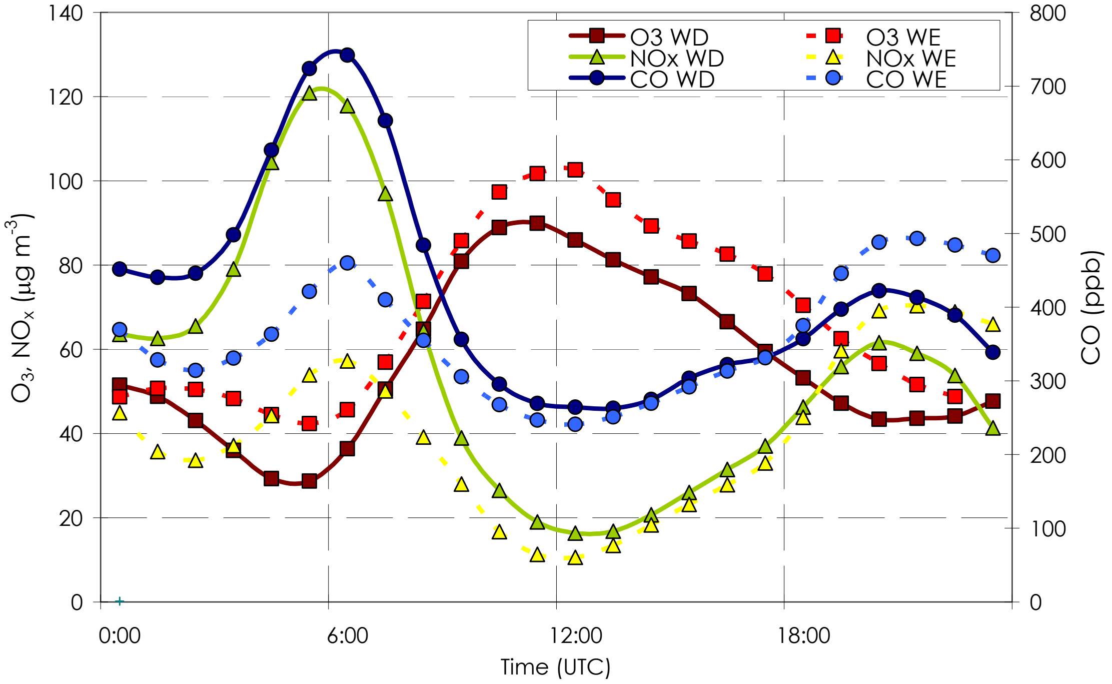


Figure 9.6. Ratio NO_x(kg km^{-2} h^{-1})/VOCs(kg km^{-2} h^{-1}) for (up) weekdays and (down) weekend in the northeastern Iberian Peninsula. On weekdays this ratio achieves 2.0-2.7, meanwhile lower NO_x emissions provide values under 1.0 on weekends.



