Fresenius Envir Bull 1: 232-237 (1992)

1018-4619/92/040226-06 $ 1.50+0.20/0

MATHEMATICAL MODELING OF PHOTOCHEMICAL AIR POLLUTION IN ATHENS, GREECE

N.M. Zoumakis, A.G. Kelessis, G. Kallos[1], B. Charalampidou, Th.I. Kozyraki, F.K. Vosniakos and M. Petrakakis[2]

Laboratory of Atmospheric Physics, Technological Education Institute (T.E.I.), P.O.Box 14561, Thessaloniki 54101, Greece.

[1]Department of Applied Physics, University of Athens, Athens 10680, Greece.

[2]Environmental Department, Municipality of Thessaloniki, E. Venizelou 45, Thessaloniki 54631, Greece.

Summary. A three-dimensional numerical model for predicting the time-dependent dynamic behavior of chemically reacting air pollutants in the Athens basin is developed. The model is used to estimate the spatial and temporal distribution of CO, SO_2, NO, NO_2 and O_3 emissions in Athens. The model results were also validated and compared with actual measurements.

Key Words: Urban air pollution models, numerical grid models, turbulent diffusion, atmospheric chemistry.

Introduction

Modeling urban scale air pollution is essentially the problem of describing the formation and transport of chemically reacting species in the turbulent planetary boundary layer. Assuming that molecular diffusion is negligible when compared with turbulent dispersion, the atmospheric diffusion equation can be expressed as follows[1]:

$$\frac{\partial C_i}{\partial t} + \frac{\partial}{\partial x}(uC_i) + \frac{\partial}{\partial y}(vC_i) + \frac{\partial}{\partial z}(wC_i) = \frac{\partial}{\partial x}\left(K_H \frac{\partial C_i}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_H \frac{\partial C_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_V \frac{\partial C_i}{\partial z}\right) + S_i + R_i \quad (1)$$

where the concentration $C_i(x,y,z,t)$, of each of the reactive pollutant species in the atmosphere must satisfy the continuity equation (modified by use of the K-theory), $U=(u,v,w)$ are the components of the wind velocity, K_H and K_V are horizontal and vertical eddy diffusion coefficients, R_i is the rate of formation of species i by chemical reactions, and S_i is the rate of emission of species i from sources.The objective of this study is to develop and validate the airshed simulation model for the prediction of photochemical air pollutants (i.e., CO, NO, NO_2, HC and O_3) and sulfur dioxide (SO_2) concentrations, and their variations in space and time in the urban Athens area.

The Model Developed in this Study

Considering the limitations[2,3] inherent in Equation (1) that restrict its applicability in describing the transport and chemical reactions of air pollutants in the atmosphere, the atmospheric diffusion equation is applicable into a grid of 80, 3x3 kilometer squares and source emissions and meteorological variables was distributed in conformance with this spatial dimension over which all quantities are averaged. The grid actually used in the solution of Equation (1) is a three-dimensional array of ten layers of cells occupying the space between the ground and the base of the inversion. To complete the mathematical formulation of the airshed model both the initial and boundary conditions need to be specified[4,5,6]. To implement the finite-difference scheme on a fixed rectangular grid, we perform the following change of variable[5]:

$$\varrho = [z-h(x,y)]/[H(x,y,t)-h(x,y)] \qquad (2)$$

where h(x,y) is the ground elevation above sea level,and H(x,y,t) is the elevation above sea level of an assumed upper limit for vertical mixing of transport. Given the structure of Equation (1) a numerical scheme based on the method of fractional steps was used to obtain the numerical integration of diffusion equation[2]. A modeling system capable of describing the time-dependent dynamic behavior of photochemical air pollutants requires the following components: (a) meteorological data, including wind speed and direction, inversion height, atmospheric stability and eddy diffusivities; (b) photochemical reaction mechanism; and (c) a source emissions inventory.A divergence-free objective analysis scheme have been applied in preparing the wind fields for the model simulation[7,8,9]. Based on extensive radiosonde measurements (which were made at Athens International Airport), we have also studied the variations in the depth of the mixing layer as a function of both location and time over Athens basin. McRae et al.[2] reviewed the literature pertaining to measurements of the turbulent diffusivity in the atmosphere and suggested a relationship:

