A Simple Modelling System to Forecast Tropospheric ozone concentrations

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ABSTRACT:
This study reports the development of a simple, operational modelling system to forecast surface ozone concentrations. The model consists of 3 modules corresponding to meteorological, emission and photochemical models linked by a program written in Visual Fortran. The system was applied during later spring-summer 2003 and 2004 in different areas of Catalonia, in north-east Spain. Accuracy in predicting maximum daily ozone concentration was between 15 and 20 μgm^{-3}, while there was a tendency to overestimate, which ranged from 0.5 to 7 μgm^{-3}. We also tested the model's ability to forecast concentrations within different levels concentrations, especially those are higher than 180 μgm^{-3}, which could be of practical use to air-quality managers. Between 65% and 90% of the forecasts were correct, depending on the area forecasted. The system was also used to make a sensitivity analysis for all areas of the simulation. This study helps to find strategies for reducing ozone levels because it provides information about how the ozone concentration responds to changes in the emissions of its precursors.
Key words: Tropospheric ozone, ozone modelling, Eulerian simulation, Lagrangian simulation, ground-level ozone forecast, sensitivity analysis.

Un Sistema de Modelización simple para Predecir las Concentraciones de Ozono Troposférico

RESUMEN:
Este estudio recoge el desarrollo de un sistema simple de modelización operacional para predecir las concentraciones de ozono superficial. El modelo consta de tres módulos correspondientes a los modelos fotoquímicos, de emisión y meteorológico que están enlazados por medio de un programa escrito en Visual Fortran. El sistema se aplicó durante el final de la primavera y el verano de los años 2003 y 2004 en diferentes áreas de Cataluña, localizada en el NE de España. La precisión en la predición de la concentración máxima diraria de ozono varía entre 15 y 20 μgm^{-3}, existiendo una tendencia a la sobreestimación entre 0,5 y 7 μgm^{-3}. También se ha probado la validez del modelo para predecir concentraciones dentro de diferentes niveles de concentración, especialmente aquellos mayores de 180 μgm^{-3}, que podría ser de uso práctico para los gestores responsables de la calidad del aire. Entre un 65% y 90% de las predicciones, dependiendo del área predicha, fueron correctas. También se probó el sistema para realizar un análisis de sensibilidad para todas las áreas de simulación. Este estudio podría ser útil para encontrar estrategias de reducción de los niveles de ozono debido a que proporciona información acerca de cómo las concentraciones de ozono responden a los cambios en la emisión de sus precursores.
Palabras clave: ozono troposférico, modelización del ozono, simulación euleriana, predicción de ozono superficial, análisis de sensibilidad.

1. INTRODUCTION

As a result of combined emissions of nitrogen oxides and organic compounds, considerable amounts of ozone have been measured in the planetary boundary layer. Tropospheric ozone is considered one of the worst pollutants in the lower troposphere. Increased concentration may contribute to potentially important climate change (Chalita et al. 1996); it is toxic to plants and reduces crop yield (Zunckel et al. 2006), it acts as 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). The phenomenon is significant in industrial areas, especially in Southern Europe (Grossi et al. 2000), due to the high levels reached in summer, since solar radiation exacerbates the effects of the ozone. This is the case in different zones of northern Spain located near urban and industrial areas, and especially those which are located downwind where local ozone precursors are lacking. 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.

In the last three decades, significant progress has been made in air-quality modelling systems. The simple Gaussian and Eulerian box models have evolved into statistical models (Schlink et al. 2006) and complex variable-grid models (Hurley et al. 2005). These latter represent the most sophisticated class of atmospheric models and they are more complex and challenging to run than Gaussian or box dispersion models. They are most often used for problems that are too complex to be handled using simple models. With continuing advances, variable-grid modelling is increasingly used in research settings for assessing air and health impacts of alternative future emission scenarios (Mauzerall et al. 2005). Models of this kind are computationally expensive to maintain and run; the size of the input and output data sets makes it difficult to perform and evaluate large numbers of sensitivity simulations, and it is not easy to determine cause and effect because of the complexity of the interactions between model components. In contrast, trajectory and box models, although they have numerous disadvantages (their representation of transport and turbulent dispersion is too simplistic and they are difficult to use for multi-day scenarios), nevertheless present several advantages (Holloway et al. 2005). The most important benefits are their computationally low cost and their simplicity and efficiency; they are easier to encode and operate than grid models; it is easy to specify model inputs and to vary inputs in sensitivity simulations, and therefore large numbers of simulations can be performed rapidly. All these reasons induced us to design a simple, functional modelling system to forecast daily ozone concentrations, which is reported in this study. It consists of three modules corresponding to the meteorological, emission and photochemical models linked by a program written in Visual Fortran. The meteorological module consists of a mesoscale model (MASS), which provides the initial conditions for a non-local boundary layer model based on the transilient turbulence model. The second module contains information on ozone precursor emissions and the third, the photochemical module, is composed by a 1-D box model OZIPR, which computes

ozone concentrations using information from the other modules. In section 3 we describe the modelling system, which is applied in Eulerian and Lagrangian modes, the latter mainly to simulate mesoscale advections such as sea breeze. The model has been validated for several periods, as described in section 4. As one of the main objectives of the ozone modelling systems is to assess the scale of ozone impacts and to develop control strategies, a sensitivity analysis is performed in section 5 to determine which strategies could be applied to the different areas considered in this study. Finally concluding remarks are presented in section 6.

2. THE AREAS STUDIED

The areas under study are located in Catalonia (Fig.1), which is dominated by several complex features, including the Mediterranean coastline.

The Pyrenees, to the north, have maximum heights above sea level of 2600 m, and the littoral and pre-littoral mountain ranges, parallel to the coast line reach heights of between 500 m and 1712 m, respectively. In weak background synoptic flow, the weather within the different areas under study, marked by a rectangle in Fig.1 is strongly influenced by mesoscale circulations, mainly the sea breeze and anabatic and katabatic winds developed during day and night time respectively. The sea breeze transports ozone and its precursors inland (Soler et al. 2004), and so it is important for the present study, which focuses on diurnal concentrations. Figs. 2 show more detailed information on the topography of each study area.

