Transactions on Ecology and the Environment vol 29 © 1999 WIT Press, www.witpress.com, ISSN 1743-3541

Applicability of a photochemical box model over complex coastal areas

G. Latini,[1] R. Cocci Grifoni,[1] G. Fava,[2] G. Passerini [1]
[1] *Dipartimento di Energetica, Università di Ancona via Brecce Bianche, 60100 Ancona, Italy*
[2] *Dipartimento di Scienza dei Materiali e della Terra, Università di Ancona via Brecce Bianche, 60100 Ancona, Italy*

Abstract

The aim of this paper is to show that a Photochemical Box Model (P.B.M) is able to describe the air pollution diurnal profiles within a typical complex coastal area. Due to the simplicity of the box model physical structure, P.B.M. is well suited for rapid assessment. In principle, it is best designed to treat low wind conditions, in presence of sunlight. It can manage point, line and area sources. The emission sources are homogeneously distributed across the surface of the volume and the volume is mixed the whole time. In this first study, atmospheric diffusion and wind shear have been neglected.

1 Introduction

The P.B.M. model is applied to calculate pollutant concentrations during one day with meteorological conditions favouring pollutant accumulation.
The single box model is the simplest air pollution model. It is based upon the principle of the conservation of mass, namely mass of pollutants, inside an Eulerian box, within which chemical reactions are computed to evaluate, between all, the concentrations of hydrocarbons and ozone. The considered pollutants are basically nitrogen oxides and hydrocarbons. The model was applied over a Coastal Area, in the middle of Italy (Marche), that comprises valleys, hills, urban and industrial zones.

A box is taken into account with horizontal dimensions of 20 Km (from Ancona to Falconara), and a height that may vary according to a non-linear growth curve that represents the depth of the mixed layer. Model simulation begins at 5.00 h, local standard time (LST) and continues throughout the day typically ending just before sunset.

Data requirements for the P.B.M. include meteorology, air quality, and emission data. It is important to provide the photochemical model with initial species concentrations, hourly input of wind speed, source emission fluxes of CO, NOx (Nitrogen Oxides), THC (hydrocarbons), reactivity classes and boundary species concentrations. Values of mixed layer depth are specified at hourly intervals throughout a semi-empirical calculation. The P.B.M evaluates a measure of air quality averaged over the entire volume of the domain. In this study the air pollution diurnal profile within a typical coastal area has been investigated during the period 1/31 July 1998. In particular, the result of a sunny day (July 16, 1998) is presented.

2 The Esino Valley

Marche is an Italian region made up of valleys nearly parallel all looking out onto the Adriatic Sea. The Esino valley (in the province of Ancona) is characterised, like most of the others, by a riverbed that is roughly perpendicular to the coast and in a NE direction. The valley is surrounded by hillsides in increasing height as they distance from the coast. The first hills rise close to the coast and at this distance the height does not exceed 100 m. A further 20 km inland, the height does not exceed 200 m, but at about 30 km the valley undergoes a sharp narrowing near the gorge "della Rossa" where the height exceeds 1000 m. The area taken into consideration will be the lower valley of Esino. The considered area covers 20 km inland from the coast and 20 km wide.

The climate in this area is classified under subcoastal. There is an all year round sea breeze although of different intensity and influenced by a heavy component from NW.

The sea breeze is caused by the different temperatures in the air bodies above the sea on one side and the coast on the other. This gives way to a meandering current along the coast with a parallel component to the coast caused by the synoptic winds; the component perpendicular to the coast, according to the direction is called coastal or sea breeze based on the origin of the winds. In presence of discontinuity as in the hillsides situated at the entrance of the valley, the force of the sea breeze enforces the breeze coming from the valley. This phenomenon is caused by a difference in temperature between the land and air around slopes. The highest intensity of the sea breeze/valley breeze occurs during the warmest hours (about 3 PM) and it starts decreasing after the sunset. During the night, you may have some hours of calm before the mountain breeze/land breeze starts again. Usually stability is associated with the mountain breeze, while unstable conditions to the sea. In this scenario, the increase of the mixed layer starts from the coast. The layer marks both the condition of stability above the MBL (Marine Boundary Layer) and the instability of the CBL

