Modelització i simulació fotoquímica mesoscalar del transport del material particulat i gasos a l'atmosfera

Raúl Arasa Agudo

Modelització i simulació fotoquímica mesoscalar del transport del material particulat i gasos a l'atmosfera

Memòria realitzada per Raúl Arasa Agudo per optar al grau de Doctor en Ciències Físiques.

Programa de Doctorat: Meteorologia (2007-2011)

Barcelona, Juny de 2011

Doctorand:

Raúl Arasa Agudo

Directora:

Dra. Maria Rosa Soler Duffour

Departament d'Astronomia i Meteorologia
Universitat de Barcelona

UNIVERSITAT DE BARCELONA

ANNEX 2: Articles publicats en revistes amb revisió per experts

A continuació es reprodueixen els articles publicats o en fase de publicació on el doctorand és primer autor:

A performance evaluation of the MM5/MNEQA/CMAQ air quality model to forecast ozone concentrations in Catalonia area. Tethys, 7, 11-22.

Numerical experiments to determine MM5/WRF-CMAQ sensitivty to various PBL and land-surface schemes in North-eastern Spain: application to a case study in summer 2009. International Journal of Environmental Pollution. In Press.

Evaluation of MM5-MNEQA-CMAQ air quality modelling system and bias-adjustment techniques to forecast ozone concentrations: application to the norteastern Spain during summers 2009 and 2010. Enviat a Science of the Total Environment.

Tethys
Journal of Mediterranean Meteorology & Climatology

Tethys 2010, **7**, 11–23
www.tethys.cat
ISSN-1697-1523
eISSN-1139-3394
DOI:10.3369/tethys.2010.7.02
Journal edited by **ACAM**

A performance evaluation of MM5/MNEQA/CMAQ air quality modelling system to forecast ozone concentrations in Catalonia

R. Arasa[1], M. R. Soler[1], S. Ortega[2], M. Olid[1] and M. Merino[1]

[1]Department of Astronomy and Meteorology, Universitat de Barcelona, Avinguda Diagonal 647, 08028 Barcelona
[2]Department of Physics and Nuclear Engineering, Universitat Politècnica de Catalunya, C/ Urgell 187, 08036 Barcelona

Received: 27-V-2009 – Accepted: 2-XII-2009 – **Original version**

Correspondence to: rosa@am.ub.es

Abstract

We examine the ability of a modelling system to forecast the formation and transport of ozone over Catalonia, at the NE of the Iberian Peninsula. To this end, the Community Multiscale Air Quality (CMAQ) modelling system developed by the United States Environmental Protection Agency (US EPA) and the PSU/NCAR mesoscale modelling system MM5 are coupled to a new emission model, the Numerical Emission Model for Air Quality (MNEQA). The outputs of the modelling system for the period from May to October 2008 are compared with ozone measurements at selected air-monitoring stations belonging to the Catalan Government. Results indicate a good behaviour of the model in reproducing diurnal ozone concentrations, as statistical values fall within the EPA and EU regulatory frameworks.

Key words: air quality modelling, meteorological modelling, CMAQ, ozone, evaluation

1 Introduction

As a result of combined emissions of nitrogen oxides and organic compounds, large amounts of ozone are found in the planetary boundary layer. Tropospheric ozone is considered one of the worst pollutants in the lower troposphere. At high concentrations ozone is toxic to plants and reduces crop yield (Guderian et al., 1985; Hewit et al., 1990; Zunckel et al., 2006). Sitch et al. (2007) suggest that the effects on plants of indirect radiative forcing by ozone could contribute more to global warming than the direct radiative forcing due to tropospheric ozone increases. Ozone is a respiratory irritant to humans, and it damages both natural and man-made materials such as stone, brick-work and rubber (Serrano et al., 1993). All these harmful effects are significant in Southern Europe (Silibello et al., 1998; Grossi et al., 2000; San José et al., 2005) as in summer solar radiation exacerbates the effects of ozone. This is the case in areas of northern Spain located near urban and industrial areas, and especially those lying downwind of such areas, where local ozone precursors are lacking (Soler et al., 2004; Aguirre-Basurko et al., 2006). Consequently, the environmental benefits of monitoring, quantifying, modelling and forecasting the dose and exposure of the human population, vegetation and material to ozone is an essential precondition to assessing the scale of ozone impacts and developing control strategies (Brankov et al., 2003).

In the last three decades, significant progress has been made in air-quality modelling systems. The simple Gaussian and box models have evolved into statistical models (Schlink et al., 2006; Abdul-Wahab et al., 2005) and Eulerian-grid models (Hurley et al., 2005; Sokhi et al., 2006). These latter represent the most sophisticated class of atmospheric models and they are most often used for problems that are too complex to solve by simple models. With continuing advances, Eulerian-grid modelling is increasingly used in research settings to assess air and health impacts of future emission scenarios (Mauzerall et al., 2005). Air-quality Eulerian models have become a useful tool for managing and assessing photochemical pollution and represent a complement that could reduce the often costly activity of air-quality monitoring.

Modelling, however, suffers from a number of limitations. Models require extensive input data on emissions and meteorology, which are not always reliable or easy to acquire. The ability of models to represent the real world

Figure 1. Location of Catalonia (left) and main geographical features (right).

is limited by many factors, including spatial resolution and process descriptions. As models remain uncertain in their predictions, extensive validation is required before they can be used and relied upon (Denby et al., 2008).

In an attempt to meet these requirements, various studies have been performed in several areas (Hogrefe et al., 2001; Zhang et al., 2006a, 2006b). Millan et al. (2000) and Gangoiti et al. (2001) studied the photo-oxidant dynamics in the North-western part of the Mediterranean area. In addition, for North-eastern Spain, several studies have evaluated the performance of the model MM5-EMICAT2000-CMAQ. This was done using a range of horizontal resolutions, comparing different photochemical mechanisms, or testing the ability of the model to predict high ozone concentrations during typical summer episodes (Jiménez et al., 2006a; Jimenez et al., 2003; Jiménez et al., 2006b).

We now report the validation of a new mesoscale air-quality modelling system. Although it is applied to the same area using the same meteorological and photochemical models, MM5 and CMAQ like in previous studies, the validation covers a longer period (6 months) and basically the system uses a new emission model MNEQA. This consists of a highly disaggregated emission inventory of gaseous pollutants and particulate matter (Ortega et al., 2009). Simulations using this new air quality system are evaluated using a network of 48 air quality stations.

A description of the modelling system MM5/MNEQA/CMAQ is presented in section 2 while the statistical air-quality model evaluation against measurements is presented in section 3. Finally, some conclusions are reported in section 4.

2 Modelling system

2.1 Area under estudy

The area of study is Catalonia, in North-East Spain. The population of Catalonia recently reached seven million, most of them living in and around the city of Barcelona. Catalonia is a Mediterranean area with complex topography. It is bounded by the Pyrenees to the North and by the Mediterranean Sea to the South and East. The territory, from a geographic point of view, can be divided into three distinct areas. One area runs more or less parallel to the coastline and includes the coastal plain, the coastal mountain range and the pre-coastal depression. The second area is called the central depression; and the third area includes the Pyrenean foothills and the Pyrenees proper. The main industrial areas and most of the population are located on the coast. In summer, there are high ozone concentration episodes inland, sometimes in rural areas, owing to the advection of pollutants by the sea-breeze, which brings them from the coast to the rural territory inland.

2.2 Meteorological model

The PSU/NCAR mesoscale model, MM5 (Grell et al., 1994), version 3.7, is used to generate meteorological fields. These have been the input for the air-quality modelling system. Meteorological simulations are performed for two two-way nested domains (Figure 2) with resolutions of 27 km, and 9 km. The coarse domain covers southern Europe, including Spain, half of France and northern Italy and an inner domain of 30×30 cells covers Catalonia.

Initial and boundary conditions for domain D1 are updated every six hours with analysis data from the European Centre of Medium-range Weather Forecast global model

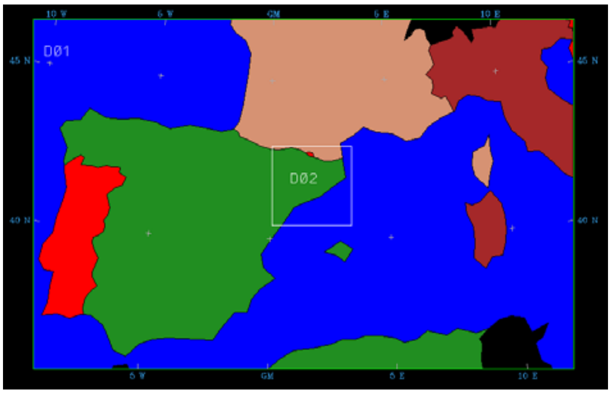


Figure 2. Model domains.

(ECMWF) with a 0.5° × 0.5° resolution. The boundary layer processes are calculated using the MRF scheme based on Troen and Mahrt (1986); the Grell scheme (Grell, 1993) is used for cumulus parameterization, while the microphysics is parameterized using the Schultz scheme (Schultz, 1995). For the land surface scheme, the five-layer soil model is activated in which the temperature is predicted using the vertical diffusion equation for the 0.01, 0.02, 0.04, 0.08, and 0.16 m layers from the surface, with the assumption of fixed substrate (Dudhia, 1996). Solar radiation is parameterized by using the cloud-radiation scheme (Dudhia et al., 2004). The vertical resolution includes 32 levels, 20 below 1500 m approximately, with the first level at approximately 15 m and domain top at about 100 hPa. The distribution of the vertical layers, higher resolution in the lower levels, is a common practice (Zhang et al., 2006a, 2006b; Bravo et al., 2008). MM5 hourly outputs files are processed with the Meteorology-Chemistry Interface Processor (MCIP) version 3.2 for CMAQ model.

2.3 Photochemical model

The chemical transport model used is the U.S. EPA model-3/CMAQ model (Byung and Ching, 1999). This model, supported by the U.S. Environmental Protection Agency (EPA), is continuously being developed. The CMAQ v4.6 simulations utilizes the CB-05 chemical mechanism and associated EBI solver (Yarwood et al., 2005), including the gas-phase reactions involving N_2O_5 and H_2O, and it removes obsolete mechanism combinations (e.g. gas+aerosols w/o). In addition to these changes, the 4.6 version includes different modifications in the aerosol module (AERO4). Additional details regarding the latest release of CMAQ can be found at the website of the Community Modelling and Analysis System (CMAS) center (http://www.cmascenter.org/help).

CMAQ model uses the same model configuration as the MM5 simulation. Boundary conditions and initialization values for domain D1 come from a vertical profile supplied by CMAQ itself, while boundary and initial conditions for domain D2 are supplied by domain D1. The model is executed taking the first 24 h as spin-up time.

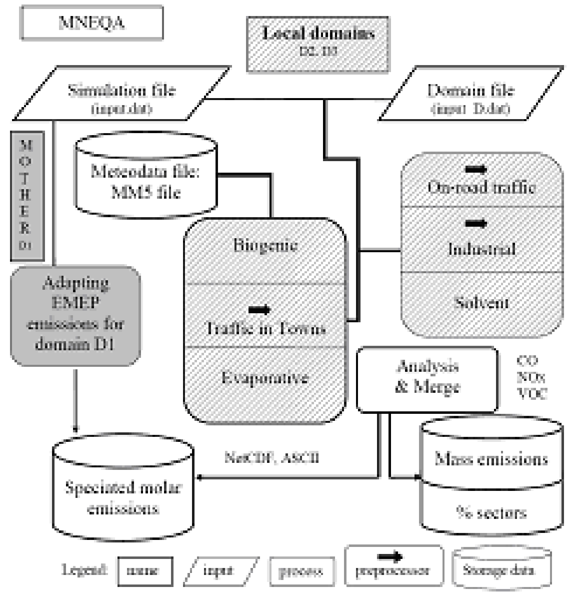


Figure 3. Flow diagram for MNEQA model. Grey is for modules in the mother domain, D1. Shading identifies modules in local domain and solid black arrows symbolize preprocessors. From Ortega et al. (2009).

2.4 MNEQA Emission model

MNEQA is an emission model developed by the authors (Ortega et al., 2009). As it is a critical part of the air quality modelling system, in this section we present a general overview and an outline of the differences in the methodology applied to D1 and D2 domains.

2.4.1 General overview

Nested domains are commonly applied to air quality modelling systems because the constituent meteorological, emission and photochemistry models must deal with grid variability and various domain ranges. As a result of the variability in spatial resolution, MNEQA methodology differs from one domain to another. The main differences between the domains are grid resolution and total range covered in one or more countries. Although the same degree of emissions description is desirable for all domains, information on emission sources and anthropogenic activities is not detailed enough or available in all jurisdictions. Nevertheless, the European Union has taken some action in this regard: it has developed the European Pollutant Emission Register (EPER http://eper.ec.europa.eu) for the reporting years 2001 and 2004, and the Pollutant Release and Transfer Registers (PRTR) for 2007.

Due to the difficulty in recording the data required by an emissions model for a very large domain, the methodol-

Table 1. Quantitative performance statistics for ozone concentration prediction, using 9 km grid domain.

Statistical parameter	Mathematical definition
Mean bias (MB)	$MB = \frac{1}{N}\sum_1^N (C_m - C_0)$
Mean normalized bias error (MNBE)	$MNBE = \frac{1}{N}\sum_1^N \left(\frac{C_m - C_0}{C_0}\right) \cdot 100\%$
Mean fractionalized bias (MFB)	$MFB = \frac{1}{N}\sum_1^N \left[\frac{C_m - C_0}{\left(\frac{C_m + C_0}{2}\right)}\right] \cdot 100\%$
Mean absolute gross error (MAGE)	$MAGE = \frac{1}{N}\sum_1^N \lvert C_m - C_0 \rvert$
Mean normalized gross error (MNGE)	$MNGE = \frac{1}{N}\sum_1^N \left(\frac{\lvert C_m - C_0\rvert}{C_0}\right) \cdot 100\%$
Normalized mean error (NME)	$NME = \frac{\sum_1^N \lvert C_m - C_0\rvert}{\sum_1^N C_0} \cdot 100\%$
Normalized mean bias (NMB)	$NMB = \frac{\sum_1^N (C_m - C_0)}{\sum_1^N C_0} \cdot 100\%$
Root mean square error (RMSE)	$RMSE = \sqrt{\frac{1}{N}\sum_1^N (C_m - C_0)^2}$
Unpaired peak prediction accuracy (UPA)	$UPA = \frac{C_m(max) - C_0(max)}{C_0(max)} \cdot 100\%$

ogy applied in the mother domain (D1) is top-down, while that applied in the inner domain (D2) is mainly bottom-up. A modular structure was developed to take into account the characteristics of every emission source. Figure 3 shows the MNEQA flow chart and its structure. The module for D1 adapts EMEP emissions (Vestreng et al., 2006) for time and space resolutions in D1. A simulation file provides general information about the simulation period to the D1 module and also to D2 (striped in Figure 3). Domain files with the description of the grid of the domain being simulated are fed to the modules. Some modules (such as: Biogenic, Traffic in Towns and Evaporative) require a meteorological data file because the emissions depend on meteorological parameters such as temperature and radiation. Preprocessors (solid black arrows in Figure 3) are available for the following modules: Traffic in Towns, Industrial and On-road Traffic. Finally, the module Analysis and Merge creates outputs (in ASCII and NetCDF formats) from MNEQA simulations: speciated molar emissions, as required by CMAQ; mass emissions for CO, NOx and VOCs and particulate matter; and mass percentage of the contribution to total emissions from every emissions module.

MNEQA uses the output from a meteorological model to calculate temperature and radiation data. Finally, the compound emissions are classified into the species used in the photochemical mechanism: MNEQA does the speciation for CB-05.

2.4.2 Emissions in D1 domain

MNEQA uses a simple top-down methodology based on emissions data from the EMEP (May, 2007) expert emissions inventory (Vestreng et al., 2006). Europe and a small section of North Africa are covered by the EMEP domain, with a 50 × 50 km^2 grid resolution. Emissions are computed from national data on 11 sectors, five main pollutants (CO, NH_3, NMVOC, NOx, SOx) and two types of particulate matter (PM 2.5 and PM coarse). The available emissions data cover a period of several years. The algorithm consisted of assigning to each mother domain cell the emissions value of the nearest EMEP cell, multiplied by a proportional factor. This factor represents the ratio between the number of D1 cells and the number of EMEP domain cells intersecting within D1.

Speciation is computed using profiles from the California Air Resources Board (CARB) website (http://arb.ca.gov/ei/speciate/dnldopt.htm#specprof). Monthly and weekly profiles (Parra, 2004) have been applied to determine an emissions value for each hour based on the day of the week and the month of the year.

2.4.3 Emissions in D2 domain

In the case of the local domain, we have used a bottom-up approach for biogenic, traffic, residential consumption and industrial emissions. Taking various geometrical characteristics into account, we distinguished between surface, linear and point sources. These geometrical characteristics

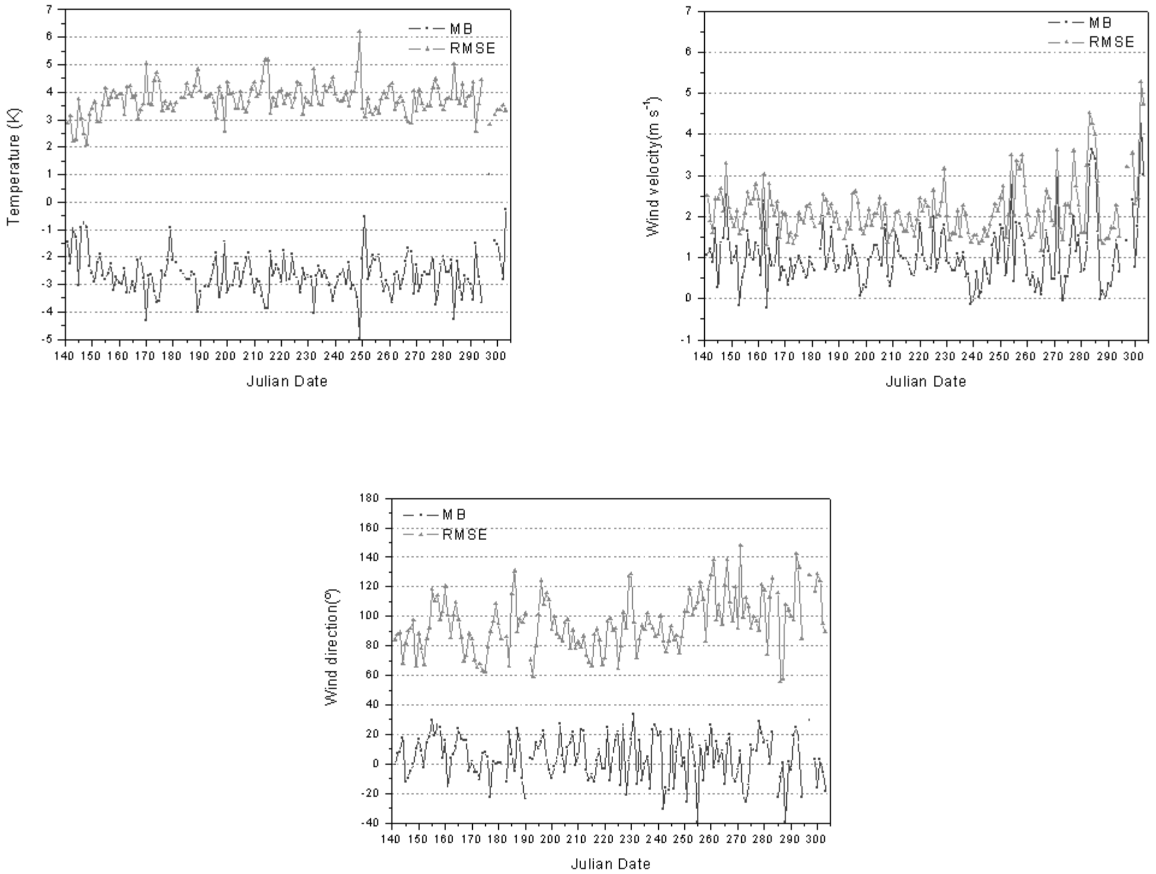


Figure 4. Evolution, for the period studied, of the daily MB and RMSE. (a) (top left) corresponds to air temperature at 1.5 m (a.g.l.); (b) (top right) corresponds to wind velocity measured at 10 m (a.g.l.) and (c) corresponds to wind direction measured at 10 m (a.g.l.).

are reflected in our calculations using a geographical information system (GIS). Finally, the emissions are merged for every grid cell because the photochemical model does not distinguish between the various types of sources; all that is required is one emissions value for each grid cell, each time step and each compound.

2.4.4 Air quality model configuration

In this section, the characteristics of the configuration used in the simulations performed with the air quality model are described. The domain D1 has a horizontal grid resolution of 27 km and the inner domain, D2, 9 km. D1 has an extension of 68×44 grid cells centred at latitude 41.42°N and longitude 1.40°E. D2 has its bottom left corner at D1 (31, 19) with 30×30 grid cells. The total number of vertical model levels is 30 for all domains, up to 100 Pa. Because the photochemical model requires boundary data, the data domains have fewer cells at each horizontal boundary. For that reason, MNEQA and CMAQ are performed in D1 with 66×42 grid cells and in D2 with 28×28 grid cells One-hour time step resolution is used in all domains and models.

3 Statistical air-quality model evaluations against measurements

As an air quality model is a conjunction of three models, meteorological, photochemical and emission, and since the latter has already been compared with other emission models (Ortega et al., 2009), in this section the results of the MM5 meteorological model and CMAQ photochemical model will be evaluated.

3.1 Evaluation of meteorological fields

Modelling results have been evaluated from a set of different surface meteorological stations distributed over Catalonia belonging to the Catalonia Meteorological Service. The evaluation includes wind velocity and wind direction measured at 10 m above ground level (a.g.l.) and air tempera-

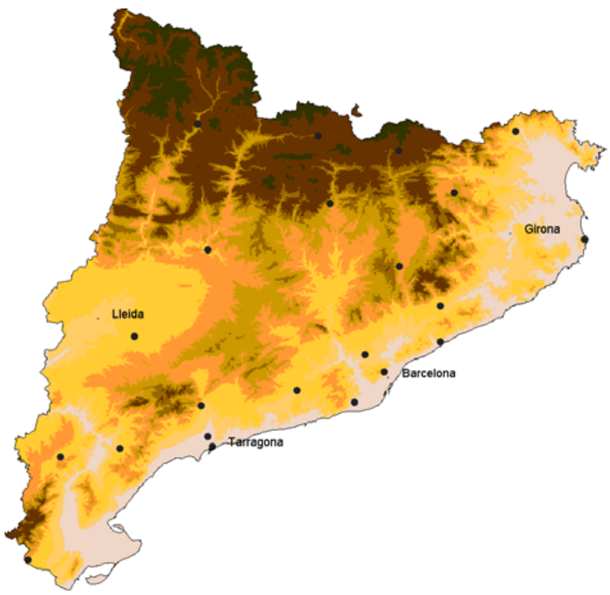


Figure 5. Topographical features of the studied area and the location of the 22 air-quality stations (•) used.