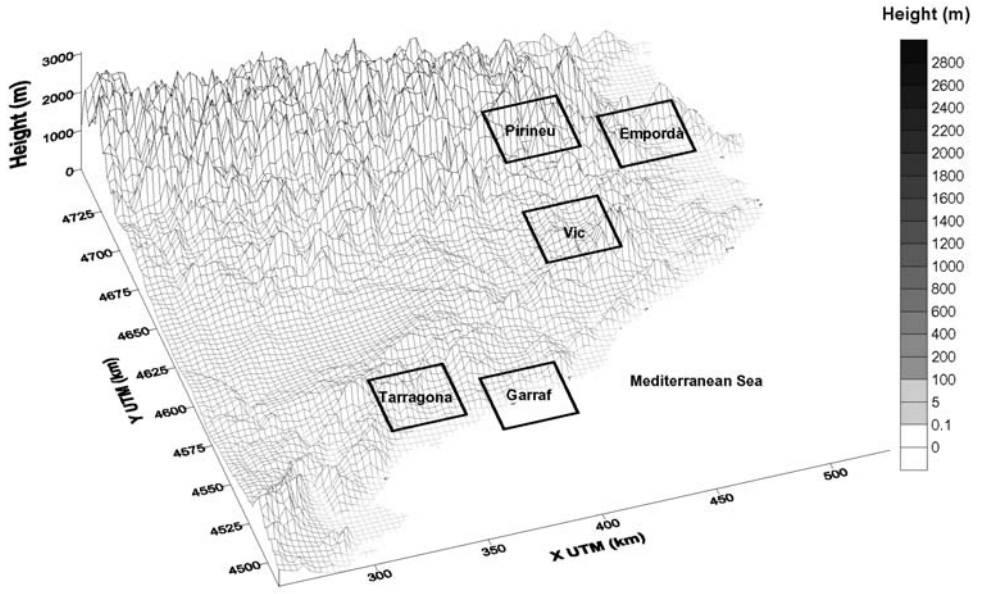

Figure 1.- Topographic map of Catalonia, contour intervals are labelled every 600m. Ozone concentration has been forecasted in the areas delimited by the rectangle.

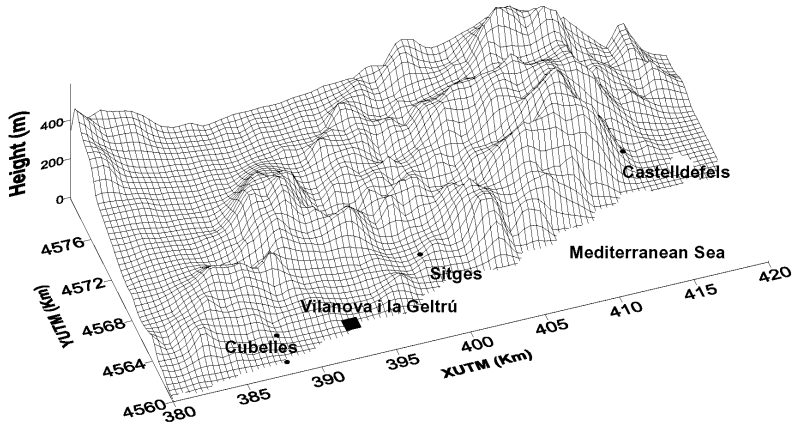

Figure 2a- Detailed information about the topographic characteristics of Garraf area showing the location of the power plant (PP), contour intervals are labelled every 200m.

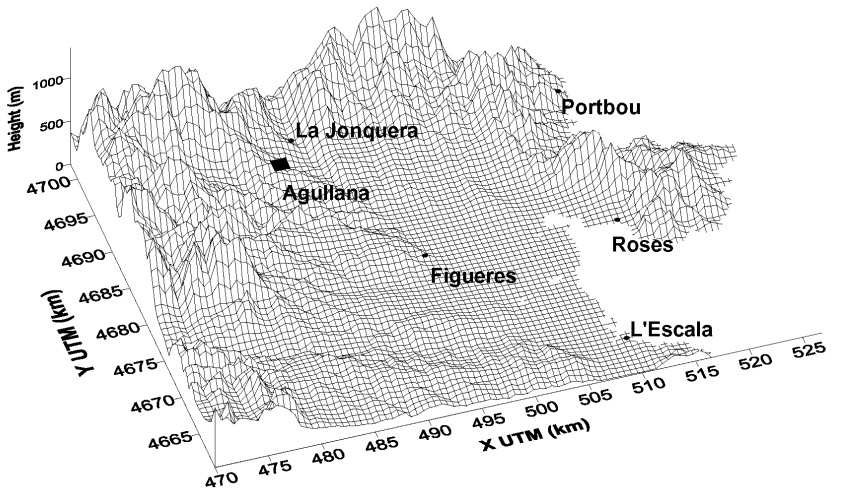

Figure 2b.- Detailed information about the topographic characteristics of Empordà area showing the location of the AP-7 motorway, contour intervals are labelled every 200m.

