10 Conclusions

The model MM5-EMICAT2000-CMAQ represents a potentially powerful tool for analyzing environmental issues related to air quality in very complex terrains, since it is fully flexible to simulate different episodes, with different resolutions and contribution for different emitter sources. The model was successfully applied to an important pollution episode that took place in the entire Western Mediterranean Basin during 13-16 August, 2000. This episode 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, and values over the European threshold of 180 $\mu g\ m^{-3}$ for ground-level O_3 established in Directive 2002/3/EC are attained. The day was characterized by a weak synoptic forcing, so that mesoscale phenomena would be dominant.

MM5-EMICAT2000-CMAQ represents the state-of-the-science of air quality modeling; and their components are highly supported and documented. The results presented constitute a valuable contribution to the use of Models-3/CMAQ in Europe with very high spatial and temporal resolution, because nowadays there is a lack of works and evaluation results for this third generation air quality model outside North America and certain regions of Asia.

Furthermore, MM5-EMICAT2000-CMAQ may set the basis for the forecasting of air quality modeling in the northeastern Iberian Peninsula, and to study future scenarios, such as the modification of land-use, characteristics of on-road traffic, modifications on climate, or requirements of the legislation (both for emissions and ground-level concentrations), just to cite some of the hot spots in current atmospheric research.

It may be stated that the objectives proposed for this Dissertation (indicated in Section 1.4) were achieved, since:

1. The use of the multiscale-nested air quality model MM5-EMICAT2000-CMAQ with a high spatial (1-2km and 16 layers covering the troposphere, with an especial interest in the low troposphere) and temporal (1h) resolution has revealed as a useful tool to assess air quality issues in very complex terrains, as the northeastern Iberian Peninsula, were its complex topography induces an extremely complicated structure of the flow. That phenomenon has important effects in the transport and transformation of pollutants that lead to the necessity of a deep and rigorous analysis of dynamics of photochemical pollutants over the area.

2. The utilization of MM5-EMICAT2000-CMAQ applied to the description of air quality issues over the northeastern Iberian Peninsula represents an useful instrument that can contribute to the optimization in the design of ambient air quality stations in the area of the northeastern

Iberian Peninsula, to the establishment of environmental managing policies and to regulatory purposes according to the actual Directive 2002/3/EC for ozone in ambient air.

10.1 Current Implications of MM5-EMICAT2000-CMAQ

A detailed analysis of results and their conclusions were included for each Chapter. The most important aspects of those conclusions, respect to the contribution of this Dissertation and the implication of MM5-EMICAT2000-CMAQ results are summarized below.

1. A methodology for the comparison and selection of photochemical mechanisms for air quality modeling was developed. The range of concentrations predicted by the box mechanisms show the state-of-the-science in tropospheric chemistry. The conclusions derived from the results indicate that even for the simulation of extremely simple situations, there can be discrepancies in predicted concentrations due to different considerations and parameterizations within the mechanisms. Furthermore, this study shows that such discrepancies are significant in most of the cases and quantifies typical biases among various mechanisms. The CBM-IV mechanism reveals as the mechanism that presents a closer behavior to the average state-of-the-science, with small plain deviations during the entire period of the simulation. In addition, it is the mechanism with a lowest number of chemical reactions, which impacts the computational time needed to solve the chemistry. This issue is important when considering air quality modeling with very high resolution, and therefore, this mechanism was implemented within MM5-EMICAT2000-CMAQ framework to represent tropospheric chemistry.

2. The problems concerning the initialization of MM5-EMICAT2000-CMAQ and the generation of the boundary conditions for the domain of the northeastern Iberian Peninsula were solved by using a multiscale approach, performing simulations in the entire Iberian Peninsula in order to provide the necessary boundaries by one-way nesting procedures. An analysis of the influences of initial conditions and their sensitivity on ozone indicates the necessity of a correct initialization of the model by means of spin-up or start-up procedures. The influence of initial conditions was minimized through a 48 hours spin-up or start-up prior to formal simulations that reduces the impact factor of initial conditions to 10% or less for ozone. However, the influence of boundary conditions is significant to a selected site when the arrival time of boundary condition is short and the species lifetime is longer, as the case of ozone. The importance of modifying ozone or precursors boundaries becomes evident for the whole period of the simulation after the arrival of upwind boundaries and cannot be minimized through spin-up processes. Therefore, the availability of accurate boundary information is essential when performing simulations in very complex terrains as the northeastern Iberian Peninsula. This problem is resolved by including all the sources that have potential effects on the given region; and by applying the nested simulation results of a larger model domain

covering the entire Iberian Peninsula to the boundary conditions of smaller nested simulation domain.

