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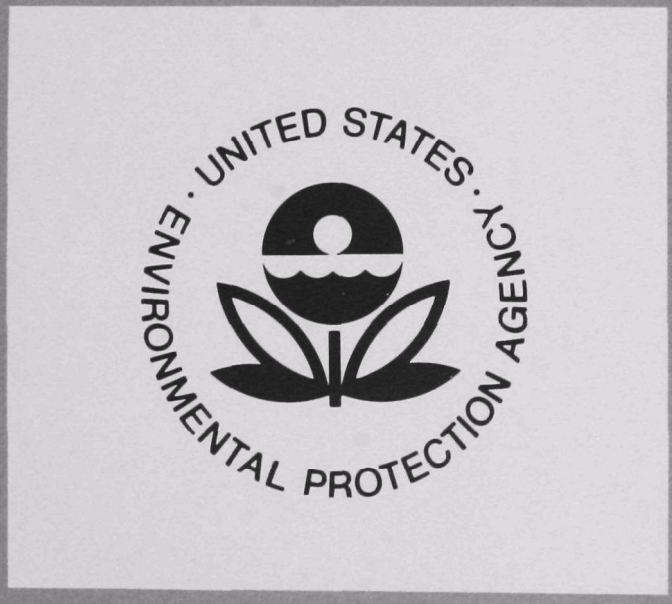
Environmental Monitoring Series

CONTINUED RESEARCH IN MESOSCALE AIR POLLUTION SIMULATION MODELING: Volume II - Refinements in the Treatment of Chemistry, Meteorology, and Numerical Integration Procedures



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CONTINUED RESEARCH IN MESOSCALE AIR POLLUTION SIMULATION MODELING: VOLUME II - REFINEMENTS IN THE TREATMENT OF CHEMISTRY, METEOROLOGY, AND NUMERICAL INTEGRATION PROCEDURES

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I INTRODUCTION

The SAI urban airshed model was originally developed for the Environmental Protection Agency (EPA) under Contracts CPA 70-148 and 68-02-0339. Two series of reports, entitled "Development of a Simulation Model for Estimating Ground-Level Concentrations of Photochemical Pollutants" and "Further Development and Evaluation of a Model for Estimating Ground-Level Concentrations of Photochemical Pollutants," describe our models development and evaluation studies. In concept, the model formulation was general, based on mass conservation relationships for a reactive species in a turbulent fluid. To implement the model, however, we assumed that we could do the following:

- Use the gradient transport hypothesis to represent pollutant transport by turbulence.
- Neglect turbulence influences on the net rate of chemical reactions.
- Neglect subgrid-scale concentration variations and their effect on reaction rates.

Volume III discusses this threefold assumption. In addition, we made several assumptions with regard to the treatment of various parameters in the model. For example, we assumed that a 15-step kinetic mechanism could be used to represent the chemical reaction processes. The nature of these assumptions reflects not only the time and funding constraints on our work then, but also the current understanding of the physical and chemical processes that occur in the urban atmosphere. In this Volume, we discuss efforts carried out under the present contract to refine further various aspects of the model and its usage.

Basically, our model refinement activities have focused on four areas:

- Chemistry-related model development activities.
- Meteorology-related model development activities.
- An evaluation of alternative techniques for integrating the species continuity equations.
- Airshed model modification for multiday simulation.

Each of these areas is the subject of a chapter in this volume.

Chapter II discusses our efforts to improve the treatment of chemical parameters in the model. Specifically, we began with a 39-step generalized kinetic mechanism and, by eliminating unimportant reactions, by invoking the steady-state assumption, and by combining reaction steps we derived a 31-step mechanism suitable for incorporation in the airshed model. In addition, we examined SO_2 chemistry and developed an interim 10-step reaction mechanism for describing both homogeneous and heterogeneous reactions. Although this mechanism has yet to be validated using smog chamber data, it does provide a starting point for treating SO_2 chemistry in the airshed model. We also determined the sensitivity of the kinetic model predictions to variations in temperature, water concentration, and H_2O_2 concentration. These results provide guidance with regard to the appropriate treatment of the spatial and temporal variations of these parameters in the airshed model. Finally, the chapter describes our experience to date in using the new 31-step mechanism in an actual simulation of a smoggy day in the Los Angeles basin.

Chapter III describes our efforts to improve the treatment of meteorological parameters in the model. We examined the impact on the model predictions of wind shear--an effect previously neglected in the model. Upon finding that wind shear has a significant influence, we extended the capabilities of the model to treat this parameter. In addition, we developed a methodology to derive improved diffusivity relationships (discussed more fully in Volume III) and examined an algorithm for rendering three-dimensional wind fields mass consistent. We gave special consideration to the treatment of elevated temperature inversions, especially with respect to possible importance of pollutant exchange between the stable inversion layer and the turbulent mixed layer as the inversion is eroded by surface heating.

Chapter IV presents our evaluation of alternative techniques for integrating the species continuity equations. Because the governing equations of the photochemical dispersion model are nonlinear, numerical techniques

must be employed to obtain approximate solutions. Since we must attempt to solve large systems of coupled, nonlinear partial differential equations, we have to be careful to choose an appropriate numerical procedure. The two most important concerns influencing this choice are the following:

> Accurate representation of the horizontal advective transport of pollutants.
> Efficient solution of large systems of nonlinear equations.

For this contract effort, we restricted our attention to the first of these areas. We carried out a comparative study of various alternative techniques that have appeared in the literature and that, if implemented in the airshed model, would represent a means for minimizing truncation error propagation effects. The methods examined include finite difference, particle-in-cell, and finite element schemes. We applied each method to the same test problem, and we compared the numerical results with analytical solutions.

Chapter V summarizes our efforts to modify the airshed model for multiday simulations. In previous photochemical modeling studies, multiday simulations have been ignored. Model applications have usually been limited to the simulation of daytime conditions. For example, a model run might start at some point in the morning preceding the rush hour and extend into the afternoon to model the buildup of O_3. Accurate nighttime simulations are hindered by the typically small size of wind speeds then and the lack of available measurements aloft. However, multiple-day simulations may prove to be extremely useful. For example, in the evaluation of an emission control strategy that is to be carried out in some future year, the model user must carefully choose the initial pollutant concentration distribution to be employed in the simulation. If a multiple-day run is made, the influence of the initial concentrations on the predictions for the second and subsequent days will not be as pronounced as it is on the first day. Furthermore, multiday simulations may uncover errors in the treatment of emission, meteorological, or chemical parameters that would otherwise remain unnoticed in a relatively short term simulation. Chapter V concludes with a presentation of the results of a 34-hour simulation of the Los Angeles basin for CO using the SAI model.

II CHEMISTRY-RELATED DEVELOPMENT STUDIES

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One of the distinguishing characteristics of models capable of estimating photochemical pollutant concentrations is that chemical reaction processes must be represented accurately. Two pollutants treated in such models for which air quality standards have been established, namely NO_2 and O_3, are not emitted from sources in appreciable quantities. These pollutants are formed in the atmosphere as the products of numerous reactions involving NO, hydrocarbons, and a variety of free radical species. Because of the inherent complexity of the overall reaction processes, care must be exercised to incorporate in a photochemical dispersion model a tractable kinetic mechanism which embodies as much chemical reaction as possible.

In this chapter we discuss efforts to improve the treatment of the atmospheric chemical reaction processes in the SAI airshed model. Previously, these processes were represented by a 15-step mechanism developed by Hecht and Seinfeld (1971). Since this mechanism was developed, however, additional efforts have been undertaken to design improved mechanisms. One of the most promising mechanisms to appear in the literature is that reported by Hecht et al. (1973). This mechanism consists of 39 reaction steps and treats four classes of hydrocarbons (paraffins, olefins, aromatics, and aldehydes). In general, this new mechanism seems to represent an advance of such importance as to warrant its incorporation in the airshed model.

In the course of reviewing modeling needs with respect to atmospheric chemistry, a number of issues were raised. These topics, which we address in this chapter, include the following:

- Development of a computer program to facilitate the evaluation of kinetic mechanisms.
- Compaction of the 39-step hydrocarbon/NO_x/O_3 mechanism to reduce its impact on computing time in the airshed model.

- Development of an interim mechanism for SO_2 reactions and sulfuric acid formation suitable for incorporation in the airshed model.
- Examination of spatial and temporal variations in temperature, water, and H_2O_2 concentration in an urban airshed such as the South Coast air basin to provide guidance with respect to the treatment of these parameters in regional models.
- Evaluation of alternative means for treating organics in the airshed model.
- Experience gained in the use of the new kinetic mechanism to perform an actual airshed simulation of the Los Angeles Basin.

Each of these issues is discussed in the succeeding sections of this chapter.

A. DEVELOPMENT OF AN AUTOMATIC COMPUTER PROGRAM FOR THE EVALUATION OF KINETIC MECHANISMS

Once a set of reactions for the formation of photochemical smog has been proposed, it is necessary to demonstrate that the mechanism is correct; i.e., that it is able to account for, within experimental error, the actual concentration of each species present in the reaction mixture at any point during the time span of the reaction. In its simplist form, this evaluation process involves the formulation and solution of the set of coupled differential equations that describe the variation in the formation and consumption of each species in the reaction mixture as a function of time. This set of equations can be expressed as follows:

$$\frac{dy_i}{dt} = \sum_{j=1}^{J} R_{f_{i,j}} - \sum_{k=1}^{K} R_{c_{i,k}} \quad , \qquad (1)$$

where

y_i = the concentration of species i,

t = time,

$R_{f_{i,j}}$ = the rate of formation of species i in reaction j of the set of J reactions in which species i is formed,

$R_{c_{i,k}}$ = the rate of consumption of species i in reaction k of the set of K reactions in which species i is consumed.

The concentrations thus calculated can be compared with those measured experimentally in the reaction mixture.

Unfortunately, the real world presents experimental, computational, and operational obstacles to the pursuit of this simple validation scheme. First, for the integrity of the reaction mixture to be preserved, the mixture must be contained in some sort of reaction chamber, which in turn gives rise to two side effects: leaks (intentional, as in sampling, or unintentional) and wall reactions. Second, when the most efficient computer codes are used, the time needed to solve the coupled differential equations increases as the square of the number of species increases. Moreover, certain sets of rates lead all too often to systems of "stiff" equations, for which the solution times can become quite large. Finally, the urge always exists to "improve" a reaction mechanism, no matter how closely it approximates the experimental data; the computer code must allow these changes to be performed with a minimum amount of effort. In dealing with these realities, the researcher is called upon to display his mettle and to tax his ingenuity. The approaches we used in this study are described in the following subsection.

1. Treatment of Chamber Effects

With few exceptions, reaction chambers are not completely airtight. Under normal operating conditions, this does not create a serious problem, since almost all chambers are maintained at atmospheric pressure, and since the small amount of interchange by diffusion can usually be ignored. However, a problem

does arise when samples are removed from the chamber for analysis. Since the species that comprise smog exist in the atmosphere in minute (1 to 1000 ppb) concentrations, sample sizes on the order of a few liters are commonly needed to obtain enough material for an accurate analysis. Moreover, samples must be withdrawn fairly frequently during the reaction to monitor species concentrations that are changing rapidly. As a result, it is not unusual for 10 to 20 percent of the chamber volume to be withdrawn through sampling procedures. The reaction simulation technique must take this "dilution" of the reaction medium into account.

In the ideal case, the gas used to replace the samples being withdrawn is inert with respect to the reaction (e.g., pure nitrogen in a smog system), or it contains only reactive species whose concentrations are so large--relative to the amounts consumed or produced by the reactions--that they can be assumed to be constant throughout the reaction (e.g., oxygen or water vapor in "clean" air). In this case, it is sufficient to apply a "dilution factor" to the concentrations of all the species (inert diluent) or to those that do not remain constant (clean air diluent). If samples of an approximately constant size are removed at reasonably uniform time intervals, the dilution factor can be considered to be a constant, Q, and the equation for the rate of change of the concentration of species i becomes

$$\frac{dy_i}{dt} = \sum_{j=1}^{J} R_{f_{i,j}} - \sum_{k=1}^{K} R_{c_{i,k}} - y_i Q \quad . \qquad (2)$$

In some chamber experiments, however, the incoming medium is just the natural atmosphere in the laboratory, which may contain concentrations of pollutant species as high as or higher than those being followed in the reaction chamber. Moreover, it may be desirable in some cases to inject pollutants or pollutant precursors deliberately into the chamber to simulate the effect of fresh emissions on the reacting mixture. As long as the concentration of species i, y_{in}, in the incoming medium is known, the effect of such inflowing species on the rate equation can be easily expressed:

$$\frac{dy_i}{dt} = \sum_{j=1}^{J} R_{f_{i,j}} - \sum_{k=1}^{K} R_{c_{i,k}} - (y_i - y_{in})\, Q \quad . \qquad (3)$$

Unfortunately, wall effects cannot be handled as neatly. Wall absorption is best determined by placing the species in question, A, in a "nonreactive" environment within the chamber and following its decay with time. One can then include within the reaction mechanism an equation such as

$$A \xrightarrow{k_a} \text{Wall} \quad , \quad \underline{\qquad k_a \qquad} \, , \qquad (4)$$

with an appropriate rate constant.

Heterogeneous catalysis by the reactor walls is even more troublesome. However, by determining reaction rates at several different surface-to-volume ratios for the reactor (e.g., through the use of "artificial" walls to partition the chamber), the rate constants for the homogeneous and heterogeneous reactions can be obtained, and both reactions can be included in the mechanism.

$$\text{Homogeneous:} \quad A + B \xrightarrow{k_c} C \quad , \qquad (5)$$

$$\text{Heterogeneous:} \quad A + B \xrightarrow{k_w} C \quad . \qquad (6)$$

2. Computational Considerations

As mentioned earlier, the computer time required to solve a set of differential equations increases at least as does the square of the number of equations to be solved (or, in the present case, as does the square of a number of distinct chemical species that appear in the reaction mechanism). Thus, any techniques that can be used to decrease the number of species concentrations that actually require coupled differential equations for their solution should be applied. Such techniques include the assumption of constant concentration; the uncoupling of product-only species; the invocation of the steady-state approximation; and the aggregation, or "lumping," of species that yield similar products. The last two techniques are the subjects of further discussion in Sections B and E and are thus not treated here.

Certain species that appear in the reaction mechanism either are present at truly constant concentrations (e.g., the reactor walls) or have concentrations so high--relative to the amounts of that species formed or consumed during the reaction--that they remain essentially constant with respect to time (e.g., oxygen). Since the change in concentration for these species is only negligibly different from zero, they can be excluded from the differential equation process.

A second category of species that need not be included in the set of coupled differential equations is those that appear in the reaction mechanism only as products (e.g., CO_2 or HNO_3). The rate of formation of these product species is, to be sure, represented by the following equation:

$$\frac{dy_i}{dt} = \sum_{j=1}^{J} R_{f_{i,j}} \quad . \tag{7}$$

However, the presence of this species has no effect on the rate of formation or depletion of any other species; thus, the differential equation describing its formation can be uncoupled from the set of all differential equations and solved independently, at a significant savings in overall computer time.

3. Ease of Changing Reactions

Most computer codes used in the simulation of reaction kinetics incorporate, in one form or another, the features described above. The major advantage offered by the present program is the ease of preparation and, particularly, the ease of alteration of the mechanism and its associated species concentrations. The user need know nothing about computer programming or the solution of differential equations, and very little about chemical reaction mechanisms, to obtain meaningful results from the program.

On the first line of input, the user specifies the run identification, the number of reactions in the mechanism to be studied, how many of these are lumped reactions, the number of each of the various types of species described in the previous subsection, and an indication of whether the reaction rates should be printed. The second line continues this specification of parameters with an indication of the frequency of printout, the time step sizes, and the dilution factor.

The user then submits his reaction mechanism, one reaction per line, restricted only by one requirement on ordering: The lumped reactions must appear last. Each reaction appears as an ordinary chemical equation, with a list of reactants, a list of products, and a rate constant. The products can have coefficients (either fractions or integers), but the reactants cannot--each reactant molecule must be entered separately. The user can choose any four-letter mnemonic he wishes for the species names.

If there are any lumped reactions, the sets of individual reactions comprising each "lump" are then entered. Their formulation is exactly the same as that of the lumped reaction, except that the name of each species that contributes to the composition of the lump appears in place of the lumped species as the first reactant.

The user than provides the list of species and their initial concentrations--one per line. The order of their types must be the same as that given on the initial parameter line, but no particular order is required within each species type.

Should any of the species be present in the gas flowing into the reaction chamber, their concentrations in the inflowing stream and, if needed, the time and new values of any change in this concentration are entered next. Finally, the user can request concentration-time plots of any species. If desired, these plots can contain experimental points with which those points calculated by the proposed mechanism can be compared.

To change a rate constant or chemical reaction, the user need merely alter the corresponding input line. New reactions can be added by insertion; old ones can be removed by deletion. A similarly easy process can be used to change an initial species concentration or to add or remove species names from the list. Species can be transferred among species types (e.g., differential to steady-state) by a single interchange of lines.

A complete user's guide to the computer program is included in Appendix A. This appendix provides detailed information on each of the features described above, descriptions and listings of all of the computer routines, and sample inputs and outputs.

B. DEVELOPMENT OF AN IMPROVED KINETIC MECHANISM FOR INCORPORATION IN PHOTOCHEMICAL DISPERSION MODELS

1. General Considerations in the Design of a Suitable Mechanism

The selection of a chemical mechanism for inclusion in an atmospheric diffusion model depends substantially on two factors:

> The accuracy of prediction of the chemistry module.
> The computing time required to evaluate the mathematical equations representing the mechanism.

From the standpoint of developing a chemical transformation model, the second factor is subordinate to the first. After a reliable mechanism has been developed, it can be condensed in several ways to reduce the computing time necessary to obtain predictions--for example, by eliminating unimportant reactions, by combining species that react in the same ways and at similar rates into a general grouping, and by invoking the steady-state approximation where applicable.

Depending on the degree to which these compaction measures are applied, the resultant mechanism can be assigned one of three broad categories: detailed mechanisms, lumped general mechanisms, or parametric models. A detailed mechanism consists entirely of elementary reactions. Because there are hundreds of different organics in the atmosphere, such a mechanism requires an extremely large number of mathematical equations to represent the chemical transformations. Although a detailed mechanism is ultimately the most accurate (in the limit if all rate constants and reactions are known), it is unsuitable for atmospheric modeling because of the second criterion listed above. A lumped general mechanism results when reactants and reactions of the same type are combined into general classes and reactions and those that clearly do not contribute to the predictions are eliminated from a detailed mechanism. A lumped general mechanism strikes a balance between detail of representation and compactness of form. The elimination of reactions that significantly affect predicted concentrations would oversimplify the mechanism to the point where it could not

provide accurate predictions unless corrective measures were taken. In particular, adjustable coefficients would have to be incorporated, forming a parametric model. For such a model, the values of the adjustable parameters are selected to minimize the discrepancies between experimental data and calculated values.

When we first began to develop a photochemical airshed model two types of chemical mechanisms were available for use. The first, a detailed model for propylene, was unsuitable because it was too narrow in scope. Its predictions for the atmosphere would have almost certainly been unreliable. The second was a parametric model, the Hecht-Seinfeld 15-reaction mechanism, for which values of the adjustable parameters had been determined for several hydrocarbon-NO_x systems using smog chamber data. These hydrocarbons included propylene, iso-butylene, toluene, and n-butane; binary mixtures of propylene and n-butane, propylene and ethane, and toluene and n-butane; and auto exhaust. Thus, to the extent that the atmosphere could be represented as a surrogate consisting of these species, the parametric mechanism could be expected to provide reasonably accurate predictions over the range of initial conditions explicitly used in selecting values of the parameters. Moreover, the mechanism was mathematically compact. The predicted time-varying behavior of the pollutants could be obtained at every time step through the solution of only four differential equations and six algebraic equations. Given a choice of these two mechanisms, we selected the parametric model for incorporation in the airshed model because it came closest to meeting our two criteria.

The compact mechanism is far from ideal, however. Recent experimental studies have demonstrated the key roles of OH and HO_2 reactions in smog formation, reactions whose importance is understated in the mechanism. Other studies have shown that O and CO are less important that we thought at the time we formulated the model. And one limitation that is particularly discomforting is the narrow range over which values of the adjustable parameters are valid. This last shortcoming would limit the accuracy of the results obtained from the atmospheric dispersion model in such applications as the evaluation of alternative emission control strategies.

The mechanism most suitable for use in atmospheric models is a lumped general mechanism. Under EPA Contract 68-02-0580, we recently undertook the development of such a general kinetic mechanism. In this mechanism, we incorporated state-of-the-art knowledge of the reaction processes, and we provided for the rapid and straight forward modeling of organic species not explicitly evaluated using smog chamber data.

In the new kinetic mechanism, the inorganic reactions common to all organic-NO_x systems are treated in great detail. We introduced generality into the model by lumping similar types of organics and free radicals into several new classes. In particular, olefins, aromatics, paraffins, and aldehydes constitute four separate classes of organics. We segregated organic free radicals into alkoxy, peroxyalkyl, and peroxyacyl subgroupings. Using propylene-NO_x, n-butane-NO_x, and propylene-n-butane-NO_x smog chamber data over a wide range of HC/NO_x ratios, we evaluated the model and showed that its predictions of the dependence of peak ozone on the initial concentrations of hydrocarbon and oxides of nitrogen qualitatively agree with experimental observations. Seinfeld et al. (1973) discussed the rationale and formulation of this lumped kinetic mechanism, and Hecht et al. (1973) and Hecht et al. (1974) presented initial and secondary evaluation results using the mechanism.

This new mechanism appears to be more accurate than the Hecht-Seinfeld mechanism that we previously employed in the atmospheric simulation model. In addition, we can easily extend the new mechanism to new organics that have not been explicitly evaluated (the values of the adjustable parameters do not need to be determined). Unfortunately, the computing time that is initially required to carry out a simulation with the new mechanism is much higher than that needed for the Hecht-Seinfeld model. At the outset of this project, representation of the chemistry of a system consisting of a paraffin, an olefin, and NO_x in air (no aromatics or CO) required 36 reactions and the solution of 16 differential equations and 4 algebraic equations to obtain predictions. Such mathematical complexity would certainly be excessive if the mechanism were imbedded in the airshed model, where the kinetics must be evaluated at every grid point for every time step. We therefore set out to reduce the computing time necessary to obtain predictions from the mechanism.

We approached the problem of long computational time requirements from two directions. Initially, we sought to condense the mechanism to the smallest number of reactions required for accurate predictions. We identified critical reactions by means of a sensitivity analysis, and we subsequently eliminated insensitive reactions from the model. We also found that taking a flexible posture toward solving the representative rate expressions resulted in time savings. Our experience in working with the kinetic mechanism showed that computation time increased approximately linearly with the number of reactions, but quadratically with the number of coupled differential equations. Thus, we identified and verified species for which the pseudo-steady-state approximation is valid; this step permitted the replacement of three coupled differential equations by three coupled algebraic equations. Next, we took advantage of the fact that differential equations describing the concentrations of species that are formed as a result of chemical reactions but do not themselves enter into reactions can be solved independently of reacting species. We separated these so-called uncoupled species from the coupled species, eliminating three coupled differential equations, but adding three uncoupled differential equations.* Finally, we eliminated one species from the mechanism by algebraic manipulation, thus reducing the number of coupled algebraic equations by one.

Since the computing time was the single greatest hindrance to our incorporating the improved kinetic mechanism in the airshed model, we focused a great deal of attention on this problem. As a result, we condensed the mechanism in both its physical and mathematical structure to a form that is amenable to diffusion modeling. We discuss the details, methodology, and results of this program below.

2. Elimination of Unimportant Reactions in the General Kinetic Mechanism

During the period in which we first formulated and subsequently modified the lumped kinetic mechanism to achieve satisfactory predictions, we added and deleted several reactions. However, we made no attempt to eliminate unimportant

*Appendix A discusses the concept of coupled and uncoupled species.

reactions. Under EPA Contract 68-02-0580, we recently completed a sensitivity analysis of the kinetic mechanism; we used the results of this study to help us select possible reactions for elimination. Our goal in the sensitivity study was primarily to identify the "critical parameters" in the model, that is, those whose uncertainties most greatly influence the reliability of predictions. In essence, we calculated the rate of change in predictions with changes in the value of each rate constant, holding all other rate constants fixed at their standard values as a measure of sensitivity. Rate constants for which the measure has a high value correspond to sensitive reactions. Low values indicate insensitive reactions that may not have to be included in the model to make accurate predictions. Before proceeding with a discussion of our results, we describe the procedures and methods that we used in the sensitivity analysis.

The sensitivity study focused on a binary hydrocarbon-NO_x system (EPA Run 352) in which the initial concentrations were as follows:

Species	Concentration (ppm)
NO_2	0.07
NO	0.27
Propylene	0.265
n-Butane	3.29

We chose this particular experiment for several reasons:

- Both high and low reactivity hydrocarbons were present initially.
- The initial concentrations of total hydrocarbons and oxides of nitrogen were typical of those found in a polluted atmosphere.
- The accumulation of ozone reached an asymptotic level during the experiment.
- We had the run modeled with reasonable success in our evaluation study.

We performed the sensitivity analysis in the following manner. Using the nominal (or base) values for all parameters reported by Hecht et al. (1973) (see Tables 14 and 16 in that reference), we obtained base concentration-time profiles for propylene, n-butane, NO, NO_2, and O_3 by integrating the governing rate equations with each parameter at its nominal value. We then increased (and subsequently decreased) one of the parameters by a fixed percentage, holding all other parameters at their nominal values. We integrated the equations twice, once for each of the two new settings (+50 percent and -50 percent) of the selected input parameter. Repeating this process for each rate constant, we carried out, for n parameters, integrations for a base case and 2n parameter variations. Finally, for each of the 2n + 1 integrations, we determined the values of the sensitivity measures or "decision variables." We compared the magnitudes of the decision variables for each variation in a parameter with those computed for the base case, and ranked the sensitivities of the parameters by tabulating the magnitudes of the differences.

a. Measurement of Sensitivity

Central to a sensitivity analysis of a mathematical model is the meaningful quantification of changes in model predictions that result from perturbing the input parameters one at a time. As the measure of sensitivity for each parameter, we chose the absolute area between the concentration-time profile for the given parameter, with all parameters held at their base values, and the profile generated when the i-th parameter was perturbed by a fixed percentage. We denote these parameters as A_{NO_2}, A_{NO}, A_{O_3}, A_{olef} (propylene), and A_{para} (n-butane). Since Hecht et al. (1973) discussed these criteria in some detail, we review their appropriateness only briefly here.

The five indices (A_{NO_2}, A_{NO}, A_{O_3}, A_{olef}, and A_{para}) constitute continuous measurements of sensitivity determined experimentally over the entire period of simulation for each species. Mathematically, we represent this relationship as follows:

$$|A| = \int_0^{400\ \text{min}} |C_i(p,t) - C_i(p + \%p,t)|\ dt \quad ,$$

where

$|A|$ = the absolute area between the concentration-time profile predicted for the i-th species, with all parameters at their base values, and the profile obtained when one parameter is perturbed by a fixed percentage.

C = the concentration of the i-th chemical species.

i = the species index--NO_2, NO, O_3, olefin, paraffin.

p = the parameter that is being perturbed.

$\%$ = the percentage perturbation in p divided by 100.

If the perturbation of a given parameter greatly alters the time history of the i-th chemical species, indicating high sensitivity to that parameter, $|A_i|$ will have a large value. But if the concentration-time trace remains essentially unchanged, the predictions of the model will be insensitive to variations in the parameter under evaluation, and $|A_i|$ will be small.

To facilitate the comparison and ranking of their sensitivities, we varied all parameters in turn by the same fixed percentage. Some of the input parameters are very poorly characterized, having associated uncertainties of up to an order of magnitude, whereas the values of other parameters are known within an uncertainty of 10 percent. The comparative table of rate constants [Table 16 in Hecht et al. (1973)] suggests that a representative "degree of precision" among the several alternative experimental determinations or theoretical estimates available for any particular parameter is on the order of 50 percent. Therefore, we used that percentage as the magnitude of perturbation for the sensitivity calculations. However, because the precision bounds of the rate constant values for individual reaction rate constants vary greatly, our choice of the "range of perturbation" was arbitrary. The significance of the 50 percent figure rests only on its approximate division of the very uncertain from the less uncertain parameters. Table 1 ranks the reactions by the amount of uncertainty. (We define the uncertainty bound for a rate constant as the range within which the "true value" of the constant can be presumed to fall with confidence.)

Table 1

THE REACTIONS RANKED BY AMOUNT OF UNCERTAINTY

	Reaction	Percent Uncertainty
1.	$N_2O_5 + H_2O$	± 100 %
2.	$NO + HNO_3$	100
3.	$HNO_2 + HNO_3$	100
4.	$NO + NO_2 + H_2O$	100
5.	$HNO_2 + HNO_2$	100
6.	$HNO_2 + h\nu$	100
7.	$OH + NO_2$	100
8.	$OH + NO + M$	100
9.	$RO_2 + NO$	100
10.	$RCO_3 + NO$	100
11.	$RCO_3 + NO_2$	100
12.	$HO_2 + HO_2$	100
13.	$HO_2 + RO_2$	100
14.	$RO_2 + RO_2$	100
15.	$RO + NO_2$	80
16.	$ALD + h\nu$	70
17.	$RO + NO$	65
18.	$OLEF + OH$	45
19.	$O + NO_2 + M$	40
20.	$O_3 + NO_2$	40
21.	$NO_3 + NO$	40

Table 1 (Concluded)

Reaction	Percent Uncertainty
22. PARA + OH	± 40 %
23. ALD + OH	40
24. RO + O_2	40
25. PARA + O	35
26. HO_2 + NO	30
27. OLEF + O_3	30
28. O + NO_2	25
29. NO_2 + hv	20
30. O_3 + NO	20
31. NO_3 + NO_2	20
32. H_2O_2 + hv	20
33. OLEF + O	20
34. O + NO + M	15
35. O + O_2 + M	10
36. N_2O_5	5

The small amount of experimental data available upon which to base our estimates limited the procedure we followed to estimate the uncertainty bound for each rate constant. In essence, we calculated the percentage deviation of the highest and lowest expected values of each rate constant, having surveyed the literature to find independent determinations of these rate constants. Thus, the so-called estimate of uncertainty bounds is, in fact, simply an indication of the degree of agreement (or more precisely, the disagreement) among a number of independent determinations of the same rate parameter. In three situations, this "definition" does not apply:

- If only a single determination was made for a given rate constant, the uncertainty bound is an indication of the precision of the experiment.
- Since photolysis rate constants (e.g., k_1) must be determined *in situ* for a smog chamber experiment, the bounds are an indication of the reliability of the experimental method.
- The uncertainty estimate for k_{37} ($HO_2 + HO_2$) was taken from Lloyd (1974), who reviewed the reactions of the HO_2 radical.

Because of the imprecision of these estimates, we assumed that the uncertainty bounds were symmetric about the nominal value. Therefore, although we estimated the uncertainties associated with several parameters to be ±100 percent, the true upper bound may be considerably higher.

b. Results of the Sensitivity Analysis

For the purpose of ranking the parameters by sensitivity, we averaged the values of the area indices calculated for plus and minus percentage variations in the parameters to obtain a single characteristic value. Although this procedure facilitated ranking, some information was lost in the process. Because each of the measures of sensitivity is based on the difference between nominal

and perturbed concentration-time profiles, the magnitude of each difference, in general, depends upon the degree of perturbation (e.g., 10, 25, 50 percent). Because the equations governing the kinetics are nonlinear, the values of the sensitivity measures typically are not identical for plus and minus perturbations in a given parameter. But, in examining the values of the "area" sensitivity measures for plus and minus perturbations, we found them to agree sufficiently well to justify using their average values to rank the parameters.

Since we were interested chiefly in quantifying the overall sensitivity (or insensitivity) associated with each reaction in the model, the use of an indicator based on the changes in the predictions of several species was appropriate. Thus, we combined the five area sensitivity measures into a single scalar, which we term the "sensitivity." We defined the synthesized sensitivity measure for each rate constant as follows:

$$\text{Sensitivity}_j = \sum_{i=1}^{5} \frac{w_i A_{ij}}{A_{\max_i}} \quad ,$$

where

- i = 1, 2, 3, 4, and 5 refer to the average area sensitivity measures for NO_2, NO, O_3, olefin, and paraffin, respectively.
- j = the number of the reaction rate constant in the kinetic mechanism.
- w_i = the weighting of the individual measure in the combined sensitivity scalar. (We weighted each of the five measures equally because, in developing and evaluating the general kinetic mechanism, we were interested in predicting the concentration-time behavior of each of these species with equal accuracy. However, we might have chosen different weights if our goals were different. For example, to predict oxidant and NO_x for evaluating alternative emission control strategies, we might have weighted O_3, NO, and NO_2 more heavily.)

A_{ij} = the average area measurement determined for the i-th criterion and the j-th reaction.

A_{max_i} = the maximum value of the i-th criterion observed for any of the reactions. (Dividing by the maximum value scales each of the arrays of the five individual area measurements between zero and one.)

Table 2 presents the values of this "sensitivity" index (seventh column), along with the values of the five averaged individual area indices. Table 3 ranks the reactions according to the combined sensitivity. As Table 3 shows, the following rate constants, presented in the order of decreasing sensitivity, display the greateast overall sensitivity:

Rate Constant	Identification
k_1	NO_2 photolysis
k_{28}	Oxidation of n-butane by OH
k_{20}	Oxidation of NO by HO_2
k_3	Reaction of O_3 with NO
k_{16}	Photolysis of HNO_2
k_{23}	Oxidation of propylene by O_3
k_{29}	Photolysis of aldehydes
k_{24}	Reaction of OH with propylene

Just as there are critical parameters in the model whose values must be determined with certainty, some parameters are almost insensitive. Large variations in the magnitude of these parameters result in small changes in model predictions. By identifying those reactions that contribute minimally to the total predicted response, the sensitivity analysis provides the basis for eliminating reactions from the mechanism. Removal, of course, is subject to further limited individual testing of each reaction over a range of initial conditions and bounds of uncertainty.

Table 2

INDIVIDUAL AREA AND SENSITIVITY INDICES

NO.	A(NO2)	A(NO)	A(O3)	A(OLEF)	A(PARA)	SENSITIVITY.
1	4.0999994E 00	3.0100000F-01	4.8099991E 01	5.9399996E 00	1.1099999E 01	6.0233879E-01
2	2.9399997E-01	1.5199995E-01	5.8699995E-01	3.7799996E-01	7.1099997E-01	4.2636652E-02
3	3.5400000E 00	2.3799998E-01	4.2899994E 01	4.4599991E 00	9.1799994E 00	5.0078332E-01
4	9.4299972E-02	5.8300000E-02	1.5199995E-01	3.4999996E-02	6.1699998E-02	1.0480803E-02
5	1.9699997E-01	4.7399998E-02	6.3000000E-01	2.5999997E-02	3.0299997E-01	1.5842065E-02
6	9.4299972E-02	5.8399998E-02	1.4699996E-01	3.4299999E-02	6.0699999E-02	1.0441024E-02
7	3.4399996E 00	1.5199995E-01	1.2000000E 01	7.7999997E-01	1.9899998E 00	1.8804300E-01
8	3.5099993E 00	9.3699992E-02	5.2399998E 00	2.8599995E-01	5.9499997E-01	1.2817216E-01
9	3.1999998E 00	8.8999987E-02	4.5699997E 00	2.4199998E-01	4.9599999E-01	1.1538500E-01
10	3.4799995E 00	9.3499959E-02	5.1799994E 00	2.8399998E-01	5.8999997E-01	1.2708902E-01
11	2.6999998E 00	9.5499992E-02	3.5699997E 00	1.3000000E-01	3.6199999E-01	9.5649123E-02
12	2.2599993E 00	7.1199954E-02	4.1699991E 00	3.0299997E-01	1.2500000E 00	9.8682284E-02
13	9.9599999E-01	5.7499997E-02	8.6199999E-01	2.6499998E-02	4.8899996E-01	3.8531106E-02
14	2.4799995E 00	1.2599993E 00	4.0699997E 00	1.4899998E 00	2.2900000E 00	2.7009088E-01
15	1.6799994E 00	7.2599995E-01	3.0799999E 00	1.0999994E 00	2.0199995E 00	1.7816830E-01
16	5.0799999E 00	1.9299994E 00	7.5000000E 00	2.7999992E 00	5.1599998E 00	4.7975492E-01
17	3.7799997E 00	1.0499992E 00	6.8199987E 00	2.3799992E 00	5.4899998E 00	3.4641325E-01
18	2.5599995E 00	1.1999998E 00	3.9299994E 00	1.4499998E 00	2.0299997E 00	2.6154286E-01
19	0.0	0.0	0.0	0.0	0.0	0.0
20	8.4699993E 00	6.4899999E-01	2.1699997E 01	3.2799997E 00	6.7199993E 00	5.1467425E-01
21	1.3699999E 00	8.7499976E-02	1.4699993E 00	2.3099995E-01	2.0499992E 00	7.3833704E-02
22	3.2299995E-01	1.2799996E-01	5.9899998E-01	3.0100000E-01	1.6999996E-01	3.3491254E-02
23	6.9899998E 00	4.5400000E-01	4.1199999E 00	7.1099997E 00	1.1199999E 00	4.4005167E-01
24	2.2399998E 00	8.2699996E-01	7.7199993E 00	5.4199991E 00	5.0999994E 00	3.7242830E-01
25	0.0	0.0	0.0	0.0	0.0	0.0
26	0.0	0.0	0.0	0.0	0.0	0.0
27	8.2799971E-02	4.9599998E-02	8.6899996E-02	1.6500000E-02	7.9099953E-02	8.6847395E-03
28	5.6199999E 00	1.5999994E 00	1.2500000E 01	1.8799996E-01	2.0699997E 01	5.5576986E-01
29	6.6099997E 00	8.7399995E-01	1.7000000E 01	2.4799995E 00	4.3899994E 00	4.2951244E-01
30	1.5799999E 00	7.5099945E-02	8.6499996E 00	1.3499994E 00	7.7999992E 00	1.9439411E-01
31	1.0400000E 00	7.9399943E-02	3.2099991E 00	1.7299998E-01	1.1399996E-01	5.2100249E-02
32	9.1899997E-01	1.7499995E-01	7.7599993E 00	7.1499997E-01	3.2099998E-01	9.5314741E-02
33	1.0499992E 00	1.1099994E-01	8.6499996E 00	7.3699999E-01	3.3099997E-01	9.6192002E-02
34	6.1299998E-01	3.4599996E-01	3.5400000E 00	6.9699997E-01	1.0299997E 00	9.4606638E-02
35	3.8299996E-01	1.2399995E-01	2.2699995E 00	4.0099996E-01	6.1999995E-01	4.8602294E-02
36	1.7699999E-01	1.0799998E-01	4.5599997E-01	1.2899995E-01	1.6499996E-01	2.2490099E-02
37	4.1499996E 00	2.7099997E-01	1.0200000E 01	1.4799995E 00	3.3099995E 00	2.4209946E-01
38	2.0400000E-01	5.8300000E-02	4.3599999E-01	1.7199997E-02	4.1499998E-02	1.3556119E-02
39	3.1699997E-01	6.2099997E-02	9.4499999E-01	2.5099996E-02	7.1799994E-02	1.9249547E-02

Table 3

THE REACTIONS RANKED BY SENSITIVITY

	Reaction	Sensitivity
1.	$NO_2 + h\nu$	0.60
2.	PARA $\pm$ OH	0.56
3.	$HO_2 + NO$	0.51
4.	$O_3 + NO$	0.50
5.	$HNO_2 + h\nu$	0.48
6.	OLEF + O_3	0.44
7.	ALD + $h\nu$	0.43
8.	OLEF + OH	0.37
9.	$OH + NO_2$	0.35
10.	NO $\pm$ $NO_2 + H_2O$	0.27
11.	OH + NO	0.26
12.	$HO_2 + HO_2$	0.24
13.	ALD $\pm$ OH	0.19
14.	$O_3 + NO_2$	0.19
15.	$HNO_2 + HNO_2$	0.18
16.	$NO_3 + NO$	0.13
17.	N_2O_5	0.13
18.	$NO_3 + NO_2$	0.12
19.	$NO + HNO_3$	0.10
20.	$RCO_3 + NO_2$	0.10
21.	$N_2O_5 + H_2O$	0.10
22.	$RCO_3 + NO$	0.10

Table 3 (Concluded)

	Reaction	Sensitivity
23.	$RO + O_2$	0.09
24.	$H_2O_2 + h\nu$	0.07
25.	$RO_2 + NO$	0.05
26.	$RO \pm NO_2$	0.05
27.	$O + O_2 + M$	0.04
28.	$HNO_2 + HNO_3$	0.04
29.	OLEF + O	0.03
30.	RO + NO	0.02
31.	$RO_2 + RO_2$	0.02
32.	$O + NO_2$	0.02
33.	$HO_2 + RO_2$	0.01
34.	O + NO + M	0.01
35.	$O + NO_2 \pm M$	0.01
36.	PARA + O	0.01

Reactions that could potentially be removed from the mechanism, based on the results of the sensitivity analysis, appear in the lower portion of Table 3. These reactions included the oxygen atom oxidation of the species tabulated below:

Species	Reaction
Paraffins	k_{27}
NO	k_4
NO_2 in the presence of a third body (M)	k_6
NO_2 second order reaction	k_5
Olefins	k_{22}

Other candidates included the following:

Species	Reaction
HNO_2-HNO_3	k_{13}
RO-NO	k_{36}
RO_2-HO_2	k_{38}
RO_2-RO_2	k_{39}

Finally, we included among the candidates for potential elimination the reaction between NO and HNO_3 (k_{12}). After carrying out the sensitivity calculations, we learned that the experimental value of this rate constant was several orders of magnitude less than our earlier estimate; this change sharply decreased the sensitivity of the reaction.

c. Elimination of Insensitive Reactions

We based the tentative conclusions reached thus far largely on the averaged sensitivity criteria characterizing a single set of initial reactant concentrations. If we were to repeat the calculations using only half the initial hydrocarbon and twice the initial NO_x used in the present study, we would expect to

find the order of parameter ranking to be somewhat different than that given in Table 3. Thus, we had to scrutinize each reaction carefully prior to its elimination; our criterion for elimination was that the reaction be "insensitive" (a term defined quantitatively shortly) over the range of initial concentrations of interest, as well as over the uncertainty bounds of the reaction rate constant (Table 1).

We chose three EPA smog chamber runs as a representative set of initial concentrations and ratios over which to evaluate the reactions for possible removal. As shown in Table 4, two of these runs are binary hydrocarbon systems; in the other experiment, propylene was the only hydrocarbon present. These three runs span a total hydrocarbon-to-NO_x initial ratio of 0.7 to 10.5 and a reactive hydrocarbon*-to-NO_x initial ratio of 0.2 to 0.8. Air quality data obtained in Los Angeles indicate that the ratios for polluted air there are often within these ranges. (In the atmosphere, the ratio can vary with both location and time of day.)

Table 4

CHARACTERISTICS OF THE SMOG CHAMBER RUNS

EPA Run	Concentrations (ppm)				Total $[HC]/[NO_x]$	High Reactivity $[HC]/[NO_x]$
	$[n\text{-butane}]_0$	$[propylene]_0$	$[NO]_0$	$[NO_2]_0$		
329	--	0.24	0.29	0.06	0.7	0.7
333	3.40	0.23	1.25	0.08	2.7	0.2
352	3.29	0.26	0.27	0.07	10.5	0.8

We considered reactions to be "insensitive" if, upon their removal individually and as a group, the remaining set of reactions was able to predict the following within 10 percent of the values predicted by the complete mechanism:

---

*Defined as propylene.

- The time to the NO_2 peak (T)
- The height of the NO_2 peak (H)
- The magnitude of the ozone peak (M).

These three scalars, all of which can be easily quantified, are of interest because the onset of formation of many secondary products formed in the atmosphere accompanies the peak concentration of NO_2 and because the intensity of smog is often associated with the ozone and NO_2 concentrations. Thus, T, H, and M constitute three major indicators of smog formation and severity. Although the choice of the 10 percent range was arbitrary, this value is lower than the uncertainty bounds associated with the experimental chamber data used to evaluate and "tune" the model. Thus, we felt that the choice was reasonable.

Consideration of the sensitivity values associated with each rate constant led us to select 10 reactions for possible removal from the mechanism, Of these, we found that only six could actually be eliminated based on the criteria cited above:

Species	Reaction
$O + NO$	k_4
$O + NO_2 + M$	k_6
$NO + HNO_3$	k_{12}
$HNO_2 + HNO_3$	k_{13}
$RO_2 + HO_2$	k_{38}
$RO_2 + RO_2$	k_{39}

As shown in Table 5, the values of T, H, and M after removal of these six reactions were within 10 percent of the values before the reactions were eliminated. Several other reactions could have been removed for one or two of the EPA runs, but not for all three. However, since their elimination would have limited the applicability of the kinetic mechanism to a narrower range of initial concentrations and ratios, we did not drop them.

Table 5

VALUES OF T, H, AND M BEFORE AND AFTER REMOVAL OF THE SIX REACTIONS

EPA Run	Time to the NO_2 Peak (T) (minutes)		Concentration (ppm)			
			Height of the NO_2 Peak (H)		Magnitude of the Ozone Peak (M)	
	Before	After	Before	After	Before	After
329	87	86	0.25	0.25	0.39	0.40
333	285	281	0.75	0.70	0.40	0.41
352	65	70	0.25	0.25	0.50	0.52

The conclusions we reached during this study were based on the lumped general mechanism. If this mechanism proves to be fundamentally inadequate, the sensitivity calculations should be repeated with the corrected mechanism, and reactions that we eliminated should be examined again to judge their sensitivity in the environment of the corrected mechanism.

3. Further Modifications To Reduce Computing Requirements

Although the elimination of unnecessary reactions saves computing time, the condensation discussed thus far focused primarily on giving prominence to the important reactions in the mechanism. Significantly greater reductions in computing time can be obtained by varying the mathematical representation of the chemical mechanism. From a purist's point of view, a series of differential rate equations most accurately represents changes in the concentrations of reactants with time. (Ideally, one would solve these equations analytically. We used numerical methods to solve the equations on the computer, but these techniques were evaluated using test systems of equations for which analytical solutions were available.) Over the years, scientists have used the following approximations and simplifications to facilitate the solution of complex kinetic systems:

- Recognizing the fundamental mathematical difference between the differential equations of species that are produced but do not enter into reactions and those of species that do react. The differential equations for reactants are often mathematically coupled and must therefore be solved simultaneously. If these coupled species have vastly different characteristic times of reaction, the equations become "stiff" numerically and must be solved using very small time steps to preserve accuracy. In contrast, the differential equations for species that do not react are not coupled and can be solved accurately one at a time using a method as simple as Simpson's rule.
- Applying the steady-state approximation. If the concentration of a species equilibrates rapidly (relative to many other species in the system), one can assume that the summation of the rate terms for formation and consumption of the species is identically zero. This assumption reduces the differential equation to an algebraic equation.
- Combining second-order reactions into higher order reactions. In some special cases, two or more reactions can be combined into a single reaction, with the elimination of an intermediate as well.

The following subsections summarize the results of applying each of these techniques to the lumped kinetic mechanism.

a. Treatment of Uncoupled Species

In a system containing propylene, n-butane, NO_x, and air, four species form that do not react subsequently: nitric acid, peroxyacylnitrates, organic nitrites, and organic nitrates. Because these products do not enter into reactions with other species present in the system, we can uncouple and solve the differential equations for each of the four species independently.

b. Invocation of the Steady-State Approximation

In earlier work, we demonstrated the validity of the steady-state approximation for O, OH, RO, and NO_3 (Hecht et al., 1973). Recently, we justified the application of the approximation to obtain predictions of the concentrations of HO_2, N_2O_5, RO_2, and RCO_3. To demonstrate the validity of the approximation for any given species, we compared the concentration-time profile for the species predicted by an algebraic description with that predicted by a differential expression. In so doing, we found that the profiles generated using the two mathematical representations agreed to within 0.1 percent for these species. Thus, we eliminated four additional coupled differential equations, which were replaced by four coupled algebraic equations.

c. Combination of Reactions into a Single Higher Order Reaction

The species N_2O_5 exists in equilibrium with NO_2 and NO_3:

$$NO_3 + NO_2 \overset{k_I}{\rightarrow} N_2O_5 \quad .$$

$$N_2O_5 \overset{k_{II}}{\rightarrow} NO_3 + NO_2 \quad .$$

The only important reaction of N_2O_5 other than Reaction II is hydrolysis to form nitric acid, a stable product in the mechanism:

$$N_2O_5 + H_2O \overset{k_{III}}{\rightarrow} 2HNO_3 \quad .$$

If we assume that N_2O_5 is in a steady-state (we have established the validity of this assumption) we can combine these reactions into the single third-order reaction:

$$NO_3 + NO_2 + H_2O \overset{k_{IV}}{\rightarrow} 2HNO_3 \quad ,$$

having the rate constant

$$k_{IV} = \frac{k_I \, k_{III}}{k_{II} + k_{III} \, H_2O} \quad .$$

The combination of these three reactions eliminates N_2O_5 as a species, thereby saving one algebraic equation and removing a net total of two reactions from the mechanism.

