

PHOTOCHEMICAL DIFFUSION MODELS FOR AIR QUALITY SIMULATION: CURRENT STATUS

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The development and implementation of photochemical diffusion models for air quality simulation provide one technique for carrying out the mandates of the 1970 amendments to the Clean Air Act. Mathematical models currently available for evaluating the impact of emissions on air quality consider source emission data, meteorological variables characterizing transport and dispersion processes, and reaction mechanisms describing chemical transformation and removal processes of atmospheric pollutant species. The purpose of this paper is to review and evaluate the status of several photochemical diffusion models currently available. These models, which vary in complexity, were developed to assess the impact of anthropogenic emissions on ambient photochemical oxidant levels in urban areas. Three approaches to photochemical air quality simulation modeling are considered: the grid point model (1, 2, 3, 4), the trajectory model (5), and the box model (6, 7).

PHOTOCHEMICAL AIR QUALITY SIMULATION MODELS

A summary of currently available photochemical air quality simulation models (PAQSM) and their characteristics is given in Table 1 (19). Three of these models were chosen for this evaluation study. A brief discussion of the formulation of the 3 models is given here to provide essential information for the evaluation.

In developing a mathematical relation for simulating the transport, dispersion, and transformation of pollutant emission into the atmosphere, one must consider the following 3 areas.

1. Chemical transformation. To understand the relation between HC-NO_x emissions and photochemical oxidant formation requires that a chemical mechanism be formulated that describes the complex HC-NO_x oxidation processes occurring in the sunlight irradiated atmosphere.

2. Source emission inventory. Model performance is critically related to the accurate description of the rates of emissions of pollutant species in space and time.

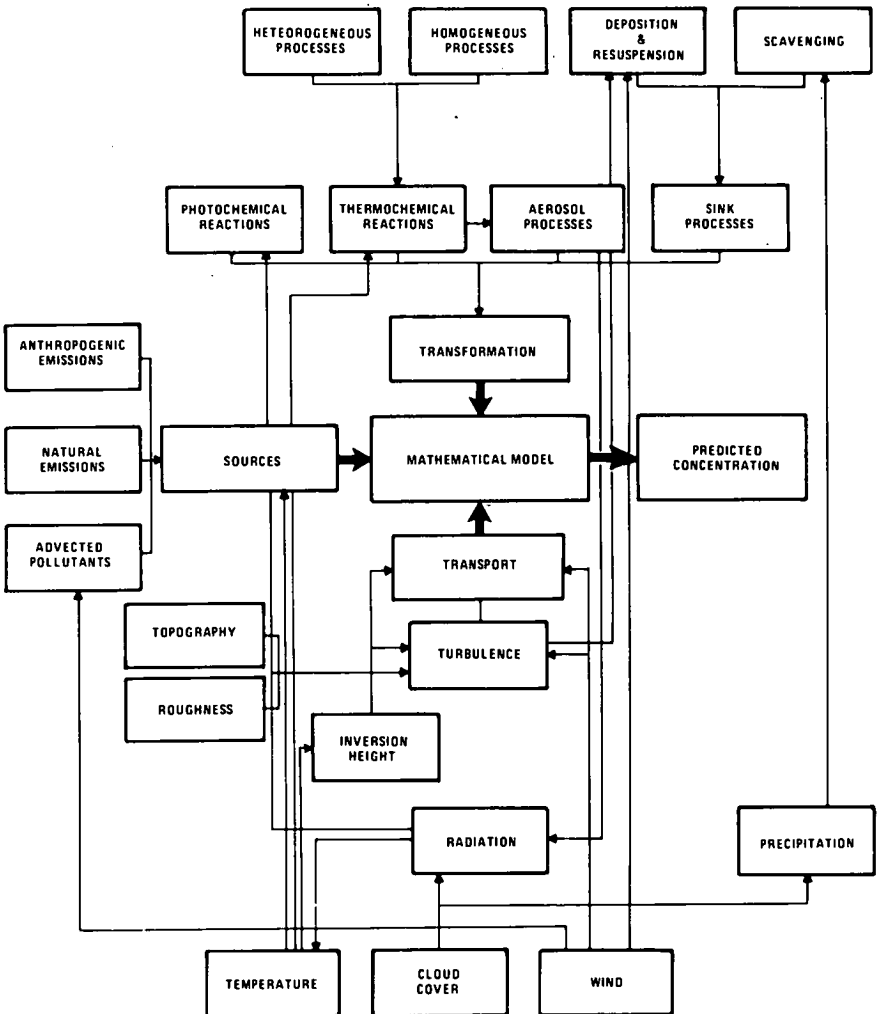
3. Meteorological factor. Methodologies must be developed for the treatment of the meteorological variables that affect pollutant transport and dispersion. The complexity of the methodology used will depend on the mathematical detail considered in describing the transport and dispersion processes in the turbulent planetary boundary layer.