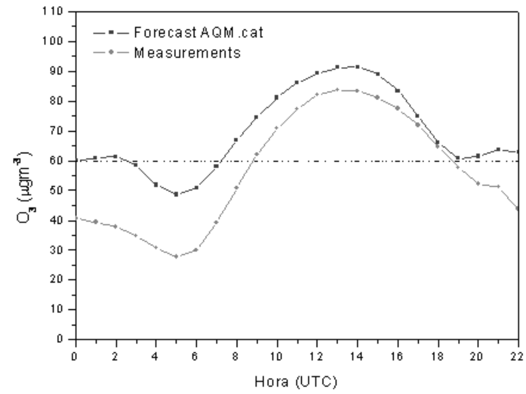


Figure 6. Time evolution of averaged hourly ozone concentrations provided by the air-quality model and the 48 air-quality stations for the studied period.

ture at 1.5 m (a.g.l.). The root mean square error (RMSE) and mean bias (MB) for these meteorological parameters have been calculated for hourly data provided by the model and observations (see Table 1 for definition), obtaining a daily statistical value. Wind statistics and wind direction are calculated for wind velocity higher than 0.5 m s^{-1}, as wind direction is not reliable for lower velocities. The computation of statistical parameters is straightforward for wind velocity and temperature, but the circular nature of wind direction makes it difficult to obtain the corresponding statistics. To avoid this problem we have used a modified wind direction, wherein 360° was either added to or subtracted from the predicted value to minimize the absolute difference between the observed and predicted wind directions (Lee and Fernando, 2004). For example, if the prediction is 10° and the corresponding observation is 340°, then a predicted value of 370° is used.

Figure 4 shows the evolution of the RMSE and MB of the wind velocity, wind direction and temperature for the studied period. Wind speed (Figure 4a) points out an RMSE delimited between 1 and 3 m s^{-1} and an MB between 0 to 2 m s^{-1} during most of the period, from May to the middle of September, from this point until the end of the period, RMSE increases to 4 m s^{-1} and MB to 3.5 m s^{-1}. The first period is mainly characterized by anticyclonic situation with small pressure gradients favouring the development of mesoscale circulations such as the sea breeze regime in the coast and mountain winds inland. Wind velocity associated with these circulation patterns is reproduced quite well by the model, although it tends to slightly underestimate wind velocity during the day and overestimate it at night. The model does not accurately reproduce very weak winds (Bravo et al., 2008), typical of the area studied at night. This causes the positive MB value during all period. During the second period, the meteorological situation has been much more variable led by synoptic scale given rise to higher MB and RMSE values.

Figure 4b shows the evolution of the RMSE and MB for wind direction. The RMSE ranges between 60° to 120° for the first period, while during the second period limits vary between 80° and 140°. MB values range from 20° to -20° with highest deviation during the second period.

The evolution of the RMSE and MB for air temperature is presented in Figure 4c. For most of the period studied, RMSE ranges between 3 and 4 degrees, while the MB ranges between -2 and -4 degrees. These values highlight the tendency to underestimate the air temperature at 1.5 m (a.g.l.).

The performance of the meteorological model agrees with several previous studies of meteorological applications for air quality modelling (Zhang et al., 2006a), especially those based on the area of study, (Jiménez et al., 2008; Jiménez et al., 2006a) where the classical statistics for surface fields have been reported (e.g., temperature, wind speed range from 1 to 4 degrees and 2 to 4 m s^{-1}). However, our statistical evaluation shows a slightly greater dispersion, mainly for wind direction. The main reason could be the horizontal resolution, as meteorological studies over complex terrains require more horizontal and vertical resolution for resolving complex mesoscale circulation patterns (Jiménez et al., 2006a).

3.2 Evaluation of the photochemical model

Statistical metrics for photochemical model performance assessment are calculated for surface ozone concentrations at 48 measurement sites in the 9 × 9 km^2 modelling domain. Although there is a newer guideline for

Table 2. Summary statistics corresponding to selected air quality stations associated with air-quality simulations of hourly and maximum 1-h and 8-h ozone average concentrations for the studied period.

Statistic	Hourly averaged (00 to 24 UTC)	Hourly averaged for ozone concentrations $\geq 60\ \mu g\ m^{-3}$	1-h max. concentration for ozone concentrations $\geq 60\ \mu g\ m^{-3}$	8-h max. concentration for ozone concentrations $\geq 60\ \mu g\ m^{-3}$
MB ($\mu g\ m^{-3}$)	1.35	-1.90	-2.34	-0.83
MAGE ($\mu g\ m^{-3}$)	31.21	16.47	14.72	11.96
MNBE (%)	6.90	-0.41	0.11	1.12
MNGE (%)	41.98	19.95	14.66	13.31
MFB (%)	-2.52	-4.61	-1.67	-0.48
RMSE ($\mu g\ m^{-3}$)	29.97	21.75	19.38	16.10
NMB (%)	0.93	-2.21	-2.42	-1.00
NME (%)	21.52	19.18	15.22	14.48
UPA (%): 11.5				

evaluating model performance, US EPA (2007), in this study we have used US EPA (2005), as the new guideline does not include range quantification in the statistical metrics. The three multi-site metrics used are the unpaired peak prediction peak accuracy (UPA), the mean normalized bias error (MNBE) and the mean normalized gross error (MNGE). As well as the general guidance and protocols for air-quality performance evaluation (Seigneur et al., 2000), new statistical metrics based on the concept of factors for overcoming the limitations of the traditional measurements are calculated. These statistics are summarized in Table 1.

For the evaluation, hourly measurements of ozone concentration from 20 May to the end of October 2008 (hereafter "studied period") are reported by 48 air-quality surface stations named XVPCA (*Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica*) belonging to the Environmental Department of the Catalan Government This network of stations covers the size of the area with an accurate territorial distribution. However, given the grid cell resolution, 9×9 Km^2, not all measurement stations satisfy the criterion for being representative of the area in which it is located. That is, if the grid cell is representative of a rural area, the measurement station cannot be located in the main town as its measurements will be representative of an urban area. Using this criterion, the validation is performed with only 22 representative stations (see Figure 5 and Table 3).

In addition to the previous metrics, the US Environmental Protection Agency (US EPA, 2005) developed a guideline indicating that it is inappropriate to establish a rigid criterion for model acceptance or rejection (i.e. no pass/fail test). However, building on past ozone modelling applications (US EPA, 1991) common values ranges for bias, error and accuracy have been established. The accepted criteria are MNBE, ± 5 to $\pm 15\%$; MNGE, +30 to +35%; UPA ± 15 to $\pm 20\%$. For the entire period studied, the results in Table 2 show averages of the statistics metrics for hourly surface concentrations, daily peak 1-h values and daily peak 8-h ozone concentrations.

For hourly averaged ozone concentrations, results indicate that the model shows a slight tendency to overestimate ground level ozone concentration (Table 2), as MB, MNBE and NMB values are positive, and although MNBE is within the EPA recommended performance goal of $\pm 15\%$, the MNGE value is higher than the accepted criterion (35%). This behaviour of 24-h average ozone concentrations is probably due to the excessive contribution of ozone concentrations during the night forecasted by the model.

The three main sources of error could be: (i) the model does not represent nocturnal physicochemical processes accurately enough (Jiménez et al., 2006b); (ii) the emission model may not calculate night-time emissions properly; (iii) meteorological parameters, such as wind velocity, wind direction and vertical mixing are not well reproduced by the model when the synoptic forcing is weak and the ambient winds are light and variable (Schürmann et al., 2009; Bravo et al., 2008).

As shown in Figure 6, the model overestimates ozone concentrations at night. To solve this problem, model evaluation statistics are often calculated using only the hourly observation-prediction pairs for which the observed concentration is greater than a specific value. This procedure removes the influence of low concentrations, such as night-time values. Various cutoff values have been used for this purpose; however, 60 $\mu g\ m^{-3}$ is frequently employed and is in accordance with EPA practice (US EPA, 1991; Sistla et al., 1996). When we apply this restriction, MNGE decreases to 19.95%, which is below the EPA's recommended performance goal of 35%, although the model tends to underestimate ozone mixing ratios, as MB, NMB, MFB and MNBE are -1.90 $\mu g\ m^{-3}$, -2.21%, -4.61% and -0.41% respectively. For 1-h maximum concentration using the same restriction, the model tends to underestimate (albeit not in all 22 stations) the maximum value, as MB is -2.34 $\mu g\ m^{-3}$, NMB is -2.42%, MFB is -1.67% and MNBE is 0.11%. In addition, MNGE is 14.66%, therefore all values are within the regulatory framework. For 8-h maximum concentration, the model behaviour is similar as MB is -0.83 $\mu g\ m^{-3}$,

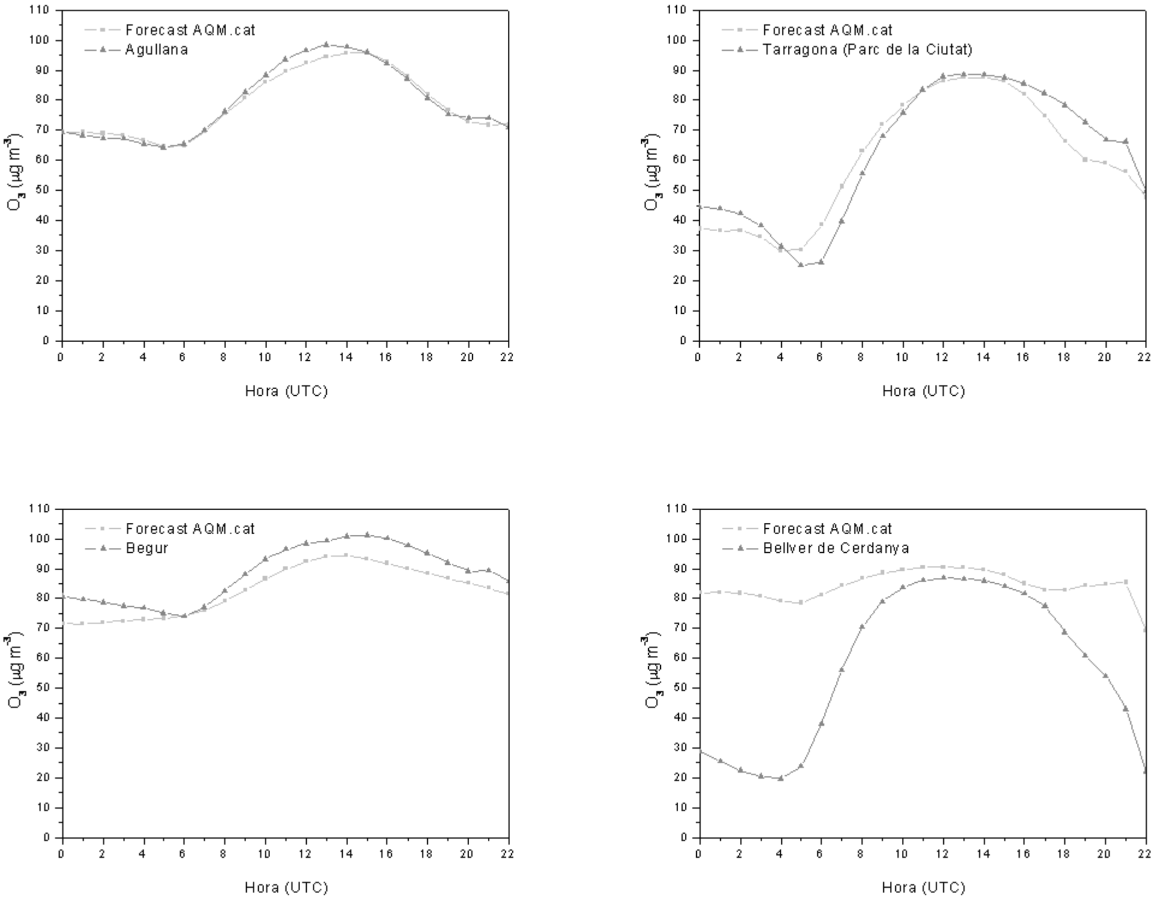


Figure 7. Time evolution of averaged hourly ozone concentrations provided by the air-quality model and some selected air-quality stations for the studied period.

MNBE is 1.12%, NMB is -1.0%, MFB is -0.48% and MNGE is 13.31%. Small positive values for MNBE, corresponding to 1-h and 8-h maximum ozone concentrations, indicate that in some stations the ratio between modelled and observed ozone concentrations is slightly higher than the unity therefore, in these locations, the modelling system overestimates ozone concentrations. The UPA value calculated as the difference between the highest observed value and highest predicted value over all hours and monitoring stations over the entire period is 11.5%, which meets the EPA's $\pm 20\%$ goal. In addition, if daily UPA values are calculated, results indicate that almost all values of this statistic (81%) are well within the EPA criteria for an acceptable model performance. As a summary of Table 2 we conclude that the model shows a slight tendency to underestimate ozone concentrations, as when we applied a reference threshold in order to avoid nocturnal values, some statistics become negative. The information provided in Table 2 is extended to each monitoring station used in this study (Table 3). In addition, some examples of time evolution of averaged hourly ozone concentrations provided by the air-quality model and selected air-quality stations are presented in Figure 7. This additional information confirms the results and conclusion derived from Table 2. The performance of the photochemical model agrees with several previous results on air quality modelling in the studied area, (Jiménez et al., 2008; Jiménez et al., 2006a), where statistical values also are within the EPA criteria.

As well as the statistical validation, unsystematic and systematic root mean square error, RMSE_u (1) and RMSE_s (2), are computed in order to evaluate the intrinsic error in the model and the random error (Appel et al., 2007).

$$RMSE_u = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(C - C_m)^2} \quad (1)$$

$$RMSE_s = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(C - C_0)^2} \quad (2)$$

Table 3. Statistics corresponding to selected air quality stations associated with air-quality simulations of hourly averaged for ozone concentrations $\geq 60\ \mu g\ m^{-3}$.

Station	MB ($\mu g\ m^{-3}$)	MNBE (%)	MFB (%)	MAGE ($\mu g\ m^{-3}$)	MNGE (%)	NME (%)	NMB (%)	RMSE ($\mu g\ m^{-3}$)
Constantí	-2.92	-2.74	-4.47	7.09	8.28	20.12	-8.28	14.12
Pardines	0.95	3.22	1.69	9.84	11.61	14.65	1.41	14.42
Agullana	-5.70	-5.10	-7.19	12.23	13.58	17.26	-8.05	17.63
Juneda	-0.23	0.87	-0.20	6.73	7.98	15.34	-0.52	12.42
Sort	0.98	2.28	1.19	6.05	7.51	14.29	2.31	11.13
S. M. Palautordera	-0.68	-0.14	-1.43	7.04	7.74	16.99	-1.65	14.11
Begur	-7.85	-5.90	-8.53	15.51	16.08	18.69	-9.46	21.51
Santa Pau	0.06	1.20	0.07	6.76	7.69	16.68	0.16	12.94
Gandesa	0.19	1.69	0.32	9.16	11.11	14.41	0.29	13.54
Bellver de C.	1.62	3.09	2.00	6.07	7.59	14.64	3.90	11.27
Ponts	-0.45	0.79	-0.19	6.48	7.23	13.97	-0.97	11.96
La Sénia	1.26	3.09	1.63	9.35	11.70	14.05	1.89	13.30
Tarragona - Ciutat	-5.55	-5.92	-9.02	9.69	11.39	20.34	-11.66	18.06
Rubí	-9.78	-11.31	-17.36	12.45	14.72	33.10	-26.00	23.37
Tona	1.12	2.40	0.89	7.72	9.07	18.18	2.64	14.15
Alcover	3.09	4.62	3.04	6.73	9.16	21.66	9.94	13.24
Guiamets	0.04	1.16	-0.24	8.33	10.16	14.04	0.07	12.97
Berga	1.40	3.06	1.79	7.45	8.89	15.58	2.93	13.00
Vilafranca del P.	-4.95	-5.14	-7.21	8.79	9.99	19.15	-10.80	15.85
Mataró	-5.30	-5.27	-7.79	10.04	11.64	20.60	-10.87	17.67
Gavà	-7.29	-7.60	-10.63	10.11	11.29	22.86	-16.47	18.48
Barcelona - V. H.	-12.52	-14.61	-21.96	15.52	18.34	31.33	-25.26	25.94

$$C = a + bC_0 \quad (3)$$

$$RMSE_s = \sqrt{(RMSE_u)^2 + (RMSE_s)^2} \quad (4)$$

C_m and C_0 values are modelled and observed concentrations, respectively; a and b are the least-squares regression coefficients derived from the linear regression between C_m and C_0; and N is the total number of model/observation pairs.

These new measurements help to identify the sources or types of error, which can be of considerable help in refining a model. The RMSE$_s$ represents the portion of the error that is attributable to systematic model errors; and the RMSE$_u$ represents random errors in the model or model inputs that are less easily addressed. For a good model, the unsystematic portion of the RMSE must be much larger than the systematic portion, whereas a high systematic RMSE$_s$ value indicates a poor model.

Results are given in Tables 4 and 5 for each month analyzed (June-September 2008). May and October are not included, as the evaluation began on May 19 and twelve days are not representative, while during October there were several gaps.

For the case studied, results for 1-h and 8-h peak ozone concentrations show that systematic error values are lower than unsystematic ones, except for September and June, respectively. However, errors are similar, which implies that the air-quality system still has to be improved and refined. To analyze these results better, we should plan to carry out an expanded detailed analysis identifying the key factors that influence these prediction biases, such as sensitivity to synoptic conditions, to the boundary layer scheme used in the MM5 meteorological model, to the boundary conditions prescribed and to the chemical mechanisms used in CMAQ model.

3.3 Modelling quality objectives for ozone "Uncertainty" defined by directive EC/2008/50

In 2008 a new European air quality directive was ratified by the European parliament (EC 2008). This directive replaced earlier directives with the intention of simplifying and streamlining reporting, as well as the introduction of new limit values concerning PM2.5. Whilst previous directives had based assessments and reporting largely on measurement data, this new directive places more emphasis on the use of models to assess air quality within zones and agglomerations. The increased focus on modelling allows the Member States more flexibility in reporting assessments and the potential to reduce the cost of air quality monitoring. However, modelling, like monitoring, requires expert implementation and interpretation. Models must also be verified and validated before they can be confidently used for air quality assessment or management (Denby et al., 2008).

The quality objectives for a model are given as a percentage uncertainty. Uncertainty is then further defined in the directive as follows: 'The uncertainty for modelling is defined as the maximum deviation of the measured and cal-

Table 4. Systematic and random errors for averaged 1-h peak ozone concentration.

Month	RMSE$_s$ (μg m^{-3})	$\left(\frac{RMSE_s}{RMSE}\right)^2 \cdot 100$ (%)	RMSE$_u$ (μg m^{-3})	RMSE (μg m^{-3})
June	11.32	(28.32)	18.01	21.27
July	14.35	(45.30)	15.77	21.32
August	9.15	(24.67)	15.99	18.42
September	15.40	(54.86)	13.97	20.79

Table 5. Systematic and random errors for averaged 8-h peak ozone concentration.

Month	RMSE$_s$ (μg m^{-3})	$\left(\frac{RMSE_s}{RMSE}\right)^2 \cdot 100$ (%)	RMSE$_u$ (μg m^{-3})	RMSE (μg m^{-3})
June	16.54	(61.09)	13.20	21.16
July	11.99	(45.70)	13.07	17.74
August	10.48	(39.35)	13.01	16.71
September	12.64	(43.83)	14.31	19.09

Table 6. RDE values calculated for the 22 representative stations taken into account all studied period.

Station	RDE for the limit of target value (%)
Constantí	27.83
Pardines	7.42
Agullana	4.92
Juneda	17.75
Sort	14.50
Sta. Maria de Palautordera	23.08
Begur	14.83
Santa Pau	19.83
Gandesa	13.25
Bellver de Cerdanya	12.17
Ponts	12.50
La Sénia	15.42
Tarragona - Parc de la Ciutat	25.08
Rubí	42.58
Tona	2.67
Alcover	34.42
Guiamets	21.33
Berga	5.83
Vilafranca del Penedès	33.17
Mataró	10.75
Gavà	25.08
Barcelona - Vall d'Hebron	32.67

culated concentration levels for 90% of individual monitoring points, over the period considered, by the limit value (or target value in the case of ozone), without taking into account the timing of the events. The uncertainty for modelling shall be interpreted as being applicable in the region of the appropriate limit value (or target value in the case of ozone). The fixed measurements that have to be selected for comparison with modelling results shall be representative of the scale covered by the model.'

3.3.1 The mathematical formulation of the Directive's quality objectives

As in the previous directives, the wording of this text remains ambiguous. Since values are to be calculated, a mathematical formula would have made the meaning much clearer. As such, the term 'model uncertainty' remains open to interpretation. Despite this, Denby et al. (2008) suggest that it should be called the Relative Directive Error (RDE) and define it mathematically at a single station as follows:

$$RDE = \frac{|O_{LV} - M_{LV}|}{LV} \tag{5}$$

where O_{LV} is the closest observed concentration to the limit value concentration or the target value for ozone and M_{LV} is the correspondingly ranked modelled concentration. The maximum of this value found at 90% of the available stations is then the Maximum Relative Directive Error (MRDE).

For ozone, average RDE values calculated as a percentage for the 22 representative stations are presented in Table 6. Results show a broad spread, ranging from low values (2.67%) in small towns to high values in cities and industrialized areas where it is difficult to take all the emissions into account.

MRDE values, calculated as percentages for each month as well as for the whole period considered are presented in Table 7. As in the previous section, May and October are not included, as the evaluation began on May 19, and twelve days is considered not representative. During October there were several gaps.

MRDE values presented in Table 6 show percentages within the regulatory framework recommended in the European Directive EC/2008/50, which is 50%.

Table 7. MRDE values for each month period as well as for all period.