4. The Present Status of the Mechanism

As a result of the procedures described thus far, we added nine reactions to the mechanism. Thus, a total of 31 reactions are necessary to represent the chemistry of a system of paraffins, olefins, NO_x, CO and air. In addition, to facilitate usage of the mechanism in the airshed model, we included two additional reactions involving O and OH reactions with aromatics. It is to be understood, however, that this is an interim treatment of the chemistry involving aromatics and is subject to revision at such time as a more suitable mechanism is developed. Table 6 presents the revised mechanism. Of the 25 species included in the mechanism, 10 are represented by coupled differential equations, 7 by algebraic equations, and 4 are constant, as shown in Table 7. Although the computing time associated with individual sets of initial conditions varies because of changes in the stiffness of the system of equations, we found that incorporating the changes presented here reduced the required computing time by approximately 50 percent over that required previously (Hecht et al. 1973). This saving is significant enough to justify the replacement of the simplified 15-step mechanism by the more accurate lumped kinetic mechanism as the kinetics module in the airshed dispersion model.

Table 6

A LUMPED KINETIC MECHANISM FOR PHOTOCHEMICAL SMOG

$NO_2 + h\nu \xrightarrow{1} NO + O$	NO_2-NO-O_3 Cycle
$O + O_2 + M \xrightarrow{2} O_3 + M$	
$O_3 + NO \xrightarrow{3} NO_2 + O_2$	
$O + NO_2 \xrightarrow{4} NO + O_2$	
$O_3 + NO_2 \xrightarrow{5} NO_3 + O_2$	Chemistry of NO_3
$NO_3 + NO \xrightarrow{6} 2NO_2$	
$NO_3 + NO_2 + H_2O \xrightarrow{7} 2HNO_3$	
$NO + NO_2 + 2H_2O \xrightarrow{8} 2HNO_2 + H_2O$	Chemistry of HNO_2
$2HNO_2 \xrightarrow{9} NO + NO_2 + H_2O$	
$HNO_2 + h\nu \xrightarrow{10} OH + NO$	
$OH + NO_2 \xrightarrow{11} HNO_3$	Important Reactions of OH with Inorganic Species
$OH + NO \xrightarrow{12} HNO_2$	
$OH + CO + (O_2) \xrightarrow{13} CO_2 + HO_2$	
$HO_2 + NO \xrightarrow{14} OH + NO_2$	Oxidation of NO by HO_2
$HO_2 + HO_2 \xrightarrow{15} H_2O_2 + O_2$	Hydroperoxy Radical Termination
$H_2O_2 + h\nu \xrightarrow{16} 2OH$	Photolysis of H_2O_2

Table 6 (Concluded)

$$HC_1 + O \xrightarrow{17} ROO + \alpha RC(=O)OO + (1-\alpha)HO_2$$

$$HC_1 + O_3 \xrightarrow{18} RC(=O)OO + RO + HC_3$$

$$HC_1 + OH \xrightarrow{19} ROO + HC_3$$

$$HC_2 + O \xrightarrow{20} ROO + OH$$

$$HC_2 + OH \xrightarrow{21} ROO + H_2O$$

$$HC_3 + h\nu \xrightarrow{22} \beta ROO + (2-\beta)HO_2$$

$$HC_3 + OH \xrightarrow{23} \beta RC(=O)OO + (1-\beta)HO_2 + H_2O$$

$$HC_4 + O \xrightarrow{24} ROO + OH$$

$$HC_4 + OH \xrightarrow{25} ROO + H_2O$$

Organic Oxidation Reactions

HC_1 = Olefins
HC_2 = Paraffins
HC_3 = Aldehydes
HC_4 = Aromatics

$$ROO + NO \xrightarrow{26} RO + NO_2$$

$$RC(=O)OO + NO + (O_2) \xrightarrow{27} ROO + NO_2 + CO_2$$

$$RC(=O)OO + NO_2 \xrightarrow{28} RC(=O)OONO_2$$

$$RO + O_2 \xrightarrow{29} HO_2 + HC_3$$

$$RO + NO_2 \xrightarrow{30} RONO_2$$

$$RO + NO \xrightarrow{31} RONO$$

Reactions of Organic Free Radicals with NO, NO_2, and O_2

Table 7

TYPE OF MATHEMATICAL REPRESENTATION REQUIRED TO PREDICT CONCENTRATIONS OF SPECIES IN THE GENERAL MECHANISM

Coupled Differential Equations	Uncoupled Differential Equations	Steady-State Algebraic Equations	Constant
NO_2	HNO_3	O	M
NO	PAN	NO_3	O_2
O_3	RNO_2	OH	H_2O
HNO_2	RNO_3	HO_2	CO_2
H_2O_2		RO	
CO		RO_2	
Olefins		RCO_3	
Paraffins			
Aldehydes			
Aromatics			

C. DEVELOPMENT OF A KINETIC MECHANISM DESCRIBING SO_2 REACTIONS AND SULFURIC ACID FORMATION

During the past decade, air pollution investigators have focused a substantial amount of scientific attention on SO_2, the precursor of sulfuric acid and sulfate, because of its effects on visibility and health. They observed that the oxidation of gaseous SO_2 occurs both through reactions with gas phase oxidants and through reactions with liquid aerosol droplets. They demonstrated that the addition of SO_2 to a reactor in which atmospheric concentrations of organics and NO_x in air are being irradiated (i.e., a smog simulation experiment)

results in a substantial decrease in visibility due to the formation of a sulfuric acid aerosol. And they established that SO_2 is oxidized in fog. In this section, we review current knowledge and speculation concerning the oxidation of SO_2 through reactions that occur in the gas phase and in solution. Since Bufalini (1971) has extensively reviewed the oxidation of SO_2 in polluted air, our discussion focuses primarily on more recent results. We conclude this section with a discussion of our efforts to model a set of dynamic organic-NO_x-SO_2 smog chamber experiments and a summarization of our future plans to simulate the chemistry of SO_2.

1. The State of the Art of Gas Phase SO_2 Kinetics

Until recently, air pollution SO_2 research focused primarily on the qualitative and semi-quantitative characterization of the interaction of SO_2 with components of smog. Scientists have been particularly interested in evaluating the effect of SO_2 on oxidant levels and visibility in simulated smog (irradiated mixtures of organics, NO_x, SO_2, and air); they have used environmental chambers extensively for this purpose. In these experiments, they observed that the concentration of SO_2 slowly diminishes with time. However, most of the early (prior to 1970) experiments were not controlled carefully enough to allow an accurate estimate to be made of the rate of SO_2 oxidation due to gas phase chemical reactions. Variations in relative humidity, the reactivity of chamber surfaces, and the accuracy of the analytical instrumentation all served to introduce imprecision into the data. And, by their very nature, smog chamber experiments provide minimal insight into the actual individual reactions by which SO_2 is oxidized in smog. Observations are limited to macroscopic changes in the concentrations of the major reactants and products with time. The results of recent chamber experiments and detailed kinetic studies of elementary reactions have provided sufficient insight so that we can now postulate a provisional mechanism for the oxidation of SO_2 by homogeneous gas phase reactions. We discuss this 10-step mechanism briefly below.

Experimental studies have indicated that peroxy radicals, diradicals, and hydroxyl radicals are the most potent gas phase oxidizing agents with respect to SO_2 in photochemical smog. Davis et al. (1973) obtained a preliminary measurement of the rate constant for the reaction

$$HO_2 + SO_2 \xrightarrow{S_1} OH + SO_3$$

of 0.45 $ppm^{-1}min^{-1}$. The observed rate is sufficiently high to suggest that the HO_2-SO_2 reaction is important at about the time that NO_2 reaches its maximum values and O_3 begins to accumulate. Studies of SO_2 in smog simulation experiments have shown that this is the time at which the oxidation rate of SO_2 is greatest. HO_2 is, of course, generally regarded as the principal oxidant of NO:

$$HO_2 + NO \rightarrow OH + NO_2 \quad .$$

Because of the functional similarity of peroxyalkyl and peroxyacyl radicals to HO_2, it does not seem unreasonable to presume that these three species would undergo the same chemical reactions with a given reductant. Both RO_2 and RCO_3 apparently oxidize NO through a reaction similar to the HO_2-NO reaction:

$$RO_2 + NO \rightarrow RO + NO_2 \quad ,$$

$$R\underset{\underset{O}{\|}}{C}OO + NO \rightarrow R\underset{\underset{O}{\|}}{C}O + NO_2 \quad .$$

Although the rate constants for these reactions are not known yet, the reactions are thought to proceed more rapdily than the HO_2-NO reaction. We feel that, because of the analogies between the structure and behavior of HO_2, RO_2, and RCO_3, the last two species oxidize SO_2 at a rate somewhat faster than that of HO_2. We therefore estimate that $k_{S_2} = k_{S_3} = 1$ $ppm^{-1}min^{-1}$:

$$RO_2 + SO_2 \xrightarrow{S_2} RO + SO_3 \quad ,$$

$$\underset{\underset{O}{\|}}{RCOO} + SO_2 \xrightarrow{S_3} \underset{\underset{O}{\|}}{RCO} + SO_3 \quad .$$

Cox and Penkett (1972) observed that SO_3 forms with reasonable rapidity when a system containing O_3, olefin, and SO_2 react, and they postulated that diradicals, products of the O_3-olefin reaction, are the species that oxidize SO_2:

$$R_2\dot{C}O\dot{O} + SO_2 \xrightarrow{S_4} R_2CO + SO_3 \quad .$$

Since diradicals apparently form in smog only as a result of O_3-olefin reactions, this reaction, depending on its rate, may be less important that Reactions S_1 through S_3 in polluted air, where normally less than 20 percent of the organics are olefinic. O'Neal and Blumstein (1973) recently reconsidered the mechanism of the O_3-olefin reaction, and they feel that the intermediate complex of the reaction may decompose to form free radicals, including H. A hydrogen atom formed in this manner could combine with O_2 to form HO_2, which is known to oxidize SO_2 (Reaction S_1). Thus, in the Cox and Penkett experiments, HO_2, rather than a diradical, may have been the specie generated by the O_3-olefin reaction that oxidized SO_2. Consequently, Reaction S_4 is very speculative.

Recent measurements of the OH-SO_2 rate constant have suggested that the reaction

$$OH + SO_2 \xrightarrow{S_5} HO\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{S}}$$

may be an important loss mechanism for SO_2 in photochemical smog. Cox (1974) obtained a value of 850 $ppm^{-1}min^{-1}$ under atmospheric conditions, and Castleman et al. (1974) found the value to be 600 $ppm^{-1}min^{-1}$.

One can only speculate as to subsequent reactions of $HOSO_2$ in smog [see, for example, Smith and Urone (1974) and references therein]. We offer one possible reaction scheme here, which is largely an analogy to reactions of organic free radicals.

We assume that O_2 adds to the $HOSO_2$ radical

$$HOSO_2 + O_2 \xrightarrow{S_6} HO\overset{\overset{O}{|}}{S}O_2\overset{|}{O}$$

and that this peroxy radical can oxidize nitric oxide:

$$\overset{\overset{O}{|}}{HOSO_2}\overset{|}{O} + NO \xrightarrow{S_7} \overset{\overset{O}{|}}{HOSO}\overset{|}{O} + NO_2 \quad .$$

The $HOSO_3$ might abstract a hydrogen atom from an organic molecule or from an HO_2 radical, forming H_2SO_4 directly:

$$\overset{\overset{O}{|}}{HOSO}\overset{|}{O} + RH \xrightarrow{S_8} \overset{\overset{O}{|}}{HOSOH}\overset{|}{O} + R\cdot \quad ,$$

$$\overset{\overset{O}{|}}{HOSO}\overset{|}{O} + HO_2 \xrightarrow{S_8} \overset{\overset{O}{|}}{HOSOH}\overset{|}{O} + O_2 \quad .$$

Or the $HOSO_3$ might undergo a unimolecular decomposition reaction to form OH and SO_3:

$$\overset{\overset{O}{|}}{HOSO}\overset{|}{O} \xrightarrow{S_9} HO + SO_3 \quad .$$

Sulfur trioxide is, of course, the anhydride of sulfuric acid:

$$SO_3 + H_2O \xrightarrow{S_{10}} H_2SO_4 \quad .$$

Although we can set forth other reactions for the HSO_x radicals describing their behavior in the presence of NO_2 and other reactive species, we cannot substantiate such reactions (including S_7 through S_{10}) with the results of experiments that have been carried out to date.

Although we did not include several reactions in the core mechanism (S_1 through S_{10}) for the oxidation of SO_2, some comments about them are in order. The O-SO_2 reaction, for example,

$$O + SO_2 + M \rightarrow SO_3 + M \quad ,$$

has a reasonably high rate constant but is, nevertheless, slow because of the extremely low concentration of oxygen atoms in smog. The direct photolysis of SO_2 in otherwise clean air results in the slow disappearance of SO_2, but the rate of SO_2 loss is not comparable to the rates observed in polluted air. Wilson and Levy (1969) showed that NO_2 reacts very slowly with SO_2. Calvert (1975) determined upper limits for the rates of reaction of NO_3 and N_2O_5 with SO_2 of 10^{-5} $ppm^{-1}min^{-1}$ and 6×10^{-8} $ppm^{-1}min^{-1}$, respectively. Consequently, both of the reactions are of negligible importance in photochemical smog. In addition, Calvert found, in agreement with others, that the O_3-SO_2 reaction is very slow, having a rate constant of about 10^{-8} $ppm^{-1}min^{-1}$. In summary, each of this last group of reactions results in the slow oxidation of SO_2 to SO_3. Although we could have included in the core SO_2 mechanism, the results of kinetic studies of these reactions suggest that their combined contribution to the total predicted loss rate of SO_2 is minor.

Because kineticists have studied in detail only two of the ten elementary reactions included in the mechanism for the gas phase oxidation of SO_2 the mechanism has an extremely high level of uncertainty. EPA is presently funding investigations of some of these reactions; therefore, more accurate values

of the corresponding rate constants may be forthcoming in the near future. Despite the uncertainty, we attempted to test this mechanism using smog chamber data. (Section C-3 describes these efforts.) However, we found that the chamber data were inadequately characterized in many important respects and, consequently, were unusable.

2. The State of the Art Regarding the Oxidation of SO_2 in Solution

A large percentage of the volume of aerosol particles consists of water. Gas phase borne SO_2 can dissolve in these particles, especially in the environment of a stack plume, where the SO_2 concentration is often high. Once SO_2 is dissolved, both direct and catalyzed reactions apparently lead to the oxidation of SO_2 to sulfate. However, it is not now possible to assess the relative importance of these competitive pathways under conditions of photochemical smog formation. Certainly, the contribution of these two types of reactions to the total SO_2 oxidation rate in solution depends on such factors as aerosol size, oxidant concentration, catalyst concentration, species of oxidant present, catalyst species present, and other chemical species in the droplet that might enter into reactions with the oxidants or the catalysts. In this section, we identify possible important direct and catalyzed reactions in solution and attempt to explain the mechanisms of these reactions.

a. Reactions of SO_2 in Solution with Oxidants Produced in the Gas Phase

Investigators have studied the reactions of SO_2 in solution with three products of photochemical smog: NO_2, O_3, and H_2SO_4.

$$NO_2 + SO_2 \xrightarrow[H_2O\ (\ell)]{} NO + SO_3 \quad .$$

$$O_3 + SO_2 \xrightarrow[H_2O\ (\ell)]{} O_2 + SO_3 \quad .$$

$$H_2SO_4 + SO_3 \xrightarrow[H_2O\ (\ell)]{} H_2SO_3 + SO_3 \quad .$$

The first of these reactions (Wilson et al., 1972) and the last (Gerhard and Johnstone, 1955) proceed very slowly. Ozone and SO_2, however, react rapidly in the presence of liquid water, and the reaction probably occurs in solution (Wilson and Levy, 1969). The rate of this aqueous reaction contrasts sharply with that of the gas phase O_3-SO_2 reaction, which is extremely slow. Thus, the reaction between SO_2 and O_3 could be significant in aerosol particles, and measurement of the rate constant of the reaction in a simulated atmospheric environment is important.

b. Direct and Catalyzed Reactions of SO_2 with Metal Ions in Solution

As reported in the literature, SO_2 is slowly oxidized when dissolved in water (probably through a direct reaction with dissolved oxygen); however, the presence of metal ions, such as Mn^{+2}, Fe^{+2}, Fe^{+3}, Ni^{+2}, and Cu^{+2}, in the solution accelerates the oxidation rate of SO_2 substantially (Urone and Schroeder, 1969; Bufalini, 1971). The metal ions can interact chemically with SO_2 in either or both of two ways: through direct reaction with SO_2 or through catalysis of the (dissolved) air oxidation of SO_2. We now turn to a discussion of each of these classes of reactions.

Direct Oxidation-Reduction Reactions Between Metal Ions and SO_2. An examination of half-cell potentials provides a straightforward means of evaluating whether a given reaction is expected to occur on the basis of purely thermodynamic considerations. In the context of this discussion, we are particularly interested in learning whether oxidation-reduction couples (i.e., reactions) between SO_2 and metal ions result in the oxidation of SO_2 to SO_3 (or $SO_4^=$) and the reduction of metal ions to some lower oxidation state*.

We first observe that according to predictions, O_2, O_3, and H_2O_2 should all oxidize SO_2. Noting that the SO_2-$SO_4^=$ half-reaction is:

*We used reduction potentials for these calculations; thus, for a reaction couple to be favored, the combined potential must be positive.

$$SO_2^\circ \times H_2O \rightarrow SO_4^{-2} + 4H^+ + (x - 2)\, H_2O + 2e^- \quad , \quad E^\circ = -0.17\ V \quad ,$$

we see that SO_2 is oxidized as a result of any of the following half-reactions:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad , \quad E^\circ = 0.682\ V \quad ,$$

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \quad , \quad E^\circ = 2.07\ V \quad ,$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad , \quad E^\circ = 1.776\ V \quad .$$

The coupled potentials are, therefore, positive by 0.51 V, 1.90 V, and 1.61 V, respectively.

Of the five metal cations known to "oxidize" SO_2, only two would be predicted to enter into direct reaction with SO_2 on the basis of thermodynamic considerations alone: Fe^{+3} and Cu^{+2}. Their respective half-cell potentials are

$$Cu^{+2} + 2e^- \rightarrow Cu^\circ \quad , \quad E^\circ = 0.34\ V \quad ,$$

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \quad , \quad E^\circ = 0.77\ V \quad .$$

Direct reactions between SO_2 and Mn^{+2}, Fe^{+2}, and Ni^{+2} are extremely unfavored. Their respective half-cell potentials are:

$$Mn^{+2} + 2e^- \rightarrow Mn \quad , \quad E^\circ = -2.375\ V \quad ,$$

$$Fe^{+2} + 2e^- \rightarrow Fe \quad , \quad E^\circ = -0.41\ V \quad ,$$

$$Ni^{+2} + 2e^- \rightarrow Ni \quad , \quad E^\circ = -0.23\ V \quad .$$

These data indicate that for the direct oxidation of SO_2 by Mn^{+2}, Fe^{+2}, and Ni^{+2} to occur, one would have to apply 2.54 V, 0.58 V, and 0.40 V, respectively, of energy to the reacting system.

Theoretical results such as these should, of course, be subjected to experimental scrutiny. In fact, experimenters have observed the direct reactions between SO_2 and O_2, O_3, and H_2O_2, in a water solution that are predicted to take place on the basis of thermodynamic principles. The two cations Fe^{+3} and Cu^{+2} are known to accelerate the rate of oxidation of SO_2. However, it has not yet been shown (to our knowledge) that the mechanism of oxidation of SO_2 by Fe^{+3} and Cu^{+2} is direct. The isolation of Fe^{+2} and Cu as products of reactions in an aqueous solution of SO_2, Fe^{+3}, and Cu^{+2} would, for example, constitute acceptable evidence for the direct oxidation mechanism. (It is important to remember the limitations of these electrochemical cell calculations. Although half-cell potentials provide a means of predicting the direction of a chemical reaction, they do not in any way indicate the rate at which the reaction will proceed.) Mn^{+2}, Fe^{+2}, and Ni^{+2} do not enter into a direct reaction with SO_2 unless energy is supplied to the system; thus, their roles in the oxidation process must be catalytic or indirect.

Catalytic Oxidation of SO_2. Catalytic oxidation may well be the principal process for SO_2 conversion under conditions of high humidity and high particulate concentration, such as those that exist in plumes from power plants. Gartrell et al. (1963) reported, for example, that the rate of SO_2 oxidation in a smoke plume was quite low for relative humidities less than 70 percent, but it increased markedly for higher humidities. In one case, they measured a rate of SO_2 conversion of 55 percent in 108 minutes. Although such a rate is too high to be accounted for by a photochemical mechanism [a conclusion based on early studies of the photochemical oxidation of SO_2 by Gerhard and Johnstone (1955)], it is similar to that expected of oxidation in solution in the presence of a catalyst. Since the metal sulfates (and chlorides) emitted in a plume from a coal-burning process are potential catalysts for the liquid phase oxidation of SO_2, a reasonable explanation for this process is that these particles act as condensation nuclei, producing droplets of metal salt solution, which then act as loci for the SO_2 conversion.

The atmospheric catalytic oxidation of SO_2 involves both water and dissolved O_2,* and it requires the presence of a catalyst:

$$2SO_2 + 2H_2O + O_2 \xrightarrow{\text{catalyst}} 2H_2SO_4 \quad .$$

Catalysts for this reaction include several metal salts, such as sulfates and chlorides of manganese and iron, which usually exist in air as suspended particulate matter. At high humidities, these particles act as condensation nuclei or undergo hydration to become solution droplets. The oxidation process then proceeds by absorption of both SO_2 and O_2 by the liquid aerosol, with a subsequent chemical reaction in the liquid phase.

Early experiments conducted by Johnstone and Coughanowr (1958) and Johnstone and Moll (1960), in which they measured SO_2 oxidation in droplets of $MnSO_4$, confirmed the basic catalytic mechanism. In addition, studies performed by Junge and Ryan (1958) of the oxidation of SO_2 in bulk catalyst solutions yielded valuable information on the effects of solution acidity on the rate of SO_2 oxidation.

Recently, Cheng et al. (1971) reported laboratory results involving the catalytic oxidation of SO_2 in aerosol drops containing metal salts. They developed an aerosol-stabilizing technique in which aerosol particles were deposited on inert supporting Teflon beads in a fluidized bed. This deposition process altered neither the physical shape nor the chemical properties of the aerosol. After packing the Teflon beads with the deposited aerosol particles into a flow reactor, in which the catalytic oxidation of SO_2 occurred, the experimenters passed a mixture of SO_2 and humid air through the reactor. The SO_2 concentrations at the reactor entrance ranged from 3 to 18 ppm. To monitor the progress of the oxidation, Cheng et al. continuously measured the SO_2 concentration at the reactor exit. They identified reaction products by analyzing the reactor contents at the completion of an experiment.

*The rate of the direct reaction of SO_2 with O_2,

$$2SO_2 + O_2 \rightarrow 2SO_3 \quad ,$$

is too slow at room temperature to be of importance in the atmospheric oxidation of SO_2.

The SO_2 conversion progressed in three stages. During the initial period, all of the influent SO_2 was converted; none appeared at the reactor exit. A transitional period followed, in which the SO_2 conversion rate decreased from the initial maximum value to a steady value. From then on, a steady-state conversion of SO_2 took place. The three-stage process can be related to the change in solubility of SO_2 in a water solution as the solution becomes more acidic. The initially rapid conversion of SO_2 apparently results from the high rate of dissolution of gaseous SO_2 into liquid catalyst drops. The increase in sulfuric acid in the drops soon affects the initial stage of rapid conversion. Because H_2SO_4 in a dilute concentration undergoes complete dissociation to HSO_4^- and H^+, the added H^+ concentration diminishes the solubility of SO_2. Finally, as the solution acid concentration exceeds a certain level, the high H^+ concentration prevents further dissociation of H_2SO_4, and the solubility of SO_2 becomes constant. In this final stage, the rate of conversion of SO_2 to sulfate equals the rate at which SO_2 is absorbed in the drops.

Although NaCl, $CuSO_4$, $MnCl_2$, and $MnSO_4$ all exhibited the same general behavior, each salt differed in effectiveness as a catalyst for the oxidation of SO_2. Table 8 shows the steady-state conversions found by Cheng et al. (1971). In the case of $CuCl_2$, Cheng et al. found that, rather than acting as a catalyst, $CuCl_2$ reacted directly with SO_2 according to the following reaction:

$$SO_2 + 2CuCl_2 + 2H_2O \rightleftarrows 2CuCl + H_2SO_4 + 2HCl \quad .$$

Although the conversion of SO_2 proceeded even at very low relative humidities (less than 40 percent), it did so slowly. Above about 70 percent relative humidity, which is the level at which the transition from solid crystals surrounded by a layer of water to actual solution drops takes place, the rate of conversion increased dramatically.

The individual steps in the liquid-phase catalytic oxidation of SO_2 are as follows:

> The gas-phase diffusion of SO_2 to the drops,
> The diffusion of SO_2 from a drop's surface to the interior,
> The catalytic reaction in the interior.

Under steady-state conditions, the slowest of these three steps limits the overall rate of SO_2 conversion. If the gas phase diffusion of SO_2 to the drops is the controlling step, then the rate of SO_2 conversion should depend on the gas velocity in the system. If the liquid-phase diffusion of SO_2 controls the conversion rate, then the rate can be expected to be independent of the type of catalyst. In varying the gas flow rate through their reactor, Cheng et al. found that the overall rate of SO_2 conversion was unaffected. Since, as the results in Table 8 show, these rates clearly depend on the type of catalyst, the rate-controlling step is the chemical reaction itself. Foster (1969) reached similar conclusions.

Table 8

THE EFFECT OF DIFFERENT CATALYSTS ON SO_2 OXIDATION

Catalyst	Weight (mg)	Mean Residence Time (min)	Influent SO_2 Concentrations (ppm)	Fraction Conversion	Effectiveness Factor*
NaCl	0.36	1.7	14.4	0.069	1.0
$CuSO_4$	0.15	1.7	14.4	0.068	2.4
$MnCl_2$	0.255	0.52	3.3	0.052	3.5
$MnSO_4$	0.51	0.52	3.3	0.365	12.2

*The catalytic effectiveness of the various materials was compared with that of NaCl. Thus, the effectiveness factor is the product of the ratio of the weight of the catalyst in the reactor, the ratio of the reactor mean residence time, and the ratio of the reaction conversion of SO_2 in the reactor. The effectiveness factor for $MnSO_4$, for example, is:

$$1.0\left(\frac{0.36}{0.51}\right)\left(\frac{1.7}{0.52}\right)\left(\frac{0.365}{0.069}\right) = 12.2 \quad .$$

For steady-state conversion in the atmosphere, Cheng et al. derived the following first-order rate expression from their data for $MnSO_4$:

$$R_{SO_2} = 0.67 \times 10^{-2}[SO_2] \quad ,$$

where R_{SO_2} is the micrograms of SO_2 converted per minute per milligram of $MnSO_4$, $[SO_2]$ is the gas phase concentration of SO_2 in micrograms per cubic meter, and the constant factor is for drops containing 500 ppm of $MnSO_4$. The factor can be altered for other catalysts using Table 8. We can compute the rate of conversion of SO_2 for conditions typical of natural fog in an urban atmosphere:

- (SO_2) = 0.1 ppm.
- The average diameter of the fog droplets is 15 μ.
- Half the fog droplets contain a catalyst capable of oxidizing SO_2 to H_2SO_4. The catalyst concentration within these droplets is equivalent to 500 ppm $MnSO_4$.
- The fog concentration is 0.2 gram of H_2O per cubic centimeter of air.

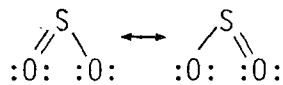
Under these assumptions, the equivalent catalyst concentration is 50 micrograms of $MnSO_4$ per cubic meter of air, and the rate of conversion of SO_2 is 2 percent per hour. Typical concentrations of catalyst metals are tabulated below:

Catalyst	Concentration ($\mu g\ m^{-3}$)
Mn	10
Cu	10
Zn	58
Fe	74
Pb	17

Thus, the conditions of the sample calculation are reasonable for actual air.

The detailed mechanism of the catalized oxidation of SO_2 is not yet known; however, the first step in the process may involve the association of a reactant with the catalyst. If the catalyst is a transition metal cation, the reactant apparently enters into a coordination complex with the cation; thus, the reactant occupies a position in the ligand field of the metal. Matteson et al. (1969) observed that catalyst potency toward the oxidation of SO_2 tends to decrease as the number of possible sites at which SO_2 can complex on the metal ion decreases. Thus, the configuration of the ligand field (e.g., square planar, octahedral) of a given metal ion strongly influences the catalytic behavior of the ion.

If the first step in catalysis is, indeed, the coordination of SO_2 with the cation, the rate of displacement of other ligands in the ligand field by SO_2 must be examined. Some species form much stronger coordination bonds with transition metal ions than others do. For example, carbon monoxide poisoning of the blood results because the binding energy of CO to the iron in hemoglobin is much greater than that of O_2. Consequently, O_2 cannot displace the CO from the iron, and the body rapidly depletes the blood of O_2. SO_2 can, in principle, coordinate with transition metals, since it contains unshared electrons--a general characteristic of ligands:



(Other ligands include, for example, H_2O, NO, and CO.) But, if, as a result of this mechanism involving transition metal cations, SO_2 is to be catalytically oxidized in aerosols, it must be able to displace other ligands from the catalyst. Because of the high concentration of water and the presumably low relative concentrations of SO_2 and catalysts in aerosols, the tendency for SO_2 to displace water from the ligand field must be especially great. Thus, an experimental investigation of the rate of H_2O displacement by SO_2 in the principal catalysts for SO_2 oxidation is clearly needed.

One explanation of the catalytic oxidation of SO_2 in solution is the series of four equilibria proposed by Matteson et al. (1969):

$$SO_2 + Mn^{+2} \underset{2}{\overset{1}{\rightleftarrows}} Mn \cdot SO_2^{+2} \quad ,$$

$$2Mn \cdot SO_2^{+2} \underset{4}{\overset{3}{\rightleftarrows}} [(Mn \cdot SO_2^{+2}) \cdot O_2] \quad ,$$

$$[(Mn \cdot SO_2^{+2}) \cdot O_2] \underset{6}{\overset{5}{\rightleftarrows}} 2Mn \cdot SO_3^{+2} \quad ,$$

$$Mn \cdot SO_3^{+2} + H_2O \underset{8}{\overset{7}{\rightleftarrows}} Mn^{+2} + HSO_4^- + H^+ \quad .$$

Matteson et al. made three crucial assumptions in this mechanism:

- SO_2 coordinates rapidly with Mn^{+2} (Step 1)
- The association of $Mn \cdot SO_2^{+2}$ complexes is likely (Step 3)
- Oxygen transfer to the $[(Mn \cdot SO_2^{+2})_2 \cdot O_2]$ complex occurs (Step 5).

Although Matteson et al. did not address these issues in formulating their mechanism, the series of reactions provides a construct for further experimental and theoretical inquiries.

It is not possible now to ascertain the extent to which the oxidation of SO_2 in solution competes with the gas phase reactions. Very little data pertaining to the kinetics of the reactions between SO_2 and dissolved salts exist that can be incorporated in a predictive model. Understanding the role of SO_2

in the atmosphere and, indeed, the formulation of effective SO_2 control strategies will critically depend on the fundamental investigation of the types of reactions discussed in this section. Without quantitative data upon which to build a model, predictions are of little significance.

3. Efforts To Test the Gas Phase Reaction Mechanism for SO_2

Shortly after the inception of the project, we received the results of a series of smog chamber experiments from EPA to use to test the 10-step mechanism described in Section C-1 as a possible explanation for the oxidation of SO_2 in the gas phase. The experiments were carried out in a dynamic flow reactor, and propylene, NO_x, SO_2, and air were used as reactants. To simulate the system, we added the SO_2 reactions (Reactions S_1 through S_{10}) to a general mechanism for smog (Hecht et al., 1974). We had previously performed extensive tests of the organic-NO_x-air reactions using propylene-NO_x-air data obtained in the same smog chamber operated in a static mode.

Unfortunately, we found that the dynamic SO_2 experiments were unsuitable for modeling for two reasons. First, the concentration of SO_2 in the inlet tube fluctuated substantially during an irradiation, but the inlet concentrations were not measured often enough to permit an accurate inflow profile of SO_2 to be generated. Second, the oxidation reactions of SO_2 are quite slow relative to the majority of other chemical transformations of interest in this particular chemical system (e.g., the oxidation of NO and organics, and the formation of O_3). The net effect of these two characteristics of the system was that the fluctuations in the inlet tube SO_2 concentrations masked any loss of SO_2 due to chemical reactions.

The mechanism evaluation procedure, therefore, became more a test of the adequacy with which the mixing and flow characteristics of the chamber were modeled than of the accuracy of the mechanism. In view of the substantial uncertainties in the inflow data, even very good agreement between the predictions and the data would not be sufficient to demonstrate the validity of the mechanism. Consequently, we suspended our efforts to test the SO_2 mechanism

until more carefully controlled smog chamber data become available. A new experimental study involving organics, NO_x, and SO_2 is now in progress; we summarize that program in the following section.

4. Future Examinations of SO_2 Chemistry

Under the direction of Dr. Arthur Levy, investigators at Battelle Memorial Laboratory are presently conducting a series of organic-NO_x-SO_2-air experiments using propylene (nine runs) and toluene (six runs) as the reactive organic. Under another EPA contract, we expect to employ these data to test the SO_2 mechanism proposed in Section C-1. The use of these data offers several advantages:

> The experiments are being conducted under static conditions. Consequently, we will not have to contend with fluctuations in inflow reactant concentrations as an additional variable in evaluating the model.
> The chamber is still in operation (the chamber used for the experiments mentioned in Section C-1 has been disassembled). Thus, any chamber effects that were not yet measured can still be determined, if needed, for the model testing exercises.
> Dr. Levy's group at Battelle has considerable experience and expertise in studying SO_2 in smog chambers. Therefore, the new SO_2 data will almost certainly be the best that are currently obtainable.

The evaluation of a mechanism describing the oxidation of SO_2 in solution or in aerosols is more difficult. To our knowledge, no systematic experimental study of this process suitable for model testing has yet been carried out. Until the oxidation rate of SO_2 in systems containing aerosol particles has been determined as a function of particle size (volume, surface area), composition and concentration of reactants in the particle, pH of the particle, and concentration of SO_2 in the gas phase, it will be difficult to propose with any confidence a physical model for the oxidation of SO_2 in solution. As a temporary

measure, it may be possible to develop a parametric model in which the oxidation of SO_2 in particles is described by the first-order reaction

$$SO_2 \xrightarrow{k_p} SO_4^{=} \quad .$$

The parameter k_p can then be estimated from the following:

- Observations of the SO_2 oxidation rate in droplets under well-controlled conditions, such as those used in the experiments of Cheng et al. (1971).
- Knowledge of the composition of atmospheric aerosols.

Although a parametric mechanism is necessarily simplistic, combined with the gas phase mechanism, it may be sufficient to predict the atmospheric conversion of SO_2 to sulfate within the uncertainty bounds of aerometric measurements. We expect to analyze the methods for selecting values of k_p during Contract 68-02-0580.

D. SPECIAL CONSIDERATIONS REGARDING THE TREATMENT OF TEMPERATURE, WATER, AND HYDROGEN PEROXIDE IN THE AIRSHED MODEL

In the process of reviewing previous airshed modeling exercises, as well as considering some of the possible difficulties that might arise in the use of the latest version of the SAI model, we identified the following three questions that seemed to need further clarification:

- To what extent should temperature effects on reaction rate constants be considered in the model?
- How important are the spatial and temporal variations in water concentration?
- Will the model predictions be sensitive to the initial concentration distribution of hydrogen peroxide?

In an attempt to answer these questions, we carried out various sensitivity studies using the kinetic mechanism, and we reviewed available measurements for some of these parameters in one of the most severe and persistent photochemical air pollution regions--the South Coast air basin of California.

It is well known that reaction rate constants are a function of temperature. This effect is commonly expressed using the Arrhenius relationship:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad ,$$

where

k = the rate constant,
A = a constant (sometimes referred to as the frequency factor),
E_a = the so-called activation energy for the reaction,
R = the gas constant,
T = the absolute temperature.

Given k at some temperature T_0 and the activation energy, the value of k at any other temperature can be estimated from

$$k(T) = k(T_0) \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad . \qquad (8)$$

Thus, we do not need to determine b. In the computer programs, we input T_0 and the values of E_a and $k(T_0)$ for each chemical reaction. Then k can be calculated at any other temperature T using Eq. (8).

Although the algorithm outlined above is not difficult to incorporate in the model, there is some question of the extent to which spatial and temporal variations in temperature must be considered. For example, complete specification of the temperature as a function of x, y, z, and time would require significant amounts of additional computer storage, not to mention the extra

effort required of the user to assemble sufficient data to estimate the complete temperature field. Thus, we undertook a study to examine the sensitivity of the kinetic mechanism to variations in temperature that might be found in an urban airshed. These results can be used as a guide for determining under what conditions spatial and temporal features of the temperature field must be considered in the model.

Similar questions arise concerning the distribution of water in the gas phase over an urban area, especially a region like the South Coast air basin, in which there are coastal areas as well as inland valleys. We note that though spatial variations of relative humidity are significant in this airshed, it is important to examine the variations in water concentration because this is the parameter entering the kinetic rate expressions. Thus, to determine the extent to which provisions for treating spatial and temporal variations in water concentration should be included in the model, we examined the sensitivity of the mechanism to variations in water concentration.

Finally, incorporation of the 31-step mechanism (excluding SO_2 chemistry) in the model will require the user to specify initial and boundary concentrations of HNO_2 and H_2O_2, two pollutants that are rarely measured routinely in most urban areas. To obtain a rough estimate of the concentrations of these pollutants, we can assume that each is in chemical equilibrium; thus, from the kinetic mechanism, we can write

$$[HNO_2] = \frac{-k_{10} + \left\{k_{10}^2 + 8k_9\left(2k_8[NO][NO_2][H_2O]^2 + k_{12}[OH][NO]\right)\right\}^{1/2}}{4k_9} \quad ,$$

$$[H_2O_2] = \frac{k_{15}[HO_2]^2}{k_{16}} \quad .$$

If a simulation is to start somewhat before dawn, use of the above relationships would be tantamount to assuming that chemical equilibrium had been approached during the preceding nighttime period. Although this assumption may be reasonable for HNO_2, we note that the H_2O_2 photolysis rate constant, k_{16}, would be

essentially zero at night. In fact, from the mechanism we see that there is no "sink" for H_2O_2 other than the photolysis reaction. Thus, the use of the equilibrium assumption for H_2O_2, especially at night, does not seem desirable. To examine this issue further, we carried out simulation runs using the mechanism to ascertain its sensitivity to the initial H_2O_2 conditions. In the following sections, we discuss the results obtained from these sensitivity studies involving temperature, water, and H_2O_2.

1. The Predicted Effects of Changes in Temperature and Water Concentration on Smog Kinetics

To determine what effect changes in temperature or water concentration have on the concentration predictions, we carried out simulations of a smog chamber experiment using the new kinetic scheme incorporated in the airshed model. The base values used were those of EPA Run 333:

> $[NO]_0$ = 1.25 ppm,
> $[NO_2]_0$ = 0.08 ppm,
> $[C_3H_6]_0$ = 0.23 ppm,
> $[n\text{-}C_4H10]_0$ = 3.41 ppm,
> $[H_2O]_0$ = 16,000 ppm,
> T = 25°C.

For each simulation run, we changed only one parameter from the base values.

We performed the simulations for two different temperatures, 15°C and 35°C, with all other factors kept the same. We calculated the rate constants at the new temperatures from the base values of the rate constants (25°C) and from measured or estimated reaction activation energies, as shown in Table 9 (Garvin and Hampson, 1974; Demerjian et al., 1974; Johnston et al., 1970). Because the majority of the reactions in the mechanism are thermal and because they have small positive activation energies, raising the temperature accelerated the conversion of NO to NO_2 and decreased the time to the onset of O_3

Table 9

ACTIVATION ENERGIES OF REACTIONS IN THE GENERAL MECHANISM

Reaction	E_A kcal mole^{-1}	Reference
$NO_2 + h\nu \xrightarrow{1} NO + O$	0	Estimate
$O + O_2 + M \xrightarrow{2} O_3 + M$	-1	Garvin and Hampson (1974)
$O_3 + NO \xrightarrow{3} NO_2 + O_2$	2.4	Garvin and Hampson (1974)
$O + NO_2 \xrightarrow{4} NO + O_2$	0.6	Garvin and Hampson (1974)
$O_3 + NO_2 \xrightarrow{5} NO_3 + O_2$	4.9	Garvin and Hampson (1974)
$NO_3 + NO \xrightarrow{6} 2NO_2$	1.4	Johnston et al. (1974)
$NO_3 + NO_2 + H_2O \xrightarrow{7} 2HNO_3$	-1.9*	Davis (1974)
$NO + NO_2 + 2H_2O \xrightarrow{8} 2HNO_2 + H_2O$	0	Demerjian et al. (1974)
$2HNO_2 \xrightarrow{9} NO + NO_2 + H_2O$	9	Demerjian et al. (1974)
$HNO_2 + h\nu \xrightarrow{10} OH + NO$	0	Estimate
$OH + NO_2 \xrightarrow{11} HNO_3$	-2.2	Garvin and Hampson (1974)
$OH + NO \xrightarrow{12} HNO_2$	-2.2	Garvin and Hampson (1974)
$OH + CO + (O_2) \xrightarrow{13} CO_2 + NO_2$	0.15	Davis (1974)
$HO_2 + NO \xrightarrow{14} OH + NO_2$	2	Estimate
$HO_2 + HO_2 \xrightarrow{15} H_2O_2 + O_2$	0	Estimate
$H_2O_2 + h\nu \xrightarrow{16} 2OH$	0	Estimate

* The value of E_A listed for this composite reaction we determined from the values of E_A for the three equivalent reactions:

Reaction	E_A	Reference
$NO_3 + NO_2 \longrightarrow N_2O_5$	-2	Demerjian et al. (1974)
$N_2O_5 \longrightarrow NO_2 + NO_3$	19.4	Garvin and Hampson (1974)
$N_2O_5 + H_2O \longrightarrow 2HNO_3$	0	Estimate

Table 9 (concluded)

Reaction	E_A kcal mole^{-1}	Reference
$HC_1 + O \xrightarrow{17} ROO + \alpha RCOO + (1-\alpha)HO_2$	0.1§	Garvin and Hampson (1974)
$HC_1 + O_3 \xrightarrow{18} RCOO + RO + HC_3$	3.8§	Garvin and Hampson (1974)
$HC_1 + OH \xrightarrow{19} ROO + HC_3$	1§	Estimate
$HC_2 + O \xrightarrow{20} ROO + OH$	5†	Estimate
$HC_2 + OH \xrightarrow{21} ROO + H_2O$	1†	Estimate
$HC_3 + h\nu \xrightarrow{22} \beta ROO + (2-\ )HO_2$	0	Estimate
$HC_3 + OH \xrightarrow{23} \beta RCOO + (1-\beta)HO_2 + H_2O$	0	Estimate
$HC_4 + O \xrightarrow{24} ROO + OH$	--	--
$HC_4 + OH \xrightarrow{25} ROO + H_2O$	--	--
$ROO + NO \xrightarrow{26} RO + NO_2$	1	Estimate
$RCOO + NO + (O_2) \xrightarrow{27} ROO + NO_2 + CO_2$	0	Estimate
$RCOO + NO_2 \xrightarrow{28} RCOONO_2$	0	Estimate
$RO + O_2 \xrightarrow{29} HO_2 + HC_3$	6	Garvin and Hampson (1974)
$RO + NO_2 \xrightarrow{30} RONO_2$	0	Estimate
$RO + NO \xrightarrow{31} RONO$	0	Estimate

§ Estimated E_A for propylene

† Estimated E_A for n-butane

accumulation, as expected. Conversely, lowering the temperature noticeably slowed the smog formation process. Figure 1 presents concentration-time profiles for NO, NO_2, O_3, and propylene for each of these two runs.

We carried out similar runs at two extreme conditions of relative humidity--0 and 100 percent--at the base temperature (25°C). These percentages correspond to 0 and 32,000 ppm of H_2O, respectively. Figure 2 shows a comparison of the predicted concentration-time profiles for these two cases with the profile for the base case. Increasing the water concentration accelerated the conversion of NO to NO_2, whereas a complete elimination of water dramatically slowed down the overall smog kinetics. Both of these effects are attributable to changes in the production rate and equilibrium level of nitrous acid, governed by the reactions

$$NO + NO_2 + H_2O \rightleftarrows 2HNO_2 \quad .$$

Because it is virtually impossible--even with pumping and baking--to obtain a water concentration of 0 ppm in existing smog chambers, we carried out one final run at 3.2 ppm of H_2O. The concentration-time profile obtained under these conditions differed from those of the completely dry run by less than 2 percent after six hours of simulation time.

In urban areas, ambient temperatures and water concentrations change considerably during the day and from one day to the next. Thus, the results of these simulation runs suggest that it may be necessary to account for variations in temperature and water concentration when modeling urban photochemical smog. Toward this end, smog chamber experiments conducted at various constant levels of temperature and water concentration would be most useful in ascertaining the effects of variations of these two parameters on smog kinetics.