The research and development of each of these areas represent a formidable task. In a latter section of this paper, a discussion and evaluation of the current state of the art of each of these areas are considered. The even greater difficulty of coupling these areas together via mathematical relations describing the physical and chemical dynamics of the atmosphere is the goal of the photochemical air quality simulation model. Figure 1 gives some indication, conceptually, of the complex nature of the

Table 1. Summary of characteristics of photochemical air quality simulation models.

Reference	Description	Results Reported
5	Trajectory model based on moving column of air in which vertical diffusion and chemical reactions take place. Column of air follows surface trajectory interpolated from monitoring station wind readings. Eschenroeder-Martinez kinetic mechanism is used.	Applied to Los Angeles for CO, NO, NO ₂ , HC, and O ₃ . Various wind trajectories on 6 validation days. Simulation period per day: 6 to 9 hours.
7	Trajectory model based on well-mixed, moving column of air in which chemical reactions take place. Column of air follows surface trajectory interpolated from monitoring station wind readings. Wayne kinetic mechanism is used.	Applied to Los Angeles for CO, NO, NO ₂ , HC, and O ₃ . Various wind trajectories on 6 validation days. Simulation period per day: 4 to 6 hours.
1, 2, 3	Grid model based on numerical solution of 3-dimensional, time-dependent atmospheric diffusion equations. Numerical solution is based on method of fractional steps. Hecht-Seinfeld kinetic mechanism is used. Three-dimensional wind field is computed from surface maps.	Applied to Los Angeles for CO, NO, NO ₂ , HC, and O ₃ . Complete spatial and temporal distributions over the basin for 6 validation days. Simulation period per day: 10 hours.
8	Grid model based on numerical solution of 3-dimensional, time-dependent atmospheric diffusion equations. Numerical solution is based on particle-in-cell method. Eschenroeder-Martinez kinetic mechanism is used. Three-dimension wind field is computed from surface maps.	Applied to Los Angeles for CO, NO, NO ₂ , HC, and O ₃ . Complete spatial and temporal distributions over the basin for one 16-hour period.
9	Multibox boundary layer model with detailed wind field, vertical profiles of velocity, and diffusivity. Gear's method is used in numerical integration of coupled ordinary differential equations. Lumped chemical kinetic mechanism is used.	Applied to San Francisco Bay Area for CO, NO, NO ₂ , HC, and O ₃ . Complete spatial and temporal distributions over the area for several days. Simulation period per day: 24 hours.
6	Cell model based on solution of dynamic mass balance equations with intercell flows neglected, for an array of well-mixed cells. Kinetic mechanism proposed by Friedlander and Seinfeld (14) is used. Single representative wind speed is estimated from available surface measurements.	Applied to Los Angeles for HC, NO, and NO ₂ . Regional average concentrations predicted for 2 days. Simulation period per day: 6 to 7 hours.

Figure 1. Schematic diagram of major components contributing to photochemical air quality simulation problem.



problem to be considered and shows the various interactions occurring among the areas of transport, source emissions, and transformation.

In developing the mathematical relations for describing the physical and chemical dynamics of the atmosphere, it became readily apparent that solutions of the 3-dimensional, time-varying equations for conservation of mass, momentum, and energy for reactive species in the turbulent planetary boundary layer have no practical application in sight. Therefore, simplified approaches had to be adopted for treating the fundamental physical and chemical processes occurring in the atmosphere. Specifically all of the currently available PAQSMs use mathematical relations derived from the observation of mass equation and are based on K-diffusivity theory. Though it is not within the scope of this paper to derive the working equations used by the various PAQSMs (5), it will be useful to write down the working equations and their entailing assumptions for the 3 PAQSMs considered.

The working equation for the grid point model is the most detailed of the 3 model classes considered and is given in equation 1.

$$\frac{\partial c_i}{\partial t} + u \frac{\partial c_i}{\partial x} + v \frac{\partial c_i}{\partial y} + w \frac{\partial c_i}{\partial z} = \frac{\partial}{\partial x} K_H \frac{\partial c_i}{\partial x} + \frac{\partial c_i}{\partial y} + \frac{\partial}{\partial z} K_V \frac{\partial c_i}{\partial z} + S_i(x, y, z, t) + R_i(c_1, c_2, \dots, c_N), i = 1, 2, \dots, N \quad (1)$$

where

- N = number of pollutant species;
- c_i = mean concentration of pollutant species i ;
- x, y, z = Cartesian coordinates;
- u, v, w = mean wind speeds in x, y , and z directions respectively;
- K_H, K_V = horizontal and vertical turbulent eddy diffusivities respectively;
- S_i = rate of injection (or removal) of species i by a volume source (or sink); and
- R_i = rate of production (or consumption) of species i through chemical reactions.

