A Review on the Photochemical Oxidant Modeling as Applied to Air Quality Studies in Complex Terrain

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The high oxidants, which occur the daily maximum concentrations in the afternoon, are transported into the other region via long range transport mechanisms or trapped within the shallow mixing boundary layer and then removed physically (deposition, transport by mountain wind, etc.) and chemically (reaction with local sources). Therefore, modeling formation of photochemical oxidants requires a complex description of both chemical and meteorological processes.

In this study, as a part of air quality studies, we reviewed various aspects of photochemical modeling on the basis of currently available literature. The result of the review shows that the model is based on a set of coupled continuity equations describing advection, diffusion, transport, deposition, chemistry, emission. Also photochemical oxidant models require a large amount of input data concerned with all aspects of the ozone life cycle. First, emission inventories of hydrocarbon and nitrogen oxides, with appropriate spatial and temporal resolution. Second, chemical and photochemical data allowing the quantitative description of the formation of ozone and other photochemically-generated secondary pollutants. Third, dry deposition mechanisms particularly for ozone, PAN and hydrogen peroxide to account for their removal by absorption on the ground, crops, natural vegetation, man-made and water surfaces. Finally, meteorological data describing the transport of primary pollutants away from their sources and of secondary pollutants towards the sensitive receptors where environmental damage may occur. In order to improve our present study, shortcomings and limitation of existing models are pointed out and verification process through observation is emphasized.

1. INTRODUCTION

Most cities frequently experience episodes of the high oxidant concentration, particularly during the summer months. These episodes are a consequence of the unique geographic setting of the region and the emission of large quantities of pollutants emitted by various sources such as diesel buses, automobiles, power plants and industries. Photochemical oxidants are generated through the photochemical and thermal reactions of hydrocarbons or nitrogen oxides in the atmo-

sphere, transported into the other region, transformed via a series of complex chemical and physical processes, and then removed. These oxidants cause the photochemical smog in urban areas during daytime and make adverse impacts on the ecosystem and human environments(Ohara et al., 1995). Also, local flows such as the mountain/valley wind and the land/sea breeze may affect the transport of pollutants when a city is close to the mountain and the ocean. Therefore the modeling of photochemical oxidants consists of complex systems which include the

meteorological, chemical and physical processes in complex terrain.

It is well known that the oxidant (O_3) unnaturally achieves high concentrations in urban areas as well as rural areas subject to anthropogenic influences. The high O_3 in rural areas is partly due to the photochemical production associated with anthropogenic and biogenic precursors in rural air(Liu et al., 1987; Sillman et al., 1990; McKeen et al., 1991), but the highest concentration of O_3 is generally believed to be associated with the direct transport of pollutants from major urban centers. Some of the highest concentration of O_3 is observed at rural sites located in the shore. The high O_3 in coastal locations has also been reported in several places(Lyons and Cole, 1975; Miller et al., 1978; Lyons et al., 1990). In the coastal region, air flow and its stratification significantly changes due to the abrupt change of surface temperature and roughness between land and sea and, in addition, land/sea breeze occurs when the geostrophic wind is weak.

Land/sea breeze has been studied in the field of meteorology and many aspects of these phenomena have been clarified not only by field observations but also by theoretical analyses. These are reviewed by Asai and Yoshikado (1973). Estoque(1961, 1962) was the first one who treated these phenomena numerically including nonlinear terms. Further development of the Pielke model was made by Mahrer and Pielke (1976) using terrain following height coordinates.

In the presence of both the land/sea breeze and the mountain/valley wind, a sea breeze may form a strong flow combined with valley wind in the afternoon, causing a long range transport of pollutants into the inland area(Kurita et al., 1985). Whereas at night two dominant local winds, i.e., the land breeze and the mountain wind which are rather weak compared to the daytime reverse

flow may result in the stagnation of pollutants in the region(Moussiopoulos et al., 1995; Dayan and Koch, 1996). This long range transport of pollutants induced by either terrain-forced local flows (thermally-driven flows) or synoptic-scale pressure systems causes regional and global pollution problems.

Under the mechanism of long range transport, chemical species such as NO_x and reactive HCs emitted from the urban industries into the atmosphere are transformed via a number of physical and chemical pathways and they are the major cause of visibility impairment. Kurita and Ueda(1986) correlated the presence of the convergence line associated with the thermal heat low generated in mountain areas during the daytime, affecting the transport of the polluted air mass.

