*UNIVERSITAT POLITÈCNICA DE CATALUNYA*
**Programa de Doctorado en Ingeniería Ambiental**


Ph.D. Thesis

# Air Quality Modeling in Very Complex Terrains: Ozone Dynamics in the Northeastern Iberian Peninsula

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*To my parents*
*and aunt*

*"Comparing the air of cities to the air of deserts and arid lands is like*
*comparing waters that are befouled to waters that are fine and pure.*
*In the city, because of the height of its buildings, the narrowness of its streets*
*and all that pours forth from its inhabitants and their superfluities,*
*the air becomes stagnant, turbid, thick, misty, and foggy [...].*
*If there is no choice in this matter, for we have grown up*
*in the cities and have become accustomed to them,*
*you should select from the cities one of open horizons,*
*endeavor at least to dwell at the outskirts of the city.*
*If the air is altered ever so slightly, the state of the*
*Psychic Spirit will be altered perceptibly.*
*Therefore you find many men in whom you can notice defects*
*in the actions of the psyche with the spoilage of the air,*
*namely, that they develop dullness of understanding,*
*failure of intelligence and defect of memory".*

*Moses Maimonides (1135-1204).*

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## *Summary*

The high levels of air pollutants over the northeastern Iberian Peninsula in summer have a strong influence both on ecosystems and human health. The region is particularly sensitive to air pollution by ozone ($O_3$), since its complex topography, that induces an extremely complicated structure of the flow that has important effects in the transport and transformation of pollutants. Despite of its complexity, the utilization of multiscale-nested air quality models has revealed as a useful tool to assess air quality issues in very complex terrains.

The third generation air quality model used to simulate air quality issues in the domain of the northeastern Iberian Peninsula is MM5-EMICAT2000-CMAQ with high spatial (1-2km) and temporal (1h) resolution. The MM5 mesoscale meteorological model was applied to simulate regional-scale atmospheric circulations. EMICAT2000 was developed by Dr. Parra within the Environmental Modeling Laboratory headed by Dr. Baldasano, in order to estimate the emission of primary pollutants in the northeastern Iberian Peninsula; and to provide the basis for work in air quality modeling using chemical transport models. The CMAQ chemical transport model has been configured with different parameterizations in order to analyze their influence in $O_3$ results. After developing a methodology for the comparison and selection of photochemical mechanisms, CBM-IV was implemented in CMAQ, coupling gas-phase and heterogeneous chemistry, since it reveals as the mechanism that presents a closer behavior to the average state-of-the-science.

Modeling was conducted for the photochemical pollution event that took place from 13-16 August, 2000. This episode corresponds to a typical summertime low pressure gradient with high levels of $O_3$ in the Iberian Peninsula that exceed the European threshold of 180 $\mu g\ m^{-3}$ established in Directive 2002/3/EC. The domain of study covers a squared area of 272x272 $km^2$ centered the northeastern Iberian Peninsula.

The problems concerning the initialization of the model and the generation of boundary conditions for the domain were solved by using a multiscale approach, performing simulations in the entire Iberian Peninsula to provide the necessary boundaries by one-way nesting procedures. The influence of initial conditions was minimized through a 48h spin-up prior to formal simulations that reduces their impact factor to lower than 10% for $O_3$.

High resolution becomes essential when describing mesoscale phenomena in very complex terrains. Some small-scale features in low-troposphere processes throughout the day appear when using a horizontal resolution of 2km and 16 vertical layers that cannot be captured with coarser horizontal and vertical resolutions. With this resolution, the MM5-EMICAT2000-CMAQ model is suitable to be used for regulatory purposes since it meets the performance criteria

established both by the USEPA and the Directive 2002/3/EC when assessed against ambient measurements.

The origin of the high levels of air pollutants in the area is conditioned by the superposition of circulations of different scale that may be described by the combination of global and regional models (ECHAM5/MESSy and MM5-EMICAT2000-CMAQ). The occurrence of high $O_3$ levels is the result of an imbalance between high local chemical production rates and dry deposition, fundamentally.

The method of photochemical indicators provides a test for sensitivity evaluation of $O_3$-$NO_x$-VOCs sensitivity in the northeastern Iberian Peninsula, showing the correlation between photochemical indicators and simulated $NO_x$-VOCs chemistry in very complex terrains. Furthermore, MM5-EMICAT2000-CMAQ provides a useful tool to set control policies for the emissions of $O_3$ precursors and to analyze their behavior in very complex industrial areas, as the area of Tarragona, where the $O_3$ chemistry is strongly controlled by the industrial emissions of VOCs.

A day-specific hourly emissions inventory considering day-to-week variations in emissions has been coupled with MM5-CMAQ to conduct a study of the $O_3$ weekend effect. On weekends, traffic from heavy-duty vehicles undergoes a substantial reduction. 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. Because of this behavior, a significant weekend increase in $O_3$ weekend concentrations is simulated in coastal urban areas. The higher proportional reduction of $NO_x$ on weekends makes $O_3$-forming photochemistry more active on weekends compared to weekdays.

Last, it should be highlighted that the utilization of MM5-EMICAT2000-CMAQ applied to the description of air quality issues over the northeastern Iberian Peninsula represents a useful instrument that may contribute to the establishment of environmental managing policies and to regulatory purposes according to the actual Directive 2002/3/EC for $O_3$ in ambient air.