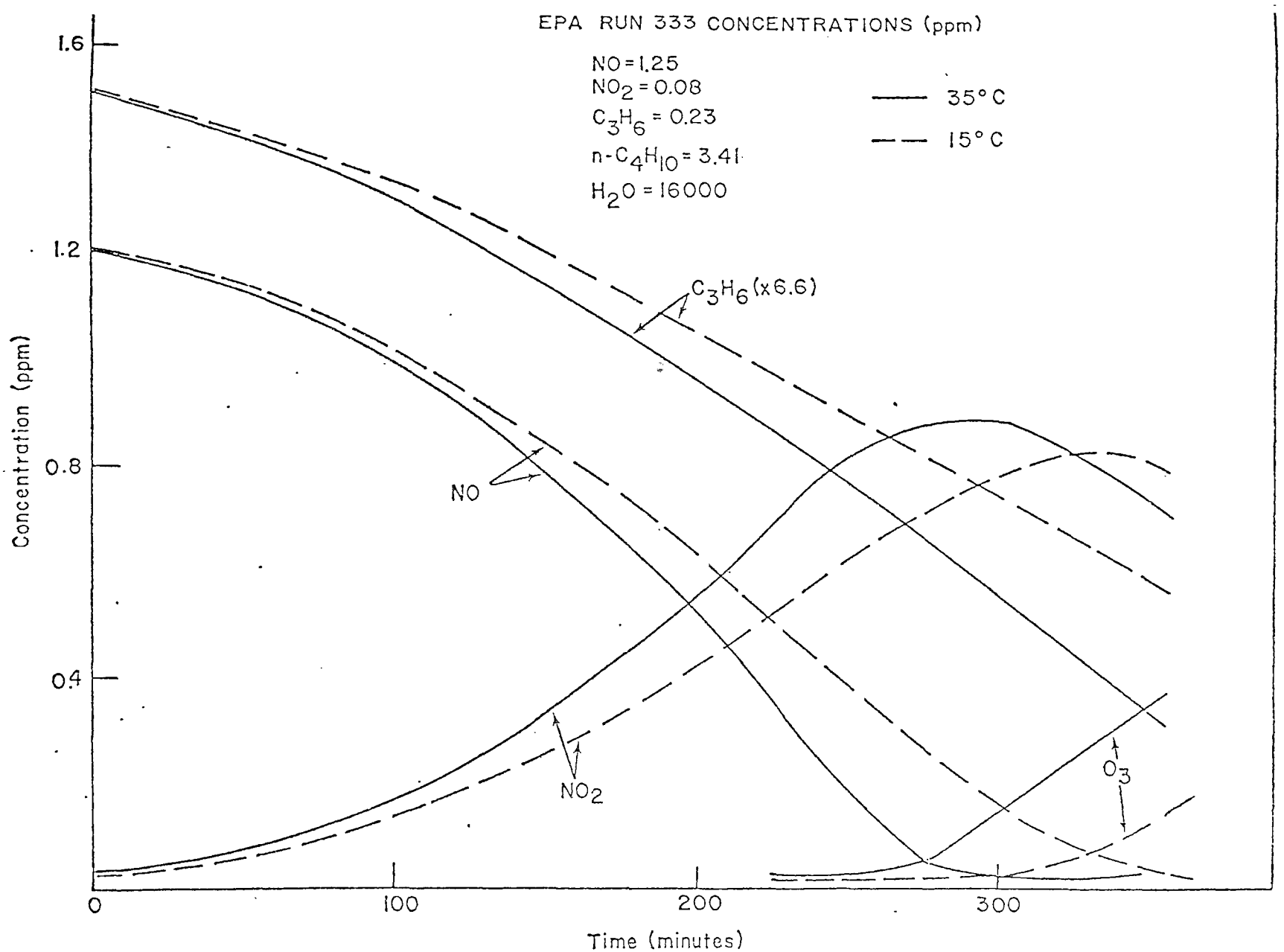


FIGURE 1. CONCENTRATION-TIME PROFILES FOR NO, NO_2, O_3, AND PROPYLENE AT 15°C AND 35°C

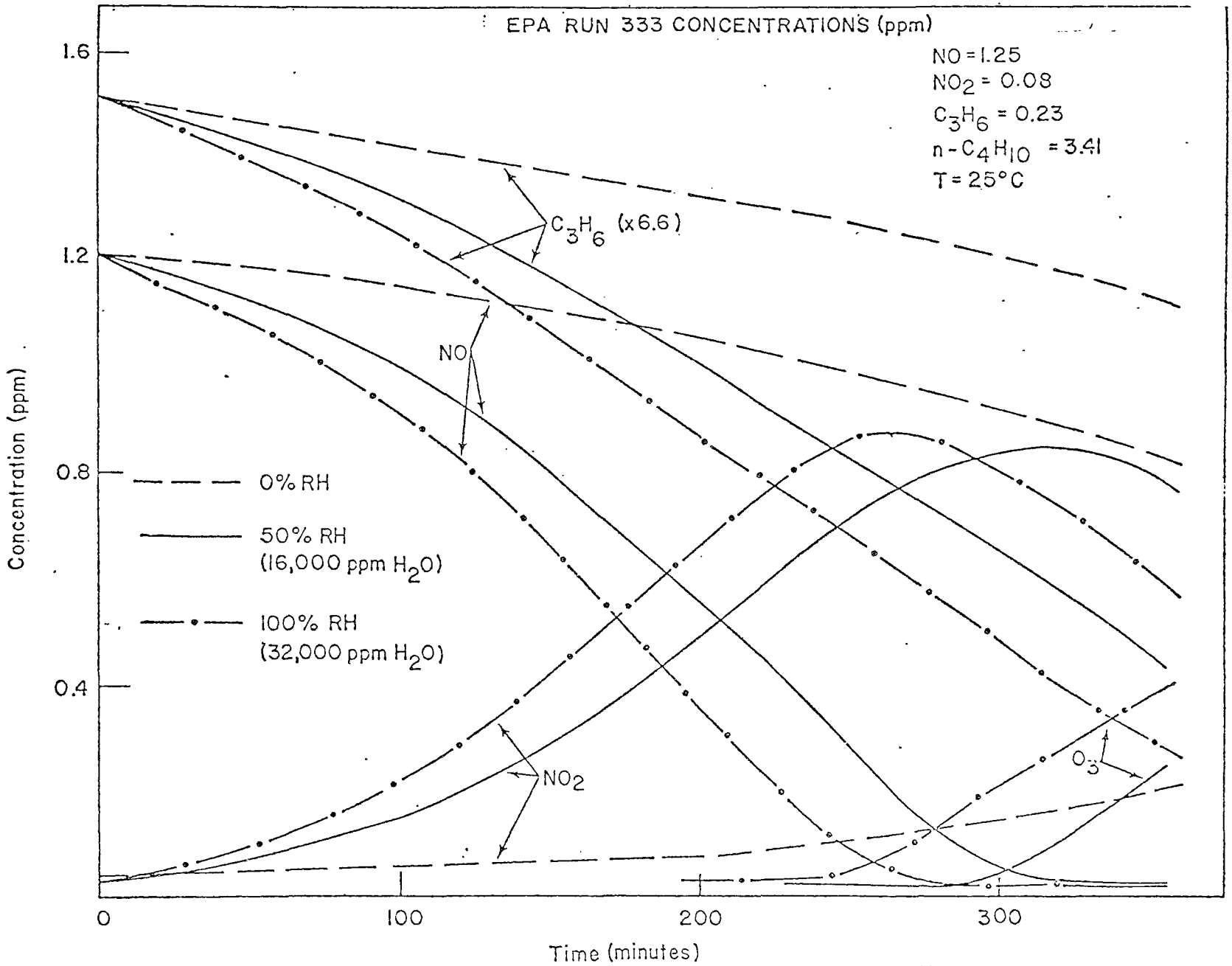


FIGURE 2. PREDICTED CONCENTRATION-TIME PROFILES FOR NO, NO2, 03, AND PROPYLENE AT 0, 50, AND 100 PERCENT RELATIVE HUMIDITY

2. Specification of the Initial Concentration of H_2O_2

With the implementation of the new kinetic scheme in the airshed model, we must now specify the emission rate and the initial and boundary concentrations of a new reactant, H_2O_2. To ascertain the accuracy with which these parameters must be determined, we carried out kinetic simulations of EPA Chamber Run 333 (under the initial conditions listed in Section D-1) at three different initial H_2O_2 concentrations: 0, 0.01, and 0.1 ppm.

The concentration-time profiles obtained for the case in which $[H_2O_2]_0$ = 0.01 ppm did not differ appreciably from those for the base case, in which $[H_2O_2]_0$ = 0 ppm. The small initial H_2O_2 concentration resulted in a five-minute reduction in the time to the NO_2 peak (305 versus 310 minutes) and a small increase in O_3 at 360 minutes (0.32 versus 0.30 ppm).

In constrast, the effect on the predictions of the presence of 0.1 ppm of H_2O_2 initially was far more visible. The conversion of NO to NO_2 was accelerated considerably, and the NO_2 peaked at 264 minutes. As a result of the substantial reduction in the time to the NO_2 peak, O_3 accumulated to 0.46 ppm before the simulation was terminated at 360 minutes.

For similar simulations of another smog chamber experiment (EPA Run 349), the initial conditions were as follows:

- $[NO]_0$ = 0.31 ppm,
- $[NO_2]_0$ = 0.03 ppm,
- $[\text{propylene}]_0$ = 0.44 ppm,
- $[\text{n-butane}]_0$ = 3.25 ppm,
- $[H_2O]_0$ = 16,000 ppm,
- T = 25°C.

In these simulations, a maximum in the O_3 concentration did occur, and the results indicate that the asymptotic ozone level is not affected appreciably (less than 2 percent) by the initial presence of as much as 0.1 ppm of H_2O_2.

However, the H_2O_2 did serve to reduce the time that elapsed before the maximum was reached. For example, the predicted O_3 maximum occurred at 194 minutes for EPA Run 349 when the initial charge contained 0.1 ppm of H_2O_2, compared with 225 minutes when H_2O_2 was absent initially.

On the basis of these simulations, we feel that an effort should be made to construct an emissions inventory for H_2O_2 only if the sources of such emissions would lead to an ambient hydrogen peroxide concentration of more than 0.01 ppm. Should H_2O_2 sources contribute less than this amount, the error incurred by neglecting these sources would be very small, especially prior to the formation of the NO_2 peak and at the O_3 asymptote.

With regard to the specification of initial and boundary concentrations in the airshed model, the sensitivity runs indicate that care should be exercised in specifying H_2O_2 concentrations when they are on the order of 0.1 ppm or larger. Data presented by Bufalini et al. (1972) suggest that H_2O_2 in the South Coast air basin may reach levels as high as 0.18 ppm during a very smoggy day. However, early morning and late afternoon levels were reported to be about 0.01 to 0.02 ppm, thus indicating that overnight carry-over effects may not be too significant. We hasten to add that these observations are based on a very limited number of ambient air measurements. Additional measurements of the diurnal behavior of H_2O_2 in an urban airshed would be useful.

3. Spatial and Temporal Variations in Temperature and Water Concentration in the South Coast Air Basin

Having shown in Section D-1 that the kinetic mechanism is somewhat sensitive to changes in temperature and water concentration, we carried out a limited effort to examine the extent of these variations in an actual airshed. We chose the South Coast air basin for this study for two reasons. First, photochemical smog is particularly severe in this region. Second, we expected that the spatial and temporal variations in temperature and water concentration found here would be as large as those found in most other airsheds where the model might be applied.

During the summer, an onshore flow of moist marine air generally keeps coastal areas relatively cool [temperatures in the 70s to 80s (°F)]. By the time the air has traveled to the inland valleys, however, significant heating has taken place, and the temperature often exceeds 100°F. In addition, relative humidities near the coast are usually higher than those measured inland. Of course, since water concentration is the parameter of interest, the effect of temperature on relative humidity must be considered.

Tables 10 and 11 present hourly ground-level temperature and relative humidity data for three smoggy days in June 1974. The station location associated with each code number is as follows:

Number	Station Name
13W	Lennox
21W	Long Beach
41W	Burbank
61W	Ontario
75W	Downtown Los Angeles

Figure 3 shows the location of each station. Lennox and Long Beach are representative of coastal locations, whereas Downtown Los Angeles, Burbank, and Ontario are representative of inland communities.

To examine variations in temperature and relative humidity with height above the terrain, we reviewed some of the measurements recently reported by Blumenthal et al. (1974). They measured the three-dimensional distribution of pollutants and meteorological parameters throughout the South Coast air basin using a fully instrumented fixed-wing aircraft. We chose to examine a two-day period--26-27 July 1973--for which numerous aircraft spirals were made, both during the day and at night.

Table 10

GROUND-LEVEL AIR TEMPERATURES IN THE LOS ANGELES BASIN ON 28-30 JUNE 1974

JOB NUMBER =GAMTABLS — AIR POLLUTION CONTROL DISTRICT - COUNTY OF LOS ANGELES
PROGRAM =GAMTABLS

DATE: 07/19/74 — TEMPERATURE / AT HOUR / IN DEGREES FAHRENHEIT — VA 74

STA — HOUR PST — 6/28/74

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	AVE	N	MAX
13W							64	70	75	77	76	77	78	79	79	79	79	76	75	69					75.2	14	80
21W							65	70	75	81	84		90	93	92	92	90	88	84	77					83.2	13	96
41W							68	74	79	85	92	97	99	99	99	98	96	95	89	85					89.6	14	99
61W							67	75	83	88	93	98	103	105	106	106	102	98							93.7	12	106
75W							67	70	74	79	86	93	96	89	89	88	88	87	86	84					84.0	14	96

STA — HOUR PST — 6/29/74*

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	AVE	N	MAX
13W							63	65	69	71	69	72	72	72	72	72	70	67	64	63					68.6	14	73
21W							64	65	68	70	72	73	74	77	77	76	75	72	73	68					71.7	14	79
41W							65	70	74	79	84	86	86	87	89	88	84	83	80	75					80.7	14	89
61W							65	69	77	81	86	92	95	97	95	93	92	88	84	77					85.1	14	97
75W							67	69	72	74	76	80	81	81	83	85	83	80	78	73					77.3	14	85

STA — HOUR PST — 6/30/74*

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	AVE	N	MAX
13W							62	62	63	66	69	69	71	71	70	71	70	67	65	64					67.1	14	72
21W							63	63	64	64	68	70	71	71	72	72	69	67	67	66					67.6	14	74
41W							62	63	66	70	74	76	79	80	78	79	78	75	71	67					72.7	14	80
61W							57	58	61	67	77	82	85	87	88	87	83	81	76	70					75.6	14	88
75W							66	66	66	70	72	76	77	78	77	77	75	75	74	70					72.8	14	78

Table 11

GROUND-LEVEL RELATIVE HUMIDITIES IN THE LOS ANGELES BASIN ON 28-30 JUNE 1974

JOB NUMBER =GAMTABLS — AIR POLLUTION CONTROL DISTRICT - COUNTY OF LOS ANGELES

PROGRAM =GAMTABLS

DATE: 07/19/74 — RELATIVE HUMIDITY / AT HOUR / IN PERCENT — VA 76

STA	HOUR PST																							6/28/74		
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	AVE	N	MIN
13W							87	76	60	58	58	52	48	44	44	44	42	48	50	63					55.3	14	42
21W							65	59	50	36	43		32	31	31	28	26	29	31	40					38.5	13	26
41W							37	40	31	28	17	12	12	19	19	13	14	14	19	17					20.9	14	12
61W							38	30	27	23	20	13	10	10	10	11	11	13							18.0	12	10
75W							65	61	56	51	39	35	32	48	46	43	40	39	38	38					45.1	14	32

STA	HOUR PST																							6/29/74*		
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	AVE	N	MIN
13W							90	90	78	73	76	68	66	66	68	68	73	81	84	87					76.3	14	66
21W							75	73	65	63	59	57	55	52	50	52	52	57	55	65					59.3	14	50
41W							43	46	43	38	36	40	42	40	30	31	42	38	46	56					40.8	14	30
61W							47	47	36	35	25	17	16	21		25	28	34	36	50					32.1	13	16
75W							82	80	73	69	65	54	60	57	54	56	60	65	68	80					65.9	14	54

STA	HOUR PST																							6/30/74*		
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	AVE	N	MIN
13W							90	90	87	78	70	70	64	66	66	66	68	76	81	84					75.4	14	64
21W							73	73	70	70	61	57	57	59	57	57	63	65	65	68					63.9	14	57
41W							81	78	70	63	60	58	52	51	54	51	51	53	61	68					60.8	14	51
61W							100	100	93	76	54	44	36	32	32	34	41	46	54	66					57.7	14	32
75W							83	82	81	76	70	62	67	63	62	68	67	70	77	80					71.6	14	62

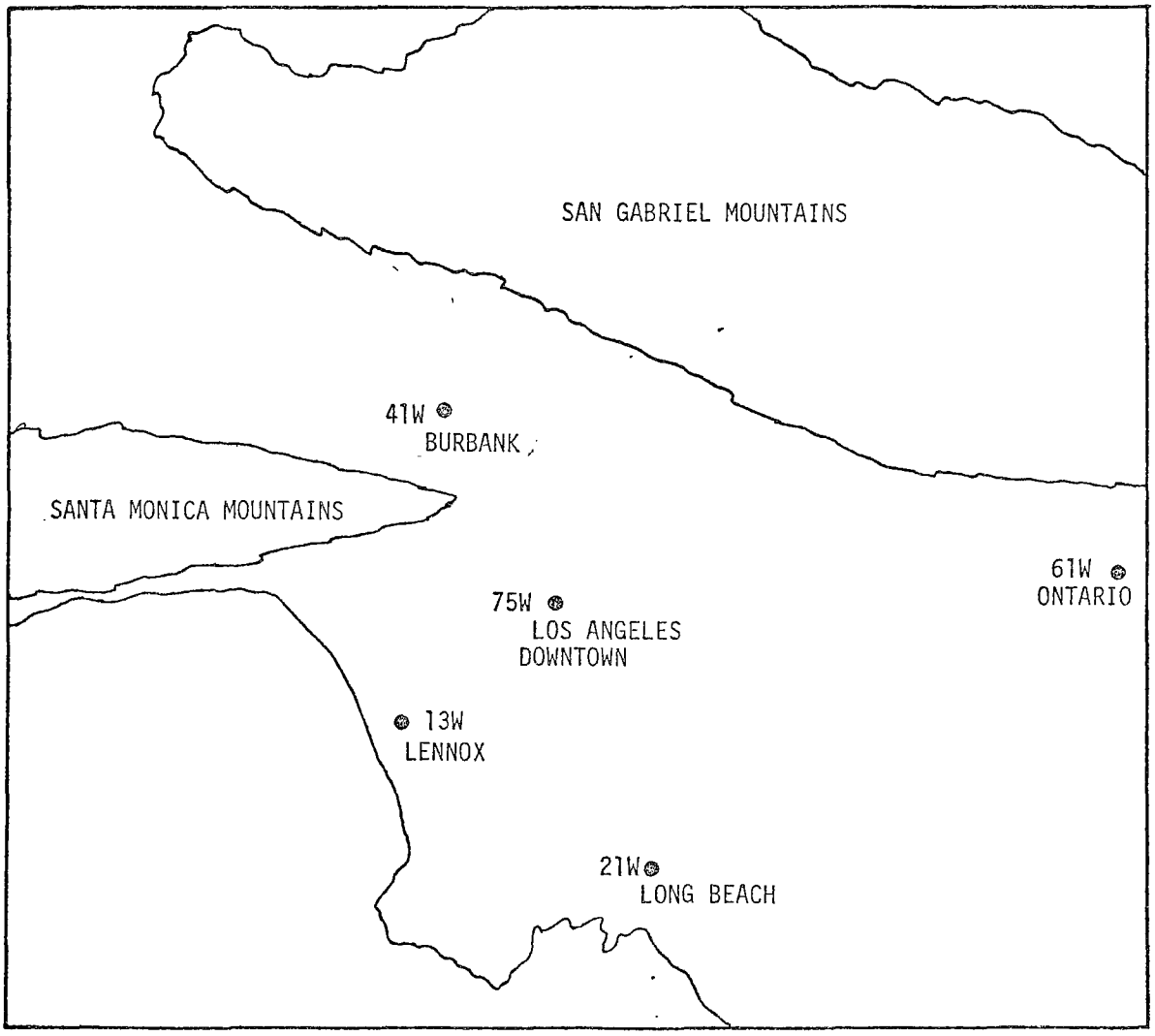


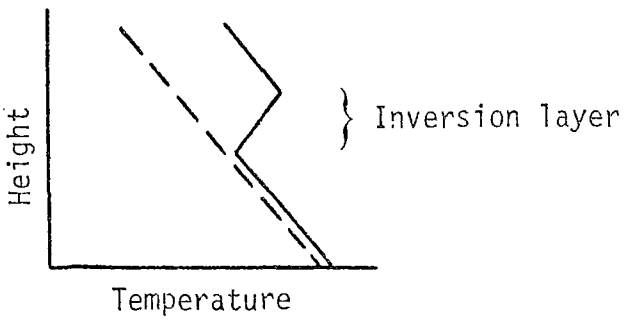
FIGURE 3. LOCATIONS OF TEMPERATURE AND RELATIVE HUMIDITY MONITORING SITES

From the data presented in Table 10, we note that the maximum difference in temperature at any hour during the day and the variation in average air temperatures across the basin for each of the three days are as follows:

	Maximum Spatial Temperature Difference		Average Spatial Temperature Difference	
Day	°C	°F	°C	°F
June 28	15	27	10	18.5
June 29	14	25	9	16.5
June 30	10	18	5	8.5

Thus, spatial variations in temperature of as much as 15°C may exist in the Los Angeles area during the middle of the day. However, on the average, the variations in temperature are somewhat smaller.

To show temperature variations aloft, we plotted in Figure 4 temperature profiles above Rialto, California, at five times on 26-27 July 1973. The 13:07 sounding on July 26 exhibits a temperature difference of about 9°C. If adiabatic conditions had persisted, we would have expected the temperature gradient to be -0.01°C $m.^{-1}$ Thus, over a 1000m interval, the temperature difference would be 10°C, which is approximately the amount observed at Rialto at 13:07. As illustrated below, when an elevated inversion layer is present, the temperature differences in this situation may be smaller than those that would exist under adiabatic conditions:



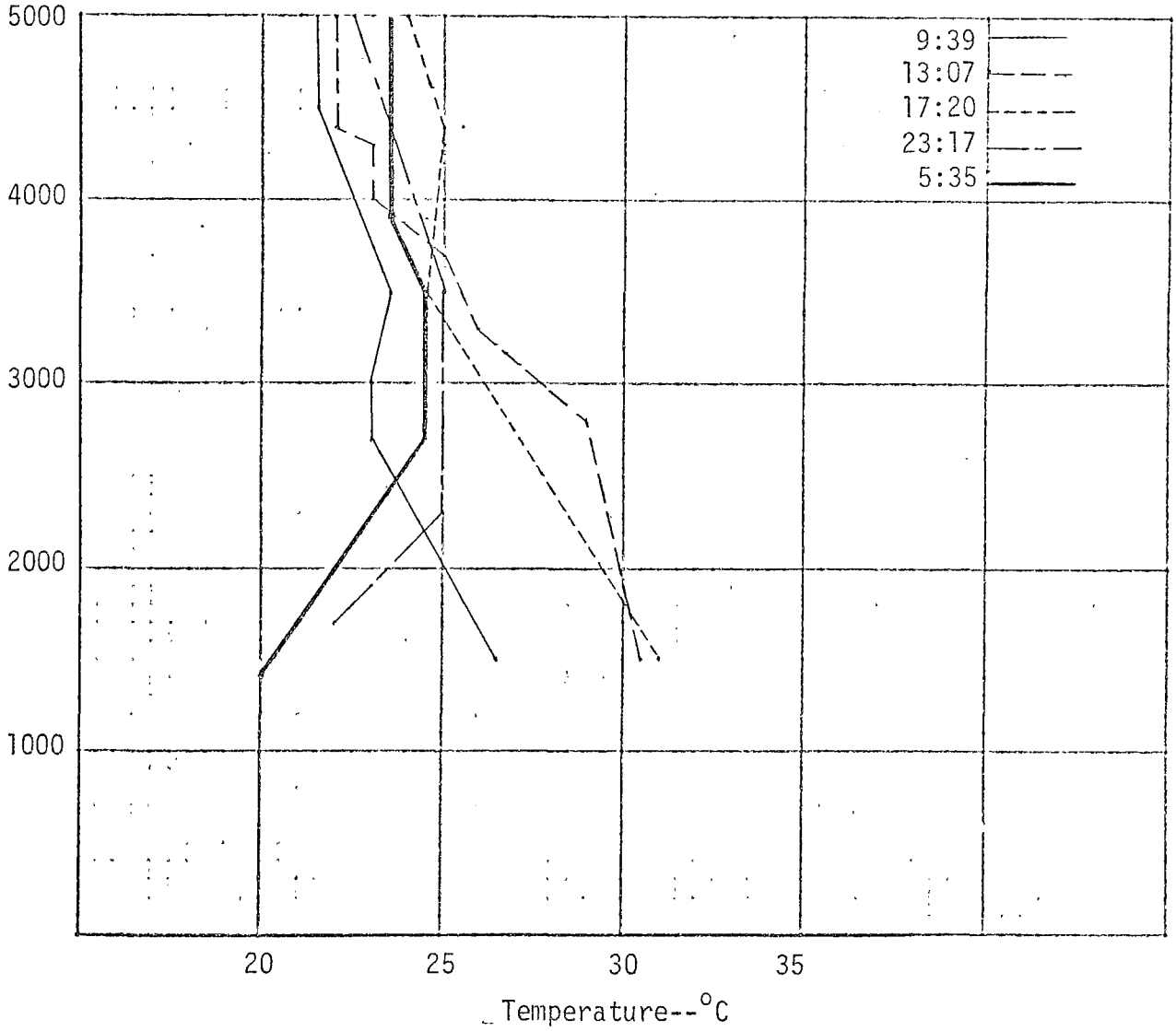


FIGURE 4. DISTRIBUTION OF THE TEMPERATURE ALOFT ABOVE RIALTO ON 26-27 JULY 1973

For a modeling region extending to, say, 1000m in height above the terrain, vertical temperature differences may be as large as horizontal variations.

In considering the distribution of water in the basin, we must first convert relative humidity measurements to water concentration in ppm. Using the definition of relative humidity, we can calculate the concentration of water, $[H_2O]$, in ppm from the following formula:

$$[H_2O] = \frac{RH \times P(T)}{760} \times 10^4 \quad ,$$

where

RH = relative humidity (in percent),

P = vapor pressure of water (in mm Hg) at temperature T.

Figure 5 illustrates the temporal variation of water concentration at the five ground stations on 28 June 1974. The two coastal locations tend to exhibit similar behavior, as do the two inland locations. Concentrations at the Downtown Los Angeles site seem to be more characteristic of those found near the coast than those observed farther inland. In general, the spatial variation in water concentration is about 7000 to 11,000 ppm.

Examining the temperature and humidity profiles observed at Rialto on 26-27 July 1973, we calculated vertical profiles of water concentration for five times during this two-day period. These profiles are illustrated in Figure 6. The maximum variation in concentration measured on these days was about 8000 ppm, as shown in the 17:20 profile for July 26.

In the analyses described above, we found that spatial variations in temperature and water concentration in the Los Angeles basin can be as large as 15°C and 11,000 ppm, respectively. Of course, since only a very limited number of days were examined, it is highly probable that even greater variations frequently occur. Considering the sensitivity results presented in Section D-1 and the variations in temperature and water concentration cited above, it is

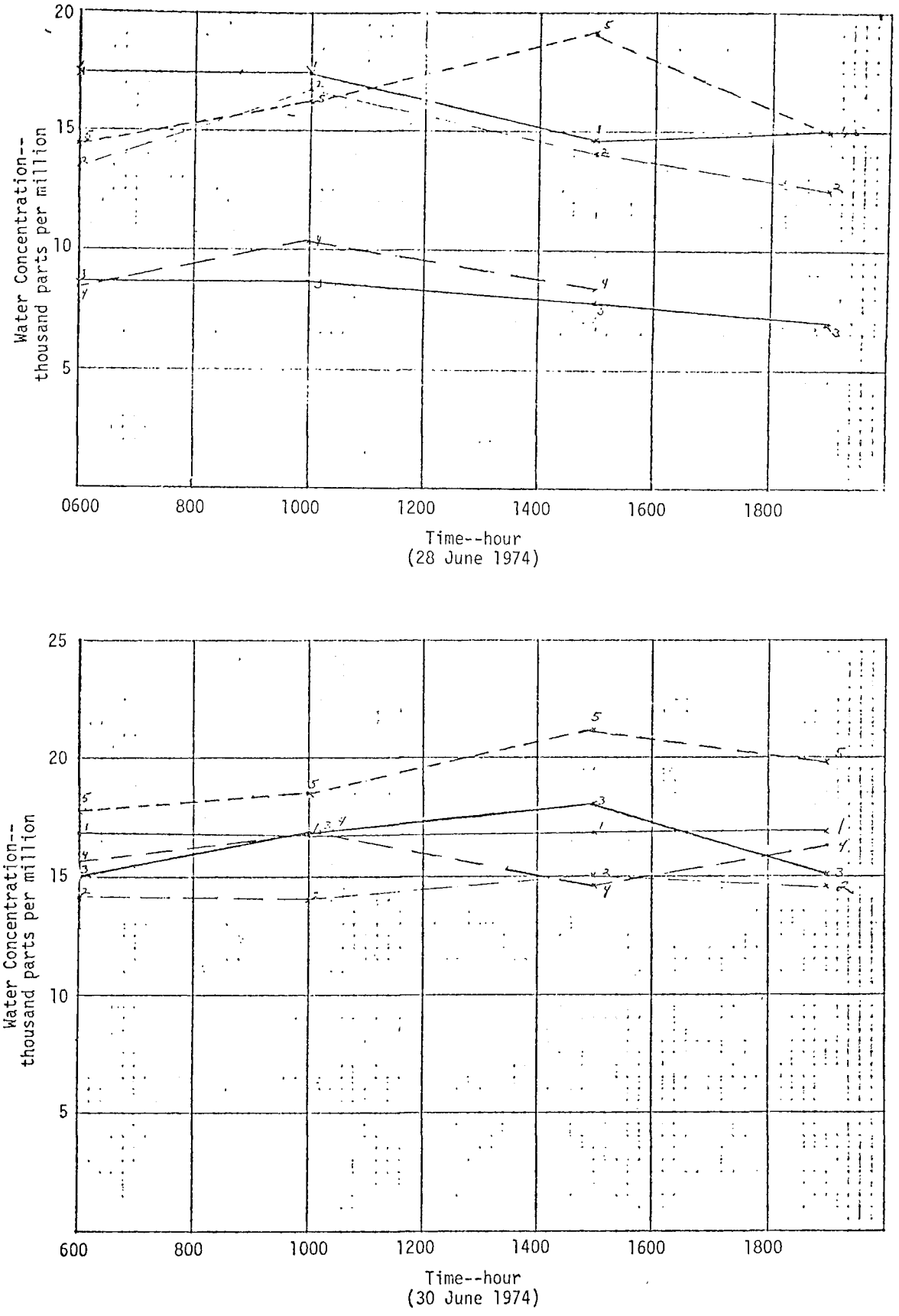


FIGURE 5. TEMPORAL VARIATIONS IN WATER CONCENTRATION AT FIVE LOCATIONS IN THE LOS ANGELES BASIN

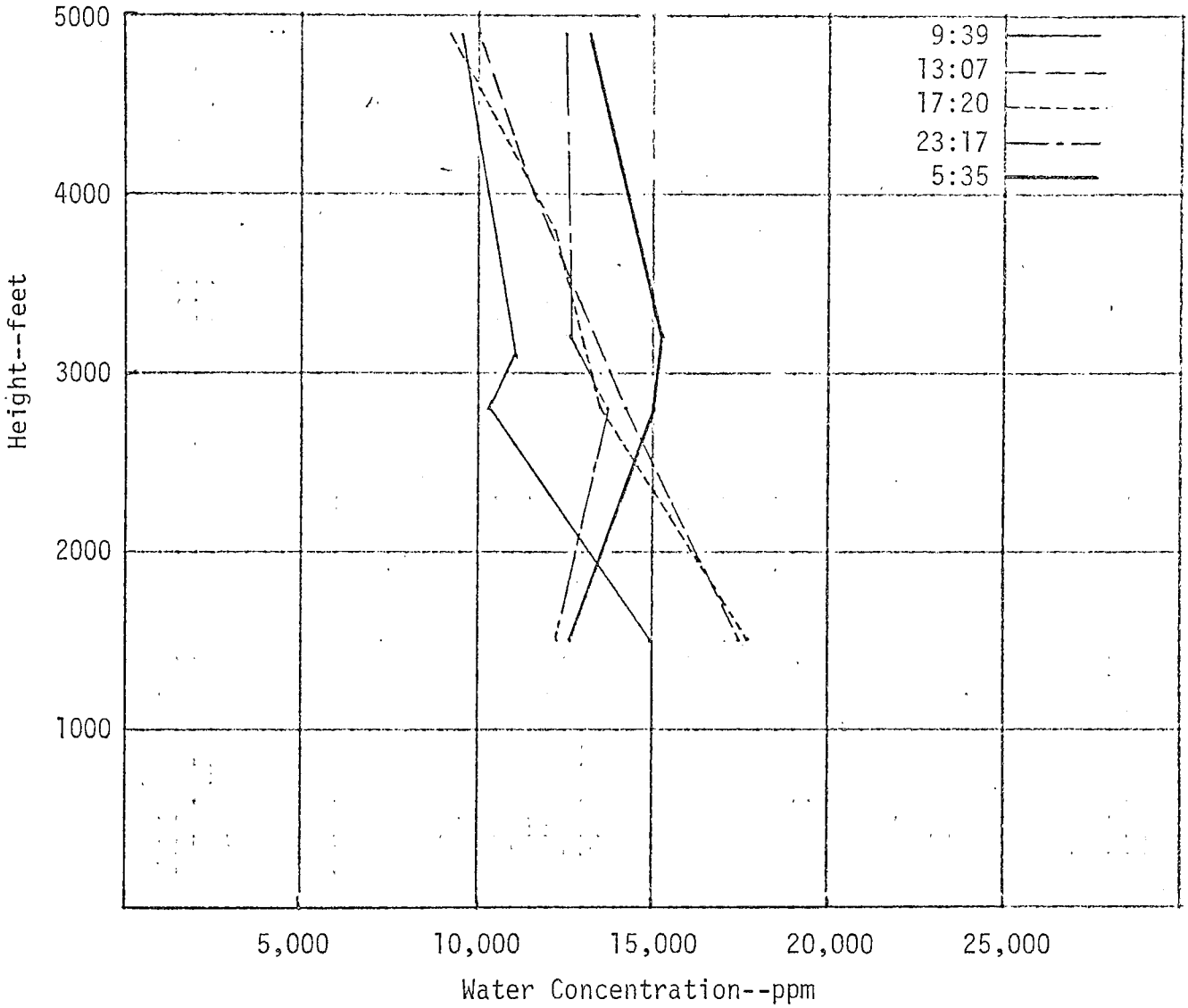


FIGURE 6. DISTRIBUTION OF THE WATER CONCENTRATION ALOFT ABOVE RIALTO ON 26-27 JULY 1973

difficult to conclude that these variations can be completely ignored. Therefore, we recommend that future studies be carried out using the airshed model itself to test various alternative strategies for treating temperature and water. Such strategies might include treating temperature or water concentrations as functions of

- Time only
- z and time
- x, y, and time
- x, y, z, and time.

Toward this end we have included provisions in the computer codes to allow the user to input temperature and relative humidity fields that vary in both space and time.

E. TREATMENT OF ORGANICS IN THE AIRSHED MODEL

Use of the kinetic mechanism discussed in Section B-1 requires that the organic species be grouped into four classes: paraffins, olefins, aromatics, and aldehydes. To treat a mixture of numerous organics, such as those found in the atmosphere, "average" rate constants must be estimated for O, OH, and O_3 attack, as appropriate, for each of the four organic groups. In general, specification of a single set of average rate constants that are invariant in space and time is possible only if the individual members of each particular group are of similar reactivity (neglecting spatial and temporal temperature effects). Table 12 presents rate constants for O, OH, and O_3 attack on various hydrocarbons. Because of the abundance of methane in the atmosphere and the wide disparity in reactivities of various paraffins, we conducted a study to ascertain the best treatment of this hydrocarbon group in the airshed model.

We considered four strategies for grouping paraffins:

(1) One reactive group including all paraffins.
(2) Two reactive groups--C_1 through C_3 low reactive; C_4, C_5, ... high reactive.
(3) Two groups--C_1 through C_3 nonreactive; C_4, C_5, ... reactive.
(4) Two groups--methane nonreactive; C_2, C_3, ... reactive.

Strategy 3 has been employed in previous applications of the airshed model.

Table 12

RATE CONSTANTS FOR O, OH, AND O_3 ATTACK ON VARIOUS HYDROCARBONS

	O		OH		O_3	
Hyrdrocarbon	Rate Constant	Reference	Rate Constant	Reference	Rate Constant	Reference
Paraffins						
Methane	1.8×10^{-2}	Herron and Huie (1969	1.6 x 10	Greiner (1967)		
Ethane	1.37	Herron and Huie (1969)	4.5×10^{2}	Greiner (1967)		
Propane	1.23 x 10	Heicklen (1967)	1.8×10^{3}	Greiner (1967)		
Butane	3.2 x 10	Herron and Huie (1969)	5.72×10^{3}	Greiner (1967)		
Isobutane	8.8	Wright (1965)	5.12×10^{3}	Greiner (1967)		
n-pentane	8.5 x 10	Herron and Huie (1969)	5.81×10^{3}	Greiner (1967)		
Isopentane	1.9×10^{2}	Herron and Huie (1969)	6.76×10^{3}	Greiner (1967)		
2,2-dimethylbutane	3.0×10^{2}	Herron and Huie (1969)	2.80×10^{3}	Greiner (1967)		
Cyclopentane	2.9×10^{2}	Herron and Huie (1969)	1.11×10^{4}	Greiner (1967)		
2,3-dimethylbutane	1.5×10^{2}	Heicklen (1967)	8.2×10^{3}	Greiner (1967)		
2-methylpentane	2.2×10^{2}	Estimate	8.41×10^{3}	Greiner (1967)		
3-methylpentane	2.2×10^{2}	Estimate	8.41×10^{3}	Greiner (1967)		
n-hexane	1.36×10^{2}	Herron and Huie (1969)	7.16×10^{3}	Greiner (1967)		
Methylcyclopentane	1.3×10^{2}	Estimate	6.87×10^{3}	Greiner (1967)		
2,4-dimethylpentane	3.3×10^{2}	Estimate	1.13×10^{4}	Greiner (1967)		
2-methylhexane	2.5×10^{2}	Estimate	1.06×10^{4}	Greiner (1967)		
3-methylhexane	2.5×10^{2}	Estimate	1.06×10^{4}	Greiner (1967)		
2,2,4-trimethylpentane	2.5×10^{2}	Herron and Huie (1969)	7.34×10^{3}	Greiner (1967)		
n-heptane	1.91×10^{2}	Herron and Huie (1969)	8.81×10^{3}	Greiner (1967)		
Methylcyclohexane	1.6×10^{2}	Estimate	8.5×10^{3}	Greiner (1967)		
2,4-dimethylhexane	3.7×10^{2}	Estimate	1.30×10^{4}	Greiner (1967)		

Table 12 (Concluded)

Hydrocarbon	O		OH		O_3	
	Rate Constant	Reference	Rate Constant	Reference	Rate Constant	Reference
2,5-dimethylhexane	3.7×10^2	Estimate	1.30×10^4	Greiner (1967)		
2,3,4-trimethylpentane	1.8×10^2	Herron and Huie (1969)	1.58×10^4	Greiner (1967)		
n-octane	2.5×10^2	Herron and Huie (1969)	1.28×10^4	Greiner (1967)		
n-nonane	2.0×10^2	Estimate	1.21×10^4	Greiner (1967)		
n-decane	2.6×10^2	Estimate	1.38×10^4	Greiner (1967)		
Olefins						
Ethylene	7.72×10^2	Cvetanovic (1963)	2.13×10^3	Morris and Niki (1971)	3.8×10^{-3}	Wei (1963)
Propylene	4.41×10^3	Cvetanovic (1963)	2.13×10^4	Morris and Niki (1971)	1.6×10^{-2}	Wei (1963)
Butenes	4.41×10^3	Cvetanovic (1963)	5.12×10^4	Morris and Niki (1971)	1.3×10^{-2}	Wei (1963)
1-pentene			5.33×10^4	Morris and Niki (1971)	1.3×10^{-2}	Wei (1963)
Trans-2-pentene			1.13×10^6	Morris and Niki (1971)	5.0×10^{-2}	Wei (1963)
Cis-2-pentene	1.69×10^4	Cvetanovic (1963)	1.13×10^6	Morris and Niki (1971)	4.1×10^{-2}	Wei (1963)
2-methyl-2-butene	6.03×10^4	Cvetanovic (1963)	1.49×10^6	Morris and Niki (1971)		
Cyclopentene	2.35×10^4	Cvetanovic (1963)				
1-hexene	5.00×10^3	Cvetanovic (1963)			1.5×10^{-2}	Wei (1963)
Cis-2-hexene					4.1×10^{-2}	Wei (1963)
1-heptene					1.21×10^{-2}	Cadle (1952)
Aldehydes						
Formaldehyde	4.41×10^2	Estimate	1.92×10^4	Morris and Niki (1971)		
Acetaldehyde	4.41×10^2	Estimate	1.92×10^4	Morris and Niki (1971)		
Propionaldehyde			3.84×10^4	Morris and Niki (1971)		
Aromatics						
Toluene	1.1×10^2	Estimate				
M-xylene, p-xylene	4.4×10^2	Estimate		Estimate		

To test these schemes, we performed smog chamber simulations for a mixture of paraffins, NO_x, and CO having proportions typical of those found in the Los Angeles atmosphere in 1969. For comparison, we carried out a baseline simulation in which each paraffin was treated as an individual reactive species in the mechanism. Thus, we compared the predictions for Strategies 1 through 4 with those for the baseline case to determine the errors introduced by each lumping scheme.

Initial conditions for the simulation runs were derived from air quality measurements taken at Commerce, California, on 30 September 1969 by Scott Research Laboratories. In particular, we used the following concentrations, which were measured at 8 a.m. on that day:

Species	Concentration (ppm)
CO	10.0
NO	0.4
NO_2	0.1
H_2O	1.6×10^4
C_1^+	4.213
C_2^+	0.476
C_1-C_3	3.944
C_4^+	0.269

The predicted values of NO, NO_2, and O_3 after 12 hours of irradiation were as follows:

	Predicted Concentration (ppm)		
Strategy	NO	NO_2	O_3
Baseline	0.05	0.30	0.05
1	0.04	0.30	0.07
2	0.05	0.30	0.05
3	0.09	0.28	0.03
4	0.05	0.30	0.05

These results indicate that Strategies 2 and 4 led to the best agreement with the baseline case. Since Strategy 2 uses two reactive species, whereas Strategy 4 involves only one, we plan to treat the paraffin class according to Strategy 4 to minimize computing costs.

Thus, five organic classes are considered in the airshed model: nonreactive hydrocarbons (methane and acetylene), nonmethane paraffins, olefins, aromatics, and aldehydes. We recommend that future studies be carried out to ascertain whether the olefins should be treated as a single lumped species or as several lumped species. In addition, it may be possible to combine the aromatics with the nonmethane paraffins, since both groups have similar reactivities and may produce similar products (according to the mechanism given in Section B-1).

F. INTRODUCTION OF THE IMPROVED KINETIC MECHANISM INTO THE AIRSHED MODEL

In Sections B and C, we delineate efforts aimed at developing improved mechanisms for describing the chemical interactions of hydrocarbons, NO_x, O_3, and SO_2. With regard to the HC-NO_x-O_3 system, the generalized mechanism discussed in Section B represents a significant improvement over the 15-step mechanism previously employed in the airshed model. Thus, we have incorporated the expanded mechanism into the model. In addition, we have implemented in the model the SO_2 mechanism described in Section C, even though the mechanism has yet to be validated using smog chamber data. In the present section, we discuss our efforts to use the improved kinetic mechanism in an actual airshed simulation.

Installation of the new mechanism in the airshed model required that numerous changes be made in the computer codes. Particular difficulties arose because the number of species that must be followed in the airshed model increased from 6 to 12 (NO, NO_2, O_3, H_2O_2, HNO_2, nonmethane paraffins, olefins, aromatics, aldehydes, SO_2, CO and unreactive hydrocarbons). Moreover, the programs were to be exercised on the CDC 7600 computer, which has only a limited amount of small core memory, at Lawrence Berkeley Laboratory. Thus, we

restructured the programs somewhat to make efficient use of available small core memory, as well as the more abundant amounts of extended core memory. After the coding changes were made, we checked the programs by running several test cases.

To gain some experience in using the new mechanism in airshed simulations, we decided to exercise the model using meteorological and emissions inputs derived in previous model evaluation efforts. We felt that using the same meteorological and emissions inputs, to the extent possible would provide a means for ascertaining how sensitive the model predictions were to the change in the kinetic mechanism itself. Because of our previous experience in simulating the Los Angeles basin on 29 September 1969, we chose that day for our initial model application effort.

Before the simulations could be carried out, we first had to compute new splits for hydrocarbon emissions and initial and boundary concentrations. Previously, available hydrocarbon emissions and air quality data were divided into two groups--reactive and unreactive hydrocarbons. To use the new mechanism, we revised the categories to reflect the new definition of the five organic classes--nonmethane paraffins, olefins, aromatics, aldehydes, and nonreactive hydrocarbons (methane and acetylene).

Organics are emitted from a variety of sources in the Los Angeles basin, including motor vehicles, refineries, and numerous other stationary sources. Although the organic composition of automobile emissions has been documented by several investigators, very little information is available for use in establishing guidelines for estimating the composition of the stationary source emissions. For the purposes of this study, we assumed that the composition of stationary source emissions is the same as that for automobiles. Although we recognize that this is not necessarily a good assumption, our main objective was simply to make "reasonable" estimates of the emission splits to exercise the model. A more refined inventory can be derived using the results of a recent study of organic emission control strategies carried out by Trijonis and Arledge (1975). Unfortunately, their results were not available in time for inclusion in this study.

Using organic composition data derived from tests of 10 automobiles reported by the Bureau of Mines (1973), we estimated the following mass emission splits:

Group	Mass Split (percent)
Nonmethane paraffins	29
Olefins	30
Aromatics	23
Aldehydes*	5
Nonreactive hydrocarbons	18

Thus, we added previous estimates of reactive and nonreactive hydrocarbon emissions to estimate the spatial and temporal distribution of total hydrocarbon emissions. Then, we multiplied the emission splits cited above by the total hydrocarbon emissions in each grid cell to estimate the distribution of emissions for each of the five classes.

We calculated initial and boundary concentrations using our previous estimates of reactive and nonreactive hydrocarbon concentrations in conjunction with gas chromatographic analyses of ambient air in the basin for 29 September 1969 reported by Scott Research Laboratories (1970). We derived the following relationships:

$$[\text{Olefins}] = 0.211[C_R],$$

$$[\text{Paraffins}] = 0.414[C_R] + 0.057[C_{NR}],$$

$$[\text{Aromatics}] = 0.376[C_R] + 0.003[C_{NR}],$$

$$[\text{Aldehydes}] = 0.04 \text{ ppm},$$

$$[\text{Nonreactive hydrocarbons}] = 0.94[C_{NR}],$$

where $[C_R]$ and $[C_{NR}]$ are the original estimates of reactive and nonreactive hydrocarbon concentrations, respectively.

*Aldehyde emissions are estimated to be about 5 percent of the total hydrocarbon emissions. Since aldehydes were not included in the original SAI inventory for Los Angeles, the total percentage adds up to 105 percent. Thus, we increased the total organic emissions by 5 percent to reflect the additional aldehyde emissions.

Figures 7 through 12 illustrate some of the predictions obtained from the SAI model using the 31-step kinetic mechanism and the emissions and air quality inputs described above. These figures also show the predictions from the analogous simulation in which the 15-step mechanism was employed. In general, the most obvious characteristic of these results is that the O_3 production seems to have been accelerated, leading to higher predicted O_3 levels. However, in many instances the NO_2 predictions are in better agreement with the measurements, especially during the late morning and early afternoon.

It is difficult to make any assessment now of the enhanced reliability of the model resulting from the incorporation of the new 31-step mechanism. However, considering the nature of the available model inputs used in this study, the results are encouraging. We recommend that a greater effort be expended in future work to assemble an appropriate organic emissions inventory. Furthermore, the enhanced production of O_3 observed in the results presented here may be caused in part by inaccuracies in the treatment of aldehyde photolysis or NO removal in the mechanism. We assumed that aldehyde photolysis is proportional to that for NO_2. However, shifts in the UV spectrum throughout the day may invalidate this assumption. Finally, NO may be removed too rapidly in the mechanism, thus, allowing O_3 levels to build up prematurely. These issues can be resolved only by subjecting the model to a comprehensive evaluation. We recommend that such an undertaking be considered in the near future.

