

## **8 Control of Ozone Precursors in a Very-Complex Industrial Terrain by Using Multiscale-Nested Air Quality Models with Fine Spatial Resolution (1 km<sup>2</sup>)**

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### **8.1 Introduction**

The complex topography of the northeastern Iberian Peninsula induces an extremely complicated structure of the flow because of the development of  $\alpha$ - and  $\beta$ -mesoscale phenomena that interact with synoptic flows. The characteristics of the breezes have important effects in the dispersion of pollutants. 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.

Therefore, air pollution studies in very complex terrains as the northeastern Iberian Peninsula require high-resolution modeling of air quality (with a resolution of 1km or finer) for resolving very complex structures such as flow channeling in valleys or the influence of line and point sources (Kessler *et al.*, 2001; Jiménez *et al.*, 2004). In order to deal with the influence of larger scale transport, however, high resolution models have to be nested in larger models (e.g. treating larger areas with lower resolution) in order to generate appropriate initial and boundary conditions for the finer resolution domains, as discussed in Chapter 4.

As commented in Chapter 7, the kinetics of ozone (O<sub>3</sub>) chemistry and its two main precursors, nitrogen oxides and volatile organic compounds, represent an important source of uncertainty in atmospheric chemistry and photochemical modeling (Atkinson, 2000). This complexity affects the design of control strategies to reduce tropospheric O<sub>3</sub> production. Nowadays, considerable interest exists in finding observable indicators of how real air masses are likely to respond to emission controls. A major problem for the study of O<sub>3</sub>-NO<sub>x</sub>-VOCs sensitivity has been the inability to gain evidence based on direct measurements rather than theoretical calculations (Sillman, 1999), and therefore air quality models are an useful tool to establish policies for controlling the emissions of the species that act as precursors of tropospheric ozone.

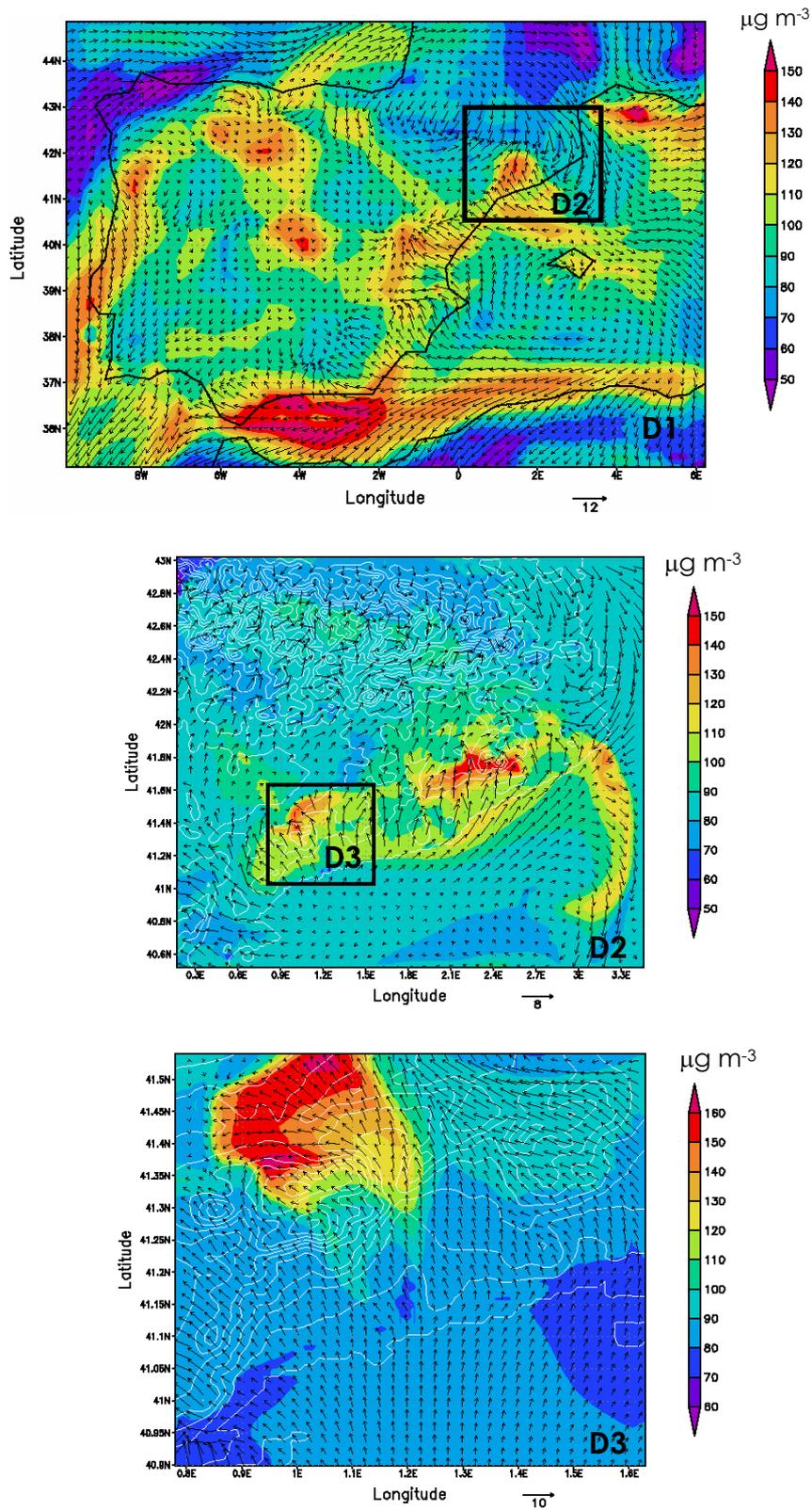
This work shows the results obtained through the utilization of the MM5-EMICAT2000-CMAQ multiscale-nested air quality model relating the sensitivity regimes for O<sub>3</sub>-NO<sub>x</sub>-VOCs in an area of high geographical complexity like the industrial area of Tarragona, located in the northeastern Iberian Peninsula. The aforementioned model was applied with fine temporal and spatial resolution (1h and 1km<sup>2</sup>) to represent the chemistry and transport of tropospheric O<sub>3</sub> and other photochemical species with respect to different hypothetical scenarios of emission controls. The area of Tarragona contains very important industrial sources, such as two refineries, several chemical complexes, co-generation power plants and incinerators, among others. The analyses presented here provide an assessment of the effectiveness of different policies for control of precursors by comparing the modeled results for different scenarios.

## 8.2 Methods

Simulations with MM5-EMICAT2000-CMAQ were performed for 15 August, 2000 (see description in Chapter 2). The particular characteristics of the northeastern Iberian Peninsula, generally, and the industrial area of Tarragona, particularly, force to the use of complex multiscale-nested models with very high resolution in order to properly generate the initial and boundary conditions in the area of study. Therefore, three different nested domains were defined for performing simulations (Figure 8.1): (1) a 1392x1104 km<sup>2</sup> domain (D1) centered in the Iberian Peninsula, that covers the Iberian Peninsula, northern Africa and the Western Mediterranean Basin with a horizontal resolution of 24km and 16 vertical layers in sigma-coordinates (having the first layer an altitude around 36 m agl). Emissions of this domain were obtained from EMEP data for year 2000 ([www.emep.int](http://www.emep.int)); (2) a 272x272 km<sup>2</sup> domain (D2) covering the northeastern Iberian Peninsula with a horizontal resolution of 2km and identical vertical resolution; and (3) a 40x40 km<sup>2</sup> domain (D3) centered in the city of Tarragona that covers the industrial complex around this city. Horizontal resolution is 1km and 16 vertical layers cover the troposphere. Emissions for D2 and D3 were generated with EMICAT2000 emission model (Parra, 2004).

### 8.2.1 Hypothesis for the Control of Emissions of Ozone Precursors

The Gothenburg Protocol and the Directive 2001/81/EC (EU, 2001) were adopted in order to abate the acidification, eutrophication and ground-level ozone and to set national emission ceilings for certain atmospheric pollutants. These documents established emission limits for the year 2010 for different photochemical species (nitrogen oxides, volatile organic compounds and sulfur compounds, among others), and the reductions set for the ozone precursors are considered with respect to the reference year of 1990: 41% in the case of NO<sub>x</sub>; 40% in the case of VOCs and 63% for SO<sub>2</sub>. If we focus in ozone precursors, reductions of 27% are achieved for NO<sub>x</sub> and VOCs during the period 1990-2000 in the case of the northeastern Iberian Peninsula; therefore reductions around 20% until year 2010 are needed to agree with the hypothesis of the Gothenburg Protocol and Directive 2001/81/EC (Table 8.1).