Fig. 2a corresponds to the Garraf area, where low mountains (about 500 m) lie near the sea. The power plant in Cubelles and the sea breeze give rise to ozone episodes downwind. Maximum values occur in the afternoon around 17 UTC, when the sea breeze has veered to the southwest. Fig. 2b corresponds to the Empordà Plain, where there is a large motorway, AP-7, which is a source of additional ozone during the summer holiday. Fig. 2c corresponds to the Tarragona area, where the sea breeze transports pollutants inland from the petrochemical complex on the coast. Fig. 2d includes the Eastern Pyrenees and

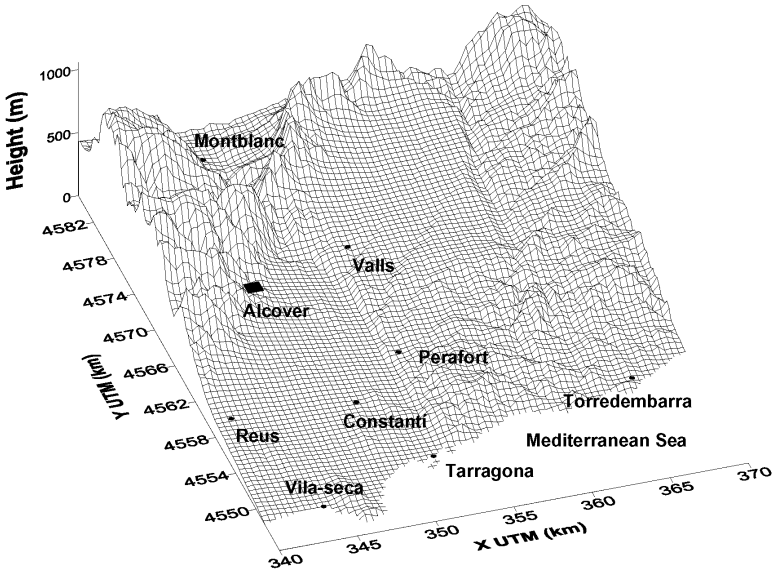

Figure 2c.- Detailed information about the topographic characteristics of the Tarragona area showing the location of the petrochemical area (PA), contour intervals are labelled every 200m.

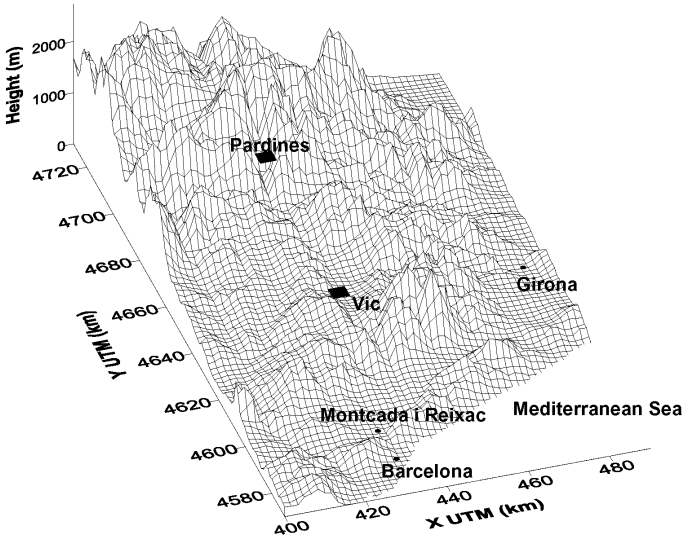

Figure 2d.- Detailed information about the topographic characteristics of La Plana de Vic and Eastern Pyrenees, contour intervals are labelled every 200m.

the Vic Plain near the Barcelona metropolitan area, which is an important anthropic source of ozone and its precursors. One of the causes of ozone episodes in Vic Plain is the pollutants' advection as a result of the sea breeze. In

addition, stronger sea breezes raise ozone concentrations in the pre-Pyrenean zone in the late afternoon. For each area, a representative monitoring station (located respectively in Vilanova i la Geltrú, Agullana, Alcover, Vic and Pardines) (Figures 2) was selected. Hereafter, we identify each area by its monitoring station.

3. THE MODELLING SYSTEM

The forecast system used in this study, (Fig. 3), is composed of three modules corresponding to the meteorological, emission and photochemical models.

3.1. METEOROLOGICAL MODELS

This module consists of two models. An upgrade of the Mesoscale Atmospheric Simulation System, hereafter referred to as MASS (Zack and Kaplan, 1987), which is the operational model of the Catalan Weather Service, and the 1-D atmospheric boundary layer (ABL) model based on the transilient turbulence scheme (Stull, 1984).

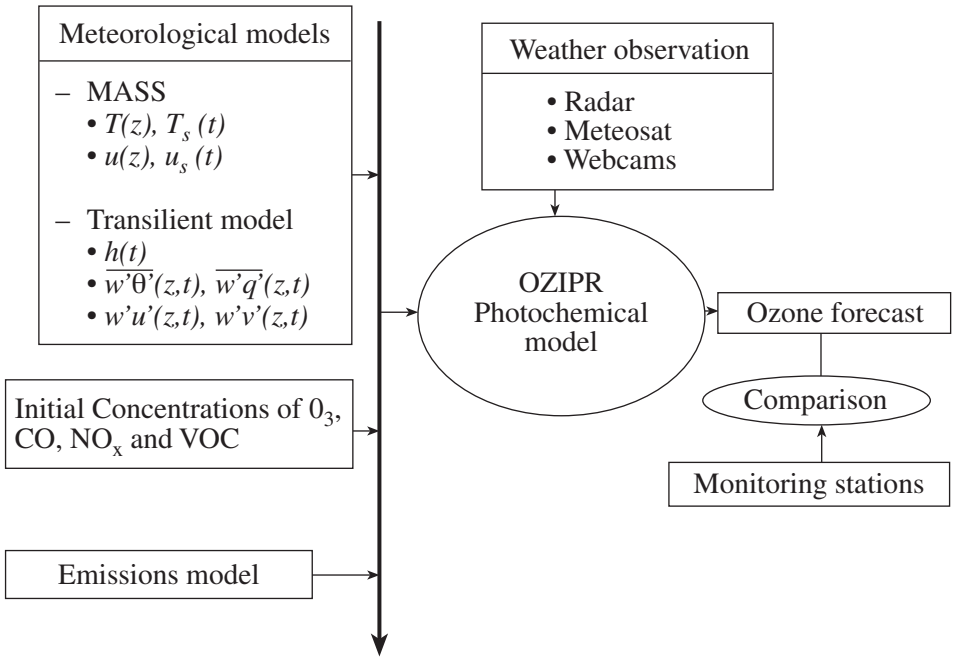

Figure 3.- Diagram of the modelling system components.