The increasing availability of inexpensive and highly performing computers has made possible the replacement of the simpler Gaussian plume and the Lagrangian puff models of atmospheric dispersion with the more computationally intensive (and more accurate) 3-D Lagrangian particle dispersion models(LPDMs). LPDMs simulate the transport and diffusion of tracer releases by the mean-wind and turbulence-driven motion of a large number of individual particles. Studies of small-scale dispersion with LPDMs include those of Hanna(1978), van Dop et al.(1985), and Luhar and Britter(1989). Applications of the LPDMs to mesoscale dispersion studies were attempted by McNider et al.(1980), Yu and Pielke(1986), Kao and Yamada(1988), and Uliasz(1990). All studies mentioned in the above employed the one-particle model. Durbin(1980) and Thomson(1986) have used the two-particle Lagrangian model to study concentration fluctuations and relative dispersion. The Lagrangian trajectory model can be either receptor-oriented, in which trajectories are calculated backward in time from the arrival of an air

parcel at a receptor of interest(Eliassen and Saltbones, 1975; Ottar, 1979; Olson *et al.*, 1979), or source-oriented, in which trajectories are calculated forward in time from the release of a pollutant-containing air parcel from an emissions source(Johnson *et al.*, 1978; Mancuso *et al.*, 1979; Bhumralkar *et al.*, 1980). There are also a few hybrid approaches, in which the Lagrangian trajectory technique is used to simulate the horizontal transport and diffusion, and the Eulerian grid technique is used to simulate vertical diffusion (Draxler, 1977; Meyers *et al.*, 1979).

In order to develop a control strategy based on chemical principles, it is necessary to understand the chemical reactions controlling the gas phase concentrations of O_3, H_2O_2, and, in particular, the OH radical. Thus the atmospheric chemistry of hydrocarbon/NO_x photooxidations must be included in chemical mechanisms for the long-range transport modeling(Calvert *et al.*, 1983). Extensive studies conducted up to date concerning the development of gas phase chemical mechanisms for urban scale applications(Niki *et al.*, 1972; Demerjian *et al.*, 1974; Falls and Seinfeld, 1978; Atkinson *et al.*, 1982) can be utilized for regional scale applications. A number of kinetic mechanisms for the photochemical smog have been proposed (Eschenroeder, 1969; Friedlander and Seinfeld, 1969; Wayne *et al.*, 1970).

The purpose of this study is to develop mesoscale photochemical oxidant model which can describe the formation, transport, transformation and deposition processes of photochemical oxidants in the atmosphere and to evaluate and predict urban air qualities and to provide an improved tool for assessing air quality strategies by reviewing various aspects of photochemical oxidant models through literatures.

First of all, we will review the classifications and characteristics of photochemical oxidant models and the general structure, i.e., wind field, transport, photochemistry, and deposition and propose the most ideal photochemical oxidant model. Finally, conclusions and suggestions for future studies will be made.

2. A REVIEW ON PHOTOCHEMICAL OXIDANT MODELS

The goal of air quality modeling is to supply pertinent information in the decision - making processes within the framework of air quality management systems, especially in connection with control strategy. The fundamental problem which has to be solved is to calculate air concentrations of one or more species in space and time as related to the independent variables such as the emissions into the atmosphere, the meteorological variables, and parameters which describe the transformation and removal processes.

Air quality models are broadly divided into a descriptive, statistical and physical model. Descriptive model is subdivided into the steady-state model which contains the Gaussian plume and puff model, and the non-steady state, time-dependent model, which includes Eulerian grid, Lagrangian trajectory, hybrid Lagrangian-Eulerian, random walk trajectory particle, box, and spectral model. The statistical model contains regression, empirical orthogonal function model, and the physical model includes fluid flow channel and wind tunnel. As a matter of fact, the models which aim at air quality prediction among these air quality models are the time dependent model group.

When we reviewed photochemical oxidant models on literatures, most of the models are the Eulerian type or the Lagrangian type which is applicable to urban, meso as well as regional

Table 1. The characteristics of the photochemical oxidant models currently available in the literature.

RESEARCHER	MODEL CHARACTERISTICS		
	Name	Type	Spatial Scale
Schere & Demerjian, 1984	PBM	single-cell Eulerian	urban
Ames et al., 1985	UAM	Eulerian	urban, regional
Baer & Nester, 1987	DRAIS	"	meso
Carmichael et al., 1986	STEM-II	"	meso, regional
Lamb & Novak, 1983	ROM	Eulerian	regional
Meinl & Builtjes, 1984	PHOXA	"	"
Ames et al., 1985	SAI-AirShed Model	"	"
Chang et al., 1987	RADM	"	"
Venkatram et al., 1988	ADOM	"	"
Yamartino et al., 1989	CALGRID	"	"
Builtjes et al., 1991	LOTOS	"	"
Hall et al., 1975	LPDM	Lagrangian	small
Mcnider et al., 1980		"	meso
Meyer & Brugues, 1989	EKMA	Lagrangian trajectory	local, urban