In the derivation of equation 1, the following assumptions were made:

1. Pollutant species do not affect atmospheric temperature and velocity, and thus the equations of conservation of species can be solved independently of the equations of momentum and energy;
2. Molecular diffusion is negligible;
3. Atmospheric flow is incompressible;
4. The system is isothermal;
5. Wind velocities and concentrations may be represented as the sum of deterministic and stochastic components;
6. The average value of the stochastic components of concentration is zero;
7. The turbulent fluxes are linearly related to the gradients in the mean concentrations; and
8. Terms of the type $\langle c'_i c'_j \rangle$ arising from the inclusion of chemical reactions are negligible (c' being the stochastic component of concentration).

In the case of the moving cell or trajectory approach, equation 1 reduces to equation 2

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial z} K_V \frac{\partial c_i}{\partial z} + S_i(x, y, z, t) + R_i(c_1, c_2, \dots, c_N), i = 1, 2, \dots, N \quad (2)$$

with the following additional assumptions:

1. The motion of an air parcel corresponds to the local surface wind velocities in the modeling region;
2. Horizontal transport of materials across cell boundaries does not occur; and
3. Variation in wind velocity with height is neglected.

Finally, the box model approach, which assumes constant wind velocity and mixing height and does not consider diffusional effects, reduces to equation 3.

$$\frac{d(c_i)}{dt} = \frac{S_i}{Z} - \frac{uc_i}{\Delta x} - R_i(c_1, c_2, \dots, c_N), i = 1, 2, \dots, N \quad (3)$$

where

Z = depth of mixing layer,
 Δx = box width, and
 u = wind speed.

EVALUATION OF MODELS

The lack of an extensive air monitoring data base needed for carrying out a comprehensive model validation study has necessitated the adoption of alternative approaches to assess model performance. Several techniques will be considered in evaluating the performance of PAQSM. Although, in the final analysis, the evaluations cannot substitute for a validation study, they do provide qualitative and sometimes quantitative information on the overall performance of models and their components. In the discussions that follow, evaluations are considered by relating to the basic assumptions made in deriving the working equations, the methodologies and assumptions used by PAQSM components, and the model initial and boundary concentrations.

Evaluating the validity of the diffusion equation has been discussed in detail by Lamb and Seinfeld (11). This work indicates that working equation 1 is a valid representation of atmospheric transport and chemical reactions if the following criteria are met.

1. Source emission function

$$\frac{1}{S_i} \frac{\partial S_i}{\partial t} \ll 10^{-3} \text{ sec}^{-1}$$

$$\frac{1}{S_i} \frac{\partial S_i}{\partial x_k} \ll \frac{1}{2000} \text{ meter}^{-1}, k = 1, 2$$

2. Chemical reaction rate

$$\frac{1}{R_i} \frac{\partial R_i}{\partial t} \ll 10^{-3} \text{ sec}^{-1}$$

3. Mean velocity components

$$\frac{1}{\bar{u}_i} \frac{\partial \bar{u}_i}{\partial t} \ll 10^{-3} \text{ sec}^{-1}$$

$$\ll \frac{1}{2000} \text{ meter}^{-1}, k = 1, 2$$

$$\frac{1}{\bar{u}_i} \frac{\partial \bar{u}_i}{\partial x_k} \ll \frac{1}{20} \text{ meter}^{-1}, k = 3$$

4. Turbulent velocity components

$$\frac{1}{\langle u_i' u_j' \rangle} \frac{\partial \langle u_i' u_j' \rangle}{\partial t} \ll 10^{-3} \text{ sec}^{-1}$$

$$\ll \frac{1}{2000} \text{ meter}^{-1}, k = 1, 2$$

$$\frac{1}{\langle u_i' u_j' \rangle} \frac{\partial \langle u_i' u_j' \rangle}{\partial x_k} \ll \frac{1}{20} \text{ meter}^{-1}, k = 3$$

Primed terms in these expressions represent stochastic components of the property, and barred terms represent mean quantities. The limiting conditions, based on measurements of wind turbulence of Lamb and Neiburger (12) and averaging times of 0.3 hour, reflect less stringent limits than expected with hourly averaged data, which is more commonly used. Based on these criteria, model resolution is of the order of 1 hour in time, 8000 m in horizontal space, and 80 m in vertical space. Source emissions and averaging times used by the model should reflect this order of resolution. It should be noted, though, that the above criteria only establish conditions sufficient for the valid application of the diffusion equation. The limiting conditions provide no information with regard to necessity for the valid application of the diffusion equation.

The evaluation of grid and trajectory approaches to PAQSMs has been studied by Liu and Seinfeld (13). Using analytic solutions to simplified forms of the atmospheric diffusion equation, Liu and Seinfeld formulated numerical experiments to assess absolute errors introduced by assumptions made in the 2 modeling approaches. The results of this study are given in Table 2. It should be noted that (a) these results are based on simplified forms of the working equations considered by the PAQSMs and, therefore, may not reflect the true total errors resulting from the assumption; (b) the inclusion of vertical winds in the trajectory approach is quite feasible, but wind shear consideration would seem questionable; and (c) in theory the grid point model can consider wind shear, but currently available models do not include it.