(Convective Boundary Layer) on the coast. The meteorological output data here in analysed, is related to the measurements performed by the Italian Air Force Weather Station in Falconara Marittima (ISTAT), located in Chiaravalle airport, 2 km from the coast and more or less in the middle of the Esino valley (43.37 Lat-13.22 Long-12 m height). The output data comes from the observations performed hourly and gives information in both frequencies and monthly/seasonal distribution of speed, direction and directional persistence of wind, atmospheric stability and air temperature.

3 The Model

The approach adopted is an Eulerian dispersion model that solves numerically the simplified diffusion equation given by

$$\frac{\partial c_i}{\partial t} = u\frac{\partial c_i}{\partial x} + \frac{\partial z}{\partial t}\frac{\partial c_i}{\partial z} + \frac{Q_i}{z} + R_i(c_i,......,c_n) \qquad (1)$$

where c_i denotes the mean concentration of species *i* within the domain, *u* is the mean wind speed within the domain, Q_i is the source emission flux of species i into the domain and R_i the rate of production and/or destruction of species *i* from chemical species.

This equation represents the principle of conservation of mass, and it is solved numerically within the P.B.M for the concentrations c_i as a function of time. The P.B.M. evaluates, as results, hourly averaged concentrations.

Since the P.B.M is a photochemical model, a set formed by 63-step chemical kinetic mechanisms has been considered to study the influence of the pollutant photochemistry in the mesoscale transport. The main four reaction, mainly between Oxygen and Nitrogen Oxides, are only reminded:

$NO_2 + h\nu => NO + O$
$O + O_2 + M => O_3 + M$
$O_3 + NO => NO_2 + O_2$
NO_2 +. O3 => $NO_3 + O_2$

The Ozone, a natural constituent of stratosphere formed by photolysis of molecular oxygen, can be transported by atmospheric circulation into the lower atmosphere. Natural hydrocarbons including those from trees and vegetation are also subject to photochemical reaction producing oxidants. Ozone is one of the strongest oxidising agents.

The P.B.M system is appropriate for typical ozone episodes and it includes three main components: a meteorological data editor (for hourly data) with its preprocessor (PBMMET), an air quality and emission data editor with its preprocessor (PBMAQE), and the dynamic Photochemical Box Model (PBM).

4 Data Requirements

The P.B.M. requires three main sets of data (K.L Schere and K.L. Demerjian[1]): meteorological data, air quality data, and emission data

4.1 Meteorological Data

The P.B.M requires values of specific meteorological parameters in order to solve (eqn 1). Required data are listed below:

- date (day, month, year; starting time is fixed at 05.00 local time);
- location (latitude, longitude);
- wind speed (hourly, meter/second; the wind speed is assumed to be measured at 10 m above ground);
- mixing height (hourly, meters above the ground);
- total solar (TSR) or ultra-violet radiation (ly/minute, optional);
- ambient air temperature (hourly, degree Centigrade, optional);
- cloudiness (coverage, height, optional).

The meteorological data related to July 1998 (temperature and wind speed) have been supplied by IRPEM department of National Centre of Research (C.N.R), Ancona (see Table 1).