scale(Table 1). In the case of PBM(Photochemical Box Model) with the single Eulerian type, we can describe the height of mixed layer with time, and change of each pollutant which is generated and removed by the chemical reaction using the 63-step kinetic mechanism. The current version of this model has been further developed to evaluate both simple and complex chemical mechanisms. UAM(Urban Airshed Model), DRAIS and CALGRID are Eulerian photochemical models that simulate the emission, transport, dispersion, chemical transformation, and removal of inert and chemically reactive species in the atmospheric boundary layer. ROM(Regional Oxidant Model) is intended to evaluate the effectiveness of emission control strategies. PHOXA(Photochemical Oxidants and Acid Deposition Model Application), ADOM (Acid Deposition Oxidant Model), RADM(Regional Acid Deposition Model), and STEM2(Sulfur Transport Eulerian Model 2) were developed for acid deposition adding transport and scavenging by cloud and precipitation processes, and trans-

formation by gas-phase and aqueous-phase chemistry. Mathur et al.(1995) attempts to investigate the relative predictability of RADM and ROM by comparing concentration predictions for various atmospheric chemical species. In the case of LPDM(Lagrangian Particle Dispersion Model) as Lagrangian random work model type, turbulent dispersion is modeled. A more advanced land-surface/PBL model(1995) is implemented in the Penn State/NCAR Mesoscale Model Version 4(MM4) which is utilized to provide meteorological data to the Regional Acid Deposition Model (RADM). The PBL is strongly dependent on surface fluxes of heat, moisture, and momentum. These fluxes are largely controlled by soil moisture and vegetative evapotranspiration. The MM4 was unable to respond to dynamic soil moisture conditions, leading to unrealistic partitioning of the surface energy budget between sensible and latent heat fluxes. The new model includes explicit soil moisture and evapotranspiration, as well as improved
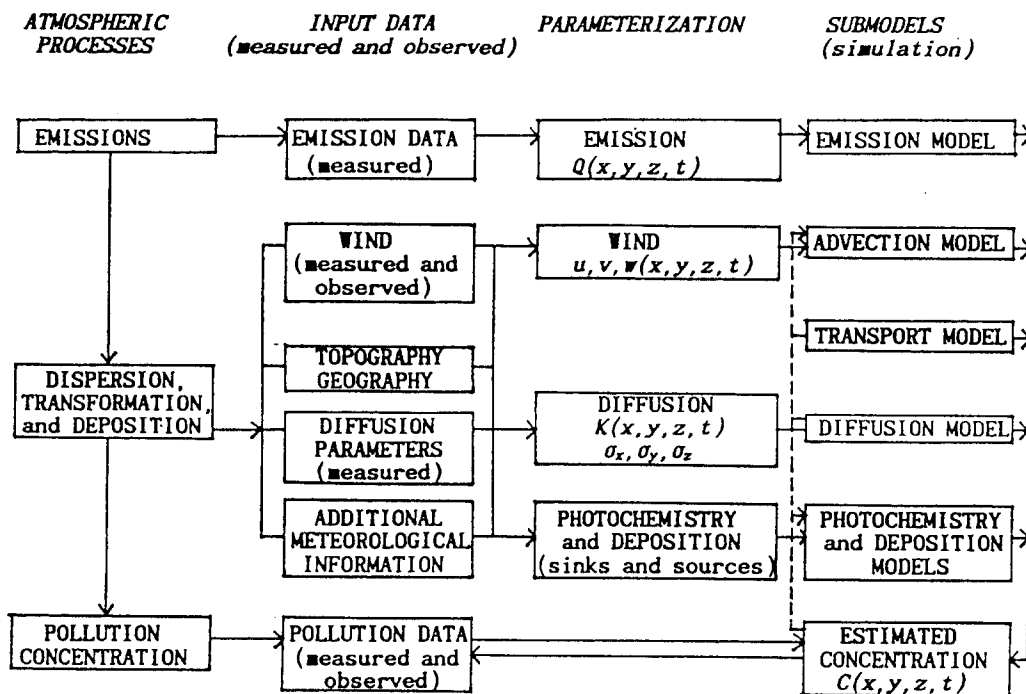
ATMOSPHERIC PROCESSES	INPUT DATA (measured and observed)	PARAMETERIZATION	SUBMODELS (simulation)