EVALUATION OF METHODOLOGIES AND ENTAILING ASSUMPTIONS USED IN MODELS

As mentioned earlier, the 3 major areas considered in formulating a mathematical model for simulating photochemical air quality are chemical transformations, source emissions, and the meteorological factor. The significant role played by each component in determining the overall performance of a model is considered in this section.

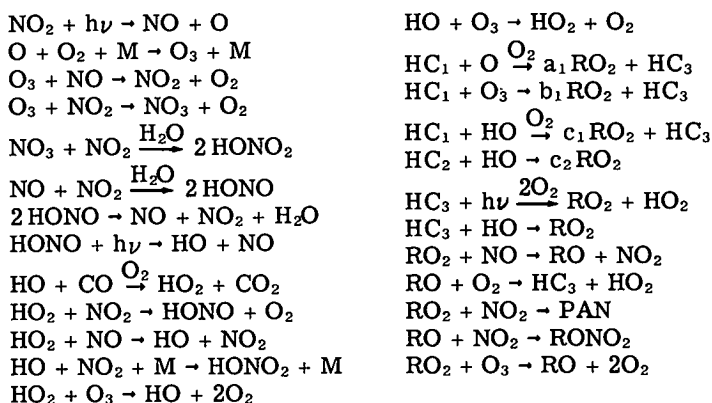
Chemical Transformations

The prediction of photochemical oxidant is critically related to the chemical kinetic mechanism used by the PAQSMs. The development and evaluation of chemical kinetic mechanisms have proceeded by comparing numerical solutions of coupled ordinary

differential equations derived from a postulated reaction set, with concentration versus time profiles observed under controlled laboratory conditions for various initial hydrocarbons with NO_x , hydrocarbon- NO_x levels, and hydrocarbon- NO_x ratios. The assumption is that experimental smog chamber studies are analogs of the chemical transformation processes occurring in urban polluted atmospheres. Therefore, chemical kinetic mechanisms that accurately simulate smog chamber results should also accurately simulate chemical reaction processes in polluted atmospheres.

In the early stages of chemical mechanism development for use in the simulation of atmospheric transformation processes, it became readily apparent that inclusion of detailed reaction processes for the individual hydrocarbons present in urban polluted atmospheres was an impossible task. The hundreds of organic species emitted by anthropogenic sources as well as those occurring naturally would necessitate the consideration of thousands of chemical reactions in describing these individual hydrocarbon oxidation processes. Even if all these specific chemical reactions were known and their rate constants determined, their inclusion into the transport model would prove to be a computational nightmare and economically unfeasible. Therefore, techniques had to be devised for generalizing the chemical kinetics such that computational requirements would be met without losing the major features of the hydrocarbon- NO oxidation processes.

The so-called "lumping" technique has become the prevalent approach used by PAQSMS. This technique lumps together the various reactive hydrocarbons present in the polluted atmosphere into one or more classes. Reactions are specified by hydrocarbon class with specific inorganic species (e.g., O-atom, O_3 , and HO) that result in the formation of products and lumped hydrocarbon free radical species. The inorganic reactions occurring in the atmosphere are considered specifically, but with varying levels of detail. The following are types of reactions that might be considered in a typical lumped reaction mechanism. A summary of the characteristics of generalized chemical kinetic mechanisms currently in use in PAQSMS is given in Table 3.



The sources of errors in the development of generalized chemical kinetic mechanisms stem from 2 primary areas: those associated with the smog chamber data base and those associated with the kinetic mechanism. In the case of chamber data used for mechanism development and verification, errors may be introduced for the following reasons:

1. Inadequate or no control and measurement of levels of H_2O in the chamber,
2. Impurities in background chamber air,
3. Inadequate or no measurements of the spectral distribution and intensity of the chamber irradiation system,
4. Inaccurate or ambiguous analytical methods,

5. Nonhomogeneity due to inadequate stirring or poor chamber design,
6. Adsorption and desorption of reactants and products on chamber walls,
7. Chemical reactions occurring on chamber surfaces, and
8. Inadequate control and measurement of chamber temperature.

Errors associated with the chemical kinetic mechanism include

1. Uncertainties in experimental determinations of specific reaction rate constants;
2. Variations of rate constants with temperature either uncertain or unknown;
3. Inadequacies in lumping due to the nonrepresentativeness of lumped class reactions relative to specific species within the class, e.g., reaction rates, products, and stoichiometric coefficients; and
4. Inaccuracies in the mechanism due to insufficient verification studies.

Smog chamber data available within the past 2 or 3 years have been well characterized with respect to most of the errors outlined above. In these cases, therefore, errors can be taken into consideration in the development and verification of the chemical kinetic mechanism. The major shortcoming in recent years has been the limited quantity of quality smog chamber data available for development and verification of mechanisms.

The sensitivity of the chemical mechanisms to uncertainties in specific reaction rate constants as well as to temperature variations has been assessed by several workers (3, 16, 17). In a recent study by Dodge and Hecht (16), a combined uncertainty and sensitivity factor for reactions was used as an index for ranking possible sources of error in the Hecht, Seinfeld, and Dodge mechanism (15). These results indicated that at least 12 reactions of the generalized mechanism need to be more accurately determined.