**Figure 8.1.** Ozone results for different nested domains at 1200UTC on 15 August, 2000: Peninsular domain (D1, up); northeastern Iberian Peninsula (D2, center); and Tarragona (D3, down).

**Table 8.1.** Emissions of NO<sub>x</sub>, VOCs and SO<sub>2</sub> in Catalonia for 1990 and 2000 (Parra, 2004) and objectives to achieve in year 2010 according to Gothenburg Protocol (kt y<sup>-1</sup>).

	<b>NO<sub>x</sub></b>	<b>VOCs</b>	<b>SO<sub>2</sub></b>
Year 1990	147.3	136.6	116.6
Year 2000	106.9	99.3	64.7
Objective 2010	86.9	82.0	43.1
Reduction 1990-2000	<b>27.4%</b>	<b>27.3%</b>	<b>56.0%</b>
Required Reduction 2000-2010	<b>18.7%</b>	<b>17.4%</b>	<b>33.4%</b>

Considering that most of the industrial emissions in the northeastern Iberian Peninsula are located in the area of Tarragona (D3), and that these industries in D3 do not exhibit a considerable seasonal fluctuation in their emissions (Parra, 2004), hypothetical uniform reductions during the entire year have been considered for setting control policies of industrial sources in the zone of Tarragona and to assess their effect in the sensitivity regimes of O<sub>3</sub>-NO<sub>x</sub>-VOCs.

The effects in the air quality of this area were evaluated for the following scenarios: (1) Base case for year 2000 with emissions estimated by EMICAT2000 (vegetation, traffic, industrial emissions, and also associated to the domestic and commercial use of solvents and fossil fuels); (2) Scenario 1: Reduction of 25% in the industrial emissions of nitrogen oxides emissions in the area of Tarragona (D3); (3) Scenario 2: Reduction of 25% in the industrial emissions of volatile organic compounds in the area of Tarragona (D3); (4) Scenario 3: Reduction of 25% in the industrial emissions of both nitrogen oxides and volatile organic compounds in the area of Tarragona (D3); (5) Scenario 4: Reduction of 50% in the emissions derived from on-road traffic in the area of Tarragona (D3); (6) Scenario 5: Reduction of 100% in the emissions of the refinery located in D3; and (7) furthermore, in order to estimate the contribution of biogenic emissions in this domain, an additional scenario was included (Scenario 6: Reduction of 100% in biogenic emissions in D3).

### **8.2.2 Base Case Emissions**

The main emission sources in the northeastern Iberian Peninsula (D2) are located on the coast, especially in the Barcelona Geographical Area and the Tarragona industrial zone. The importance of biogenic emissions is high in D2, representing a 34% of total annual VOCs emissions, and are a source of reactive compounds such as aldehydes and isoprene (Parra, 2004). Traffic emissions on an annual cycle represent a 58% of the emissions of NO<sub>x</sub> and 36% of VOCs in D2, especially olefins and aromatic compounds. During 15 August, 2000, emissions are supposed to have an additional weight, since traffic increases because of the vacation period and the contribution of foreign vehicles. Main emitters are located in the axis of roads parallel to the littoral and the cities of Barcelona and Tarragona. Industrial emissions are located mainly in D3 and represent a 39% of the emissions of NO<sub>x</sub> and 17% of the emissions of VOCs; meanwhile the

domestic and commercial use of solvents represents 13% of the VOCs emissions in D2. The emissions of precursors attributable to the industrial sector in the northeastern Iberian Peninsula add up 41 kt yr<sup>-1</sup> of NO<sub>x</sub> and 23 kt yr<sup>-1</sup> of VOCs. In the annual cycle, total emissions of ozone precursors in D2 are 106.9 kt yr<sup>-1</sup> of NO<sub>x</sub> (58% traffic emissions; 39% industrial emissions) and 99.3 kt yr<sup>-1</sup> of NMVOCs (34% biogenic emissions; 36% on-road traffic emissions; 17% industrial emissions). Total percentages of the contribution of different sources to total emissions in D2 are summarized in Table 8.2.

**Table 8.2.** Summary of emissions in the northeastern Iberian Peninsula for the base case (%) in year 2000.

Source	Primary Pollutants					Total
	NO <sub>x</sub>	NMVOCs	CO	SO <sub>2</sub>	TSP	
1. Biogenic Emissions		34.33				7.83
2. On-Road Traffic	58.37	36.24	96.86	2.01	66.81	64.75
3. Industrial Emissions	38.54	16.69	2.73	94.44	31.91	23.35
Power Generation	14.03	0.51	0.79	44.05	7.23	8.01
Cement Factories	8.98	0.22	1.31	2.16	17.87	3.17
Refining	7.95	4.69	0.41	38.64	3.83	6.99
Olefins	2.71	1.76	0.00	9.58	2.98	2.04
Fugitive Emissions		8.05				1.84
Others	4.86	1.46	0.22	0.00	0.00	1.30
4. Energetic Consume Domestic & Commercial	3.09	0.15	0.41	3.55	1.28	1.20
5. Use of Solvents		12.59				2.87
Total	100	100	100	100	100	100

Emissions of ozone precursors during 15 August, 2000, were 236 t d<sup>-1</sup> for nitrogen oxides and 172 t d<sup>-1</sup> for VOCs. The ratio NO<sub>x</sub>/NMVOCs, which is 0.78 for the annual cycle, decreases to 0.58 for this episode of photochemical pollution due to the high temperatures and solar radiation, that promote evaporative emissions from on-road traffic and vegetation.

Most of anthropogenic emissions derived from on-road traffic and the domestic sector are located in the Barcelona Geographical Area and in the axis of the highways oriented parallel to the coastline. Industrial emissions are located principally in D3, in the industrial area of Tarragona, where there are two refineries, several chemical complexes, co-generation power plants and incinerators, among others. In this D3, EMICAT2000 estimates a total of 15.7 kt yr<sup>-1</sup> of NO<sub>x</sub> and 20.2 kt yr<sup>-1</sup> of NMVOCs for industrial activities. These values represent 15% of total emissions in the northeastern Iberian Peninsula (D2). Industrial emissions of NO<sub>x</sub> and VOCs in D3 represent 38% and 88%, respectively, of the total industrial emissions in D2. In the case of the refinery, the most important industrial source in D3, annual emissions of O<sub>3</sub> precursors are 7.2 kt yr<sup>-1</sup> of NO<sub>x</sub> and 5.3 kt yr<sup>-1</sup> of NMVOCs.

## 8.3 Results

### 8.3.1 Evaluation of Nested Domains

The precise definition of the grid resolution is an important decision when applying an air quality model. Jiménez *et al.* (2004) showed that ozone is highly sensitive to the grid size employed in the simulations (Chapter 5), and very high spatial and temporal resolution is needed to capture the small-scale features in very complex terrains.

Air quality stations hourly data averaged over the domain of study were used in order to report the difference in the forecasted ozone levels for the base case with the different nested domains and their performance results. Hourly values of ground-level O<sub>3</sub> were provided by twelve air quality surface stations located in D3, which belong to the Environmental Department of the Catalonia Government (Spain). 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. Therefore, the maximum simulated value in the domain (182 µg m<sup>-3</sup>) may not be predicted in the location of any stations, as shown in this work (1-h peak ozone concentrations were 147 µg m<sup>-3</sup> and 127 µg m<sup>-3</sup> for measurements and simulations, respectively, at 1200UTC for both values). The statistical evaluation procedures have been described in Chapter 5 of this work. Table 8.3 collects the results of both the discrete statistical analysis.

**Table 8.3.** Statistical measures of model performance for 1-hr O<sub>3</sub> for the different nested configurations during 15 August, 2000.