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┌───────────┐      ┌──────────────┐      ┌──────────────┐      ┌──────────────┐
│ EMISSIONS │─────▶│ EMISSION DATA│─────▶│   EMISSION   │─────▶│EMISSION MODEL│──▶
└───────────┘      │  (measured)  │      │   Q(x,y,z,t) │      └──────────────┘
      │            └──────────────┘      └──────────────┘
      │
      │            ┌──────────────┐      ┌──────────────┐      ┌──────────────┐
      │            │     WIND     │─────▶│     WIND     │─────▶│ADVECTION MODEL│──▶
      │            │ (measured and│      │ u,v,w(x,y,z,t)│      └──────────────┘
      │            │   observed)  │      └──────────────┘
      │            └──────────────┘                            ┌──────────────┐
      ▼                                                        │TRANSPORT MODEL│──▶
┌───────────────┐  ┌──────────────┐                           └──────────────┘
│ DISPERSION,   │  │  TOPOGRAPHY  │      ┌──────────────┐
│TRANSFORMATION,│  │   GEOGRAPHY  │      │  DIFFUSION   │      ┌──────────────┐
│and DEPOSITION │  └──────────────┘      │  K(x,y,z,t)  │─────▶│DIFFUSION MODEL│──▶
└───────────────┘  ┌──────────────┐      │  σx, σy, σz  │      └──────────────┘
      │            │  DIFFUSION   │─────▶└──────────────┘
      │            │  PARAMETERS  │
      │            │  (measured)  │      ┌──────────────┐      ┌──────────────┐
      │            └──────────────┘      │PHOTOCHEMISTRY│      │PHOTOCHEMISTRY│
      │            ┌──────────────┐      │and DEPOSITION│─────▶│and DEPOSITION│──▶
      │            │  ADDITIONAL  │─────▶│(sinks and    │      │    MODELS    │
      │            │METEOROLOGICAL│      │  sources)    │      └──────────────┘
      │            │ INFORMATION  │      └──────────────┘
      ▼            └──────────────┘
┌───────────────┐  ┌──────────────┐                           ┌──────────────┐
│   POLLUTION   │─▶│POLLUTION DATA│                           │  ESTIMATED   │
│ CONCENTRATION │  │ (measured and│◀──────────────────────────│CONCENTRATION │◀─
└───────────────┘  │  observed)   │                           │  C(x,y,z,t)  │
                   └──────────────┘                           └──────────────┘
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Fig. 1. Flow scheme for photochemical oxidant model.

radiation and cloud cover algorithms, flux-profile relationships, and PBL mixing. To prepare for future Eulerian air quality modeling needs and to reduce the duplication of effort in maintaining multiple modeling systems, the U. S. Environmental Protection Agency is developing a third -generation comprehensive air quality modeling system, Model-3, employing an incremental prototyping strategy.

These models are effective for air quality prediction but may cause a problem in wind field for complex terrain. Therefore, considering the factors required to fit photochemical ozone to mesoscale air quality modeling in complex terrain they are presented as Fig. 1 which shows flow scheme for photochemical oxidant model. The following components can be identified as common to most current models: emission inventories which presents emission characteristics of precursors with input data; meteorological data which describe the transport of primary pollutants away from their sources and of secondary pollutants toward the sensitive receptors; chemical and photochemical data which depict formation of ozone and other photochemical (secondary) pollutants quantitatively; dry eposition data which describe removal procedure. By parameterization of these components, we are able to simulate the concentration by several submodels such as emission model, advection model, transport model, photochemistry model, and deposition model. Finally by comparing this estimated concentration with the observed concentration, the validity of the model can be discussed.

3. THE PHOTOCHEMICAL OXIDANT MODEL

3.1. GENERAL STRUCTURE OF THE PHOTO-CHEMICAL OXIDANT MODEL

In the x, y, ρ system, the mass conservation equation that forms the basis for the transport model can be written as

$$\frac{\partial C_i}{\partial t} = -u\frac{\partial C_i}{\partial x} - v\frac{\partial C_i}{\partial y} - w^*\frac{\partial C_i}{\partial \rho} + \frac{1}{\pi^2}\frac{\partial}{\partial \rho}(K_V\frac{\partial C_i}{\partial \rho})$$
$$+ \frac{\partial}{\partial x}(K_H\frac{\partial C_i}{\partial x}) + \frac{\partial}{\partial y}(K_H\frac{\partial C_i}{\partial y}) + R_i + S_i \quad (1)$$

where C_i is the pollutant concentration, K_H is the horizontal diffusivity, K_V is the vertical diffusivity, R_i is the chemical reaction term, S_i is the source term which could be a major cause of high concentration episode requiring the accurate survey of emissions, and u, v and w are the velocity components in the cartesian coordinate system, x, y and z. w^* is the vertical velocity component in terrain following coordinate system, x, y, and ρ.

The vertical limit of the domain is appropriated, which accommodates the high terrain in the region as well as the mixed layer heights during summer. The actual vertical coordinate system is terrain following. Because the largest vertical gradients of the important variables such as concentrations, turbulences, and winds occur near the ground, the vertical resolution of the grid system used is finer near the ground than the loft. The terrain following coordinate system requires the formulation of a vertical coordinate ρ, defined by,

$$\rho = \frac{[z - h(x, y)]}{\pi(x, y)}$$

$$\pi(x, y) = H - h(x, y) \quad (2)$$

where x, y, z is the cartesian coordinate system, $h(x, y)$ is the height of the terrain, and

H is the specified top of the model domain.