3.1.1. MASS model

The mesoscale model (MASS) used in this study was version 5.13 (Meso.inc). Two one-way nested domains are defined using resolutions of 30 and 8 km. The dimensions of each domain are 55x55 grid points for the outer domain and 103x103 grid points for the inner domain. The vertical resolution the ABL model was 21 levels with higher resolution at the lower levels located at 10, 25 and 50 m respectively. More characteristics of the simulation are described in Beneito (2006).

3.1.2. The atmospheric boundary layer model

The 1-D atmospheric boundary layer model is based on non-local transilient turbulence closure, first developed by R. B. Stull (1984) as an alternative to local closure schemes such as K-theory and higher-order closure. It is a non-local first-order closure approach that describes resolvable-scale vertical mixing when horizontal turbulence is unresolved (as in many meso-, synoptic- and climate-scale forecast models with large horizontal sizes but smaller vertical sizes). The model provides mean wind, potential temperature and specific humidity profiles. Moreover, turbulence profiles of kinematic turbulent fluxes are calculated using the transilient turbulent closure scheme. This information enable us to calculate the height of the boundary layer defined as the height of most negative heat flux or as the average base of the overlying stable layer. The height of the boundary layer is the height of the photochemical box model, so its calculation is very important in determining ozone concentration (Berman et al. 1997). In addition, the role of vertical mixing and therefore the mixing height is very important in the temporal evolution of the ground level ozone concentration. Several studies have demonstrated that vertical mixing contributes significantly to the ozone build-up at ground level in the morning when the top of the mixed layer reaches the ozone- and precursors-rich layer trapped aloft in the nocturnal residual layer.

3.2. EMISSION MODEL

Emissions are calculated over a domain of 3x3 km^2, covering the areas studied, an extensive description of the emission model can be founded in Ortega et al. (2006) here we only outline the most important characteristics. Two types of emission are distinguished: anthropogenic and biogenic. Anthropogenic emissions are basically produced by traffic and industrial activity. To calculate emissions for traffic, databases distinguish motorways, roads and hourly mean daily traffic intensity for heavy and light vehicles. To calculate emissions from vegetation, the procedure of Pierce et al. (1998) was followed. Only isoprene, the major biogenic Volatile Organic Compound (VOCs), and nitrogen oxide are included. To compute emissions surface air and subsoil temperatures are calculated by the MASS

model. Photosynthetically active radiation,(PAR), is obtained from measured global radiation, on the assumption that 48% of global radiation is PAR (McCree, 1972). Classes of land use are provided from the same database used by the MASS model.

3.3. PHOTOCHEMICAL MODEL

The photochemical model used is the OZIPR model (Ozone Isopleth Plotting Program Research) (Gery and Crouse, 1990), which is a column or box model developed by the EPA (Environmental Protection Agency). It is a single-day forecast model designed to focus on the atmospheric chemistry that leads to ozone. The idealized column contains specified initial concentrations of VOCs, CO and NOx and updated emissions from the surface and elevated sources, which are included during the day. The model is executed in Eulerian and Lagrangian modes. In the first mode, the air mass, which was taken as 20X20 km^2 over a region, is treated as a box into which pollutants are emitted. Transport into and out of the box by meteorological processes and dilution is included. In the Lagrangian mode this idealized column is transported by the wind (along the air mass trajectory), but cannot expand horizontally. Emissions are included as the air column passes over emission sources, since the hourly emissions into the air mass are taken from the 3x3 km^2 grid-based emission list. With the Lagrangian simulation the ozone entering the idealized columns is taken into account as advection. In both simulations air from above the column is mixed in as the inversion rises during the day and dilution occurs during the simulation, in which chemical reactions convert the VOCs and NO_x to O_3 and other secondary pollutants. The chemical mechanism used is the carbon bond approach (Gery and Crouse 1990) for the lumping of organic species. Dry deposition on the surface is included in the model in a simple way: for each species, values are set for two types of surface, urban and rural.

As well as initial concentrations and hourly emissions, other inputs in the OZIPR model are temperature, relative humidity and mixing height, which is the height of the column model. The hourly evolution of the mixing height is one of the critical parameters of the calculations needed for the OZIPR model, as the rate of dilution of atmospheric pollutants depends on the diurnal change in mixing height.

3.3.1. Photochemical model application

As stated in the previous section, the photochemical model is applied in Eulerian and Lagrangian modes. In the first mode, the air mass, which is treated as fixed, is centred over Vilanova i la Geltrú, Agullana, Alcover, Vic and Pardines. However, in this Eulerian mode, mesoscale effects such as sea breeze are not considered. To take these into account, therefore, the box model must be applied in the Lagrangian mode following the trajectory backward in time, which is calculated using a trajectory model (Alarcon and Alonso 2001). This model is based on a simple

transport model developed at the Air Resources Laboratory (NOAA), adapted to short trajectories corresponding to mesoscale transport (tens of km).