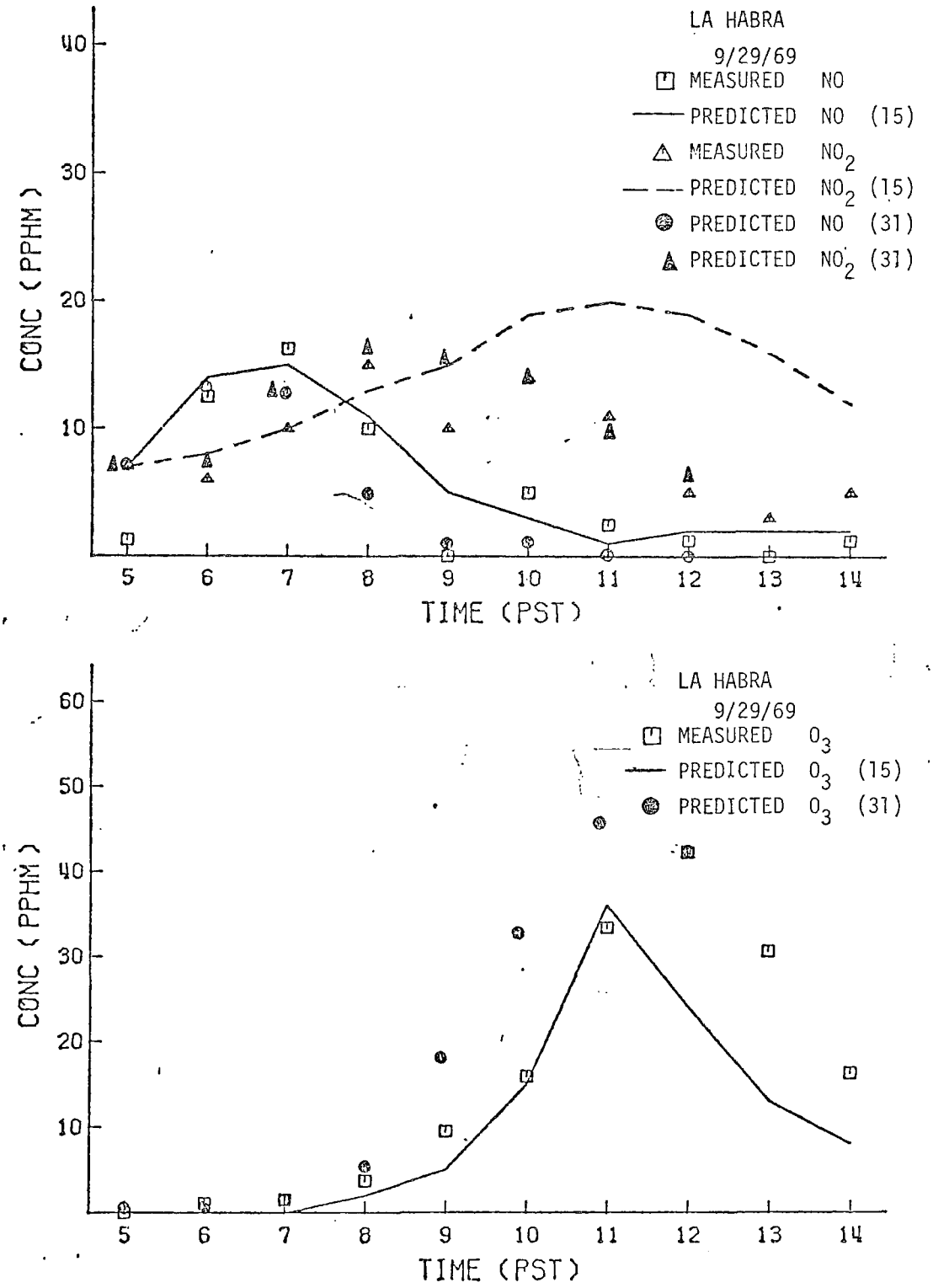
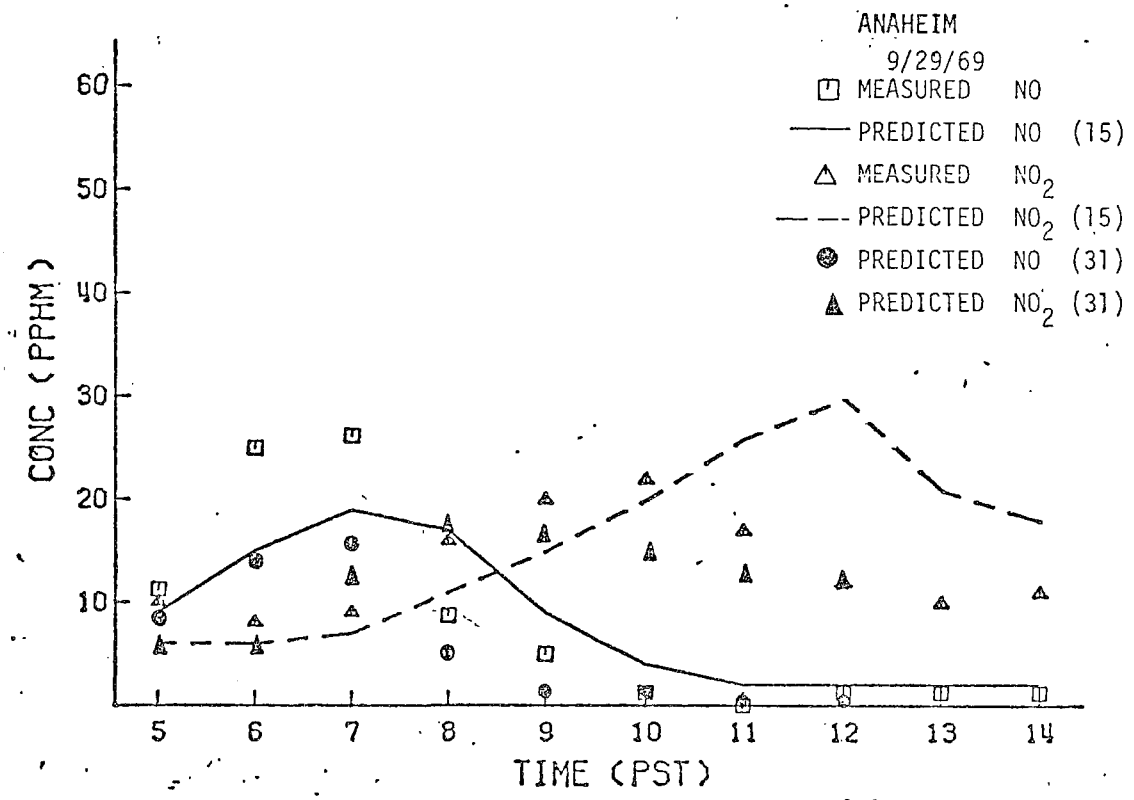


FIGURE 7. PREDICTED AND MEASURED CONCENTRATIONS FOR LA HABRA USING THE 15- AND 31-STEP KINETIC MECHANISMS



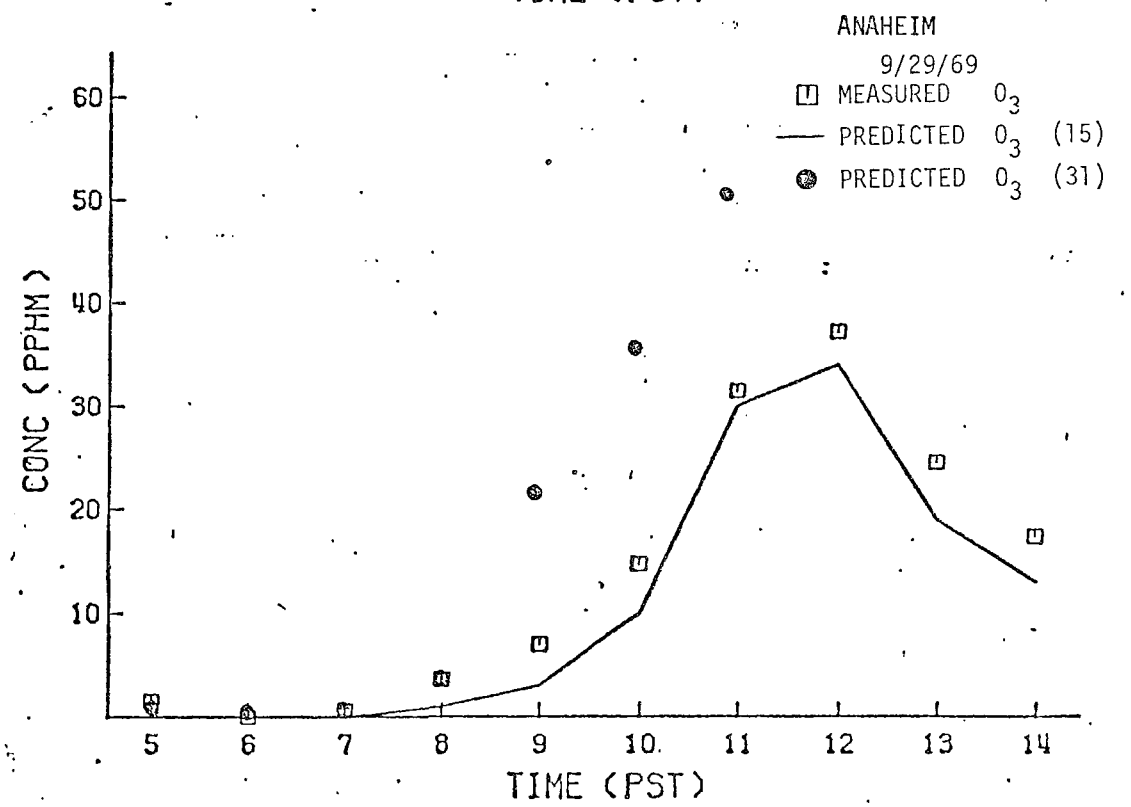


FIGURE 8. PREDICTED AND MEASURED CONCENTRATIONS FOR ANAHEIM USING THE 15- AND 31-STEP KINETIC MECHANISMS

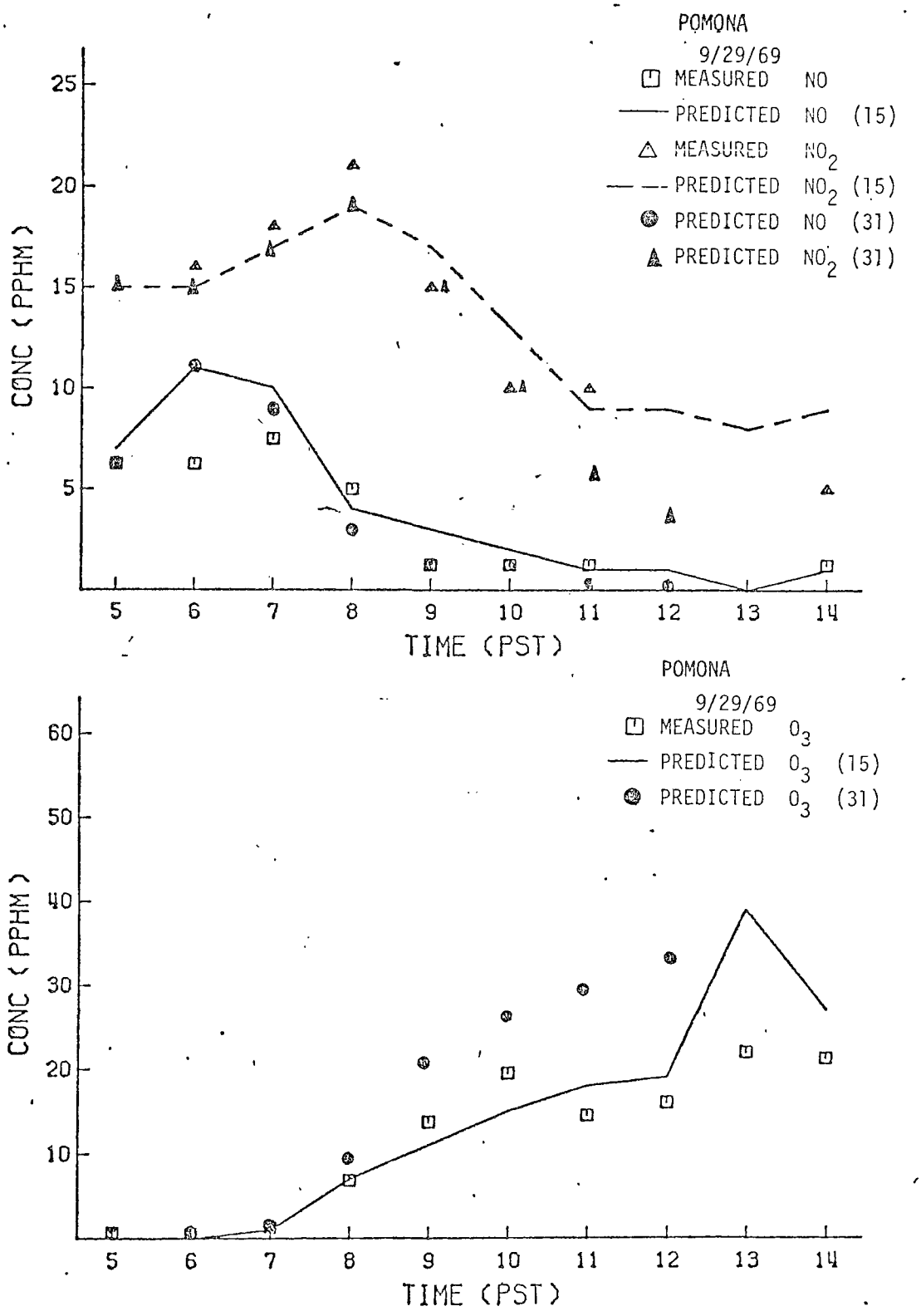


FIGURE 9. PREDICTED AND MEASURED CONCENTRATIONS FOR POMONA USING THE 15- AND 31-STEP KINETIC MECHANISMS

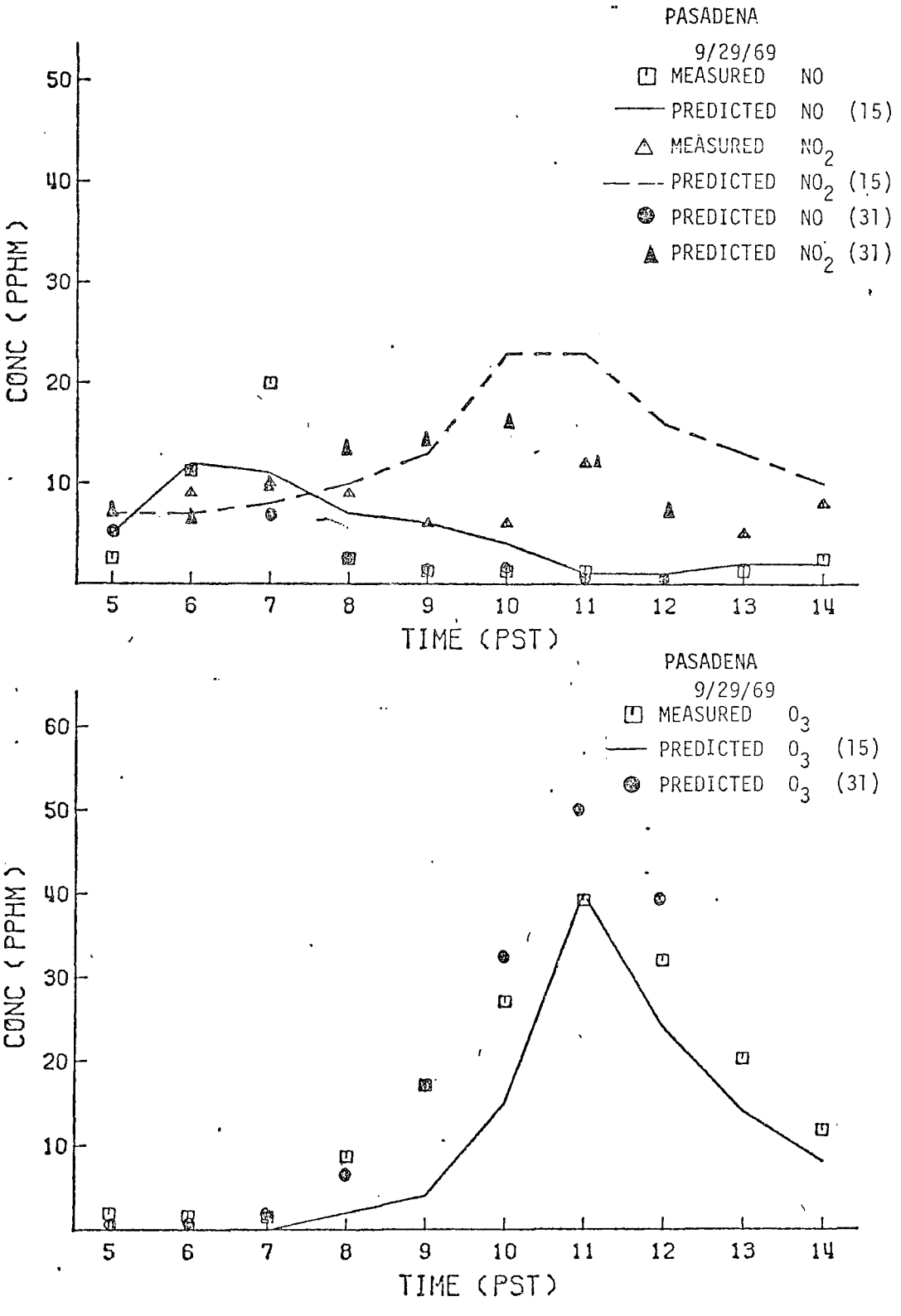


FIGURE 10. PREDICTED AND MEASURED CONCENTRATIONS FOR PASADENA USING THE 15- AND 31-STEP KINETIC MECHANISMS

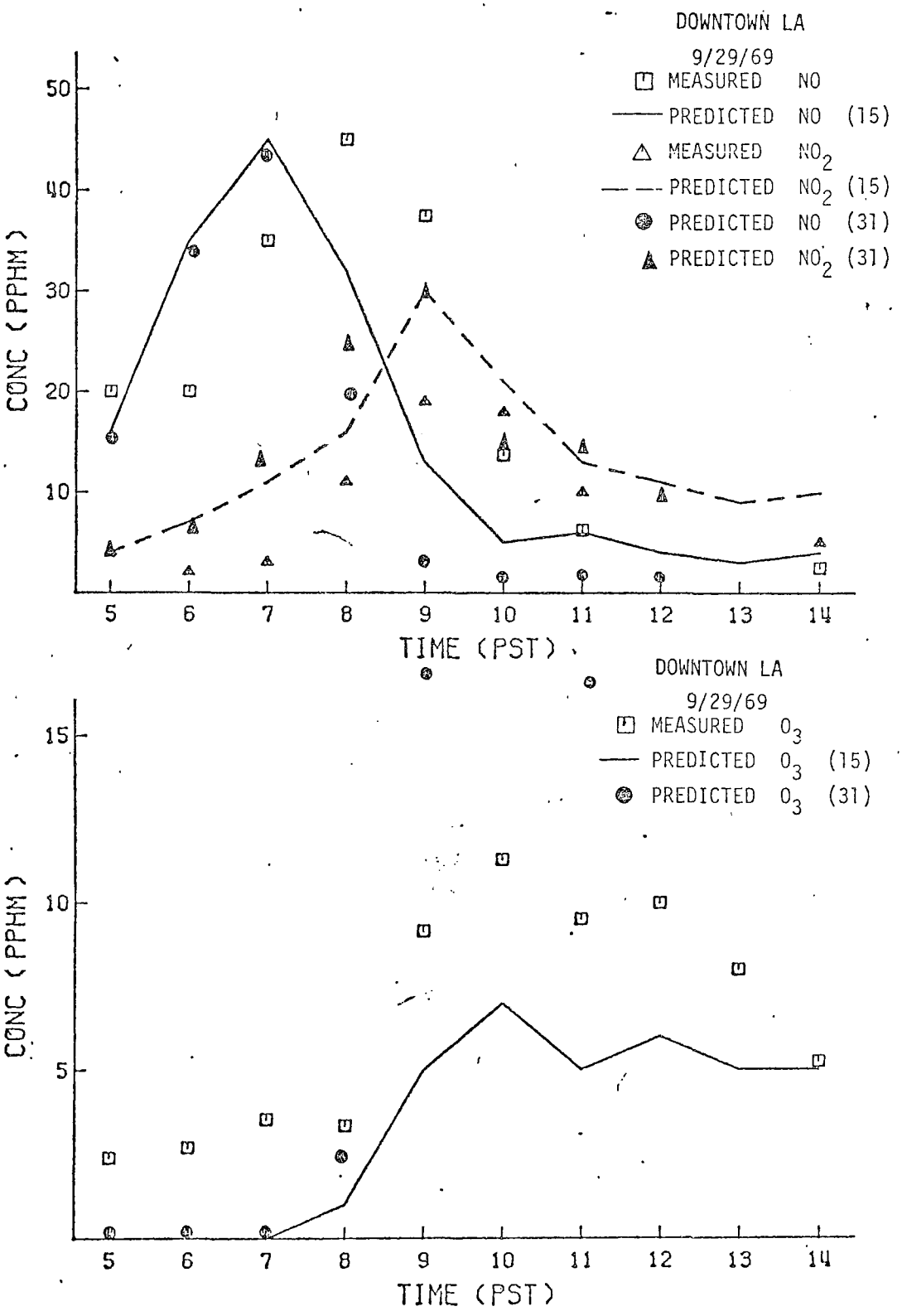


FIGURE 11. PREDICTED AND MEASURED CONCENTRATIONS FOR DOWNTOWN LOS ANGELES USING THE 15- AND 31-STEP MECHANISMS

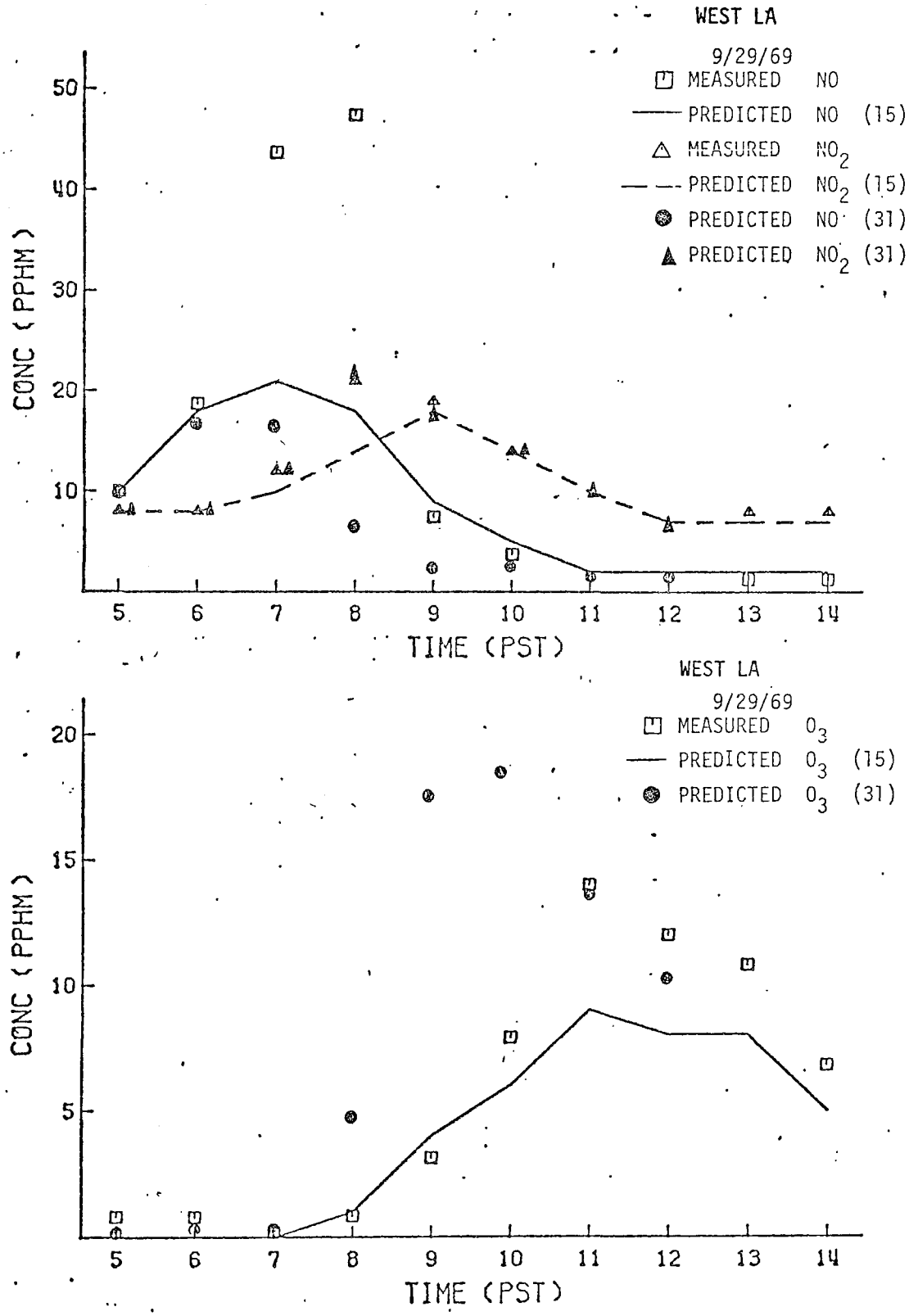


FIGURE 12. PREDICTED AND MEASURED CONCENTRATIONS FOR WEST LOS ANGELES USING THE 15- AND 31-STEP MECHANISMS

III METEOROLOGY-RELATED DEVELOPMENT ACTIVITIES

Steven D. Reynolds
Mark A. Yocke
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In our previous model development and application efforts, we made several assumptions about the treatment of meteorological parameters. Among these, the most notable are the following:

> Wind shear effects can be neglected.
> A diffusivity algorithm that is solely a function of wind speed and height can be used.
> The base of an elevated inversion layer is a suitable choice for the top of the modeling region.

However, these assumptions clearly introduce inaccuracies. First, the wind flow field is fully three-dimensional and should be treated accordingly. Second, the magnitude of the turbulent diffusivity depends on atmospheric stability and surface roughness, as well as on wind speed and height. Third, significant quantities of pollutants trapped in an elevated inversion layer may be injected into the mixed layer as the stable layer is eroded by surface heating effects. Moreover, ground-based inversions frequently occur at night. Thus, further consideration needs to be given to the definition of the modeling region and the treatment of inversion layers in the model. In the following sections, we discuss our efforts to improve the treatment of wind fields, diffusivities, and inversions in the airshed model.

A. MODEL SENSITIVITY TO THE INCLUSION OF WIND SHEAR

The results of model sensitivity studies reported in Volume I indicate the importance of accurately specifying the wind speed and direction throughout the region of interest. In this section, we discuss additional sensitivity studies that were carried out to assess the importance of characterizing wind shear effects. The results of this effort will be useful for establishing (1) the need to extend our existing meteorological algorithms to treat

wind shear and (2) the extent to which vertical wind soundings should be taken over urban areas.

Accurate specification of winds aloft is usually hampered in a grid model by a dearth of appropriate measurements. Since the full three-dimensional structure of the wind field must be input to the model, particular attention must be given to this aspect of model usage. The following are four possible means for establishing the complete wind field:

(1) Assumption of a "flat" velocity profile, where the estimated ground-level wind speeds and directions are assumed to be invariant with height (i.e., wind speeds and directions are a function only of x, y, and t).
(2) Calculation of the winds aloft by scaling the ground-level winds according to the findings of previous wind shear studies (i.e., assumption of a form for the wind shear, such as a power law profile).
(3) Interpolation for the wind speeds and directions using actual wind soundings aloft.
(4) Prediction of the wind flow field using a numerical simulation model.

The first alternative, which is the simplest, is useful for establishing the basic characteristics of the flow field. Previous SAI simulations have used this approach. For more refined estimates of the wind field when no measurements aloft are available, the second technique can be used. The last two alternatives afford the best means of specifying winds aloft, provided that--for Alternative 3--the measurement network is sufficiently dense and that--for Alternative 4--the model has been validated. At present, Alternatives 2 and 3 appear to represent the best means for accurately specifying winds aloft.

An important step in procuring a data base for describing the upper level winds is being made in the RAPS program for St. Louis. One aspect of this comprehensive data gathering study will be the regular monitoring of winds aloft

at two to four sites in this metropolitan area. Using the surface wind data in conjunction with the upper wind measurements, one should be able to estimate with reasonable accuracy the structure of the wind field over this urban area.

To gain some insight into the importance of wind shear effects on the predictions obtained from the photochemical airshed model, we carried out a series of comparative simulations for the Los Angeles basin, using both "flat" and power law wind velocity profiles. Since vertical wind soundings were not available for Los Angeles, we used only the surface-based measurements to generate both wind fields. In the following subsections, we further describe the treatment of wind shear and discuss the results of the simulations.

1. Wind Velocity Profile

Variations in horizontal wind with height have been the subject of intensive study in meteorology for years. Assuming neutral stability conditions, von Kármán derived a logarithmic relationship for the mean wind velocity in the sublayer (surface layer) of the atmospheric boundary layer from theoretical considerations (Plate, 1971):

$$\frac{U}{u_*} = \frac{1}{K} \ln\left(\frac{Z}{Z_0}\right) \quad , \tag{9}$$

where

U = wind speed at height Z,
u_* = the friction velocity,
Z_0 = the roughness parameter,
K = the von Kármán constant.

Subsequently, this relationship was verified through experiment. For diabatic conditions, Laikhtman (1944) and Deacon (1949) proposed that the expression

$$\frac{U}{u_*} = \frac{1}{K(1-\beta)}\left[\left(\frac{Z}{Z_0}\right)^{1-\beta} - 1\right] \tag{10}$$

be used, where β is a function of atmospheric stability.

Within the remainder of the atmospheric boundary layer (i.e., above the sublayer), wind profiles are usually characterized by an empirical power law. Blasius was the first to describe the mean velocity distribution by the following general relationship:

$$\frac{\underset{\sim}{U}}{\underset{\sim}{U}_R} = \left(\frac{Z}{Z_R}\right)^M \quad , \tag{11}$$

where $\underset{\sim}{U}_R$ is the wind velocity vector at a reference height Z_R. The exponent M is a function of ground surface roughness and atmospheric stability. DeMarrais (1959), Davenport (1965), Shellard (1965), and Jones et al. (1971) performed experiments to derive quantitative relationships for M. On the basis of their findings, they estimated that M is likely to be within the following range:

$$0.4 > M > 0.2 \quad .$$

Because of its applicability over the entire boundary layer, we selected the mean velocity power law relationship [Eq. (11)] as the most suitable available description of the wind speed shear. We chose 0.2 as a representative value of M for an urban area, such as Los Angeles.

2. Implementation of the Wind Velocity Profile

The numerical integration scheme used in the grid model requires that the average wind velocity be specified at each grid cell interface. The integration of Eq. (11) along the vertical axis from the lower cell boundary to the upper, followed by division by the cell depth, yields the expression for the mean horizontal wind velocity over a horizontal cell interface:

$$\underset{\sim}{U} = \frac{\underset{\sim}{U}_R}{(Z_t - Z_b)Z_R^M(M+1)} \cdot \left(Z_t^{M+1} - Z_b^{M+1}\right) \quad , \tag{12}$$

where Z_t is the elevation at the top of the cell and Z_b is the elevation at the bottom of the cell. Equation (12) can be used to obtain both the x and y components of the mean velocity for each horizontal grid cell interface within the modeling region. Assuming that turbulent atmosphere flow is incompressible, the vertical advective velocity, w, can be computed from the continuity relationship:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad . \tag{13}$$

3. Computer Coding

To incorporate the wind shear algorithms given by Eqs. (12) and (13), we made appropriate coding changes in the computer programs embodying the airshed model. The result of these alterations was a slight increase in both machine storage requirements and CPU time.

4. Description of the Experiment

After we altered the computer codes, we designed an experiment to examine the sensitivity of the airshed model to wind shear effects. To insure that the deviations in predicted concentrations are caused only by dissimilarities in the prescribed wind fields, we made test runs using both the original code (in which a flat profile was assumed) and the newly revised code with M set equal to zero. From Eq. (12), if M = 0, we obtain the same flat wind profile as was used in the original formulation of the model. Meteorological and emissions data for Los Angeles on 29 September 1969 served as input data for predicting concentrations of RHC, URHC, NO, NO_2, O_3, and CO, using both the modified and unmodified programs for the hours 0500 through 1500 PST. The two programs produced identical predictions, thus indicating that all coding alterations had been implemented properly.

Finally, we ran the modified program using a value for M of 0.2, and we compared the output of this program with the previous unmodified computations (assuming a flat velocity profile). Figures 13 through 20 show plots of the average and maximum deviations in ground-level concentrations for each species as a function of time. Here, the concentration deviations are defined as the predicted concentrations with wind shear minus the corresponding concentrations predicted when wind shear is neglected.

5. Discussion of the Results

An examination of the simulation results reveals the significance of incorporating the power law wind profile in the grid model. Because the velocities are systematically altered through the application of the wind profile algorithm, the computed wind velocities at the inversion base and ground-level heights were increased, relative to the straight profile values ($M = 0$), by as much as 70 and 20 percent, respectively. The wind velocities averaged over the entire mixing depth were consistently much larger than the uniform profile values. As one would expect, therefore, the results of the sensitivity experiment, which was performed with a 25 percent increase in all wind velocities (see Chapter IV of Volume I), are strikingly similar to those shown here.

A characteristic of both the wind speed and wind shear sensitivity studies is that, when the concentration maps are compared with those generated for the base case, a perceptible translation of concentration isopleths toward the northeast, the prevailing wind direction, is observed. In addition, the majority of maximum concentrations are located in Grid Columns 20 through 25; this result was expected because the translation of concentration isopleths is greatest when the path of travel is longest. The fact that average overall deviations for all species are negative also supports the hypothesis that the net effect of the inclusion of wind shear is similar to that resulting from a simple increase in wind speeds.