3.2. WIND FIELD

In order to predict movements of air pollutants in the atmosphere reliably, applying mass-consistent three-dimensional gridded wind fields is of great importance. Due to the complexity of the terrain within the modeling region and the scarcity of information on surface and upper level winds, the wind field is one of the most difficult inputs to specify. Two methods of wind field generation are used: one based on interpolation of surface wind and the other based on a prognostic mesoscale model.

3.2.1. THE INTERPOLATION SCHEME

The horizontal interpolation scheme is estimated using power law and inverse-distance-squared method and the vertical interpolation scheme employed linear or cubic spline interpolation scheme. In order to obtain hourly three-dimensional mass consistent wind fields, assuming incompressible fluid the equation of continuity can be written as

$$\frac{\partial U}{\partial x} + \frac{\partial V}{\partial y} + \frac{\partial W}{\partial \rho} = 0 \quad (3)$$

where $U = Hu$, $V = Hv$, and $W = w - u(\frac{\partial h}{\partial x}) - v(\frac{\partial h}{\partial y})$.

A problem to determine unknown functions, U, V and W to minimize a function,

$$E(U, V, W) = \int_\Omega [\alpha_1^2(U - U_0)^2 + \alpha_1^2(V - V_0)^2 + \alpha_2^2(W - W_0)^2]dxdyd\rho \quad (4)$$

under a constraint of the continuity equation can be transformed into an equivalent problem without the constraint by introducing the Lagrangian multiplier λ, i.e., the problem to determine U, V, and W minimizing the following function,

$$E(U, V, W, \lambda) = \int_{\Omega} \alpha_1^2 (U - U_0)^2 + \alpha_1^2 (V - V_0)^2$$
$$+ \alpha_2^2 (W - W_0)^2 + \lambda \left(\frac{\partial U}{\partial x} + \frac{\partial W}{\partial \rho} \right) dx \, dy \, d\rho \quad (5)$$

The procedure to solve this problem leads to the following equation:

$$\frac{\partial^2 \lambda}{\partial x^2} + \frac{\partial \lambda}{\partial y^2} + \left(\frac{\alpha_1}{\alpha_2} \right)^2 \frac{\partial \lambda^2}{\partial \rho^2} =$$
$$-2\alpha_1^2 \left(\frac{\partial U_0}{\partial x} + \frac{\partial V_0}{\partial y} + \frac{\partial W_0}{\partial \rho} \right) \quad (6)$$

with the boundary conditions, i.e., at the bottom boundary,

$$\frac{\partial \lambda}{\partial \rho} = -2\alpha_2^2 W_0 \quad (7)$$

and at the other boundaries,

$$\lambda = 0 \quad (8)$$

In equations (5) and (6), α_1 and α_2 denote the parameters to be determined by considering the typical value of the ratio of vertical – to horizontal – wind velocity and so on (Kitada *et al.*, 1983). The subscript 0 indicates the initially estimated value based on the observations, e.g., $W_0 = w_0 - u_0 \left(\frac{\partial h}{\partial x} \right) - v_0 \left(\frac{\partial h}{\partial y} \right)$. The mass-consistent wind field U, V, and W (or u, v and w) is derived from the calculated λ field as

$$U = U_0 + \frac{1}{2\alpha_1^2} \frac{\partial \lambda}{\partial x}$$
$$V = V_0 + \frac{1}{2\alpha_1^2} \frac{\partial \lambda}{\partial y} \quad (9)$$
$$W = W_0 + \frac{1}{2\alpha_1^2} \frac{\partial \lambda}{\partial \rho}$$

Equation (6) is solved using the SOR(Successive Over Relaxation) method after applying a centered difference approximation to the equation.

3.2.2. THE PROGNOSTIC MESOSCALE MODEL

The mesoscale model is a hydrostatic, prog-

nostic, three-dimensional model based on the equation of momentum, mass and energy balance. It employs a terrain following coordinate system. The prognostic equation set is as follows:

$$\frac{du}{dt} = fv - c_p \theta \frac{\partial \Pi}{\partial x} + g\rho \left(\frac{\partial h}{\partial x} \right) - g\rho \frac{\partial H}{\partial x}$$
$$+ \left(\frac{1}{\pi} \right)^2 \frac{\partial}{\partial \rho} \left(K_V \frac{\partial u}{\partial \rho} \right) + \frac{\partial}{\partial x} \left(K_H \frac{\partial u}{\partial x} \right)$$
$$+ \frac{\partial}{\partial y} \left(K_H \frac{\partial u}{\partial y} \right) \quad (10)$$