3.4. OPERATIONAL DESIGN

The forecasting system (Fig. 3) is designed to be as simple as possible. We begin with an initial meteorological profile calculated from the MASS model at 0600 UTC, corresponding to the grid point where the photochemical model would later forecast ozone. A pre-processing step consisting of certain interpolations is taken to provide high vertical resolution in the ABL. This information and turbulent surface fluxes are provided hourly to the transilient model, which supplies the time evolution of temperature, wind speed and turbulent heat flux profiles and then the mixing height. All this information and initial concentrations of NO_x, VOCs and O_3 provided by the surface monitoring stations combined with the emissions inventory is transferred to the photochemical model, which gives the hourly ozone forecast continuously checked against the values provided by the network of monitoring stations. Simultaneously, as solar radiation and cloud cover are important in ozone formation, RADAR and METEOSAT images are also used as a diagnostic tool to improve ozone forecasting. If hourly ozone concentration predictions do not agree with surface measurements, mainly because cloud cover, wind vector or temperature predicted by meteorological models do not correspond to real measurements or observed weather, we run the model again incorporating updated versions of the cloud fraction, surface sensible and latent heat fluxes, and initial values of NO_x, VOCs and O_3 concentrations. Furthermore, using meteorological stations we can manually update meteorological data on temperature or wind vector, allowing us to correct the output of the meteorological models. This new information is again checked with data provided by monitoring stations to test the reliability of the new prediction. This procedure is repeated every time the weather prediction fails.

4. OZONE FORECAST VERIFICATION

To evaluate the model statistically we computed several verification statistics (EPA, 1999). Although the model computes the hourly concentration values on a daily basis, the statistics are computed in two different ways. The first computation predicts discrete forecasts, like the mean hourly maximum value registered during the day or the mean hourly daily peak. The second computation is based on different category forecasts; in this study we have considered three categories, defined as follows:

❶ $[O_3]_{max} \leq 120\ \mu g\ m^{-3}$
❷ $120 < [O_3]_{max} \leq 180\ \mu g\ m^{-3}$
❸ $[O_3]_{max} > 180\ \mu g\ m^{-3}$

These intervals are delimited according to legislation and can easily be modified. For the daily peak forecast we calculate the accuracy A (mean absolute error) and the bias B (mean error). The accuracy measures the average proximity or coincidence between the maximum values forecast and the maximum values observed for all forecasts, while the bias indicates whether the maximum forecasts are under- or over-predicted.

Table I presents the results obtained in the 2003 (Alcover, Pardines and Vic areas) and 2004 (Alcover, Pardines, Vic, Agullana and Vilanova areas) ozone forecasts.

Table I.- Accuracy and Bias for the maximum daily ozone concentration

Indexes (μg m$^{-3)}$		**Agullana**	**Alcover**	**Pardines**	**Vic**	**Vilanova**
2003	Accuracy	—	16.8	17.2	14.8	—
	Bias	—	5.8	3.5	0.5	—
2004	Accuracy	18.2	19.1	15.6	15.5	20.2
	Bias	7.4	2.6	4.5	6.2	6.6
Mean value	Accuracy	18.2	17.9	16.4	15.1	20.2
	Bias	7.4	4.2	4.0	3.3	6.6

The mean values indicate that the best results were obtained in Vic and Pardines (due to their lower uncertainty) and the worst results were those corresponding to Vilanova i la Geltrú and Agullana. One of the reasons for this discrepancy could be the presence of thin fog in the Vilanova area, which was not accounted for in the MASS model. Thin fog reduces the incoming solar radiation and therefore the formation of ozone. Another factor could be the uncertainty of emissions coming from the motorway AP-7, from the petrochemical industry of Tarragona or, especially from the power plant of Cubelles. The plant responds to the demand for power, and it is not in continuous operation. The second parameter, the bias, indicates that the modelling system always tends to overestimate ozone concentration (positive B). The discrepancies between measurements and simulations could be due to several sources of error, such as uncertainties in the definition of the column depth, but mainly the lack of determination in the emission model and the cloud cover. Summer 2004 was characterized by a high frequency of low clouds, which were not always correctly predicted by the MASS model. As solar radiation is one of the main factors causing ozone formation, its forecast is vital to the reliability of ozone predictions. Nevertheless, although better accuracy and little bias is always desirable, the results shown in this study are similar to results found in other studies with other models (Silibello et al.1998). .

To evaluate the forecast related to a prescribed threshold, we followed the method described in EPA (1999), creating the contingency tables, which are the basis for calculating some verification statistics for category forecast as the accuracy, the bias, and the effective probability of detection. The accuracy, A, is the percentage of

forecasts which correctly predicted the event or non-event. High numbers are better. The bias, B, indicates, on average, whether forecasts are under predicted (false negatives) or over predicted (false positives), values closer to 1 are the best. Values <1 indicate under-forecasting (i.e. the event occurred more frequently than was predicted). Values >1 indicate over-forecasting. The effective probability of detection, EPD, indicates the ability to predict pollution events (i.e. at or above the threshold).

Tables II and III show results of these indexes for the 2003 (Alcover, Pardines and Vic areas) and 2004 (Alcover, Pardines, Vic, Agullana and Vilanova areas) ozone forecast campaigns. These tables illustrate the ability of the model to forecast ozone concentrations above the warning threshold (180 μgm^{-3}).

Table II.- Evaluation of maximum ozone forecast related to prescribed thresholds, ❷ $120 < [O_3]_{max} \leq 180\ \mu g\ m^{-3}$

Indexes			Optimum	Agullana	Alcover	Pardines	Vic	Vilanova
❷	2003	Accuracy (%)	100	—	78	80	90	—
		Bias	1	—	1.23	1.16	1.11	—
		EPD (%)	100	—	96	96	99	—
❷	2004	Accuracy (%)	100	65	75	70	77	69
		Bias	1	1.84	1.34	1.64	1.29	2.26
		EPD (%)	100	94	93	98	97	83
❷	Mean	Accuracy (%)	100	65	76.5	75	83.5	69
		Bias	1	1.84	1.28	1.4	1.2	2.26
		EPD (%)	100	94	94.5	97	98	83

Table III.- Evaluation of maximum ozone forecast related to prescribed thresholds, ❸ $[O_3]_{max} > 180\ \mu g\ m^{-3}$