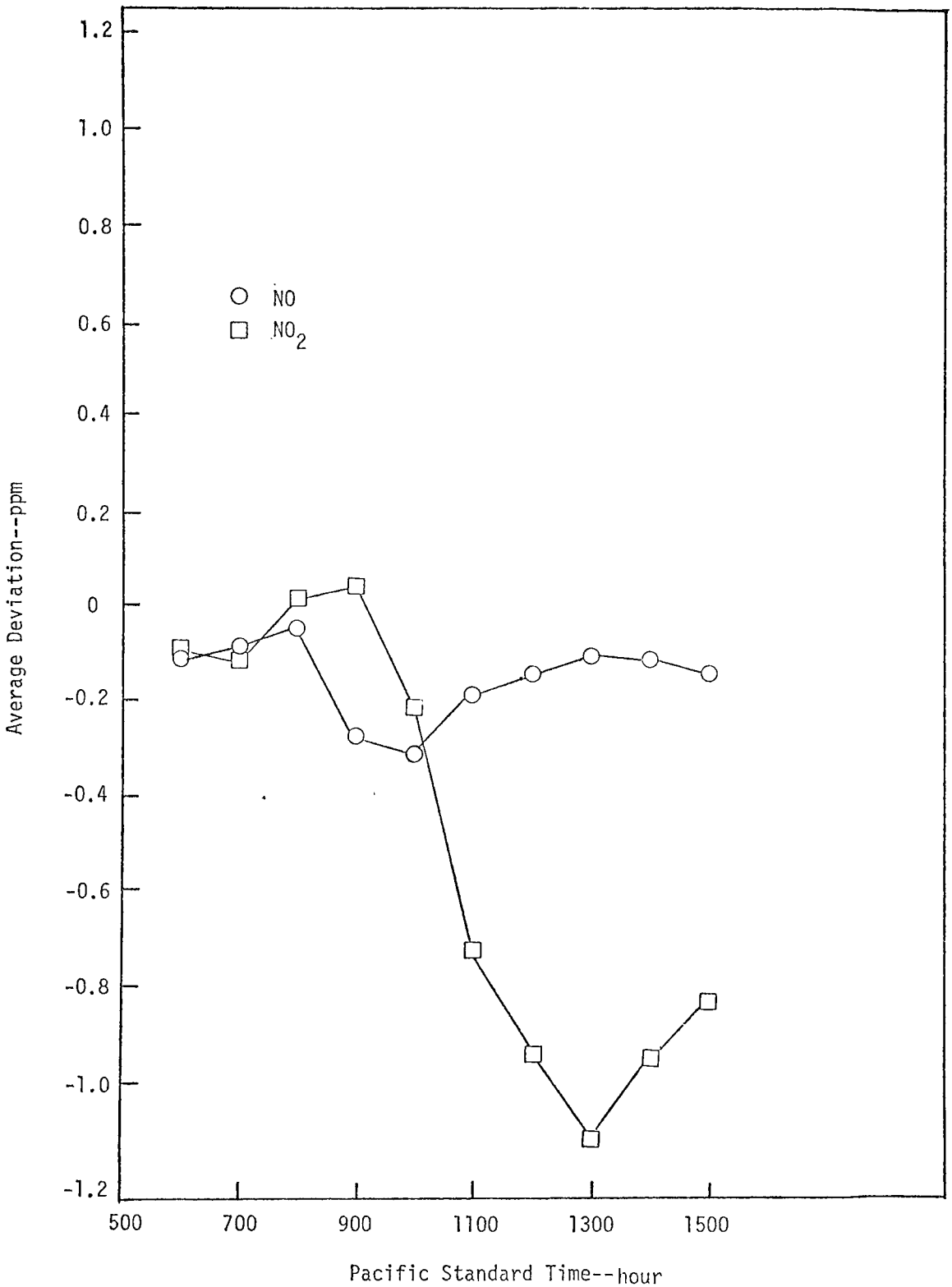


FIGURE 13. THE EFFECT--EXPRESSED AS AVERAGE DEVIATION--OF VARIATIONS IN VERTICAL WIND SHEAR ON NO AND NO_2

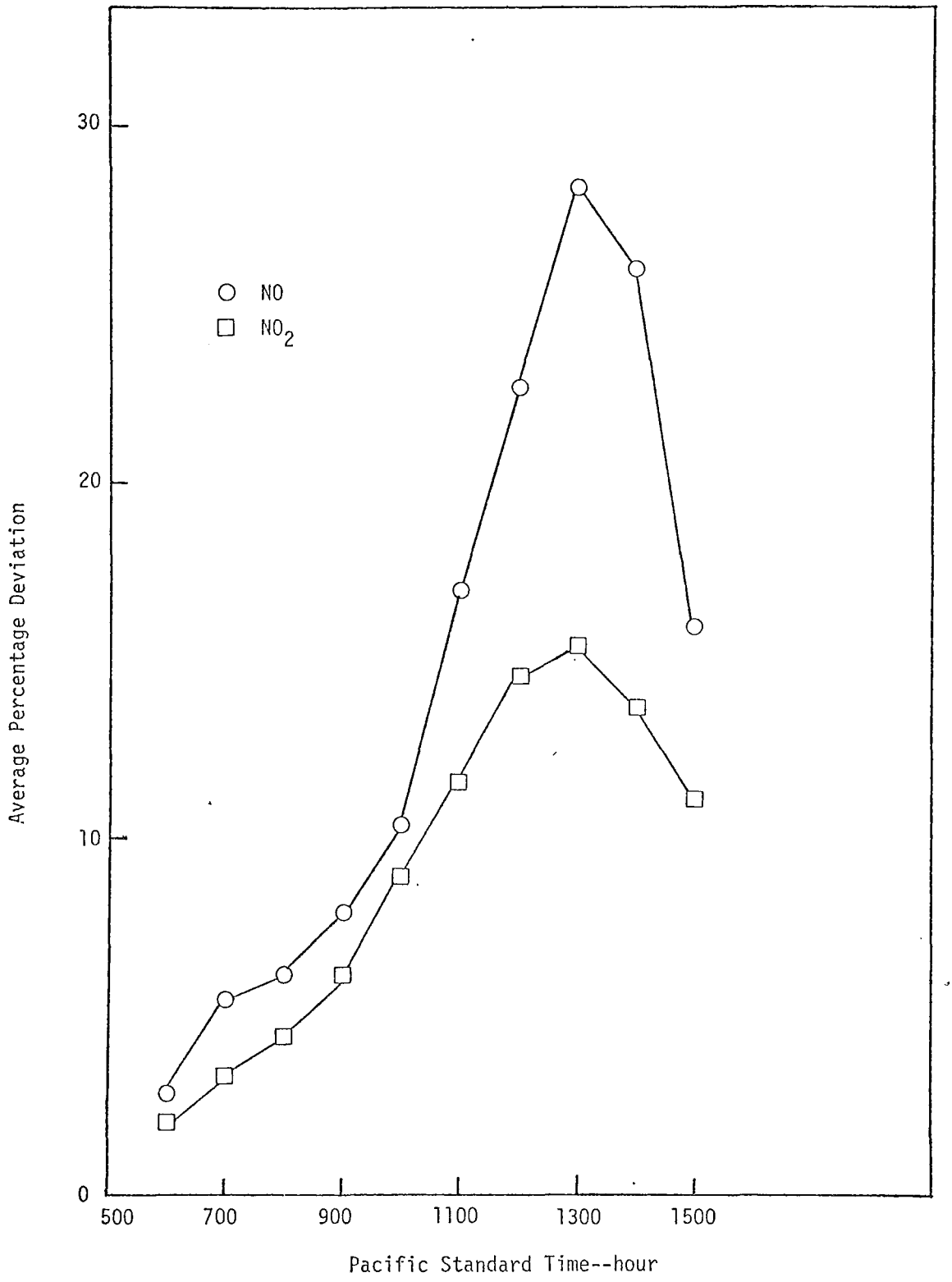


FIGURE 14. THE EFFECT--EXPRESSED AS PERCENTAGE DEVIATION--OF VARIATIONS IN VERTICAL WIND SHEAR ON NO AND NO_2

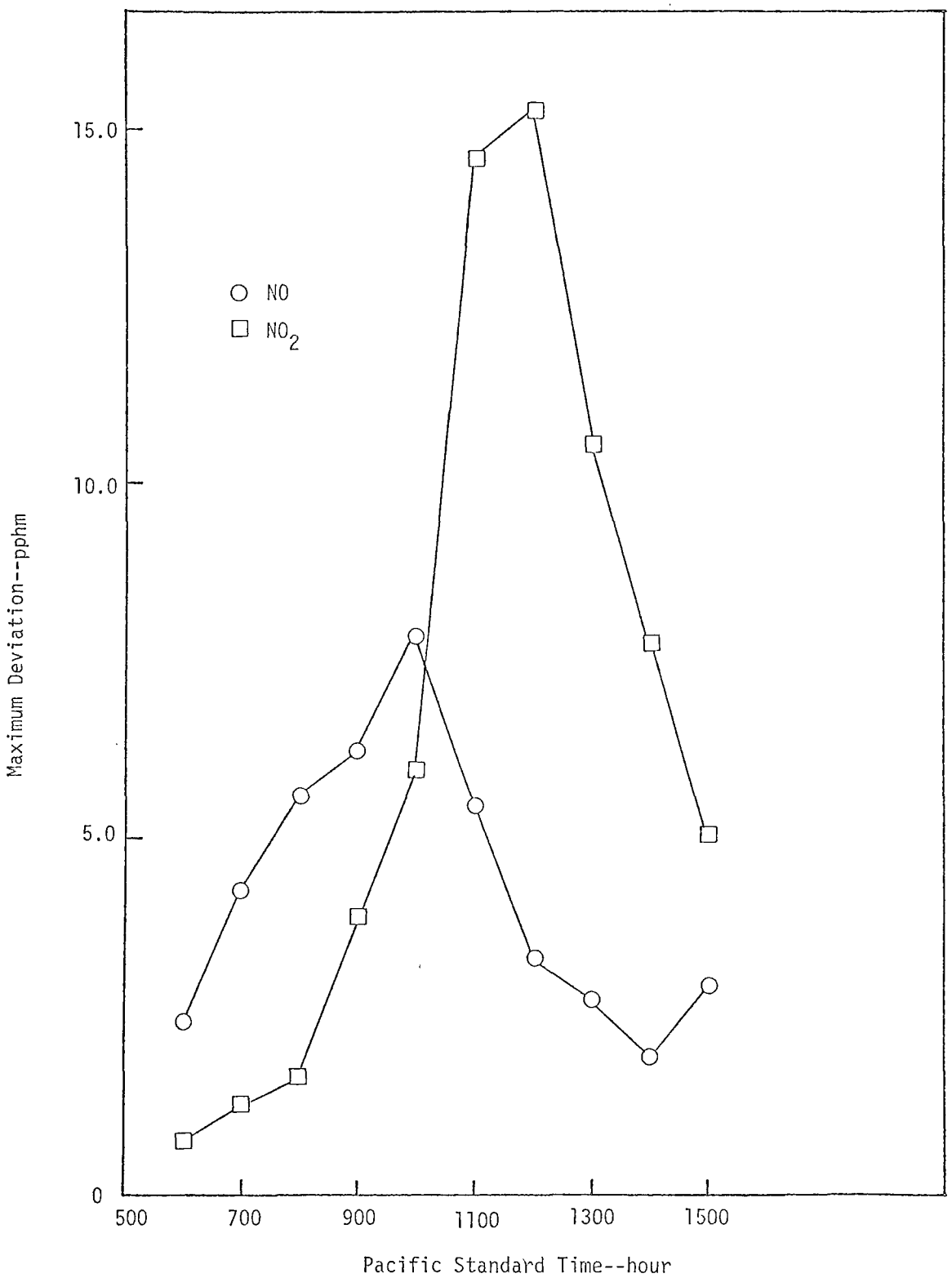


FIGURE 15. THE EFFECT--EXPRESSED AS MAXIMUM DEVIATION--OF VARIATIONS IN VERTICAL WIND SHEAR ON NO AND NO_2

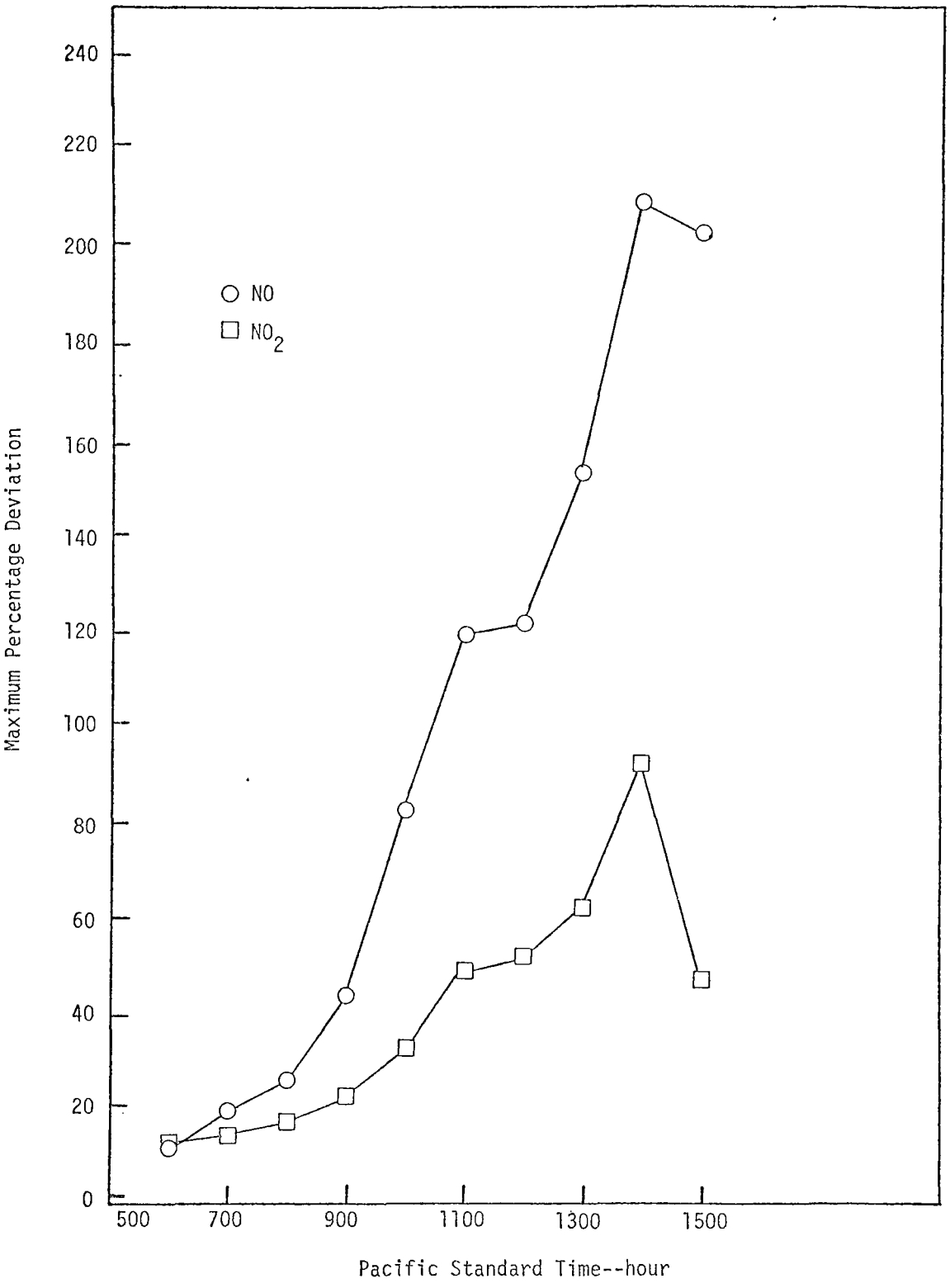


FIGURE 16. THE EFFECT--EXPRESSED AS PERCENTAGE MAXIMUM DEVIATION--OF VARIATIONS IN VERTICAL WIND SHEAR ON NO AND NO_2

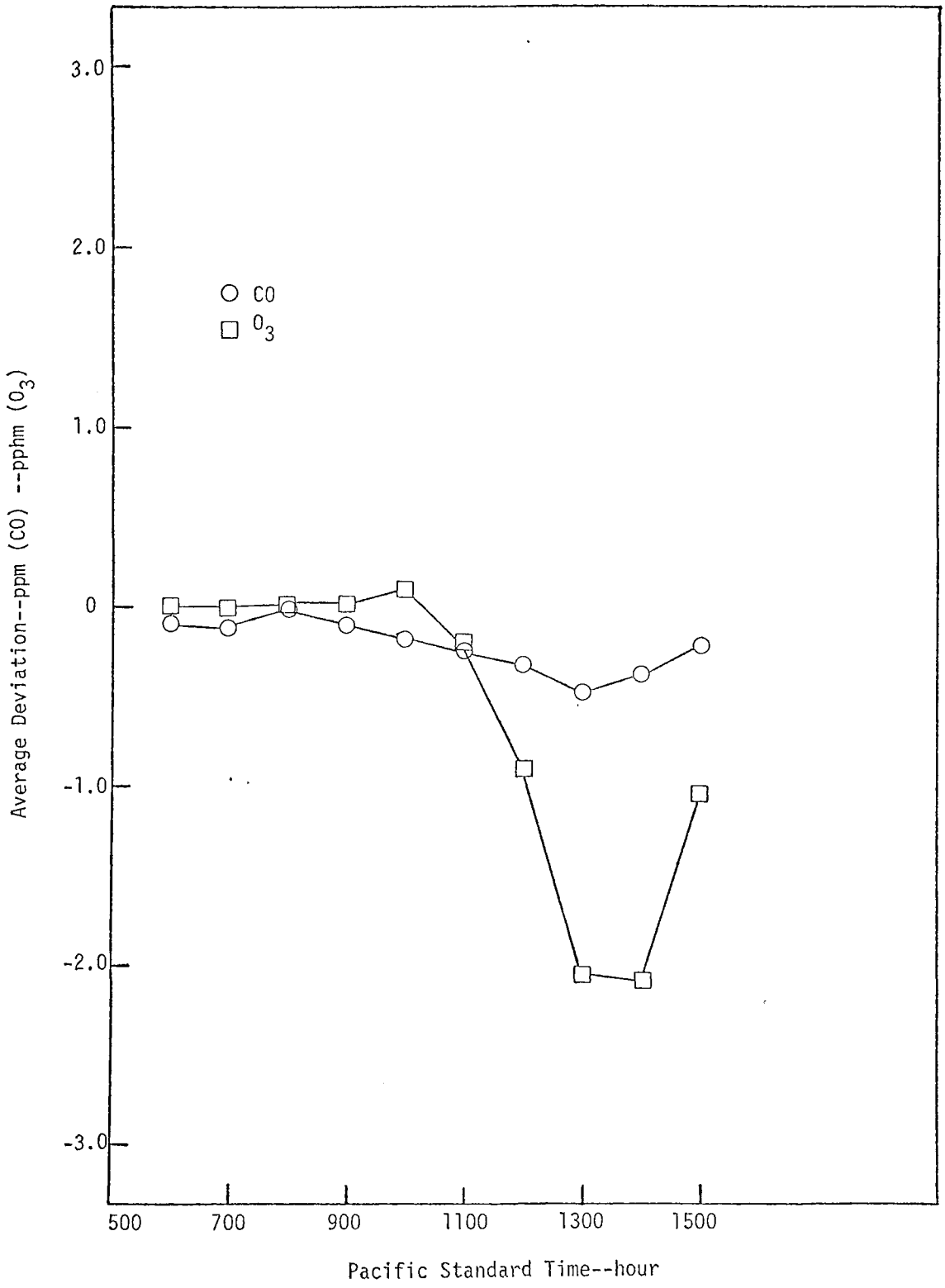


FIGURE 17. THE EFFECT--EXPRESSED AS AVERAGE DEVIATION--OF VARIATIONS IN VERTICAL WIND SHEAR ON CO AND O_3

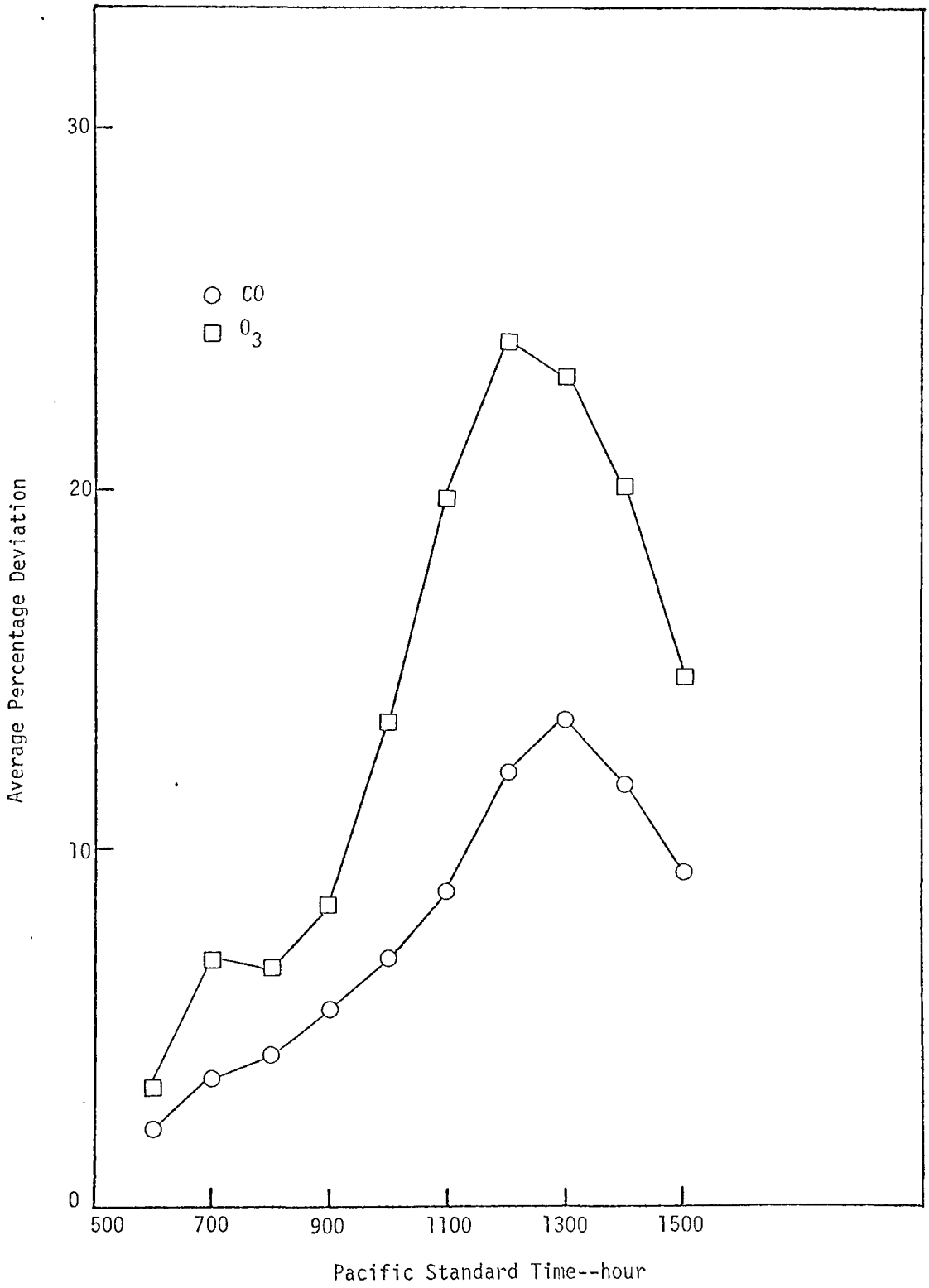


FIGURE 18. THE EFFECT--EXPRESSED AS PERCENTAGE DEVIATION--OF VARIATIONS IN VERTICAL WIND SHEAR ON CO AND O_3

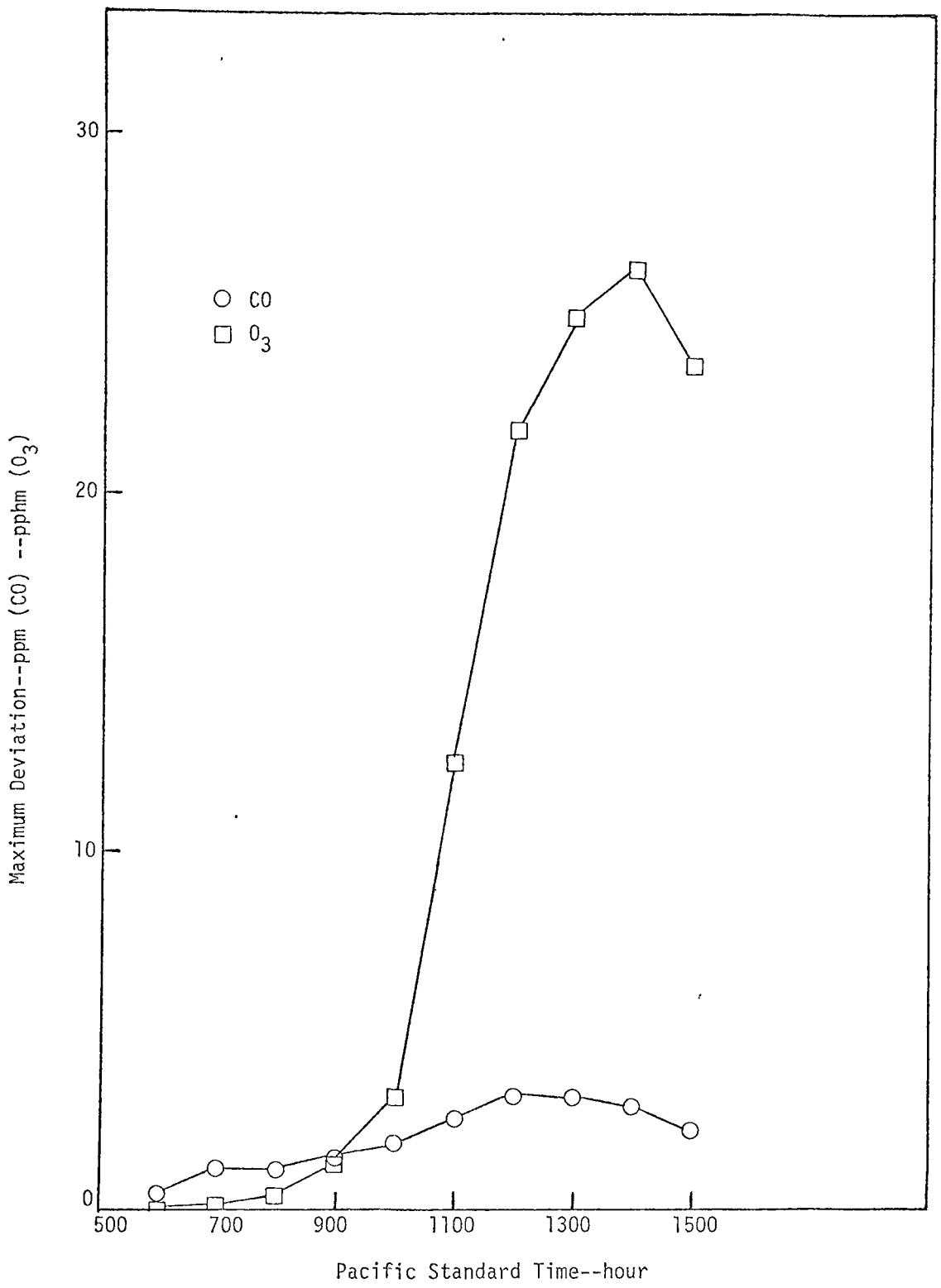


FIGURE 19. THE EFFECT--EXPRESSED AS MAXIMUM DEVIATION--OF VARIATIONS IN VERTICAL WIND SHEAR ON CO AND O_3

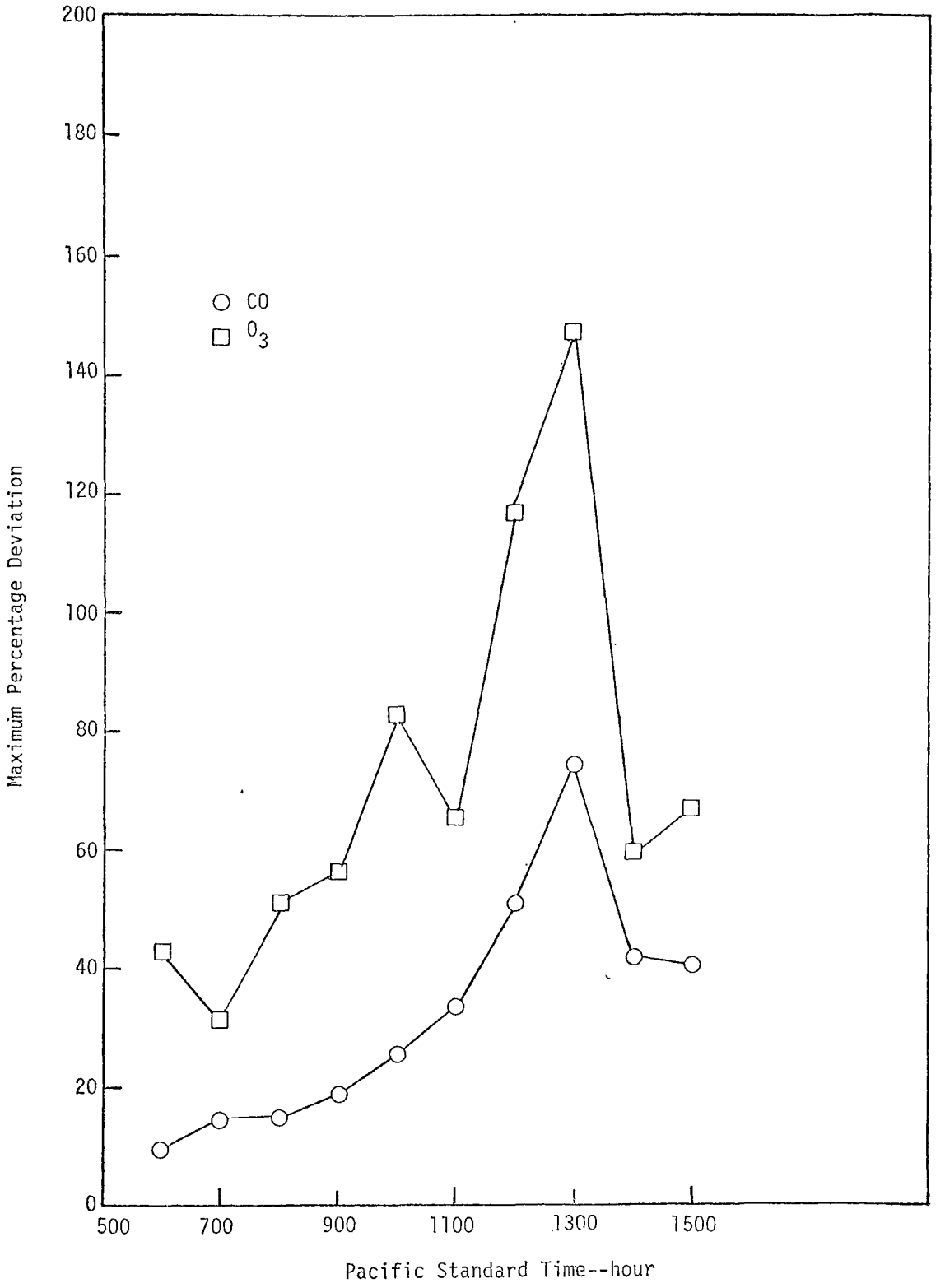


FIGURE 20. THE EFFECT--EXPRESSED AS PERCENTAGE MAXIMUM DEVIATION--OF VARIATIONS IN VERTICAL WIND SHEAR ON CO AND O_3

The results of this study clearly indicate that wind shear phenomena should be included in the airshed model. Of course, it would be most helpful in the construction of velocity profiles to have wind data taken aloft in cities where the model is to be applied.

B. TREATMENT OF WIND SHEAR IN THE AIRSHED MODEL

On the basis of the sensitivity results presented in the previous section, we included provisions in the computer programs for treating a fully three-dimensional wind field. To facilitate usage of either theoretical wind shear relationships or actual wind data aloft, we structured the air quality simulation program to accept the three-dimensional wind field inputs directly from the meteorological data file. The user assembles the wind field inputs by employing the Automated Meteorological Data Preparation Program. Thus, all wind shear algorithms and interpolation routines are embedded in the meteorological data program. By structuring the airshed simulation package in this way, we have enabled changes in the treatment of wind shear to be accomplished without modifying the photochemical dispersion model code.

In many urban areas, sufficient soundings of the winds aloft are seldom available for use in constructing the complete flow field. Therefore, we initiated efforts to derive a set of theoretical wind shear relationships using results obtained from Deardorff's planetary boundary layer model. These relationships are presented and discussed in Chapter II of Volume III. For use in those urban areas where numerous pibal or other suitable data are available, we recommend that an algorithm be developed and installed in the Automated Meteorological Data Preparation Program for the construction of wind fields aloft using the available wind soundings.

C. EXAMINATION OF AN ALGORITHM FOR DERIVING MASS-CONSISTENT WIND FIELDS

One of the assumptions commonly invoked in airshed modeling is that the air flow in the planetary boundary layer is incompressible. Under these conditions, the velocity components satisfy the following continuity relationships:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad , \tag{14}$$

where u, v, and w are the x, y, and z components, respectively, of the wind velocity vector. In the SAI model, the z coordinate is normalized by the depth of the modeling region, in which case Eq. (14) becomes

$$\frac{\partial u \Delta H}{\partial x} + \frac{\partial v \Delta H}{\partial y} + \frac{\partial W}{\partial \rho} = 0 \quad , \tag{15}$$

where

$$\begin{aligned}
\rho &= [z - h(x,y)]/[H_t(x,y,t) - h(x,y)], \\
H_t &= \text{the elevation of the top of the modeling region,} \\
h &= \text{the terrain elevation,} \\
\Delta H &= H_t(x,y,t) - h(x,y), \\
W &= w - u[(\partial h/\partial x) + \rho(\partial \Delta H/\partial x)] - v[(\partial h/\partial y) + \rho(\partial \Delta H/\partial y)] \quad .
\end{aligned}$$

In typical airshed model applications, estimates of u(x,y,z,t) and v(x,y,z,t) are obtained from the available data on wind speed and direction, both at ground level and aloft. Once the horizontal components are specified, Eq. (15) can be solved for W. Writing this equation in finite difference form, we obtain

$$W_{i,j,k+\frac{1}{2}} = W_{i,j,k-\frac{1}{2}} - \frac{\Delta\rho}{\Delta x}\left[(u\Delta H)_{i+\frac{1}{2},j,k} - (u\Delta H)_{i-\frac{1}{2},j,k}\right]$$

$$- \frac{\Delta\rho}{\Delta y}\left[(v\Delta H)_{i,j+\frac{1}{2},k} - (v\Delta H)_{i,j-\frac{1}{2},k}\right] \quad , \tag{16}$$

where the integer triple (i,j,k) designates the center of a grid cell. Equation (15) is solved subject to the constraint of

$$W = 0 \tag{17}$$

at $\rho = 0$, which simply states that either the wind speed is zero at the ground or the wind is flowing parallel to the terrain. By first estimating the horizontal wind components and subsequently solving Eq. (15) for W, we insure that the net flux of air into each grid cell is zero.

One difficulty associated with the wind field methodology described above is that nonzero vertical velocities may be calculated at the top of the modeling region. Thus, pollutants may be advected out of the modeling region, even though a stable capping inversion layer is present. This situation is somewhat contrary to the usual belief that an elevated inversion layer suppresses vertical transport, although buoyant air parcels may penetrate the stable layer to some extent. It is important to note that the calculated vertical motions are, in part, the result of inaccuracies in the predicted horizontal wind components, especially aloft, where few measurements are generally available.

In previous efforts, we examined means for removing convergence and divergence areas in the flow field aloft (see Roth et al., 1971). However, these attempts to force the vertical velocities to obey some specified constraint, such as a zero velocity at the inversion base, failed to produce acceptable wind fields. In many instances, the algorithms generated horizontal wind speeds aloft in excess of 40 mph. Under the present contract, we revisited this issue of constructing mass-consistent wind fields in light of the findings of recent studies in this area reported in the literature.

1. The Governing Equations

The problem that we address here is as follows: Given a set of initial estimates of u and v over the modeling region, how should these wind speeds be adjusted to yield vertical wind velocities that not only satisfy Eq. (14), but also obey some imposed constraint. The methodology described below is similar to that given by Fankhauser (1974).

Let u_0 and v_0 designate the initial estimates of the horizontal wind components, which have been obtained through, say, the application of interpolation procedures. The values of u and v to be employed in the grid model are obtained by defining a function ϕ in the following manner:

$$u\Delta H = (u\Delta H)_0 + \frac{\partial \phi}{\partial x} \quad , \tag{18}$$

$$v\Delta H = (v\Delta H)_0 + \frac{\partial \phi}{\partial y} \quad . \tag{19}$$

Note that we attempt here to adjust only u_0 and v_0, not ΔH. Substituting Eqs. (18) and (19) into Eq. (15), we obtain

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = - \frac{\partial W}{\partial \rho} - \frac{\partial (u\Delta H)_0}{\partial x} - \frac{\partial (v\Delta H)_0}{\partial y} \quad . \tag{20}$$

We define the terms on the right-hand side of Eq. (20) as follows:

$$D = - \frac{\partial W}{\partial \rho} \quad , \tag{21}$$

$$D_0 = \frac{\partial (u\Delta H)_0}{\partial x} + \frac{\partial (v\Delta H)_0}{\partial y} \quad . \tag{22}$$

Thus, Eq. (20) becomes

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = D - D_0 \quad . \tag{23}$$

At this point, recall that from Eq. (17) W must be zero at the ground. Furthermore, we wish to impose a constraint such as

$$W = W_T \tag{24}$$

at the top of the modeling region. If we set $W_T = 0$, then pollutants will not be allowed to advect up into the inversion layer.

Operationally, Eq. (23) is written in finite difference form and is solved on successive layers of grid cells in the x-y plane. Thus, in finite difference notation, Eq. (23) becomes

$$[\nabla^2\phi]_{i,j,k} = D_{i,j,k} - (D_0)_{i,j,k} \quad , \tag{25}$$

where $[\nabla^2\phi]_{i,j,k}$ is the usual five-point difference operator for the Laplacian. Before Eq. (25) can be solved numerically, however, an additional relationship for $D - D_0$ must be determined, and appropriate boundary conditions must be specified.

In a study carried out by O'Brien (1970), a general objective analysis technique is described for adjusting the divergence and vertical wind speeds associated with wind fields derived from mesoscale rawinsonde data. The essence of this work is that expressions for $D - D_0$ can be derived on the basis of an assumed form of the errors associated with the values of D_0. For example, if the errors in D_0 are independent of height, then it can be shown that

$$D_{i,j,k} - (D_0)_{i,j,k} = \frac{\left[(W_{i,j,k+\frac{1}{2}})_0 - W_T\right]}{\Delta\rho(K)} \quad , \tag{26}$$

where K is the total number of grid cells in the vertical direction. Furthermore, if the errors in D_0 are assumed to be proportional to height above the terrain, then

$$D_{i,j,k} - (D_0)_{i,j,k} = \frac{2k\left[(W_{i,j,k+\frac{1}{2}})_0 + W_T\right]}{\Delta\rho(K)(K+1)} \quad . \tag{27}$$

If numerous ground-level meteorological monitoring sites were scattered over an urban area of interest, and few upper-level soundings were available, then it seems reasonable that the errors in the estimated winds aloft would be somewhat larger than those for winds near the ground. Thus, Eq. (27) may provide a

more satisfactory relationship for $D - D_0$. Note that the perturbations to the flow field near the surface are significantly smaller if one uses Eq. (27) than they are if Eq. (26) is used, as demonstrated in the next section.

In specifying boundary conditions, one has two possible choices: the Dirichlet ($\phi = 0$) or the Neumann ($\partial\phi/\partial n = 0$) boundary condition. Physically, the former treatment leaves the u component of the velocity unaltered along boundaries parallel to the x-axis and the v component unaltered on boundaries parallel to the y-axis. In the latter case, just the opposite is true. Fankhauser (1974) employed the Dirichlet condition in his study, and Liu et al. (1974) report that in simulations using a similar type of model, the results were not significantly influenced by the choice of one formulation over the other.

2. Tests of the Model

To test the model described in the previous section, we carried out a study to determine the magnitude of the alterations that would be predicted for the typical wind fields previously used as input to the SAI airshed model. Thus, we rendered the wind fields used in the 29 September 1969 model evaluation study for Los Angeles (see Reynolds et al., 1973) mass consistent; moreover, we constrained the vertical velocity W to be zero at the base of the inversion layer. We used a 25 x 25 x 5 grid layout, where $\Delta x = \Delta y = 2$ miles and $\Delta\rho = 0.2$. Since wind shear was neglected in the Los Angeles study, we considered u_0 and v_0 to be functions only of x, y, and time. Tables 13 through 15 illustrate the nominal wind speeds and directions and mixing depths for 6 a.m. and 3 p.m. on 29 September 1969. These maps served as the inputs to the mass-consistent wind algorithm.

In performing the calculations with the model, we wished to assess the sensitivity of the predictions to (1) the manner in which $D - D_0$ is approximated [i.e., the use of Eq. (26) or (27) and (2) the choice of either Dirichlet or Neumann boundary conditions. Furthermore, we examined the nature

Table 13

HOURLY AVERAGED WIND SPEED AND DIRECTION IN THE LOS ANGELES BASIN ON 29 SEPTEMBER 1969 AT 6:00 a.m. PST

(a) Wind Speed

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	1.0	1.0	1.5	2.0	3.0	4.0	3.0	3.0	2.5	2.5	2.5	2.0	2.0	2.0	2.0	2.0	2.5	2.5	3.0	3.0	3.0	3.5	3.5	4.0	4.0
24	1.0	1.0	1.5	2.0	2.5	3.0	3.0	3.0	2.5	2.5	2.5	2.0	2.0	2.0	2.0	2.0	2.5	2.5	2.5	3.0	3.0	3.5	3.5	4.0	4.0
23	1.0	1.0	1.5	2.0	2.0	3.0	3.0	3.0	2.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.5	3.0	3.0	3.0	3.5	3.5	4.0	4.0	4.0
22	1.0	1.0	2.0	2.0	2.0	3.0	3.0	3.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.5	3.0	3.0	3.5	3.5	3.5	4.0	4.0	4.0
21	1.0	1.5	2.0	3.0	3.0	3.0	3.0	2.0	2.0	2.0	2.0	2.0	2.5	2.0	2.0	2.5	3.0	3.5	3.5	3.5	4.0	4.0	4.0	4.0	4.0
20	1.0	1.5	1.5	2.0	2.0	2.0	2.0	1.0	1.0	2.0	2.0	2.5	2.5	2.0	2.0	3.0	4.0	4.0	3.5	4.0	4.0	4.0	4.0	4.0	4.0
19	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.0	2.0	2.5	2.5	2.5	3.0	3.0	4.0	5.0	5.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
18	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.0	2.0	2.0	3.0	3.0	3.0	4.0	4.0	4.0	5.0	5.0	4.5	4.0	4.0	4.0	4.0	4.0	4.0
17	1.0	1.0	1.0	1.0	1.5	1.0	1.0	2.0	2.5	3.0	3.5	4.0	4.0	4.0	4.5	5.0	5.0	4.5	4.0	4.0	4.0	4.0	3.0	3.0	3.0
16	2.0	2.0	2.0	2.0	2.0	2.0	2.0	3.0	3.0	4.0	4.0	4.0	5.0	5.0	5.0	5.0	5.0	4.5	4.0	4.0	3.0	3.0	2.5	2.5	2.5
15	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	4.0	4.0	4.5	4.5	5.0	5.0	5.0	5.0	4.5	4.0	4.0	3.0	3.0	2.5	2.5	2.5	2.5
14	3.0	3.0	3.0	3.0	3.0	3.0	3.0	4.0	4.5	4.0	4.5	5.0	5.5	5.0	5.0	5.0	4.0	4.0	3.0	3.0	2.5	2.5	2.5	2.5	2.5
13	2.5	2.5	2.5	2.5	2.5	2.5	3.0	4.0	4.0	5.0	5.0	6.0	6.0	6.0	5.0	5.0	4.0	3.0	3.0	2.0	2.0	2.0	2.5	2.0	2.0
12	2.5	2.5	2.5	2.5	2.5	2.5	2.5	3.0	4.0	5.0	5.0	7.0	7.0	6.0	6.0	5.0	5.0	4.0	4.0	3.0	2.0	2.0	2.0	2.0	2.0
11	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	3.0	4.0	5.0	6.0	6.0	6.0	5.0	5.0	5.0	5.0	4.0	3.0	2.0	2.0	2.0	2.0	2.0
10	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	3.0	3.0	4.0	5.0	5.0	4.0	4.0	4.0	4.0	4.0	3.0	2.5	2.0	2.0	2.0	2.0	2.0
9	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.5	2.5	3.0	3.0	3.5	3.0	3.0	3.0	3.0	3.0	2.5	2.5	2.0	2.0	2.0	2.0	2.0
8	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.5	2.5	3.0	3.0	3.0	3.0	2.5	2.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0
7	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.5	2.5	2.5	2.5	2.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
6	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
5	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
4	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
3	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
2	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
1	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

(b) Wind Direction

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	98	103	108	113	118	123	128	136	141	146	148	149	150	150	150	150	151	151	151	150	150	150	150	150	150
24	89	93	97	106	115	121	127	132	137	142	147	140	148	149	140	146	144	144	144	140	140	140	140	140	140
23	80	85	91	98	112	119	126	132	138	145	147	148	147	146	146	145	143	140	136	136	131	120	120	120	120
22	75	79	84	96	110	118	125	132	139	147	147	148	147	146	142	138	135	133	129	125	120	117	115	113	110
21	76	80	85	95	100	115	121	128	135	142	146	147	147	142	138	135	130	125	120	115	110	107	105	103	100
20	77	81	85	94	105	112	117	124	131	138	146	145	144	139	135	133	128	123	117	110	95	93	92	91	90
19	77	81	86	93	102	109	114	120	126	133	138	142	141	136	133	130	125	120	110	100	95	93	92	91	90
18	78	82	86	92	99	105	110	116	122	129	131	137	135	133	130	127	119	113	106	100	95	93	92	91	90
17	79	83	87	91	97	102	106	111	117	125	126	130	129	130	128	123	115	110	105	98	95	93	92	91	90
16	79	83	87	91	95	99	103	107	112	119	120	123	123	120	126	120	113	108	105	100	95	93	92	91	91
15	80	84	88	92	96	100	104	107	110	113	115	117	117	110	110	117	112	107	104	100	95	95	93	91	91
14	81	84	88	91	94	97	100	103	106	100	113	116	117	118	117	116	111	107	107	101	96	92	90	90	90
13	82	84	87	90	92	94	96	99	102	107	111	115	117	118	118	116	114	105	106	101	97	93	90	90	90
12	83	85	87	89	90	91	93	95	99	105	109	114	117	120	122	122	122	105	102	100	95	93	93	93	93
11	84	85	86	88	88	89	90	91	96	103	108	113	117	120	123	125	125	125	125	105	96	92	92	92	92
10	84	85	86	87	88	89	90	90	96	103	108	113	117	119	123	126	120	122	116	107	98	95	92	91	91
9	85	86	87	88	89	90	92	93	98	103	107	111	115	118	123	126	121	115	111	108	101	99	96	92	92
8	87	88	88	89	90	92	94	96	99	103	107	110	113	118	124	128	130	130	126	100	96	96	92	90	90
7	88	89	90	91	92	94	76	98	100	104	106	109	111	117	124	128	130	130	120	115	110	100	95	91	90
6	90	91	92	93	94	96	98	100	102	104	106	108	110	110	125	125	127	124	113	104	90	93	90	90	90
5	90	91	92	93	94	96	90	100	102	104	106	108	110	111	112	115	119	120	116	109	103	96	92	90	90
4	90	91	92	93	94	96	98	100	102	104	106	108	110	110	110	112	111	111	109	104	104	100	92	90	90
3	90	91	92	93	94	96	90	100	102	104	106	108	110	110	110	110	110	108	106	108	107	92	90	90	90
2	90	91	92	93	94	96	90	100	102	104	106	108	110	110	109	109	111	111	111	105	100	92	90	90	90
1	90	91	92	93	94	96	98	100	102	104	106	108	110	110	109	109	111	111	111	105	100	92	90	90	90

Table 14

HOURLY AVERAGED WIND SPEED AND DIRECTION IN THE LOS ANGELES BASIN
ON 29 SEPTEMBER 1969 AT 3:00 p.m. PST

(a) Wind Speed

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	7.0	8.0	9.0	9.0	9.0	9.0
24	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	7.0	8.0	9.0	9.0	9.0	9.0	9.0	9.0
23	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	7.0	7.0	8.0	9.0	9.0	9.0	6.0	9.0	9.0
22	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	7.0	8.0	8.0	9.0	9.0	9.0	9.0	9.0	9.0	8.0
21	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	7.0	7.0	8.0	9.0	9.0	10.0	10.0	10.0	10.0	9.0	8.0	8.0
20	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	7.0	8.0	8.0	9.0	10.0	10.0	11.0	11.0	10.0	9.0	8.0	7.0	7.0
19	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	7.0	8.0	9.0	10.0	10.0	11.0	12.0	11.0	10.0	9.0	8.0	7.0	7.0	6.0
18	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	7.0	8.0	9.0	10.0	11.0	11.0	12.0	12.0	10.0	9.0	8.0	8.0	7.0	7.0	6.0
17	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	7.0	7.0	8.0	9.0	9.0	10.0	12.0	12.0	11.0	10.0	9.0	8.0	8.0	7.0	6.0	6.0	6.0
16	6.0	6.0	7.0	7.0	7.0	7.0	7.0	8.0	8.0	8.0	9.0	10.0	10.0	12.0	11.0	10.0	10.0	9.0	8.0	7.0	7.0	6.0	6.0	6.0	6.0
15	7.0	7.0	8.0	8.0	9.0	9.0	9.0	8.0	9.0	9.0	10.0	11.0	12.0	11.0	10.0	9.0	9.0	8.0	7.0	7.0	6.0	5.0	5.0	5.0	5.0
14	8.0	8.0	9.0	9.0	9.0	9.0	9.0	9.0	10.0	10.0	11.0	12.0	11.0	10.0	9.0	8.0	8.0	7.0	6.0	6.0	5.0	5.0	5.0	5.0	5.0
13	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	10.0	11.0	12.0	13.0	11.0	10.0	9.0	8.0	8.0	7.0	7.0	6.0	5.0	5.0	5.0	5.0	4.0
12	9.0	9.0	9.0	8.5	8.5	8.5	9.0	9.0	10.0	11.0	13.0	15.0	13.0	11.0	10.0	9.0	8.0	8.0	7.0	6.5	6.0	5.0	5.0	4.0	4.0
11	8.5	8.5	8.5	8.0	8.0	8.0	8.0	9.0	10.0	11.0	12.0	14.0	13.0	11.0	10.0	10.0	9.0	9.0	8.0	7.0	6.0	5.0	4.0	4.0	4.0
10	8.5	8.0	8.0	8.0	8.0	8.0	8.0	8.0	9.0	10.0	12.0	13.0	13.0	11.0	10.0	9.0	9.0	8.0	7.0	6.0	5.0	4.0	4.0	4.0	4.0
9	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.5	9.0	10.0	11.0	12.0	13.0	11.0	10.0	9.0	8.0	7.0	6.0	5.0	4.0	4.0	4.0	4.0	4.0
8	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.5	9.0	9.0	10.0	11.0	10.0	9.0	8.0	7.0	6.0	5.5	5.5	4.5	4.0	4.0	4.0	4.0
7	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.5	8.5	8.5	9.0	10.0	9.0	8.0	7.0	6.0	5.5	5.0	5.0	4.5	4.5	4.0	4.0	4.0
6	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.5	8.5	9.0	8.0	7.0	6.0	5.5	5.0	5.0	5.0	5.0	4.5	4.0	4.5	4.5
5	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	7.0	6.0	5.5	5.0	5.0	5.0	5.0	5.0	5.0	4.5	4.5	4.5
4	8.0	8.0	8.0	8.0	8.0	8.0	8.0	7.5	7.0	7.0	7.0	7.0	7.0	6.0	6.0	6.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	4.5
3	8.0	8.0	8.0	8.0	8.0	7.5	7.5	7.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
2	8.0	8.0	8.0	7.5	7.5	7.0	7.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
1	8.0	8.0	7.5	7.5	7.0	7.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0

(b) Wind Direction

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	125	115	106	105	99	95	90	85	78	70	65	63	60	55	36	86	85	85	85	85	85	84	32	30	30
24	131	125	110	107	98	94	90	85	78	70	65	60	37	33	36	36	36	36	36	35	34	31	30	30	30
23	126	126	112	110	99	95	90	83	03	63	60	47	38	36	36	36	37	37	37	37	36	33	30	30	30
22	116	116	116	111	100	95	90	80	77	63	55	50	41	40	40	40	40	39	38	38	36	33	30	30	30
21	110	110	110	110	103	95	90	79	73	63	50	48	41	40	43	44	45	39	37	37	37	36	35	35	43
20	90	90	90	90	90	88	87	83	68	65	46	46	48	49	49	49	49	45	45	43	40	40	43	45	50
19	80	80	80	78	78	76	75	70	60	60	46	49	50	53	50	50	50	50	50	44	44	44	45	53	58
18	82	82	80	78	77	75	75	70	53	50	50	50	55	54	53	52	51	50	50	50	50	60	62	65	66
17	80	80	80	75	70	68	60	57	50	58	59	59	57	55	56	56	54	52	58	60	65	65	72	72	73
16	75	75	75	70	63	62	60	60	60	63	60	59	69	60	60	56	56	60	63	65	67	70	72	72	73
15	72	72	70	65	63	65	66	65	64	64	63	62	60	60	59	59	60	63	63	65	65	67	72	72	73
14	70	69	66	65	65	66	66	66	65	65	64	62	62	61	61	60	60	63	63	65	65	70	72	73	73
13	70	69	66	66	66	67	67	66	66	65	64	62	62	62	62	62	62	66	66	68	68	72	73	74	74
12	69	66	66	69	69	68	68	66	66	64	63	62	62	62	64	64	64	68	68	70	70	74	75	75	73
11	70	69	69	70	71	69	68	66	65	64	62	62	62	64	66	68	68	70	72	72	73	74	75	75	75
10	71	71	72	72	70	68	67	66	64	64	62	64	70	66	68	72	72	72	72	72	73	74	75	75	75
9	72	72	72	70	70	68	66	64	64	66	66	66	73	72	72	72	72	72	72	72	73	74	75	75	76
8	72	72	72	72	69	68	68	68	68	70	71	72	72	72	72	72	72	72	73	73	74	74	76	76	76
7	73	73	73	73	72	70	70	70	70	73	72	72	72	72	72	73	73	73	73	73	75	75	76	76	76
6	73	73	73	74	73	73	73	73	73	73	73	73	73	73	73	73	73	73	73	73	76	76	77	77	78
5	74	74	74	75	75	73	73	73	73	73	73	73	73	73	73	73	73	73	74	74	77	77	79	79	80
4	76	76	75	75	75	73	73	73	73	73	73	73	73	73	73	73	73	73	75	77	79	82	83	83	83
3	76	76	75	74	74	73	73	73	73	73	73	73	73	73	73	73	73	73	75	77	79	82	83	83	83
2	75	74	74	73	73	73	73	73	73	73	73	73	73	73	73	73	73	73	75	77	79	82	83	83	83
1	75	74	74	73	73	73	73	73	73	73	73	73	73	73	73	73	73	73	75	77	79	82	83	83	83

Table 15

MIXING DEPTHS IN THE LOS ANGELES BASIN ON 29 SEPTEMBER 1969 AT 6:00 a.m. AND 3:00 p.m. PST

(a) 6:00 a.m.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	100	100	100	100	100	100	100	100	100	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
24	100	100	100	100	100	100	100	100	100	150	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
23	100	100	100	100	100	100	100	100	100	100	150	150	150	200	200	200	200	200	200	200	200	200	200	200	200
22	100	100	100	100	100	100	100	100	100	100	100	100	100	150	200	200	200	200	200	200	200	200	200	200	200
21	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	175	200	200	200	
20	100	100	100	100	100	100	150	150	150	150	100	100	100	100	100	100	100	100	100	100	125	150	150	150	
19	200	200	200	200	200	200	200	200	200	200	150	140	120	100	100	100	100	100	100	100	100	100	100	150	
18	300	300	300	300	300	275	250	250	250	225	200	170	150	125	100	100	100	100	100	100	100	100	100	100	100
17	400	400	400	400	375	325	300	300	275	250	225	200	175	150	125	100	100	100	100	100	100	100	100	120	150
16	500	500	500	480	450	410	350	325	300	275	250	225	200	175	150	125	100	100	100	100	100	123	140	160	150
15	500	500	500	500	495	460	410	350	325	300	275	250	225	200	175	150	125	100	100	100	100	125	150	150	150
14	500	500	500	500	500	470	425	375	350	325	300	275	250	225	200	175	150	125	125	125	125	150	200	200	200
13	500	500	500	500	500	480	450	400	375	350	325	300	275	250	230	225	200	150	150	150	150	175	200	200	200
12	500	500	500	500	500	500	490	450	400	375	350	325	300	300	280	270	225	200	175	175	175	200	200	200	200
11	500	500	500	500	500	500	470	460	430	400	375	350	350	350	340	330	250	250	200	200	200	225	225	225	250
10	500	500	500	500	500	500	495	450	450	400	400	400	400	400	400	375	300	300	250	225	225	250	250	250	20
9	500	500	500	500	500	500	500	480	430	400	425	430	450	450	450	400	350	330	300	275	250	250	250	275	20
8	500	500	500	500	500	500	400	350	350	400	450	450	480	475	470	450	400	370	350	325	300	300	300	300	250
7	500	500	500	500	500	500	400	350	350	350	480	495	495	490	485	475	450	400	400	375	350	325	325	325	32
6	500	500	500	500	500	500	500	500	400	350	485	500	500	500	500	500	400	450	450	425	400	375	350	350	350
5	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	495	490	400	450	425	400	375	375	350
4	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	490	495	480	460	425	400	400	400
3	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	480	450	425	400	400
2	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	480	400	350	35	
1	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	400	350	300		

(b) 3:00 p.m.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	2500	2500	2500	2500	2500	2300	2400	2300	2200	2000	1800	1500	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200
24	2500	2500	2500	2500	2500	2500	2400	2300	2200	2000	1900	1700	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500
23	2500	2500	2300	2500	2500	2300	2200	2200	2200	2000	1900	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800
22	2400	2400	2400	2400	2400	2200	2100	2100	2200	2000	1900	1900	1900	2000	2100	2200	2200	2200	2200	2200	2200	2200	2200	2200	2200
21	2000	2000	2000	2000	2000	2000	2000	2000	2200	2000	1800	1800	1800	2000	2300	2300	2300	2300	2300	2300	2300	2300	2300	2300	2300
20	1500	1500	1600	1500	1500	1500	1500	1500	1800	1700	1500	1500	1500	1800	2000	2300	2500	2500	2500	2500	2500	2500	2500	2500	2500
19	1200	1200	1200	1200	1200	1200	1200	1200	1500	1400	1300	1300	1300	1500	1700	2000	2300	2500	2500	2300	2300	2300	2300	2300	230
18	900	900	900	900	900	900	900	900	1000	1000	1100	1100	1100	1200	1400	1700	2200	2500	2500	2300	2200	2200	2200	2200	2200
17	600	600	600	600	600	600	600	600	800	900	950	950	950	950	1000	1400	2000	2200	2300	2200	2200	2200	2200	2200	2200
16	550	550	550	550	550	575	600	600	650	675	700	725	750	775	825	1200	1500	1800	2000	2000	2000	2000	2000	2000	2000
15	550	550	550	550	550	550	575	600	630	650	600	700	720	740	800	1200	1400	1600	1800	1800	1800	1800	1800	1800	1800
14	550	550	550	550	550	550	600	600	600	630	660	690	700	800	900	1100	1300	1500	1500	1500	1500	1600	1600	1600	1600
13	550	550	550	550	550	550	550	575	600	630	650	700	700	700	800	1000	1100	1300	1300	1300	1300	1400	1400	1400	1400
12	550	550	550	550	550	550	550	575	600	630	650	700	750	800	850	900	1000	1100	1100	1100	1100	1200	1200	1200	1200
11	550	550	550	550	550	550	550	575	575	610	650	670	700	730	775	800	850	950	1000	1000	1000	1100	1100	1100	1100
10	550	550	550	550	550	550	550	575	575	600	625	640	650	700	700	700	750	900	900	900	900	1000	1000	1000	1000
9	550	550	550	550	550	550	550	550	550	575	600	600	600	625	625	650	650	800	800	800	800	850	850	850	850
8	550	550	550	550	550	550	550	500	500	575	575	575	575	575	575	600	600	700	750	750	750	750	750	750	750
7	550	550	550	550	550	550	550	500	500	550	550	550	550	550	550	575	600	600	650	675	675	675	675	675	675
6	550	550	550	550	550	550	550	500	500	550	550	550	550	550	550	550	575	600	600	600	600	600	600	600	600
5	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	575	575	575	575	575	575	575	575
4	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550
3	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	525	500	500	500
2	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	550	525	500	500	450	
1	500	550	550	500	500	550	550	550	550	550	550	500	500	550	550	550	550	550	500	550	550	550	525	500	450

of the changes in the flow field at two levels on the grid: near the surface and at the top of the modeling region (i.e., k = 1 and k = 5)*. The results of these simulations are presented in Tables 16 through 23. Table 24 summarizes the nature of the inputs and the treatment of the parameters in the wind algorithms corresponding to each table. The predicted changes in wind speed and direction given in these tables are defined as follows:

$$\Delta S = (u^2 + v^2)^{1/2} - \left(u_0^2 + v_0^2\right)^{1/2} \quad ,$$

$$\Delta\theta = 57.2958 \left[\tan^{-1}\left(\frac{u}{v}\right) - \tan^{-1}\left(\frac{u_0}{v_0}\right)\right] \quad ,$$

where ΔS and $\Delta\theta$ are the reported changes in wind speed and direction, respectively.

3. Discussion of the Results

Reviewing Tables 16 through 23, we note that wind speed and direction are altered by no more than about 11 mph and 93°, respectively. To place some perspective on these results, we must consider the magnitude of the errors associated with the input wind fields themselves. Typically, the uncertainties in the wind fields employed in airshed simulations are on the order of 2 mph in speed and 60° in direction. For the most part, the predicted perturbations in wind direction are smaller than 60°. However, significant alterations in the wind speed are predicted for the 3 p.m. wind inputs. These predictions are the result of generally higher wind speeds and a greater degree of convergence and divergence in the interpolated wind field.

*Since u_0 and v_0 are considered to be independent of z, the perturbations calculated using Eq. (26) are the same in each layer of grid cells. Thus, the change in speed and direction is reported only for the bottom layer of cells (i.e., k = 1).