	<b>EPA Goal</b>	<b>Nested D1 (24km)</b>	<b>Nested D2 (2km)</b>	<b>Nested D3 (1km)</b>
Observed peak (µg m <sup>-3</sup> )		147		
Modeled peak (µg m <sup>-3</sup> )		97	111	127
UPA (%)	<±20	-33.8	-24.7	-13.8
MNBE (%)	<±15	-17.8	-19.1	-13.1
MNGE (%)	<+35	19.3	19.6	13.6

The European Directive 2002/3/EC (EU, 2002) related to ozone in ambient air establishes an uncertainty of 50% for modeling assessment during daytime hours as the quality objective. This uncertainty is defined as the maximum error of the measured and calculated concentration levels. In addition, this value is less demanding than US EPA (1991) standards, and is achieved by simulations with every resolution considered. An improvement in the unpaired peak accuracy (UPA) is produced with an increase in resolution from the most coarse domain (D1) to the second nest (D2) is indicated in the results (-33.8% to -24.7%, respectively). However, these values are not within the standard of ±15–20% set for the prediction of the peak; a finer resolution of 1km

(D3) is needed to meet this objective (-13.8%). The negative values for UPA in each nested domain indicate an underprediction in the simulated values with respect to the maximum measured peak in the stations of the domain of Tarragona ( $147 \mu\text{g m}^{-3}$ ).

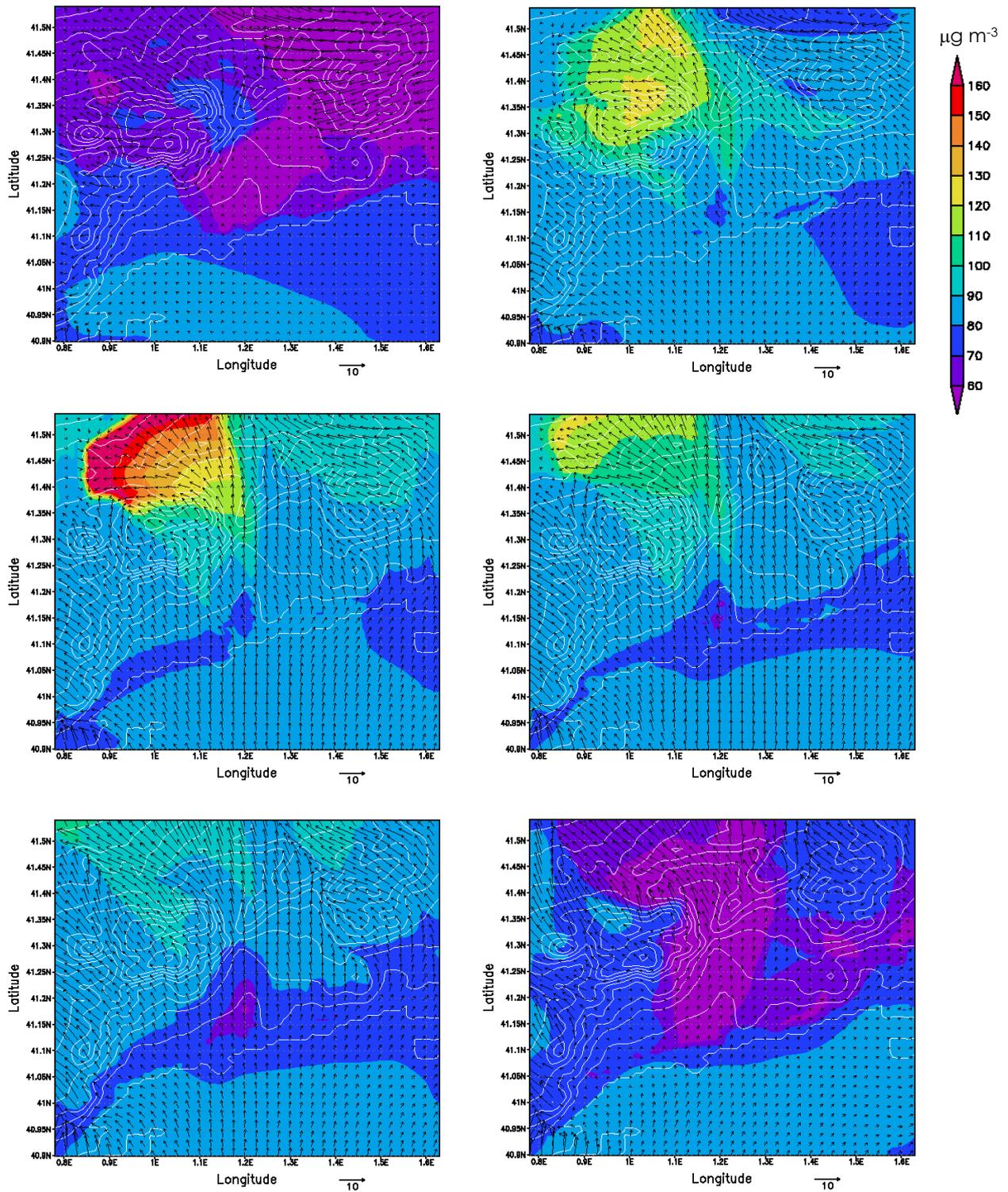
For the mean normalized bias error (MNBE), these indicators do not get better when increasing the resolution from 24 km in D1 to 2km in D2 (values over the US EPA standard of  $\pm 10\text{--}15\%$  for normalized bias), but an important improvement is shown in the case of D3, where MNBE descends to -13.1%, meeting the aforementioned guidelines. Negative values of MNBE indicate that the model, with different nested resolutions, tends to underpredicts the ozone levels achieved in the area.

The mean normalized gross error (MNGE) is met by all nested configurations (19.3%, 19.7% and 13.6% for D1, D2 and D3, respectively), but results from D3 improve with respect to other nested configurations. Therefore, results indicate that a resolution of at least 1km, is needed when studying the phenomena of air pollution occurring in the very complex industrial area of Tarragona and to predict correctly the low-troposphere processes throughout a daily cycle. In addition, Lyons *et al.* (1995) indicated that horizontal resolutions up to 1-km should be considered when simulating vertical motion of pollutants associated with sea breezes. Hence, a horizontal resolution of 1km was selected for the study of the  $\text{O}_3$  response to the emission controls of its precursors.

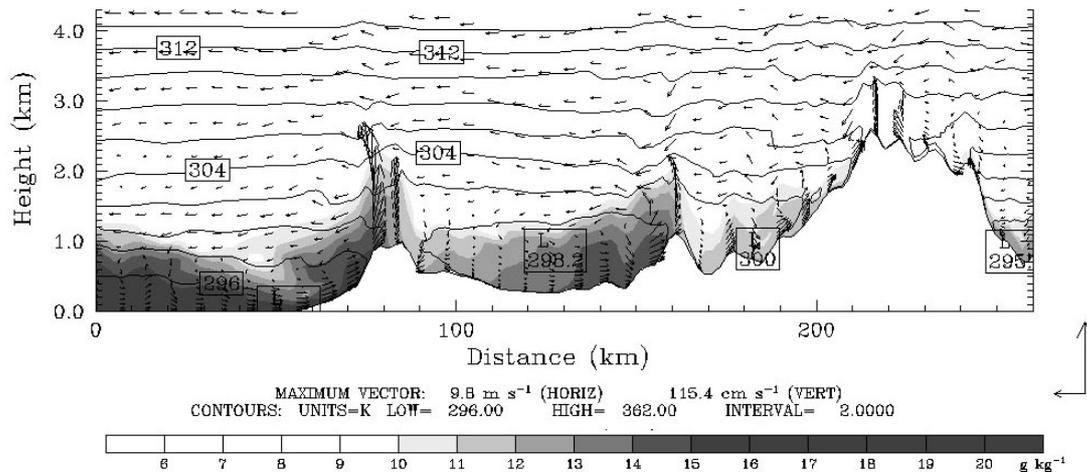
### **8.3.2 Description of Pollutants Dynamics for 15 August, 2000 (Base Case)**

The dynamics of the daily cycle of ground-level ozone are depicted in Figure 8.2. The behavior of nocturnal flows in the D3 presents calm winds during nocturnal nights and the development of the sea breeze from 0800UTC. The canalizations observed come conditioned because of the particular orography of the northern Mediterranean littoral of the Iberian Peninsula. At night, the dominant reaction is the depletion of ozone with the abundant NO emissions in the industrial zone of Tarragona through the reaction  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ , where ozone oxidizes nitrogen monoxide, being consumed in the process.

Coastal mountain ranges in D3 promote the formation of katabatic winds from 0800UTC that facilitate the establishment of the breeze regime, when the superficial heating of the air induces the thermal circulation. At this time, mountain winds inland are well developed, helping the penetration of the breeze. Afterwards, the altitude of the mountain ranges hinders the advance of the sea breeze producing the accumulation of precursors; and the presence of solar radiation begins the formation of ozone. Orographic forcings undergone by the breeze front contribute to the vertical injection of air masses with high levels of photochemical pollutants in this region. These injections can be stressed with the convergence on mountaintops of the breeze front and anabatic winds of the northern slopes (Figure 8.3).



