Ozone isopleths for Mexico City using CBM4 within AQUAMI

R. Muñoz-Ledo[a], J.R. Varela[b], C. Reyes-López[a], M. Ley-Koo[a]

[a] *Depto. de Fisico-Química Aplicada, Instituto de Investigaciones Eléctricas, Cuernavaca, Mor. 62000, Mexico*

[b] *Depto. de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, México, D.F. 09340 Mexico*

ABSTRACT. AQUAMI is a microcomputer based software package which includes a module to account for photochemical process taking place in the atmosphere; when coupled to kinetic mechanisms as the so-called CBM4, it allows the calculation of pollutants concentration in a system containing NO_x and HC's. From such calculations the so-called Isopleths, which are level curves representing the maximum Ozone concentration in terms of NO_x and HC's concentrations at the beginning of the solar day, may be constructed. Such curves have been widely used for the analysis of "scenarios" in various cities through out the world. In this work we describe the use of CBM4 within AQUAMI and a parametrization to simulate local conditions, as actinic flux, for Mexico City so that Ozone isopleths may be obtained. CBM4 has been selected as the chemical model since it is faster than the so-called CBM-X model and although the latter includes more reactions, CBM4 has those which are relevant for the present work; it should be pointed out that the resulting computer program can be handled by an IBM compatible personal computer involving small CPU times, which is important since several simulations are required for each isopleth. The simulation is done for irradiation conditions at several months of the year, keeping the same patterns for pollutant emissions.

Introduction

Development of air quality models is of current interest due to the role they play in computer simulators used to analize "scenarios" whose results lead to the design of contingency plans. The purpose of this work is to describe the use of AQUAMI[1], which is briefly described in the next section, together with the so-called CBM4[3] chemical mechanism to estimate Ozone concentrations, in a system involving NO_x and HC's, as a function of time and under different initial conditions. The Ozone concentrations are used to construct the so-called Ozone Isopleths, which are level curves representing the maximum Ozone concentration reached during the day. Among others, the advantage of using AQUAMI cou-

pled to CBM4 is that the resulting computer program may be used in an IBM compatible personal computer, yielding results comparable to those measured and involving reasonable CPU time; since for each isopleth several simulations are needed the reduced mechanism CBM4 is preferred over the more complete so-called CBM-X[5].

Description of AQUAMI

AQUAMI is a computer package developed by Varela *et al.*[1] to deal with the detailed analysis of photochemical processes taking place in a polluted atmosphere and, as such, it is of interest to mention some features that are important for this work. Ozone is the product of a photochemical reaction and as such, it requires the knowledge of the intensity of solar radiation at a given locality; AQUAMI includes a module to estimate dissociation frequencies for each photolizable specie, involved in a given mechanism, as well as the actinic flux characteristic of Mexico City. In addition, it also contains a module to estimate the behavior of the mixing layer, as far as temperature and width is concerned, and which is important to establish the chemical reactions that can take place.

The inputs required by AQUAMI are:

- chemical mechanism, provided as an ASCII file containing the chemical reactions to be considered and which is interpreted internally through a module named GenCod2[2] to generate the corresponding computer code to represent the differential equations describing the chemical mechanism;

- emissions, a file containing emission data of NO_x and HC's, initial Methane, air (in terms of Oxygen and Nitrogen), and CO concentrations as well as humidity; and

- information concerning the sunrise and sunset times, which are characteristic of the season and are used to determine the behavior of the mixing layer as a function of time throughout the day and temperature.

The output provided by AQUAMI includes the concentration of chemical species, according to the given mechanism, as function of time.

Description of CBM4

CBM4 is an abbreviation of Carbon Bond Mechanism-IV, developed by Gery *et al.*[3]; such mechanism is an improved version of the so-called Carbon-Bond Mechanism that was previously developed by Whitten *et al.*[4], the difference being the chemical kinetics of aromatic species, and is a condensed version of the so-called CBM-X developed by the same authors[5], since it involves a reduced number of reactions (81) and species (37). However, both lead to similar predictions for Ozone concentrations and have been tested against experimental results from smog chamber data.