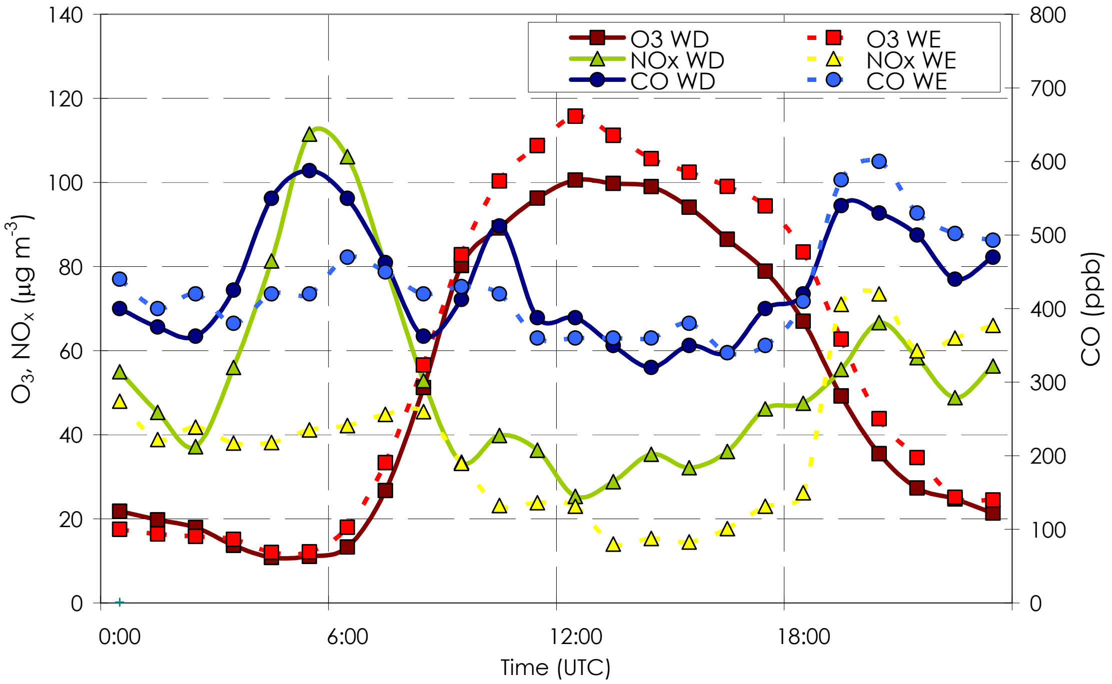


Figure 9.7. Averaged hourly weekday (solid) and weekend (dashed) ozone (squares) and precursors (NO_x, triangles; CO, circles) for the northeastern Iberian Peninsula during the episode of 13-16 August, 2000; (up) simulations; and (down) measurements.

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 (Figure 9.8). Nevertheless, night-time 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 precursors (represented by CO) is not as important (reductions of –4% for simulated maximum and average levels). Therefore, Vic constitutes a 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 (Figure 9.9).

9.3.5 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 destroy (quench) 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 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 9.2), 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.