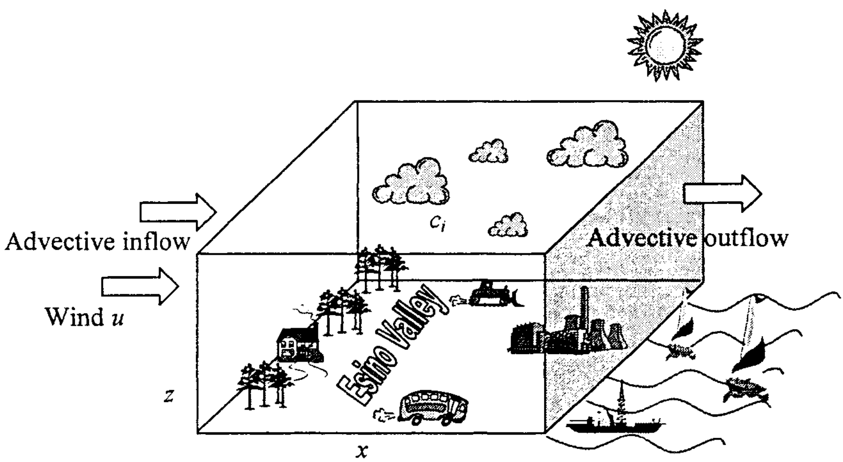

Figure 1: photochemical box model applies over Esino Valley

Transactions on Ecology and the Environment vol 29 © 1999 WIT Press, www.witpress.com, ISSN 1743-3541

DAY	WIND [M/S]	TEMPERATURE [°C]
16/7/98 5.00	1.30	19.5
16/7/98 6.00	1.11	21.0
16/7/98 7.00	0.85	21.5
16/7/98 8.00	0.56	22.5
16/7/98 9.00	0.18	23.0
16/7/98 10.00	-0.21*	23.2
16/7/98 11.00	-0.17*	23.6
16/7/98 12.00	-0.45*	24.0
16/7/98 13.00	-1.53*	24.7
16/7/98 14.00	-2.46*	24.6
16/7/98 15.00	-2.96*	24.5
16/7/98 16.00	-2.67*	24.3
16/7/98 17.00	-1.16*	24.4
16/7/98 18.00	-0.46*	23.9
16/7/98 19.00	0.85	23.0
16/7/98 20.00	0.96	22.4
16/7/98 21.00	0.58	21.9
(*the minus symbol denotes a wind directed out of the box)		

Table 1

The mixing height (Table 2) is evaluated in the complex terrain with a semiempirical estimate of boundary layer parameters like Monin-Obukhov length and roughness length z_0 (Latini et al.[2]).

It is important to take in account the orography of the Esino Valley because it strongly influences the atmospheric flows and therefore advection and mixing of pollutants. The investigated area is the Esino watershed (near Ancona), a slightly valley faced to middle Adriatic Sea. This area includes a refinery on the estuary of the Esino River, urban zones like Iesi, hills, and some main road (Figure 1).

DAY	HMIX [M]	DAY	HMIX [M]
16/7/98 5.00	61.21	16/7/98 14.00	782.30
16/7/98 6.00	669.07	16/7/98 15.00	780.02
16/7/98 7.00	348.30	16/7/98 16.00	741.29
16/7/98 8.00	484.37	16/7/98 17.00	759.51
16/7/98 9.00	561.56	16/7/98 18.00	691.19
16/7/98 10.00	591.10	16/7/98 19.00	552.47
16/7/98 11.00	645.68	16/7/98 20.00	479.81
16/7/98 12.00	707.13	16/7/98 21.00	400.43
16/7/98 13.00	809.65		

Table 2

Transactions on Ecology and the Environment vol 29 © 1999 WIT Press, www.witpress.com, ISSN 1743-3541

4.2 Air Quality Data

Air quality data are required to compute values for some c_i terms in (eqn 1). Initial conditions are needed for $\partial c_i/\partial t$ terms, lateral boundary conditions for $\partial c_i/\partial x$ terms, and boundary conditions at the top of the domain for $\partial c_i/\partial z$:

- initial condition concentrations (ppm);
- boundary concentrations (ppm);
- observed concentrations (ppm, optional);
- hydrocarbons speciation factors for initial concentrations;
- hydrocarbons speciation factors for boundary concentrations;
- hydrocarbons speciation factors for observed concentrations (optional).

Ambient concentrations are often available as non-methane hydrocarbons (NMHC). Since there are hundreds of specific compounds in this class, only a few major structural categories are introduced to simulate the range of all NMHC compounds.