**Figure 8.2.** Wind vectors and ozone concentrations ( $\mu\text{g m}^{-3}$ ) in the domain of Tarragona (D3) at (from top-down and left-right) 0600 UTC, 1000UTC, 1200UTC, 1400UTC, 1600UTC and 2000UTC.



**Figure 8.3.** Vertical profile of the wind vectors, potential temperature and mixing ratio for 15 August, 2000, at 1200UTC (Mediterranean Sea-Tarragona-Pyrenees profile).

During the hours of photochemical activity, air masses act as photochemical reactors, where  $\text{NO}_x$ , VOCs and solar radiation interact to form tropospheric ozone, peroxyacetyl nitrate and other photochemical pollutants.

Once the air masses overcome the mountain ranges, they are transported inland by the sea breeze, reinforced with anabatic winds, until they reach the area of Alcover, where the model provides values of  $182 \mu\text{g m}^{-3}$  of  $\text{O}_3$  at 1200UTC; exceeding the information threshold of  $180 \mu\text{g m}^{-3}$  set by Directive 2002/3/EC. Simultaneously, pollutants injected mechanically in a chimney effect are incorporated in return fluxes aloft that come towards the sea (Millán *et al.*, 1992, 1997; Baldasano *et al.*, 1994). A fraction of these air masses are transported over the mixing layer out from the domain, extracting pollutants in a short-medium scale transport. The other fraction is forced to descend as a consequence of the compensatory subsidence over the eastern coast of the Iberian Peninsula (Millán *et al.*, 1996) where they are re-circulated and increase the levels of photochemical pollutants.

At 1400UTC, winds overcome the coastal mountains, transporting pollutants inland towards domain D2 (Figure 8.2). This situation remains similar until 2000UTC, when the breeze weakens and turns towards the southwest on the coast, starting the development of the nocturnal land-breeze regime. This does not present intense draining, and the calm dominates the situation in plain areas. Katabatic winds are developed in the mountains; terral winds are reinforced by the katabatic winds of coastal mountains. During these hours the tropospheric ozone is depleted because of the emissions of nitrogen oxides, as commented for the first hours of 15 August, 2000.

## 8.4 Effect of the Control of Emitter Sources on Photochemical Pollutants in the Area of Tarragona

Tropospheric ozone is the most important photochemical pollutant in the area of Tarragona. Nevertheless, several species participate in the formation of O<sub>3</sub> and its chemistry; and also in the air quality of D3. Therefore, in order to analyze the effects of the control of ozone precursors, other species were also considered, like nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), non-methane volatile organic compounds (NMVOCs), carbon monoxide (CO), nitric acid (HNO<sub>3</sub>), peroxyacetyl nitrate (PAN) and total reactive nitrogen (NO<sub>y</sub>).

The response of O<sub>3</sub> to the reduction of its precursors can be examined in further detail if quantitative methods are employed to define the chemistry of O<sub>3</sub>-NO<sub>x</sub>-VOCs. According to Sillman *et al.* (2003), locations are defined as NO<sub>x</sub>-sensitive for a specified hour if O<sub>3</sub> in the case with 35% reduced NO<sub>x</sub> is lower than O<sub>3</sub> in both the base case and in the case with 35% reduced VOCs by at least 4 μg m<sup>-3</sup> (2 ppb). Locations are classified as VOC-sensitive if the O<sub>3</sub> in the case with reduced VOCs is lower than O<sub>3</sub> in the other cases by at least 4 μg m<sup>-3</sup>. Locations that are neither VOC-sensitive or NO<sub>x</sub>-sensitive by this definition are classified as having mixed sensitivity if O<sub>3</sub> in the cases with the reduced NO<sub>x</sub> and with reduced VOCs is lower than O<sub>3</sub> in the base case by at least 4 μg m<sup>-3</sup>; locations are classified as insensitive to NO<sub>x</sub> and VOCs otherwise. These definitions are time-dependent; that is, a model location may be NO<sub>x</sub>-sensitive at some times and VOC-sensitive at other times.

Jiménez and Baldasano (2004) performed a sensitivity study for the northeastern Iberian Peninsula, finding that at the time of maximum photochemical activity (1200UTC) of 14 August, 2000, the industrial area of Tarragona increases its levels of O<sub>3</sub> when reducing NO<sub>x</sub> emissions by 35% (Chapter 7). On the other side, a reduction of a 35% in VOCs emissions causes an important diminution in the aforementioned area; and thus, the authors indicated that this industrial area presents VOC-sensitive chemistry during the hour of maximum ozone formation. In this study, the contribution of different sources and the repercussion of their control are analyzed according to different hypothesis and with a very high spatial resolution (1km<sup>2</sup>), corresponding to very complex terrains.

### 8.4.1 Response of Ozone to Emission Controls

The results for different photochemical pollutants are summarized in Table 8.4 for peak levels for each of the seven scenarios proposed. The threshold of information set in Directive 2002/3/EC is achieved neither in the case of reducing the industrial emissions of VOCs by 25%, nor in the scenario where both NO<sub>x</sub> and VOCs are reduced by 25%. Additionally, Table 8.5 shows the reduction percentages of peak concentrations for each scenario with respect to the base case.

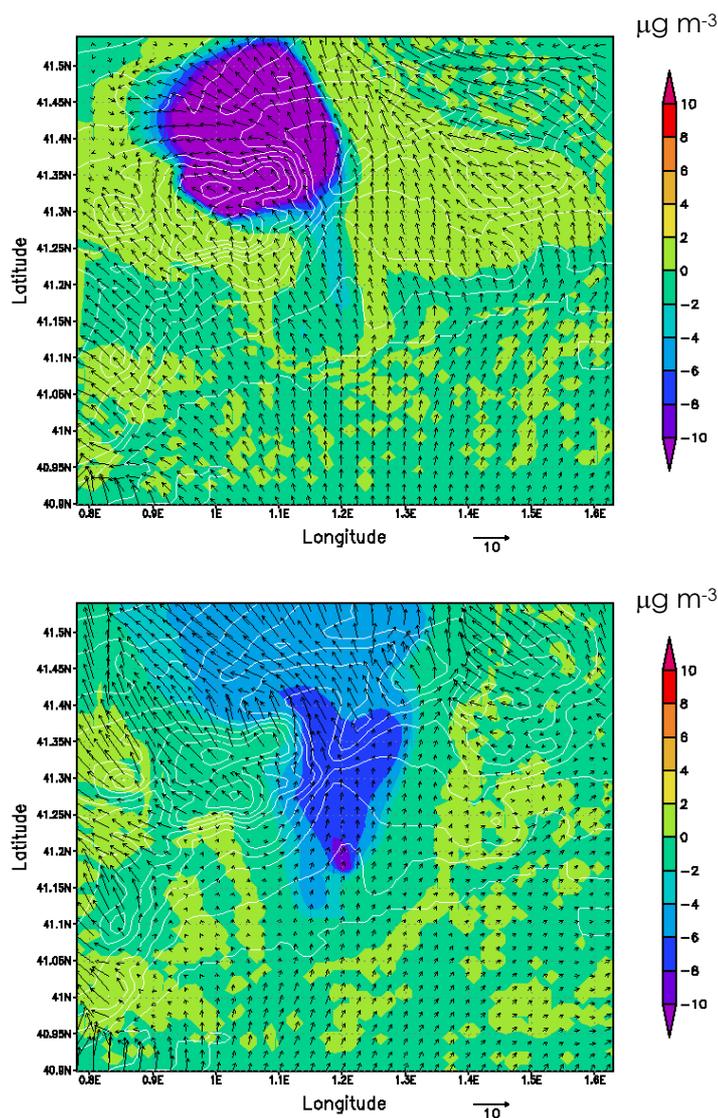
**Table 8.4.** Peak hourly values in domain D3 for different scenarios. Red color indicates an increment in the level of the pollutant respect to the base case. Green color indicates a reduction in the level of the pollutant respect to the base case.