## *Resumen*

Los altos niveles de contaminantes atmosféricos en el nordeste de la Península Ibérica tienen un fuerte impacto tanto en los ecosistemas como en la salud humana. Esta región es particularmente sensible a la contaminación por ozono ($O_3$), debido a su compleja topografía, que induce una estructura del flujo que tiene importantes efectos en el transporte y la transformación de contaminantes fotoquímicos. A pesar de esta complejidad, la utilización de modelos de calidad del aire multiescala y anidados se ha revelado como una herramienta útil a la hora de evaluar fenómenos relacionados con la calidad del aire en terrenos muy complejos.

El modelo de calidad de aire de tercera generación empleado para simular la problemática de contaminación atmosférica en el nordeste de la Península Ibérica es MM5-EMICAT2000-CMAQ, configurado con alta resolución espacial (1-2km) y temporal (1h). El modelo meteorológico de mesoescala MM5 fue aplicado para simular las circulaciones atmosféricas en una escala regional. EMICAT2000 fue desarrollado por el Dr. Parra dentro del Laboratorio de Modelización Ambiental, bajo la dirección del Dr. Baldasano, con el fin de estimar las emisiones de contaminantes primarios en el noreste peninsular; y para proporcionar la información requerida por el modelo de transporte químico CMAQ. Este modelo ha sido configurado con diferentes parametrizaciones para analizar su influencia en los resultados de $O_3$ troposférico. Tras desarrollar una metodología de comparación y selección de mecanismos fotoquímicos, el mecanismo CBM-IV fue implementado en CMAQ para representar la química en fase gas y heterogénea, puesto que este mecanismo presentó un comportamiento medio y representativo del actual estado de los conocimientos en la materia.

El episodio de contaminación fotoquímica seleccionado tuvo lugar entre el 13 y el 16 de agosto del año 2000. Este episodio corresponde a una situación típica de verano de bajo gradiente bárico con altos niveles de $O_3$ en toda la cuenca Mediterránea que sobrepasan el umbral de 180 $\mu g\ m^{-3}$ establecido en la Directiva 2002/3/CE. El dominio de estudio cubre un área de 272x272 $km^2$ centrado en el nordeste de la Península Ibérica.

Los problemas derivados de la inicialización del modelo y de la generación de condiciones de contorno para el dominio se solucionaron empleando una aproximación multiescala, realizando simulaciones para toda la Península Ibérica y suministrando la información al dominio del noreste peninsular a través de procedimientos de anidamiento unidireccionales. La influencia de las condiciones iniciales fue minimizada mediante un *spin-up* de 48 horas previo a las simulaciones reales, que reduce el impacto de las condiciones iniciales a un factor por debajo del 10% en el caso del $O_3$.

La aplicación de una alta resolución resulta esencial a la hora de describir los fenómenos mesoescalares en terrenos muy complejos. Ciertas particularidades de pequeña escala aparecen cuando se usa una resolución horizontal de 2km y 16 capas verticales, que no pueden ser capturadas por resoluciones con menos nivel de detalle. Con la resolución propuesta, el modelo MM5-EMICAT2000-CMAQ puede ser aplicado para usos regulatorios, ya que alcanza los criterios de exactitud establecidos tanto por la USEPA como por la Directiva 2002/3/CE cuando se evalúa frente a datos de estaciones de medida de calidad del aire.

El origen de los altos niveles de contaminación atmosférica en el área de estudio está condicionado por la superposición de circulaciones de diferente escala que pueden ser descritos por la combinación de modelos globales y regionales, como ECHAM5/MESSy y MM5-EMICAT2000-CMAQ, respectivamente. La presencia de niveles altos de $O_3$ es el resultado de las interacciones de diferentes procesos en los que domina la fotoquímica local y la deposición seca, fundamentalmente.

El método de los indicadores fotoquímicos presentado proporciona un test para la evaluación de la sensibilidad del sistema $O_3$-$NO_x$-COVs en el noreste de la Península, mostrando la correlación entre indicadores fotoquímicos y la química de $NO_x$ y COVs en terrenos muy complejos. Adicionalmente, MM5-EMICAT2000-CMAQ es una herramienta útil a la hora de establecer políticas de control de emisión de precursores de $O_3$ y para analizar su comportamiento en áreas industriales muy complejas como es el caso de Tarragona, donde la química de $O_3$ está fuertemente controlada por las emisiones industriales de COVs.

Con el fin de estudiar el efecto fin de semana, se acopló a MM5-CMAQ un inventario de emisiones considerando diferencias entre los distintos días de la semana. Durante los fines de semana, las emisiones de vehículos pesados experimentan una reducción substancial. El retraso de 1-2 horas en los picos de las emisiones de precursores en los fines de semana produce que se genere $O_3$ más eficientemente que con las emisiones de $NO_x$ durante los días de semana laborables. Debido a este comportamiento, un importante incremento en los niveles de $O_3$ es simulado y observado en las zonas costeras urbanas. La mayor reducción proporcional de $NO_x$ durante los fines de semana hace que el potencial de formación de $O_3$ sea más activo en los fines de semana comparado con los días laborables.

Por último, cabe destacar que la aplicación de MM5-EMICAT2000-CMAQ a la descripción de la problemática de calidad del aire sobre el nordeste de la Península Ibérica representa un instrumento que puede contribuir a establecer políticas de gestión ambiental y legislativas dentro del marco de la actual Directiva 2002/3/CE para $O_3$ en aire ambiente.

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