Indexes			Optimum	Agullana	Alcover	Pardines	Vic	Vilanova
❸	2003	Accuracy (%)	100	—	84	79	98	—
		Bias	1	—	1.12	1.59	1.03	—
		EPD (%)	100	—	89	72	90	—
❸	2004	Accuracy (%)	100	90	81	92	84	89
		Bias	1	1.08	1.46	0.77	1.28	2.14
		EPD (%)	100	100	89	85	95	86
❸	Mean	Accuracy (%)	100	90	82.5	85.5	91	89
		Bias	1	1.08	1.29	1.18	1.1	2.14
		EPD (%)	100	100	89	78.5	92.5	86

In Alcover and Pardines areas the model's ability to forecast ozone values exceeding 180 μgm^{-3} is satisfactory, while in Vic and Agullana areas the results are better. The worst results are for the Vilanova area, due to high values of bias associated with uncertainty in emissions from the Cubelles power plant. In general, the model forecasts overestimate ozone concentrations above this threshold, as bias is positive. Aside from emissions uncertainty, one of the reasons for these false alarms could be erroneous predictions about the sea breeze inland, which are supplied by the meteorological model, causing an overestimation of ozone levels. The entrance of the sea breeze requires absence of background synoptic flow and mainly cloudless sky. If the MASS model predicts this last condition but clouds appear at noon, the sea breeze becomes too weak reach the areas considered in this study, especially the Pyrenees.

High bias can also be observed in the Vilanova area for threshold ❷, indicating that forecasts often overestimate ozone concentration. As has been commented previously, the main reason for the poor result in this area could be the high frequency of low cloud occurrence during summer 2004, which was not predicted by the meteorological model, and uncertainty in the estimation of emissions from the power plant. In the Agullana area, results also show discrepancies from measurements, as accuracy is slightly lower than the other places and the bias is moderate. Ozone concentration forecasts in this area are severely affected by the uncertainty in the forecast of traffic intensity for the motorway which crosses it.

5. SENSITIVITY ANALYSIS

The mechanisms by which the primary emissions, especially VOCs and NO_x, affect the concentrations of secondary pollutants such as ozone are very complex. Thus the relations between the concentrations of primary and secondary pollutants are, in many conditions, nonlinear. One approach is to use computer models to simulate one hour peak of O_3 formed when mixtures of known initial concentrations of VOCs and NO_x are considered. The results, usually tested in an environmental chamber, are often displayed in the form of 2- or 3-dimensional isopleths indicating whether VOCs or NO_x or both, would be most effective in controlling ozone. According to Finlayson-Pitts and Pitts (2000), at high VOCs/NO_x, decreasing VOCs alone at constant NO_X, gives slowly decreasing O_3. However, decreasing NO_x at constant VOCs, is very effective in decreasing ozone. In the opposite case, low VOCs/NO_x ratios, reducing VOCs at constant NO_x gives an important decrease in ozone. However, reducing NO_x at constant VOCs, leads to an increase in O_3.

To perform a similar test in every area where daily ozone concentration is forecasted, a simple study (Jiang et al. 1997) is performed. The study analyses the variation of ozone concentration in response to changes in precursor emissions, mainly total VOCs and NO_x. Selected sensitivity tests to the response of O_3 concentration to the total VOCs emission are executed. VOCs emission is multiplied by 0, 0.8,…..2.0, while NO_x and CO emissions are kept to the base-case amount which are the usual values for a typical summer day. These values are introduced in

the modelling system and the ozone forecast is calculated. Results indicate that by increasing VOCs and keeping NO_x and CO constant, O_3 levels are increased; while decreasing VOC emissions reduce ozone concentrations. These results were as expected, since all the areas under study are characterized by a low ratio of VOCs to NO_x emissions. The reason for this pattern is that high VOCs concentrations activate the formation of peroxy radical RO_2 through the reaction of hydrocarbons with the hydroxyl radical, OH. Later the RO_2 radical reacts with NO to give NO_2 and then ozone. The results of the sensitivity test show similar patterns in all the areas studied and therefore we will show only the most representative. However, some local factors, like topography, must be taken into account as contribute to the dispersion. Again, the proximity of the area to the Mediterranean Sea influences temperature, sea breeze inland, cloud cover and humidity. As an example, Figure 4 shows changes in ozone concentration in response to variations of emissions in the Alcover area with clear sky.

The sensitivity is maximum when the base case is multiplied by 2, but it decreases as emission values move away from this case. In general, the O_3 concentrations increase with VOCs emissions. However, between 8:00 and 9:00 UTC all air masses have lower reactivity in terms of O_3 production, even when VOCs emissions are doubled. This can be explained by the predominance of NOx in this hour. O_3 titration by NO is the predominant chemical process at this time. In fact, the O_3 destruction by NO is so strong in the morning that it is not totally offset by the O_3 production process until about 10:00 UT even if VOCs

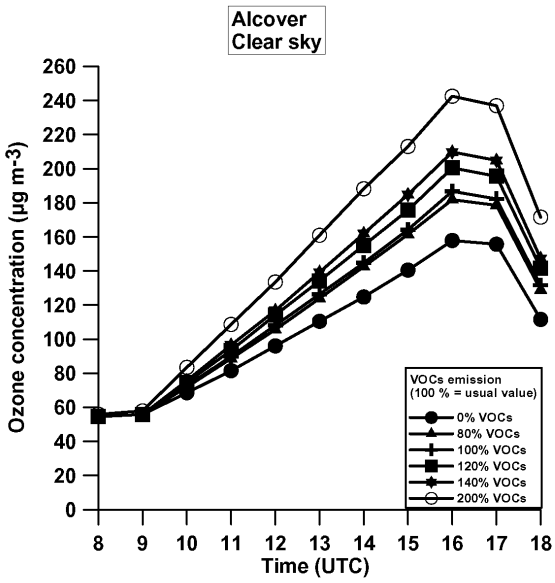

Figure 4.- Sensitivity of hourly ozone concentrations values to changes of VOCs emissions in the Alcover area with clear skies. Legends examples 80% VOCs indicate the base case VOCs emissions are multiplied by 0.8, while NO_x and CO emissions are kept to the base-case amount.

emissions are doubled. These results agree with those found by Jiang et al. (1997) in Canadian Lower Fraser Valley. The difference between several ozone forecasts made with different precursor emissions is greatest at 16 UTC, which is the time of daily maximum temperature. When temperatures are higher, chemical reactions are faster, so ozone formation is enhanced when VOCs emission conditions are optimal for ozone formation. This factor accounts for differences between ozone concentrations produced in optimal and non-optimal emission conditions.