	<i>Base Case</i>	<i>Scenario 1</i>	<i>Scenario 2</i>	<i>Scenario 3</i>	<i>Scenario 4</i>	<i>Scenario 5</i>	<i>Scenario 6</i>
		<i>Reduction 25% NO<sub>x</sub></i>	<i>Reduction 25% VOCs</i>	<i>Reduction 25% NO<sub>x</sub>, VOCs</i>	<i>Reduction 50% Traffic</i>	<i>Reduction 100% Refinery</i>	<i>Reduction 100% Biogenic</i>
O <sub>3</sub> (μg m <sup>-3</sup> )	182	201	161	179	181	189	181
NO <sub>x</sub> (μg m <sup>-3</sup> )	133	113	133	113	133	112	134
SO <sub>2</sub> (μg m <sup>-3</sup> )	583	583	583	583	583	493	583
CO (ppb)	578	578	578	578	537	532	578
NMVOCS (ppm)	1.92	1.92	1.61	1.61	1.90	1.75	1.91
HNO <sub>3</sub> (ppb)	10.76	9.28	10.20	9.50	10.63	8.59	10.78
PAN (ppb)	3.15	3.78	2.54	3.03	3.09	3.44	3.03
NO <sub>y</sub> (ppb)	100	83	98	82	99	81	100

**Table 8.5.** Percentage of reduction in peak hourly values in domain D3 for different scenarios. Red color indicates an increment in the level of the pollutant respect to the base case. Green color indicates a reduction in the level of the pollutant respect to the base case.

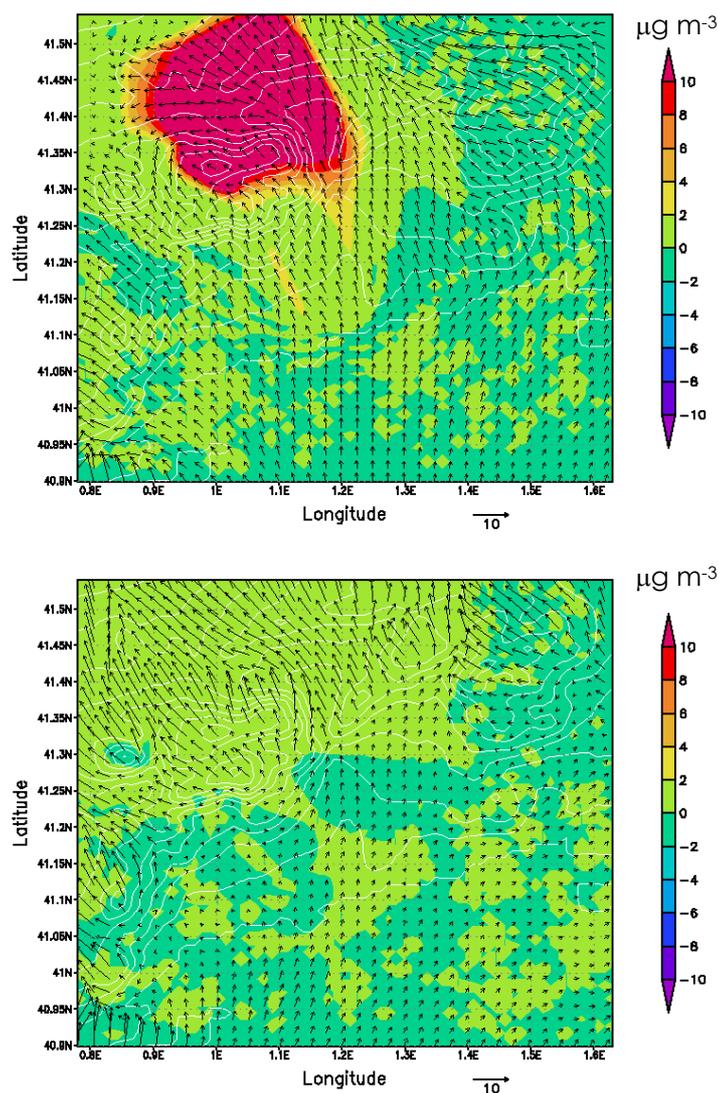
	<i>Scenario 1</i>	<i>Scenario 2</i>	<i>Scenario 3</i>	<i>Scenario 4</i>	<i>Scenario 5</i>	<i>Scenario 6</i>
	<i>Reduction 25% NO<sub>x</sub></i>	<i>Reduction 25% VOCs</i>	<i>Reduction 25% NO<sub>x</sub>, VOCs</i>	<i>Reduction 50% Traffic</i>	<i>Reduction 100% Refinery</i>	<i>Reduction 100% Biogenic</i>
O <sub>3</sub> (%)	10.2	-11.6	-2.0	-0.7	3.9	-0.9
NO <sub>x</sub> (%)	-15.3	0.0	-15.6	-0.6	-16.0	0.1
SO <sub>2</sub> (%)	0.0	0.0	0.0	0.0	-15.3	0.0
CO (%)	0.0	0.0	0.0	-7.0	-7.9	0.1
NMVOCS (%)	0.0	-16.1	-16.0	-0.8	-8.9	-0.1
HNO <sub>3</sub> (%)	-13.8	-5.2	-11.7	-1.2	-20.1	0.2
PAN (%)	20.2	-19.4	-3.8	-1.7	9.2	-3.7
NO <sub>y</sub> (%)	-16.9	-1.2	-17.6	-0.8	-18.9	0.0

**Scenario 1: Reduction of industrial NO<sub>x</sub> emissions (25%).** Tables 8.4 and 8.5 and Figure 8.4 show that a reduction of 25% in the emissions of industrial NO<sub>x</sub> represents an increase of 10% in the peak levels of tropospheric ozone in D3, achieved at 1200UTC (hour of maximum photochemical formation in the area), increasing O<sub>3</sub> levels from 182 μg m<sup>-3</sup> for the base case to 201 μg m<sup>-3</sup> in Scenario 1. This difference is principally observed downwind of the emission area (Alcover). Figure 8.4 also depicts that, at 2000UTC, the lower industrial emissions of NO<sub>x</sub> provoke an inferior destruction (or titration) of tropospheric ozone through the reaction  $O_3 + NO \rightarrow NO_2 + O_2$ .



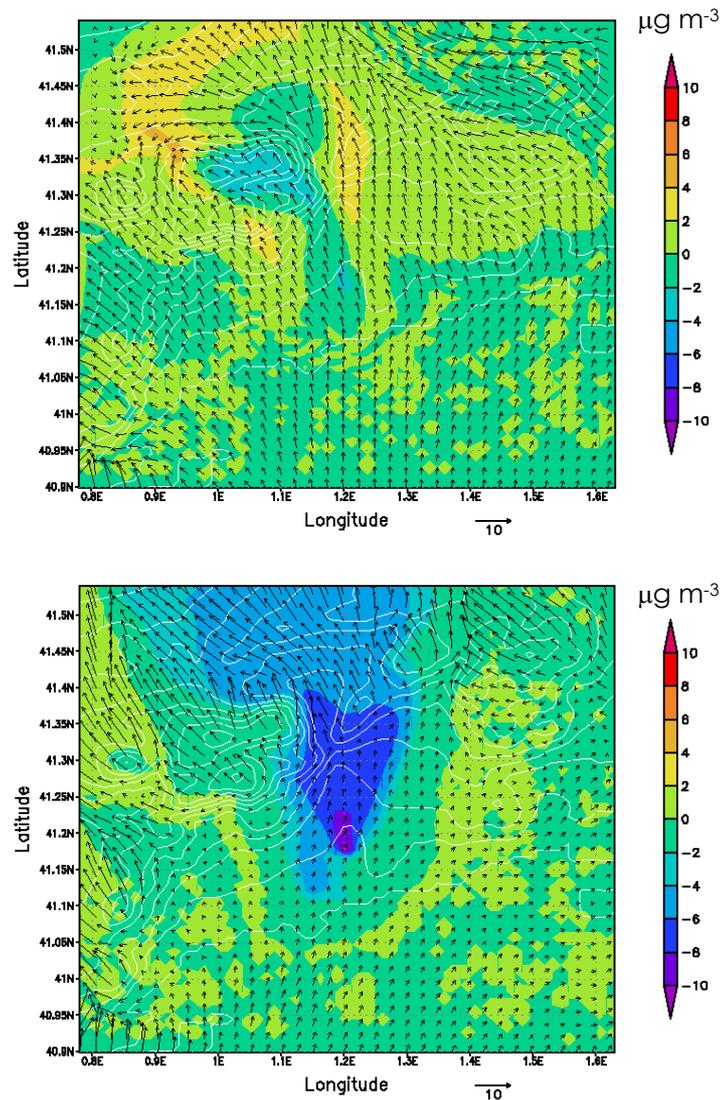
**Figure 8.4.** Difference between the base case and the scenario of reduction of industrial  $\text{NO}_x$  emissions (25%) at 1200UTC (up) and 2000UTC (down). A positive value indicates a reduction in the levels of  $\text{O}_3$  in Scenario 1; a negative value indicates an increase in the levels of  $\text{O}_3$  in Scenario 1 respect to the base case.