3. Air quality models are very sensitive to the degree of resolution. High horizontal and vertical resolution becomes essential when describing mesoscale phenomena in very complex terrains, since they are very sensitive to the degree of topographical smoothing. Some small-scale features appear when using a resolution of 2-km that cannot be captured with coarser horizontal resolutions. Resolutions of 2km or finer must be applied in order to capture the characteristics of emission patterns, since higher resolutions do not allow a clear definition of emissions cities, on-road traffic and other emitter areas; however, higher resolutions become necessary in order to provide the information needed to perform nested simulations in order to initialize the model in the northeastern Iberian Peninsula. Outputs from the chemical transport model were sensitive to the grid size employed in the simulations, presenting a higher dependence on horizontal grid than on the vertical resolution when simulating O_3; nevertheless, high vertical resolution was found to be as important as horizontal resolution to properly simulate other photochemical pollutants such as NO_x. Therefore, the model should have enough horizontal (2km) and vertical resolution (16 layers) in order to represent correctly the low-troposphere processes throughout the day; and that was the resolution applied in subsequent case studies for the northeastern Iberian Peninsula.

4. The MM5-EMICAT2000-CMAQ model is suitable to be used for regulatory purposes since it meets the performance criteria established both by the Unites States Environmental Protection Agency and the European Directive 2002/3/EC for model evaluations when assessed against ambient measurements from 48 air quality stations located in Catalonia (Spain) for the episode 13-16 August, 2000. The simulations with coarser grids tend to underestimate maximum ozone, carbon monoxide and nitrogen oxides levels with regards to the finer grids. Vertical qualitative evaluation of the regional model with LIDAR profiles obtained over the city of Barcelona (41.361N – 2.181E) indicates that modeled profiles are similar to measurements, accurately capturing the layering of pollutants over this part of the Mediterranean produced during re-circulation processes. The model simulates a realistic ozone gradient between the boundary layer and the free troposphere.

5. The origin of the high levels of photochemical pollutants and their dynamics over the Western Mediterranean Basin, and specifically, over the northeastern Iberian Peninsula, are conditioned by the superposition of circulations of different scale (local, regional and global circulations) that may only be described by the combination of global and regional models, such as ECHAM5/MESSy and MM5-EMICAT2000-CMAQ, respectively. Air masses of the lower troposphere have a local origin mainly due to re-circulation processes (caused by the orographic forcing), which are common in the Western Mediterranean Basin during this kind of synoptic situation. The canalization between the Pyrenees and the Central Massif introduced northwestern flows of Atlantic air masses into the northeastern Iberian Peninsula. The strength of the sea breeze and the complex orography of the eastern Iberian coast

produce several vertical injections and layering of pollutants. The development of the Iberian Thermal Low forces the convergence of surface winds from the coastal areas towards the central plateau injecting polluted air masses aloft. Once in this region, northwesterly winds transport pollutants in a stratified layer in an altitude of 3500m heights towards the northwestern Mediterranean Basin, where they sink as a consequence of the compensatory subsidence. Strong thermally or mechanically driven convections appear at the central plain of the northeastern Iberian Peninsula injecting low-troposphere air masses rich in photochemical pollutants up to middle troposphere (over 3500m). Once the air masses are injected in altitude, they incorporate to the dominant synoptic flux and are transported towards the coast.

6. The occurrence of high ozone concentrations is the result of an imbalance between high local chemical production rates and dry deposition, fundamentally. The contribution of advective transport is limited due to the low baric pressure gradient, and simulations with ECHAM5/MESSy and MM5-EMICAT2000-CMAQ estimate that its contribution to maximum peak ozone levels is in the order of just 2.5-5.0%. The steady increase in chemical production of ozone during the day exceeds vertical convection and dry deposition removal rates and leads to peak ozone concentrations during the mid-afternoon.

7. The method of photochemical indicators was successfully used to evaluate O_3-NO_x-VOCs sensitivity in the northeastern Iberian Peninsula, showing the correlation between photochemical indicators and simulated NO_x-VOCs sensitivity in very complex terrains. The methodology proposed provides a test for sensitivity evaluation. O_3 chemistry in the Barcelona city plume is close to the transition between VOC-sensitive and NO_x-sensitive conditions. Nevertheless, the city and Barcelona and Alcover industrial area present a high VOC-sensitive behavior due to the high traffic and industrial NO_x emissions. NO_x-sensitive chemistry is associated with lower O_3 and NO_y. The variations in the behavior of the indicator are analytically linked to the variations in the O_3 production efficiency per primary radical production. In general, H_2O_2- and HNO_3- derived indicators entail higher uncertainties since transition regimes between NO_x and VOCs sensitivity cover a wide range, because those indicators (and their ratio) are affected by changes in environmental conditions. NO_y and O_3/NO_y are revealed as the most accurate figures to assess sensitivity in the domains studied, attending to the narrow transition regime between NO_x- and VOC-sensitive chemistry and the low uncertainty observed. The results given in this study indicate the necessity to consider the differences in the conditions of the domains when applying the indicator approach.