Air quality data (CO, NOx, NMHC) were supplied by IRPEM department of National Centre of Research (C.N.R), Ancona.

As regards the ozone, it is photochemically produced in the atmosphere when certain precursor pollutants (VOC and NOx) are mixed together in presence of sunlight. To develop an effective ozone control strategy, we need an inventory of, at least, the most important emission sources (plants, business. etc.) of precursor pollutants. The emission inventory should basically identify the source types present in the area and the amount of each pollutant emitted. Such data are not available for the Esino area and so the default value has been considered (O_3=0.030 ppm) for initial concentration and top condition.

4.3 Emission data

Data from source-specific emission tests or continuous emission monitors are usually preferred for estimating emissions related to a source since those data provide best representation of emission sources. However, data from individual sources, in the Esino valley, are not always available and, when available, they could not reflect the actual variability of emissions over time. Thus, emission factors are frequently applied as the choice method for estimating emissions, in spite of their limitations. Normally, emission estimates must be referred to the territory, so each activity has to be quantified with a parameter related to the emission factors defined on.

The general equation for emission estimation is:

$$E = A \times EF$$

Transactions on Ecology and the Environment vol 29 © 1999 WIT Press, www.witpress.com, ISSN 1743-3541

where E represents the emissions, A is the activity rate, and EF is the emission factor.

An emission factor (Gaudioso et al.[3], Veldt et al.[4]) is a representative value that attempts to relate the quantity of a pollutant released into atmosphere to an activity associated with the release of that pollutant. Usually emission estimates (Latini et al.[5]) are referred to the territory, and each activity extension has to be quantified by a parameter related to the emission factors.

The emission data required within P.B.M input are:

- source emission rate of CO from area and line sources (Kg/hour);
- source emission rate of CO from point sources (Kg/hour);
- source emission rate of NOx from area and line sources (Kg/hour);
- source emission rate of NOx from point sources (Kg/hour);
- source emission rate of total hydrocarbons (THC) from point sources (Kg/hour);
- source emission rate of total hydrocarbons (THC) from line and area sources (Kg/hour);
- source emission rate of hydrocarbons classes from point sources (mole/hour);
- source emission rate of hydrocarbons classes from line and area sources (mole/hour);
- ratio of NO_2/NOx in area and line source NOx emissions (default values);
- ratio of NO_2/NOx in point source NOx emissions (default values);
- ratio of CH_4/THC in area and line source THC emissions (default values);
- ratio of CH_4/THC in point source THC emissions (default values).

The default values are reported in Table 3.

	NO_2/NO_X	CH_4/THC
Point source	0.10	0.06
Area and line source	0.10	0.00

Table 3

5 Results

The air quality model generates the diurnal level concentrations for CO, NO, NO_2, and O_3. To validate the model results, in terms of diurnal trend, the obtained results are compared with the data monitored by two continuos emission monitors within the area of study (Chiaravalle and Falconara).

Table 4 summarises the results for PBM O_3 values and monitored O_3 values (O_3 MN).

Day	O3 PBM [ppm]	O3 MN [ppm]
16/7/98 6.00	0,0283	0,0119
16/7/98 7.00	0,0282	0,01335
16/7/98 8.00	0,0285	0,01824
16/7/98 9.00	0,0298	0,02342
16/7/98 10.00	0,033	0,0276
16/7/98 11.00	0,0386	0,0343
16/7/98 12.00	0,0458	0,0352
16/7/98 13.00	0,053	0,0376
16/7/98 14.00	0,066	0,0315
16/7/98 15.00	0,091	0,04
16/7/98 16.00	0,0713	0,03645
16/7/98 17.00	0,042	0,036
16/7/98 18.00	0,0326	0,03738
16/7/98 19.00	0,029	0,03713
16/7/98 20.00	0,026	0,0334
16/7/98 21.00	0,0249	0,0212

Table 4

The Figure 2 demonstrates that the model can reproduce the diurnal trend.

