Photochemical air pollution model for the Madrid area

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ABSTRACT

This paper presents an Eulerian Three Dimensional Photochemical Urban Model (E3PUM) which has been implemented into an Eulerian Transport System. The integrated system has been developed for specific applications over urban areas. The model is integrated into a system which contains a mesoscale meteorological model (MEMO), an eulerian transport model (E3DUSM), a high resolution emission model (HREMOD) and a detailed dry deposition model (DEPO). We have run the model over the Madrid (Spain) Area under different scenarios.

INTRODUCTION

Ozone forms in the lower atmosphere through a complex series of chemical reactions involving manmade and natural emissions. Once formed, ozone is transported and dispersed by the wind, removed at the earth’s surface through a variety of mechanisms, and undergoes further chemical interactions leading to other photochemical oxidants such as peroxyacetyl nitrate (PAN). Attempts to account qualitatively for the transport, dispersion, transformation and removal of ozone in the lower atmosphere within a mathematical framework represent what is commonly known as photochemical dispersion modelling [1, 2].

Photochemical dispersion models are composed of four basic components: a chemical kinetic mechanism, an emission model(s), a meteorological model of pollutant transport and removal -which includes a set of numerical algorithms for integrating the governing species conservation equations-. The sophistication
of each component varies widely depending upon the intended model application. In the scientific literature, the photochemical and meteorological models, the chemical kinetic mechanisms, the emission inventorying techniques, the numerical methods and the data base preparation techniques can be found [3, 6]. In this paper we present the preliminary results of a new photochemical model (E3PUM) which has been applied to the Madrid Area.

THE METEOROLOGICAL MODEL

This model is composed on a mesoscale meteorological module which is called MEMO (Mesoscale Model). This model was developed by Flassak and Moussiopoulou [7, 8]. This is a non-hydrostatic mesoscale meteorological model which produces wind and temperature fields over complex mesoscale orography. This model solves numerically the Navier-Stokes equations by using finite differential and spectral techniques. This model has proved the accuracy of the results under different simulations found in the literature [9, 10]. The model includes three-dimensional windfields, vertical thermal structure and mixing height of each location in the modelling domain as a function of time; surface temperature field and solar intensity. Figure 1 shows a YZ plane for the 15th of August of 1991 over the Madrid domain.
THE TRANSPORT MODEL

The approach adopted was an eulerian dispersion model that solves numerically the advection-diffusion equation on a staggered grid. The form of the equation we adopted is

\[
\frac{\partial c_s}{\partial t} + \sum_{i} \left( \frac{\partial (u_i c_s)}{\partial x_i} \right) = \sum_{j} \left( \frac{\partial}{\partial x_j} \left( K_{c_i} \frac{\partial c_s}{\partial x_j} \right) \right) + \sum_{i} \left( S_{c_i} \right) + \sum_{i} \left( P_{c_i}(c) \right) + \sum_{i} \left( L_{c_i}(c) \right)
\]  

(1)

where \( c_s \) denotes the gas phase concentrations of pollutants, \( u_i \) are the wind velocity components and \( K_c \) is the eddy-diffusivity for scalars (K-theory is used thereof). The \( I \) term is the inertia or storage, \( A \) corresponds to the advection, \( D \) to diffusion, \( E \) to emission (for point and area sources inside the domain), and \( CH_1 \) and \( CH_2 \) stands for production and loss terms, respectively, regarding gas-phase chemistry.

The 3D eulerian model uses the same computational domain (\( \sigma \)-coordinates, expanding vertical grid, etc.) as the mesoscale meteorological model, but the time step used was \( \Delta t = 30 \) s. The temporal discretization adopted makes use of the 2"nd Order Adams-Bashforth scheme. The vertical diffusion is implemented with the Crank-Nicholson method. For the \( A \) term a modification of the original 1D TVD (total variation diminishing) method for the three dimensional case was introduced by Harten [11]. This method achieves a great reduction in the undesirable numerical diffusion but we should point out that this spurious diffusion is not completely removed.