$$\frac{dv}{dt} = -fu - c_p \theta \frac{\partial \Pi}{\partial y} + g\rho \left(\frac{\partial h}{\partial y} \right) - g\rho \frac{\partial H}{\partial y}$$
$$+ \left(\frac{1}{\pi} \right)^2 \frac{\partial}{\partial \rho} \left(K_V \frac{\partial v}{\partial \rho} \right) + \frac{\partial}{\partial x} \left(K_H \frac{\partial v}{\partial x} \right)$$
$$+ \frac{\partial}{\partial y} \left(K_H \frac{\partial v}{\partial y} \right) \quad (11)$$

$$\frac{d\theta}{dt} = \left(\frac{1}{\pi} \right)^2 \frac{\partial}{\partial \rho} \left(K_V \frac{\partial \theta}{\partial \rho} \right) + \frac{\partial}{\partial x} \left(K_H \frac{\partial \theta}{\partial \rho} \right)$$
$$+ \frac{\partial}{\partial y} \left(K_H \frac{\partial \theta}{\partial y} \right) \quad (12)$$

$$\frac{dq_V}{dt} = \left(\frac{1}{\pi} \right)^2 \frac{\partial}{\partial \rho} \left(K_V \frac{\partial q_V}{\partial \rho} \right) + \frac{\partial}{\partial x} \left(K_H \frac{\partial q_V}{\partial \rho} \right)$$
$$+ \frac{\partial}{\partial y} \left(K_H \frac{\partial q_V}{\partial y} \right) \quad (13)$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w^*}{\partial \rho} - \frac{1}{\pi} \left(u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial y} \right)$$
$$+ \frac{1}{\pi} \left(\frac{\partial H}{\partial t} + u \frac{\partial H}{\partial x} + v \frac{\partial H}{\partial y} \right) = 0 \quad (14)$$

$$\frac{\partial \Pi}{\partial \rho} = -\pi \frac{g}{C_p \theta} \quad (15)$$

$$\frac{\partial T_s}{\partial t} = \frac{\partial}{\partial z} \left(K_S \frac{\partial T_s}{\partial z} \right) \quad (16)$$

where,

$$w^* = w \frac{1}{\pi} + \frac{\rho}{\pi} \left(u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial y} \right)$$
$$- \frac{\rho}{\pi} \left(\frac{\partial H}{\partial t} + u \frac{\partial H}{\partial x} + v \frac{\partial H}{\partial y} \right) \quad (17)$$

$$\Pi = \left(\frac{P}{P_{00}} \right)^{R_d/C_p}, \quad \theta = T \left(\frac{P_{00}}{P} \right)^{R_d/C_p}, \quad f = 2\Omega \sin \phi, \text{ and}$$

$$\frac{d}{dt} = \frac{\partial}{\partial t} + u \frac{\partial}{\partial x} + \omega^* \frac{\partial}{\partial z^*}.$$

3.3. TRANSPORT

The wind and turbulence fields computed by the mesoscale model are used as input data for the Lagrangian model. The model consists of tracking the release of a large number of particles, representing a pollutant air mass, transported and diffused in a three-dimensional domain, using the formulation,

$$x_i(t+\delta t) = x_i(t) + [u_i(t) + u_i'(t)]\delta t$$
$$: i = 1,2,3 \qquad (18)$$

where $x_i(t)$ is the antecedent x, y, z position of the particle and $x_i(t+\delta t)$ is its position after time interval δt; u_i represents the u, v and w velocity components, respectively, and u'_i represents the corresponding turbulence velocity fluctuations, parameterized statistically and based on boundary layer prediction of the mesoscale model.

Following Hanna(1979) the turbulence velocity are given by:

$$u_i'(t) = u_i'(t-\delta t)R(\delta t) + u_i''$$
$$: i = 1,2,3 \qquad (19)$$

where $R(\delta t)$ is a Lagrangian autocorrelation function and u''_i is a random component (Wilson et al., 1981) with a Gaussian distribution of zero mean, and a variance defined by the variance in local turbulence.

3.4. PHOTOCHEMISTRY

The most important fact in the photochemical oxidant model is the chemical reaction mechanism. The representation of the detailed chemical and photochemical mechanisms may cause significant problems in photochemical models and their representation is often a compromise. The more detailed mechanism offers the prospect of a greater realism but only with the involvement of significantly greater computer resources and with the requirements for a great deal of input data. For some modeling approaches, only highly simplified chemical mechanisms can be implemented, requiring a considerable amount of scrutiny and development time. There has been little uniformity in the approaches to develope chemical mechanisms in the various models and so it is only possible to classify them in broad terms following Derwent and Hough(1989).

We have reviewed twenty-six with a view to understanding their relative merits when applied to the description of photochemical oxidants formation. Table 2 refers to the mechanisms reviewed. These chemical mechanisms are used for photochemical oxidant models in Table 1 and they are applicable to photochemical oxidants modeling that we are going to describe. According to our review, condensed mechanism developed by Lurmann(1986) is most suitable for use in urban-scale photochemical modeling. This mechanism includes numerous reactions for night-time and successive day simulations. It is a condensed mechanism which formed similarly to the detailed mechanism over long-range transport application, and then obtained a very good result through chamber experiment.