Table 16

PREDICTED CHANGES IN WIND SPEED AND DIRECTION FOR CASE 1*

(a) Wind Speed

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-.0	-.1	-.0	-.0	-1.2	-1.0	-.8	-.7	-.3	-.2	-.2	-.1	-.1	-.1	-.2	-.2	-.3	-.3	-.5	-.4	-.4	-.6	-.3	.0	.0
24	-.0	-.0	-.0	-.0	-1.1	-.9	-.9	-.6	-.3	-.2	-.2	.0	-.0	-.1	-.2	-.2	-.3	-.3	-.2	-.5	-.4	-.3	-.0	.1	.1
23	-.0	-.1	-.0	-1.0	-.7	-1.1	-.0	-.5	-.1	.5	.4	.3	.2	-.0	-.2	-.3	-.5	-.5	-.3	-.0	-.0	-.5	-.1	.2	.4
22	.0	.1	-.0	-.0	-.0	-1.2	-.8	-.5	.6	.8	.7	.7	.6	.0	-.2	-.1	-.4	-.7	-.6	-.8	-.4	-.3	-.4	-.0	.2
21	.2	-.0	-.4	-1.2	-1.1	-.9	-.0	.3	.5	.7	.0	.9	.3	.2	.1	-.2	-.6	-1.1	-1.1	-.7	-.0	-.7	-.4	-.0	.2
20	.3	-.1	-.2	-.0	-.7	-.5	-.2	.0	1.0	.2	.5	.1	.1	.3	.2	-.5	-1.3	-1.4	-1.1	-1.2	-.9	-.7	-.4	.0	.2
19	.1	.1	-.1	-.2	-.2	-.1	.3	.5	-.3	-.0	-.3	-.3	-.3	-.0	-1.2	-1.0	-2.3	-2.1	-1.6	-1.0	-.0	-.6	-.2	.1	.1
18	.1	.0	-.0	-.1	-.1	.1	.4	-.4	-.3	-.4	-.0	-.7	-.9	-1.7	-2.1	-2.0	-2.6	-2.0	-1.2	-1.0	-.5	-.4	-.1	.0	.0
17	.0	.0	-.0	-.1	-.1	.0	.0	-.3	-.0	-.7	-1.0	-1.2	-1.3	-1.0	-1.9	-2.5	-2.3	-1.5	-1.1	-.0	-.4	-.4	.0	.1	.0
16	.0	-.0	-.1	-.1	-.0	.1	.2	-.5	-.4	-1.1	-.9	-.0	-1.7	-1.7	-1.0	-1.9	-1.0	-1.1	-.0	-.0	.3	-.1	.1	-.0	-.0
15	-.0	-.0	-.1	-.1	-.1	-.1	-.0	.0	-.9	-.7	-.0	-.0	-1.3	-1.2	-1.3	-1.0	-1.2	-.6	-.5	.4	.2	.3	-.0	-.1	-.0
14	-.0	-.1	-.1	-.2	-.2	-.0	.3	-.4	-.6	-.6	-.4	-.9	-1.4	-1.0	-1.1	-1.3	-.6	-.7	.2	.2	.6	.2	-.0	-.0	.0
13	-.0	-.1	-.1	-.2	-.1	.1	.1	-.4	-.4	-.7	-.5	-1.3	-1.2	-1.2	-.6	-1.1	-.6	-.1	-.3	.6	.7	.1	-.1	.1	.0
12	-.0	-.1	-.1	-.2	-.1	-.1	.1	-.0	-.4	-.7	-1.1	-1.6	-1.9	-.7	-1.1	-.6	-.7	-.1	-.5	.2	.8	.4	.1	.0	.0
11	-.0	-.1	-.1	-.1	-.1	-.1	-.0	.1	-.5	-.9	-1.4	-1.1	-.7	-.7	-.7	-.6	-.7	-1.0	-.5	.2	.7	.3	.1	.1	.0
10	-.0	-.1	-.1	-.1	-.2	-.1	-.1	.1	-.0	-.6	-1.4	-.4	-.2	-.9	-.7	-.5	-.4	-.4	.3	.0	.0	.3	.0	-.0	.0
9	-.0	-.1	-.1	-.2	-.2	-.2	-.2	-.1	-.6	-.0	-.0	-.6	-.0	-.6	-.4	-.2	-.1	.1	.4	.2	.0	.2	.0	-.1	.0
8	-.0	-.1	-.1	-.2	-.2	-.3	-.2	-.3	-.4	-.4	-.7	-.6	-.9	-.7	-.5	-.4	-.0	.0	.3	.2	.1	.1	-.0	-.0	-.0
7	-.0	-.1	-.1	-.2	-.3	-.3	-.3	-.3	-.3	-.4	-.5	-.9	-.8	-.0	-.4	-.2	.2	.3	.1	-.0	-.0	-.0	.0	.0	.0
6	-.0	-.1	-.1	-.2	-.2	-.3	-.3	-.3	-.3	-.4	-.6	-.6	-.9	-.0	-.2	-.0	.1	.2	.1	-.0	-.0	-.0	.0	.0	.0
5	-.0	-.1	-.1	-.2	-.2	-.2	-.3	-.3	-.3	-.4	-.5	-.6	-.5	-.0	-.2	-.0	.0	.1	-.0	-.1	-.1	-.1	-.0	.0	.0
4	-.0	-.1	-.1	-.2	-.2	-.2	-.3	-.3	-.3	-.4	-.4	-.5	-.4	-.3	-.2	-.1	-.0	.0	-.0	-.1	-.1	-.1	-.0	.0	.0
3	-.0	-.1	-.1	-.1	-.2	-.2	-.0	-.3	-.3	-.4	-.4	-.4	-.4	-.0	-.0	-.2	-.1	-.0	-.1	-.2	-.2	-.1	-.0	.0	.0
2	-.0	-.1	-.1	-.1	-.2	-.2	-.0	-.3	-.3	-.4	-.4	-.4	-.3	-.0	-.0	-.2	-.1	-.1	-.1	-.2	-.2	-.2	-.0	.0	.0
1	-.0	-.0	-.1	-.1	-.2	-.2	-.0	-.3	-.3	-.4	-.4	-.4	-.0	-.0	-.0	-.2	-.2	-.1	-.1	-.2	-.0	-.2	-.1	.0	.0

(b) Wind Direction

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-2	-2	4	10	19	23	21	20	14	10	9	5	7	9	13	16	20	22	22	23	23	22	11	2	-0
24	0	1	5	10	23	32	30	30	24	17	10	7	8	9	13	16	21	24	24	25	26	30	18	6	2
23	2	2	0	10	22	31	29	30	20	26	22	16	14	13	14	15	17	10	18	16	17	24	22	14	10
22	-1	-1	-2	5	15	26	27	26	25	26	28	26	26	23	19	19	21	20	14	14	16	15	16	13	11
21	-13	-14	-11	-3	1	15	24	24	24	27	28	29	32	39	39	38	42	40	32	25	19	15	15	15	14
20	-21	-22	-21	-11	6	19	27	28	31	29	26	30	33	38	38	34	34	31	23	16	19	18	21	24	21
19	-18	-20	-21	-14	1	12	22	20	18	18	20	21	22	27	21	17	15	9	6	8	7	11	15	18	16
18	-12	-12	-11	-10	-7	-2	3	6	6	8	10	7	7	10	5	2	2	-0	-1	-0	2	5	9	11	9
17	-4	-4	-4	-4	-5	-7	-5	0	0	1	0	-1	-3	-2	-7	-12	-12	-11	-8	-4	-1	3	5	6	3
16	-0	-0	-1	-1	-1	-5	-8	-4	-2	-3	-2	-2	-2	-7	-11	-13	-18	-17	-13	-10	-4	1	2	-1	-1
15	2	0	-0	-1	-2	-5	-7	-5	-2	-4	-1	-0	1	-0	-4	-7	-15	-18	-14	-12	-7	-4	-3	-4	-4
14	1	0	0	-0	-0	-0	-1	-1	-0	0	-0	0	0	-0	-1	-2	-8	-15	-17	-15	-11	-6	-6	-6	-5
13	0	0	0	0	1	1	-0	0	1	0	0	-0	-1	-2	-2	-0	-2	-8	-14	-19	-18	-12	-9	-8	-8
12	0	0	0	0	1	0	-1	0	2	0	-1	-3	-4	-5	-5	-6	-8	-3	-6	-14	-16	-14	-13	-11	-11
11	-0	-0	0	0	1	1	-0	0	1	1	2	1	1	-0	-2	-6	-10	-16	-22	-13	-11	-9	-10	-12	-13
10	0	0	0	1	0	-0	-1	-2	-3	0	9	9	7	5	1	-2	-1	-4	-7	-8	-8	-8	-8	-11	-14
9	0	0	0	0	-0	-2	-4	-6	-3	8	11	10	7	8	6	3	1	6	3	-3	-6	-9	-10	-9	-11
8	-0	-0	-0	-0	-1	-3	-4	-6	-2	4	10	11	8	4	3	1	-4	-2	-5	7	2	-3	-5	-4	-5
7	-1	-1	-1	-1	-1	-0	-0	-3	-3	-0	6	9	11	8	7	5	-0	-1	-0	-7	-10	-8	-7	-4	-4
6	-2	-2	-2	-2	-1	-0	0	-1	-2	-2	1	7	14	17	10	8	1	0	2	2	1	-1	-3	-4	-4
5	-2	-2	-2	-1	-1	-0	0	0	0	-1	0	6	13	15	16	11	5	-0	-1	-2	-2	-3	-4	-4	-4
4	-1	-1	-1	-1	-0	-0	0	0	0	0	2	6	9	12	13	10	9	6	4	1	-1	-7	-5	-4	-4
3	-1	-0	-0	-0	-0	-0	0	0	1	3	5	7	8	9	8	7	7	6	6	-2	-6	-4	-4	-4	-1
2	-0	-0	-0	-0	-0	0	0	1	1	2	3	4	5	6	6	5	4	3	2	2	3	-1	-3	-3	-3
1	-0	-0	-0	0	0	0	1	1	2	3	3	4	4	4	4	3	2	2	1	2	1	-0	-0	-1	-1

* See Table 24 for a description of the experimental conditions.

Table 17

PREDICTED CHANGES IN WIND SPEED AND DIRECTION FOR CASE 2*

(a) Wind Speed

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-.0	.1	-.2	-.2	-.5	-.9	-.2	-.3	-.1	-.1	-.1	-.0	-.0	-.1	-.1	-.1	-.2	-.2	-.3	-.2	-.2	-.3	-.2	-.1	-.1
24	-.0	.1	-.2	-.3	-.4	-.4	-.4	-.8	-.1	-.1	-.1	.0	-.0	-.0	-.1	-.1	-.2	-.1	.0	-.2	-.1	-.5	-.1	-.1	-.0
23	-.0	.1	-.2	-.4	-.1	-.6	-.3	-.3	-.2	.2	.2	.1	.1	-.0	-.1	-.1	-.2	-.4	-.4	-.2	-.4	-.1	-.1	.1	.1
22	.0	.2	-.5	-.3	-.1	-.6	-.3	-.4	.2	.2	.2	.2	.2	-.0	-.1	.0	-.1	-.3	-.2	-.4	-.2	-.1	-.3	-.0	.0
21	.1	-.0	-.0	-.6	-.4	-.4	-.5	.2	.0	.2	.2	.3	-.1	-.0	-.0	-.2	-.3	-.5	-.5	-.2	-.4	-.3	-.2	-.0	.0
20	.2	-.1	.0	-.4	-.2	-.2	-.2	.4	.5	-.1	.2	-.1	-.1	.1	.1	-.2	-.6	-.6	-.3	-.5	-.4	-.3	-.2	-.0	.0
19	.0	.0	-.0	-.1	-.1	-.0	.1	.3	-.3	.0	-.2	-.1	-.1	-.4	-.3	-.7	-1.0	-.0	-.6	-.2	-.3	-.2	-.1	-.0	.0
18	.0	.0	-.0	-.0	-.0	.0	.3	-.3	-.0	-.2	-.3	-.2	-.2	-.7	-.7	-.5	-1.0	-.7	-.3	-.4	-.1	-.1	-.0	-.0	.0
17	.0	.0	-.0	-.0	-.1	.3	.0	-.1	-.2	-.2	-.4	-.0	-.4	-.6	-.6	-.9	-.9	-.4	-.5	-.1	-.1	-.3	.3	.0	-.0
16	.0	-.0	-.0	-.0	-.0	.0	.2	-.4	.0	-.0	-.3	-.1	-.3	-.6	-.7	-.7	-.7	-.4	-.1	-.4	.3	-.1	.1	-.0	-.0
15	-.0	-.0	-.0	-.0	-.0	-.0	-.0	.2	-.5	-.2	-.3	-.2	-.4	-.4	-.4	-.5	-.4	-.2	-.4	.3	-.0	.2	-.0	-.0	-.0
14	-.0	-.0	-.0	-.1	-.1	-.0	.2	-.2	-.3	-.2	-.0	-.3	-.6	-.2	-.4	-.5	-.1	-.5	.2	-.1	.3	.1	-.0	-.0	-.0
13	-.0	-.0	-.1	-.1	-.0	.1	.1	-.2	-.2	-.4	-.0	-.6	-.4	-.0	-.0	-.5	-.1	.1	-.3	.3	.3	-.1	-.1	.1	.0
12	-.0	-.0	-.0	-.1	-.0	-.0	.1	.1	-.2	-.3	-.4	-.7	-.7	-.1	-.6	-.1	-.4	.1	-.3	.0	.4	.1	.0	.0	.0
11	-.0	-.0	-.0	-.0	-.0	-.0	-.0	.2	-.2	-.3	-.6	-.3	-.2	-.2	-.2	-.3	-.3	-.7	-.3	-.1	.4	.1	.0	.0	.0
10	-.0	-.0	-.0	-.0	-.1	-.0	-.0	.2	-.4	-.0	-.8	.1	.1	-.4	-.2	-.1	-.1	-.2	.2	.1	.3	.1	.0	-.0	-.0
9	-.0	-.0	-.0	-.1	-.1	-.1	-.1	.0	-.3	-.1	-.3	-.2	-.2	-.2	-.1	.0	.0	.0	.2	-.0	.2	.1	-.0	-.0	-.0
8	-.0	-.0	-.0	-.1	-.1	-.1	-.1	-.1	-.1	-.0	-.3	-.1	-.4	-.3	-.2	-.2	.0	-.1	.2	.0	.1	.0	-.0	-.0	-.0
7	-.0	-.0	-.0	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.4	-.3	-.2	-.1	-.1	.2	.1	.0	-.1	-.1	-.0	-.0	-.0	-.0
6	-.0	-.0	-.0	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.2	-.1	-.5	-.1	-.0	-.0	.0	.1	.0	.0	.0	.0	.0	.0	.0
5	-.0	-.0	-.0	-.1	-.1	-.1	-.1	-.1	-.1	-.2	-.2	-.1	-.2	-.1	-.0	-.0	.0	-.0	-.0	-.0	-.0	-.0	-.0	-.0	.0
4	-.0	-.0	-.0	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.2	-.1	-.1	-.1	-.0	-.0	.0	.0	-.0	-.0	-.0	-.0	.0	.0
3	-.0	-.0	-.0	-.0	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.0	-.0	-.0	-.1	-.1	-.1	-.0	.0	.0
2	-.0	-.0	-.0	-.0	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.0	-.0	-.0	-.1	-.1	-.1	-.0	.0	.0
1	-.0	-.0	-.0	-.0	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.0	-.0	-.1	-.1	-.1	-.0	.0	.0

(b) Wind Direction

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-2	-3	-0	0	3	7	3	6	2	2	3	0	2	3	4	4	6	5	6	6	5	6	2	0	-0
24	0	0	2	2	5	10	7	9	6	5	3	1	2	2	4	3	5	6	7	9	7	5	4	1	-0
23	1	1	-0	3	4	9	7	9	5	3	9	3	5	4	4	2	4	4	4	3	4	3	3	4	3
22	0	1	0	1	3	7	6	7	7	9	11	10	11	7	6	6	7	7	3	3	5	3	4	3	3
21	-3	-3	-3	-1	-1	2	7	6	7	10	11	11	12	13	11	11	12	11	8	7	4	3	4	4	5
20	-7	-7	-5	-2	2	5	11	11	16	19	8	10	11	14	12	9	9	8	4	3	8	7	8	10	4
19	-6	-7	-7	-3	2	7	11	7	6	5	7	6	5	8	2	1	2	0	1	4	2	3	5	6	5
18	-5	-4	-3	-3	-1	-0	-0	1	1	2	4	1	0	2	0	-0	1	0	-0	-0	0	1	3	3	3
17	-1	-1	-1	-1	-1	-2	-1	1	0	0	0	-1	-1	-0	-2	-3	-1	-2	-2	-0	-0	1	1	2	2
16	-0	-0	-0	-0	0	-1	-2	-0	-1	-1	-0	-1	-0	-4	-4	-3	-4	-4	-4	-3	-1	1	0	-0	-0
15	1	0	-0	-0	-1	-2	-3	-2	-0	-2	0	-0	2	1	-0	-1	-4	-5	-4	-3	-2	-2	-1	-1	-1
14	0	0	-0	-0	-0	-0	-0	-0	-0	5	-0	0	0	0	-0	0	-2	-5	-6	-6	-4	-1	-1	-2	-1
13	-0	0	0	0	0	0	-0	0	0	-1	-0	0	-0	-0	-0	1	0	-1	-3	-6	-7	-4	-2	-2	-2
12	0	0	0	0	0	0	-0	0	0	-0	-1	-2	-2	-3	-3	-3	-3	2	2	-4	-6	-5	-5	-4	-4
11	-0	-0	0	0	0	0	0	0	1	0	1	0	0	-0	-1	-3	-5	-0	-13	-5	-4	-2	-3	-4	-4
10	0	0	0	0	0	0	-0	-0	-0	-0	4	3	3	2	0	-1	0	-0	-1	-2	-3	-3	-2	-3	-4
9	0	0	0	0	-0	-0	-1	-2	-0	0	4	2	2	3	3	2	1	6	2	-2	-4	-4	-4	-3	-4
8	-0	-0	0	0	-0	-0	-1	-1	-0	1	3	3	2	0	0	0	-3	-2	-5	7	3	-0	-0	-1	-1
7	-0	-0	-0	-0	-0	-0	-0	-0	-0	-0	1	2	4	1	2	2	-0	-0	-0	-6	-7	-4	-3	-1	-1
6	-1	-1	-1	-1	-0	-0	-0	-0	-1	-0	0	2	4	6	1	3	-0	-0	2	3	3	1	0	-1	-1
5	-0	-0	-0	-0	-0	-0	0	0	0	-0	0	1	4	4	6	4	1	-0	-2	-2	-1	-0	-1	-1	-1
4	-0	-0	-0	-0	-0	-0	0	0	0	0	0	1	2	3	4	3	4	3	1	0	-0	-4	-2	-1	-1
3	-0	-0	-0	-0	-0	-0	0	0	0	0	1	1	2	2	2	2	2	3	3	3	-2	1	-1	-1	-1
2	-0	-0	-0	-0	-0	0	0	0	0	0	1	1	1	1	2	2	1	0	-0	-0	2	-0	-1	-1	-1
1	-0	-0	-0	0	0	0	0	0	0	0	1	1	1	1	1	1	0	0	0	0	0	-0	-0	-0	-0

* See Table 24 for a description of the experimental conditions.

Table 18

PREDICTED CHANGES IN WIND SPEED AND DIRECTION FOR CASE 3*

(a) Wind Speed

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-.0	-.2	-.6	-1.2	-1.7	-1.9	-1.1	-.8	-.4	-.4	-.0	-.2	-.2	-.2	-.2	-.8	-.3	-.8	-.9	-.4	-.4	-.7	-.4	.1	.1
24	-.0	-.2	-.9	-1.6	-1.6	-1.0	-.9	-.6	-.2	-.2	-.2	.0	-.0	-.1	-.2	-.3	-.4	-.3	-.2	-.5	-.4	-.6	.2	.4	.3
23	-.0	-.3	-1.0	-1.6	-1.0	-1.3	-.8	-.4	.2	.9	.7	.6	.4	.0	-.2	-.4	-.6	-1.0	-1.0	-.8	-1.0	-.3	.1	.3	.0
22	.0	-.0	-1.2	-1.8	-1.3	-1.5	-.9	-.3	1.1	1.5	1.4	1.4	1.1	.2	-.1	-.2	-.5	-.9	-.9	-1.1	-.6	-.4	-.4	.1	.3
21	.3	-.0	-.6	-1.0	-1.0	-1.3	-.8	.6	1.1	1.4	1.0	1.0	.9	.8	.6	.3	-.1	-.8	-1.1	-.9	-1.0	-.9	-.0	.1	.3
20	.0	.0	-.2	-1.2	-1.2	-.6	-.1	1.2	1.0	.0	1.1	.0	.0	.8	.0	-.3	-1.2	-1.6	-1.4	-1.6	-1.3	-1.1	-.3	.4	.0
19	.3	.2	-.0	-.3	-.4	-.1	.0	.8	-.2	-.0	-.3	-.3	-.3	-.9	-1.5	-2.5	-3.3	-3.3	-2.6	-1.6	-1.3	-.9	-.2	.4	.4
18	.2	.1	-.0	-.1	-.1	.1	.4	-.0	-.0	-.7	-1.1	-1.2	-1.5	-2.7	-3.3	-3.5	-4.1	-3.3	-2.1	-1.6	-.8	-.6	-.1	.2	.1
17	.1	.0	-.1	-.1	-.1	.5	.1	-.4	-.0	-1.1	-1.6	-1.9	-2.2	-2.9	-3.2	-3.6	-3.5	-2.4	-1.8	-.9	-.6	-.5	.4	.2	.0
16	.0	-.0	-.1	-.1	-.1	.1	.3	-.7	-.7	-1.7	-1.5	-1.4	-2.5	-2.7	-2.0	-2.9	-2.5	-1.6	-.0	-.6	.3	-.0	.1	-.0	-.0
15	-.0	-.1	-.1	-.2	-.2	-.1	-.0	-.1	-1.3	-1.2	-1.0	-1.4	-2.1	-2.1	-2.2	-2.3	-1.7	-.7	-.6	.3	.9	.4	-.1	-.1	-.0
14	-.0	-.1	-.2	-.3	-.3	-.0	.3	-.6	-1.0	-1.0	-.9	-1.4	-2.2	-1.8	-1.9	-2.0	-1.2	-.8	.3	.3	.9	.4	-.1	-.1	.0
13	-.0	-.2	-.2	-.3	-.2	.1	.0	-.6	-.7	-1.1	-1.0	-2.0	-2.0	-1.9	-1.2	-1.7	-1.1	-.3	-.2	1.0	1.1	.0	-.1	.2	.1
12	-.0	-.1	-.2	-.3	-.2	-.1	.0	-.1	-.7	-1.2	-1.6	-2.4	-2.1	-1.2	-1.6	-1.0	-1.1	-.3	-.6	.4	1.2	.6	.2	.1	.1
11	-.0	-.1	-.2	-.2	-.2	-.2	-.1	.1	-.8	-1.5	-2.2	-1.8	-1.2	-1.1	-1.2	-1.2	-1.0	-1.2	-.3	.4	1.1	.6	.2	.2	.1
10	-.0	-.1	-.2	-.2	-.3	-.2	-.1	-.1	-1.1	-1.2	-2.0	-.8	-.6	-1.3	-1.1	-.8	-.6	-.6	.4	.8	.9	.5	.1	.0	.1
9	-.0	-.1	-.2	-.3	-.3	-.3	-.3	-.3	-.9	-.9	-1.2	-1.0	-1.0	-1.0	-.7	-.4	-.2	.1	.6	.4	.7	.4	.0	-.1	.0
8	-.0	-.1	-.2	-.3	-.4	-.5	-.4	-.4	-.6	-.7	-1.1	-1.0	-1.4	-1.1	-.8	-.6	-.0	.1	.5	.3	.2	.1	-.0	-.1	.0
7	-.0	-.1	-.2	-.3	-.4	-.5	-.5	-.5	-.6	-.7	-.9	-1.3	-1.2	-1.0	-.6	-.3	.3	.4	.2	.0	-.0	-.0	.0	.0	.0
6	-.0	-.1	-.2	-.3	-.4	-.4	-.5	-.5	-.5	-.7	-1.0	-1.0	-1.3	-.6	-.2	.0	.2	.2	.1	-.0	-.0	.0	.1	.1	.0
5	-.0	-.1	-.3	-.3	-.3	-.4	-.4	-.5	-.5	-.7	-.9	-.9	-.7	-.5	-.3	-.1	.1	.1	.0	-.1	-.1	-.1	-.0	.0	.0
4	-.0	-.1	-.2	-.3	-.3	-.4	-.4	-.5	-.6	-.7	-.7	-.5	-.6	-.5	-.3	-.2	-.0	.0	-.0	-.1	-.2	-.2	-.0	.0	.0
3	-.0	-.1	-.2	-.2	-.3	-.4	-.4	-.5	-.6	-.6	-.7	-.7	-.6	-.5	-.4	-.2	-.1	-.1	-.1	-.3	-.3	-.2	-.0	.1	.0
2	-.0	-.1	-.2	-.2	-.3	-.4	-.4	-.5	-.6	-.6	-.6	-.6	-.6	-.5	-.4	-.3	-.2	-.2	-.2	-.4	-.4	-.3	-.1	.1	.1
1	-.0	-.1	-.2	-.2	-.3	-.4	-.4	-.5	-.5	-.6	-.6	-.6	-.6	-.5	-.0	-.4	-.3	-.2	-.2	-.4	-.4	-.4	-.1	.1	.0

(b) Wind Direction

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-2	-1	13	33	48	49	47	39	27	19	16	11	12	17	23	31	36	40	39	40	42	40	20	4	-3
24	0	2	11	36	61	61	60	54	42	30	10	13	14	16	23	30	37	41	42	44	47	53	01	10	4
23	3	4	1	35	59	61	57	51	46	40	32	24	22	22	25	30	33	36	37	33	35	41	35	22	15
22	-3	-5	-8	16	47	56	52	44	38	36	39	36	37	37	32	34	38	37	30	27	28	28	28	22	10
21	-22	-34	-24	-8	18	35	44	39	35	38	39	40	46	58	59	60	70	72	64	48	36	29	28	25	23
20	-32	-35	-40	-31	16	36	42	39	39	41	39	46	50	56	59	58	64	64	53	36	34	32	33	37	31
19	-20	-32	-35	-30	-1	19	30	30	31	31	33	37	42	51	58	52	45	30	17	15	14	21	26	29	25
18	-19	-19	-19	-17	-13	-4	6	11	13	16	19	16	19	20	30	20	4	-3	-3	-1	4	10	16	18	15
17	-6	-6	-7	-8	-9	-10	-8	-8	1	3	1	-1	-6	-7	-23	-45	-44	-20	-17	-9	-1	5	9	10	9
16	-0	-0	-1	-2	-3	-0	-13	-8	-5	-6	-4	-5	-6	-15	-24	-35	-43	-35	-25	-17	-7	2	8	-1	-2
15	2	1	-0	-1	-4	-7	-10	-7	-4	-6	-2	-1	0	-3	-10	-18	-31	-33	-26	-19	-12	-6	-5	-7	-7
14	2	1	0	-0	-0	-0	-1	-2	-1	6	0	0	0	-2	-4	-6	-16	-26	-27	-24	-17	-10	-11	-11	-10
13	0	6	0	1	1	1	-0	0	2	1	1	-1	-4	-5	-5	-3	-5	-16	-24	-29	-26	-20	-16	-14	-14
12	0	0	0	1	2	0	-1	1	3	1	-1	-5	-6	-8	-9	-11	-14	-9	-15	-22	-23	-21	-20	-18	-16
11	-0	0	1	1	2	1	-0	0	0	1	3	1	2	-0	-4	-10	-16	-24	-32	-19	-16	-14	-17	-20	-21
10	0	0	1	1	1	-0	-2	-5	-6	1	17	17	13	9	2	-3	-4	-8	-12	-13	-13	-13	-14	-19	-23
9	0	0	0	0	-1	-4	-8	-12	-6	7	22	22	16	14	10	4	1	6	8	-4	-9	-13	-15	-15	-17
8	-1	-1	-0	-1	-2	-5	-8	-10	-4	8	23	23	17	11	7	2	-5	-3	-5	7	1	-7	-9	-8	-9
7	-2	-2	-2	-2	-2	-0	-0	-5	-7	-6	14	22	25	17	13	8	0	-1	-1	-9	-12	-12	-11	-7	-6
6	-4	-4	-4	-4	-3	-0	1	-1	-4	-5	2	19	30	32	19	13	3	0	2	1	0	-3	-6	-7	-8
5	-3	-3	-3	-3	-2	-0	0	1	0	-3	1	14	27	29	27	19	9	1	-1	-3	-3	-5	-7	-7	-7
4	-2	-2	-2	-2	-1	-0	0	0	1	1	5	12	19	22	23	18	15	10	6	2	-2	-10	-8	-7	-7
3	-1	-1	-1	-1	-0	-0	0	1	2	3	7	11	14	16	16	15	12	11	10	8	-1	-2	-7	-7	-7
2	-0	-0	-0	-0	-0	0	1	2	3	5	7	9	11	12	12	10	7	5	4	4	5	-2	-5	-6	-5
1	-0	-0	-0	0	0	1	2	0	4	5	7	8	9	9	8	6	4	3	3	3	3	-0	-1	-2	-2

*See Table 24 for a description of the experimental conditions.

Table 19

PREDICTED CHANGES IN WIND SPEED AND DIRECTION FOR CASE 4*

(a) Wind Speed

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	.1	-.0	-.3	-.3	-.4	-.4	-.3	-.6	.1	1.0	1.2	1.6	1.6	1.8	.2	-.1	-.3	-.0	-.2	-.1	.0	-.0	.0	-.1	-.2
24	-.4	-.3	-.4	-.3	-.4	-.4	-.4	-.5	.3	.2	1.2	1.0	.9	.0	-.6	-1.0	-1.0	-.7	-1.0	-.9	-.9	-.4	-1.0	-1.0	-1.2
23	-.4	-.2	-.2	-.1	-.2	-.1	-.0	-.1	-.2	.7	.4	.9	.5	-.8	-1.0	-1.8	-2.2	-1.7	-1.7	-1.9	-1.6	-1.0	.4	-2.1	-2.4
22	-.1	.1	.2	.2	.2	.3	.4	.1	.4	.8	.8	.7	.3	-1.1	-1.4	-2.3	-2.8	-2.3	-2.3	-2.0	-2.0	-2.0	-2.4	-2.5	-2.6
21	.3	.2	.5	.8	.9	.9	.9	.8	.9	1.0	1.2	1.3	.1	-1.2	-1.6	-2.5	-3.2	-2.7	-3.0	-2.6	-2.4	-2.5	-2.0	-1.7	-2.2
20	.7	.6	1.0	1.4	1.6	1.7	1.8	2.0	1.8	1.7	2.1	1.8	1.1	-.4	-1.0	-2.2	-3.1	-2.4	-2.7	-2.5	-1.9	-1.7	-1.4	-1.0	-1.3
19	.6	.9	1.2	1.5	1.9	2.2	2.6	2.5	2.0	2.5	2.4	2.3	1.8	.6	-.9	-1.6	-2.7	-3.2	-2.2	-1.7	-1.5	-1.3	-1.0	-1.2	-1
18	.9	1.2	1.6	2.0	2.5	3.1	3.7	3.1	2.9	3.3	2.9	2.8	2.5	2.0	.3	-.9	-2.5	-3.1	-2.0	-1.3	-.8	-1.0	-.4	-.8	-.2
17	1.3	1.8	2.3	2.8	3.6	4.5	5.6	5.4	4.1	4.0	3.5	3.3	4.1	4.3	2.2	.1	-1.0	-1.7	-1.8	-1.4	1.0	-1.0	-.1	-.2	-.2
16	1.2	2.1	1.4	2.5	3.4	4.2	5.1	4.8	5.0	5.1	4.6	4.3	5.3	4.4	4.2	2.3	.1	-.9	-1.3	-.7	-.8	.0	-.6	.2	.9
15	.4	1.2	1.3	2.6	2.8	3.9	4.3	5.4	4.5	4.7	4.2	4.2	4.1	5.1	4.5	2.7	.8	-.1	-.4	-1.0	-.5	.0	-.2	-.1	.0
14	-.0	.8	1.0	2.1	3.0	3.6	4.0	4.6	4.0	4.2	3.4	3.1	4.2	4.4	3.9	2.9	1.1	.2	.2	-.3	.1	-.1	-.1	.0	.1
13	-.3	.4	1.3	2.0	2.8	3.5	4.1	4.6	3.9	3.2	2.4	1.6	3.5	4.1	3.7	2.9	1.3	.5	-.2	.1	.6	.1	.0	-.1	.5
12	-.4	.2	.9	2.1	2.8	3.6	3.8	4.4	3.8	3.3	1.9	.2	1.8	2.7	2.7	2.3	1.7	.1	.3	.2	.2	.0	.0	.5	.3
11	-.3	.3	.8	1.9	2.6	3.4	4.2	4.1	3.8	3.1	2.4	.5	.7	2.0	2.5	1.7	1.4	.0	.0	.2	.4	.3	.0	.4	.4
10	-.3	.5	1.0	1.6	2.3	3.1	3.8	4.4	4.0	3.5	2.0	1.1	.4	1.6	2.0	2.3	1.2	.4	.2	.4	.3	.2	.4	.4	.4
9	-.2	.3	.9	1.5	2.1	2.9	3.7	4.0	4.1	3.4	2.6	1.4	-.0	1.0	1.7	1.8	1.0	.6	.3	.5	1.0	.2	.6	.5	.5
8	-.1	.3	.8	1.4	1.9	2.5	3.4	4.4	4.3	3.3	3.1	1.9	.6	1.1	1.6	1.7	1.6	1.1	.5	.1	.6	.9	.7	.6	.5
7	-.0	.3	.5	1.3	1.8	2.3	2.9	3.8	3.7	3.1	2.7	2.0	.7	1.2	1.6	1.8	1.6	1.3	.5	.5	.2	.6	.4	.7	.6
6	.0	.3	.5	1.2	1.6	2.0	2.5	3.2	3.4	2.9	2.1	1.8	.9	1.1	1.4	1.6	1.4	.9	.9	.6	.4	.3	.6	.5	.4
5	.1	.3	.7	1.1	1.5	1.8	2.1	2.5	2.6	2.4	2.0	1.6	.9	1.0	1.4	1.3	1.4	1.1	.8	.6	.4	.3	.1	.5	.4
4	.1	.4	.7	1.0	1.3	1.6	1.7	2.2	2.5	2.2	1.8	1.3	.7	1.1	1.1	1.3	1.1	1.0	.8	.6	.4	.3	.2	.1	.4
3	.1	.3	.6	.9	1.0	1.6	1.6	1.8	2.4	2.1	1.7	1.3	.8	.8	1.1	.9	.9	.8	.6	.4	.3	.2	.2	.2	.2
2	.1	.3	.4	.9	.9	1.4	1.2	1.9	1.6	2.1	1.7	1.3	1.0	.8	.8	.8	.7	.6	.5	.3	.1	.1	.1	.1	.1
1	.0	.1	.6	.6	1.1	1.0	1.7	1.4	2.0	1.7	1.5	1.2	.9	.8	.8	.7	.6	.5	.4	.2	.1	-.0	-.0	-.0	.0

(b) Wind Direction

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-1	1	1	1	0	0	0	0	2	5	7	9	14	20	9	2	-2	-4	-3	-2	-0	1	3	3	1
24	-6	-7	-2	-0	1	2	3	5	8	9	12	17	32	25	15	8	1	1	1	1	3	5	10	6	5
23	-9	-12	-5	-3	0	2	6	10	9	20	26	39	42	34	20	17	9	9	7	7	7	9	17	12	14
22	-4	-5	-9	-4	1	5	9	15	19	20	35	42	47	30	35	24	15	14	11	11	14	17	25	22	23
21	1	0	-2	-3	0	6	11	21	23	33	43	46	49	41	33	26	16	18	15	16	19	23	27	20	23
20	23	21	20	18	15	16	17	21	29	34	48	46	40	33	29	23	17	16	13	15	21	22	23	23	22
19	36	35	33	33	31	31	32	36	36	39	45	38	34	27	26	22	15	11	12	17	20	21	22	16	17
18	39	37	36	34	32	32	32	35	42	44	37	32	25	22	20	17	11	9	13	13	18	10	10	8	9
17	45	43	39	38	38	38	43	42	33	31	25	18	18	16	12	9	4	4	3	3	2	1	0	1	3
16	48	44	37	36	39	39	37	32	27	22	19	15	12	9	5	8	-1	-5	-4	-2	-0	-2	-8	0	-0
15	38	35	32	34	33	30	26	25	21	18	13	8	7	4	1	-2	-8	-11	-8	-6	-3	-1	-3	-1	-2
14	32	30	29	29	27	26	24	22	19	15	10	5	2	0	-3	-5	-11	-13	-14	-13	-7	-7	-6	-6	-4
13	26	24	25	25	23	22	20	19	16	13	9	3	1	-0	-3	-7	-11	-14	-15	-14	-12	-12	-11	-10	-10
12	22	23	22	19	18	18	17	16	13	12	8	4	3	1	-3	-6	-10	-14	-15	-14	-13	-14	-14	-12	-12
11	17	17	17	16	13	13	13	13	11	9	6	2	2	-1	-4	-8	-10	-13	-14	-13	-14	-13	-13	-12	-12
10	13	13	12	11	12	11	10	9	8	6	3	-0	-5	-4	-7	-12	-15	-15	-15	-15	-15	-13	-13	-13	-13
9	9	10	9	11	9	9	9	8	6	1	-1	-4	-9	-9	-11	-12	-15	-15	-16	-16	-16	-15	-15	-15	-16
8	7	7	7	7	8	6	4	2	-0	-4	-9	-12	-12	-11	-12	-13	-15	-15	-15	-14	-14	-15	-17	-17	-16
7	4	4	4	4	3	3	1	-0	-3	-7	-10	-12	-13	-12	-12	-13	-14	-15	-14	-12	-12	-13	-14	-15	-16
6	2	3	3	2	1	-0	-1	-3	-6	-7	-9	-11	-13	-12	-11	-11	-11	-12	-12	-11	-11	-11	-12	-13	-14
5	0	0	0	0	-0	-0	-1	-2	-4	-5	-7	-9	-10	-9	-9	-9	-10	-10	-10	-10	-11	-10	-11	-12	-13
4	-1	-0	-0	-0	-1	-0	-1	-2	-3	-4	-5	-6	-7	-6	-5	-6	-7	-8	-9	-10	-11	-12	-12	-12	-13
3	-1	-1	-1	-0	-0	-0	-1	-1	-2	-3	-3	-4	-4	-2	-2	-3	-4	-5	-6	-7	-8	-9	-9	-9	-9
2	-0	-0	0	0	0	0	0	0	0	0	-1	-1	-1	-0	-0	-0	-1	-1	-2	-3	-3	-4	-5	-5	-6
1	-0	-0	0	1	1	1	2	2	3	3	2	2	1	1	1	1	1	0	0	-0	-0	-1	-1	-1	-1

*See Table 24 for a description of the experimental conditions.

Table 20

PREDICTED CHANGES IN WIND SPEED AND DIRECTION FOR CASE 5*

(a) Wind Speed

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	.2	.0	-.1	-.1	-.2	-.2	-.2	-.4	.6	.5	.4	.5	.4	.4	.0	.0	-.0	-.2	.1	.1	.1	-.1	.0	-.0	-.1
24	-.2	-.1	-.2	-.1	-.2	-.1	-.1	-.4	.2	-.1	.5	.2	.2	.0	-.3	-.4	-.3	-.1	-.3	-.3	-.5	-.1	-.1	-.3	-.4
23	-.2	-.1	-.1	-.0	-.1	-.0	-.0	-.0	-.3	.3	-.2	.2	.1	-.5	-.3	-.6	-.8	-.5	-.6	-.8	-.6	-.7	1.1	-.9	-1.3
22	-.0	.1	.0	.1	.0	.1	.1	-.1	-.0	.2	.0	-.2	-.1	-.7	-.6	-.9	-1.1	-.7	-.8	-.6	-.6	-.7	-1.3	-1.2	-1.0
21	.1	-.1	.1	.2	.2	.3	.1	.2	.2	.1	.1	.1	-.3	-.9	-.8	-1.0	-1.3	-.9	-1.2	-1.0	-1.0	-1.3	-1.0	-.6	-1.0
20	.2	.0	.3	.4	.5	.5	.4	.6	.4	.2	.5	.1	-.1	-.5	-.3	-.8	-1.2	-.7	-1.1	-1.1	-.8	-.6	-.6	-.2	-.6
19	-.0	.1	.2	.3	.4	.5	.6	.5	.5	.5	.4	.3	.2	-.1	-.7	-.6	-1.0	-1.4	-.9	-.0	-.6	-.6	-.3	-.7	-.1
18	.0	.1	.0	.9	.0	.0	1.0	1.1	.4	.0	.0	.0	.0	.4	-.2	-.3	-1.1	-1.4	-.7	-.0	-.3	-.5	.0	-.4	.1
17	.0	.2	.4	.0	.9	1.1	1.6	1.3	.9	1.2	1.0	.9	1.4	1.0	.3	-.2	-.3	-.5	-.6	-.0	1.2	-.7	.1	-.0	-.1
16	-.1	.0	-.3	.4	.7	.9	1.4	1.0	1.4	1.6	1.4	1.2	2.0	.9	1.4	.9	-.1	-.3	-.4	-.0	-.4	.2	-.4	.2	.0
15	-.2	.2	-.1	.0	.4	.9	1.0	1.9	1.2	1.6	1.4	1.4	1.0	1.7	1.0	1.1	.2	-.1	-.0	-.5	-.2	.1	-.1	-.0	.0
14	-.3	.1	-.1	.4	.7	.9	1.1	1.4	1.0	1.4	1.1	.8	1.5	1.5	1.4	1.1	.3	.0	.2	-.3	.2	-.1	-.1	-.0	.0
13	-.3	-.1	.2	.4	.7	1.0	1.2	1.5	1.2	1.0	.8	.2	1.4	1.4	1.3	1.1	.3	.3	-.3	.0	.4	.0	-.0	-.2	.3
12	-.3	-.1	.1	.0	.0	1.2	1.1	1.5	1.2	1.2	.5	-.5	.4	1.0	.8	.7	.7	-.2	.1	-.0	-.0	.3	-.2	.3	.1
11	-.2	.0	.1	.0	.0	1.1	1.0	1.3	1.2	1.0	.9	-.3	.0	.0	.9	.3	.0	-.2	-.1	.0	.1	.1	.4	.1	.1
10	-.2	.2	.3	.5	.7	1.0	1.2	1.6	1.3	1.3	.0	.3	-.2	.7	.0	.9	.2	.1	.0	.1	.1	.4	.1	.1	.1
9	-.1	.1	.2	.4	.7	.9	1.3	1.3	1.4	1.1	.8	.0	-.6	.7	.0	.0	.0	.1	.0	.2	.4	.3	.1	.1	.1
8	-.1	.1	.3	.4	.6	.8	1.1	1.6	1.5	1.0	1.2	.7	-.2	.3	.0	.0	.0	.4	.2	-.2	.2	.3	.2	.2	.1
7	-.0	.1	.3	.4	.6	.8	1.0	1.3	1.2	1.0	1.0	.7	-.1	.3	.0	.0	.0	.0	.1	.2	-.0	.3	.0	.3	
6	-.0	.1	.3	.4	.5	.7	.9	1.1	1.1	1.0	.6	.7	.0	.3	.4	.0	.0	.2	.4	.2	.1	-.0	.2	.1	.1
5	.0	.1	.2	.4	.5	.6	.7	.0	.0	.0	.6	.5	.1	.3	.0	.4	.5	.3	.2	.2	.1	.1	-.1	.2	.1
4	.0	.1	.2	.3	.4	.5	.5	.7	.9	.7	.6	.4	.1	.4	.4	.5	.4	.3	.2	.2	.1	.1	.1	-.1	.2
3	.0	.1	.2	.3	.3	.0	.9	.5	1.0	.7	.0	.0	.2	.3	.9	.3	.3	.0	.2	.1	.1	.1	.0	.0	.0
2	.0	.1	.0	.0	.2	.0	.0	.0	.4	.9	.0	.4	.0	.0	.0	.0	.0	.2	.2	.2	.1	.0	.0	.0	.0
1	.0	-.0	.3	.1	.4	.2	.7	.0	.0	.0	.0	.4	.0	.0	.3	.2	.2	.2	.1	.1	.0	-.0	-.0	-.0	.0

(b) Wind Direction

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-0	1	1	0	0	0	0	0	0	1	2	3	4	10	2	0	-0	-1	-1	-1	-0	-0	1	1	0
24	-4	-3	-0	0	0	1	1	1	3	2	4	4	14	8	4	2	-0	0	0	0	1	1	5	2	1
23	-3	-6	-1	-1	0	0	2	3	1	8	9	16	15	9	8	4	1	3	2	1	2	1	5	1	4
22	-1	-1	-4	-1	0	1	3	5	7	11	13	15	16	9	10	6	3	4	2	2	3	4	9	6	6
21	-1	-1	-2	-4	-2	1	3	6	9	12	16	16	17	12	10	6	2	6	4	5	6	7	8	9	6
20	10	9	9	8	6	5	6	6	11	12	20	18	14	9	8	6	3	4	3	4	7	6	6	6	6
19	15	15	14	14	14	14	15	17	14	15	19	14	13	8	8	7	4	2	2	6	6	7	8	4	4
18	13	13	14	13	13	13	12	14	19	31	16	14	9	9	6	6	4	2	5	4	8	1	3	1	5
17	16	16	14	15	16	17	22	21	14	13	9	6	7	6	4	3	1	1	0	-0	-1	-1	-1	-0	0
16	17	17	13	14	17	18	18	15	12	9	8	6	5	3	2	1	-0	-2	-2	-1	0	-1	-0	0	-0
15	13	13	11	14	14	13	11	11	8	8	5	3	3	1	0	-0	-4	-4	-2	-2	-0	0	-1	-0	-0
14	10	11	11	11	10	10	10	10	7	6	3	1	0	-0	-1	-2	-4	-5	-4	-5	-2	-2	-2	-2	-0
13	8	8	9	9	9	9	8	8	6	5	3	0	0	-0	-1	-2	-4	-5	-5	-5	-4	-4	-3	-3	-1
12	7	9	8	7	7	7	7	7	5	5	3	1	1	1	-1	-2	-3	-5	-4	-5	-4	-4	-5	-4	-4
11	5	5	5	6	4	5	5	5	5	3	2	0	1	-0	-1	-2	-2	-4	-4	-6	-4	-4	-4	-4	-4
10	4	4	3	3	4	6	4	3	3	2	2	-0	-3	-0	-2	-5	-6	-5	-5	-5	-5	-4	-4	-4	-1
9	2	3	3	4	3	3	6	4	3	1	-0	-0	-4	-3	-4	-4	-5	-5	-5	-6	-6	-5	-5	-3	-5
8	2	2	2	2	3	3	2	0	-0	-2	-4	-5	-5	-4	-4	-4	-5	-5	-5	-4	-4	-5	-6	-6	-6
7	1	1	1	1	1	1	0	0	-1	-3	-3	-4	-5	-4	-4	-5	-5	-5	-5	-4	-4	-4	-5	-5	-5
6	1	1	1	0	0	-0	-0	-1	-3	-3	-3	-4	-5	-4	-4	-4	-4	-4	-4	-4	-4	-4	-4	-4	-4
5	0	0	0	-0	-0	-0	-0	-0	-1	-2	-2	-3	-4	-3	-3	-3	-3	-4	-4	-3	-3	-2	-3	-4	-4
4	-0	-0	-0	-0	-0	-0	-0	-1	-1	-1	-2	-2	-3	-2	-2	-2	-2	-2	-3	-4	-4	-5	-4	-4	-5
3	-0	-0	-0	0	-0	0	-0	-0	-0	-1	-1	-1	-1	-1	-1	-1	-1	-1	-2	-2	-2	-3	-3	-3	-3
2	-0	0	0	0	0	0	-0	0	0	0	-0	-1	-1	-0	-0	-0	-0	-0	-0	-1	-1	-1	-1	-1	-2
1	-0	-0	0	0	0	0	0	0	1	1	1	0	0	0	0	0	0	0	0	-0	-0	-0	-0	-0	-0

*See Table 24 for a description of the experimental conditions.