It should mentioned that CBM4 was originaly developed for a location of 30°N at sea level and zenith of 0°; however, Mexico City is located 2240 mts. above sea level at 20°N, so that photolytic rates must be calculated accordingly. To do so, AQUAMI uses a parabolic fit to estimate photolytic rates[6] as a function of time along the day and in terms of the season.

As pointed out before, the condensed CBM4 leads to a reduced number of equations to be handled by AQUAMI, so that the CPU requirements may be covered with an IBM compatible personal computer.

Pollutant concentrations

Once the initial concentrations of Methane, CO, H_2O, Oxygen and Air, as third body, are given, AQUAMI calculates the concentrations of species through the solution to the set of corresponding differential equations, according to the reactions included in CBM4. Such solution involves integrations in time steps provided by the user; in this case, the chosen sizestep was 1 min and the integration procedure, used by AQUAMI, is EPISODE[7,8,9]. The concentrations for the 37 species considered in CBM4, are stored in file for each time step and, at the same time, they can be visualized through a plot on the computer's monitor; due to the chosen time step this may be considered a real time simulation. As the results are stored, they are analized to obtain that corresponding to the maximum concentration of the specie of interest as well as the time at which the maximum occurs; they may also be plotted, as shown in fig. 1, for further analysis.

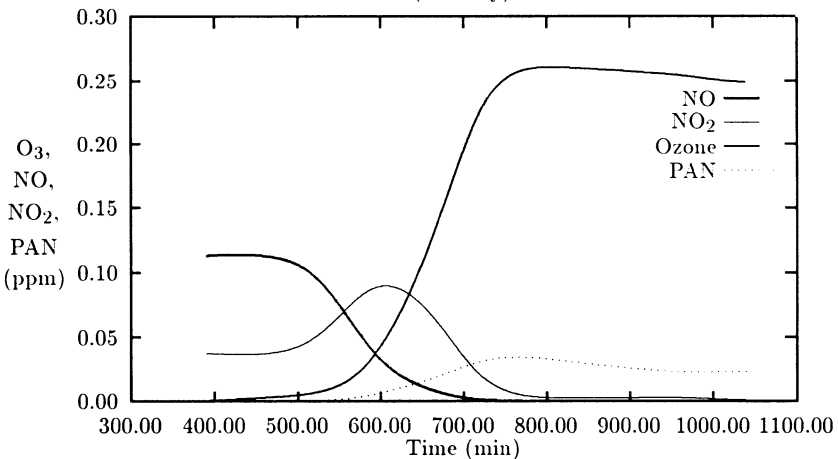HC = 0.25 ppmC, NO_x = 0.15 ppm initial concentration
(January)

Figure 1. Concentration of O_3, NO. NO_2 and PAN as a function of time during a solar day in Winter.

The sunrise and the sunset times are used as the begining and the end of daily simulations, such simulations will be characteristic of the season and will give the maximum Ozone concentration and the time of its occurence for given NO_x and HC's initial concentrations; these values are also stored but in a separate file.

Ozone isopleths

The preceding results correspond to a set of intial conditions, as far as NO_x and HC's concentrations are concerned, so that they will only provide one point of an isopleth. As the initial conditions are changed, the maximum concentrations for the species of interest may be obtained, but there is no warranty that all the maxima, from different initial conditions, will correspond to the same isopleth. Therefore, an algorithm to construct the complete isopleth is required.

The algorithm to construct a complete isopleth is based upon the observation that the discrete change of initial conditions carries along a grid and, therefore, once the daily simulations have been performed for all the sets of initial concentrations, each point of the grid will have associated the maximum Ozone concentration and the time of its occurrence, in addition to the NO_x and HC's initial concentrations.

The next step is the selection and the linking of points belonging to a given isopleth; that is points having the same maximum value for the Ozone concentration. To select the points, it is convenient to recall that for each daily simulation there is a small file with the value for the maximum concentration corresponding to a given set of initial concentrations, so that by looking through all such files those for the isopleth of interest may be singled out. In this process, one looks for the value, or the two nearest (lower and higher), associated to the maximum Ozone concentration of interest; the latter values will be used, if needed, to interpolate the corresponding values of the initial NO_x or HC's concentrations.