Month	MRDE for the limit of target value (%)
June	34.42
July	31.33
August	27.83
September	33.50
All period	33.17

4 Conclusions

This paper describes the evaluation of a coupled regional modelling system used to simulate ozone air quality over the North-Western Mediterranean area (Catalonia) during late spring, summer and early autumn, 2008. The modelling system consists of the MM5 mesoscale model, the MNEQA emission model and the CMAQ photochemical model. Although the same meteorological and photochemical models have been applied in Catalonia in recent years, they have been evaluated during short periods and using a different emission model. This study has demonstrated the ability of the air quality modelling system MM5/MNEQA/CMAQ to forecast ozone concentrations with sufficient accuracy, as the statistics fell within the EPA and European recommended performance goals. Daytime results for average, 1-h and 8-h predictions indicate satisfactory behaviour of the model. However, modelled ozone concentrations at night are beyond measure and some statistics lie outside the regulatory framework. This behaviour of the model could be attributed to several factors, such as poor calculation of emissions at night, the failure to represent nocturnal physicochemical processes with sufficient accuracy, and finally, the inability of the model to reproduce certain meteorological parameters, such as wind velocity and wind direction at night. Results from systematic and unsystematic errors show similar values, although unsystematic errors tend to be slightly larger. In addition, although the model statistics are within the performance goals, some of these statistics, when calculated locally, do not meet regulatory targets. This evaluation also evinces a set of problems that need to be solved in future validations. The domain resolution over Catalonia must be improved, as air pollution dispersion studies in complex terrain require high resolution modelling of air quality in order to resolve complex circulation patterns like sea breezes, drainage flows or channelling flows, which are not always seen by the meteorological model using coarse horizontal resolution. In addition, by increasing resolution, a greater number of stations could be included in the validation. A new 3 km resolution is currently being introduced.

Acknowledgements. This research was supported by the Catalan Government under contracts FBG-304.471 and FBG-304.980. The authors gratefully acknowledge the technicians of this department for providing information about the emissions inventory and air-quality measurements. Thanks are extended to the Catalan Meteorological Service for providing the initial and boundary meteorological fields for executing MM5.

References

Abdul-Wahab, S. A., Bakheit, C. S., and Al-Alawi, S. M., 2005: *Principal component and multiple regression analysis in modelling of ground-level ozone and factors affecting its concentration*, Environ Modell Softw, **20**, 1263–1271.

Aguirre-Basurko, E., Ibarra-Berastegui, I., and Madariaga, I., 2006: *Regression and multilayer perceptron-based models to forecast hourly O3 and NO2 levels in the Bilbao area*, Environ Modell Softw, **21**, 430–446.

Appel, K. W., Gilliland, A. B., Sarwar, G., and Gilliam, R. C., 2007: *Evaluation of the Community Multiscale Air Quality (CMAQ) model version 4.5: Sensitivities impacting model performance. Part I-Ozone*, Atmos Environ, **41**, 9603–9615.

Brankov, E., Henry, R. F., Civerolo, K. L., Hao, W., Rao, S. T., Misra, P. K., Bloxam, R., and Reid, N., 2003: *Assessing the effects of transboundary ozone pollution between Ontario, Canada and New York, USA*, Environ Pollut, **123**, 403–411.

Bravo, M., Mira, T., Soler, M. R., and Cuxart, J., 2008: *Intercomparison and evaluation of MM5 and Meso-NH mesoscale models in the stable boundary layer*, Bound-Layer Meteor, **128**, 77–101.

Byung, D. W. and Ching, J. K. S., 1999: Science algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modelling System, U.S. EPA/600/R-99/030.

Denby, B., Larssen, S., Guerreiro, C., Douros, J., Moussiopoulos, N., Fragkou, L., Gauss, M., Olesen, H., and Miranda, A. I., 2008: Guidance on the use of models for the European air quality directive, ETC/ACC Report.

Dudhia, J., 1996: A multi-layer soil temperature model for MM5. Preprints, Sixth PSU/NCAR Mesoscale Model Users' Workshop, NCAR, Boulder, CO, 49-50.

Dudhia, J., Gill, D., Manning, K., Wang, W., and Bruyere, C., 2004: PSU/ NCAR mesoscale modeling system tutorial class notes and user's guide: MM5 modeling system version 3, NCAR, http://www.mmm.ucar.edu/mm5/documents/tutorial-v3-notes.html.

EMEP, 2007: EMEP/MMSC-W Technical Report 1/2006 ISSN 1504-6179, http://www.emep.int.

Gangoiti, G., Millan, M., Salvador, R., and Mantilla, E., 2001: *Long-range transport and re-circulation of pollutants in the western Mediterranean during the project Regional Cycles of Air Pollution in the West-central Mediterranean Area*, Atmos Environ, **35**, 6267–6276.

Grell, G., 1993: *Prognostic evaluation of assumptions used by cumulus parameterizations*, Mon Weather Rev, **121**, 764–787.

Grell, G., Dodhia, J., and Stauffer, D., 1994: A Description of the Fifth Generation Penn State/ NCAR Mesoscale Model (MM5), NCAR. Tech. Note TN-398+STR, NCAR, Boulder, CO, 117 pp.

Grossi, P., Thunis, P., Martilli, A., and Clappier, A., 2000: *Effect of sea breeze on air pollution in the greater Athens area: Part II: Analysis of different Emissions Scenarios*, J Appl Meteorol, **39**, 563–575.

Guderian, R., Tingey, D. T., and Rabe, R., 1985: Effects of photochemical oxidants on plants. Air Pollution by Photochemical Oxidants, Guderian R., Springer, Berlin, pp. 129-333.

Hewit, C., Lucas, P., Wellburn, A., and Fall, R., 1990: *Chemistry of ozone damage to plants*, Chem Ind, **15**, 478–481.

Hogrefe, C., Rao, S. T., Kasibhatla, P., Kallos, G., Tremback, C. T., Hao, W., Sistla, G., Mathur, R., and McHenry, J., 2001: *Evaluating the performance of regional-scale photochemical modelling systems: Part II- ozone predictions*, Atmos Environ, **35**, 4175–4188.

Hurley, P. J., Physick, W. L., and Luhar, A. K., 2005: *TAPM: a practical approach to prognostic meteorological and air pollution modelling*, Environ Modell Softw, **20**, 737–752.

Jimenez, J., Baldasano, J. M., and Dabdub, D., 2003: *Comparison of photochemical mechanisms for air quality modeling*, Atmos Environ, **37**, 4179–4194.

Jiménez, P., Jorba, O., Parra, R., and Baldasano, J. M., 2006a: *Evaluation of MM5-EMICAT2000-CMAQ performance and sensitivity in complex terrain: High-resolution application to the Northeastern Iberian Peninsula*, Atmos Environ, **40**, 5056–5072.

Jiménez, P., Lelieveld, J., and Baldasano, J. M., 2006b: *Multiscale Modelling of air pollutants Dynamics in the North-Western Mediterranean Basin during a typical summertime episode*, J Geophys Res, **111**, D18 306.

Jiménez, P., Jorba, O., Baldasano, J. M., and Gassó, S., 2008: *The Use of a Modelling System as a Tool for Air Quality Management: Annual High-Resolution Simulations and Evaluation*, Sci Total Environ, **390**, 323–340.

Lee, S. and Fernando, H. J. S., 2004: *Evaluation of Meteorological Models MM5 and HOTMAC Using PAFEX-I Data*, J Appl Meteorol, **43**, 1133–1148.

Mauzerall, D. L., Sultan, B., Kim, J., and Bradford, D., 2005: *NOx emissions: variability in ozone production, resulting health damages and economic costs*, Atmos Environ, **39**, 2851–2866.

Millan, M., Mantilla, E., Salvador, R., Carratala, A., Sainz, J. M., Alonso, L., Gangoiti, G., and Navazo, M., 2000: *Ozone cycles in the western Mediterranean basin: Interpretation of monitoring data in complex coastal terrain*, J Appl Meteorol, **39**, 487–508.

Ortega, S., Soler, M. R., Alarcón, M., and Arasa, R., 2009: *MNEQA: An emissions model for photochemical simulations*, Atmos Environ, **43**, 3670–3681.

Parra, R., 2004: Desarrollo del modelo EMICAT2000 para la estimación de emisiones de contaminantes del aire en Cataluña y su uso en modelos de dispersión fotoquímica, PhD Dissertation, Universitat Politècnica de Catalunya, Spain, PhD Dissertation, http://www.tdx.cat/TDX-0803104-102139.

San José, R., Stohl, A., Karatzas, K., Bohler, T., James, P., and Pérez, J. L., 2005: *A modelling study of an extraordinary night time ozone episode over Madrid domain*, Environ Modell Softw, **20**, 587–593.

Schlink, U., Herbarth, O., Richter, M., Dorling, S., Nunnari, G., Gawley, G., and Pelikan, E., 2006: *Statistical models to assess the health effects and to forecast ground level ozone*, Environ Modell Softw, **21**, 547–558.

Schultz, P., 1995: *An explicit cloud physics parameterization for operational numerical weather prediction*, Mon Weather Rev, **123**, 3331–3343.

Schürmann, G. J., Algieri, A., Hedgecock, I. M., Manna, G., Pirrone, N., and Sprovieri, F., 2009: *Modelling local and synoptic scale influences on ozone concentrations in a topographically complex region of Southern Italy*, Atmos Environ, **43**, 4424–4434.

Seigneur, C., Pun, B., Pai, P., Louis, J. F., Solomon, P., Emery, C., Morris, R., Zahniser, M., Worsnop, D., Koutrakis, P., White, W., and Tombach, I., 2000: *Guidance for the performance evaluation of three-dimensional air quality modeling systems for particulate matter and visibility*, J Air Waste Manage Assoc, **50**, 588–599.

Serrano, E., Macias, A., and Castro, M., 1993: *An improved direct method of rubber craking analysis for estimating 24-hour ozone levels*, Atmos Environ, **27**, 431–442.

Silibello, C., Calori, G., Brusasca, G., Catenacci, G., and Finzi, G., 1998: *Application of a photochemical grid model to Milan metropolitan area*, Atmos Environ, **32**, 2025–2038.

Sistla, G., Zhou, N., Hao, W., Ku, J. Y., and Rao, S. T., 1996: *Effects of uncertainties in meteorological inputs of Urban Airshed Model predictions and ozone control strategies*, Atmos Environ, **30**, 2011–2025.

Sitch, S., Cox, P. M., Collins, W. J., and Huntingford, C., 2007: *Indirect Radiative Forcing of Climate Change through Ozone Effects on the Land-Carbon Sink*, Nature, **448**, 791–794.

Sokhi, R. S., San José, R., Kitwiroon, N., Fragkou, E., Pérez, J. L., and Middleton, D. R., 2006: *Prediction of ozone levels in London using the MM5-CMAQ modelling system*, Environ Modell Softw, **21**, 566–576.

Soler, M. R., Hinojosa, J., Bravo, M., Pino, D., and Vilà Guerau de Arellano, J., 2004: *Analyzing the basic features of different complex terrain flows by means of a Doppler Sodar and a numerical model: Some implications to air pollution problems*, Meteorol Atmos Phys, **85**, 141–154.

Troen, I. S. and Mahrt, L., 1986: *A simple model of the atmospheric boundary layer; sensitivity to surface evaporation*, Bound-Layer Meteor, **37**, 129–148.

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

US EPA, 2005: Guidance on the use of models and other analyses in attainment demonstrations for the 8-hour ozone NAAQS, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, US, US EPA Report No. EPA-454/R-05-002. October 2005, 128 pp.

US EPA, 2007: Guidance of the use of models and other analysis for demonstrating attainment of air quality goals for ozone, PM2.5 and Regional haze, US Environmental protection Agency, Research Triangle Park, North Carolina, US, EPA-454/B-07-002.

Vestreng, V., Rigler, E., Adams, M., Kindbom, K., Pacyna, J. M., Denier van der Gon, H., Reis, S., and Travnikov, O., 2006: Inventory review. Emission data reported to LRTAP and NEC Directive; Stage 1, 2, and 3 review; Evaluation of inventories of HMs and POPs.

Yarwood, G., Roa, S., Yocke, M., and Whitten, G., 2005: Updates to the carbon bond chemical mechanism: CB05, Final report to the US EPA, RT-0400675, http://www.camx.com.

Zhang, Y., Liu, P., Pun, B., and Seigneur, C., 2006a: *A Comprehensive Performance Evaluation of MM5-CMAQ for the Summer 1999 Southern Oxidants Study Episode, Part-I. Evaluation Protocols, Databases and Meteorological Predictions*, Atmos Environ, **40**, 4825–4838.

Zhang, Y., Liu, P., Queen, A., Misenis, C., Pun, B., Seigneur, C., and Wu, S. Y., 2006b: *A Comprehensive Performance Evaluation of MM5-CMAQ for the Summer 1999 Southern Oxidants Study*

Episode, Part-II.Gas and Aerosol Predictions, Atmos Environ, **40**, 4839–4855.

Zunckel, M., Koosailee, A., Yarwood, G., Maure, G., Venjonoka, K., van Tienhoven, A. M., and Otter, L., 2006: *Modelled surface ozone over southern Africa during the Cross Border Air Pollution Impact Assessment Project*, Environ Modell Softw, **21**, 911–924.

Numerical experiments to determine MM5/WRF-CMAQ sensitivity to various PBL and land-surface schemes in North-eastern Spain: application to a case study in summer 2009

Raúl Arasa *

Department of Astronomy and Meteorology, Faculty of Physics, University of Barcelona, Avinguda Diagonal 647, 08028 Barcelona, Spain. Telephone: (+34)934039229; Fax: (+34)934021133; e-mail: rarasa@am.ub.es. * Corresponding author

Maria Rosa Soler

Department of Astronomy and Meteorology, Faculty of Physics, University of Barcelona, Avinguda Diagonal 647, 08028 Barcelona, Spain. Telephone: (+34)934021129; Fax: (+34)934021133; e-mail: rosa@am.ub.es.

Miriam Olid

Department of Astronomy and Meteorology, Faculty of Physics, University of Barcelona, Avinguda Diagonal 647, 08028 Barcelona, Spain. Telephone: (+34)934039229; Fax: (+34)934021133; e-mail: molid@am.ub.es.

Abstract: The Community Multiscale Air Quality (CMAQ) model was used along with the Weather Research and Forecasting (WRF) model to study air quality modelling sensitivity to the various planetary boundary layer (PBL) schemes and land surface models (LSM). The performance is assessed and quantified by comparing results with surface observations and the outputs provided by the 5th generation Mesoscale Model (MM5) when coupled to CMAQ model. Data were provided by 35 meteorological and 51 air-quality monitoring stations in North-eastern Spain. The evaluated meteorological variables include 1.5-m temperature, 10-m wind speed and direction and 2-m mixing ratio, while the CMAQ species evaluation focuses on ozone concentrations. Results show several differences across the meteorological simulations affecting CMAQ performance. Differences were observed in circulatory patterns between the two meteorological models, which influence spatial ozone distributions. In addition, differences in several meteorological variables such as PBL height modulate pollutant mixing capability, differences in predicted cloud cover affect incoming solar radiation, and differences in temperature influence biogenic emissions. These different model behaviours are discussed, as they could account for the differences in the values predicted for ozone concentrations.

Keywords: Model sensitivity, Planetary boundary layer, Air quality simulation, CMAQ, MM5, WRF, Ozone.

R. Arasa, M.R. Soler and M. Olid

Raúl Arasa is an Assistant Lecturer in the Department of Astronomy and Meteorology at the University of Barcelona. He is currently pursuing his PhD in mesoscale modelling systems and he is involved in several environmental studies assessing the scale of ozone impacts and developing control strategies. His recent research focuses on the implementation of mesoscale air quality modelling to forecast photochemical pollutants and particulate matter in the area of Catalonia. This research has been published and presented to several international and national conferences.

Maria Rosa Soler is a Professor in the Department of Astronomy and Meteorology at the University of Barcelona. Her major research interests are testing and modelling the meteorological phenomena associated to the atmospheric micro and mesoscale. In addition, she has participated in many studies related to the problem of photochemical pollutant transport and diffusion. She is involved in many national and international projects, and she is the author of more than 70 papers that have been published in national and international journals and conference proceedings.

Miriam Olid is a researcher in the Department of Astronomy and Meteorology at the University of Barcelona. She has participated in the implementation of a mesoscale air quality modelling system for the area of Catalonia, focussing on air emission modelling. She has carried out several studies for modelling and assessment of air pollution. Her research has been published and presented in national and international conferences.

1. Introduction

In recent decades, the 5th generation Mesoscale Model (MM5) (Grell et al., 1994) has been one of the most popular models used to provide the meteorological data required for photochemical models such as the U.S. EPA model-3/CMAQ model (Byun and Ching, 1999). For the periods May-September 2008, 2009 and 2010, an air-quality modelling system composed of MM5, CMAQ and the emission model MNEQA (Numerical Emission Model for Air Quality) (Ortega et al., 2009) was applied to the North-East part of Spain (Catalonia) to forecast ozone concentrations. The performance of this system has been evaluated (Arasa et al., 2010) and found to be able to forecast ozone concentrations with sufficient accuracy as the statistics fell within the U.S. Environmental Protection Agency (EPA) and European recommended performance goals. However, releases of new versions of MM5 by the community have ceased since the Weather Research and Forecasting model (WRF) (Skamarock and Klemp, 2008) has taken its place. Both models have a modular design which allows users to choose several options for the physics involved. However, WRF presents accurate numerical and high-quality mass conservation characteristics, as well as accurate parameterizations to represent physical processes. Several physical schemes in WRF for boundary layer turbulence and surface processes were tested as they play an important role in the simulation of lower atmospheric winds, temperature, cloud cover and mixing layer height. The behaviour of these variables in turn affects the dispersion simulations, the surface pollutant concentrations and the production of secondary species. While other studies have tested the sensitivity of the WRF model to various PBL schemes and surface processes on meteorological fields, few of them specifically compared the performance of WRF driven CMAQ model simulations (Appel et al., 2009). The present study examines the operational performance of the CMAQ model during two ozone episodes in summer 2009, using meteorological data provided by MM5 and WRF. Evaluation results for each simulation are presented and reasons for differences in performance are discussed.

2. Methodology

2.1. Modelling approach

Meteorological numerical simulations were performed using the WRF-ARW version 3.1.1 and the mesoscale model, MM5, version 3.7. Both models were configured with three nested domains that have grids of 27, 9 and 3 km (Fig. 1), with a two-way interface with the smallest grid. D3, the inner domain, corresponds to Catalonia (NE Spain) and covers 94x94 grid cells. The vertical grid is common to all the domains, with 31 vertical levels, 20 below 1500 m approximately and domain top at 100hPa. The distribution of the vertical layers, higher resolution in the lower levels, is a common practice, thus enabling low-level flow details to be captured. Initial and boundary conditions were taken from the European Centre for Medium Range Weather Forecasts (ECMWF) every 6 hours, and so boundary conditions can be updated at this time interval. MNEQA is an emissions model developed at the University of Barcelona. It includes emissions from both natural sources (particles from dust or hydrocarbons emitted by vegetation) and anthropogenic sources (mainly traffic and industry). The photochemical model used in this study to simulate pollutant dispersion is the EPA model-3/CMAQ model. The CMAQ v4.6 simulations use the CB-05 chemical mechanism (Yarwood et al., 2005) and the aerosol module AERO4 (Bhave et al., 2005). Boundary conditions and initialization values come from a vertical profile for outer domain (D1) supplied by CMAQ itself. For inner domains (D2 and D3) boundary conditions come from concentrations predicted in a CMAQ mother domain. This consideration can introduce error on the system, providing an overestimation of low ozone concentration values (Borge et al., 2010) and affecting each numerical simulation analyzed. To minimize this problem the authors consider coupling a chemical transport global model to the system in a near future. The model is executed with 24h as spin-up.

Figure 1. Model domains.

In order to explore the sensitivity to the PBL and land surface (LS) schemes of the WRF model, five sets of numerical experiments or simulations were performed. The first compared solutions using one MM5 configuration, while simulations 2 to 5 compared solutions using different PBL and LS schemes but the same parameterizations for cumulus, microphysics and radiation (Table 1). All parameterizations used in Table 1 are referenced in Grell et al. (1994) and Skamarock and Klemp (2008). Although it was intended to isolate the PBL scheme as the sole cause of the model sensitivity, as each of the five PBL schemes required a specific LS model, model sensitivity was due to the PBL and LSM associated.

2.2. Area characteristics, data used and episode selection

The area of study was Catalonia in North-East Spain. The population of Catalonia recently reached seven million, most of whom live in and around the city of Barcelona. Catalonia is a Mediterranean area with complex topography. It is bounded by the Pyrenees to the North and by the Mediterranean Sea to the South and East. The main industrial areas and most of the population are located along the coast. In summer, there are high ozone concentration episodes inland, sometimes in rural areas, due to the advection of pollutants by the sea breeze, which brings them from the coast to the rural territory inland (Soler et al., 2010). Meteorological modelling results were evaluated from a set of 35 surface meteorological stations belonging to the Catalonia Meteorological Service that are distributed throughout Catalonia. The evaluation included wind speed and wind direction measured at 10 m above ground level (a.g.l.), air temperature at 1.5 m a.g.l. and air humidity measured at 2 m a.g.l. The air-quality evaluation, which focussed on ozone concentrations, was performed using hourly measurements of ozone (O_3) concentrations reported by 51 air-quality surface stations belonging to the regional Catalan Environmental Agency and covering with an accurate territorial distribution the size of the area. Two ozone episodes, 27-28 July 2009 and 05-06 August 2009, were selected for the simulation, as they represent typical summer weather conditions characterized by an anticyclonic situation with slight pressure gradients favouring the development of mesoscale circulations such as the sea breeze. This thermally induced circulation transports pollutants to areas well away from their source, resulting in poor air quality and an increase in potential health problems.

Table 1. Physical options for MM5 and WRF simulations.