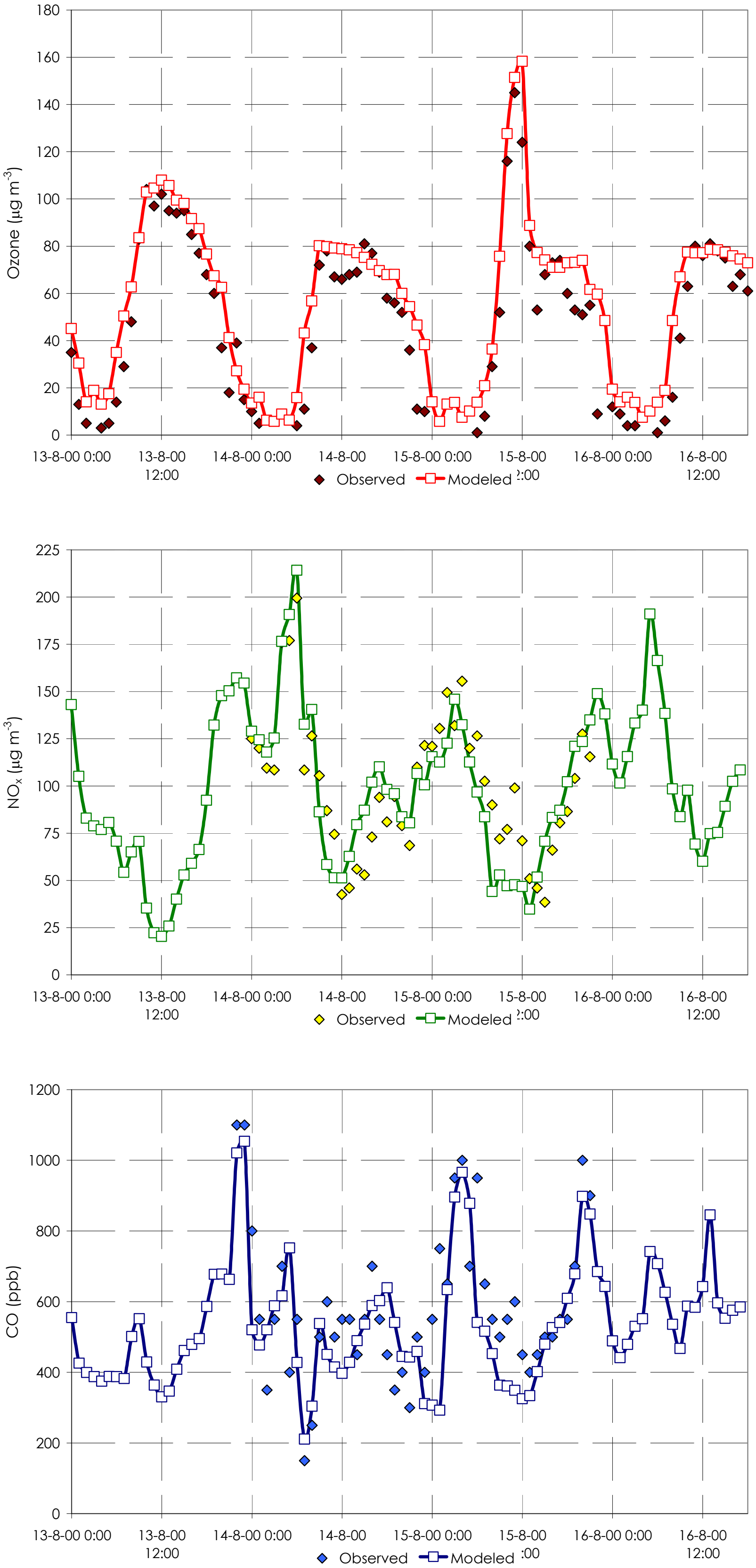


Figure 9.8. Time series for (a) ozone; (b) NO_x and (c) CO both for observations (diamonds) and simulations (solid line) in the area of Barcelona (upwind) for 13-16 August, 2000.