**Scenario 2: Reduction of industrial VOCs emissions (25%).** In the case of reducing industrial VOCs emissions by 25%, a clear diminution of 12% is observed in the peak levels of tropospheric ozone at 1200UTC in D3 (Table 8.5), with concentrations reducing from  $182 \mu\text{g m}^{-3}$  for the base case to  $161 \mu\text{g m}^{-3}$  in Scenario 2 (Table 8.4 and Figure 8.5); with reductions of up to  $20 \mu\text{g m}^{-3}$  in the downwind area of Alcover. With the results of Scenario 1 and 2, and according to the definition of Sillman *et al.* (2003), D3 undergoes a VOC-limited chemistry. Nocturnal chemistry is not altered by the reductions of VOCs, since organic compounds do not significantly contribute to night-chemistry of  $\text{O}_3$ ; and therefore, no differences are observed in D3.



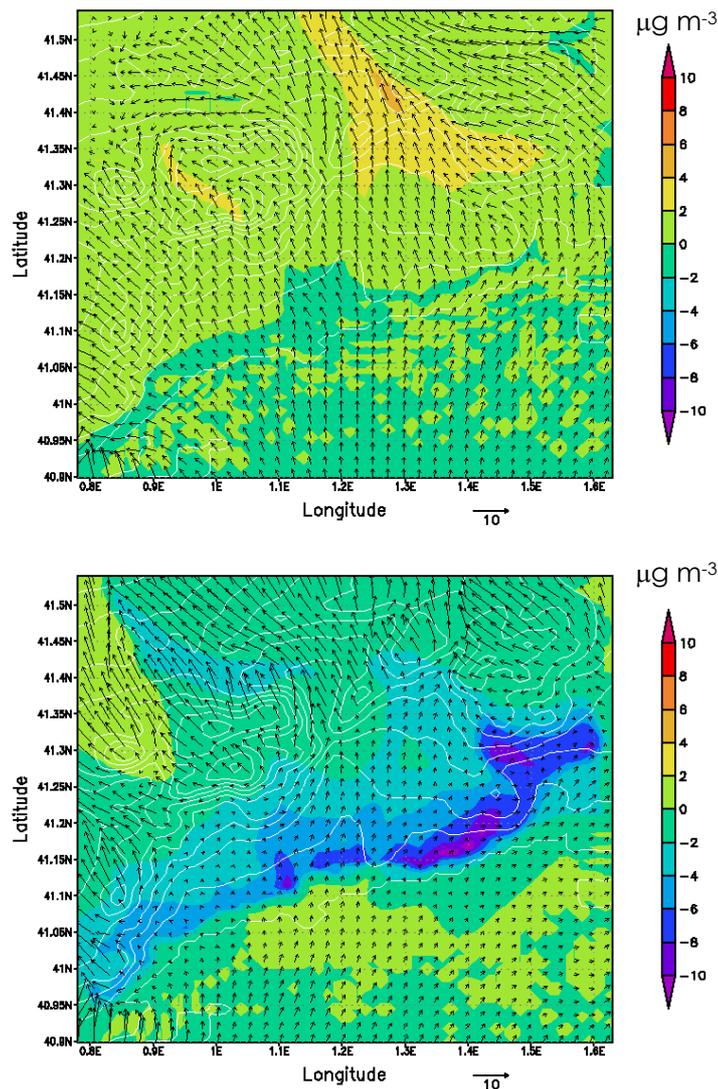
**Figure 8.5.** Difference between the base case and the scenario of reduction of industrial VOCs emissions (25%) at 1200UTC (up) and 2000UTC (down). A positive value indicates a reduction in the levels of  $\text{O}_3$  in Scenario 2; a negative value indicates an increase in the levels of  $\text{O}_3$  in Scenario 2 respect to the base case.

**Scenario 3: Reduction of industrial  $\text{NO}_x$  (25%) and VOCs emissions (25%).** Simultaneous reductions of industrial  $\text{NO}_x$  and VOCs emissions lead to decreases of just  $3 \mu\text{g m}^{-3}$  (Table 8.4 and Figure 8.6) in the domain of Tarragona, with  $182 \mu\text{g m}^{-3}$  in the base case and  $179 \mu\text{g m}^{-3}$  in Scenario 3, since this zone is strongly VOC-limited. That represents a decrease of just a 2% in peak levels of tropospheric ozone at 1200UTC (Table 8.5). At 2000UTC, when photochemical activity ceases, the reduction in  $\text{NO}_x$  emissions provokes a lower titration of tropospheric ozone, as commented before, allowing a higher accumulation of this photochemical pollutant and higher nocturnal levels.



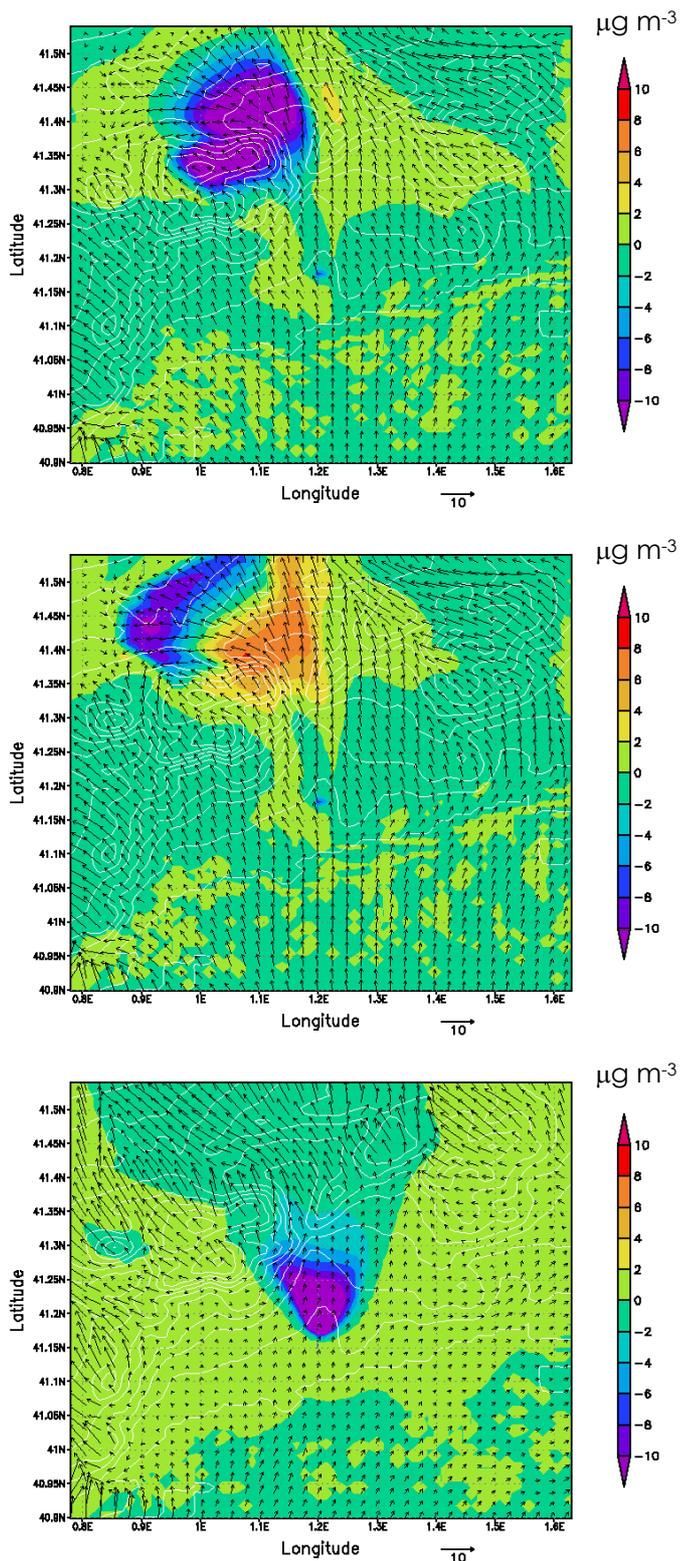
**Figure 8.6.** Difference between the base case and the scenario of reduction of industrial  $\text{NO}_x$  (25%) and VOCs emissions (25%) at 1200UTC (up) and 2000UTC (down). A positive value indicates a reduction in the levels of  $\text{O}_3$  in Scenario 3; a negative value indicates an increase in the levels of  $\text{O}_3$  in Scenario 3 respect to the base case.