$$K = K(u_*,z_0,L,Z_i) \qquad (3)$$

expresses the variation of the eddy diffusion coefficients[10] K_H and K_V with the surface friction velocity u*, roughness height z_0, Monin-Obukhov stability length L, and mixed layer depth Z_i. The Monin-Obukhov stability length L can be derived by using the bulk Richardson number Ri_b approach :

$$(z-z_0)/L = F(Ri_b) \qquad (4)$$

where the analytical forms for $F(Ri_b)$ may be taken from Byun[11]. However, if Ri_b-measurements are not available, each Pasquill stability class can be approximated[12] by a single straight line of

1/L against z_0. Lateral and vertical dimensions of the plume are obtained by assuming a Gaussian profile in each direction[2]. The photochemical mechanism adopted in this work is based on that of McRae et al.[2]. To validate the model, the pollutant (SO_2, NO_x, CO, HC) emissions (see Table 1) must be specified as a function of time and location in Athens basin[13,14]. Hourly wind speed, wind direction, and mixing depth maps and a complete emissions inventory are prepared for each validation period.

Table 1. Emissions of SO_2, CO, NO_x, HC in the Athens basin (tons/year).

Emission source	SO_2		CO		NO_x		HC	
	t/y	%	t/y	%	t/y	%	t/y	%
Automobiles	1400	4.9	390000	99.7	18500	67.3	49000	68.8
Industries	22600	79.3	500	0.15	7500	27.3	22000	30.9
Space heating	4500	15.8	500	0.15	1500	5.4	200	0.3
Total	28500		391000		27500		71200	

Results and Discussion

Hourly averaged ground-level (in ppb) SO_2, NO, NO_2, and O_3 concentrations, and CO concentrations (in ppm) were estimated at 00:00-24:00 (local time), for winter and summer period. Figure 1 shows the predicted contours of equal ground NO and O_3 concentrations, at 08:00 and 14:00 (local time) and SO_2 concentrations, at 09:00 and 22:00 (local time). Validation of the model was carried out for nitric oxide (NO), nitrogen dioxide (NO_2), ozone (O_3), sulfur dioxide (SO_2) and carbon monoxide (CO) concentrations. Figure 2 presents the observed and predicted average diurnal variation of the ground-level NO, NO_2, O_3, SO_2 and CO concentrations, at several locations in the region of Athens. The comparison plots indicate that the computed results agree favorably with the experimental measurements. Carbon monoxide and nitric oxide are emitted by automobiles (the major source of these pollutants in Athens) and observed CO and NO concentrations tend to have a similar pattern of variation during the morning traffic rush hours (Figure 2). However, the direct result of the street canyon effect [3,4] is that the box-model underestimate the carbon monoxide and nitric oxide concentrations. The rising sun initiates the photochemical reactions which convert the nitric oxide to nitrogen dioxide. Within a few hours the nitrogen dioxide reaches a maximum during which it photochemically reacts to form ozone and other oxidants. As ozone forms during the late morning hours, NO tends to decrease and O_3 reaches a maximum during the midday to afternoon period. The model also calculated the percent contribution of each activity to the total SO_2 in each cell. It is found that the mean contribution of space heating to the total mean daily SO_2 is about 65-70% for the central area of Athens, for the cold period. In conclusion, the suggested mathematical model of photochemical air pollution is capable of accurate predictions over a range of meteorological and source emission conditions and it can be used as an important aid in urban and regional planning.