Source Emissions

The accurate description of pollutant emissions within some time and space frame is obviously a critical factor in the performance of all types of air quality simulation models. Emissions are usually characterized as being in point, line, or area source configurations. In many cases individual sources may fall into one or more configurations, and the choices made will depend on the particular area and detail emphasized by the model. Table 4 gives some indication of the types of sources considered in each configuration and the necessary input information used by the methodologies. In the development of emissions inventories for PAQSMS, the emphasis is on HC, NO_x, and CO emissions and, therefore, in general, one might consider line sources in more detail than point and area sources. Even this, though, depends on the particular area being modeled.

The overall uncertainties in the generated emission rates can be considerable and will vary with respect to source type, methodology, and quality of input parameters and data used in the emission model. To my knowledge, the only emission models that have undergone some validation are those for point sources. This is not surprising in that line and area source emission validation would be tied directly to the air quality simulation model, which in itself has not yet been validated. Presumably, evaluations of the emission rate estimates can be made based on the overall uncertainties of various components used in the computation. Such an evaluation will not be attempted here, though indications are that uncertainties of the order of ± 50 percent in emission rates are not inconceivable.

To gain some insight into the sensitivity of PAQSMS to uncertainties in pollutant emission, Liu and Whitney (18) performed grid point model calculations, varying emission rates uniformly by ± 15 percent in individual runs. Comparisons with base calculations showed maximum percentage deviations of the order of 10 percent for CO, 26 percent for NO, 58 percent for O₃, and 17 percent for NO₂. The local maximum deviations were 1.4 ppm for CO, 5.7 pphm for NO, 6.3 pphm for O₃, and 5.7 pphm for NO₂.

Table 2. Evaluation of assumptions used in grid point and trajectory approaches.

Model	Assumption	Errors Introduced
Trajectory	Neglect of horizontal diffusion Neglect of vertical winds	<10 percent after 9 hours of simulation (a) dependent on meteorological conditions and (b) can be as large as 1 order of magnitude
	Neglect of wind shear	(a) dependent on meteorological conditions and (b) can be more than 50 percent after 9 hours of simulation
Grid point	Neglect of numerical errors	(a) dependent on grid cell size, time interval, numerical scheme used, and physical parameters used; and (b) can be as large as 50 percent after 9 hours of simulation

Table 3. Summary of characteristics of generalized chemical kinetic mechanisms.

Reference	Description	Comments
14	Seven-step reaction mechanism that lumps reactive hydrocarbons into single class and assumes O-atom and O ₃ as the hydrocarbon oxidizing species. Contains limited information on inorganic reactions.	Limited comparison studies performed with smog chamber data. Does not include HO reactions, which represent major oxidation path for hydrocarbon species. Mechanism has been used in box model approach (5) with limited success.
1, 3	Fifteen-step reaction mechanism that lumps reactive hydrocarbons into single class and assumes O-atom, O ₃ , and HO as the hydrocarbon oxidizing species. Contains moderate information on inorganic reactions.	Comparison studies performed with 14 smog chamber runs considering 4 hydrocarbon-NO _x systems. HC and NO _x initial conditions used in chamber studies were significantly higher than those observed in urban polluted atmospheres. Mechanism is currently used in grid-point approach (1, 2, 3) with moderate success.
5	Sixteen-step reaction mechanism that lumps reactive hydrocarbons into a single class and assumes O-atom, O ₃ , and HO as the hydrocarbon oxidizing species. Contains moderate information on inorganic reactions.	Comparison studies performed same as above. Mechanism currently is used in trajectory approach (4) with moderate success.
13	Thirty-nine-step reaction mechanism that lumps reactive hydrocarbons into 4 classes. Hydrocarbon oxidizing species include O-atom, O ₃ , and HO as well as direct photooxidation for the aldehyde class of hydrocarbon. Contains rather detailed information on inorganic reactions.	Comparison studies performed include above 14 chamber runs and chamber results from an ongoing program at University of California, Riverside. New chamber data base uses HC-NO _x initial conditions more representative of urban polluted atmospheres. Incorporation of mechanism in grid-point approach is under way. Available June 1976.
6	Thirty-three-step reaction mechanisms based on propylene photooxidation. Atmospheric hydrocarbon is specified as propylene and lumped less reactive hydrocarbon species. Hydrocarbon oxidizing species include O-atom, O ₃ , HO, HO ₂ , and CH ₃ O ₂ .	Comparison studies performed same as in 2 and 3 above. Mechanism currently is used in trajectory approach (6) with moderated success.

Table 4. Emission inventory.