Physical Options	MM5	WRF configurations	
Cumulus	Grell	Grell 3D	
PBL Scheme	Medium Range Forecast Model (MRF)	WRF-1:Yonsei University (YSU)	WRF-2: Mellor-Yamada-Janjic (MYJ)
		WRF-3: Asymmetrical Convetive Model 2 (ACM2)	WRF-4: Quasi-Normal Scale Elimination (QNSE)
Microphysic	Schultz	Lin	
Radiation Scheme	Rapid Radiative Transfer Model (RRTM) lw & Cloud-radiation sw	RRTM lw & RRTM for Global climate models (RRTMG) sw	
Surface Scheme	Noah LSM	WRF-1: Noah LSM	WRF-2: Eta similarity
		WRF-3: Pleim Xiu	WRF4: QNSE

3. Results and discussion

3.1. WRF sensitivity to PBL and LS schemes

To evaluate the different simulations we compared surface measurements with model results. The statistics selected and benchmarks values to drive the evaluation are taken from Denby et al. (2008) and EPA (2009) respectively. The basic statistical measures used to evaluate MM5 and WRF forecasts were the mean bias (MB), the mean absolute gross error (MAGE), the root-mean-square error (RMSE) and the index of agreement (IOA). Tables 2 and 3 present the statistics, corresponding to the two analyzed periods. For the 28 July 2009 simulation, statistics values presented in Table 2 showed that the 10-

m wind speed MB was always positive. This indicates an overestimation of the wind speed; YSU and ACM2 schemes yielded the best values of MB and RMSE; QNSE yielded the largest MB value, while IOA values are similar. For wind direction, MYJ yielded the best MAGE while ACM2 yielded the largest. The poor performance found for this variable could be attributed to the complex topography of the simulated area. For air temperature, all five simulations resulted in slightly negative biases: the lowest value was for the YSU scheme and the largest was for MRF in the MM5 model. MAGE values were similar: the largest value also corresponded to the MRF scheme in the MM5 model. Finally, for specific humidity, the best MAGE was for the YSU scheme, while the MRF scheme in MM5 had the largest value. All simulations resulted in poor IOA in specific humidity, and good IOA in temperature. Our results agree with those found by Borge et al., (2008) for the Iberian Peninsula. For this first set of simulations WRF forecasted temperature, wind and specific humidity better than MM5-MRF did. Related to differences in circulatory patterns between the two meteorological models, Figure 2 shows an example of the wind fields simulated by MM5-MRF and WRF-YSU at 0800UTC, where we can see that during the night MM5-MRF forecasts a recirculation centred on the metropolitan area of Barcelona. In WRF configurations, this recirculation is not so clear or not reproduced. In addition, during day time hours WRF-YSU forecasts more intense sea-breezes than MM5 does. These differences in circulatory patterns directly influence the distribution of ozone concentrations in CMAQ simulations, as we will see in the next section.

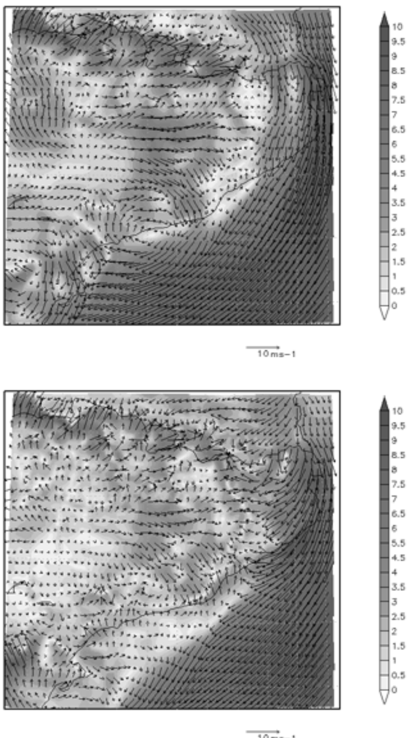


Figure 2. Surface wind fields simulated at 0800 UTC by MM5-MRF (upper panel) and WRF-YSU (lower panel) for the 28 July 2009 simulation.

For the 06 August 2009 simulation, statistics presented in Table 3 showed that the 10-m wind speed MB was always positive. This indicates an overestimation of the wind speed; MRF and YSU schemes yielded the best values of MB and RMSE, while MYJ yielded the largest MB and the best IOA values. For wind direction, MRF yielded the best MAGE while QNSE yielded the largest. For air temperature, all five simulations resulted in negative bias: the lowest value was for the YSU scheme and the largest was for QNSE. Finally, for specific humidity, the best MAGE was for the MRF scheme, while the QNSE scheme had the largest value. All simulations resulted in poor IOA in wind speed, and good IOA in temperature and specific humidity, mainly during the day. Wind speeds and wind directions forecasted by MM5-MRF reproduce the measurements better than WRF configurations do. In general, WRF configurations yield higher wind speeds than MM5-MRF does and different wind field patterns. Otherwise, WRF configurations forecast lower specific humidity values than MM5-MRF does. This means that MM5-MRF simulation produce higher wet deposition than

WRF does. For air temperature and surface solar radiation, WRF forecast higher values than MM5-MRF does, suggesting less overall cloud cover in WRF simulations.

Table 2. Statistics corresponding to MM5 and WRF model evaluation for the 28 July 2009 simulation.

Meteorological variable	**Statistic**	**Bench-mark**	**MM5 MRF**	**WRF-1 YSU**	**WRF-2 MYJ**	**WRF-3 ACM2**	**WRF-4 QNSE**
Wind speed	RMSE (ms^{-1})	<2.00	1.73	1.60	1.86	1.61	1.84
	MB (ms^{-1})	<±0.50	0.60	0.53	0.94	0.59	0.97
	IOA	≥0.60	0.64	0.70	0.66	0.67	0.66
Wind direction	MAGE (º)	<30.00º	56.43	58.28	57.55	61.58	60.03
	MB (º)	<±10º	4.21	5.50	1.03	7.25	3.35
Temperature	MAGE (K)	<2.00	2.10	1.88	1.75	1.68	1.83
	MB (K)	<±0.50	-1.83	-0.77	-0.95	-0.94	-1.13
	IOA	≥0.80	0.89	0.90	0.91	0.93	0.91
Specific humidity	MAGE ($g\ kg^{-1}$)	<2.00	1.78	1.58	1.79	1.74	1.74
	MB ($g\ kg^{-1}$)	<±1.00	1.24	0.60	0.50	0.84	0.48
	IOA	≥0.60	0.41	0.46	0.29	0.35	0.31

Table 3. Statistics corresponding to MM5 and WRF model evaluation for the 06 August 2009 simulation.

Meteorological variable	**Statistic**	**Bench-mark**	**MM5 MRF**	**WRF-1 YSU**	**WRF-2 MYJ**	**WRF-3 ACM2**	**WRF-4 QNSE**
Wind speed	RMSE (ms^{-1})	<2.00	1.63	2.03	2.60	2.10	2.57
	MB (ms^{-1})	<±0.50	0.64	1.23	1.85	1.33	1.81
	IOA	≥0.60	0.65	0.60	0.47	0.56	0.48
Wind direction	MAGE (º)	<30.00º	50.63	54.94	56.84	53.27	57.36
	MB (º)	<±10º	11.38	15.00	16.22	19.68	20.41
Temperature	MAGE (K)	<2.00	1.61	2.19	2.41	2.70	2.48
	MB (K)	<±0.50	-1.28	-1.24	-1.40	-1.56	-1.64
	IOA	≥0.80	0.95	0.91	0.90	0.90	0.89
Specific humidity	MAGE ($g\ kg^{-1}$)	<2.00	1.80	2.05	2.05	1.95	2.05
	MB ($g\ kg^{-1}$)	<±1.00	1.11	0.40	-0.16	0.17	-0.34
	IOA	≥0.60	0.70	0.70	0.71	0.72	0.70

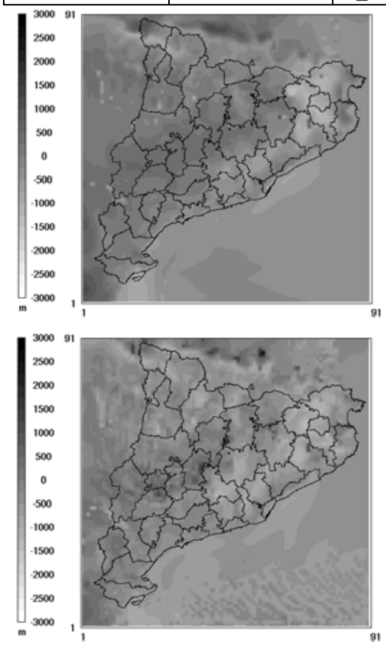


Figure 3. PBL height differences between YSU and MRF (upper panel) and MYJ and MRF (lower panel) on 28 July 2009 at 1400 UTC.

Related to PBL height forecasts, Figure 3, as an example, shows a map of the PBL height differences between the YSU, MYJ and MRF schemes at 1400 UTC, which corresponds to a typical summer afternoon when PBL was fully developed. The differences of the mixing depth varied over a broad range. Generally, the MRF scheme produced higher mixing depths near and over the coast, while in the rest of the domain MRF yielded lower mixing depths than those yielded by WRF options. The fundamental difference between the MRF PBL and YSU PBL scheme is the definition of the critical bulk Richardson number (Rib_{cr}), Rib_{cr}=0.5 in MRF and Rib_{cr}=0 in YSU. Consequently, if we compare MRF results, we find that YSU increases boundary layer mixing in the thermally-induced free convection regime and decreases it in the mechanically-induced forced convection regime, which is dominant in topographically complex coastal areas.

3.2. CMAQ sensitivity to PBL and LS schemes

Differences in ozone concentrations forecasted by MM5-CMAQ and WRF-CMAQ can be due to several causes, which can be attributed to different PBL and LS parameterizations used in the various simulations. As we noticed in the last section, the incoming solar radiation forecasted by WRF is higher than that predicted by MM5. This difference is a result of the difference in cloud cover (de Meij et al., 2009). The smaller cloud fraction in WRF-CMAQ favours greater O_3 production, as it is used in the calculation of the photolysis rate for O_3 (Appel et al., 2009). It is difficult to quantify the impact of these differences on O_3 concentration and besides, the impact of this effect is local. In addition, the larger surface solar radiation, together with higher temperatures in the WRF-CMAQ simulation, provides greater biogenic emissions in MNEQA. Biogenic Volatile Organic Compounds (VOCs) provided by WRF-MNEQA are between 10% and 16 %, higher than those provided by MM5-MNEQA, while for nitrogen oxides (NO_x) this difference is between 6% and 17 %. This effect increases ozone concentrations in rural and suburban areas. Another explanation of the differences in ozone concentrations forecasted by WRF-CMAQ and MM5-CMAQ may be the O_3 dry deposition values forecasted by the two systems, as there are significant differences in the LS schemes implemented in the two models. Simulations provided by WRF-CMAQ yield between 1% and 18% lower deposition velocities of O_3 than those given by MM5-CMAQ, which results in higher ambient ozone concentrations. Also, the impact of PBL parameterizations, especially the PBL height, plays an important role in air quality modelling. Focusing on ozone concentrations and taking into account the previous results found for PBL depth, we expect that WRF-CMAQ will provide higher O_3 concentrations in coastal areas while throughout a large portion of the domain ozone concentrations will be lower.

To evaluate the accuracy of the ozone concentration forecast provided by MM5-MRF-CMAQ and WRF-CMAQ configurations, several statistical metrics were calculated for surface ozone concentrations at 51 measurement sites in the modelling domain. The four multi-site metrics used are the unpaired peak prediction accuracy (UPA), the mean normalized bias error (MNBE), the mean normalized gross error (MNGE) and the index of agreement (IOA) (EPA, 2009). The statistical parameters were applied to hourly values, maximum 1-h and 8-h concentration (Tables 4 and 5), using only the hourly observation-prediction pairs for which the observed concentration is greater than a specific value (cut-off: $60 \mu g m^{-3}$); this procedure, used for several authors, removes the influence of low concentrations such as night-time values.

For the 28 July 2009 simulation (Table 4), the hourly values show an improvement of the WRF-CMAQ forecast compared to the MM5-CMAQ forecast. For 1-h and 8-h maximum concentrations, both modelling systems tend to overestimate ozone concentrations, although the value of MNGE in the WRF-CMAQ simulation is between 9% and 18% lower than that in MM5-CMAQ. Within configurations, WRF-2 provided the best results in this case. Besides, differences in circulatory patterns, (commented in Section 3.1), directly influence the distribution of ozone concentrations in CMAQ simulations, as we can see in Figure 4, representing 1-h maximum ozone concentrations. The location of the ozone peaks and the shape of the ozone plumes depend on the modelling system. These results agree with those reported by Pirovano et al. (2007).

For the simulation of 06 August 2009 (Table 5), differences in the mean values of ozone concentration are greater than differences in geographical distribution, which is consistent with the results of Minguzzi et al. (2007). The statistical values corresponding to WRF configurations evaluation show similar or slightly better values than those corresponding to MM5-CMAQ, with WRF-3 providing the best results. For this simulation, both modelling systems underestimate ozone concentrations, as MNBE and UPA values for hourly and 1-h and 8-h maximum concentrations are negative. If we compare the performance of the two modelling systems for the two periods, MM5-CMAQ forecast efficiency is similar for both periods, but WRF-CMAQ efficiency is worse for the second period. One explanation for this behaviour could be the high O_3 concentrations recorded for this period, usually associated with local re-circulations, which are not well forecasted by either modelling system.

Table 4. Summary statistics corresponding to air quality stations associated with air-quality simulations of ozone concentration for the period 28 July 2009.

Values	**Statistic**	**Bench-mark**	**MM5 MRF**	**WRF-1 YSU**	**WRF-2 MYJ**	**WRF-3 ACM2**	**WRF-4 QNSE**
Hourly	MNBE (%)	<±15.00	1.46	-2.20	-2.67	1.59	-0.51
	MNGE (%)	<35.00	26.51	20.48	19.33	22.53	20.42
	IOA	--	0.550	0.678	0.770	0.673	0.706
Maximum 1-h	MNBE (%)	<±15.00	19.84	8.62	6.99	16.53	7.86
	MNGE (%)	<35.00	37.28	25.78	20.86	30.55	24.46
	IOA	--	0.526	0.584	0.733	0.563	0.602
	UPA (%)	<±20.00	15.92	5.08	-2.45	10.34	-2.48
Maximum 8-h	MNBE (%)	<±15.00	11.02	4.40	3.21	9.63	5.26
	MNGE (%)	<35.00	30.48	21.07	17.09	24.10	20.97
	IOA	--	0.726	0.857	0.908	0.808	0.855
	UPA (%)	<±20.00	6.83	12.65	5.11	20.71	4.61

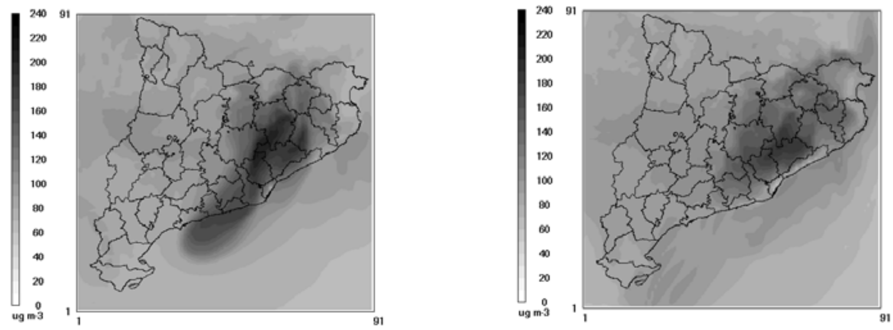


Figure 4. Maximum 1-h ozone concentrations for the 28 July 2009 simulation predicted by MM5-MRF (left panel) and WRF-YSU (right panel).

Table 5. Summary statistics corresponding to air quality stations associated with air-quality simulations of ozone concentration for the period 06 August 2009.

Values	**Statistic**	**Bench-mark**	**MM5 MRF**	**WRF-1 YSU**	**WRF-2 MYJ**	**WRF-3 ACM2**	**WRF-4 QNSE**
Hourly	MNBE (%)	<±15.00	-19.69	-20.18	-22.61	-18.78	-17.10
	MNGE (%)	<35.00	23.08	23.88	25.95	23.29	21.54
	IOA	--	0.693	0.692	0.656	0.700	0.705
Maximum 1-h	MNBE (%)	<±15.00	-15.01	-13.74	-13.28	-10.00	-12.88
	MNGE (%)	<35.00	17.02	15.79	14.72	14.17	15.21
	IOA	--	0.775	0.801	0.808	0.833	0.767
	UPA (%)	<±20.00	-8.19	-17.11	-14.67	-15.10	-21.82
Maximum 8-h	MNBE (%)	<±15.00	-15.63	-15.62	-16.44	-13.60	-13.99
	MNGE (%)	<35.00	17.48	16.90	16.90	15.97	15.21
	IOA	--	0.908	0.920	0.919	0.921	0.923
	UPA (%)	<±20.00	-12.81	-16.07	-12.81	-15.43	-18.39

4. Conclusions

A numerical experiment was conducted over two ozone episodes in summer 2009, to study air-quality modelling sensitivity to various PBL schemes used in WRF. The YSU, MYJ, ACM2 and QNSE schemes as well as MRF in MM5 were used in the sensitivity simulations. Although it was intended to isolate the PBL scheme as the sole cause of model sensitivity, as each of the five PBL schemes required specific LSM, model sensitivity was due to the PBL and its associated LSM. We evaluate the differences in meteorological parameters and the accuracy of temperature, wind and specific humidity forecasts. Overall, the performances of the two models are similar, although some differences are observed. The WRF model usually produces higher wind velocities and temperature than MM5, and lower specific humidity and cloud cover. Related to wind fields we observed differences affecting the distribution of ozone concentration and ozone maximums. This finding emphasizes the important role of circulation patterns in photochemical simulations. The photochemical CMAQ model is sensitive to various meteorological inputs and several direct and indirect causes lead to differences between the ozone concentrations predicted by MM5-CMAQ and WRF-CMAQ simulations. PBL height determines the mixing capability of pollutants and their concentration, thus affecting both ozone, and ozone precursor concentrations. WRF configurations predict lower PBL heights than MM5 near and over the coast, while in a large portion of the domain WRF predicts greater depths. Therefore, if we consider only this effect WRF-CMAQ would provide higher O_3 concentrations in coastal areas, while in a large portion of the domain ozone concentrations would be lower. In addition, changes in the meteorological inputs provided by MM5 and WRF configurations affect the photolysis rate for O_3 and the emission model MNEQA. Less cloud cover and higher temperature input in WRF simulations induced greater biogenic emissions. In particular MNEQA provided at the most 17% greater NO_x emission and 16% greater VOCs emission when meteorological inputs came from the WRF model. Another possible explanation of the differences in ozone concentrations predicted by WRF-CMAQ and MM5-CMAQ is the O_3 dry deposition values forecasted by each system. Simulations provided by WRF-CMAQ yield between 1% and 18 % lower deposition rates of O_3 than those provided by MM5-CMAQ, which results in higher ambient ozone concentrations. Within configurations, WRF-MYJ provides the best results for ozone concentration on 28 July 2009 simulation. Although to achieve conclusive results will be necessary to extend this study to a large period.

Acknowledgements

This research was supported by the Spanish Government through project CGL 2009-12797-C03-02.

References

Appel, K.W., Roselle, S.J., Gilliam, R.C. and Pleim, J.E. (2009) ‘Sensitivity of the Community Multiscale Air Quality (CMAQ) Model v4.7 results for the eastern United States to MM5 and WRF meteorological drivers’, *Geoscientific Model Development Discussions*, Vol. 2, pp.1081-1114.

Arasa, R., Soler, M.R., Ortega, S., Olid, M. and Merino, M. (2010) 'A performance evaluation of MM5/MNEQA/CMAQ air quality modelling system to forecast ozone concentrations in Catalonia', *Tethys*, 7, 11-23.

Bhave, P., Nolte, C., Pleim, J.E., Schwede, D., Roselle, S.J. (2005) *Recent developments in the CMAQ modal aerosol module*. In: The 2005 Models-3 Users Workshop, Chapel Hill, NC, 26-28 Sept. 2005. Available at: http://www.cmascenter.org/conference/2005/ppt/p17.pdf

Borge, R., Alexandrov, V., Del Vas, J.J., Lumbreras, J. and Rodríguez, E. (2008) 'A comprehensive sensitivity analysis of the WRF model for air quality applications over the Iberian Peninsula', *Atmos. Env.*, Vol. 42, pp.8560-8574.

Borge, R., López, J., Lumbreras, J., Narros, A., Rodríguez, E. (2010) 'Influence of boundary conditions on CMAQ simulations over the Iberian Peninsula', *Atmos. Env.*, Vol. 44, pp.2681-2695.

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

De Meij, A., Gzella, A., Cuvelier, C., Thunis, P., Bessagnet, B., Vinuesa, J.F., Menut, L. and Kelder, H.M. (2009) 'The impact of MM5 and WRF meteorology over complex terrain on model CHIMERE calculations', *Atmospheric Chemistry and Physics*, Vol. 9, pp.6611-6632.

Denby, B., Larssen, S., Guerreiro, C., Douros, J., Moussiopoulos, N., Fragkou, L., Gauss, M., Olesen, H., Miranda, A.I. (2008*) Guidance on the use of models for the European air quality directive*. ETC/ACC Report.

EPA Draft (2009) *Reassessment of the Interagency Workgroup on Air Quality Modeling (IWAQM)* Phase 2 Summary Report: Revisions to Phase 2 Recommendations.

Grell, G.A., Dudhia, J., Stauffer, D.R. (1994) 'A description of the fifth-generation Penn State/NCAR mesoscale model (MM5)' *NCAR Tech*, Note NCAR/TN-398+STR, p.117.

Minguzzi, E., Bedogni, M., Carnevale, C. and Pirovano, G. (2005) 'Sensitivity of CTM simulations to meteorological input', *International Journal of Env. and Pollution*, Vol. 24, pp.36-50.

Ortega, S., Soler, M.R., Alarcón, M. and Arasa, R. (2009) 'MNEQA, an emissions model for photochemical simulations', *Atmos. Env.t*, Vol. 43, pp.3670-3681.

Pirovano, G., Coll, I., Bedogni, M., Alessandrini, S., Costa, M.P., Gabusi, V., Lasry, F., Menut, L. and Vautard, R. (2007) 'On the influence of meteorological input on photochemical modelling of a severe episode over a coastal area', *Atmos. Env.*, Vol. 41, pp.6445-6464.

Skamarock, W.C. and Klemp, J.B. (2008) 'A time-split non-hydrostatic atmospheric model', *Journal of Computational Physics,* Vol. 227, pp.3465-3485.

Soler, M.R., Arasa, R., Merino, M., Olid, M. and Ortega, S. (2010) 'Modelling local sea-breeze flow and associated dispersion patterns over a coastal area in north-east Spain: A case study'. *Boundary-Layer Meteorology*, in press.

Yarwood, G., Rao, S., Yocke, M., Whitten, G. (2005) *Updates to the Carbon Bond chemical mechanism: CB05*. Report to the U.S. Environmental Protection Agency, RT-04-00675. http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf

EVALUATION OF MM5-MNEQA-CMAQ AIR-QUALITY MODELLING SYSTEM AND BIAS-ADJUSTMENT TECHNIQUES FOR FORECASTING OZONE CONCENTRATIONS: APPLICATION TO NORTH-EASTERN SPAIN DURING SUMMER 2009 AND 2010.