THE PHOTOCHEMICAL MODEL

The system formed by the main four reactions from the \( O_3 - NO_x \) cycle has been selected to study the influence of pollutant photochemistry in the mesoscale transport. Because this is the first preliminary test of the integrated air quality system, we have preferred to start with this simple scheme (although essential in the atmospheric photochemistry). On the other hand, the high computer speed demands for this task advice to start with simple schemes to test the consistency and other parameters of the model. Figure 2 shows a Conceptual representation of the different components of a photochemical model.
The chemical reaction scheme adopted is:

\[ NO + O_3 \xrightarrow{k_1} NO_2 + O_2 \]  
\[ 2NO + O_2 \xrightarrow{k_2} 2NO_2 \]  
\[ NO_2 + O_2 + h\nu \xrightarrow{k_3} NO + O_3 \]  
\[ NO_2 + O_3 \xrightarrow{k_4} NO_3 + O_2 \]

the temperature effect on the conversion rate constant \( k_1 \) [12] and \( k_2 \) [13] are parameterized as follows

\[ k_1 = 2.310^{-12} \times e^{-1450/T} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \]  
\[ k_2 = 1.510^{-40} \times e^{-1780/T} \text{ cm}^6 \text{ mole}^{-2} \text{ s}^{-1} \]
The reaction constant for $NO_2$ photodissociation, $k_3$ is a function of u.v. light intensity. Here, the empirical expression proposed by Leighton has been chosen:

$$k_3 [O_2] = 0.0047 \text{ min}^{-1}$$

where $I$ is the intensity of the u.v. light in W m$^{-2}$. On summer days, maximum values of $k_3 [O_2] = 6.210^{-3} s^{-1}$ have been reported for latitudes around 50° N. The functional dependence on temperature is unknown.

Following the suggestion of Burton et al. during nocturnal conditions, reaction 4 is excluded and chemical reaction 5 is included with a rate constant $k_4$:

$$k_4 = 1.210^{-13} e^{-24450 \over T} \text{ cm}^3 \text{mole}^{-1} \text{s}^{-1}$$

This reaction scheme ignores many important reactions involved into the photochemical $O_3 - NO_x$ cycle e.g. the production of very reactive hydroxyl radicals from ozone photolysis. The kinetic system for the simplified reaction scheme is:

$$\frac{\partial [NO_2]}{\partial t} = k_1 [NO] [O_3] + k_2 [NO]^2 - k_3 [NO_2] - k_4 [NO_2] [O_3]$$

$$\frac{\partial [NO]}{\partial t} = -k_1 [NO] [O_3] + k_2 [NO]^2 + k_3 [NO_2]$$

$$\frac{\partial [O_3]}{\partial t} = -k_1 [NO] [O_3] + k_2 [NO_2] - k_4 [NO_2] [O_3]$$

To solve this stiff system of ordinary differential equations, a Gear method has been employed. For every model time step and for each of the 5 $10^4$ cells a ODE system must be solved. As a consequence, very efficient implementations of the algorithm (in FORTRAN-90) and accurate vectorization in the grid-cell dimension should be used.

THE EMISSION MODEL

The working area has bee divided into 4 km$^2$ square cells. The $SO_2$ and $NO_x$ emissions (kg s$^{-1}$ m$^{-2}$) were determined for each cell. The CORINAIR methodology has been applied, although many emission have been obtained from the US EPA.

Only antropogenic emissions have been taken into account. We have considered the road traffic, large industries and residential activities as sources. Concerning industrial activities, since the simulation day is holiday in the Madrid Area we have not considered area industrial sources (most of small and medium-sized industries were closed), reducing industrial emissions to point industrial sources. It
was assumed that these large industrial sites operate continuously all over the day. At present, many industries include air pollution abatement devices. Therefore, when actual emission data were unknown, it was assumed an emission reduction of 50% (INYPSA). The point source emissions depend on fuel consumptions as well as the production processes. CORINAIR factors were used for both parameters.

Regarding residential activities -mainly the production of warm water (15% of the total emission in typical winter situations)-, the emissions for pollutant $s$ are computed with the following CORINAIR expression,

$$\frac{N_i}{N} \sum_f G_f \cdot EF_{fs}$$

where $N_i$ and $N$ are the inhabitants in cell $i$ and the whole domain, respectively; $G_f$ is the consumption of fuel $i$ per unit of time in the work area, and $EF_{fs}$ is the emission factor for fuel $i$ and pollutant $s$ given by EPA and shown in Table 1.