Configuration	Source Type	Methodology Input Parameters
Point	Power plant	Plant identification
	Large processing plant	Spatial coordinates Stack parameters Fuel content Processing materials Operation characteristics Process identification Emission factors Control equipment
Line	Highway, mobile	Spatial coordinates
	Rail and river vessels	Vehicle miles traveled Speed Operation characteristics Vehicle mix Emission factors
Area	Stationary	Spatial coordinates
	Airports Refineries Off highway, mobile	Population distribution Temporal apportioning factors Operation characteristic Emission factors

Note: Emission inventory is distributed in space and time.

Meteorological Factor

All of the PAQSMs developed to date are deterministic in nature; that is, meteorological data are treated entirely as input to the model, and no attempt is made to forecast any meteorological information. Therefore, methodologies must be developed for treating the meteorological data so as to make them amenable to the transport and dispersion portions of the PAQSMs. A summary of the meteorological parameters and related methodologies considered by PAQSMs is given in Table 5. The uncertainties in individual parameters are difficult to assess. Some parameters may be in error by as much as 1 order of magnitude. As with the emissions, an indication of the importance of these parameters on PAQSM predictions can be gained via the sensitivity studies of Liu and Whitney. Table 6 gives their sensitivity analysis results for a grid point PAQSM.

EVALUATION OF INITIAL AND BOUNDARY CONDITIONS OF MODELS

All PAQSMs must take into consideration the initial or boundary or both conditions of the area being modeled. In the case of the grid point approach, boundary pollutant concentrations must be specified for each hour for all grid cells that lie along an inflow boundary from the ground to the inversion base. The horizontal boundary conditions are established, when possible, by using nearby monitoring data as a guide. When such information is unavailable, estimates used are made solely on a judgmental basis. Concentrations are assumed invariant in the Z direction for any given x, y, and t. Initial concentrations are specified in each ground-level grid cell by interpolation using the data collected at monitoring stations during the hour at which the model run is initiated. For trajectory approaches, only initial concentrations need to be specified. The usual approach is to initiate the trajectory in the vicinity of an air monitoring station and use the observed measurements as initial concentrations in the trajectory cell.

To illustrate the importance of boundary concentrations on grid point model calculations, comparative simulations for Los Angeles on September 29, 1969, were made first by using the standard prescribed boundary concentrations and then using a reduced set of nominal boundary concentrations. All other conditions remained the same. Average ozone concentrations for the Los Angeles basin between 1 and 2 p.m. are shown in Figures 2 and 3 for the respective simulations. A comparison of the results shows that only minor differences are observed at the eastern and northern edges of the basin where the maxima occur, but significant differences are observed at the western and central portions of the basin. The overall effect of the reduced boundary conditions was to bring an additional 904 miles² (2341 km²) of the basin below the oxidant standard. This represents a 237 percent improvement in oxidant air quality in the modeling region due to the boundary condition reductions.

The impact of initial conditions on ozone predictions using a trajectory model approach is shown in Figure 4. In this case comparative trajectory simulations were run for Los Angeles on September 29, 1969, for the original initial concentrations prescribed for the cell and ± 20 percent of those values.

Even if model performance is assumed quite good, the serious impact that boundary and initial concentrations have on model predictions indicates that these model inputs must be accurately specified. Schemes must be devised for forecasting these input conditions so that impact assessments of various control strategies on future air quality can be made.

VALIDATION OF MODELS

The development and refinement of PAQSMs have proceeded at a reasonable pace during the past several years, but with little or no validation of the models developed. This is due to the lack of an adequate air monitoring data base against which to test the

Table 5. Summary of meteorological parameters and related methodologies considered by PAQSM.

Meteorological Parameter*	Meteorological Data	Related Methodology
Wind field	Wind speed and direction (s, y, z, t)	Linear interpolation Objective analysis
Inversion height and thickness	Temperature (x, y, x, t)	Mass consistent approach Analysis and interpolation of vertical temperature profile when available
Vertical turbulent diffusivity	Turbulent energy dissipation rate, surface roughness, wind speed and direction, and temperature	Data based on climatological observations Lack of sufficient data dictates use of simple empirical relations
Solar radiation	Radiometric (x, y, x, t)	Lack of sufficient data dictates use of functional forms based on clear sky conditions

*All parameters averaged in time and space.

Table 6. Summary of sensitivity of grid point model to variations in meteorological parameters.

Input Parameter	Variation	Local Maximum Deviation	
		CO (ppm)	O ₃ (pphm)
Wind direction	Station measurements randomly perturbed by 0 or ±22.5 deg	[1.75]	
	Values at each grid point randomly perturbed by 0 or ±22.5 deg	[2.81]	
Wind speed	Station measurements randomly perturbed by 0 or ±1 mph	[1.24]	
	Values at each grid point randomly perturbed by 0 or ±1 mph	[1.73]	
	Station measurements decreased by 50 percent	+5.3	+43.7
	Station measurements decreased by 25 percent	+2.4	+24.5
	Station measurements increased by 25 percent	-2.4	-19.6
	Station measurements increased by 50 percent	-4.2	-34.5
Horizontal diffusivity (base value 50 m ² /s)	Decreased to 0	[0.04]	
	Increased to 500 m ² /s	[0.3]	
Vertical diffusivity (base value 5 m ² /s)	Decreased to 0.5 m ² /s	+5.8	+36.3
	Increased to 50 m ² /s	-3.0	-16.0
Mixing depths	Decreased by 25 percent	+2.6	+15.3
	Increased by 25 percent	-1.5	-8.5
Radiation intensity	Decreased by 30 percent	0	-19.0
	Increased by 30 percent	0	+14.0

Figure 2. Predicted ozone concentrations in Los Angeles basin using standard model boundary concentrations.