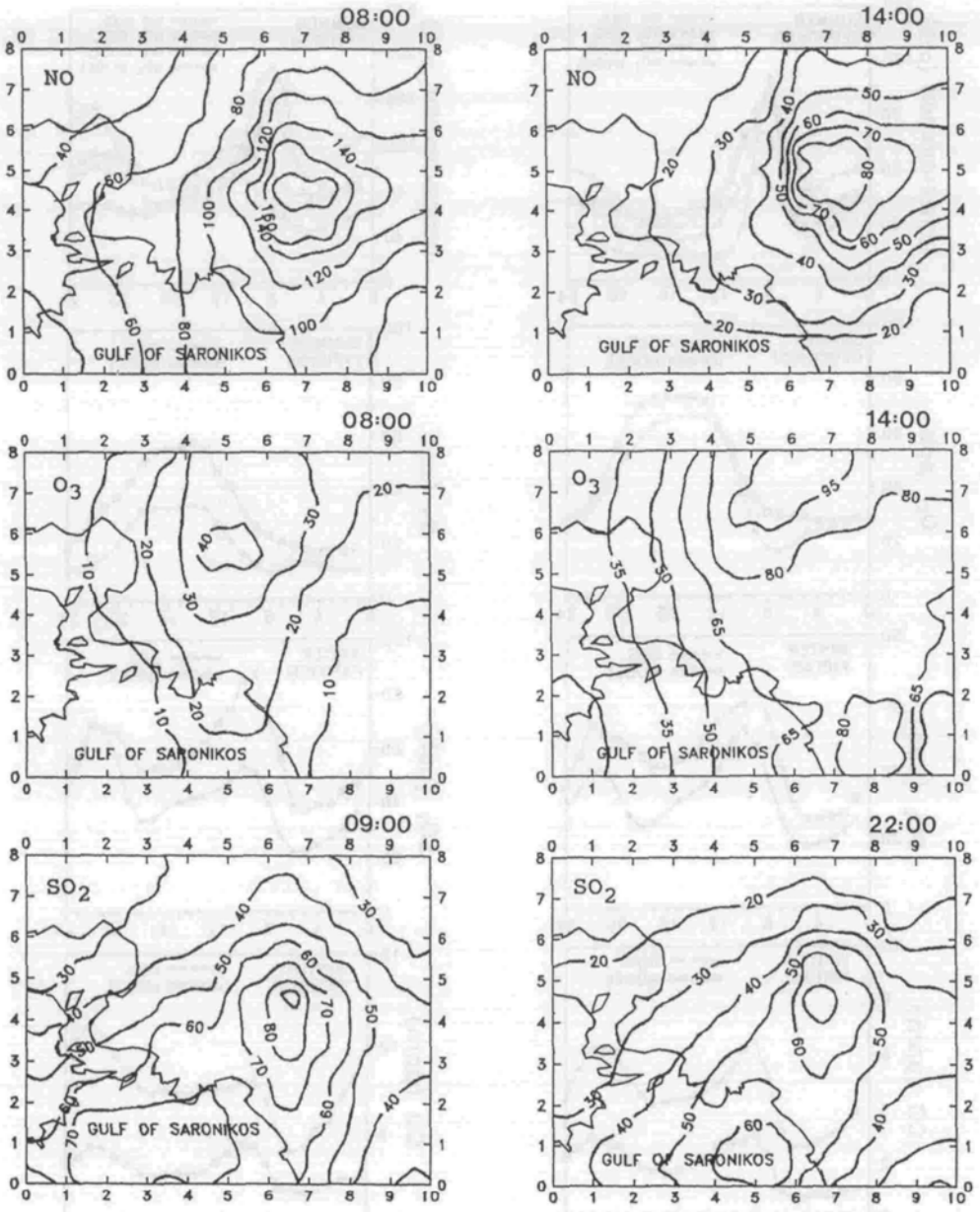

Figure 1 Predicted contours of equal ground-level NO and O_3 concentrations (in ppb) at 08:00 and 14:00 local time, and SO_2 concentrations (in ppb), at 09:00 and 22:00 local time.