8. Multiscale-nested air quality models provide a useful tool to set control policies for the emissions of ozone precursors and to analyze their in very complex industrial areas, as the 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, expect in the case of carbon monoxide. Policies leading to reductions in the industrial emissions of nitrogen oxides contribute to a strong increment in hourly maximum concentrations of ground-level ozone; however, the control of industrial NO_x emissions (alone or combined with reductions of VOCs) 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 in the area. Emissions from refineries are responsible for a high percentage of the emissions of primary pollutants (NO_x, VOCs, SO_2 and CO) in the area of Tarragona. The improvement of air quality related to CO and SO_2 is noticeable when removing refinery emissions; nevertheless, it is also an important source of NO_x that, when removed in VOCs-limited domains, produces a slight increment in tropospheric ozone concentrations. The study of different indicates that air quality modeling may be a useful tool to evaluate the chemical sensitivity of the system O_3-NO_x-VOCs and to establish environmental policies of emissions controls in the area.

9. 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. 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. 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. Emissions of NO are greater during the morning on weekdays than on weekends, highly contributing to the ozone quenching effect. Because of this behavior of emissions, a significant weekend increase in ozone weekend concentrations is simulated in coastal urban areas. On the other side, areas downwind the Barcelona Geographical Area reduce or even reverse the weekend effect. Several factors 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. The higher proportional reduction of NO_x at weekends makes O_3-forming photochemistry more active on weekends compared to weekdays.

10.2 Future Implications and Works to Develop

The potential future applications and the improvements to perform in the framework of MM5-EMICAT2000-CMAQ cover a wide range. In addition, the line of research that may be derived from the work compiled in this Dissertation could focus in:

1. The next stage of application of MM5-EMICAT2000-CMAQ may include the interaction existing between the gas-phase chemistry and aerosols. Despite the model has been parameterized in order to represent the heterogeneous chemistry, the problem derives from the implementation of a particulate matter (PM) module into EMICAT2000. The input data needed to represent air quality issues related to particulate matter would be: (1) speciation of the TSP of EMICAT2000 into $PM_{2.5}$ and PM_{10}; (2) addition of the emissions of sulfates, nitrates, ammonia and particle re-suspension; (3) inclusion of marine aerosols; (4) emissions derived from biomass burning; and (5) the characterization and inclusion of external contribution of particles into the domain (e.g. the transport of natural aerosols as Saharan dust outbreaks).

2. The line of research of the Environmental Modeling Laboratory of the Technical University of Catalonia about satellite data information may provide real-information about parameters required by the different submodules of MM5-EMICAT2000-CMAQ (land-use data, solar radiation, albedo, soil temperature, etc.) with a high resolution; information that currently must be interpolated from the limited accessible and spatially restrained data provided from different net of measurements.

3. MM5-EMICAT2000-CMAQ has been fitted to provide a useful tool to analyze future scenarios. The flexibility of the model allows the performance of simulations with new established hypothesis (related to meteorological fields, emission patterns, or new developments in tropospheric chemistry) just by actualizing the input data required by the different submodules. Nowadays, some hot spots in atmospheric research are related to the new environmental policies, implications of new fuels on air pollution, changes of land-uses, etc. In this sense, the coupling of a regional model as MM5-EMICAT2000-CMAQ with global circulations model may provide a useful tool to deepen in the understanding of the interactions chemistry-climate.

4. One of the most far-reaching developments resulting from the enhanced capabilities in air quality modeling is the possibility of performing predictions. The implications derived from the forecasting of air pollution are principally related to public health problems. MM5-EMICAT2000-CMAQ could be implemented, in a further stage of research, to provide a 48-72h forecasting system for air quality over the region of study. The coupling between meteorological, emissions and photochemical processes is full in the framework of MM5-EMICAT2000-CMAQ, and just an automatization of the data acquisition procedures would be needed. The feasibility of having an air-quality forecast system in the Iberian Peninsula comes conditioned mainly because of the limitation of computational resources.