The methodology applied to test the sensitivity of ozone to the total amount of NO_x is similar to the previous one. NO_x emissions are multiplied by different factors ranging from 0 to 2.0, while VOCs and CO emissions are fixed to the base amount. Results indicate that the highest O_3 level occurs when NO_x emissions are reduced to between 60% and 20%. As before, this result depends on the location and therefore the local NO_x emission levels. In the opposite case, when NO_x emission are 1.4 and 2.0 times the base value, O_3 concentration is always lower than the case of zero NO_x emissions. The main reason for this pattern is that, at these high NO_x concentrations, NO_2 competes with VOCs for the OH radical by forming HNO_3. This terminates the chain oxidation of VOCs and removes NO_2 from the system without forming O_3. As an example, Figure 5 shows changes in ozone concentration in response to variations of NO_x emissions in the Alcover area with a clear sky.

It seems clear that to achieve minimum values of O_3 concentrations it is necessary to attain a local equilibrium between VOCs and NO_x emissions.

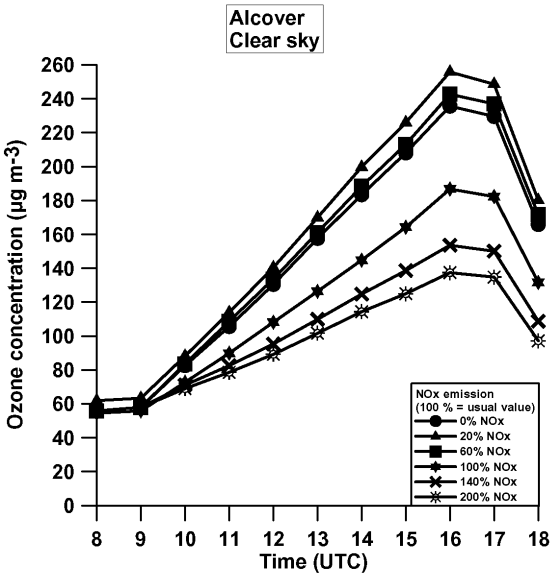

Figure 5.- Sensitivity of hourly ozone concentrations values to changes of NO_x emissions in the Alcover area with clear skies. Legends examples: 80% NO_x indicate the base case VOCs emissions are multiplied by 0.8, while VOCs and CO emissions are kept to the base-case amount.

We also tested the sensitivity of ozone to the total amount of CO, but the results were not significant. This may be because the effect of CO is somewhat substitutive of hydrocarbons. That is, although both gases become oxidised by the –OH radical to form NO_2 after a sequence of reactions, the oxidation of hydrocarbons is more likely to produce ozone than CO. Therefore, in the presence of sufficient hydrocarbons, the oxidation of CO contributes relatively little to ozone formation.

In the final stage of the sensitivity analysis related to precursor emissions, we had considered both effects, variations in VOCs and NO_x emissions, by increasing and decreasing the traffic intensity data by several percentage points. Results for the Agullana area (Fig. 6) indicate that increasing traffic emissions from the AP-7 motorway by up to 300%, always increases ozone concentrations.

This increment can be considered a realistic approximation to the changes in traffic density observed at the beginning and the end of the summer holiday period.

In addition to the previous sensitivity test related to the importance of precursors in the formation of ozone, there are several uncontrollable meteorological factors such as temperature, solar radiation and humidity which influence photochemical reactions involved in the ozone formation rate and must therefore be taken into consideration. For this reason, we also performed a simple, although not exhaustive, sensitivity analysis related to the previous meteorological variables: changes in temperature, humidity and solar radiation are

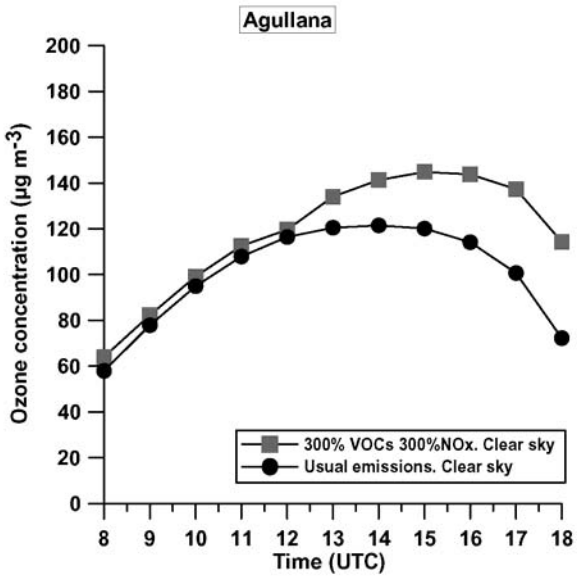

Figure 6.- Sensitivity of hourly ozone concentrations values to changes of VOCs and NO_x emissions due to the increment of traffic intensity. The area simulated is Agullana and the defined condition is clear sky. Legend examples: 300% VOCs-300% NO_x indicates the base case VOCs - NO_x emissions are multiplied by 3, while CO emissions are kept to the base-case amount.

introduced in the model. Changes in air temperature will affect the relative importance of the various reactions involved for O_3 formation and their kinetics. As an example, peroxyacetyl nitrate (abbreviated PAN) formation from NO_2 is reversible; lower temperature activate their formation, while at higher temperatures PAN is thermally decomposed, releasing NO_2 and an organic free radical. It can thus, act as an NO_x reservoir and ultimately as a source of OH and ozone (Jacobson 2002). Under clear polluted conditions the effect of temperature on reaction is almost negligible. However, when pollution increases, the rate of ozone production rises with temperature.