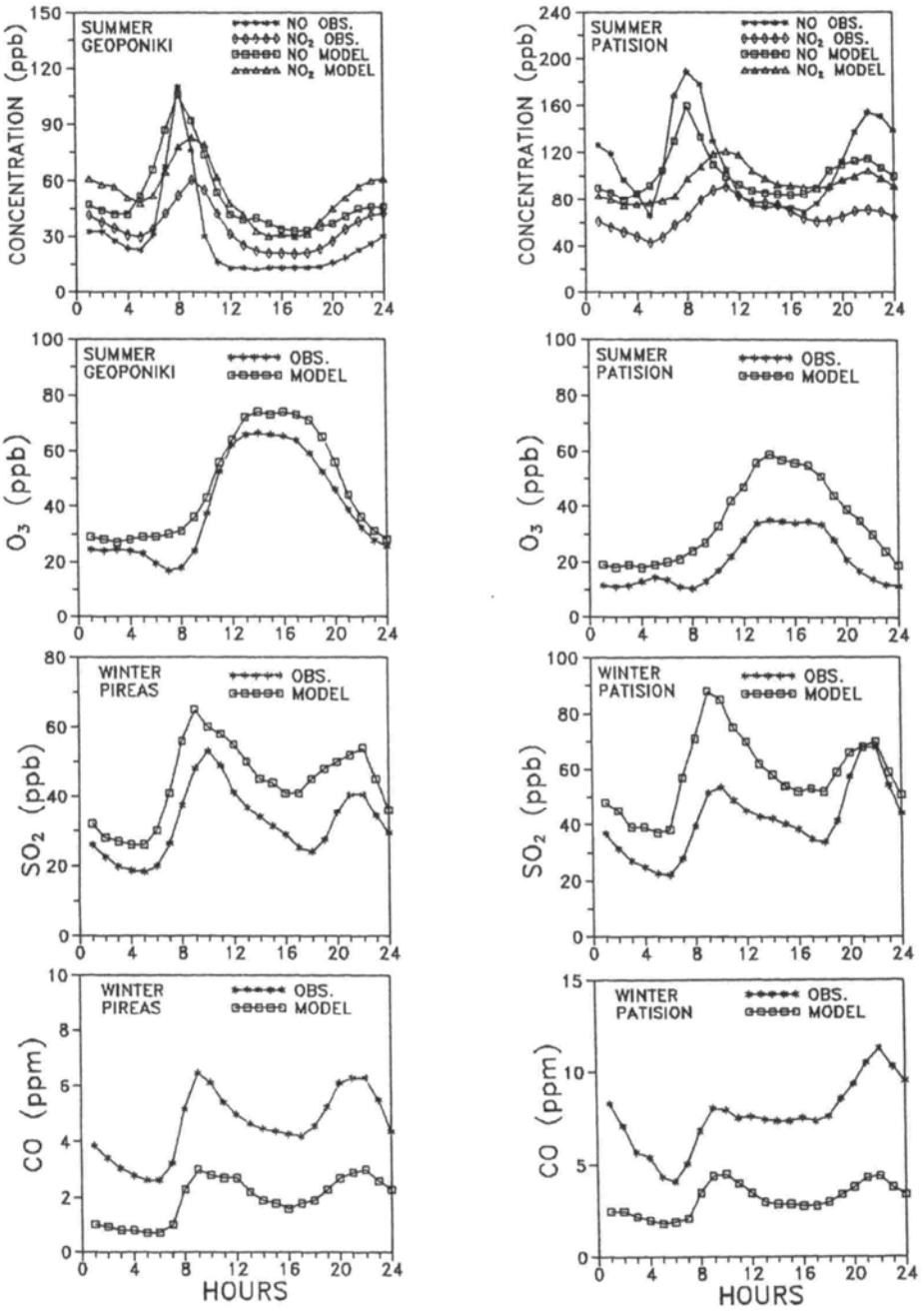

Figure 2 The observed and predicted NO, NO_2, O_3, SO_2 and CO concentrations, at several locations in the region of Athens.

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Accepted 5 February 1992