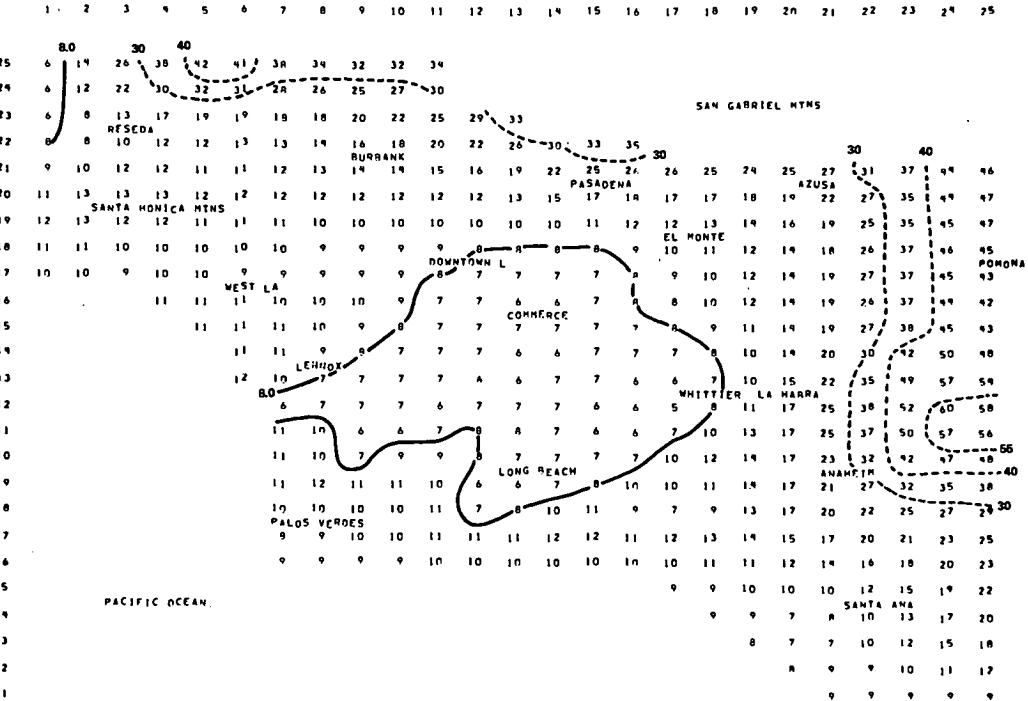


Figure 3. Predicted ozone concentration in Los Angeles basin using reduced nominal boundary conditions.