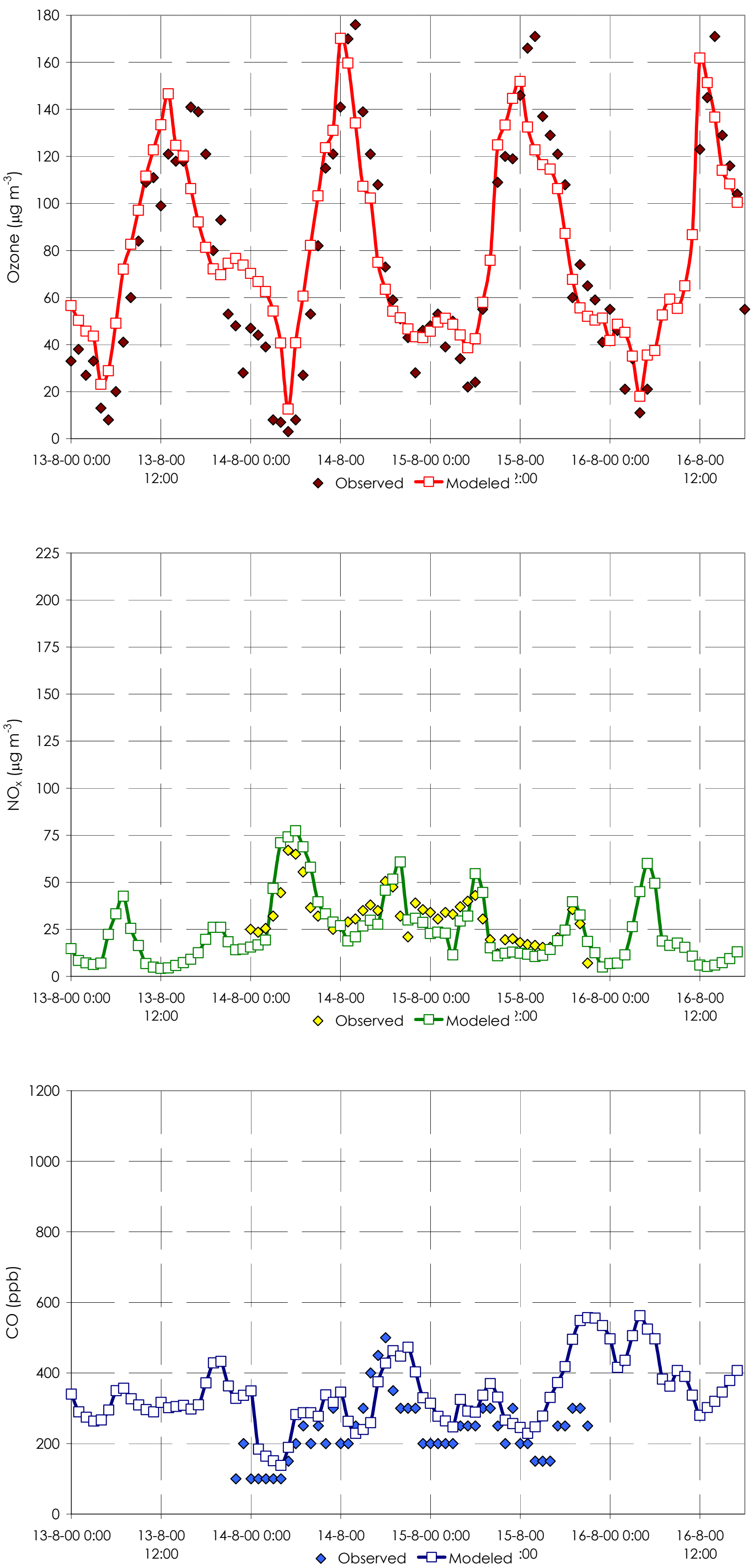


Figure 9.9. Times series for (a) ozone; (b) NO_x and (c) CO both for observations (diamonds) and simulations (solid line) in the area of Vic (downwind) for 13-16 August, 2000.

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 weekdays.

9.3.6 Carryover Contribution to the Weekend Effect

Increased VOCs 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 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. Figure 9.10 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 in O_3 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 0200UTC. 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 do not appear to be a significant cause in the study case for northeastern Iberian Peninsula ozone weekend effect.

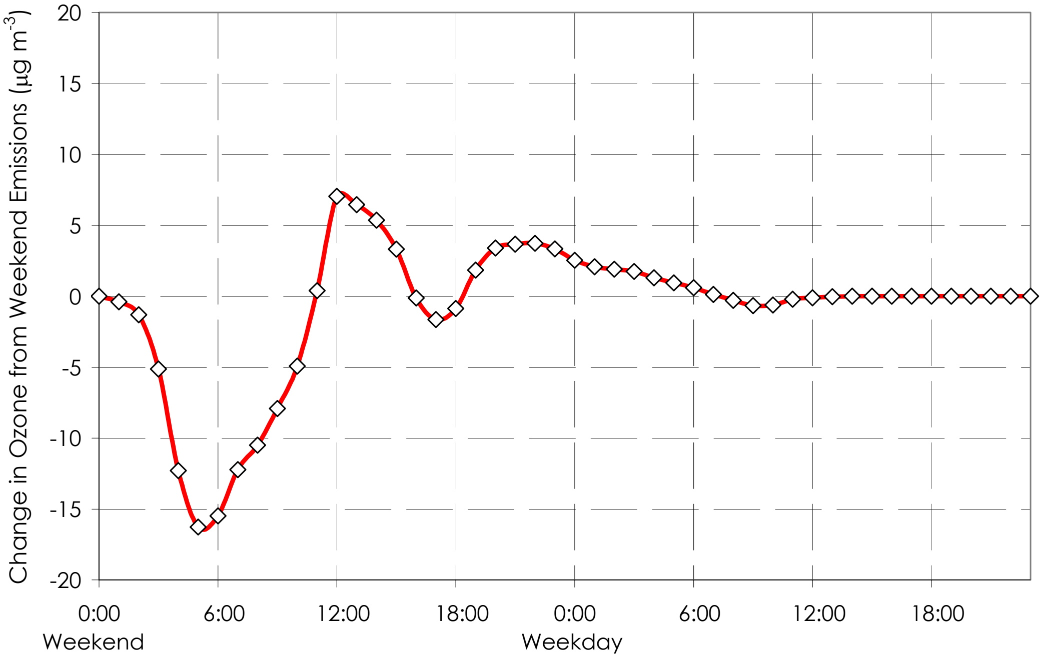


Figure 9.10. Analysis of carryover impact from weekends to weekdays by changing weekend / weekday emissions. Differences measured in ground-level O_3 return to values under 2 μg m^{-3} around 0200UTC of the following day due to pervasive early morning emissions.

9.4 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-hr 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 of O_3 precursors 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 TSP reductions in emissions are 13% and 12% respectively on weekends. The shift of 1-2 hours 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 0200UTC. 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.

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