Table 21

PREDICTED CHANGES IN WIND SPEED AND DIRECTION FOR CASE 6*

(a) Wind Speed

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	.1	-.1	-.5	-.6	-.7	-.7	-.8	-.9	.1	1.4	2.0	2.7	2.9	2.3	.5	-.2	-.5	-.8	-.8	-.3	-.6	.1	.0	-.1	-.4
24	-.5	-.4	-.6	-.5	-.7	-.6	-.6	-.7	.5	.6	1.9	2.6	1.9	1.2	-.6	-1.6	-1.7	-1.4	-1.6	-1.4	-1.4	-.5	-1.3	-1.7	-1.9
23	-.6	-.2	-.1	-.2	-.3	-.1	.0	-.1	.6	1.2	1.3	2.3	1.6	-.2	-1.0	-2.7	-3.4	-2.0	-2.7	-2.0	-2.5	-2.3	.1	-2.9	-3.5
22	-.1	.3	.7	.9	.4	.6	.8	.5	1.0	1.9	2.3	2.4	1.0	-.3	-1.2	-2.9	-4.0	-3.5	-3.6	-3.1	-3.0	-2.9	-2.8	-3.1	-3.5
21	.5	.4	.9	1.3	1.5	1.6	1.7	1.7	1.9	2.5	3.1	3.6	2.2	-.2	-1.3	-3.1	-4.4	-4.0	-4.3	-3.7	-3.1	-2.9	-2.2	-1.8	-2.4
20	1.3	1.3	1.9	2.5	2.9	3.1	3.4	3.7	3.9	3.8	4.0	4.6	3.4	.9	-.6	-2.7	-4.3	-3.7	-3.8	-3.4	-2.4	-1.9	-1.5	-1.1	-1.3
19	1.9	2.2	2.7	3.2	3.7	4.3	5.0	5.1	4.2	5.2	5.4	5.2	4.3	2.2	-.3	-1.9	-4.0	-4.7	-3.3	-2.4	-1.9	-1.3	-1.2	-1.5	-.6
18	2.6	3.1	3.6	4.2	5.0	5.9	7.0	7.7	6.2	6.7	6.1	5.7	5.5	4.2	1.4	-.9	-3.7	-4.6	-3.1	-1.8	-1.0	-1.4	-.7	-1.1	-.4
17	3.0	4.2	4.9	5.6	6.9	8.5	10.3	10.3	8.0	7.3	6.5	6.1	7.2	7.3	4.2	.6	-1.7	-2.9	-3.0	-2.1	.5	-1.3	-.4	-.3	-.3
16	3.5	4.6	5.9	6.5	7.0	8.3	9.4	9.8	9.1	9.0	8.1	7.6	8.0	7.9	7.0	3.6	.2	-1.5	-2.1	-1.4	-1.1	-.1	-.8	.1	-.0
15	2.1	3.1	3.5	5.4	6.1	7.6	8.2	9.4	8.1	8.1	7.3	7.1	7.2	8.5	7.5	4.4	1.5	-.0	-.7	-1.4	-.7	-.1	-.3	-.2	.0
14	1.2	2.3	2.9	4.6	5.9	6.9	7.4	8.1	7.4	7.1	6.9	6.5	7.0	7.2	6.5	4.7	2.1	.6	.4	-.3	.1	-.2	-.2	.1	.2
13	.0	1.6	2.9	4.2	5.3	6.5	7.4	7.9	6.9	5.7	4.2	3.1	5.7	6.8	6.2	4.7	2.4	1.0	.1	.4	.9	.4	.2	.0	.2
12	.1	1.1	2.3	3.9	5.0	6.3	6.9	7.4	6.6	5.0	3.4	1.1	2.6	4.5	4.5	3.9	2.8	.7	.7	.6	.7	.9	.3	.8	.2
11	-.0	.9	1.9	3.4	4.6	5.9	7.1	7.8	6.6	5.4	3.8	1.3	1.4	3.2	4.0	3.1	2.5	.5	.3	.6	.8	.7	1.0	.8	.1
10	-.3	.7	1.8	2.9	4.1	5.4	6.5	7.3	6.8	5.8	3.5	2.0	1.0	2.6	3.5	3.9	2.4	1.0	.6	.9	1.1	1.2	.9	.9	.8
9	-.1	.0	1.6	2.6	3.7	4.9	6.2	6.9	6.9	5.7	4.3	2.4	.0	2.4	3.0	3.3	3.0	1.3	.7	1.1	1.6	1.2	1.1	1.0	1.0
8	-.1	.0	1.5	2.4	3.3	4.3	5.6	7.2	7.0	5.6	5.0	3.2	1.4	2.1	2.8	3.0	2.9	1.9	1.0	.4	1.1	1.5	1.3	1.2	1.1
7	-.0	.0	1.4	2.2	3.1	3.8	4.9	6.3	6.3	5.2	4.6	3.5	1.8	2.2	2.7	2.7	2.7	2.2	1.2	1.0	.0	1.1	1.0	1.3	1.1
6	.0	.0	1.3	2.0	2.7	3.4	4.2	5.3	5.6	4.8	3.7	3.2	1.9	2.1	2.5	2.8	2.4	1.8	1.0	1.1	.7	.0	1.0	.9	.9
5	.1	.0	1.2	1.8	2.4	3.0	3.6	4.1	4.4	4.0	3.4	2.5	1.7	1.8	2.3	2.3	2.3	1.8	1.4	1.1	.8	.0	.4	.9	.5
4	.2	.0	1.1	1.6	2.2	2.7	3.0	3.7	4.1	3.7	3.0	2.2	1.4	1.7	1.8	2.0	1.8	1.6	1.3	1.0	.8	.0	.4	.3	.1
3	.2	.5	1.0	1.4	1.8	2.6	2.6	3.0	3.0	3.5	2.8	2.1	1.4	1.4	1.7	1.6	1.5	1.3	1.0	.7	.5	.4	.4	.4	.4
2	.1	.0	.7	1.0	1.0	2.3	2.2	3.1	2.9	3.4	2.8	2.1	1.6	1.0	1.3	1.3	1.2	1.0	.8	.5	.2	.1	.1	.1	.2
1	.1	.3	.9	1.1	1.7	1.8	2.6	2.4	3.2	2.9	2.5	2.0	1.6	1.4	1.3	1.2	1.1	.9	.6	.4	.1	-.0	-.1	.0	.6

(b) Wind Direction

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-2	0	1	1	1	1	1	1	4	7	10	13	20	28	15	3	-3	-7	-6	-4	-0	2	6	4	2
24	-12	-11	-4	-0	1	3	6	9	13	15	19	26	45	39	20	15	4	2	1	2	5	9	16	12	11
23	-15	-18	-10	-5	0	4	11	16	17	31	38	55	62	57	52	39	22	19	14	14	15	19	30	26	23
22	-7	-9	-13	-7	1	8	14	23	29	41	51	60	68	64	63	51	36	30	24	24	29	35	46	44	30
21	4	2	-1	-2	2	11	10	30	37	47	59	64	71	66	62	54	40	37	32	32	37	43	49	51	49
20	34	31	28	25	22	23	25	31	42	47	63	61	58	52	51	46	39	33	20	30	30	42	43	42	41
19	52	50	46	44	41	41	41	47	49	52	60	52	48	42	43	40	32	24	24	31	37	30	39	31	30
18	55	52	50	47	43	42	41	45	54	56	49	43	35	32	32	29	21	18	24	24	29	19	18	15	17
17	61	60	52	50	49	47	51	51	42	40	32	26	25	22	18	14	9	8	8	8	6	4	2	3	7
16	66	59	51	49	51	49	46	41	35	29	25	21	16	12	7	4	-2	-9	-7	-3	-1	-3	-0	-0	0
15	56	51	47	47	43	40	35	33	20	24	18	12	9	6	2	-3	-13	-18	-15	-12	-6	-3	-5	-3	-3
14	49	46	43	41	38	35	32	29	26	21	15	8	3	1	-4	-8	-16	-22	-23	-21	-13	-12	-11	-10	-3
13	41	38	37	35	33	30	28	26	22	19	13	6	2	-0	-4	-10	-17	-23	-24	-23	-20	-19	-10	-17	-16
12	37	36	30	28	26	24	23	22	18	17	13	7	4	0	-5	-10	-16	-23	-24	-23	-21	-22	-22	-19	-18
11	29	28	26	23	20	19	18	17	15	13	9	4	3	-2	-6	-12	-16	-21	-23	-22	-22	-20	-21	-20	-20
10	22	21	19	17	17	16	14	12	12	8	5	-0	-8	-7	-11	-16	-22	-24	-25	-24	-23	-21	-21	-21	-21
9	16	16	15	16	13	13	12	11	8	2	-2	-7	-14	-14	-17	-19	-23	-24	-25	-25	-25	-23	-23	-23	-24
8	12	12	12	10	11	9	6	3	-0	-6	-12	-17	-19	-18	-18	-19	-22	-23	-23	-22	-21	-23	-25	-25	-25
7	7	7	7	7	5	5	2	-0	-5	-10	-14	-18	-20	-19	-18	-19	-20	-22	-21	-20	-19	-20	-22	-23	-24
6	4	4	4	3	2	0	-1	-4	-8	-10	-14	-17	-19	-18	-17	-17	-17	-19	-19	-18	-18	-18	-20	-20	-22
5	1	1	1	0	-0	-0	-2	-4	-6	-8	-11	-13	-15	-14	-13	-13	-14	-15	-16	-16	-17	-16	-18	-20	-21
4	-2	-1	-1	-1	-1	-1	-2	-3	-5	-6	-8	-10	-11	-9	-8	-9	-10	-12	-13	-15	-17	-18	-19	-19	-20
3	-2	-1	-1	-0	-0	-0	-1	-2	-3	-4	-5	-6	-6	-4	-4	-4	-6	-7	-9	-11	-13	-14	-15	-15	-15
2	-0	-0	-0	0	1	0	0	1	0	0	-1	-2	-1	-0	-0	-1	-1	-2	-4	-5	-6	-7	-8	-9	-9
1	-0	-0	1	1	2	2	3	3	4	3	3	3	3	2	2	2	1	1	0	-0	-1	-1	-2	-2	-2

*See Table 24 for a description of the experimental conditions.

Table 22

PREDICTED CHANGES IN WIND SPEED AND DIRECTION FOR CASE 7*

(a) Wind Speed

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-.0	.1	.0	.1	-.1	-.6	-.2	-.5	-.5	-.5	-.5	-.4	-.3	-.2	-.2	-.1	-.2	-.2	-.4	-.4	-.4	-.7	-.6	-.6	-.1
24	.1	.5	-.0	-.0	-.4	-.7	-.9	-1.0	-.7	-.8	-.7	-.4	-.3	-.3	-.2	-.2	-.4	-.4	-.4	-.7	-.7	-1.0	-.3	.2	.3
23	.2	.5	-.1	-.5	-.3	-1.0	-1.0	-.9	-.6	-.0	.1	.1	.1	-.1	-.2	-.3	-.0	-.0	-.0	-.5	-.7	-.2	.2	.9	.7
22	.3	.5	-.5	-.5	-.4	-1.2	-.9	-.6	.6	.6	.6	.6	.4	-.1	-.2	-.2	-.5	-.0	-.5	-.6	-.1	.2	.2	.9	.7
21	.4	.3	-.1	-1.0	-.9	-.7	-.5	.7	1.0	.9	.9	.8	.0	.6	.1	-.1	-.7	-1.1	-.6	.3	.3	.2	.3	1.0	.7
20	.2	-.0	-.0	-.7	-.5	-.2	.1	1.3	1.4	.9	.0	.0	-.1	.3	.2	-.6	-1.5	-1.4	-.5	-.0	.0	.0	.7	1.3	.8
19	-.1	-.1	-.1	-.2	-.1	.2	.7	1.0	-.1	.1	-.3	-.4	-.4	-.9	-1.2	-1.8	-2.4	-1.8	-.6	.0	1.0	1.2	1.0	1.3	.9
18	-.1	-.2	-.1	-.1	.1	.4	.7	-.2	-.2	-.4	-.8	-.0	-.9	-1.9	-2.8	-1.7	-2.2	-1.2	.1	.7	1.4	1.5	1.7	1.0	.1
17	-.1	-.2	-.1	-.1	-.0	.7	.3	-.1	-.5	-.7	-1.1	-1.3	-1.4	-1.9	-1.8	-1.9	-1.4	-.2	.0	1.4	1.0	1.0	3.2	1.3	.7
16	-.1	-.2	-.2	-.1	.0	.8	.0	-.4	-.4	-1.2	-1.0	-.8	-1.0	-1.8	-1.6	-1.3	-.6	.5	1.3	1.0	2.4	1.7	1.3	1.1	.5
15	-.1	-.2	-.3	-.2	-.1	.0	.2	.2	-.9	-.7	-.8	-.8	-1.4	-1.3	-1.1	-1.0	-.1	1.2	1.5	2.7	2.5	2.1	1.7	1.2	.6
14	-.1	-.2	-.5	-.3	-.2	.1	.5	-.3	-.7	-.6	-.7	-.9	-1.5	-1.0	-.9	-.9	.2	.7	2.0	2.2	2.6	1.0	1.1	1.0	.5
13	-.1	-.2	-.3	-.2	-.1	.2	.2	-.3	-.4	-.7	-.6	-1.5	-1.4	-1.2	-.4	-.8	.0	1.1	1.2	2.4	2.5	1.5	1.0	1.3	.0
12	-.1	-.2	-.2	-.2	-.1	.0	.2	.1	-.4	-.8	-1.4	-1.9	-1.5	-.6	-.9	-.3	-.1	.5	.0	1.0	2.4	1.0	1.4	1.3	.0
11	-.1	-.2	-.2	-.2	-.1	-.1	.1	.3	-.5	-1.1	-1.7	-1.3	-.7	-.5	-.6	-.5	-.1	-.2	.0	1.0	2.2	1.7	1.3	1.2	.0
10	-.0	-.1	-.2	-.2	-.1	-.1	.1	.2	-.0	-.0	-1.5	-.3	-.1	-.0	-.6	-.2	.1	.3	1.4	1.9	2.0	1.5	1.2	1.0	.7
9	-.0	-.1	-.1	-.2	-.2	-.2	-.1	-.0	-.6	-.5	-.7	-.5	-.6	-.6	-.2	.2	.0	.9	1.4	1.3	1.7	1.4	1.1	1.2	.7
8	-.0	-.0	-.1	-.2	-.3	-.3	-.1	-.1	-.2	-.2	-.6	-.3	-.9	-.7	-.3	.0	.0	.0	1.2	1.1	1.1	1.0	.9	1.0	.0
7	-.0	-.0	-.1	-.2	-.3	-.3	-.1	-.1	-.1	-.2	-.4	-.9	-.7	-.5	-.0	.3	.9	1.1	.9	.0	.7	.0	.9	.9	.3
6	-.0	-.0	-.1	-.1	-.2	-.2	-.2	-.1	-.0	-.2	-.5	-.3	-.7	-.1	.3	.0	.5	.9	.7	.0	.0	.7	.5	.5	.4
5	-.0	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.2	-.4	-.4	-.2	.1	.3	.0	.7	.7	.0	.3	.0	.3	.0	.7	.4
4	-.0	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.1	-.2	-.1	.0	.2	.3	.5	.0	.0	.0	.4	.4	.4	.5	.0	.3
3	-.0	-.0	-.0	-.1	-.1	-.1	-.1	-.0	-.0	-.0	-.0	.0	.1	.2	.3	.5	.0	.0	.5	.3	.3	.2	.4	.5	.2
2	-.0	-.0	-.0	-.0	-.0	-.0	-.0	.0	.0	.0	.1	.1	.2	.3	.4	.4	.5	.4	.4	.2	.2	.1	.3	.4	.2
1	-.0	.0	.0	.0	.0	.0	.0	.0	.0	.1	.1	.1	.1	.2	.2	.2	.2	.2	.1	.1	.1	.0	.0	.0	-.0

(b) Wind Direction

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	-2	1	2	-1	-3	-3	-11	-11	-15	-10	-6	-10	-6	-4	-3	-3	-1	-4	-4	-4	-7	-7	-7	-4	-0
24	0	7	9	2	0	0	-11	-13	-26	-16	-15	-20	-16	-13	-10	-8	-1	-2	-6	-5	-6	-3	-9	-18	-7
23	2	6	5	3	2	7	0	-1	-6	-2	-0	-7	-8	-9	-10	-12	-7	-7	-10	-13	-10	-0	1	-5	-3
22	4	7	3	1	-2	5	6	3	-0	2	6	2	2	-0	-3	-3	-1	-3	-11	-10	-6	-4	-2	-5	-3
21	3	-3	-8	-5	-6	4	9	6	4	7	9	9	12	13	7	8	13	8	-2	-5	-5	-2	-0	-1	-1
20	1	-13	-20	-15	-1	9	17	15	16	15	9	11	12	12	7	7	9	2	-8	-9	-2	0	6	8	2
19	-0	-17	-22	-18	-4	3	13	12	10	8	7	3	0	-0	-17	-17	-14	-17	-16	-10	-8	-4	0	2	0
18	-3	-11	-12	-13	-12	-7	-0	0	-1	0	-1	-8	-14	-17	-35	-40	-30	-24	-18	-14	-9	-5	-2	-0	0
17	-1	-4	-5	-6	-8	-11	-10	-5	-5	-6	-9	-14	-20	-25	-36	-43	-39	-29	-21	-14	-9	-4	-2	-0	0
16	-0	-1	-1	-2	-3	-8	-13	-9	-8	-10	-10	-11	-14	-23	-30	-35	-36	-30	-23	-17	-9	-2	-1	-3	-0
15	0	0	-0	-1	-4	-7	-10	-0	-6	-8	-5	-5	-4	-9	-15	-21	-20	-27	-21	-16	-9	-5	-3	-2	-0
14	0	0	-0	-0	-0	-0	-1	-2	-1	5	-1	-1	-3	-6	-7	-10	-17	-22	-21	-17	-11	-4	-3	-2	0
13	-0	-0	0	1	2	2	0	0	2	1	0	-3	-5	-7	-7	-5	-9	-12	-17	-19	-15	-9	-5	-1	0
12	0	0	0	2	2	1	-0	2	4	1	-1	-5	-6	-8	-10	-11	-14	-7	-9	-14	-12	-9	-6	-3	-1
11	-0	0	1	2	4	3	1	2	2	2	3	1	1	-1	-5	-10	-16	-22	-28	-13	-7	-3	-3	-3	-4
10	0	1	2	3	3	2	0	-1	-3	3	15	15	10	7	0	-4	-3	-0	-9	-8	-4	-3	-1	-2	0
9	0	1	1	2	1	-1	-3	-6	-1	9	20	19	14	11	7	2	0	5	4	-1	-2	-4	-3	-1	-1
8	-0	0	1	1	1	-1	-2	-3	1	11	20	21	16	10	6	1	-5	-4	-5	11	7	1	1	1	0
7	0	0	0	0	1	3	4	0	0	5	14	20	22	15	11	6	-0	-1	0	-4	-5	-2	-1	0	0
6	-0	-1	-1	-0	0	3	5	3	1	2	8	19	26	29	16	12	4	2	5	7	7	5	3	1	0
5	0	-0	-0	0	1	3	4	5	5	4	7	16	25	27	26	19	11	5	3	3	4	4	2	1	0
4	0	0	0	1	2	3	4	5	6	7	10	15	20	23	24	21	19	14	12	9	6	1	2	1	0
3	0	0	0	1	2	3	5	6	7	9	11	15	17	20	21	20	18	18	17	17	7	10	5	2	0
2	0	0	1	2	3	4	5	6	8	9	11	14	16	18	19	19	17	15	13	14	16	14	11	6	0
1	0	0	0	1	1	2	2	3	4	4	5	7	7	9	10	10	9	8	7	7	8	8	9	5	0

*See Table 24 for a description of the experimental conditions.

Table 23

PREDICTED CHANGES IN WIND SPEED AND DIRECTION FOR CASE 8*

(a) Wind Speed

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	.2	.2	.0	.1	-.0	-.0	-.0	-.2	.2	.6	.8	.2	-.2	-.4	-.7	-.3	.1	.3	1.0	1.3	1.6	1.4	1.1	.9	-.0
24	.1	.1	-.0	-.3	-.4	-.3	-.3	-.3	.2	.1	.0	.4	-.0	-.3	-1.8	-2.6	-1.2	-.2	.2	.9	1.2	2.2	1.4	1.3	.3
23	-.2	-.4	-.4	-.3	-.3	-.1	-.1	-.3	-.3	.0	.1	.7	.1	-1.6	-2.1	-3.2	-3.2	-2.3	-1.8	-1.6	-.9	-.4	2.2	.3	.2
22	-.3	-.0	-.3	-.0	.1	.3	.4	-.0	.3	.9	1.0	.9	.4	-1.3	-2.2	-3.7	-4.3	-3.5	-3.3	-2.6	-2.3	-2.1	-1.9	-1.1	.1
21	-1.0	-1.3	-.3	.0	.9	1.0	1.1	1.0	1.1	1.4	1.8	2.1	.7	-1.4	-2.4	-4.0	-5.1	-4.4	-4.5	-3.8	-3.4	-3.3	-2.6	-1.8	-.7
20	-1.0	-1.4	.1	1.2	1.8	2.2	2.4	2.6	2.0	2.5	3.3	3.0	1.9	-.5	-1.8	-3.7	-5.1	-4.3	-4.4	-4.0	-3.3	-3.0	-2.8	-2.2	-1.1
19	-.5	-.6	.0	1.5	2.3	2.9	3.6	3.6	3.0	3.8	3.9	3.7	2.8	.7	-1.7	-3.1	-4.9	-5.4	-4.7	-3.3	-3.2	-3.1	-3.0	-3.4	-1.6
18	.2	.6	1.3	2.2	3.2	4.2	5.2	5.9	4.7	5.0	4.5	4.2	4.0	2.7	.0	-2.1	-4.5	-5.3	-4.0	-3.0	-2.7	-3.3	-3.0	-3.7	-2.0
17	1.0	2.1	2.7	3.7	5.1	6.6	8.4	8.3	6.3	5.8	5.1	4.8	5.7	5.8	2.9	-.5	-2.4	-3.5	-3.9	-3.2	-.6	-2.8	-2.6	-3.2	-2.2
16	1.7	3.7	2.9	4.4	5.8	6.9	8.1	7.9	7.8	7.5	6.7	6.2	7.3	6.5	5.9	2.7	-.4	-1.9	-2.8	-2.5	-2.6	-2.0	-3.2	-2.8	-2.1
15	1.9	4.1	4.1	5.5	5.9	6.9	7.4	8.4	7.1	7.0	6.3	6.2	6.2	7.4	6.0	3.6	1.1	-.4	-1.2	-2.2	-2.1	-1.9	-2.6	-3.1	-2.2
14	2.2	4.8	4.8	5.7	6.6	7.0	7.1	7.4	6.6	6.2	5.1	4.9	6.4	6.6	6.0	4.2	1.8	.3	.1	-.9	-1.0	-1.9	-2.5	-2.9	-2.3
13	2.4	5.2	5.7	6.1	6.6	7.1	7.6	7.6	6.4	6.0	5.6	5.7	6.1	6.1	5.5	4.2	2.0	.5	-.4	-.4	-.3	-1.4	-2.1	-2.9	-1.7
12	2.7	5.5	5.7	6.4	6.8	7.4	7.4	7.6	6.8	6.2	5.0	.6	2.1	3.9	3.9	3.2	2.2	.0	-.1	-.6	-1.0	-1.2	-2.2	-2.1	-2.1
11	2.9	5.8	5.6	6.2	6.7	7.4	8.1	7.5	6.7	5.3	3.7	1.1	1.0	2.7	3.3	2.3	1.7	-.4	-.8	-.9	-1.1	-1.6	-1.6	-2.3	-2.1
10	2.6	5.7	5.6	5.8	6.3	7.1	7.7	8.1	7.3	6.8	3.7	2.1	.9	2.4	3.0	3.3	1.8	.2	-.3	-.5	-.7	-1.1	-1.8	-2.3	-2.0
9	2.5	5.2	5.2	5.5	5.9	6.6	7.5	7.9	7.7	6.3	4.8	2.9	.9	2.4	2.8	2.9	2.6	.6	-.1	-.1	.0	-.9	-1.6	-2.3	-2.0
8	2.3	4.7	4.8	5.0	5.4	6.0	7.0	8.4	8.1	6.4	5.9	4.2	2.2	2.6	3.0	2.8	2.7	1.4	.2	-.8	-.6	-.8	-1.3	-2.2	-1.9
7	2.0	4.2	4.4	4.6	4.9	5.4	6.1	7.6	7.5	6.2	5.1	4.7	2.9	3.0	3.3	3.0	2.7	1.9	.5	-.2	-1.2	-1.2	-1.9	-2.2	-1.7
6	1.7	3.6	3.7	4.0	4.3	4.7	5.2	6.4	6.8	5.8	4.9	4.4	3.2	3.1	3.3	3.3	2.6	1.7	1.1	.1	-.9	-1.0	-1.9	-2.6	-1.5
5	1.4	2.9	3.1	3.3	3.6	4.0	4.4	5.0	5.3	5.0	4.5	3.8	3.1	3.1	3.2	3.0	2.9	2.0	1.2	.5	-.4	-1.3	-2.1	-2.2	-1.4
4	1.0	2.2	2.4	2.6	3.0	3.3	3.6	4.3	4.8	4.6	4.2	3.6	2.9	3.1	3.0	3.0	2.7	2.2	1.5	.8	.0	-.7	-1.5	-2.0	-1.0
3	.6	1.4	1.7	1.9	2.1	2.8	2.9	3.3	4.4	4.4	4.1	3.7	3.1	3.0	3.1	2.8	2.6	2.3	1.7	1.0	.3	-.3	-.8	-1.3	-.8
2	.2	.7	.8	1.0	1.5	2.1	2.1	3.0	3.1	4.1	4.2	4.0	3.6	3.3	3.0	2.9	2.7	2.4	1.9	1.3	.6	.1	-.3	-.5	-.3
1	-.0	-.0	.3	.2	.6	.4	1.0	.7	1.4	1.3	1.5	1.6	1.5	1.4	1.3	1.2	1.1	1.0	.8	.6	.4	.2	.1	.0	-.0

(b) Wind Direction

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	0	4	3	1	-0	-1	-2	-5	-6	-8	-7	-5	-0	10	6	3	-0	-2	-4	-6	-6	-6	-3	-2	0
24	-3	-4	0	0	-1	-2	-3	-5	-5	-6	-0	7	29	50	20	7	-3	-6	-8	-9	-8	-5	0	3	4
23	-0	-10	-7	-5	-2	-1	1	5	4	16	25	44	54	48	42	22	4	2	-1	-2	-2	-0	7	6	4
22	3	-3	-13	-9	-3	1	5	13	19	31	42	53	63	58	55	38	17	11	6	5	7	9	16	10	2
21	0	1	-5	-8	-4	3	9	21	28	38	51	58	65	60	55	43	24	19	13	13	16	17	17	6	-3
20	3	10	18	15	12	13	16	22	33	39	56	55	52	45	43	37	26	19	13	14	19	17	9	-7	-10
19	2	21	26	29	20	29	31	37	40	44	52	44	41	34	34	30	21	12	11	13	17	10	-2	-20	-15
18	-0	13	21	24	25	27	20	33	43	47	40	34	26	24	23	20	10	5	9	7	8	-7	-18	-37	-14
17	1	11	16	21	26	29	37	36	61	29	22	16	15	13	8	4	-2	-6	-10	-14	-20	-28	-37	-45	-11
16	2	11	14	21	29	31	31	27	22	17	14	9	6	2	-3	-6	-16	-26	-30	-29	-28	-36	-44	-56	-14
15	4	10	14	22	24	23	21	19	15	12	6	0	-1	-4	-9	-15	-27	-36	-39	-41	-40	-46	-59	-66	-14
14	4	11	15	18	18	18	17	15	12	8	2	-3	-8	-11	-16	-21	-32	-42	-46	-53	-53	-60	-65	-71	-13
13	4	9	13	14	14	13	13	12	9	6	0	-5	-9	-12	-17	-24	-33	-43	-49	-54	-56	-63	-69	-80	-18
12	5	12	11	9	8	9	8	8	5	4	0	-4	-7	-11	-18	-24	-33	-44	-49	-53	-55	-64	-74	-93	-19
11	4	8	7	6	3	4	4	4	2	0	-3	-8	-10	-15	-20	-27	-33	-41	-47	-49	-54	-62	-76	-91	-17
10	4	5	3	2	2	2	1	-0	-1	-4	-7	-14	-22	-22	-27	-35	-40	-46	-51	-55	-60	-67	-77	-86	-13
9	4	4	3	3	0	-0	-0	-1	-4	-10	-16	-21	-30	-31	-34	-37	-43	-48	-56	-61	-66	-71	-78	-88	-16
8	4	4	2	-0	-0	-2	-5	-9	-13	-20	-27	-33	-36	-36	-38	-40	-45	-49	-54	-57	-60	-65	-72	-81	-14
7	3	2	0	-2	-5	-6	-10	-14	-19	-26	-30	-35	-39	-39	-40	-43	-46	-50	-53	-54	-55	-57	-60	-64	-11
6	3	2	-1	-4	-7	-12	-14	-19	-23	-27	-31	-36	-40	-41	-41	-43	-44	-47	-49	-50	-52	-51	-50	-46	-6
5	2	0	-3	-7	-11	-13	-16	-20	-23	-27	-31	-35	-39	-40	-41	-42	-43	-45	-46	-46	-46	-42	-39	-32	-4
4	1	-1	-5	-9	-13	-15	-18	-22	-25	-29	-32	-36	-39	-40	-40	-40	-41	-42	-43	-44	-42	-40	-33	-22	-3
3	0	-2	-6	-9	-13	-16	-20	-24	-28	-31	-35	-38	-39	-39	-39	-39	-39	-39	-39	-39	-37	-34	-27	-16	-1
2	0	-2	-6	-10	-14	-18	-22	-26	-30	-34	-38	-41	-41	-40	-38	-37	-37	-36	-35	-34	-31	-26	-20	-11	-0
1	-0	-2	-3	-6	-8	-11	-14	-17	-20	-23	-25	-26	-23	-24	-23	-23	-21	-20	-19	-17	-14	-11	-7	-3	0

*See Table 24 for a description of the experimental conditions.

Table 24

CONDITIONS REPRESENTED IN TABLES 16 THROUGH 23

Case	Table	Time		$D - D_0$		Grid Level		Boundary Conditions	
		6 a.m.	3 p.m.	Eq. (26)	Eq. (27)	k = 1	k = 5	$\partial\phi/\partial n = 0$	$\phi = 0$
1	16	X		X		X		X	
2	17	X			X	X		X	
3	18	X			X		X	X	
4	19		X	X		X		X	
5	20		X		X	X		X	
6	21		X		X		X	X	
7	22	X			X		X		X
8	23		X		X		X		X

In addition to the general observations given above, we can also make the following specific comments:

- Perturbations obtained at ground level from the use of Eq. (26) to estimate $D - D_0$ are larger than those generated from the use of Eq. (27) (compare Tables 16 and 17 and Tables 19 and 20). The opposite is true at the top of the region (compare Tables 16 and 18 and Tables 19 and 21).
- When Eq. (27) is used to estimate $D - D_0$, the perturbations aloft are much larger than those predicted at ground level (compare Tables 17 and 18 and Tables 20 and 21).
- The choice of boundary conditions employed does have some influence on the magnitude of the predicted changes in wind speed and direction. As expected, this influence is greatest near the boundary (compare Tables 18 and 22 and Tables 21 and 23).

To explain the first two observations cited above, we note that the forcing function in Eq. (23) follows the same pattern of behavior. This can be illustrated by considering the ratio of the forcing functions employed in each case. If we let $\Delta D_{26}(K)$ and $\Delta D_{27}(k,K)$ represent the values of $D - D_0$ calculated using Eqs. (26) and (27), respectively, then we can write the ratio of the forcing function corresponding to the comparisons made above as follows:

$$\frac{\Delta D_{26}(K)}{\Delta D_{27}(1,K)} = \frac{K + 1}{2} \quad ,$$

$$\frac{\Delta D_{26}(K)}{\Delta D_{27}(K,K)} = \frac{K + 1}{2K}$$

$$\frac{\Delta D_{27}(1,K)}{\Delta D_{27}(K,K)} = \frac{1}{K} \quad ,$$

where K is the number of vertical layers of grid cells. In this study, K has a value of 5.

The experience gained in this brief study indicates that the use of algorithms similar to those given in the previous section provides a viable means of producing mass-consistent wind fields. Although such algorithms are relatively simple to employ, they are deficient in the treatment of momentum and energy balance relationships. However, until complete planetary boundary layer models suitable for predicting flow fields over urban areas can be developed and validated, photochemical modeling efforts will undoubtedly continue to rely on wind fields derived from actual field measurements. Thus, the use of mass-consistent wind algorithms should be considered as an interim means for removing excessive convergence and divergence effects in the flow field. The need for such usage may also be enhanced by the inclusion of wind shear in the airshed model, since the extent of convergence and divergence in the predicted flow field aloft may be larger than that previously experienced near the ground.

In future work, we recommend that mass-consistent wind algorithms be employed in conjunction with interpolation procedures for predicting flow fields over an urban area where a reasonably dense meteorological network has been established. In this way, tests can be designed to evaluate the performance of the methodology. The RAPS study in St. Louis may provide such a data base. In addition, further consideration should be given to the manner in which the quantity $D - D_0$ is estimated. Examination of the characteristics of flow fields over urban areas may provide some guidance in this matter.

D. ADOPTION OF AN IMPROVED ALGORITHM FOR ESTIMATING TURBULENT DIFFUSIVITIES

Pollutants are dispersed through advection and turbulent diffusion. In the horizontal directions, the advective mass flux is usually much larger than the diffusive flux. However, vertical transport is often dominated by turbulent diffusion. The usual means for treating vertical diffusion is through the assumption that the turbulent mass flux, F_t, is proportional to the gradient of the mean concentration field. That is,

$$F_t = -K_v \frac{\partial \langle c \rangle}{\partial z} \quad , \tag{28}$$

where

K_v = turbulent diffusivity,
$\langle c \rangle$ = mean concentration.

Turbulent diffusivities are extremely difficult to measure in the field, and their parameterization has been the subject of numerous studies. Upon reviewing the algorithm we employed in the 1969 validation study to calculate K_v, discussed in Roth et al. (1971), we found that there was sufficient justification to formulate a new algorithm. This new algorithm includes important atmospheric parameters, heretofore omitted, that are known to have a significant effect on the value of the diffusivity. Specific criticisms of the diffusivity algorithm that we used previously are as follows:

- The diffusivity is assumed to depend only on the wind speed. Using measured diffusivity data reported by Hosler (1969), Eschenroeder et al. (1972) found that the diffusivity does not correlate well with wind speed alone. This finding is not surprising, since we would expect that, for a given wind speed, the value of K_v for stable atmospheric conditions would be much less than its value under unstable conditions. Clearly, an algorithm for K_v must include the effect of atmospheric stability.
- Surface roughness effects are not explicitly included in the formulation of K_v. Recent studies by Lissaman (1973) and Ragland (1973) indicate that ground-level pollutant concentrations are significantly influenced by the value of the surface roughness.

In reviewing previous efforts to parameterize the diffusivity reported in the literature, we found that guidelines appear to exist that are sufficiently well developed for use in estimating the value of K_v in the surface layer (up to about 100 m). However, for the remaining portion of the planetary boundary layer above an urban area, we have not found a definitive treatment of the diffusivity that is both general and simple enough to include in an airshed model. Also of concern is the objective for multiday simulations of defining the vertical extent of the modeling region to include the inversion layer, if present. The "trapping" effect of the elevated temperature inversion would be treated through the use of the vertical diffusivity profile. Thus, a relatively sophisticated treatment of K_v is required aloft, a region of the planetary boundary layer where few measurements are generally available.

Realizing that a completely satisfying treatment of K_v may not be attainable at the present time, but also recognizing the need to improve the algorithm previously employed in the SAI airshed model, we initiated efforts to develop an algorithm for K_v that includes, at a minimum, both atmospheric

stability and surface roughness effects. Several schemes for computing K_v have been proposed in the literature, including those described by Blackadar (1962), Wu (1965), Hino (1968), Pandolfo et al. (1971), Eschenroeder et al. (1972), Ragland (1973), Bergstrom and Viskanta (1973), and Shir and Shieh (1973). However, each of these approaches is to some extent heuristic, and their validity is somewhat uncertain.

To alleviate the difficulties associated with basing a diffusivity algorithm on field measurements, we developed a methodology that uses the predictions of a sophisticated numerical planetary boundary layer model developed by Deardorff. Although the present K_v algorithm is applicable for only neutral and slightly unstable atmospheric stability regimes, the methodology can be extended to other regimes. For a more detailed discussion of this algorithm, we refer the reader to Chapter II of Volume III.

E. MODIFIED TREATMENT OF THE INVERSION LAYER IN THE AIRSHED MODEL

In previous studies, the modeling region has been defined to extend from the ground level to the base of an elevated temperature inversion. However, a major difficulty arises when using this approach for multiday simulations: A significant amount of pollutants can be reintroduced into the mixed layer from aloft as the inversion is eroded away during each daytime period. Unless the pollutants that are trapped in the inversion on the previous day are retained in the modeling region, it will be difficult to account properly for their reintroduction into the mixed layer on a given day. As an example of the O_3 levels that have been observed aloft, we present in Figure 21 a cross section of the pollutant distribution in a portion of the Los Angeles basin on the morning of 11 July 1973 (Jerskey et al., 1975).

As an alternative definition of the modeling region, we propose to include the portion of the atmosphere bounded below by the terrain and bounded aloft by the top of the inversion layer. All governing equations and coordinate transformations used previously still apply, except that the term ΔH should be interpreted as

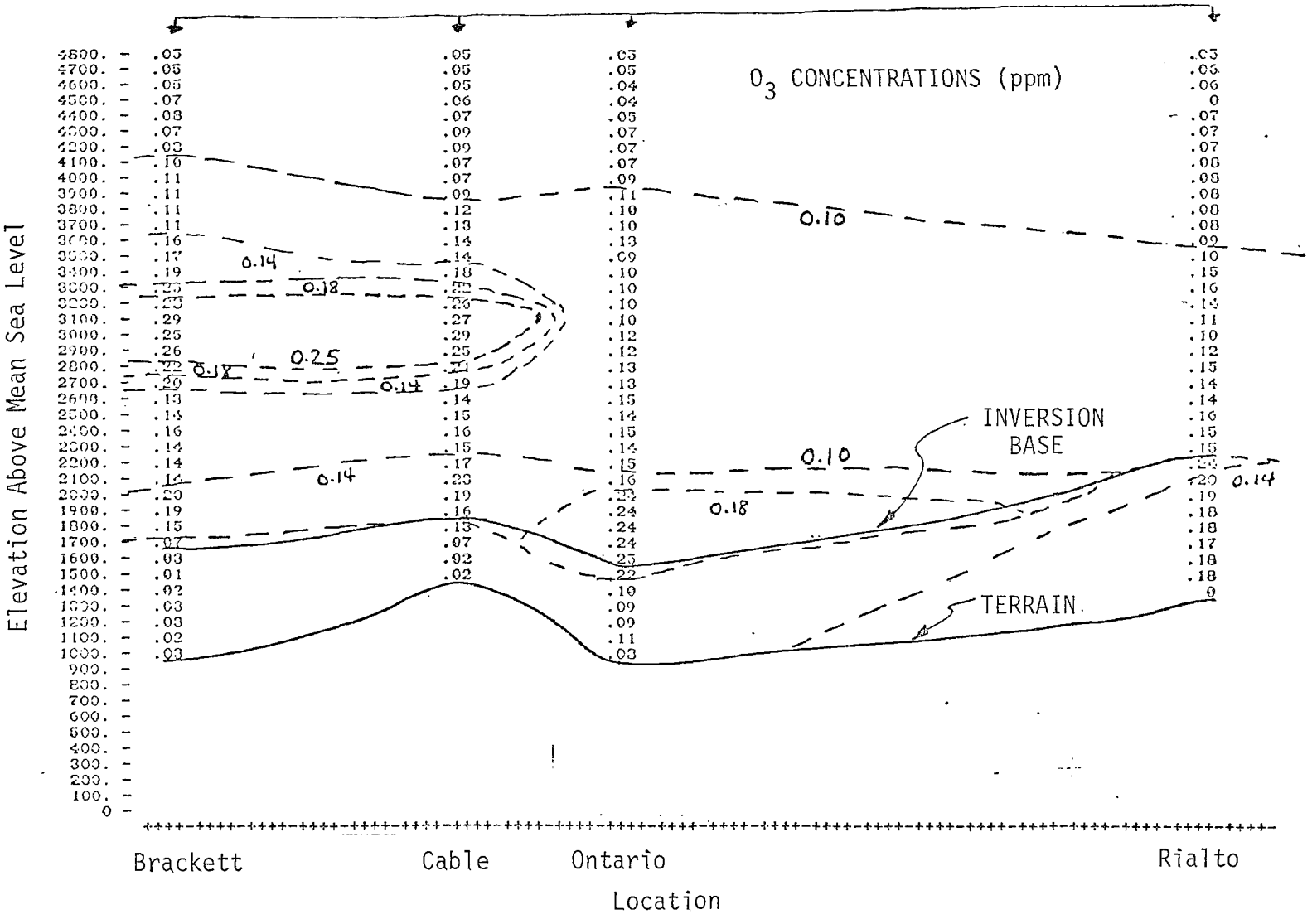


FIGURE 21. DISTRIBUTION OF O_3 ALOFT BETWEEN BRACKETT AND RIALTO DURING THE MORNING OF 11 JULY 1973

$$\Delta H = H_t(x,y,t) - h(x,y) \quad ,$$

where

$H_t(x,y,t)$ = elevation of the top of the inversion layer,
$h(x,y)$ = terrain elevation.

The effect of trapping pollutants below the inversion layer can be accounted for through the height dependence of the vertical diffusivity. Whereas relatively large values of K_v are used in the mixed layer, the values in the stable inversion layer are much smaller, reflecting the suppression of turbulent mixing.

IV EVALUATION OF ALTERNATIVE TECHNIQUES FOR INTEGRATING THE SPECIES CONTINUITY EQUATIONS

James P. Meyer

A. INTRODUCTION

In essence, the SAI atmospheric photochemical simulation program is based on the solution of the nonlinear, multidimensional species transport equation

$$\frac{\partial c_i}{\partial t} + \underset{\sim}{v} \cdot \underset{\sim}{\nabla} c_i = \nabla \cdot K \nabla c_i + R_i + S_i \quad , \tag{29}$$

which, for convenience, has been transposed [Reynolds et al. (1973)] into the form

$$\frac{\partial (\Delta H c_i)}{\partial \tau} + \frac{\partial}{\partial \rho}(u \Delta H c_i) + \frac{\partial}{\partial \eta}(v \Delta H c_i) + \frac{\partial}{\partial \rho}(w c_i)$$

$$= \frac{\partial}{\partial \rho}\left(K_H \Delta H \frac{\partial c_i}{\partial \rho}\right) + \frac{\partial}{\partial \eta}\left(K_H \Delta H \frac{\partial c_i}{\partial \eta}\right) + \frac{\partial}{\partial \rho}\left(K_V \Delta H \frac{\partial c_i}{\partial \rho}\right)$$

$$+ R_i \Delta H + S_i \Delta H \quad . \tag{30}$$

In general, no closed-form analytical solution exists for this highly complex partial differential equation for all possible initial and boundary conditions. Hence, one is forced to resort to approximation techniques, most notably finite difference schemes, to find a solution.

The choice of an appropriate numerical technique for inclusion in the airshed model involves two primary considerations. First, the accuracy of the solution obtained must be such that the error in the predicted concentrations is predominately the result of errors in model inputs rather than errors introduced by the numerical technique itself. Second, the final choice between alternative techniques capable of solving the governing equations to a specified error tolerance should be based on minimizing computing costs. In view of these considerations and the variety of numerical techniques available for solving the equations of interest, care must be taken to choose a method that offers an optimal blend of numerical accuracy and computational efficiency.

Currently, a finite difference approach termed the method of fractional steps [Yanenko (1969)] is employed in the SAI model. The basic feature of this method is that the four-dimensional governing equation in (ζ,η,ρ,τ) is split into three two-dimensional equations in (ζ,τ), (η,τ), and (ρ,τ). The details of this analysis are given elsewhere [Reynolds et al. (1973)]. With this type of approach, errors are introduced into the solution in the following ways:

- Through the introduction of truncation errors caused by the finite differencing of the partial derivatives in the transport equation.
- Through the decomposition of a three-dimensional equation into a sequence of three two-dimensional equations.

As an example of truncation error effects, Harlow and Amsden (1970) showed that for the one-dimensional advection equation

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = 0 \quad , \tag{31}$$

a numerical solution involving a first-order finite difference approximation introduces an error on the order of

$$u \frac{\delta x}{2} \left(1 - u \frac{\delta t}{\delta x}\right) \frac{\partial^2 c}{\partial x^2} \tag{32}$$

into the calculation. Since the term $\partial^2 c/\partial x^2$ appears, this error has been called "numerical diffusion." Its effect is to smooth an initially peaked distribution over a large portion of the modeling area. This reduces the resolution of the solution so much that in extreme cases it becomes nonexistent. In an attempt to reduce the truncation error effects in the SAI model arising from the treatment of the horizontal advection terms, we previously carried out numerical experiments using various second- and fourth-order difference approximations. Although we observed some reduction in truncation error using the higher order methods, many of these techniques also had the undesirable property of producing negative concentrations in the vicinity of steep concentration gradients. We finally selected an uncentered second-order method described by Price et al. (1966), which is somewhat more accurate than the first-order advection approximations, and which, at the same time, presented no difficulties with regard to the prediction of negative concentrations in the initial application of the model to the Los Angeles basin.

In the fractional step technique, the decomposition process for the η,ζ, and ρ directions introduces a sequence of higher order partial derivatives that would not normally appear in the transport equation. Although the effect of these terms is difficult to quantify a priori, their impact on model predictions can be examined by comparing predicted pollutant concentrations with known analytical solutions of the governing equations. In the discussion presented in Volume I of the validity of the grid and trajectory model concepts, we noted that errors introduced into the grid model predictions by the numerical integration technique can be as large as 50 percent in some situations. These errors are mainly due to the finite

difference treatment of the horizontal advection terms. Thus, the objective of the present study is to test and assess various alternative numerical approximations to the transport terms in the governing equations. In this analysis, our aim is to provide recommendations regarding the course of future efforts to improve the numerical integration procedure employed in the airshed model.

In the work described next, the emphasis was on the development of an analytical solution to the diffusion equation and on a comparison of the analytical results with the corresponding results obtained from various approximate integration schemes. Because of the difficulties involved in developing solutions to the diffusion equation, only a simplified one-dimensional, linear, time-dependent result could be obtained. Thus, we are able to assess the errors associated with various numerical methods for a one-dimensional flow problem in which the pollutant is allowed to undergo a first-order chemical reaction. Clearly, this test situation is not completely representative of a full photochemical airshed simulation. However, numerical techniques incapable of producing sufficiently accurate results in a one-dimensional linear problem cannot be expected to perform better in a multidimensional nonlinear application.

Since it was not possible to carry out the tests for photochemical pollutants, we are unable to assess the effect of inaccuracies introduced in the treatment of the transport terms on error propagation, especially when nonlinear chemical interactions are taking place. In addition, the test results do not illustrate the errors caused by using the fractional step methodology to treat a multidimensional problem. In spite of these limitations, however, we have been able to delineate two numerical methods that seem to represent a significant improvement over the finite difference scheme currently employed in the SAI airshed model.

B. AVAILABLE METHODS

A variety of methods have been developed to solve partial differential equations. In general, they fall into two categories: finite difference schemes and particle techniques. The former, which are well developed, include the work of Price et al. (1966), Fromm (1969), Crowley (1968), and, more recently, Boris and Book (1973). In contrast, particle-in-cell methods are relatively current; they include the contributions of Sklarew et al. (1971) and Egan and Mahoney (1972).

For the purpose of analysis, a simplified solution of the diffusion equation was developed and the results of this calculation were compared to the results of the suitably programmed approximation schemes. The equation chosen for this work was the one-dimensional transport equation,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} - kc \quad , \tag{33}$$

in which u, D, and k were considered constant. The following boundary conditions were imposed:

> Initially, no material is in the modeling region, i.e.

$$c(0,x) = 0 \quad . \tag{34}$$

> There is zero concentration gradient at infinity, i.e.,

$$\frac{\partial c}{\partial x}(t,\infty) = 0 \quad . \tag{35}$$

> There is a uniform concentration at the inlet, i.e.,

$$c(t,0) = 1 \quad . \tag{36}$$

We evaluated the following methods:

> Price scheme
> Crowley second- and fourth-order methods
> SHASTA method
> Galerkin method
> Particle-in-cell techniques
> Egan and Mahoney method.

In the following subsections we briefly describe each method.

1. The Price Scheme

Currently, the SAI model uses a method proposed by Price, Varga, and Warren (1966). For the test problem selected, this method has the finite difference form

$$c_j^{n+1} = c_j^n + \frac{K_H \delta t}{(\delta x)^2}\left(c_{j+1}^n - 2c_j^n + c_{j-1}^n\right) - \frac{u\delta t}{2\delta x}\left(3c_j^n - 4c_{j-1}^n + c_{j-2}^n\right) - k\delta t c_j^n \quad . \tag{37}$$

This approximation has errors that are first order in time (δt) and second order in distance $(\delta x)^2$.

Since the solution is explicit in time, definite limits of stability exist. These limits can be developed by assuming that the solution of the transient equation can be written in the complex Fourier form

$$c(t, j\Delta x) = \psi(t)\, e^{ij\Delta x} \quad , \tag{38}$$

where

$$i = \sqrt{-1} \quad . \tag{39}$$

After considerable algebraic manipulation and stipulation of the requirement

$$\left|\frac{\psi(t + \Delta t)}{\psi(t)}\right| < 1 \quad , \tag{40}$$

we obtain

$$k\delta t < 2 \quad , \tag{41}$$

$$u \frac{\delta t}{\delta x} < 1 \quad , \tag{42}$$

$$u \frac{\delta t}{2\delta x} + K_H \frac{\delta t}{(\delta x)^2} + k \frac{\delta t}{4} < \frac{1}{2} \tag{43}$$

as the conditions required for stability to occur.

2. The Crowley Second- and Fourth-Order Methods

To enhance the accuracy of the finite difference approximations used in formulating the advective terms of the governing equations, Crowley (1965) developed both second- and fourth-order centered difference algorithms for these terms. For the test problem, the second-order method has the expansion

$$c_j^{n+1} = \left(\beta - \frac{\alpha}{2} + \frac{\alpha^2}{2}\right) c_{j+1}^n + \left(1 - 2\beta - \alpha^2 - k\delta t\right) c_j^n + \left(\beta + \frac{\alpha}{2} + \frac{\alpha^2}{2}\right) c_{j-1}^n \quad , \tag{44}$$

where

$$\beta = \frac{K_H \delta t}{(\delta x)^2} \quad , \tag{45}$$

$$\alpha = \frac{u\delta t}{\delta x} \quad . \tag{46}$$

The corresponding fourth-order expansion has the form

$$c_j^{n+1} = \left(\frac{\alpha}{16} - \frac{\alpha^2}{48} - \frac{\alpha^3}{12} + \frac{\alpha^4}{24}\right)c_{j+2}^n + \left(\beta - \frac{5\alpha}{8} + \frac{7}{12}\alpha^2 + \frac{1}{6}\alpha^3 - \frac{1}{6}\alpha^4\right)c_{j+1}^n$$

$$+ \left(1 - 2\beta - k\delta t - \frac{27}{24}\alpha^2 + \frac{\alpha^4}{4}\right)c_j^n + \left(\beta + \frac{5\alpha}{8} + \frac{7}{12}\alpha^2 - \frac{1}{6}\alpha^3 - \frac{1}{6}\alpha^4\right)c_{j-}^n$$

$$+ \left(\frac{-\alpha}{16} - \frac{\alpha^2}{48} + \frac{\alpha^3}{12} + \frac{\alpha^4}{24}\right)c_{j-2}^n \quad . \tag{47}$$

The terms "second order" and "fourth order" refer to the relative amount of error incurred by these expansions; the sizes of such error are $(\delta x)^2$ and $(\delta x)^4$, respectively.