Raúl Arasa [1], Maria Rosa Soler [1], Miriam Olid [1]

[1] Department of Astronomy and Meteorology, Faculty of Physics, University of Barcelona. Avinguda Diagonal 647, 08028 Barcelona (Spain). Telephone: (+34)934039229, Fax: (+34)934021133

Abstract

We present a detailed evaluation of the seasonal performance of the Community Multiscale Air Quality (CMAQ) modelling system and the PSU/NCAR meteorological model coupled to a new Numerical Emission Model for Air Quality (MNEQA). The combined system simulates air quality at a fine resolution (3 km as horizontal resolution and 1 h as temporal resolution) in north-eastern Spain, where problems of ozone pollution are frequent. An extensive database compiled over two periods, from May to September 2009 and 2010, is used to evaluate meteorological simulations and chemical outputs. Our results indicate that the model accurately reproduces hourly and 1-h and 8-h maximum ozone surface concentrations measured at the air quality stations, as statistical values fall within the EPA and EU recommendations. Mean normalized bias errors (MNBE) are less than 15% for both hourly and peak (1-h and 8-h) ozone concentrations, whilst mean normalized gross errors (MNGE) are less than 35% for both. Related to EU recommendations, the maximum relative directive error (MRDE) is lower than 50%. To further improve forecast accuracy, three simple bias-adjustment techniques —mean subtraction (MS), ratio adjustment (RA) and hybrid forecast (HF)— based on 10 days of available comparisons are applied. The results show that the MS technique performed better than RA or HF, although all the bias-adjustment techniques significantly reduce the systematic errors in ozone forecasts. MNGE and MNBE metrics are reduced at most by 4.5% and 14.5% respectively, whilst MRDE is reduced by between 4% and 9%.

Keywords: air-quality modelling, meteorological modelling, bias-correction, CMAQ, ozone, evaluation.

1. INTRODUCTION

As a result of combined emissions of nitrogen oxides and organic compounds, large amounts of ozone are found in the planetary boundary layer. Tropospheric ozone is considered one of the worst pollutants in the lower troposphere. At high concentrations, ozone is toxic to plants and reduces crop yield (Guderian et al., 1985; Hewit et al., 1990; Zunckel et al., 2006). Sitch et al. (2007) suggest that the effects on plants of indirect radiative forcing by ozone could contribute more to global warming than direct radiative forcing due to tropospheric ozone does. Ozone is a respiratory irritant to humans, and it damages both natural and man-made materials such as stone, brickwork and rubber (Serrano et al., 1993). All these harmful effects are significant in Southern Europe (Silibello et al., 1998; Grossi et al., 2000; San José et al., 2005) as in summer solar radiation exacerbates the effects of ozone. This is the case in areas of northern Spain located near urban and industrial areas, and especially those lying downwind of such areas, where local ozone precursors are absent (Soler et al., 2004; Aguirre-Basurko et al., 2006). Consequently, the environmental benefits of monitoring, quantifying, modelling and forecasting the dose and exposure of the human population, vegetation and materials to ozone is an essential precondition for assessing the scale of ozone impact and developing control strategies (Brankov et al., 2003).

In the last three decades, significant progress has been made in air-quality modelling systems. The simple Gaussian and box models have evolved into statistical models (Abdul-Wahab et al., 2005; Schlink et al., 2006); stochastic models based on neuronal networks (Lissens et al., 2000; Niska et al., 2004); and Eulerian grid models (Hurley et al., 2005; Sokhi et al., 2006). The latter represent the most sophisticated class of atmospheric models and they are most often used for problems that are too complex to solve using simple models. With continuing advances, Eulerian-grid modelling is increasingly used in research settings to assess the air and health impacts of future emission scenarios (Mauzerall et al., 2005). Air-quality Eulerian models have become a useful tool for managing and assessing photochemical pollution and they represent a complement that could reduce the often costly activity of air-quality monitoring.

Modelling, however, suffers from a number of limitations. Models require the input of extensive emissions and meteorology data, which are not always reliable or easy to acquire. The capacity of models to represent the real world is limited by many factors, including spatial resolution and process descriptions. As models remain uncertain in their predictions, extensive validation is required before they can be used and relied upon (Denby, 2010).

In an attempt to meet such requirements, various studies have been performed in several areas (Hogrefe et al., 2001; Zhang et al., 2006a, b). Millán et al. (2000) and Gangoiti et al. (2001) studied photo-oxidant dynamics in the north-western part of the Mediterranean area. In addition, for north-eastern Spain, several studies have evaluated the performance of the model MM5-EMICAT2000-CMAQ using a range of horizontal resolutions, comparing different photochemical mechanism, and testing the capacity of the model to predict high ozone concentrations during typical summer episodes (Jiménez et al., 2003; 2006a, b; Jiménez et al., 2008).

We now report the validation of a new mesoscale air-quality modelling system evaluated in north-eastern Spain, called AQM.cat, although the methodology and the modelling system can be applied to any area. It is important to notice that, although the validation is applied over the same area and using the same meteorological and photochemical models, MM5 and CMAQ, as in previous studies, the validation covers a longer period (5 months in each of 2009 and 2010) and the system uses a new emission model, the Numerical Emission Model for Air Quality, MNEQA (Ortega et al., 2009). This model consists of a highly disaggregated emission inventory of gaseous pollutants and particulate matter. A preliminary version of this air-quality modelling system was evaluated in Arasa et al. (2010), and showed the capacity of the system to forecast ozone concentrations with sufficient accuracy. Since that validation, the modelling system has been continuously improved: we use higher horizontal resolution than in previous version (from 9 km to 3 km), in 2010 we changed the floor value of the vertical coefficient of turbulent diffusivity, $\underline{K_z}$, in the CMAQ model (Zhang et al., 2006a) and we also updated the emission model, using for this article the most actual version of the model, MNEQAv4.0. In addition, in this study, in order to improve operational AQM.cat ozone forecasts several bias-adjustment techniques have been incorporated. Utilization of a post-processing bias-adjustment method incorporates recent model forecasts combined with observations to adjust current model forecasts. Previous biases in the forecast values are used to estimate the systematic errors in the forecast. Conceptually, once the future bias has been estimated, it can be removed from the forecast; such and adjusted forecast should be statistically more accurate than the forecast based on the raw model output.

It is difficult to justify the use of bias-adjustment techniques to analyse model deficiencies or performance, but it is useful if a simple bias correction can lead to significantly improved forecasts from an operational forecast viewpoint (McKeen et al., 2005). For several decades, post processing of model predictions is used to improve weather forecasts of surface variables such as temperature, dewpoint or precipitation. One of the principal reasons for this is that despite years of refinement and improvement, meteorological models still contain significant errors (Wilczak et al., 2006; Kang et al., 2010). Air-quality modelling systems have even greater errors because they include the meteorological model errors and also the photochemical and emission model errors. Numerous sensitivity studies have indicated the important role that emissions play in air-quality model forecasts (Hanna et al., 1998; 2001; Baertsch-Ritter et al., 2003), and that highly uncertain emissions are the principal propagator of uncertainty in air-quality modelling systems. In the last years, several studies have been published focusing on the bias-correction in operational air-quality forecast (McKeen et al., 2005; Wilczak et al., 2006; Kang et al., 2008, 2010; Djalalova et al., 2010). A second reason for the use of bias-adjustment techniques in air-quality forecasting is that the measurement point sites used in the evaluation may not be representative of the forecast concentrations averaged over an area equal to that of a model grid cell (Wilczak et al., 2006).

The objectives of this study are to: (1) evaluate the MM5-MNEQA-CMAQ air-quality modelling system, (2) certificate the efficacy of post-processing techniques to improve operational ozone forecasts, and (3) analyse and compare several bias-adjustment techniques.

Descriptions of the modelling system used, MM5-MNEQA-CMAQ, are presented in section 2 while the post processing bias-adjustment methods, the statistical air-quality model forecast and the evaluation of adjusted forecasts against measurements are presented in section 3. Finally, some conclusions are reported in section 4.

2. EXPERIMENTAL SET-UP AND MODELS

In the following sections we comment the characteristics of the studied area, the data used for the evaluation of meteorological and photochemical simulations and a description of the modelling system.

2.1. Area characteristic and data used

The area of study was Catalonia in north-eastern Spain. The population of Catalonia recently reached seven million, most of whom live in and around the city of Barcelona. Catalonia is a Mediterranean area with complex topography, bounded by the Pyrenees to the north and by the Mediterranean Sea to the south and east. From a geographic point of view, the territory can be divided into three different areas. One area runs more or less parallel to the coastline and includes a coastal plain, coastal mountain range and pre-coastal depression. The second area is a central depression; and the third area includes the Pyrenean foothills and the Pyrenees Mountains proper (Figure 1). This complex topography induces an extremely complicated flow structure because of the overlap of local mesoscale circulations with the synoptic flow. Modelling results indicate that during summertime, sea-breeze flow and channelling effects due to terrain features strongly influence the dynamics of the circulatory patterns. This therefore affects the location of the pollutant plumes (Soler et al., 2011), as the main emission sources in the domain of study are located on the coast, especially in the Barcelona urban area and the Tarragona industrial zone. Nitrogen monoxide and dioxide (NO_x) from the metropolitan area of Barcelona represent 23% of total emissions in the domain of study, and 26% of total traffic emissions. Non-methane volatile organic compounds (NMVOCs) from the industrial area of Tarragona represent 64% of total industrial emissions in the area of study. Biogenic sources are also of great importance near the Mediterranean coast; they represent approximately 30% of the total annual NMVOC emissions in the MNEQA model. These emissions are particularly important during summertime because of the higher temperatures and solar radiation intensity, which promote photochemical build-up of ozone and other pollutants.

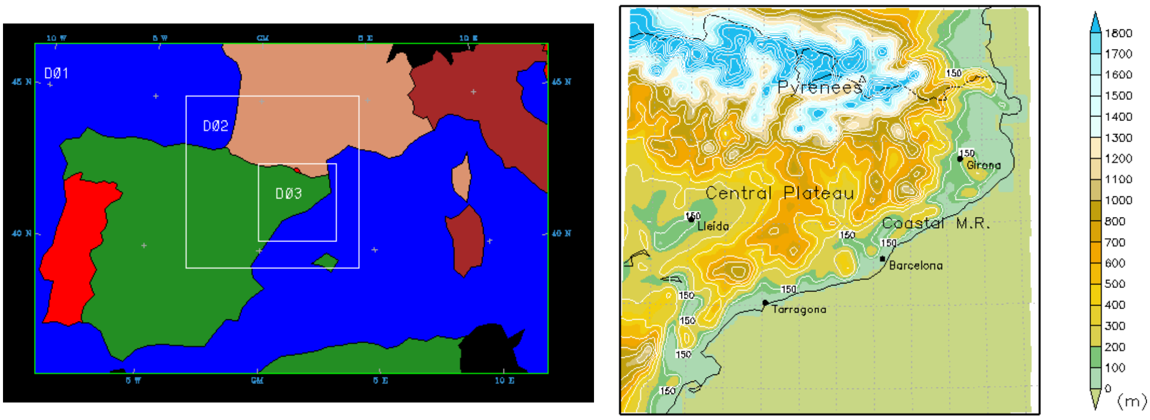


Figure 1. Model domains for MM5 simulations (left panel), and topographical features of Catalonia (right panel).

Meteorological modelling results were evaluated using a set of 35 surface meteorological stations distributed throughout Catalonia that belong to the Catalonian Meteorological Service. The evaluation included wind speed and wind direction measured at 10 m above ground level (a.g.l.), air temperature and specific humidity measured at 1.5 m a.g.l. The air-quality evaluation, focussed on ozone concentrations, was performed using hourly automatic measurements of ozone (O_3) concentration reported by 51 air-quality surface stations named XVPCA (Xarxa de Vigilància I Previsió de la Contaminació Atmosfèrica) that belong to the Environmental Department of the Catalonia Government, which covers the whole of territory considered with an accurate territorial distribution. XVPCA network includes rural, urban and suburban stations providing air-quality data from intensive traffic, industrial and background areas.

The evaluation covers two periods: from May to September in both 2009 and 2010, hereafter referred to as summer 2009 and summer 2010. Both periods are mainly characterized by typical summertime situations with low-pressure conditions favouring the development of thermal circulations, such as mountain winds and sea-breeze circulations (especially in the coastal area) that advect pollutants from the highly urbanized and industrialized coastal zones to the inland regions. The strength of the on-shore flows and the complex topography of the northwest Mediterranean coast produce several pollutant injections due to topographic forcing. As the sea-breeze front advances inland and reaches the mountain ranges located nearly parallel to the coast, topographic injections occur at different altitudes (Jorba et al., 2003; Soler et al., 2011). A number of studies have shown that during summertime, layering and accumulation of pollutants such as ozone and aerosols take place along the eastern Iberian Peninsula (Millán et al., 1992, 1997; Pérez et al., 2004). These mechanisms, together with the development of the thermal internal boundary layers in the coastal areas (Soler at al., 2011), are mainly responsible of the high levels of air pollutants observed, resulting in adverse air quality and an increased potential for health problems.

2.2. Modelling approach

Meteorological numerical simulations were performed using the PSU/NCAR mesoscale model, MM5 (Grell et al., 1994), version 3.7. The MM5 model was configured with three nested domains that have grids of 27, 9 and 3 km (Figure 1), with a two-way interface with the smallest grid. The innermost domain, D1, covers 69x45 grid cells; D2, 70x70 cells; and D3, the inner domain corresponding to Catalonia (NE Spain) covers 94x94 grid cells. Initial and boundary conditions for domain D1 are updated every six hours with analysis data from the European Centre for Medium-range Weather Forecast global model (ECMWF) with a 0.5ºx0.5º resolution. The boundary layer processes are calculated using the MRF scheme based on Troen and Mahrt (1986); the Grell scheme (Grell, 1993) is used for cumulus parameterization, while the microphysics is parameterized using the Schultz scheme (Schultz, 1995). For the land surface scheme, a five-layer soil model is applied in which the temperature is predicted using the vertical diffusion equation for the 0.01, 0.02, 0.04, 0.08, and 0.16 m deep layers from the surface, with the assumption of a fixed substrate (Dudhia, 1996). Solar radiation is parameterized using the cloud-radiation scheme (Dudhia et al., 2004). The vertical resolution includes 32 levels, 20 below (approximately) 1500 m, with the first level at approximately 15 m and the domain top at about 100 hPa. The distribution of the vertical layers, with higher resolution in the lower levels, is a common practice (Zhang et al., 2006a, b; Bravo et al., 2008). The temporal length of meteorological simulations was 48 h and they were performed for each day of each period. A one-hour time-step resolution is used in all domains and models. MM5 hourly outputs files are processed with the Meteorology-Chemistry Interface Processor (MCIP) version 3.2 for the CMAQ model

The photochemical model used in this study to simulate pollutant dispersion is the U.S. Environmental Protection Agency (EPA) model-3/CMAQ model (Byun and Ching, 1999). This model, supported by the U.S. EPA, undergoes continuous development and consists of a suite of programs for conducting air quality model simulations. The CMAQ v4.6 simulations use the CB-05 chemical mechanism and associated EBI solver (Yarwood et al., 2005) including the gas-phase reactions involving nitrogen pentoxide (N_2O_5) and water (H_2O), and it removes obsolete mechanism combinations in the three phases: gas, aerosol (solid or liquid) and aqueous. In addition to these changes, we use version 4.6 which includes modifications in the aerosol module, AERO4 (Bhave et al., 2005; Shankar et al., 2005) with a preliminary treatment of sea salt emissions and chemistry. For treating clouds in the model, we use the asymmetric convective module, ACM (Pleim and Chang, 1992). Additional details regarding the latest release of CMAQ can be found on the Community Modelling and Analysis System (CMAS) Center website: (http://www.cmascenter.org). The CMAQ model uses the same configuration as the MM5 simulation. Boundary conditions and initial values for domain D1 come from a vertical profile supplied by CMAQ itself, while boundary and initial conditions for domains D2 and D3 are supplied by domain D1 and D2 respectively. The model is executed for 48 h, taking the first 24 h as spin-up time to minimize the effects of initial conditions.

MNEQA is an emissions model developed by the Mesoscale and Microscale Atmospheric Modelling and Research Group (MAiR) of the Department of Astronomy and Meteorology at the University of Barcelona (Ortega et al., 2009). In this paper we use the new version 4.0 of the model which is applied to the area of Catalonia, but few modifications should be required to use the model in other regions, with adequate use of local data. MNEQA takes into account different emission sources and distinguishes between surface and elevated sources (at 8 vertical levels). MNEQA includes emissions from natural sources, such as dust particles from erosion and hydrocarbons emitted by vegetation, as well as several anthropogenic sources, such as traffic, industry and residential consumption. Chemical speciation is computed in the model using profiles from the California Air Resources Board (CARB) website (http://arb.ca.gov/ei/speciate/dnldopt.htm#specprof), which is adequate for gas and aerosol mechanisms in CMAQ. Monthly and weekly profiles from the Unified EMEP model (http://www.emep.int/OpenSource/index.html) are applied to determine the value of an emission for each month and day of the year.

Nested domains are commonly applied to air-quality modelling systems because the constituent meteorological, emissions and photochemistry models must deal with grid variability and various domain ranges. As a result of the variability in spatial resolution, the MNEQA method differs from one domain to another. For smaller domains such as D3, MNEQA uses a bottom-up method to calculate pollutant emissions. This involves working on each type of source in a particular way using local information.

MNEQA incorporates an industrial emissions inventory from the Catalan Environmental Department. Traffic and residential consumption emissions are calculated by emission factors using different traffic and residential parameters (length of roads, average speeds on roads, and vehicle type distribution and population) (Ortega et al., 2009). Natural emissions are computed in MNEQA using different parameterizations, and several MM5 model outputs. To incorporate particles from dust erosion, MNEQA uses the windblown dust model from Marticorena and Bergametti (1995) and Vautard (2005), whilst biogenic emissions are incorporated via the method described by Guenther et al. (1994). For larger domains (D1 and D2), MNEQA uses a top-down method, which incorporates into the model pollutant emissions from the European annual inventory EMEP/CORINAIR (http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-2009). Europe and a small section of North Africa are covered by the EMEP domain, with a 50 x 50 km^2 grid resolution. Emissions are computed from national data referring to 11 different sectors (combustion plants, production processes, solvents, waste treatment, agriculture, etc.) and seven pollutants (CO, NH_3, NMVOC, NO_x, SO_x, $PM_{2.5}$ and PM_{coarse}). The top-down method consists of a disaggregation model based on soil uses CLC2000 (Corine Land Class 2000) with 250 m resolution, coupled with different statistical functions, including socio-economic variables (Maes et al., 2009). We associate EMEP sectors with soil uses CLC2000 to allocate geographical distributions of emissions with horizontal resolutions of 9 km (D2) and 27 km (D1). Statistical functions are used as weighting functions to accurately distribute an emission value over the different grid cells. Finally, the emissions are merged for every grid cell using a geographical information system (GIS), because the photochemical model does not distinguish between the various types of sources; all that the CMAQ model requires is one emission value for each grid cell, each time step and each chemical species. MNEQAv4.0 is executed daily to calculate hourly emissions for 24- and 48-hour simulations.

3. STATISTICAL AIR-QUALITY MODELLING SYSTEM EVALUATION

As an air-quality modelling system is a conjunction of three models: meteorological, photochemical and emission, and since the last of these has already been compared with other emission models (Ortega et al., 2009), in this section the results of the MM5 meteorological model and CMAQ photochemical model will be evaluated using the classic approach; we compare discrete values corresponding to surface measurements and model results. The statistics selected to drive the evaluation are taken from Denby (2010) and EPA (2009) as suggested by Emery et al. (2001) and Tesche et al. (2002). The mathematical definition and the associated benchmarks are summarized in Table 1.

Table 1. Quantitative performance statistics for meteorology variables and/or ozone concentrations. M is the forecast value and O the measurement.

Statistical Parameter / Mathematical Definition	Variable	Benchmark
$MB = \frac{1}{N}\sum_{i=1}^{N}(M_i - O_i)$	Wind Speed	$< \pm 0.5$ ms^{-1}
	Wind Direction	$< \pm 10$º
	Temperature	$< \pm 0.5$ K
	Specific Humidity	$< \pm 1$ g kg^{-1}
$MAGE = \frac{1}{N}\sum_{i=1}^{N}\lvert M_i - O_i\rvert$	Wind Direction	< 30º
	Temperature	< 2 K
	Specific Humidity	< 2 g kg^{-1}
$MNBE = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{M_i - O_i}{O_i}\right)\cdot 100\%$	O_3 concentration	$< \pm 15$ %
$MNGE = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\lvert M_i - O_i\rvert}{O_i}\right)\cdot 100\%$	O_3 concentration	< 35 %
$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(M_i - O_i)^2}$	Wind Speed	< 2 ms^{-1}
$IOA = 1 - \frac{\sum_{i=1}^{N}(M_i - O_i)^2}{\sum_{i=1}^{N}\left[\lvert M_i - \overline{M}\rvert + \lvert O_i - \overline{O}\rvert\right]^2}$	Wind Speed	≥ 0.6
	Temperature	≥ 0.8
	Specific Humidity	≥ 0.6
$UPA = 100\cdot\frac{M_{max} - O_{max}}{O_{max}}$	O_3 concentration	$< \pm 20$ %

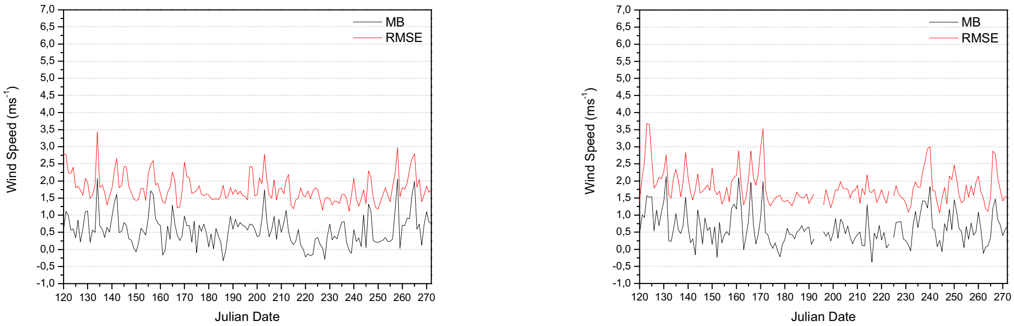
3.1. Evaluation of the meteorological model performance

As detailed above model results were evaluated from a set of different surface meteorological stations distributed over Catalonia. The root mean square error (RMSE), the mean absolute gross error (MAGE), the mean bias (MB) and the index of agreement for these meteorological parameters were calculated for hourly data provided by both the model and observations (see Table 1 for definition) resulting in a daily statistical value (Figure 2), a statistical value for the whole period (Table 2) and a hourly statistical value (Figure 3). Wind statistics and wind direction are calculated for wind speed higher than 0.5 m s^{-1}, as wind direction is not reliable for lower speeds. The computation of statistical parameters is straightforward for wind speed, specific humidity and temperature, but the circular nature of wind direction makes it difficult to obtain the corresponding statistics. To avoid this problem we used a modified wind direction, wherein 360º was either added to or subtracted from the predicted value to minimize the absolute difference between the observed and predicted wind directions (Lee and Fernando, 2004; Soler et al., 2011). For example, if the prediction is 10º and the corresponding observation is 340º, then a predicted value of 370º is used.