Results

The set of isopleths shown in fig.2 were obtained for Mexico City considering actinic fluxes which are representatives of two months, January (Winter) and July (Summer). As mentioned before, Mexico City is at 2240 meters above sea level; this modifies the concentrations of the fixed species used in CBM4, in the following manner

Concentration of fixed species in ppm

| Species	CBM4	Mexico City
Air (third body)	1.000E+06	7.700E+05
O_2	2.095E+05	1.600E+05
H_2O		2.450E+05
CH_4	1.850E+00	1.500E+00

Also, the photolytic rates will be changed, since the actinic flux varies with latitude, which is 20°N for Mexico City, as well as with the season. AQUAMI calculates the photolytic rates as a function of time along the day through a parabolic fit, whose coefficients vary from season to season; the changes being

<div align="center">

Photolytic rates $(min)^{-1}$; zenith angle=0°

</div>

Species	30°N (sea level) (Summer)	Mexico City (Winter)	Mexico City (Summer)
NO_2	0.485E+00	0.503E+00	0.540E+00
$HCHO_r$	1.575E-03	1.837E-03	1.900E-03
$HCHO_s$	1.898E-03	1.987E-03	2.200E-03
O_3	2.370E-03	2.465E-03	3.100E-03
ALD_2	0.346E-03	0.351E-03	0.440E-03

According to SEDUE[10], the mexican enviromental ministry, the annual emission of pollutants is such that, when divided by 365, the average daily emissions are 4.85E+08 gr./day of NO_x and 1.54E+09 gr./day of HC's; the partitioning of HC's has been taken to be that proposed by Jeffries[11]. It has been assumed a temperature profile consistent with that for the mixing layer but varying from 10°C to 30°C, and an atmospheric pressure of 0.77Atm. It has been found that the interesting part of the Ozone isopleths, as shown in fig. 2, lies in the range of 0.01 to 0.35 ppm for NO_x and 0.01 to 1.0 ppm for HC's, so that the above mentioned grid has been generated using stepsize of 0.02 ppm for NO_x, while HC's concentrations changed in steps of 0.01.
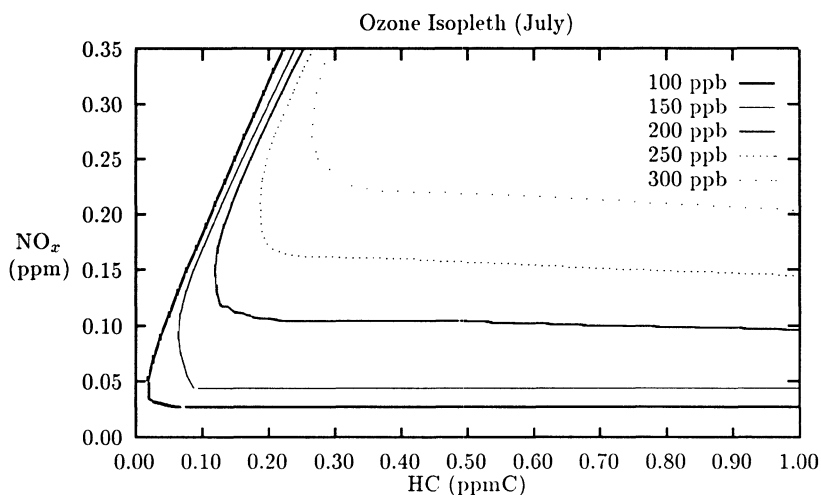