**Scenario 4: Reduction of on-road traffic (50%).** This scenario intends to quantify the influence of road traffic in the levels of tropospheric ozone; therefore, a reduction of 50% in the total emissions from road traffic causes a diminution of peak  $\text{O}_3$  levels of just  $1 \mu\text{g m}^{-3}$  (Figure 8.7) at 1200UTC (reduction of 0.7%) (Tables 8.4 and 8.5). On the contrary, the impact on  $\text{NO}_x$  emissions is important; and thus, night concentrations of ozone at 2000UTC are increased because of the lower destruction associated to lower ground-levels of nitrogen monoxide.



**Figure 8.7.** Difference between the base case and the scenario of 50% reduction of on-road emissions at 1200UTC (up) and 2000UTC (down). A positive value indicates a reduction in the levels of  $O_3$  in Scenario 4; a negative value indicates an increase in the levels of  $O_3$  in Scenario 4 respect to the base case.

**Scenario 5: Reduction of emissions of refinery (100%).** The refinery is located in the D3 and represents a huge source of photochemical precursors and other pollutants; and thus, it is interesting to remove the emissions of this refinery as a theoretical scenario. Results (Tables 8.4 and 8.5) indicate that the peak ozone level ( $189 \mu\text{g m}^{-3}$ ) rises by 4% in the domain of study with respect to the levels of the base case,  $182 \mu\text{g m}^{-3}$  (increment of  $7 \mu\text{g m}^{-3}$ ). Scenario 5 presents a peculiar behavior, with a change in the photochemical regime between 1100UTC and 1200UTC (Figure 8.8). First, we would observe an increase in tropospheric ozone levels as a consequence of the diminution of  $\text{NO}_x$  emissions, mainly, if reduction of 100% in the emissions of this source is considered.



**Figure 8.8.** Difference between the base case and the scenario of reduction of the refinery emissions (100%) at 1100UTC (up), 1200UTC (center) and 2000UTC (down). A positive value indicates a reduction in the levels of  $\text{O}_3$  in Scenario 5; a negative value indicates an increase in the levels of  $\text{O}_3$  in Scenario 5 respect to the base case.

Later, the aging of the air mass promotes a diminution in photochemical formation and the transition of chemical regimes (Dommen *et al.*, 1999), which is observed in D3 next to the coastal mountain range. At night (2000UTC), the behavior is similar to Scenario 3, where both NO<sub>x</sub> and VOCs are reduced, and the lack of nitrogen monoxide allows the accumulation and the increment of O<sub>3</sub>. It should be considered that the uncertainty levels associated to the estimation of the emissions from the refinery are particularly high; therefore, results shown here are an approach to the behavior of photochemical pollutants when removing the emissions from the refinery.

**Scenario 6: Reduction of biogenic emissions (100%).** The last scenario responds to the necessity of quantifying the influence of biogenic emissions in the area of study. Biogenic emissions contribute mainly with volatile organic compounds (terpenes, aldehydes and paraffins). The high reactivity of biogenic species makes a significant contribution to atmospheric chemistry (Atkinson and Arey, 1998). Those emissions may have a significant influence in the values of ozone (Solmon *et al.*, 2004). In D3, Figure 8.9 shows that the contribution to its peak values is negligible because of the huge weight of industrial emissions in the area. Nevertheless, as shown in Tables 8.4 and 8.5, it would have a similar effect on ozone as Scenario 4 (reduction of 50% of on-road emissions), with drops in O<sub>3</sub> concentrations of less than 1 µg m<sup>-3</sup> (0.9% respect to the base case) at the time of maximum photochemical formation, and they minimize during nighttime. Thus, the contribution of biogenic emissions to night chemistry is negligible.

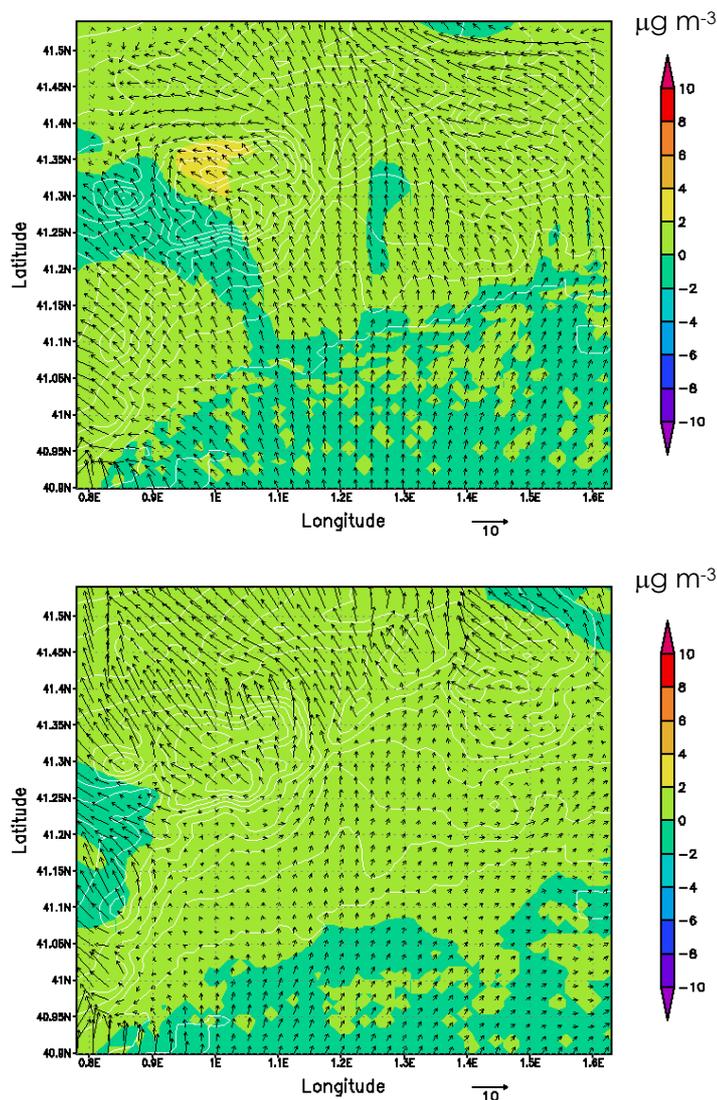
#### **8.4.2 Response of Other Photochemical Pollutants to Emission Controls**

This section briefly depicts the response of other photochemical pollutants included in Tables 8.4 and 8.5 in the different scenarios previously stated.

**Nitrogen Oxides (NO<sub>x</sub>).** Ozone concentrations are sensitive to NO and NO<sub>2</sub> concentrations and their reactions in the troposphere, and also to the NO<sub>2</sub> photolysis rate and PAN formation and loss rates (Gao *et al.*, 1996). At the same time, the concentrations of nitrogen oxides play an essential role in the formation of nitrate radical and nitric acid (Atkinson, 2000). Results indicate that higher reductions in ground-level NO<sub>x</sub> are achieved in the case of removing the emissions from the refinery (133 µg m<sup>-3</sup> in the base case vs. 112 µg m<sup>-3</sup> in Scenario 5, a 16% decrease). Similar reductions are presented when reducing NO<sub>x</sub> emissions by 25% (113 µg m<sup>-3</sup>, Scenarios 2 and 3). The control of traffic emissions has no implications in peak concentrations of NO<sub>x</sub> within D3, meaning that this high concentration is due to industrial emissions. In all scenarios, NO<sub>x</sub> levels are under the value of 200 µg m<sup>-3</sup> set by European Directive 1999/30/EC as a maximum hourly value (EU, 1999).

**Non-Methane Volatile Organic Compounds (NMVOCs).** The presence of hydrocarbons is essential for the production of hydroxyl radicals, which are included in the cycle of formation of tropospheric ozone and other photochemical oxidants as nitric acid or PAN (Luecken *et al.*,

1999). The reduction of 25% in the emissions of industrial VOCs produces reductions of 16% in the levels of NMVOCs (1.92 ppm in the base case and 1.61 ppm in Scenarios 2 and 3).



**Figure 8.9.** Difference between the base case and the scenario of reduction of biogenic emissions (100%) at 1200UTC (up) and 2000UTC (down). A positive value indicates a reduction in the levels of O<sub>3</sub> in Scenario 6; a negative value indicates an increase in the levels of O<sub>3</sub> in Scenario 6 respect to the base case.