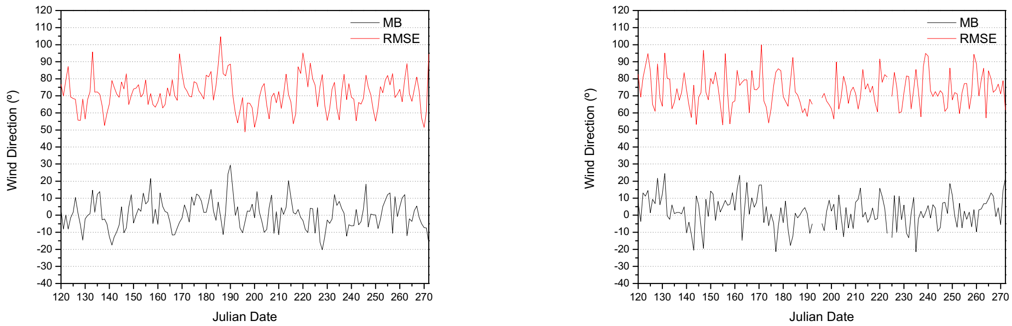
Table 2. Statistics corresponding to MM5 model evaluation taking into account the whole studied period.

Meteorological variable	Statistic	AQM.cat 2009	AQM.cat 2010
Wind Speed	RMSE (ms^{-1})	1.82	1.89
	MB (ms^{-1})	0.57	0.63
	IOA	0.66	0.65
Wind Direction	MAGE (º)	69.35	70.90
	MB (º)	0.62	2.11
Temperature	MAGE (K)	1.97	1.87
	MB (K)	-0.88	-0.56
	IOA	0.93	0.95
Specific Humidity	MAGE (g kg^{-1})	1.26	1.42
	MB (g kg^{-1})	0.22	0.36
	IOA	0.89	0.86

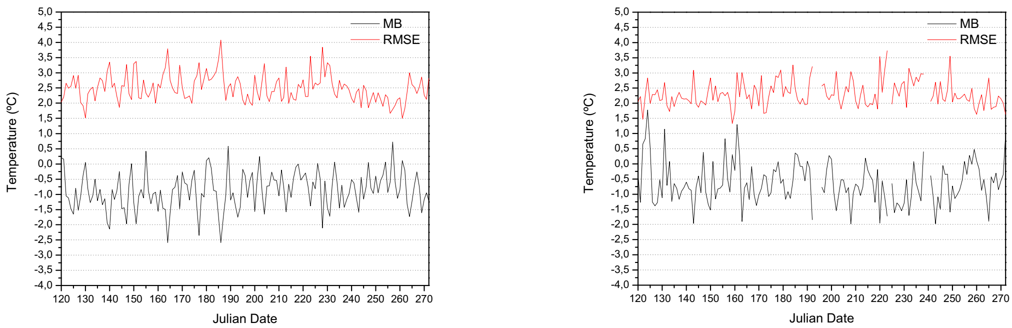
(a)



(b)



(c)



(d)

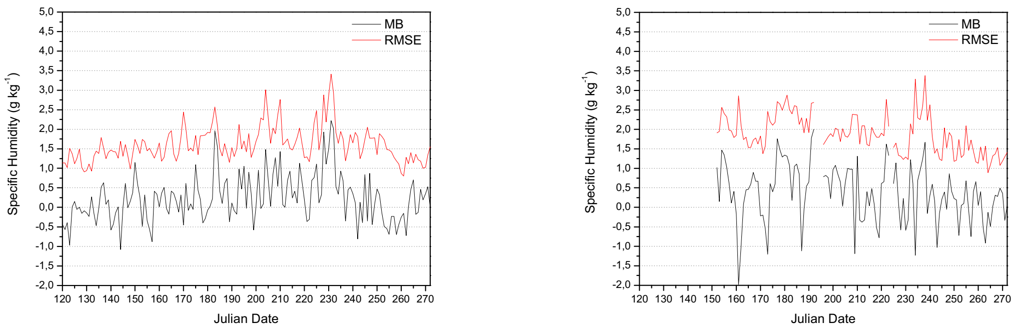


Figure 2. Evolution of the daily RMSE and MB errors for the summer 2009 period (left panel) and summer 2010 period (right panel): (a) wind speed measured at 10 m (a.g.l.); (b) wind direction measured at 10 m (a.g.l.); (c) air temperature at 1.5 m (a.g.l.); (d) specific humidity at 1.5 m (a.g.l).

To evaluate the accuracy of the meteorological predictions of the air-quality modelling system, in Table 2 global statistical values for the whole period are compared with the benchmarks in Table 1 from Denby (2010) and EPA (2009). The results show that statistical values corresponding to specific humidity and wind speed fall within recommendations, or are very close to them. Wind speed is slightly overestimated by the model, while wind direction statistics show a slightly greater dispersion: with 69.35º (2009) and 70.90º (2010) as MAGE values. This characteristic is associated with the complex topography and it is reproduced by several authors working in this area with different meteorological models (Borge et al., 2008; Jiménez et al., 2006a; 2008). For temperature, the underestimation (-0.88K and -0.56K) is higher than that suggested (-0.50K), but MAGE and IOA values fall within the recommendations.

Figures 2 and 3 show the daily and hourly evolution respectively of RMSE and MB values corresponding to wind speed, wind direction, temperature and specific humidity for the period studied. Wind speed (Figure 2a) shows an RMSE of between 1 and 3 m s^{-1} and an MB of between 0 and 2 m s^{-1} for the whole period. As we commented in section 2.1, typical summer weather conditions are anticyclonic with a slight pressure gradient favouring the development of mesoscale circulations such as a sea-breeze regime on the coast and mountain winds inland. The wind speed associated with these circulation patterns is reproduced quite well by the model, although it tends to overestimate wind speed, only slightly during the day but more at night, with values of MB between 0.5 and 1.0 m s^{-1} (Figure 3a). Figure 2b shows the daily evolution of RMSE and MB values corresponding to wind direction, with values ranging between 60º and 90º, and -10º to 10º respectively, whilst Figure 3b shows the hourly evolution of RMSE and MB for the same variable. During the diurnal hours, RMSE values decrease strongly indicating that the model performs well; however, at night, the model does not reproduce very weak winds accurately (Bravo et al., 2008), with the RMSE values increasing to 80-90 degrees. The poor performance for this variable could be attributed to the complex topography of the area studied. For air temperature, daily evolutions of RMSE and MB are presented in Figure 2c. For most of the period studied, the RMSE ranges between 2 and 3 degrees, while the MB ranges between 0 and -1.5 degrees. These results highlight the tendency of the MM5 model to underestimate the air temperature at a height of 1.5 m during diurnal hours (Figure 3c). At night, the model slightly overestimates the temperature. This results in a negative MB value for the whole period. Finally, Figures 2d and 3d show daily and hourly evolutions of RMSE and MB for specific humidity. Daily RMSE ranges between 1 and 2.5 g kg^{-1} while MB values range from -1 to 1 g kg^{-1}. Similarly to the case of wind direction and temperature evaluation, the model reproduces specific humidity better during daytime than during night-time.

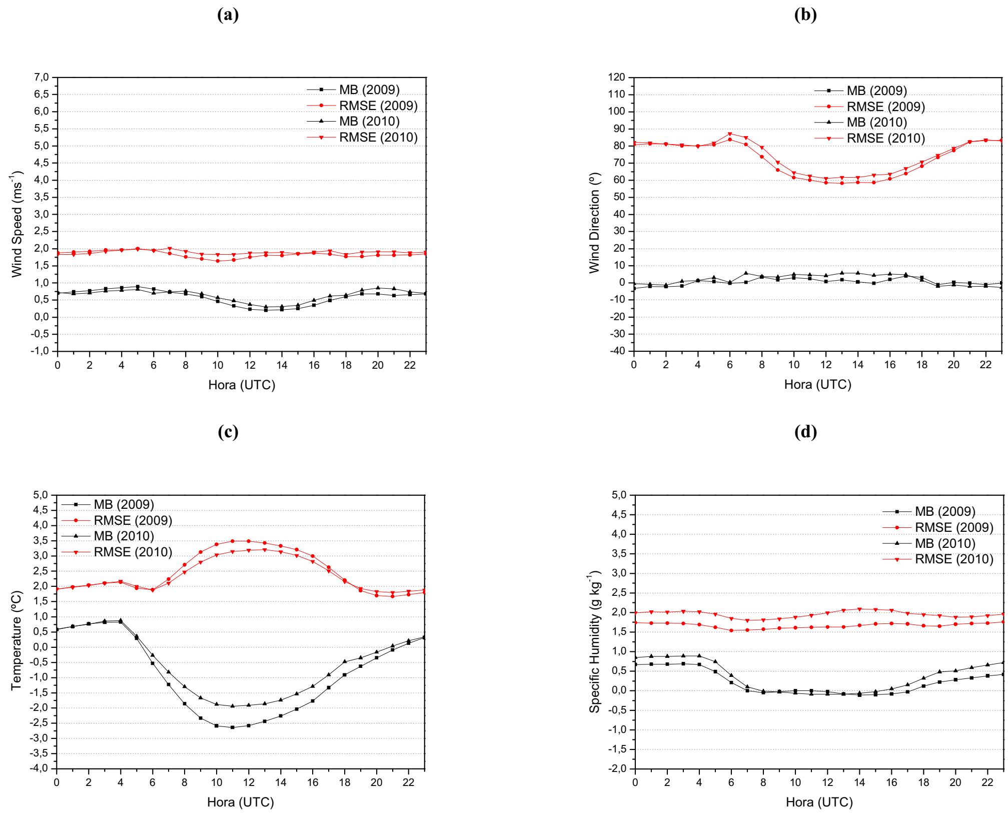


Figure 3. Time evolution of hourly – averaged mean bias and root mean square error for the summer 2009 period and summer 2010 period: (a) wind speed measured at 10 m (a.g.l.); (b) wind direction measured at 10 m (a.g.l.); (c) air temperature at 1.5 m (a.g.l.); (d) specific humidity at 1.5 m (a.g.l).

The performance of the meteorological model agrees with several previous studies of meteorological applications for air-quality modelling (Zhang et al., 2006a), especially those based on the area of study (Jimenez et al., 2006a), where classical statistics for surface fields have been reported. In comparison with previous results of this air-quality modelling (Arasa et al., 2010), the use of higher horizontal resolution yields better results, especially for temperature and wind direction. Meteorological predictions over complex terrain require fine horizontal and vertical resolution for resolving complex mesoscale circulation patterns, especially during night-time. It is known that during the day, under weak synoptic-scale conditions, the lower part of the atmosphere (the atmospheric boundary layer) is mainly governed by thermal effects; buoyancy is the dominant mechanism driving turbulence, which is assumed to be correctly described by existing similarity theories in the model. In contrast, during the night, turbulent mixing is greatly reduced or even completely suppressed, or it becomes intermittent. Various observations and studies (Mahrt et al., 1999, 2002; Cuxart et al., 2000; Poulos et al., 2002) have revealed a wide variety of nocturnal boundary layer situations, with sporadic and intermittent turbulence. In addition, this stable stratification in a non-uniform terrain induces local circulations, such as drainage flows (Soler et al., 2004), and leads to several phenomena such as gravity waves, density currents (Tarradellas et al., 2005), intrusions and meandering, with the frequent presence of low-level jets (Conangla and Cuxart, 2006). The misrepresentation of these effects can lead to incorrect estimates of vertical turbulent transport in the nocturnal boundary layer, resulting in an erroneous amount of exchange of heat and momentum over wide areas of the planet (Bravo et al., 2008). If we focus on the mesoscale, namely the basin scale as in this exercise, an incorrect treatment of the stable boundary layer can produce errors of several degrees in the temperature at 1.5 m and moisture levels that are too high or too low, and it may fail to adequately capture fog events, and lead to 100% errors in the wind speed or direction, if the local physiographical features are not well represented in the model.

3.2. Evaluation of the photochemical model

Statistical metrics for photochemical model performance assessment are calculated for surface ozone concentrations measured at 51 measurement sites in the 3x3km^2 modelling domain. Measurement stations are listed in Table 3 which shows their emplacement as well as the average observed ozone concentration values versus the simulated values for the summers of 2009 and 2010. The results indicate that the model has a tendency to underestimate the ground-level ozone concentration at different stations. Observed and modelled values show quite significant correlation, with coefficient correlations of 0.710 and 0.607 for 2009 and 2010 respectively.

The US Environmental Protection Agency (EPA, 2005) developed guidelines indicating that it is inappropriate to establish a rigid criterion for model acceptance or rejection (i.e. no pass/fail test). However, building on past ozone modelling applications (EPA, 1991) a common range of values for bias, error and accuracy has been established. The three multi-site metrics used are the unpaired peak prediction peak accuracy (UPA), the mean normalized bias error (MNBE) and the mean normalized gross error (MNGE). These statistics and the accepted EPA (1991) criteria are showed in Table 1. The statistical parameters are applied to hourly and to both 1-hour (1-h) and 8-hour (8-h) maximum ozone surface concentrations, using only the hourly observation-prediction pairs for which the observed concentration is greater than a specific value (cut-off: 60 μgm^{-3}; Sistla et al., 1996; Hogrefe et al., 2001), thus removing the influence of low concentrations such as night-time values.

Table 3. Location of measurement stations with average summer observed values and simulated concentrations of troposheric ozone.

Station	LON (º sexag.)	LAT (º sexag.)	2009 - O_3 measured ($\mu g\ m^{-3}$)	2009 - O_3 modelled ($\mu g\ m^{-3}$)	2010 - O_3 measured ($\mu g\ m^{-3}$)	2010 - O_3 modelled ($\mu g\ m^{-3}$)
Constantí	1.219	41.156	67	60	69	58
Vila-seca	1.153	41.113	66	64	68	62
Manresa	1.826	41.731	52	70	57	63
Martorell	1.922	41.477	45	47	52	41
Igualada	0.627	41.579	64	67	57	62
Lleida	0.617	41.617	69	66	66	62
Sant Celoni	2.497	41.690	58	63	48	56
Sabadell	2.103	41.562	53	71	55	62
Reus	1.121	41.152	73	66	73	62
Pardines	2.215	42.313	86	85	78	86
Agullana	2.843	42.393	91	71	82	70
Juneda	0.818	41.551	80	69	76	67
Sort	1.131	42.407	67	79	68	78
Amposta	0.583	40.708	73	66	77	65
Sta. Maria de Palautordera	2.443	41.692	67	73	66	66
St. Cugat del Vallès	2.090	41.789	60	53	58	46
Begur	3.214	41.960	92	71	88	71
Vilanova i la Geltrú	1.722	41.220	69	65	75	63
Santa Pau	2.513	42.146	64	76	60	77
Gandesa	0.441	41.059	84	70	96	71
Bellver de Cerdanya	1.778	42.369	70	79	69	78
Granollers	2.280	41.601	60	61	62	51
Ponts	1.196	41.905	77	75	75	73
La Sénia	0.289	40.644	93	69	91	69
Vic	2.240	41.937	66	71	67	64
Tarragona - Parc de la ciutat	1.243	41.119	65	61	67	58
Rubí	2.044	41.493	61	52	80	46
Tona	2.222	41.848	78	80	78	77
Alcover	1.181	41.280	79	70	76	69
Guiamets	0.756	41.102	85	71	91	72
Berga	1.849	42.097	80	82	67	79
Terrassa	2.009	41.557	58	62	56	54
Manlleu	2.288	42.004	63	78	57	73
Mollet del Vallès	2.213	41.550	48	51	48	44
Vilafranca del Penedès	1.688	41.347	75	66	65	59
Mataró	2.444	41.548	62	61	77	56
Sta. Perpètua de la Mogoda	2.218	41.537	55	57	54	48
Barcelona – Poblenou	2.189	41.388	49	43	57	26
L'Hospitalet del Llobregat	2.116	41.372	61	56	66	47
St. Adrià del Besòs	2.223	41.427	62	54	57	42
Badalona	2.240	41.445	56	56	65	46
Montcada i Reixac	2.190	41.483	48	53	54	46
St. Vicenç dels Horts	2.011	41.393	50	47	58	41
St. Andreu de la Barca	1.976	41.452	47	45	51	40
Barcelona – Eixample	2.155	41.386	42	53	44	38
Sta. Coloma de Gramanet	2.210	41.448	56	54	56	45
Barcelona – Gràcia	2.154	41.400	47	54	49	41
Barcelona - Ciutadella	2.205	41.405	49	61	63	51
Gavà	1.993	41.304	58	57	54	55
Barcelona – Vall d'Hebron	2.149	41.427	62	59	69	44
Vandellòs	0.833	41.016	69	72	95	72

3.2.1. Bias-adjustment techniques

As we comment in the introduction, during recent years several studies have been published that focus on the application of bias-correction methods to operational air-quality forecasting. A range from highly-sophisticated mathematical algorithms to simple algorithms has been studied and evaluated. Among them, a sophisticated technique used in recent years is the Kalman Filter (KF) (Kalman, 1960) predictor forecast method, described in detail in Delle Monache et al. (2006). This technique has been shown to improve accuracy in forecasts and represents the current status of knowledge in bias-adjustment techniques. Even so, techniques based on very simple mathematical algorithms have been incorporated into air quality modelling systems, showing similar performance to that achieved with the KF technique in improving the accuracy of forecast models by reducing forecast errors (McKeen et al., 2005; Wilczak et al., 2006; Kang et al., 2008). For this reason, in order to improve the AQM.cat ozone operational forecasts in this study and to evaluate the performance of bias-adjustment techniques, three simple bias-correction approaches are applied and analysed. However, the authors do not rule out the possibility of incorporating the KF technique into the air quality modelling system in future work.

The first approach, hereafter referred to as mean subtraction (MS) (McKeen et al., 2005), is the standard and most-used bias correction in meteorological analysis. The second approach, hereafter refereed to as multiplicative ratio adjustment (RA) (McKeen et al., 2005), is an alternative correction that may be more suitable for ozone predictions since corrected mixing ratios will always be a non-negative technique, and the third approach applied is the hybrid forecast, hereafter referred to as (HF) (Kang et al., 2008).

The bias-correction algorithms are applied to hourly and 1-h maximum surface ozone concentrations. The mathematical formulation of each technique is presented and commented in the next lines.

The MS method is based in an additive correction to correct the model forecast M given in expression (1).

$$MS(i,h) \equiv M(i,h) - MB(i,h) \qquad (1)$$

where i corresponds to each ozone monitor site and h to the hourly value. The correction given by the expression (2) is calculated as an evaluation of the systematic error within the model, M, and the observations, O, during a number of days ago (d). The parameter N is taken as 10 days in this study. The selection of a 10-day period for the calculation of the running mean bias correction is based on the results of Wilczak et al. (2006).

$$MB(i,h) \equiv \frac{1}{N}\sum_{d}\left[M(i,h,d) - O(i,h,d)\right] \qquad (2)$$

The second method considered is the multiplicative or RA bias correction. The mathematical formulation of this method is given by expression (3). It is based on the application of a correction factor over the forecast model. This coefficient is calculated as the quotient between the additions of observed and modelled values over the last 10 days.

$$RA(i,h) \equiv M(i,h) \cdot \frac{\sum_{d} O(i,h,d)}{\sum_{d} M(i,h,d)} \qquad (3)$$

The HF approach is based on the simple assumption that the model is capable of predicting the change in the pollutant mixing ratio from one day to the next due to changes in the synoptic or large-scale forcing (Kang et al., 2008). In this way, the forecast value can be improved by combining the observed value at the previous time with the forecast model change from the previous to current time. The bias-adjusted hybrid forecast $HF_{t+\Delta t}$ for a future time can be represented as:

$$HF(i,h)_{t+\Delta t} \equiv O(i,h)_{t} + \left(M(i,h)_{t-\Delta t} - M(i,h)_{t}\right) \qquad (4)$$

Where O_t are observations at time t, and, $M_{t+\Delta t}$ and M_t are modelled ozone forecast values at time $t+\Delta t$ and t respectively. Here Δt is 24 h.

3.2.2. Model and bias-corrected ozone forecast

In Figure 4 we can see the averaged hourly evolution of measurements, modelling system forecasts (MOD), and bias-corrected forecasts for each bias-correction method (MOD_MS, MOD_RA, MOD_HF). It shows a diurnal underestimation of forecasts, and a nocturnal overestimation, which is more significant in summer 2009 than in 2010. The diurnal underestimation could be caused by: (1) sea-breeze and land-breeze circulations that are difficult to reproduce, associated with the important role of circulation patterns in photochemical simulations (Pirovano et al., 2007); (2) a tendency to underpredict ozone precursors (nitrogen oxides, carbon monoxide and volatile organic compounds) in air-quality modelling systems (Russell and Dennis, 2000); (3) the uncertainty in the emissions coming from the MNEQA model and in its temporal distribution; and (4) underestimation of temperature forecasts in the model MM5 (Ortega et al., 2010), which is more important in summer heat episodes. Three main sources of nocturnal overestimation could be: (1) the model does not represent nocturnal physicochemical processes accurately enough (Jimenez et al., 2006b); (2) the MNEQA emission model may not calculate night-time emissions properly; (3) meteorological parameters, such as wind speed, wind direction and vertical mixing, are not well reproduced by the model when the synoptic forcing is weak and the ambient winds are light and variable (Schürman et al., 2009; Bravo et al., 2008). This nocturnal overestimation is reduced in summer 2010, probably due to several different reasons, such as: (1) changes in the minimum value of the vertical coefficient of turbulent diffusivity, K_z, from a constant value of $1 m^2 s^{-1}$ (summer 2009) to a variable value depending on the urban fraction, from $0.5 m^2 s^{-1}$ for rural areas to $2 m^2 s^{-1}$ for urban areas; and (2) emissions coming from the MNEQA model are updated. As we commented previously, to remove the influence of low concentrations, such as night-time values, evaluation statistics are calculated using only observation-prediction pairs for which the observed concentration is greater than 60 $\mu g\ m^{-3}$.