This model adapts a two-layer approach(see Fig. 2) with a boundary layer which has a process of the pollutant emissions and removal during daytime and with a reservoir layer which has a process of the nocturnal storage of pollutants above the shallow inversion layer during nighttime.

$$\frac{d}{dt} C_i = \frac{E_i}{Ah_l} + P_i - L_iC_i + \frac{V_{gi}}{h_l} C_i$$
$$+ \frac{1}{h_l} \frac{dh_l}{dt}(C_i - B_i) \qquad (20)$$

Table 2. The chemical mechanisms from the literature used in modelling photochemical air pollution formation.

No.	Mechanism	Simplications used	Reference
1	Harwell	Complete	Derwent & Hough, 1988
2	Harwell simple	Direct	Hough, 1987
3	EM	Direct	Eschenroeder & Martinez, 1972
4	RCV	Direct	Rodhe et al., 1981
5	ALW	Direct	Atkinson et al., 1982
6	BS	Parameterized	Bottenheim & Strausz, 1982
7	EMEP	Direct	Eliassen et al., 1982
8	FS	Direct	Falls & Seinfeld, 1982
9	NCAR	Direct	Stockwell & Calvert, 1982
10	NCAR simple	Direct	Stockwell, 1986
11	DCM	Direct	Schere & Demerjian, 1984
12	CBM-I	Parameterized	Killus & Whitten, 1982
13	CBM-II	Parameterized	Killus & Whitten, 1982
14	CBM-III	Parameterized	Killus & Whitten, 1982
15	CBM-IV	Parameterized	Whitten & Gery, 1985
16	CBM-IV unmodified	Parameterized	Whitten & Gery, 1985
17	CBM-X	Parameterized	Whitten et al., 1985
18	CBM-X unmodified	Parameterized	Whitten et al., 1985
19	PHOXA CBM-IV unmodified	Parameterized	Stewart et al., 1987
20	LS	Complete	Leone & Seinfeld, 1985
21	LLA	Parameterized	Lurmann et al., 1986
22	LLA simple	Parameterized	Lurmann et al., 1986
23	CB4	Parameterized	Gery et al., 1988
24	CAL	Parameterized	Lurmann et al., 1987
25	RADM-II	Parameterized	Stockwell, 1988, 1990
26	SAPRC	Complete	Carter, 1988, 1990
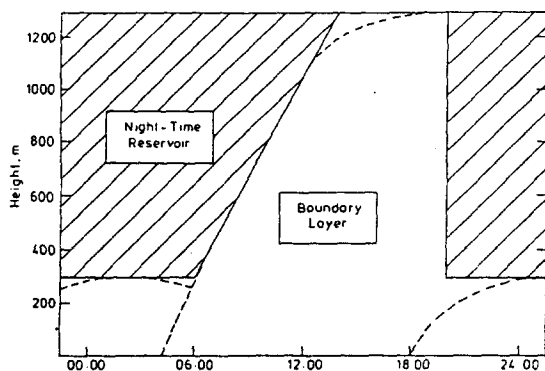
Figure 2. The two - layer approach adopted in the Harwell photochemical trajectory model.

$$\frac{d}{dt} B_i = Q_i - M_i B_i + \frac{1}{h_u} \frac{dh_u}{dt} (C_i - B_i) \qquad (21)$$

where B_i and C_i are the concentrations of species i in the reservoir and boundary layers, respectively, Q_i and P_i are the photochemical production rates of species i in the reservoir and boundary layers, respectively, $M_i B_i$ and $L_i C_i$ are the photochemical destruction rates of species i in the reservoir and boundary layers, respectively, V_{gi} is the species dependent dry deposition velocity, h_l and h_v are the depths of the boundary and reservoir layers, E_i is the emission rate of species i through the lower surface

of the model, and A is the area of the base of the air parcel.

Even though the chemical mechanisms developed have greatly simplified the atmospheric chemistry, the trade off between chemical complexity and computational efficiency still leaves important issues for further studies in considering the development of 3-D air quality models.

3.5. DRY DEPOSITION

Dry deposition is handled as a boundary condition at $\rho = 0$ in equation (1). The concept of dry deposition velocity is used to calculate the deposition flux F_i to the ground.

$$F_i = V_{di} C_i \qquad (22)$$

For the parameterization of dry deposition velocity, the electrical resistance analog is used. The deposition velocity of gases is represented by three resistances in series:

$$V_{di} = \frac{1}{R_a + R_b + R_s} \qquad (23)$$

where R_a = aerodynamic resistance, R_b = deposition layer resistance, and R_s = surface(canopy) resistance.