Ozone Isopleth (January)
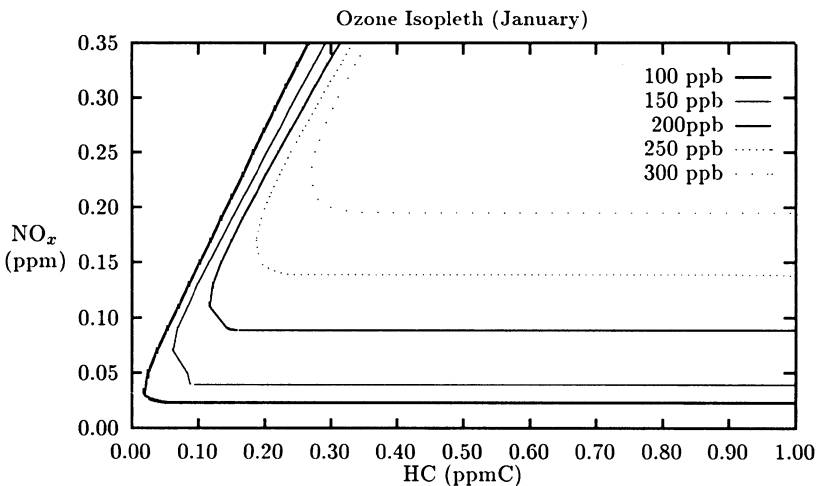
Figure 2. Ozone isopleths for Mexico City for Winter and Summer

References

1. J.R. Varela, E. Torijano, A. Vázquez and L.S. García-Colín
   "AQUAMI: air quality model in Mexico City"
   Air Pollution '93; Computational Mechanics Pub.; P. Zannetti, C.A. Breb-
   bia, J.E. García-Gardea and G. Ayala Milian Eds.; Elsevier (1993) PP.
   243-251.

2. J.R. Varela, E. Torijano A. Vázquez R. Muñoz-Ledo and M. Ley-Koo
   "Computer code generator for chemical reactions"
   Air Pollution '93; Computational Mechanics Pub.; P. Zannetti, C.A. Breb-
   bia, J.E. García-Gardea and G. Ayala Milian Eds.; Elsevier (1993) PP.
   305-312.

3. M.W. Gery, G.Z. Whitten and J.P. Killus
   "Development and testing of the CBM-IV for urban and regional modelling"
   EPA 600/388/012, US Enviromental Protection Agency. Research Triangle
   Park, N.C. (1988)

4. G.Z. Whitten, H. Hogo and J.P. Killus
   "The Carbon-Bond Mechanism: A condensed kinetic mechanism for pho-
   tochemical smog"
   Environm. Sci. Techn. **14**, 690-700 (1980)

5. G.Z. Whitten and M.W. Gery
   "Development of the CBM-X mechanism for urban and regional AQSMs"
   EPA 600/386/012, US Enviromental Protection Agency. Research Triangle
   Park, N.C. (1986)

6. E. Torijano, J.R. Varela and A. Vázquez
"Disociación fotolítica de NO_2, NO_3, HCHO, R-CHO y Ozono para las
condiciones de la ciudad de México
XVI Reunión de Energía Solar, pp 199-204 (1992)

7. A.C. Hindmarsh
"GEAR: Ordinary Differential Equation System Solver"
Lawrence Livermore Laboratory, Report UCID-30001, Rev.3 (1974)

8. A.C. Hindmarsh, G.D. Byrne
"EPISODE: "An Experimental Package for Integration of Sistems of Ordi-
nary Differential Equations"
Lawrence Livermore Laboratory, Report UCID-30112 (1975)

9. A.C. Hindmarsh, G.D. Byrne
"Application of EPISODE: An Experimental Package for Integration of
Sistems of Ordinary Differential Equations"
Numerical Methods for Differential Systems; L. Lapidus and W.E. Schiesser
Eds.; Academic Press (1976) pp 147-166

10. SEDUE (Secretaría de Desarrollo Urbano y Ecología) (1990)

11. H.E. Jeffries, K.G. Sexton and J.R. Arnold
"Validation testing of new mechanisms with outdoor chamber data"
Vol.2: Analysis of VOC data for the CBM4 and CAL photochemical mech-
anisms"
EPA/600/389/010b, US Enviromental Protection Agency. Research Trian-
gle Park, N.C. (1989)