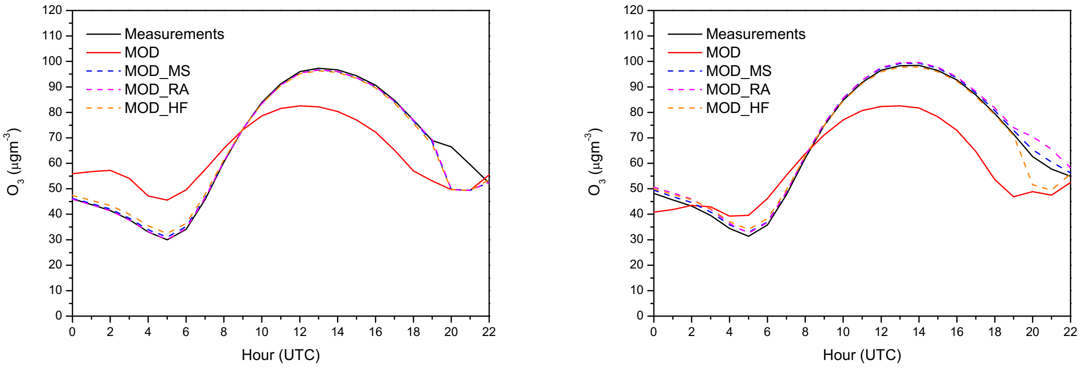


Figure 4. Time evolution of averaged hourly ozone concentrations provided by the air-quality model and bias-corrected forecast at the 51 air-quality stations for the summer 2009 period (left panel) and summer 2010 period (right panel).

Averages of the statistics metrics for hourly and daily 1-h and 8-h peak surface ozone concentrations for summer 2009 and 2010 are presented in Table 4 and Table 5 respectively. Statistical parameter values indicate that the model shows a tendency to underestimate ground-level ozone concentration, as MB and MNBE values are negative for hourly and 1-h and 8-h maximum surface ozone concentrations. MNBE values are slightly higher than the recognized criterion in several cases, -16.72% and -20.18% for hourly values during summer 2009 and summer 2010 respectively, and -15.52% and -15.67% for 1-h and 8-h maximum surface ozone concentrations in summer 2010. MNGE and UPA values are within the EPA recommendations while IOA values show significant accuracy for hourly and 1-h maximum surface ozone concentrations, and good accuracy for 8-h maximum values. The performance of the air-quality modelling system agrees with some previous results on air-quality modelling in the studied area (Jiménez et al., 2006a; Jiménez et al., 2008) where statistical values are also within the EPA criteria.

The impact of the application of the bias-correction techniques to surface ozone concentrations forecast by the model is to tend to improve the statistical parameter values: MNBE, MNGE and UPA values are within the EPA recommendations. In this way, hourly surface ozone concentration underestimation is reduced by between 10% and 15%, while 1-h and 8-h maximum underestimation is reduced by between 14 and 23%. In addition, the performance changes to a slight overestimation. However, in some cases the application of the bias-correction techniques makes the forecast worse or the errors become very similar. As an example, we observe that IOA is reduced by 14% or 8% when RA is applied to 1-h and 8-h maximum ozone surface concentrations in summer 2010. The reason for this behaviour is that the RA mathematical algorithm increases the width of the concentration distribution around the mean value and therefore increases the standard deviation as we can see in table 6. The RA method reproduces very high levels of ozone concentration, but this forecast does not always provide realistic values. In the operational daily forecasts we observed situations where the quotient between observations and model forecasts is greater than 1.25, which indicates that in these situations the bias-corrected forecast does not provide good results.

Table 4. Summary statistics corresponding to air-quality stations associated with air-quality simulations of ozone concentration for summer 2009.

Values	Statistic	MOD	MOD_MS	MOD_RA	MOD_HF
Hourly	MB (μgm^{-3})	-17.28	-6.47	-6.31	-6.60
	MAGE (μgm^{-3})	22.09	17.81	18.73	21.96
	MNBE (%)	-16.72	-5.69	-5.56	-6.10
	MNGE (%)	23.20	20.03	21.06	24.98
	RMSE (μgm^{-3})	27.81	22.59	23.84	28.29
	IOA	0.551	0.703	0.687	0.640
1-h Maximum	MB (μgm^{-3})	-17.43	-2.50	0.91	4.41
	MAGE (μgm^{-3})	24.53	18.34	20.95	20.73
	MNBE (%)	-13.71	0.17	3.63	6.38
	MNGE (%)	22.03	17.59	20.46	20.45
	RMSE (μgm^{-3})	30.33	23.26	27.72	26.64
	UPA (%)	-17.47	2.31	19.99	4.40
	IOA	0.551	0.684	0.620	0.666
8-h Maximum	MB (μgm^{-3})	-15.60	-2.10	-1.37	-0.59
	MAGE (μgm^{-3})	20.62	15.40	16.26	18.09
	MNBE (%)	-13.73	-0.02	0.73	1.34
	MNGE (%)	20.41	16.43	17.37	19.52
	RMSE (μgm^{-3})	25.41	19.28	20.53	23.10
	UPA (%)	-16.44	1.28	8.22	6.27
	IOA	0.818	0.853	0.837	0.808

Table 5. Summary statistics corresponding to air-quality stations associated with air-quality simulations of ozone concentration for summer 2010.

Values	Statistic	MOD	MOD_MS	MOD_RA	MOD_HF
Hourly	MB (μgm^{-3})	-20.97	-5.35	-4.39	-6.89
	MAGE (μgm^{-3})	25.36	19.57	22.88	23.33
	MNBE (%)	-21.36	-4.41	-3.24	-6.57
	MNGE (%)	27.12	22.04	26.03	26.57
	RMSE (μgm^{-3})	32.51	25.36	30.63	30.25
	IOA	0.532	0.670	0.597	0.631
1-h Maximum	MB (μgm^{-3})	-19.23	0.28	9.61	5.62
	MAGE (μgm^{-3})	25.04	19.58	27.47	22.39
	MNBE (%)	-15.52	2.93	12.72	7.83
	MNGE (%)	22.16	18.81	27.39	22.15
	RMSE (μgm^{-3})	32.20	25.38	38.14	39.36
	UPA (%)	0.30	1.89	3.42	3.36
	IOA	0.550	0.658	0.473	0.636
8-h Maximum	MB (μgm^{-3})	-16.75	-0.24	2.77	-0.13
	MAGE (μgm^{-3})	21.51	17.12	20.12	19.42
	MNBE (%)	-14.99	1.91	5.18	1.63
	MNGE (%)	21.03	18.07	21.46	20.84
	RMSE (μgm^{-3})	27.21	22.12	26.51	25.22
	UPA (%)	-1.40	8.22	12.54	13.89
	IOA	0.802	0.807	0.735	0.783

Histograms of model forecast errors (bias error) of the daily 1-h and 8-h maximum surface ozone concentrations are shown in Figure 5, with and without applying bias-correction techniques. The negative bias of the air-quality modelling system predicting ozone concentrations is observed as a shift of the peak in the distribution toward negative values, while the distributions shift the peak close to zero when the model forecast is corrected. In some cases the bias-correction techniques enlarge the height of the distribution peak, therefore increasing the number of forecasts with bias close to zero and reducing the width of the distribution with the consequent decrease of the standard deviation, σ. To evaluate the shift in the peak and the width of the distribution when we apply bias-correction techniques to air-quality modelling system outputs, we adjust the distribution to a Gaussian function. The results of this adjustment are presented in Table 6.

Table 6. Width and shift of the Gaussian adjustment calculated over the distributions of the air-quality modelling system and bias-corrected 1-h and 8-h maximum surface ozone concentration forecast.

Parameter	Values	Year	MOD	MOD_MS	MOD_RA	MOD_HF
Width (2σ)	1-h Maximum	2009	45.84	44.44	47.91	48.55
(μgm^{-3})		2010	44.96	45.34	54.04	50.71
	8-h Maximum	2009	40.30	38.78	40.40	42.92
		2010	41.61	40.86	46.30	43.91
Shift	1-h Maximum	2009	-16.05	-0.79	-0.07	5.24
(μgm^{-3})		2010	-14.99	2.80	6.68	4.66
	8-h Maximum	2009	-13.32	0.17	0.05	1.72
		2010	-12.80	2.22	3.90	0.27

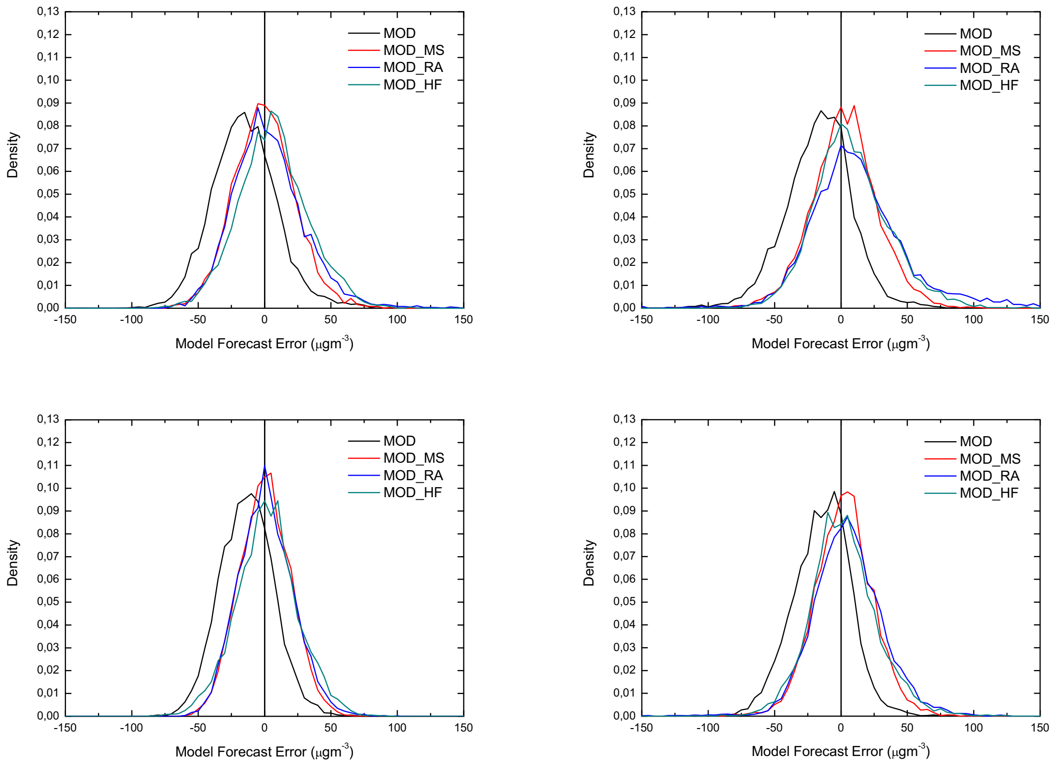


Figure 5. Histograms of model forecast error in the daily maximum 1-h surface ozone concentrations (upper panel) and maximum 8-h surface ozone concentrations (lower panel) for model predictions and bias-corrected forecasts in summer 2009 (left panel) and 2010 (right panel).

Quantitative results showed in the tables and histograms of Figure 5, demonstrate that MS is the technique that leads to the greatest adjustment. In addition, the operational daily forecast contributes to some conclusions regarding the accuracy of each technique in different situations. MS and RA provided better results than HF when the area studied is dominated by stagnant meteorological situations, prevailing mesoscale circulations such as a sea-breeze, which are mainly associated with high ozone episodes. However, the mathematical formulation of MS produces distributions with lower standard deviation if we compare them with those corresponding to RA. Otherwise, HF provides the best results when it is applied to meteorological conditions characterized by changes in the synoptic or large-scale forcing, assuming that the model is capable of predicting the change in the pollutant mixing ratio from one day to the next.

To explore forecast performance as a function of the measurement emplacement, we have classified the 51 monitoring stations as rural, urban or suburban. A monitor location is considered representative of an urban measurement when within an area of 1 km^2, at least 90% of the terrain is urbanized; it is considered rural when within an area of 100 km^2, at most 10% of the terrain is urbanized; and it is considered suburban when neither the urban not the rural definition applies (Catalan Environmental Agency, 2001).

Table 7 shows the results of the statistical parameters MNBE, MNGE and IOA as a function of measurement emplacement. We chose MNBE and MNGE values to estimate the bias and gross error of the air-quality forecast because we can compare these values with EPA recommendations. We complete the table with IOA because this parameter provides a measure of the agreement and accuracy of the forecast. We considered MS as the only bias-correction technique because it presents the best results and minimizes the width of the distribution, as commented above.

Table 7. Statistics corresponding to air-quality stations associated with air-quality simulations of ozone concentration according to the monitor location classification (urban, suburban, rural and all locations).

Year	Monitor Location Classification	Number	Hourly MNBE (%)		1-h Max MNBE (%)		8-h Max MNBE (%)	
			MOD	MOD-MS	MOD	MOD-MS	MOD	MOD-MS
2009	All data	51	-16.72	-5.69	-13.71	0.17	-13.73	-0.02
	Urban	18	-16.14	-9.57	-8.18	0.00	-9.63	-1.93
	Suburban	17	-18.16	-5.79	-12.60	1.29	-13.37	0.38
	Rural	16	-16.05	-3.06	-20.21	-0.83	-17.65	1.23
2010	All data	51	-21.36	-4.41	-15.52	2.93	-14.99	1.91
	Urban	18	-26.34	-6.89	-15.43	3.25	-15.62	1.14
	Suburban	17	-23.02	-5.10	-14.44	3.00	-14.95	1.40
	Rural	16	-16.32	-1.99	-16.70	2.53	-14.41	3.17
			Hourly MNGE (%)		1-h Max MNGE (%)		8-h Max MNGE (%)	
			MOD	MOD-MS	MOD	MOD-MS	MOD	MOD-MS
2009	All data	51	23.20	20.03	22.03	17.59	20.41	16.43
	Urban	18	24.75	22.82	21.48	19.18	20.45	17.69
	Suburban	17	24.82	20.59	21.61	18.20	19.87	16.70
	Rural	16	21.01	17.77	23.00	15.40	20.93	15.06
2010	All data	51	27.12	22.04	22.16	18.81	21.03	18.07
	Urban	18	32.25	24.10	23.29	19.95	22.84	18.97
	Suburban	17	29.03	22.70	22.03	19.53	21.25	18.58
	Rural	16	21.77	19.98	20.82	16.91	19.07	16.71
			Hourly IOA		1-h Max IOA		8-h Max IOA	
			MOD	MOD-MS	MOD	MOD-MS	MOD	MOD-MS
2009	All data	51	0.551	0.703	0.551	0.684	0.818	0.853
	Urban	18	0.537	0.641	0.558	0.644	0.855	0.879
	Suburban	17	0.557	0.683	0.568	0.655	0.838	0.850
	Rural	16	0.539	0.731	0.518	0.665	0.747	0.793
2010	All data	51	0.532	0.670	0.550	0.658	0.802	0.807
	Urban	18	0.489	0.623	0.513	0.602	0.816	0.827
	Suburban	17	0.532	0.679	0.564	0.666	0.810	0.816
	Rural	16	0.550	0.682	0.548	0.666	0.763	0.755

Results show that MNBE and MNGE values corresponding to the hourly air-quality model forecasts are better in rural sites, for instance MNGE in this area is reduced by between 4% and 10% compared to the gross error found in urban and suburban areas. The same value is reduced by between 3% and 5% if we apply MS. This characteristic is associated with the difficulty air-quality modelling systems encounter in reproducing ozone levels in urban areas, mainly due to the important variability of traffic emissions, which it is difficult to reflect in the emission mode; and the poor representations of the nocturnal physicochemical processes in the photochemical model (Jiménez et al., 2008). Concerning the IOA parameter, 8-h maximum forecasts for the air-quality model forecast are better in urban and suburban sites; its value is between 6 and 14% higher than those found in rural areas. If we apply MS IOA increases by between 7% and 11%. The 1-h maximum error values do not show clear differences between rural, urban and suburban sites: its behaviour depends on the measurement station considered and therefore we cannot extract conclusive results.

In the applications presented in this study, the bias-adjustment techniques provide different corrected forecast values corresponding with the model grid cell where the measurement point is. The extension of these methods to develop bias-adjusted values for every 3 km x 3 km grid cell, covering all the D3 domain for operative forecasts, requires the application of objective analysis techniques with successive corrections (Thiébaux and Pedder, 1987) based on the Cressman scheme (Cressman, 1959). These methods are usually used in meteorological models to incorporate information from observations. This is ongoing research and results are not yet conclusive.

3.2.3. Unsystematic and systematic error

As well as the statistical validation, unsystematic and systematic root mean square error, $RMSE_u$ and $RMSE_s$ defined in expressions (5) and (6), were computed in order to evaluate the intrinsic error in the model and the random error (Appel et al., 2007).

$$RMSE_u = \sqrt{\frac{1}{N}\sum_{1}^{N}(C - C_m)^2} \quad (5)$$

$$RMSE_s = \sqrt{\frac{1}{N}\sum_{1}^{N}(C - C_o)^2} \quad (6)$$

$$C = a + b * C_o \quad (7)$$

$$RMSE = \sqrt{(RMSE_u)^2 + (RMSE_s)^2} \quad (8)$$

$\underline{C_m}$ and $\underline{C_o}$ values are modelled and observed concentrations, respectively; a and b are the least squares regression coefficients derived from the linear regression between $\underline{C_m}$ and $\underline{C_o}$; and N is the total number of model/observation pairs. These new measurements help to identify the sources or types of error, which can be of considerable help in refining a model. The $RMSE_s$ represents the portion of the error that is attributable to systematic model errors; and the $RMSE_u$ represents random errors in the model or model inputs that are less easily addressed. For a good model, the unsystematic portion of the RMSE is much larger than the systematic portion: whereas a high systematic $RMSE_s$ value indicates a poor model.

Results are given in Table 8 for each summer, 2009 and 2010. For the case studied, results for 1-h and 8-h peak surface ozone concentrations show that systematic error values are higher than unsystematic ones, which implies that air-quality system still has to be improved and refined. To analyse these results more thoroughly, we plan to carry out and expand detailed analysis to identify the key factors that influence these prediction biases, such as sensitivity to synoptic conditions, difference between meteorological models, emissions model adjustments and the influence of boundary conditions on CMAQ simulations over Catalonia. However, when bias-correction techniques are applied, $RMSE_s$ is reduced (expected result) while the unsystematic portion is increased, providing a lower RMSE than without corrections. Between correction algorithms, MS provided the best results, which demonstrates once more that MS is the best adjustment technique applied.

Table 8. Systematic and random errors for averaged 1-h and 8-h maximum surface ozone concentrations

Parameter	Year	Statistical	MOD	MOD_MS	MOD_RA	MOD-HF
1-h Maximum	2009	$RMSE_s$ (μgm^{-3})	23.99	13.13	13.27	12.00
		$RMSE_u$ (μgm^{-3})	18.55	19.20	24.33	23.78
		RMSE (μgm^{-3})	30.33	23.26	27.72	26.64
	2010	$RMSE_s$ (μgm^{-3})	24.84	13.23	19.23	12.56
		$RMSE_u$ (μgm^{-3})	20.49	21.66	32.81	26.54
		RMSE (μgm^{-3})	32.20	25.38	38.03	29.36
8-h Maximum	2009	$RMSE_s$ (μgm^{-3})	19.13	10.84	10.54	9.24
		$RMSE_u$ (μgm^{-3})	15.08	15.95	17.61	21.17
		RMSE (μgm^{-3})	24.36	19.28	20.53	23.10
	2010	$RMSE_s$ (μgm^{-3})	29.75	10.60	10.96	8.27
		$RMSE_u$ (μgm^{-3})	18.44	19.46	24.09	23.89
		RMSE (μgm^{-3})	35.00	22.16	26.46	25.28

These effects summarize current and future lines of work in this air-quality modelling system: (1) to analyse the sensitivity of the system to changes in emissions and meteorological conditions, and tune models to achieve more accurate results; and (2) to improve operational forecasts evaluating bias between observed and modelled values.

3.2.4. Modelling quality objectives for ozone "Uncertainty" defined by directive EC/2008/50.

In 2008 a new European air-quality directive was ratified by the European Parliament (EC 2008). This directive replaced earlier directives with the intention of simplifying and streamlining reporting. Whilst previous directives, largely based assessments and reporting on measurement data, this new directive places more emphasis on the use of models to assess air-quality within zones and agglomerations. The increased focus on modelling allows the Member States more flexibility in reporting assessment and the potential to reduce the cost of air-quality monitoring. However, modelling, like monitoring, requires expert implementation and interpretation. Models must also be verified and validated before they can be confidently used for air-quality assessment or management (Denby, 2010).

The quality objectives for a model are given as a percentage uncertainty. Uncertainty is then further defined in the directive as follows: *'The uncertainty for modelling is defined as the maximum deviation of the measured and calculated concentration levels for 90% of individual monitoring points, over the period considered, by the limit value (or target value in the case of ozone), without taking into account the timing of the events. The uncertainty for modelling shall be interpreted as being applicable in the region of the appropriate limit value (or target value in the case of ozone). The fixed measurements that have to be selected for comparison with modelling results shall be representative of the scale covered by the model.'*

As in the previous directives, the wording of this text remains ambiguous. Since values are to be calculated, a mathematical formula would have made the meaning much clearer. As such, the term 'model uncertainty' remains open to interpretation. Despite this, Denby (2010) suggests that it should be called the Relative Directive Error (RDE) and defines it mathematically at a single station as follows:

$$RDE = \frac{|O_{LV} - M_{LV}|}{LV} \qquad (9)$$

where O_{LV} is the closest observed concentration to the limit value (LV) concentration or the target value for ozone and M_{LV} is the correspondingly ranked modelled concentration. The maximum of this value found at 90% of the available stations is then the Maximum Relative Directive Error (MRDE), whose value recommended in the European Directive EC/2008/50 is 50%. MRDE values calculated with the AQM.cat model without and with bias-corrected techniques for all periods evaluated are presented in Table 9. The results of the evaluation are 43% in 2009 and 46% in 2010, within the regulatory framework recommended in the European Directive EC/2008/50. The application of bias-correction techniques also improves air-quality forecasts, reducing the MRDE value significantly; the HF technique minimizes this value. For this reason, the air quality modelling system presented in this paper can be used for the aims the Directive considers.