The aerodynamic resistance R_a is associated with atmospheric turbulence and depends on the roughness length, the friction velocity, and the Monin-Obukhov length, and is givened by

$$R_a = \frac{1}{\chi u_*} [\ln(\frac{z}{z_0}) - \psi_h(\frac{z}{L})] \qquad (24)$$

where ψ_h is the nondimensional universal function, z_0 is the surface roughness at the given locality, u_* is the friction velocity, and L is the Monin-Obukhov length.

The deposition layer resistance for gases is estimated from the following relation(Wesely and Hicks, 1977; Pleim et al., 1984),

$$R_b = \frac{1}{u_*} (\frac{\nu}{D_j})^{2/3} \qquad (25)$$

where ν is the viscosity of air and D_j is diffusivity of species j.

The surface resistance (or canopy resistance), R_s, depends on the type of surface factors, the chemical species and the meteorological conditions. The R_s is broken into several components. This components are summarized as follows (Padro et al., 1991).

$$\frac{1}{R_s} = \frac{1}{R_p} + \frac{1}{R_{cut}} + \frac{1}{R_{cw}} + \frac{1}{R_g} \qquad (26)$$

$$R_p = R_{st} + R_m = \frac{r_{st} + r_m}{LAI} \qquad (27)$$

$$R_{cut} = \frac{r_{cut}}{LAI * (1 - CWC)} \qquad (28)$$

$$r_{cut} = \frac{A_0}{A_j} r_{cut_0} \qquad (29)$$

$$R_{cw} = \frac{r_{cw}}{LAI \times CWC} \qquad (30)$$

$$r_{cw} = \frac{H_j}{\alpha_j^*} (\frac{10^5}{u}) \qquad (31)$$

$$R_g = \frac{A_0}{A_j} R_{g0} \qquad (32)$$

where LAI denotes the leaf area index and R_p denotes the sum of the canopy stomatal (R_{st}) and mesophyll (R_m) resistances. The leaf stomatal resistance r_{st} is parameterized as in O'Dell et al. (1977),

$$r_{st} = \frac{P}{(B * D_j)} \qquad (33)$$

where B is the stomatal slit width and P is a

stomatal constant corresponding to the charac-
teristics of the leaf physiology and its value is
$2.3 \times 10^{-8} m^2$. B is highly parameterized as,

$$B = B_{max} \sin((t - t_d)\frac{\pi}{12}) + B_{min} \qquad (34)$$

where t is the time of day, t_d is the time at
dawn, $B_{max} = 10 \mu m$ and $B_{min} = 0.1 \mu m$.

Similarly, canopy resistance R_{cut} and R_{cw} are
obtained from the local leaf resistance r_{cut} and
r_{cw}, respectively, through division by LAI and
CWC (in fraction of area) contribution. Where H_j
is Henry's Law constant and parameter a_j^* is an
effective enhancement of the solubility of the gas
in water (Slinn et al., 1978). Surface resistance
R_g largely depends on the soil wetness.

4. CONCLUSIONS AND RECOMMENDATIONS

When we reviewed photochemical oxidant
models to study the air quality in complex
terrain, we found as follows.

Photochemical oxidant models are broadly
classified into Lagrangian or Eulerian type, and
spatial scale is small, urban, meso, or regional.
And photochemical oxidant models consist of
several submodels, such as emission, advection,
diffusion, photochemistry, and deposition models
and we propose that a perfect model can be
made by combining these submodels well. In
emission model, actual terrain data and surround-
ing condition reflecting topographical characteris-
tics should be considered.

The previous models used to assess the
concentration of air pollutant have managed
transport problems in the Eulerian grid, and
these models have a merit in describing nonlinear
chemistry like photochemical smog. But Lag-

rangian particle diffusion model will be more
effective in illustrating long range transport
problem. Also the most important fact in the
photochemical oxidant model is the chemical
reaction mechanism, thus development of chem-
ical reaction mechanism which enough to depict
atmospheric phenomenon is essential considering
the trade off between chemical complexity and
computational efficiency.

Grid resolution significantly influences the
magnitude of O_3 formation and loss processes,
especially chemistry and vertical transport. Most
models which use one to three kilometers grid
interval will be able to describe terrain effect in
detail by more reducing vertical and horizontal
grid size, and will be able to improve its
prediction rate by raising capability of spatial
resolution. Jang et al.(1995) examines the sensi-
tivity of ozone predictions to grid resolution in
Eulerian grid models. A high-resolution version
of the regional acid deposition was developed and
applied to simulate O_3 formation at different grid
resolutions. Horizontal grid-cell sizes of 20, 40,
and 80km were selected for this sensitivity
study. Individual meteorological and chemical
processes that contribute to O_3 and its precursors
were further separated and analyzed to determine
their importance to O_3 formation and effects of
grid resolution on these regulating processes.

Finally, verification process through horizontal
and vertical observation is emphasized in order
to improve prediction efficiency for the model.

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