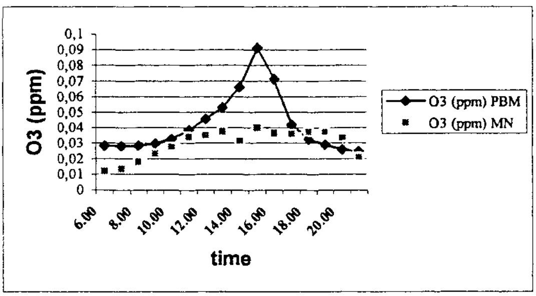

Figure 2

The hourly averaged simulation results for CO specie are overestimated. This could be due to the fact that the Esino Valley is an area with no heavy traffic. This is the reason why the CO concentration is expected lower compared to the average air quality in the area.

Transactions on Ecology and the Environment vol 29 © 1999 WIT Press, www.witpress.com, ISSN 1743-3541

Table 5 summarises the results for PBM NO values (NO-PBM) and monitored NO values (NO-MN):

TIME	NO-PBM [ppm]	NO-MN [ppm]
6.00	0.00036	0.000729
7.00	0.00087	0.00103
8.00	0.000185	0.000539
9.00	0.00027	0.000182
21.00	0.0000103	0.000544

Table 5

Unfortunately, NO concentrations in the middle of the day are not available, but there is an acceptable agreement between the two sets of data.

Finally the results for PBM NO_2 values (NO_2-PBM) and monitored NO_2 values (NO_2-MN) are summarised in the Table 6:

TIME	NO_2-PBM	NO_2-MN	TIME	NO_2-PBM	NO_2-MN
9.00	0.00515	0.0917	15.00	0.00914	0.0245
10.00	0.00632	0.071	16.00	0.0138	0.0177
11.00	0.00739	0.0552	17.00	0.0240	0.0202
12.00	0.00739	0.0485	18.00	0.0418	0.0706
13.00	0.00740	0.04275	19.00	0.0559	0.0421
14.00	0.00789	0.025			

Table 6

Statistical evaluation procedures show that for these test concentrations the overall error is less than 50%.

This can be claimed acceptable since the original code of "multi-purpose" PBM was not modified for this special application in a somewhat hard-to-model environment. Even many of the inputs had to be assumed equal to those, again "multi-purpose", proposed by PBM itself. This is mainly due to the lack of data and a certain difficulty to obtain them. This made difficult to evaluate many of the input parameters required by PBM. In the future works we will run the model under different condition and with adapted, ad-hoc, input parameters.

6 Conclusions

In this preliminary work a relatively good agreement between observed and predicted values has been showed. In particular the comparison between ozone observations in the Esino Valley and the ozone levels predicted by the PBM model is encouraging. Further work is necessary to assess the confidence of the model. Several additional, more precise, evaluative tests are necessary to establish the uncertainty and the capabilities of the model in a coastal area.

References

1. Shere, K.L & Demerijan, K.L., *User's guide for the photochemical Box Model (PBM)*, EPA 600/8-84022A, Environmental Sciences Research Lab. Research Triangle Park, North Carolina, Nov. 1984.

2. Latini, G., Cocci Grifoni, R., Passerini, G. & Tirabassi, T., Evaluation of Mixing Height over Complex Coastal Terrain, to be presented at *Air Pollution 99* Conference.

3. Gaudioso, D., Napolitano, C., Bocola, W. & Trozzi, C., Guida ai fattori di emissione degli inquinanti atmosferici, *ENEA RT/Studi/89/07*, 1989.

4. Veldt, C. & Bakkum, A., *CORINAIR emission factors,* ECC-DG XI, pp.88-385, 1988.

5. Latini, G., Fava, G., Tirabassi, T. & Vitali, G., A database for emission in a multi-sources area, Air Pollution Modelling, Monitoring and Management, eds. C.A. Brebbia & P. Zannetti, Comput. Mech. Pub., pp755-766, 1996