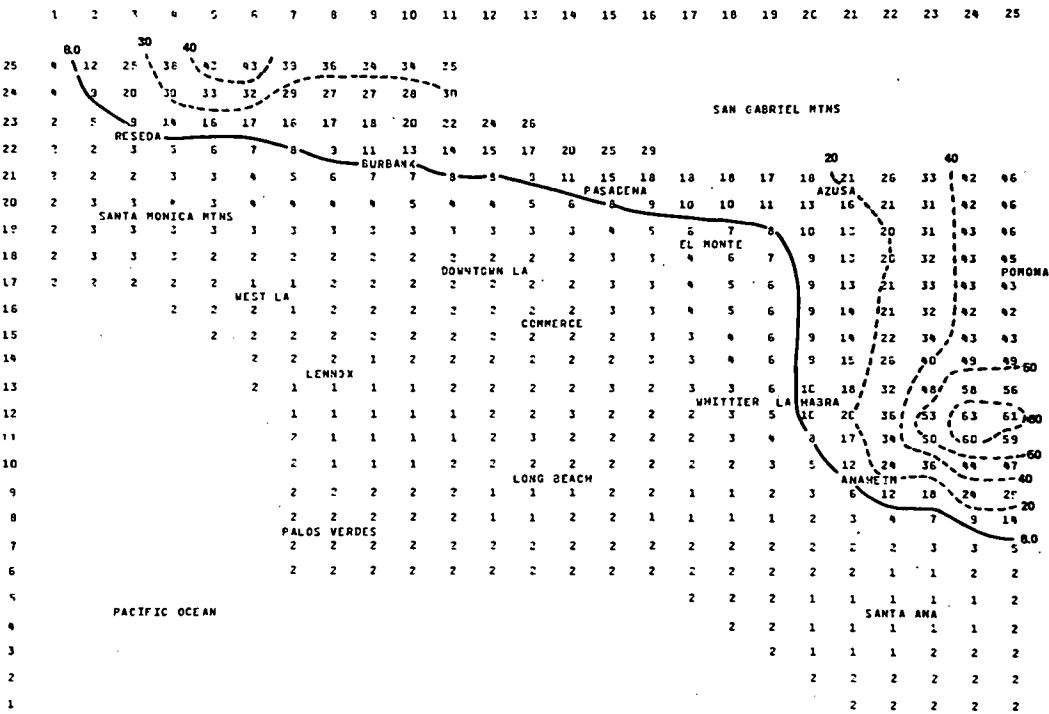
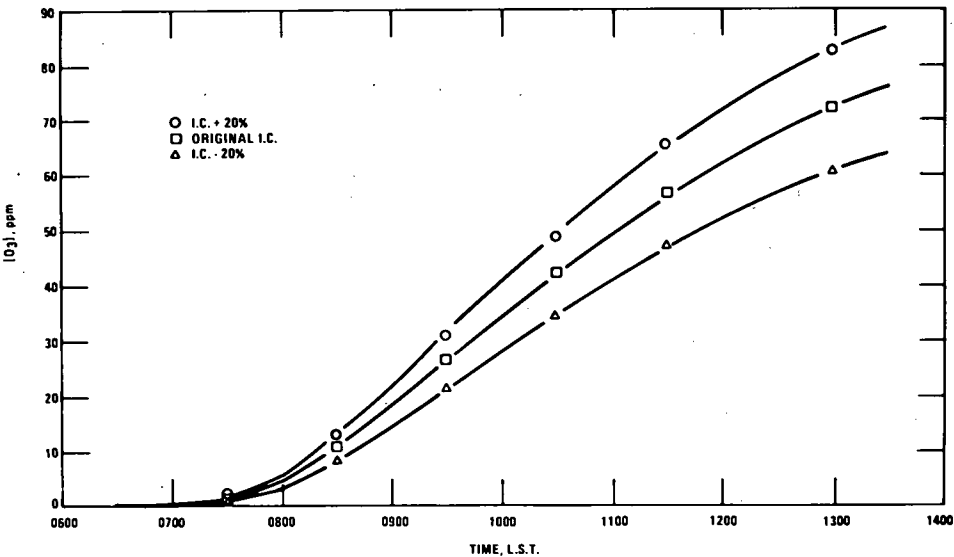


Figure 4. Predicted ozone concentrations in the Los Angeles basin using original and ± 20 percent of initial concentration in trajectory cell.



models. The most extensive testing to date of PAQSMs has been for the 3 models developed under EPA contract (1, 2, 3, 5, 7), which were run on 6 preselected days in the Los Angeles area in the fall of 1969. But even these results must be questioned in that data from many of the monitoring stations used in making comparisons of observed and predicted concentration levels were known to be local source affected and, therefore, did not reflect the spatially averaged concentrations predicted by the models. A statistical analysis of the results from the 3 models previously mentioned has been reported by Liu et al. (18). A tabulation of the statistics has not been presented here, for the results are subject to major interpretation and can be misleading at face value.

Model validation, therefore, provided a major stimulus for the St. Louis Regional Air Pollution Study (RAPS), a 5-year EPA field program initiated in 1972 (20). RAPS objectives include the development and validation of improved air quality simulation models. This requires gathering of an extensive meteorological and air quality data base as well as developing a detailed emission inventory. The monitoring network, which came on line early in 1975, consists of 25 monitoring stations spatially distributed in a spiral configuration covering approximately a 2500-mile² (6400-km²) area. The measurements include total and nonmethane HC, total sulfur, H₂S, SO₂, NO, NO₂, NO_x, CO, total suspended and fine particulate, wind speed and direction, temperature, dew point, barometric pressure, back scatter, and solar radiation.

The model validation studies, encompassing scores of comparisons between computer simulations and monitoring data, will provide the first adequate set of statistical criteria on which to judge model performance. This will, in the final analysis, provide the necessary information for assessing and selecting models for various application purposes.

SUMMARY AND CONCLUSIONS

This paper provides an overview of the various photochemical air quality simulation models currently available and considers evaluations for the various assumptions, methodologies, and input used by the model. The results indicate that the potential for serious error is present in every PAQSM currently available and that extensive verification is necessary to assess the accuracy and utility of these models.

It should be noted, though, that, even in their present uncertain form, PAQSMs provide unique information unavailable from currently applied methods for relating ambient oxidant to precursor emissions. One such example is the ability of PAQSMs to resolve, both in space and time, the impact of new precursor source emissions on ambient levels of oxidant. Therefore, some exercising of the models may be warranted to provide insight into problems for which no other techniques are currently available. This would especially be reasonable in areas where the models have been used or where data bases sufficient to run the models exist.

Verification studies for PAQSMs under RAPS are scheduled to begin in the fall of 1976. Preliminary assessment of several models should be available by early 1977. With the completion of verification and sensitivity studies, an evaluation will be made regarding potential applications of the models.

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