Fig. 7 shows an example from the Vic area. These results agree with those found by Walcek and Yuan (1995). The results for incoming solar radiation and sunlight intensity indicate that cloud cover affects the ozone formation rate by modifying the intensity of the photolysis involved. For example, in polluted air masses with high concentrations of formaldehyde (HCHO) photolysis becomes an important source of the perhydroxyl radical HO_2, which catalyzes the formation of ozone. Walcek and Yuan (1995) conclude than in polluted air masses there is a quadratic or possibly exponential increase in the ozone formation rate as the photolysis rate increases. The results shown in Fig. 8 are consistent with these findings, as the ozone concentration increases with incoming solar radiation.

Water vapour plays an important role in regulating concentrations of radical HO and HO_2 in the troposphere, necessary constituents for ozone formation. As with previous sensitivity studies there is greater impact under polluted conditions than

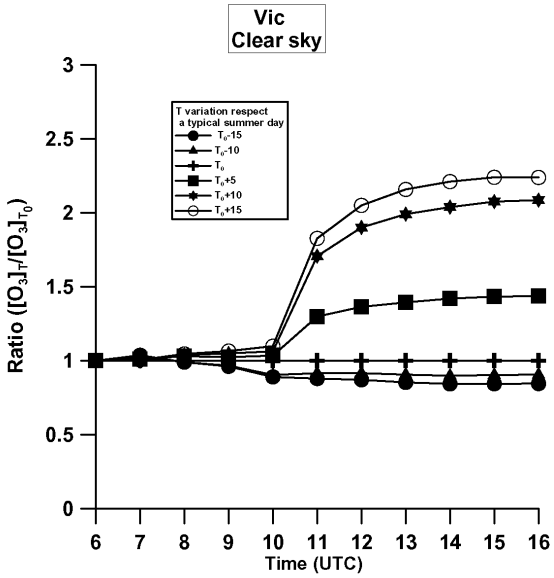

Figure 7.- Sensitivity of hourly ozone concentrations values to variations of temperature in Vic area with clear skies. Legend examples: T_0+5 indicates the base case temperature is incremented in five degrees, while the emissions and others meteorological variables are kept to the base-case amount.

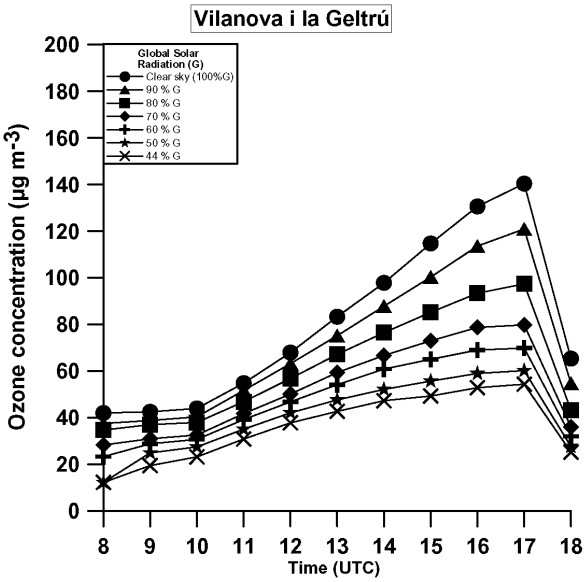

Figure 8.- Sensitivity of hourly ozone concentrations values to variations of global radiation in Vilanova area. Legend examples: 70% G indicates the base case global radiation is multiplied by 0.7, while the emissions and others meteorological variables are kept to the base-case amount.

under clean conditions, as water vapour enhances both the production and destruction of HO_x radicals, but in both cases (not shown) increasing the water vapor mixing ratio increases the ozone formation rate.

6. CONCLUSIONS

We describe the development, application and validation of an operational simple new modelling system to forecast hourly surface ozone concentrations. This is the first application of an ozone modelling system in Catalonia to predict daily ozone levels. It can, however, be applied anywhere, provided the meteorological data, emissions and initial concentrations are appropriately adjusted for the areas of application. One of the main advantages of the system is its low computational cost and its simplicity and efficiency. It is simple to encode and operate compared to grid models; it is easy to specify model inputs and also to vary inputs in sensitivity simulations, therefore large numbers of simulations can be performed rapidly.

In order to check its effectiveness and accuracy, the model was applied to five areas of Catalonia during 2003 and 2004. Forecasts validation shows the reliability of the model in producing accurate predictions, although uncertainties in the determination of various inputs such as cloud cover, emissions and wind field (sea breeze inland) are the main causes of error in the forecasts. We deduce that accurate prediction of cloud

cover is critical to the success of predictions for coastal locations, whereas accurate prediction of sea breeze inland is the main factor for mountainous areas (the Pyrenees). For all areas, satisfactory knowledge of emission levels is essential.

After checking the reliability of the model, a sensitivity analysis was carried out. Our main conclusion is that specific strategies to reduce ozone concentration must be developed for every area forecasted depending on its main ozone precursors. For example, in areas near motorways, one strategy could be to control traffic intensity, or in areas with high industrial activity (power plant, petrochemicals) new technology should be applied to treat exhaust gases before they are vented to the atmosphere. However, some general issues are common to all areas: an increase in VOCs emissions implies an increase in ozone concentration; high temperatures are a determinant factor in producing high ozone concentrations; a reduction of 50 % of incoming solar radiation causes a considerable decrease in ozone concentration. The extent to which ozone concentrations can be predicted and reduced depends on the area for which the prediction is made, as the emission, topography and climatology are different in each case.

7. ACKNOWLEDGEMENTS

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