Table 9. MRDE values calculated with air-quality model forecast and bias-corrected forecast taking into account the whole period studied.

MRDE (%)	MOD	MOD_MS	MOD_RA	MOD_HF
2009	43	39	40	39
2010	46	37	41	27

4. CONCLUSIONS

This paper describes the evaluation of a coupled regional air-quality modelling system used to simulate ozone over the north-western Mediterranean area (Catalonia) during two periods: from May to September in both 2009 and 2010. The air-quality modelling system consists of the MM5 mesoscale model, the MNEQA emission model and the CMAQ photochemical model. Although the same meteorological and photochemical models have been applied in Catalonia in recent years, they have been evaluated either over shorter periods or using a more coarse horizontal resolution. The meteorological and photochemical forecasts are compared with observations from 35 surface meteorological stations belonging to the Catalonian Meteorological Service and 51 air-quality surface stations of the Environmental Department of the Catalonia Government (Spain).

This study demonstrates the capacity of the air-quality modelling system MM5-MNEQA-CMAQ to forecast ozone concentrations with sufficient accuracy, as the statistics fell within the recommended EPA and European performance goals. Daytime forecasts for hourly and 1-h and 8-h maximum surface ozone concentrations indicate satisfactory behaviour of the model; however, modelled ozone concentrations are underestimated during the day while during the night they are overestimated. The reasons for all these failures could be associated with: the uncertainty of the emissions model, mainly during night-time and in urban areas; the poor representations of the nocturnal physicochemical processes in the photochemical model; and finally, the failure of the meteorological model to reproduce certain parameters, such as wind direction and temperature which it is underestimated, mainly during daytime. Hourly surface ozone concentration forecasts are more accurate in rural areas whilst 1-h and 8-h maximum are better in urban and suburban areas. Results from systematic and unsystematic errors show that, although the air-quality model forecasts meet the European Directive, systematic error values are higher than unsystematic ones, which implies that the air-quality system still has to be improved and refined.

One method for achieving this goal and to reduce model errors (including the uncertainty of the meteorological, emission and photochemical models, and the fact that measurement point sites used in the evaluation may not be representative of the forecast concentrations averaged over an area equal to that of a model grid cell) is to apply post-processing bias-adjustment techniques to the modelling system outputs. In this study, three methods, MS, RA and HF, are coupled and applied to the air-quality modelling system. Results reveal a significant improvement in the statistical parameters considered in the operational ozone forecast evaluation, and an appreciable reduction of the systematic component of the error. The analysis of each bias-correction technique applied to the air-quality modelling system outputs concludes that MS method provides the best forecasts and minimizes the width of the concentration distribution. MS and RA provide better results in stagnant meteorological situations while HF better reproduces situations when it is applied to meteorological conditions characterized by changes in the synoptic or large-scale forcing, assuming that the model is capable of predicting the change in the pollutant mixing ratio from one day to the next. Related to this technique, corrected forecasts fail when the quotient between observations and model forecasts exceed a determinate value,

The final performance of bias-adjusted forecast techniques depends on the performance of the model to which the bias-adjusted technique is applied. Since bias-adjusted techniques can only reduce systematic errors inherent in the model, additional improvements in the model physics, and emissions inventory and chemistry are needed to reduce both systematic and unsystematic model errors to further improve forecast performance.

Acknowledgements

This research was supported by the Spanish Government through the project CICYT CGL 2009-12797-C03-02. The authors gratefully acknowledge the technicians at the regional Catalan Environmental Agency for providing information regarding the emissions inventory and air-quality measurements. Thanks are extended to the Catalan Meteorological Service for providing the initial and boundary meteorological fields for executing MM5.

REFERENCES

Abdul-Wahab, S.A., Bakheit, C. S., Al-Alawi, S.M. Principal component and multiple regression analysis in modelling of ground-level ozone and factors affecting its concentration. Environmental Modelling and Software 2005; 20: 1263-71.

Aguirre-Basurko, E., Ibarra-Berastegui, I., Madariaga, I. Regression and multilayer perceptron-based models to forecast hourly O3 and NO2 levels in the Bilbao area. Environmental Modelling and Software 2006; 21: 430-46.

Appel, K.W., Gillilan, A.B., Sarwar, G., Gilliam, R.C. Evaluation of the Community Multiscale Air Quality (CMAQ) model version 4.5: Sensitivities impacting model performance Part I – Ozone. Atmospheric Environment 2007; 41: 9603-15.

Arasa, R., Soler, M.R., Ortega, S., Olid, M., Merino, M.. A performance evaluation of MM5/MNEQA/CMAQ air quality modelling system to forecast ozone concentrations in Catalonia. Tethys 2010; 7: 11-22.

Baertsch-Ritter, N., Prevot, A.S.H., Dommen, J., Andreani-Aksoyoglu, S., Keller, J. Model study with UAM-V in the Milan area (I) during PIPAPO: simulations with changed emissions compared to ground and airborne measurements. Atmospheric Environment 2003; 37: 4133-47.

Bhave, P., Nolte, C., Pleim, J.E., Schwede, D., Roselle, S.J. Recent developments in the CMAQ modal aerosol module. In: The 2005 Models-3 Users Workshop, Chapel Hill, NC; 2005. Available at: http://www.cmascenter.org/conference/2005/ppt/p17.pdf

Borge, R., Alexandrov, V., Del Vas, J.J., Lumbreras, J. and Rodríguez, E. A comprehensive sensitivity analysis of the WRF model for air quality applications over the Iberian Peninsula, Atmospheric Environment 2008; 42: 8560-74.

Brankov, E., Henry, R.F., Civerolo, K.L., Hao, W., Rao, S.T., Misra, P.K. et al. Assessing the effects of transboundary ozone pollution between Ontario, Canada and New York, USA. Environmental Pollution 2003; 123 : 403-11

Bravo, M., Mira, T., Soler, M.R., Cuxart, J. Intercomparison and evaluation of MM5 and Meso-NH mesoscale models in the stable boundary layer. Boundary-Layer Meteorology 2008; 128: 77-101.

Byun, D.W., Ching, J.K.S. Editors. Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. Environmental Protection Agency; 1999.

Catalan Environmental Agency, 2001. Implantació de la nova legislació europea sobre avaluació i gestió de la qualitat de l'aire a Catalunya. Delimitació de zones de qualitat de l'aire. http://www20.gencat.cat/docs/dmah/Home/Ambits%20dactuacio/Atmosfera/Qualitat%20de%20laire/Avaluacio/Xarxa%20de%20Vigilancia%20i%20Previsio%20de%20la%20Contaminacio%20Atmosferica%20(XVPCA)/Zones%20de%20qualitat%20de%20laire%20(ZQA)/43_32454.pdf

Conangla, L., Cuxart, J. On the turbulence in the upper part of the low-level jet: an experimental and numerical sutyd. Boundary-Layer Meteorology 2006; 118: 379-400.

Cuxart, J., Yagüe, C., Morales, G., Terradellas, E., Orbe, J. Stable Atmospheric Boundary-Layer Experiment in Spain (SABLES 98): A Report. Boundary-Layer Meteorology 2000; 96: 337-70.

Cressman, G.P. An operational objective analysis system. Monthly Weather Review 1959; 87: 367-74.

Delle Monache, L., Nipen, T., Deng, X., Zhou, Y., Stull, R.. Ozone ensemble forecast: 2. A Kalman filter predictor bias correction. Journal of Geophysical Research 2006; 111: D05038. doi:10.1029/2005JD006311.

Denby, B. (Ed.). Guidance on the use of models for the European air quality directive. A working document of the Forum for Air Quality Modelling in Europe FAIRMODE. ETC/ACC Report. Version 6.2; 2010.
http://fairmode.ew.eea.europa.eu/fol404948/guidance-document/model_guidance_document_v6_2.pdf.

Djalalova, J., Wilczak, J., McKeen, S., Grell, G., Peckham, S., Pagowski, M. et al. Ensemble and bias-correction techniques for air quality model forecasts of surface O_3 and $PM_{2.5}$ during the TEXAQS-II experiment of 2006. Atmospheric Environment 2010; 44: 455-67.

Dudhia J. A multi-layer soil temperature model for MM5. Preprints, Sixth PSU/NCAR Mesoscale Model Users' Workshop, Boulder, CO, NCAR; 199., p. 49–50.

Dudhia J, Gill D, Manning K, Wang W, Bruyere C. PSU/ NCAR mesoscale modeling system tutorial class notes and user's guide: MM5 modeling system version 3. NCAR; 2004. http://www.mmm.ucar.edu/mm5/documents/tutorial-v3-notes.html.

Emery, C., E. Tai. Enhanced Meteorological Modeling and Performance Evaluation for Two Texas Ozone Episodes, Final report submitted to Texas Natural Resources Conservation Commission, prepared by ENVIRON, International Corp, Novato, CA; 2001.

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

EPA. Guidance on the use of models and other analyses in attainment demonstrations for the 8-hour ozone NAAQS. US EPA Report No.EPA-454/R-05-002. Office of Air Quality Planning and Standards, North Carolina; 2005. 128pp.

EPA. Reassessment of the Interagency Workgroup on Air Quality Modeling (IWAQM) Phase 2 Summary Report: Revisions to Phase 2 Recommendations. Draft for Internal Review. US EPA Report No.EPA-454/R-09-XXX. Office of Air Quality Planning and Standards, North Carolina; 2009. 56pp.

Gangoiti G., Millán M., Salvador, R., Mantilla E. Long-range transport and re-circulation of pollutants in the western Mediterranean during the project Regional Cycles of Air Pollution in the West-central Mediterranean Area. Atmospheric Environment 2001; 35: 6267-76.

Grell, G. Prognostic evaluation of assumptions used by cumulus parameterizations. Monthly Weather Review 1993; 121: 764-87.

Grell G, Dodhia J, Stauffer D. A Description of the Fifth Generation Penn State/ NCAR Mesoscale Model (MM5). NCAR. Tech. Note TN-398+STR, NCAR, Boulder, CO. 117pp; 1994.

Grossi, P., Thunis, P., Martilli, A., Clappier, A. Effect of sea breeze on air pollution in the greater Athens area: Part II: Analysis of different Emissions Scenarios. Journal of Applied Meteorology 2002; 39: 563-75.

Guderian, R., Tingey, D.T., Rabe, R. Effects of photochemical oxidants on plants. In: Guderian, R. (Ed.), Air Pollution by Photochemical Oxidants, Springer, Berlin; 1985. p.129-333.

Hanna, S.R., Chang, J.C., Fernau, M.E. Monte Carlo estimates of uncertainties in predictions by a photochemical grid model (UAM-IV) due to uncertainties in input variables. Atmospheric Environment 1998; 32: 3619-28.

Hanna, S.R., Lu, Z., Frey, H.C., Wheeler, N., Vukovich, J., Arunachalam, S. et al. Uncertainties in predicted ozone concentrations due to input uncertainties for the UAM-V photochemical grid model applied to the July 1995 OTAG domain. Atmospheric Environment 2001; 35: 891-903.

Hewit, C., Lucas, P., Wellburn, A., Fall, R. Chemistry of ozone damage to plants. Chemistry and Industry 1990; 15: 478-81.

Hogrefe, C., Rao, S.T., Kasibhatla, P., Kallos, G., Tremback, C.T., Hao et al . Evaluating the performance of regional-scale photochemical modelling systems: Part II- ozone predictions. Atmospheric Environment 2001; 35: 4175-88.

Hurley, P.J., Physick, W. L., Luhar, A. K. TAPM: a practical approach to prognostic meteorological and air pollution modelling. Environmental modelling and software 2005; 20: 737-52.

Jiménez, J., Baldasano, J.M., Dabdub, D. Comparison of photochemical mechanisms for air quality modeling, Atmospheric Environment 2003; 37**:** 4179–94.

Jiménez, P., Jorba, O., Parra, R., Baldasano, J.M. Evaluation of MM5-EMICAT2000-CMAQ performance and sensitivity in complex terrain: High-resolution application to the Northeastern Iberian Peninsula. Atmospheric Environment 2006a; 40: 5056-72.

Jiménez, P., Lelieveld, J., Baldasano, J.M. Multi-scale Modelling of air pollutants Dynamics in the North-Western Mediterranean Basin during a typical summertime episode. Journal of Geophysical Research 2006b; 111: D18306. doi:10.1029/2005JD006516.

Jiménez, P., Jorba, O., Baldasano, J.M., Gasso, S. The use of a modelling system as a tool for air quality management: Annual high-resolution simulations and evaluation. Science of the Total Environment 2008; 390: 323-40.

Jorba, O., Gassó, S., Baldasano, J.M. Regional circulations within the Iberian Peninsula east coast. In: Kluwer Academic/Plenum Publishers, editor. 26th Int. Tech. Meeting of NATO-CCMS on Air Pollution Modelling and its application; 2003. p. 388-95.

Kalman, R.E. A new approach to linear filtering and prediction problems. J. Basic Eng 1960; 82: 35-45.

Kang, D., Mathur, R., Rao, S. T., Yu, S. Bias adjustment techniques for improving ozone air quality forecasts. Journal of Geophysical Research 2008; 113: D23308, doi:10.1029/2008JD010151.

Kang, D., Mathur, R., Rao, S.T. Real-time bias-adjusted O_3 and $PM_{2.5}$ air quality index forecasts and their performance evaluations over the continental United States. Atmospheric Environment 2010; 44: 2203-12.

Lee, S., Fernando, H.J.S. Evaluation of Meteorological Modells MM5 and HOTMAC Usinf PAFEX-I Data. Journal of Applied Meteorology 2004; 43: 1133-48.

Lissens, G., Mensink, C., Dumont, G. SMOGSTOP: A new way of forecasting ozone concentrations at ground level. International Journal of Environment and Pollution 2000 ; 14: 418-24.

Maes, J., Vliegen, J., Van de Vel, K., Janssen, S., Deutsch, F., De Ridder, K. Spatial surrogates for the disaggregation of CORINAIR emission inventories. Atmospheric Environment 2009; 43: 1246-54.

Mahrt, L. Stratified atmospheric boundary layers. Boundary-Layer Meteorology 1999; 90: 375-96.

Mahrt, L., Vickers, D. Contrasting vertical structures of nocturnal boundary layers. Boundary-Layer Meteorology 2002; 105: 351-83.

Marticorena, B., Bergametti, G. Modelling the atmospheric dust cycle: 1. Design of a soil-derived dust emissions scheme. Journal of Geophysical Research 1995; 100: D8, 16415-30.

Mauzerall, D.L., Sultan, B., Kim, J., and Bradford, D. NOx emissions: variability in ozone production, resulting health damages and economic costs. Atmospheric Environment 2005; 39: 2851-66.

McKeen, S., Wilczak, J., Grell, G., Djalalova, I., Peckham, S., Hsie, E.-Y. et al. Assessment of an ensemble of seven real-time ozone forecasts over eastern North America during the summer of 2004. Journal of Geophyisical Research 2005; 110: D21307, doi:10.1029/2005JD005858.

Millán, M.M., Artiñano, B., Alonso, L., Castro, M., Fernandez-Patier, R., Goberna, J. Mesometeorological cycles o fair pollution in the Iberian Peninsula. Air Pollution Research Report 44, Brussels, Belgium. Commission of the European Communities; 1992. 219pp.

Millán, M.M., Salvador, R., Mantilla, E. Photooxidant dynamics in the Mediterranean basin in summer. Resuls from European research projects. Journal of Geophysical Research 1997; 102: D7, 8811-23.

Millán, M., Mantilla, E., Salvador, R., Carratala, A., Sainz, J.M., Alonso, L., Gangoiti, G., Navazo, M.. Ozone cycles in the western Mediterranean basin: Interpretation of monitoring data in complex coastal terrain. Journal of Applied Meteorology 2000; 39: 487-508.

Niska, H., Hiltunen, T., Karppinen, A., Ruuskanen, J., Kolehmainen, M. Evolving the neural network model for forecasting air pollution time series. Engineering Applications of Artificial Intelligence 2004; 17: 159-67.

Ortega, S., Soler, M.R., Alarcón, M., Arasa, R. MNEQA: An emissions model for photochemical simulations. Atmospheric Environment 2009; 43: 3670-81.

Ortega, S., Soler, M.R., Alarcón, M., Arasa, R.. The role of temperature in tropospheric ozone. International Journal of Environment and Pollution 2010; in press.

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

Pirovano, G., Coll, I., Bedogni, M., Alessandrini, S., Costa, M.P., Gabusi, V. et al. On the influence of meteorological input on photochemical modelling of a severe episode over a coastal area. Atmospheric Environment 2007; 41: 6445-64.

Pleim, J.E., Chang, J.S. A non-local closure model for vertical missing in the convective boundary layer. Atmospheric Environment 1992; 26A: 965-81.

Poulos, G.S., Blumen, W., Fritts, D., Lundquist, J., Sun, J., Burns, S. et al. CASES99: A comprehensive investigation of the Stable Nocturnal Boundary Layer. Bull Amer Meteorol Soc 2002; 83: 555-81.

Russell, A., Dennis, R. NARSTO critical review of photochemical models and modelling. Atmospheric Environment 2000; 34: 2283-324.

San José, R., Stohl, A., Karatzas, K., Bohler, T., James, P., Pérez, J.L. A modelling study of an extraordinary night time ozone episode over Madrid domain. Environmental Modelling and Software 2005; 20: 587-93.

Schlink, U., Herbarth, O., Richter, M., Dorling, S., Nunnari, G., Gawley, G. et al. Statistical models to assess the health effects and to forecast ground level ozone. Environmental Modelling and Software 2006; 21: 547-58.

Schultz, P. An explicit cloud physics parameterization for operational numeric weather prediction. Monthly Weather Review 1995; 123: 3331-43.

Serrano, E., Macias A., Castro M. An improved direct method of rubber cracking analysis for estimating 24-hour ozone levels. Atmospheric Environment 1993; 27: 431-42.

Shankar, U., Bhave, P.V., Vukovich, J.M., Roselle, J.S. Implementation and initial applications of sea salt aerosol emissions and chemistry algorithms in the CMAQv4.5 – AERO4 module. In: The 2005 Models-3 Users Workshop, Chapell Hill, NC; 2005. Available at: http://www.cmascenter.org/conference/2005/abstracts/p7.pdf

Silibello, C., Calori, G., Brusasca, G., Catenacci, G., Finzi, G. Application of a photochemical grid model to Milan metropolitan area. Atmospheric Environment 1998; 32: 2025-38.

Sistla, G., Zhou, N., Hao, W., Ku, J.Y., Rao, S.T. Effects of the uncertainties in meteorological inputs of Urban Airshed Model predictions and ozone control strategies. Atmospheric Environment 1996; 3: 2011-25.

Sitch, S., Cox, P.M., Collins, W.J., Huntingford, C. Indirect Radiative Forcing of Climate Change through Ozone Effects on the Land-Carbon Sink. Nature 2007; 448: 791-94.

Sokhi, R.S., San José, R., Kitwiroon, N., Fragkou, E., Pérez, J.L., Middleton, D.R. Prediction of ozone levels in London using the MM5-CMAQ modelling system. Environmental Modelling and Software 2006; 21: 566-76.

Soler, M.R., Infante, C., Buenestado, P., Mahrt, L. Observations of Nocturnal Drainage Flows in a Shallow Gully. Boundary-Layer Meteorology 2002; 105: 253-73.

Soler, M.R., Hinojosa, J., Bravo, M., Pino D., Vilà Guerau de Arellano, J. Analyzing the basic features of different complex terrain flows by means of a Doppler Sodar and a numerical model: Some implications to air pollution problems. Meteorology and Atmospheric Physics 2004; 85: 141-54.

Soler, M.R., Arasa, R., Merino, M., Olid, M., Ortega, S. High vertical resolution numerical simulation of the sea-breeze flow in Catalonia. Implications to spatial and temporal variability of ozone and PM10 levels. Boundary-Layer Meteorology 2011; in press.

Terradellas, E., Soler, M.R., Ferreres, E., Bravo, M. Análisis of oscillations in the stable atmospheric boundary layer using wavelet methods. Boundary-layer meteorology 2005; 114: 489-518.

Tesche, T.W., D.E. McNally, and C. Tremback. Operational Evaluation of the MM5 Meteorological Model Over the Continental United States: Protocol for Annual and Episodic Evaluation. Prepared for US EPA by Alpine Geophysics, LLC, Ft. Wright, KY, and ATMET, Inc., Boulder, CO; 2002. http://www.epa.gov/scram001/reports/tesche_2002_evaluation_protocol.pdf

Thiébaux, H.J, Pedder, M.A. Spatial Objective Analysis: with Application in Atmospheric Science. Academic Press; 1986. 299pp.

Troen, I.S., Mahrt, L. A simple model of the atmospheric boundary layer; sensitivity to surface evaporation. Boundary-Layer Meteorology 1986; 37: 129-48.

Vautard, R., Bessagnet, B., Chin, M., Menut, L. On the contribution of natural Aeolian sources to particulate matter concentrations in Europe: Testing hypotheses with a modelling approach. Atmospheric Environment 2005; 39: 3291-303.

Wilczak, J., McKeen, S., Djalalova, I., Grell, G., Peckham, S., Gong, W. et al. Bias-corrected ensemble and probabilistic forecasts of surface ozone over eastern North America during the summer of 2004. Journal of Geophysical Research 2006; 111: D23S28, doi:10.1029/2006JD007598.

Yarwood, G., Rao, S., Yocke, M., Whitten, G. Updates to the Carbon Bond chemical mechanism: CB05. Report to the U.S. Environmental Protection Agency, RT-04-00675; 2005. http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf

Zhang, Y., Liu, P., Pun, B., Seigneur, C. A comprehensive performance evaluation of MM5-CMAQ for the Summer 1999 Southern Oxidants Study episode – Part I: Evaluation protocols, databases, and meteorological predictions. Atmospheric Environment 2006a; 40: 4825-38.

Zhang, Y., Liu, P., Queen, A., Misenis, C., Pun, B., Seigneur, C. et al. A Comprehensive Performance Evaluation of MM5-CMAQ for the Summer 1999 Southern Oxidants Study Episode, Part-II. Gas and Aerosol Predictions. Atmospheric Environment 2006b; 40: 4839-55.

Zunckel, M., Koosailee, A., Yarwood, G., Maure, G., Venjonoka, K., van Tienhoven, A.M. et al. Modelled surface ozone over southern Africa during the Cross Border Air Pollution Impact Assessment Project. Environmental Modelling and Software 2006; 21: 911-24.