Furthermore, the removal of the emissions from the refinery reduces the NMVOCs levels by 9% (1.75 ppm). Last, the control of on-road and biogenic emissions (Scenarios 5 and 6) have a minor influence on peak NMVOCs (reductions of around 1%).

**Sulfur Dioxide (SO<sub>2</sub>).** The role of SO<sub>2</sub> in atmospheric chemistry is related to eutrophication, acid rain and heterogeneous chemistry (Seinfeld and Pandis, 1998). The high levels of this pollutant in D3 are mainly due to the refinery, as derived from simulations. The removal of this source decreases SO<sub>2</sub> ground-levels by 15% (583 µg m<sup>-3</sup> in base case vs. 493 µg m<sup>-3</sup> in Scenario 5);

however, these levels are over the 1-hr threshold of  $350 \mu\text{g m}^{-3}$  set in European Directive 1999/30/EC. The rest of the scenarios do not show noteworthy variations regarding the base case.

**Carbon Monoxide (CO).** The atmospheric oxidation of CO in the presence of the hydroxyl radical can be viewed as a catalytic oxidation of CO to  $\text{CO}_2$  with the formation of a molecule of ozone (Wayne, 2000). The scenarios that undergo more important reductions in CO levels with respect to the base case (578 ppb) are Scenario 4 (reduction of 50% of on-road traffic, 537 ppb) and Scenario 5 (reduction of 100% of refinery emissions, 532 ppb). These cuts in ground levels represent a reduction of 7% and 8%, respectively. In the rest of the scenarios, maximum concentrations of CO are not observed.

**Nitric Acid ( $\text{HNO}_3$ ).** The majority of  $\text{HNO}_3$  produced in all simulations during daylight hours is through the  $\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$  reaction, which is one of the most important daytime reactions affecting tropospheric ozone (Seinfeld and Pandis, 1998). Therefore, the formation of nitric acid is not only related to the presence of  $\text{NO}_2$ , but also to the radical amount (in whose formation NMVOCs participate). The base case levels of  $\text{HNO}_3$  are 10.76 ppb, and important reductions in them are obtained when controlling industrial emissions of  $\text{NO}_x$  (because of the diminution of  $\text{NO}_2$ ), VOCs (reduction of OH radicals) and both  $\text{NO}_x$  and VOCs. The most favorable scenario is the reduction of 100% in the emissions from the refinery, where peak concentrations of nitric acid reduced by 20% (8.59 ppb of  $\text{HNO}_3$ ). The reduction of traffic does not significantly affect the concentrations of this pollutant; meanwhile the removal of biogenic emissions in D3 slightly raises the levels of  $\text{HNO}_3$ .

**Peroxyacetyl nitrate (PAN).** PAN has long been known to be an important atmospheric species. It acts as a reservoir for  $\text{NO}_x$  and acetyl peroxy radicals ( $\text{C}_2\text{O}_3$ ) (Stockwell *et al.*, 1995). PAN and analogues are formed during degradation of aldehydes, by the reaction of alkyl and acyl peroxy radicals with  $\text{NO}_2$ . The thermal decomposition of PAN leads to the formation of  $\text{CO}_2$ ,  $\text{NO}_2$  and peroxy radicals. In turn, the reactions of peroxy radicals lead to production of  $\text{HO}_2$  and formaldehyde, which contribute to photochemical reactions including ozone formation.

Variations of PAN are related to those of ozone (Grosjean *et al.*, 2001); therefore, in a VOCs-limited regime, a reduction of  $\text{NO}_x$  would lead to an increase of PAN levels. A control in the levels of VOCs improves the problems related to this photooxidant. Base case concentrations reach 3.15 ppb, that would increase to 3.78 and 3.44 in Scenario 1 (reduction of 25% in industrial  $\text{NO}_x$ ) and Scenario 5 (removal of the refinery), respectively. These variations imply increments of 20% and 9% having the base case as reference. A reduction is observed in the case of controlling industrial VOCs (19%, 2.54 ppb) and when controlling simultaneously  $\text{NO}_x$  and VOCs emissions (4%, 3.03 ppb). At the same time, concentrations of PAN would drop by 4% if removing biogenic emissions, since they are an important source of aldehydes (Parra *et al.*, 2004), whose degradation because of OH radicals actively participate and the generation of peroxy acetyl

radical that lead to PAN and its derivatives (Aschmann *et al.*, 2002). The control of traffic emissions would only reduce the levels of this photooxidant by 2%.

**Total Reactive Nitrogen (NO<sub>y</sub>).** NO<sub>y</sub> is the sum of the ground-level concentration of nitrogen oxides and all nitrogen oxidation products by organic species. This is a good indicator of the sensitivity to NO<sub>x</sub> and VOCs since NO<sub>y</sub> is related to the balance of both species within an air mass and allows us to have a global idea of the control of precursors (Jiménez and Baldasano, 2004). For this species, all scenarios (except removal of biogenic emissions) lead to diminutions with respect to the base case (100 ppb). The most relevant case is the reduction by 100% of the emissions of the refinery that limits both NO<sub>x</sub> emissions and the oxidation of nitrogen because of the reduction of volatile organic compounds. In this scenario, NO<sub>y</sub> ground-levels drop off to 81 ppb (reduction of 19%). The control of the industrial NO<sub>x</sub> emissions is effective (83 ppb, reduction of 17%) and also the control of both industrial NO<sub>x</sub> and VOCs emissions (82 ppb, reduction of 18%). On-road traffic reduction and the control of industrial VOCs emissions lead to drops in NO<sub>y</sub> levels around 1%.

## 8.5 Conclusions

A multiscale-nested approach was applied in order to simulate photochemical pollution in very complex terrains, as the northeastern Iberian Peninsula (D2), and, more specifically, the industrial domain of Tarragona (D3). Results indicate that a very high resolution grid (1km) and a time resolution of 1h are needed when describing the dynamics of ozone and other photochemical pollutants, and also to achieve the goals for model performance established by the US EPA and the European Legislation.

According to the Gothenburg Protocol and Directive 2001/81/EC, different scenarios have been set in order to establish hypothetical control policies for the emissions of ozone precursors in the industrial area of Tarragona. The ozone chemistry in the industrial domain of Tarragona is strongly sensitive to volatile organic compounds; and therefore, the high levels of ozone in the area are controlled by the industrial emissions of VOCs. At the same time, the contribution of on-road traffic and biogenic emissions in the area is much lower than the weight of industrial sources, except in the case of carbon monoxide. For this pollutant, traffic plays a determinant role in maximum levels. The higher percentages of reduction for ground-level O<sub>3</sub> are achieved when reducing by 25% the emissions of industrial VOCs. On the contrary, reductions in the industrial emissions of nitrogen oxides contribute to a strong increase in hourly maximum concentrations of ground-level ozone. The same behavior is observed in Scenario 5 (no refinery); the rest of the scenarios do not show important variations respect to the base case.

Even though results indicate that the control of industrial NO<sub>x</sub> emissions (alone or combined with reductions of VOCs) contributes to the increment of tropospheric O<sub>3</sub> concentrations, the reduction in the emissions of this primary pollutant is effective in the improvement of air quality related with

ground levels of nitrogen oxides, nitric acid (related with organic nitrogen, that participates in the formation of secondary aerosols) and total reactive nitrogen.

Scenario 5 (D3 with no refinery) deserves a special analysis, since the refinery is responsible for a high percentage of the emissions of primary pollutants ( $\text{NO}_x$ , VOCs,  $\text{SO}_2$  and CO) in the area of Tarragona. The improvement of air quality related to CO and  $\text{SO}_2$  is noticeable; nevertheless, it is also an important source of  $\text{NO}_x$  that, when removed in VOC-limited domains, produces a small increase in tropospheric ozone concentrations.

The study of the different scenarios included in this work indicates that air quality modeling could be a useful tool to evaluate the chemical sensitivity of the system  $\text{O}_3$ - $\text{NO}_x$ -VOCs when establishing policies of emissions controls from different sources. However, we should bear in mind that the regimes of chemical sensitivity vary with the hour of the day, change from event to event and with location within a same domain. The practical implementation of these results is not an easy task, since it involves not only environmental policies, but also socioeconomic parameters that are difficult to quantify. In addition, the impact of different policies in the diverse pollutants magnifies the difficulty of setting global policies.

## 8.6 References

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