<table>
<thead>
<tr>
<th>FUEL</th>
<th>UNITS</th>
<th>$SO_2$</th>
<th>$NO_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas oil</td>
<td>kg/1000 l</td>
<td>11.21</td>
<td>2.3</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>kg/1000 l</td>
<td>46.58</td>
<td>2.3</td>
</tr>
<tr>
<td>L.P.G.</td>
<td>kg/1000 l</td>
<td>0.046</td>
<td>1.0</td>
</tr>
<tr>
<td>Domestic Gas</td>
<td>kg/$10^6$ m$^3$</td>
<td>11.30</td>
<td>750</td>
</tr>
<tr>
<td>Hard Coal</td>
<td>kg/$10^6$ m$^3$</td>
<td>19.00</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 1.- Emission factors for the most common fuels in heating systems.

Exhaust emissions from road traffic were computed by using,

$$E_{is} = n_i \cdot r_i \cdot c \cdot f_{is}$$

where $i$ is the type of vehicle, $E$ is the emitted pollutant for each type (g), $n$ is the number of travelling vehicles (per hour), $r$ is the mean travel distance (km), $c$ the mean consumption (l km$^{-1}$; [19]) and $f_s$ the emission factor for each pollutant $s$. The calculation of $n$ starts from yearly averaged data, corrected with factors for a particular day/hour, extracted from data collected by the Traffic Department of Madrid Municipality. The CORINE/EPA emission factors used are presented in Table 2.

<table>
<thead>
<tr>
<th>VEHICLE TYPE</th>
<th>$SO_2$</th>
<th>$NO_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline cars$^a$ (g/l)</td>
<td>1.50</td>
<td>15</td>
</tr>
<tr>
<td>Diesel cars$^a$ (g/l)</td>
<td>8.25</td>
<td>20</td>
</tr>
<tr>
<td>LPG cars$^a$ (g/l)</td>
<td>0.01</td>
<td>1.6</td>
</tr>
<tr>
<td>Motorcycles$^b$ (g/l)</td>
<td>0.40</td>
<td>3</td>
</tr>
<tr>
<td>Buses. Diesel cars$^b$ (g/l)</td>
<td>8.00</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 2.- Emission factors for road traffic.
THE DEPOSITION MODEL

For evaluation of dry deposition fluxes, we adopted the so-called Big-Leaf or inferential method. The deposition velocity $v_d$ is calculated as the reciprocal value of the sum of three characteristic resistances:

$$v_d = \left( r_a + r_b + r_c \right)^{-1}$$

where $r_a$ and $r_b$ are the aerodynamic and bulk resistances; the canopy resistance $r_c$ takes into account the different physical, chemical and biological properties of the surface. The details of this model are described in [20] and [21].

RESULTS

We have performed several preliminary simulations over the Madrid Area corresponding to the 14-16, August, 1994. The domain is 80x100 km, centered in the Madrid City. We have taken an horizontal resolution of $\Delta x = \Delta y = 2$ Km. The vertical resolution chosen was variable, with a minimum $\Delta z = 10$ m, but expanding up $z_{top} = 6000$ m. The time resolution was close to $\Delta t = 15$ s. This low time-step was needed to achieve convergence of the numerical methods (particularly for the advection terms, since the small $\Delta z_{min}$ produces high Courant numbers, even for moderate vertical wind speeds). The model MEMO handles complex orography by using $\sigma$-coordinates, in addition to an expanding vertical gridsize. The model run used the non-hydrostatic option, and for initialization just one vertical sounding of wind and potential temperature was needed.

Figure 3 shows predicted and observed hourly averaged ozone concentrations for August, 14-16, 1991 for two different stations (14 and 22) in the Madrid Urban Area. The solid line represents hourly averaged ozone observations and the points represent the hourly averaged ozone predictions. In this preliminary work we show a relatively good agreement between observed and predicted values. Further work is necessary to assess the confidence of the model. Additional evaluative tests are necessary to establish the uncertainty of the model. Special importance should be given to emission inventory model which until now has received minimal emphasis from a model evaluation standpoint despite the widespread concern that the emissions may be the least accurate of the major inputs to photochemical models.
Figure 3.- Predicted and observed hourly averaged ozone concentrations for August, 14-16, 1991 at two different stations in the Madrid Urban Area.

Statistical evaluation procedures show that for this test case the overall error is of order 45-50%. In future works we will run the model under different scenarios and we will perform sensitivity simulations by using much more test cases.

ACKNOWLEDGEMENTS

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REFERENCES