3. The SHASTA Method

Instead of relying on conventional finite difference techniques, which occasionally predict negative concentrations--particularly in areas of strong gradients--Boris and Book (1973) developed the SHASTA method, or flux corrected transport algorithm, to model the advective part of the transport equation. This technique is based on the principle of positivity (that is, that the concentration should always be positive) and does not rely on an asymptotic ordering in the equation solution. The algorithm is stable, mass conservative, and essentially second order in regions where the concept of order is meaningful.

Conceptually, the algorithm consists of two stages: a transport step and a subsequent antidiffusion step. During the first stage, the material in adjacent cells is advected in a trapezoidal manner such that the total amount of material within the cell is conserved. During the transport process, a certain amount of numerical diffusion is introduced into the calculation. This error is removed in the antidiffusion step.

In mathematical form, the transport stage has the algebraic expression

$$\tilde{c}_j^{n+1} = \frac{1}{2}\phi_-^2(c_{j-1}^n - c_j^n) + \frac{1}{2}\phi_+^2(c_{j+1}^n - c_j^n) + (\phi_+ + \phi_-)c_j^n \quad , \qquad (48)$$

where

$$\phi_\pm = \frac{\frac{1}{2} \mp u_j^{1/2}\frac{\delta t}{\delta x}}{1 \pm \left(u_{j\pm1}^{1/2} - u_j^{1/2}\right)\frac{\delta t}{\delta x}} \quad , \quad j = 1, \ldots, n \quad , \qquad (49)$$

and where $u_j^{1/2}$ refers to the velocity at the j-th location at time $t + (\delta t/2)$. Completion of the antidiffusion step requires the expression

$$c_j^{n+1} = \tilde{c}_j^{n+1} - \frac{1}{8}\left(\tilde{c}_{j+1}^{n+1} - 2\tilde{c}_j^{n+1} + \tilde{c}_{j-1}^{n+1}\right) \quad . \qquad (50)$$

To account for cases in which material may be advected either into or out of the modeling region, the SHASTA method applies the following rules at the end points:

> Left-hand side
  --If $v_1 > 0$, then c_0 and v_0, the upwind boundary conditions, must be specified.
  --If $v_1 < 0$, then $\partial c/\partial x = 0$, and $c_0 = c_1$ and v_0 must be specified.
> Right-hand side
  --If $v_n > 0$, then $\partial c/\partial x = 0$, and $c_{n+1} = c_n$ and v_{n+1} must be specified.
  --If $v_n < 0$, then c_{n+1} and v_{n+1}, the incoming concentration and velocity, respectively, must be specified.

Since the SHASTA algorithm treats only the advective parts of the continuity equation, the concurrent diffusion and kinetic steps of the governing equation must be treated as subsequent operations. Hence, the system heavily relies on the method of fractional steps.

For the test case, the advective equation has the form

$$\tilde{c}^{*n+1}_j = \frac{1}{2}\phi_-^2\left(c^n_{j-1} - c^n_j\right) + \frac{1}{2}\phi_+^2\left(c^n_{j+1} - c^n_j\right) + (\phi_+ + \phi_-)\, c^n_j \quad , \tag{51}$$

$$\phi_\pm = \frac{1}{2} \mp u\,\frac{\delta t}{\delta x} \quad , \tag{52}$$

$$c^{*n+1}_j = \tilde{c}^{*n+1}_j - \frac{1}{8}\left(\tilde{c}^{*n+1}_{j+1} - 2\tilde{c}^{*n+1}_j + \tilde{c}^{*n+1}_{j-1}\right) \quad . \tag{53}$$

The diffusive and kinetic terms become

$$c^{n+1}_j = \beta c^{*n+1}_{j+1} + (1 - 2\beta - k\delta t)\, c^{*n+1}_j + \beta c^{*n+1}_{j-1} \quad , \tag{54}$$

$$\beta = \frac{K_H \delta t}{(\delta x)^2} \quad . \tag{55}$$

4. The Galerkin Method

Finite element methods represent a significant departure from finite difference techniques as a tool in solving partial differential equations. Unlike finite difference equations, which approximate derivatives at specific locations, finite element techniques approximate functions over an entire domain [Zienkiewicz (1971), Pinder and Gray (1974)].

To develop finite element solutions, one must follow four steps:

> Subdivide the domain of interest into a finite number of elements defined by node points.

> Approximate the dependent variables in terms of their unknown node point values within each element. This insures the continuity of the dependent variable across the element.

- Minimize an appropriate measure of error such that a set of simultaneous equations results.
- Solve the resulting set of equations for the node point values.

The distinct advantages of finite element techniques are their ability to model arbitrary geometric areas without a loss of convergence and their generally greater stability compared with corresponding finite difference systems.

Two distinct classes of finite element solutions exist. The Rayleigh-Ritz procedure requires the minimization of a function associated with a defining differential equation. Although this is an extremely useful method, often one cannot determine the functional form associated with the differential equation. Thus, the method has limited applicability. A more general, but somewhat less mathematically elegant, approach is the Galerkin technique [Keldysh (1964), McMichael and Thomas (1973)]. This method requires merely that the integral of the approximate solution be orthogonal to each of the basis functions spanning the solution space. For example, the linear differential equation

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} - D \frac{\partial^2 c}{\partial x^2} + kc = 0 \tag{56}$$

is written in operator form as

$$L(c) = \left(\frac{\partial}{\partial t} + \frac{u\partial}{\partial x} - \frac{D\partial^2}{\partial x^2} + k \right) c \tag{57}$$

and is assumed to have a solution of the form

$$\hat{c} = \sum_{i=1}^{n} a_i \phi_i \quad , \tag{58}$$

where there are n nodes in the domain of c. Then, the Galerkin procedure requires that

$$\int_V L(\hat{c})\phi_i \, dv = 0 \quad , \quad i = 1, 2, \ldots, n \quad , \tag{59}$$

so that the coefficients (a_i) can be determined.

As an illustration of the technique, consider the following sample problem:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} - D \frac{\partial^2 c}{\partial x^2} + kc = 0 \quad . \tag{60}$$

Assume a solution of the form

$$\hat{c} = \sum_{i=1}^{n} a_i(t) \, \phi_i(x) \quad . \tag{61}$$

Multiply the differential equation by ϕ_i, and integrate the result over its entire domain:

$$\int_0^L \frac{\partial \hat{c}}{\partial t} \phi_i \, dx + u \int_0^L \frac{\partial \hat{c}}{\partial x} \phi_i \, dx - D \int_0^L \frac{\partial^2 \hat{c}}{\partial x} \phi_i \, dx + \int_0^L k\hat{c}\phi_i \, dx = 0 \quad ,$$

$$i=1, \ldots, n \quad . \tag{62}$$

By using Green's theorem,

$$\int_0^L \frac{\partial^2 \hat{c}}{\partial x^2} \phi_i \, dx = -\int_0^L \frac{\partial \hat{c}}{\partial x} \frac{\partial \phi_i}{\partial x} \, dx + \phi_i \frac{\partial \hat{c}}{\partial x} \Big|_0^L \quad , \tag{63}$$

and by substituting the expanded series into the equation, we obtain

$$\int_0^L \sum_j^n \frac{\partial a_j}{\partial t} \phi_i \, dx + u \int_0^L \sum_j^n a_j \frac{\partial \phi_j}{\partial x} \phi_i \, dx + D \int_0^L \sum_j a_j \frac{\partial \phi_j}{\partial x} \phi_i \, dx + k \int_0^L \sum_j^n a_j \phi_j \phi_i \, dx$$

$$= D \phi_i \Sigma a_j \frac{\partial \phi_j}{\partial x} \Big|_0^L \quad , \qquad i = 1, 2, \ldots, n \quad . \tag{64}$$

Once the functions ϕ_i are selected, a series of matrix equations result. They are of the form

$$\underset{\approx}{A} \frac{d\underset{\sim}{a}}{dt} + \underset{\approx}{B}\underset{\sim}{a} = \underset{\sim}{S} \quad , \tag{65}$$

where

$\underset{\approx}{A}, \underset{\approx}{B}$ = coefficient matrices,

$\underset{\sim}{a}, \underset{\sim}{S}$ = column vectors.

These equations can be easily solved by using a Crank-Nicholson technique to approximate $\underset{\sim}{a}$ between times t and t + δt. The initial conditions $\underset{\sim}{a}_0$ must be specified.

For the work described in this report, we selected chapeau functions of the form

$$\phi_1 = \begin{cases} \dfrac{-x}{x_1} & , \quad 0 < x < x_1 \quad , \\ \\ 0 & , \quad \text{elsewhere} \quad ; \end{cases} \tag{66}$$

$$\phi_i = \begin{cases} \dfrac{x - x_{i-1}}{x_i - x_{i-1}} & , \quad x_{i-1} \le x \le x_i \quad , \\ \\ \dfrac{x_{i+1} - x}{x_{i+1} - x_i} & , \quad x_i \le x \le x_{i+1} \quad , \\ \\ 0 & , \quad \text{elsewhere} \quad ; \end{cases} \tag{67}$$

$$\phi_n = \begin{cases} \dfrac{x - x_{n-1}}{x_n - x_{n-1}} & , \quad x_{n-1} \leq x \leq x_n \\ 0 & , \quad \text{elsewhere} \end{cases} \quad . \tag{68}$$

Correspondingly, the matrices $\underset{\approx}{A}$ and $\underset{\approx}{B}$ had the tridiagonal form

$$\underset{\approx}{A} = \frac{\delta x}{6} \begin{bmatrix} 1 & 4 & 1 & 0 & 0 & \dots & 0 \\ 0 & 1 & 4 & 1 & 0 & \dots & 0 \\ 0 & 0 & 1 & 4 & 1 & \dots & 0 \\ 0 & \dots & 0 & \dots & 1 & 4 & 1 \end{bmatrix} \quad , \quad 1 \leq i \leq n-1 \tag{69}$$

$$\underset{\approx}{B} = \begin{bmatrix} -\alpha & \beta & -\gamma & 0 & \dots & 0 \\ 0 & -\alpha & \beta & -\gamma & \dots & 0 \\ \vdots & & & & & \\ 0 & \dots & & -\alpha & \beta & -\gamma \end{bmatrix} \quad , \tag{70}$$

where

$$\alpha = \frac{D}{\delta x} + \frac{u}{2} - \frac{k\delta x}{6} \quad ,$$

$$\beta = \frac{2D}{\delta x} + \frac{2k\delta x}{3} \quad ,$$

$$\gamma = \frac{D}{\delta x} - \frac{u}{2} - \frac{k\delta x}{2} \quad ,$$

while $\underset{\sim}{S}$ was zero everywhere. The boundary condition yielded the terms

$$a_1 = 1 \quad , \tag{71}$$

$$a_n = a_{n-1} \quad . \tag{72}$$

5. Particle-in-Cell Techniques

Harlow and Welch (1965) first developed particle-in-cell methods for use in the analysis of free-surface fluid mechanical problems. Since their initial development, these techniques have been expanded to include such variations as marker-in-cell (MAC) and HYDRO codes.

An interesting adaptation of the particle-in-cell algorithm has been developed by Sklarew (1971) to model mesoscale air pollution problems. In this variant, pollutant particles representing a fixed weight of material are generated in quantities proportional to the ambient pollutant concentration. As time passes, the particle positions are tracked in space by determining the incremental changes in their locations caused by advective and diffusive forces. Sklarew chose to rewrite the species transport equation in the form

$$\frac{\partial c}{\partial t} + \nabla \cdot (\underset{\sim}{v}c - D\nabla c) = 0 \quad , \tag{73}$$

where

$\underset{\sim}{v}$ = mean velocity,

$D\frac{\nabla c}{c}$ = diffusive velocity.

With these definitions, it is possible to increment the radial position of each particle during each time step by a corresponding contribution due to mean fluid flow ($\underset{\sim}{v}\delta t$) and diffusional motion [$(D\nabla c\delta t)/c$].

To account for photochemistry, one must assume that, within each cell, the particle weights can be summed to form a representative cell concentration and that the reaction occurs as if the material is homogeneously distributed throughout the cell. At the end of the reaction sequence, each particle is reweighted proportionally to the change in the cell concentration of the individual species:

$$m_i(t + \Delta t) = m_i(t) \frac{c(t + \Delta t)}{c(t)} \quad , \tag{74}$$

and the transport process is subsequently allowed to occur.

Hotchkiss and Hirt (1972) improved the modeling of the diffusional part of the transport process at Los Alamos. Their contribution was the representation of the diffusive movement as a random particle motion of the form

$$\delta x_{DIFF} = \sqrt{4D\delta t}\ \psi \quad , \tag{75}$$

where ψ is a randomly distributed Gaussian variable. Their work indicates that their method results in substantially better agreement than the method of Sklarew in areas of strong concentration gradients near point sources. This modification overcomes the difficulties in computing the finite difference approximation needed by Sklarew in calculating the gradient of the concentration.

Fundamentally, the problem with all particle-in-cell methods is the essential question of exactly what a particle represents and over what area should it be considered to have domain--classically an Eulerian-Lagrangian paradox. A recurrent problem in using this type of analysis is the background noise that must be accommodated when a particle leaves one cell and enters another. This quantum jump can be smoothed to some extent by volume-averaging the particle over the adjacent cells it intercepts. However, such a procedure may well extend the domain of a pollutant into regions that it does not actually represent. To circumvent this problem, one can always increase the number of particles associated with a problem, but at the added expense of dramatically increasing computer storage and computational time.

6. The Method of Egan and Mahoney

One of the more interesting developments in the analysis used in air pollution modeling has been the work of Egan and Mahoney (1970, 1971, 1972). In essence, their approach is to follow air parcels as they move within a

grid network, taking into account the zero, first, and second moments of the pollutant distribution. With this type of analysis, it is possible to maintain extremely high resolution and to eliminate almost entirely the numerical diffusion caused by errors associated with approximations for the advection terms.

Unfortunately, the method, which is owned proprietarily by Environmental Research and Technology in Lexington, Massachusetts, is only paraphrased in the open literature. Hence, the analysis presented here is cursory and represents only a superficial evaluation of the utility of this method.

C. A TEST PROBLEM

To provide a common basis of comparison for each of the methods, we posed the following two-dimensional problem (x - t).

Consider a semi-infinite strip extending from zero to infinity over which the species transport equation is assumed to hold and a first-order irreversible reaction occurs:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - kc \quad . \tag{76}$$

Specify that all parameters (u, D, and k) are constant, and impose the following boundary conditions:

> Initially no material is in the modeling region, i.e.,

$$c(0,x) = 0 \quad , \quad 0 \leq x \leq \infty \quad . \tag{77}$$

> There is zero flux of infinity, i.e.,

$$\frac{\partial c}{\partial x}(t,\infty) = 0 \quad . \tag{78}$$

> There is a uniform concentration at the inlet, i.e.,

$$c(t,0) = 1 \quad . \tag{79}$$

To develop a solution, take the Laplace transform of the defining differential equation

$$s\bar{c} + u\frac{d\bar{c}}{dx} = D\frac{d^2\bar{c}}{dx^2} - k\bar{c} \quad . \tag{80}$$

Then rearrange the equation in the form

$$D\frac{d^2\bar{c}}{dx^2} - u\frac{d\bar{c}}{dx} - (k + s)\bar{c} = 0 \quad . \tag{81}$$

Next, solve for $\bar{c}$:

$$\bar{c} = Ae^{[(Pe/2) - \phi]\lambda} + Be^{[(Pe/2) + \phi]\lambda} \quad , \tag{82}$$

where

$$Pe = \frac{uL}{D} \quad , \tag{83}$$

$$\lambda = \frac{x}{L} \quad , \tag{84}$$

$$\phi = \frac{L\sqrt{u^2 + 4D(k+s)}}{2D} \quad . \tag{85}$$

By imposing the boundary condition

$$\frac{d\bar{c}}{dx} = 0 \quad \text{at } x = \infty \quad , \tag{86}$$

we find that

$$B = 0 \tag{87}$$

and, hence,

$$\bar{c} = Ae^{[(Pe/2) - \phi]\lambda} \quad . \tag{88}$$

At the leading edge of the system,

$$\bar{c} = \frac{1}{s} = A \qquad \text{at } \lambda = 0 \quad , \tag{89}$$

and the complete solution in transform space becomes

$$\bar{c} = \frac{e^{[(Pe/2) - \phi]\lambda}}{s} \quad . \tag{90}$$

The inversion of this Laplace transform is nontrivial and requires some rather advanced techniques [Mikusinski (1959)]. Once inverted, the solution takes the form

$$c(\lambda,\eta) = \frac{1}{2}\left\{e^{[(Pe/2) - \psi]\lambda}\left[1 + \operatorname{erf}\left(\frac{\psi\eta}{2} - \frac{\lambda}{\eta}\right)\right]\right.$$

$$\left. + e^{[(Pe/2) + \psi]\lambda}\left[1 - \operatorname{erf}\left(\frac{\psi\eta}{2} + \frac{\lambda}{\eta}\right)\right]\right\} \quad , \tag{91}$$

where

$$\eta = \frac{\sqrt{4Dt}}{L} \tag{92}$$

$$\psi = \sqrt{\frac{kL^2}{D} + \left(\frac{Pe}{2}\right)^2} \quad . \tag{93}$$

Later, we will need to know the flux of material entering the system at the origin. To compute this term, we must obtain the derivative

$$\frac{\partial c}{\partial x}(0,t) \quad . \tag{94}$$

Instead of using x - t space, which involves the derivative of integrals, it is simpler to compute the derivative in x - s space and invert the obtained transform.

The inversion of the derivative

$$\frac{dc}{dx}(0,s) = \frac{1}{L}\left[\frac{Pe}{2s} - \frac{\sqrt{\left(\frac{Pe}{2}\right)^2 + \frac{L^2}{D}(k+s)}}{s}\right] \tag{95}$$

is given by

$$\frac{\partial c}{\partial x}(t,0) = \frac{u}{2D} - \left[\frac{1}{\sqrt{\pi D t}}\, e^{-\Omega t} + \sqrt{\frac{\Omega}{D}}\, \mathrm{erf}(\Omega t)\right] \quad , \tag{96}$$

where

$$\Omega = k + \frac{u^2}{4D} \quad . \tag{97}$$

Consequently, the total flux

$$N(0,t) = uc - D\frac{\partial c}{\partial x} \tag{98}$$

is represented by

$$N(0,t) = \frac{u}{2} + \sqrt{\frac{D}{\pi t}}\, e^{-\Omega t} + \sqrt{\Omega D}\, \mathrm{erf}(\sqrt{\Omega t}) \tag{99}$$

for a uniform concentration of one at the origin.

During the time interval t to t + δt, the amount of material entering the first cell,

$$\int_t^{t+\delta t} N(0,t')\, dt' = Q \quad , \tag{100}$$

can be approximated by

$$Q = u\frac{\delta t}{2} + \sqrt{\frac{D}{\Omega}}\left[\operatorname{erf}\left(\sqrt{\Omega(t+\delta t)}\right) - \operatorname{erf}(\sqrt{\Omega t})\right]$$

$$+ \frac{D\delta t}{2}\sqrt{\frac{\Omega}{D}}\left[\operatorname{erf}\left(\sqrt{\Omega(t+\delta t)}\right) + \operatorname{erf}(\sqrt{\Omega t})\right] \quad . \qquad (101)$$

Note that at long times the inflow approaches the quantity

$$Q = \left(\frac{u}{2} + \sqrt{D\Omega}\right)\delta t \quad ; \qquad (102)$$

and if $k = 0$,

$$Q = u\delta t \quad , \qquad (103)$$

and pure advection occurs. One effect of having the reactive term is to enhance the inflow above the purely advective amount.

In Section D, we present figures in which the analytical solution is always represented by continuous curves.

D. RESULTS

To test each method under conditions similar to those encountered in atmospheric modeling, we decided to allow the Peclet number (uL/D) and the kinetic rate constant to vary over a wide range of values. For each run, the incremental spatial distance was set at 2 miles, and the total length of the region was assumed to be 50 miles. Each hour was subdivided into 12 five-minute segments. In all cases, the free-stream velocity was held at 4 miles per hour, and the diffusivity was allowed to vary as shown in Table 25.

Table 25

VALUES OF DIFFUSIVITY AND PECLET NUMBER
FOR THREE CASE STUDIES

Case	Diffusivity ($m^2 sec^{-1}$)	Peclet Number
1	200	720
2	700	206
3	2000	72

These runs varied from almost a square wave propagation (Pec = 720) to a smooth diffusion problem (Pec = 72). For each method tested, we executed a series of 12 runs.

The corresponding kinetic values associated with these transport conditions are given in Table 26.

Table 26

KINETIC CONSTANTS FOR EACH CASE

Case	Kinetic Constant (sec^{-1})
1	0
2	10^{-4}
3	10^{-3}
4	2×10^{-3}

These values include the cases of both no reaction ($k = 0$), and a relatively fast reaction ($k = 2 \times 10^{-3}$). Two intermediate reaction rates were also considered.

In the presentation of the data, we included only those cases in which no reaction occurs ($k = 0$; Pec = 720, 206, and 72) and those of highest Peclet number (Pec = 720, $k = 10^{-4}$ and 10^{-3}). We chose these cases because they are somewhat representative of the range of conditions that can occur in mesoscale modeling systems. The following subsections present a brief synopsis of the performance of each numerical scheme. In each figure presenting our results, the analytical solution is given at 3, 6 and 9 hours from the start of the test.

1. The Price Method

As used in the SAI model, the Price scheme is inadequate for accurately modeling mesoscale phenomena. In all cases, the method overpredicts the actual ground-level concentration and transposes the wave to the left because of phase shift, as shown in Figures 22 through 23. Although some improvement occurs in cases having high Peclet numbers, this agreement is not substantial enough to reduce dramatically the errors involved. Thus, we rated the method as poor.

2. The Crowley Second- and Fourth-Order Methods

The accuracy of prediction can be substantially increased by using either the Crowley second-order or the Crowley fourth-order approximation, as shown in Figures 24 through 25. In cases where an extremely strong concentration gradient appears (Pec = 720), the second-order scheme exhibits some rather erratic results near the top of the wave. Aside from such cases, both methods provide essentially the same results.

In the implementation of these methods in actual simulation programs, some observers have noticed that higher order methods occasionally predict negative concentrations in regions having large concentration gradients.

Although this result did not appear in our work, one should keep it in mind as a limitation when using these methods.

3. The SHASTA Method

One of the simplest and yet most efficient methods of solving the species transport equation is the SHASTA method. Figure 26 presents its performance results. Not only does the method exhibit a relatively high degree of accuracy, but also, unlike many of the alternative finite difference methods, it never predicts negative results. Thus, it is the best choice available of an explicit solution algorithm.

4. The Galerkin Method

Of all the methods tested, the Galerkin technique provided the most accurate results over the widest range of conditions selected in this study, as shown in Figure 27. The predicted results were always within 1 percent of the analytical solution, and for many individual points in the analysis, the results exhibited zero error. Not only could the method be used to model situations in which extremely strong concentration gradients appeared, but also it could accurately treat cases involving very fast reaction schemes. Although the method is implicit and hence iterative in solution, its execution time appears to be comparable to a corresponding implicit Price scheme as currently used on the SAI model.

We thus recommend that this technique be used for cases where high resolution is desirable, even at the expense of increased computing time and programming effort.

5. Particle-In-Cell Methods

Accuracy in particle-in-cell methods is a strong function of the number of particles used. In this study, as the particle size was reduced from 80 to 40 to 20 weight units, the average error was reduced from 9.6 to 6.3 to

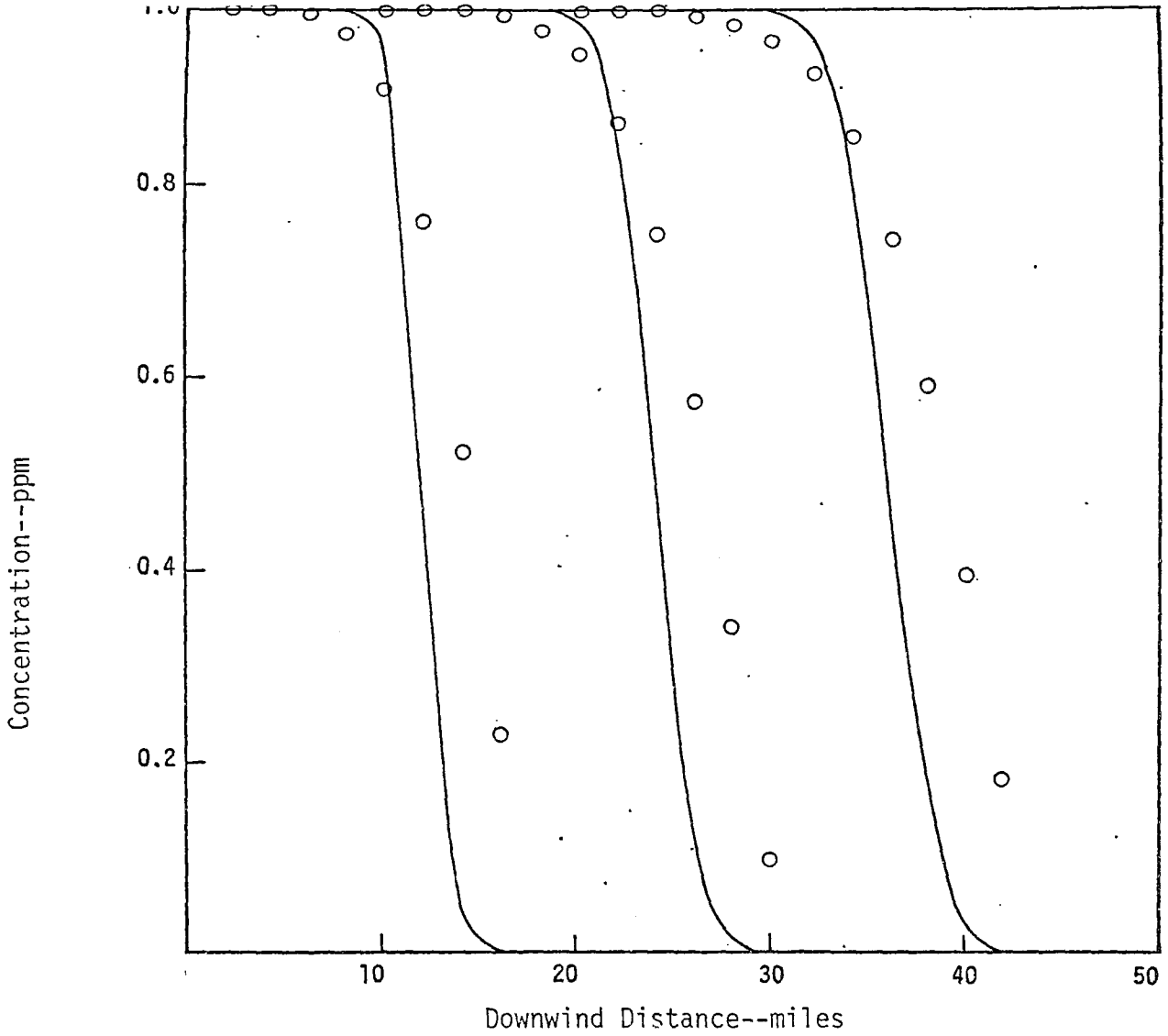
3.3 percent, respectively. Figure 28 presents the results obtained using this type of method. These methods proved successful at simulating both reactive and nonreactive systems, and they were able to treat steep gradients exceptionally well.

A rather interesting aspect of this analysis is that such techniques show greater accuracy at lower rather than higher Peclet numbers, as would normally be expected to occur. The reason for this phenomenon is probably the following: As the diffusivity is increased, the diffusive component in the Hotchkiss-Hirt analysis displaces the particle by an amount proportional to the square root of the diffusivity. For large values of the diffusion coefficient, this displacement can extend well over several cells. Hence, the method is best applied to those cases in which the diffusivity is less than 200 m^2 sec^{-1}.

One drawback of particle-in-cell methods is the amount of computing time required to solve a particular problem for a given accuracy. Since a random number must be generated for each particle at each step, computing costs can be exorbitant as the number of particles increases.

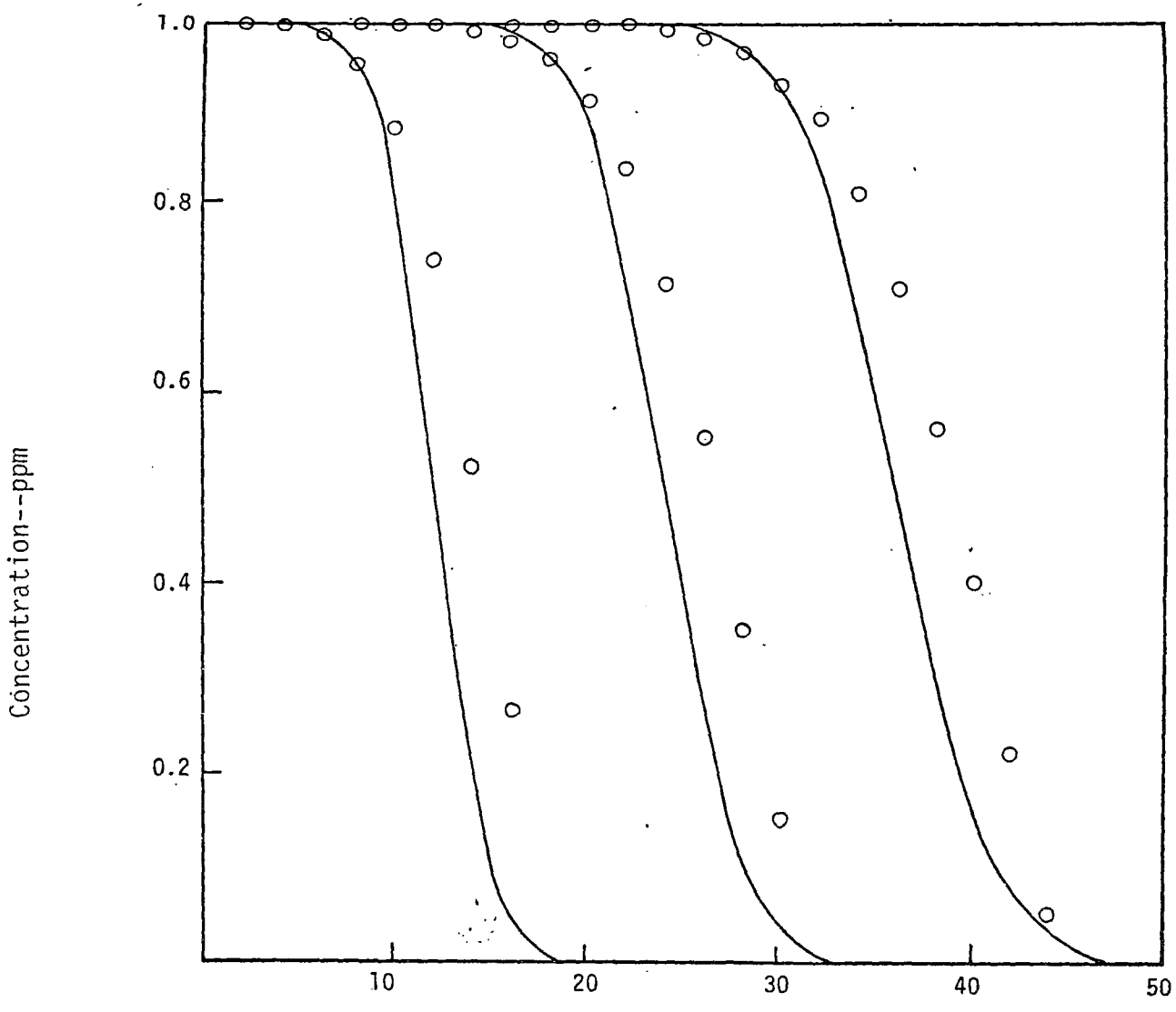
6. The Method of Egan and Mahoney

For the strictly advective case, the Egan and Mahoney method generates an extremely accurate solution with virtually no error attributable to numerical diffusion. This accuracy is particularly notable because advective phenomena have been extremely difficult to simulate using computing methods. Figure 29 presents the results obtained using this method. Unfortunately, we could not incorporate the diffusion step in this analysis because of the absence of any clear explanation of the treatment of this process in the open literature. Without this link, it is difficult to form an overall critical appraisal of the technique. In light of this limitation, this method should continue to be investigated as more material becomes available.



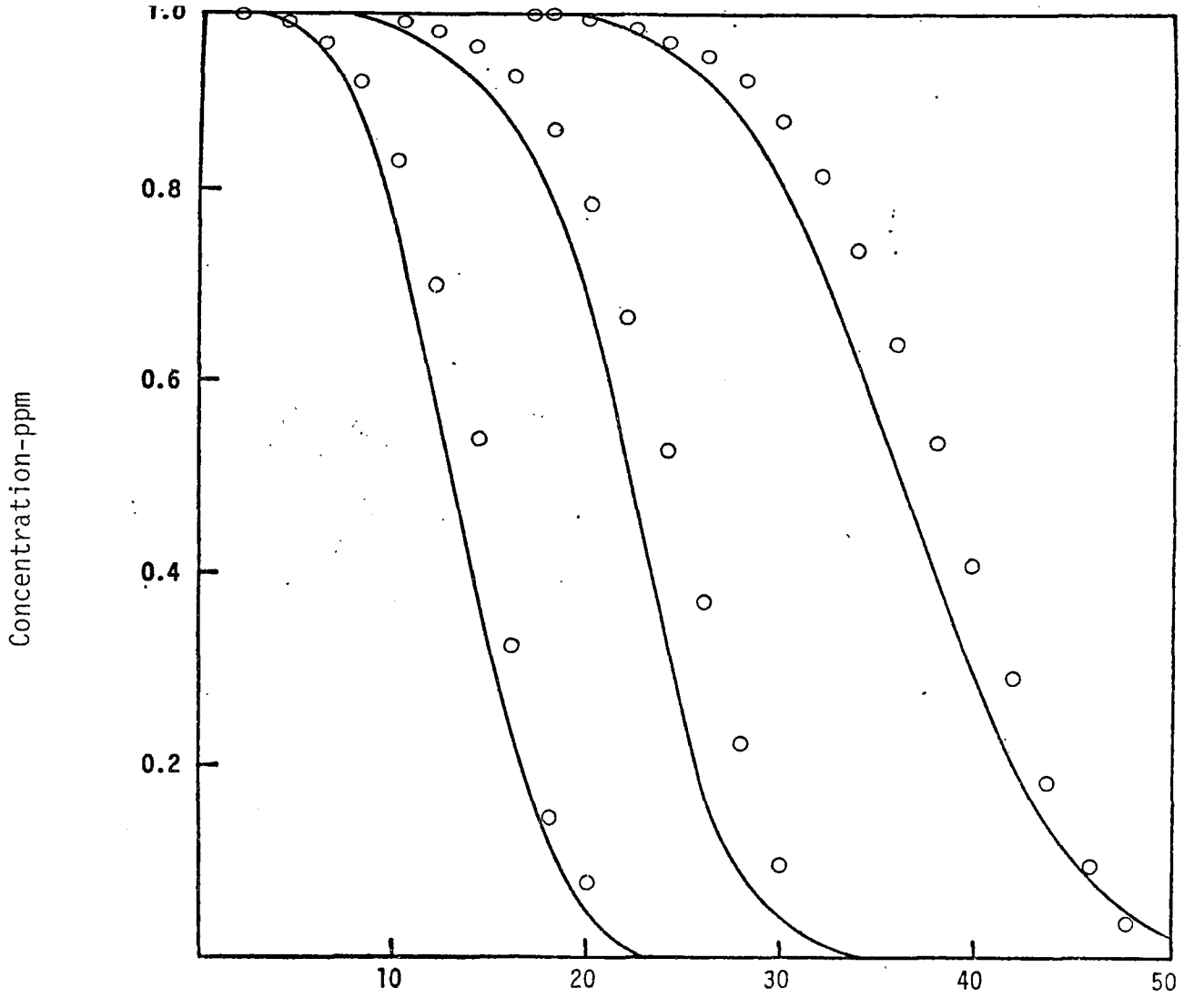
(a) Pec = 720, k = 0 sec^{-1}

FIGURE 22. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE EXPLICIT PRICE SCHEME



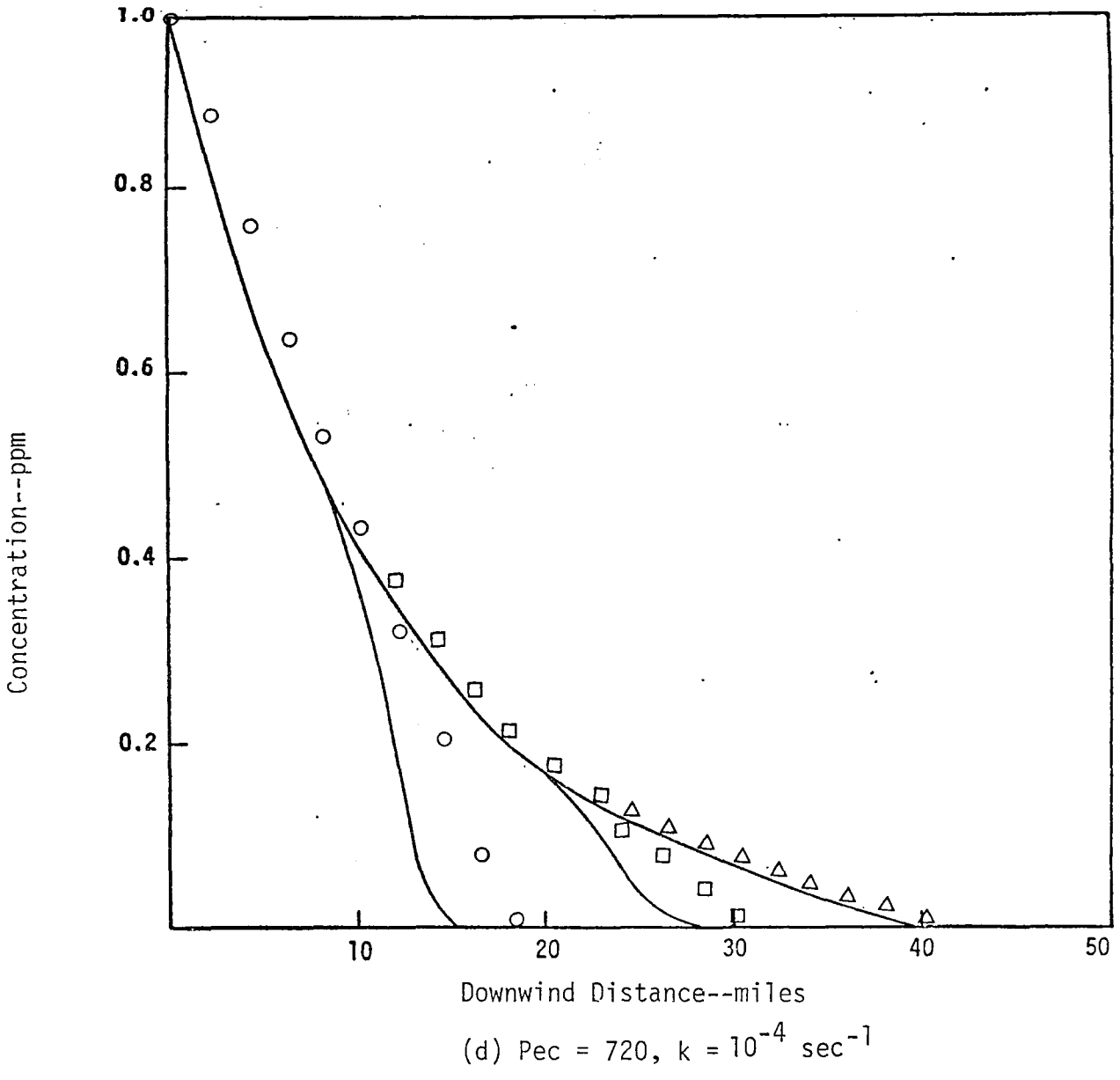
(b) Pec = 206, k = 0 sec^{-1}

FIGURE 22. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE EXPLICIT PRICE SCHEME (Continued)



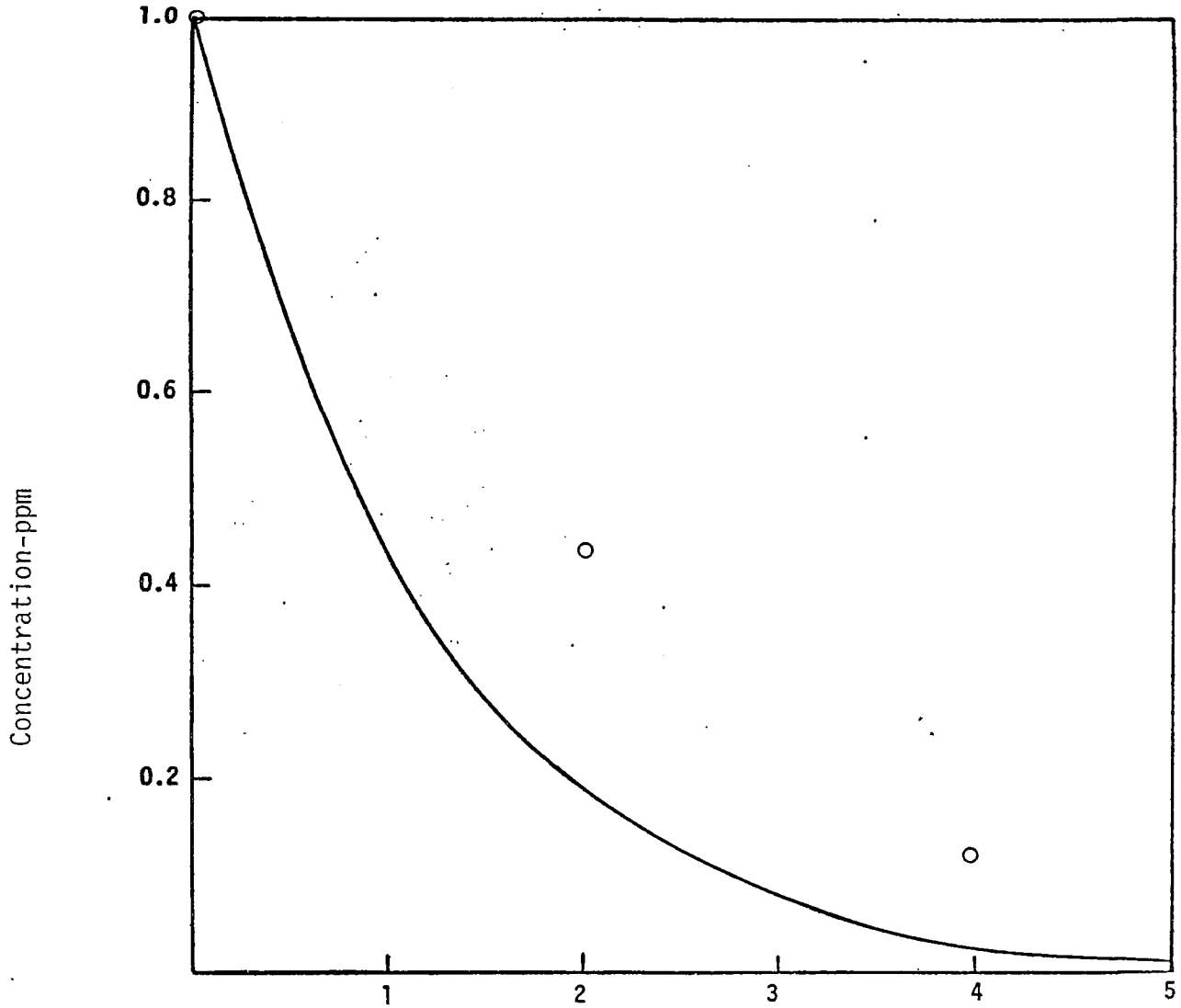
(c) Pec = 72, k = 0 sec^{-1}

FIGURE 22. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE EXPLICIT PRICE SCHEME (Continued)



(d) Pec = 720, $k = 10^{-4}$ sec^{-1}

FIGURE 22. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE EXPLICIT PRICE SCHEME (Continued)



(e) Pec = 720, $k = 10^{-3}$ sec^{-1}

FIGURE 22. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE EXPLICIT PRICE SCHEME (Concluded)

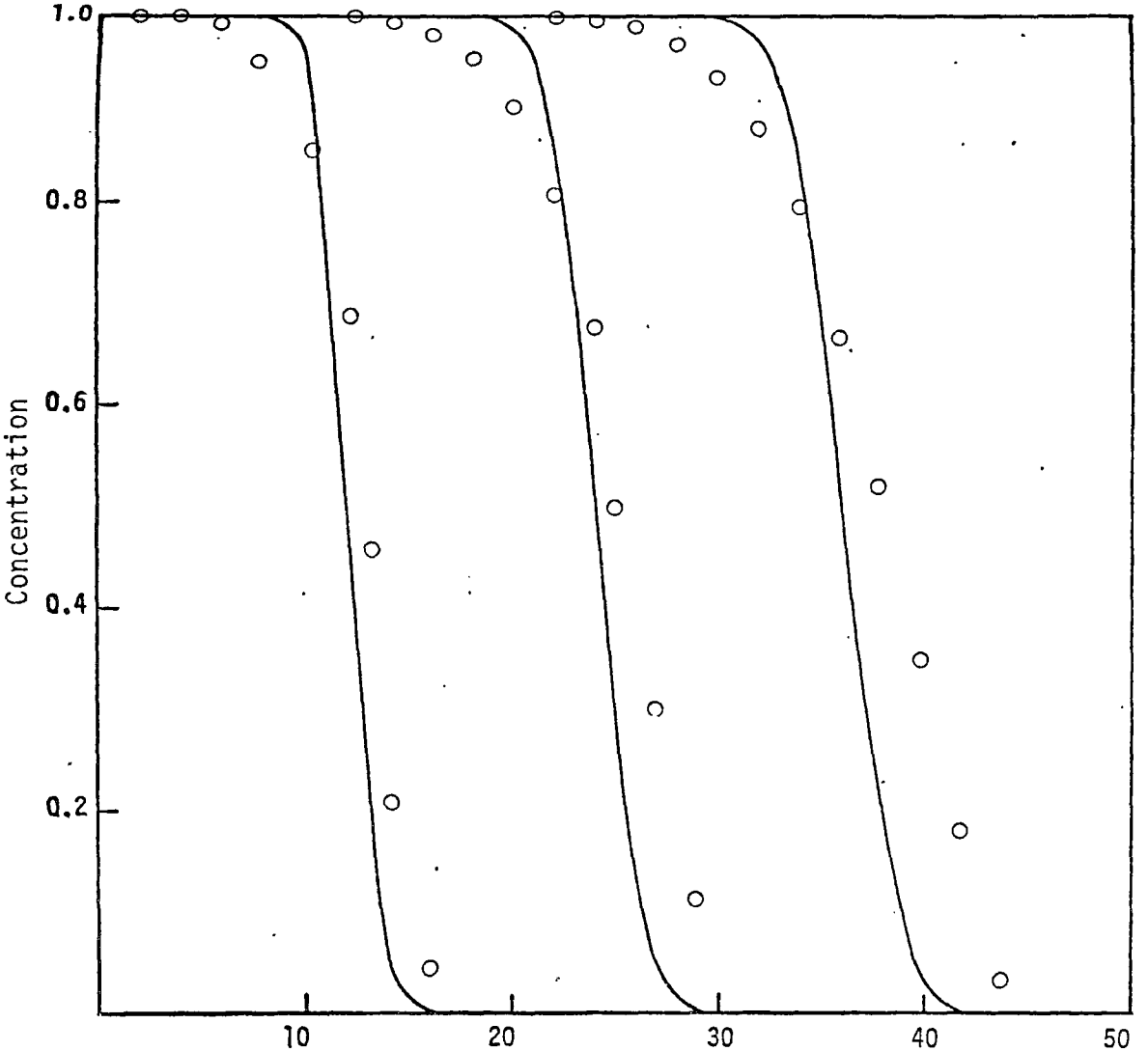
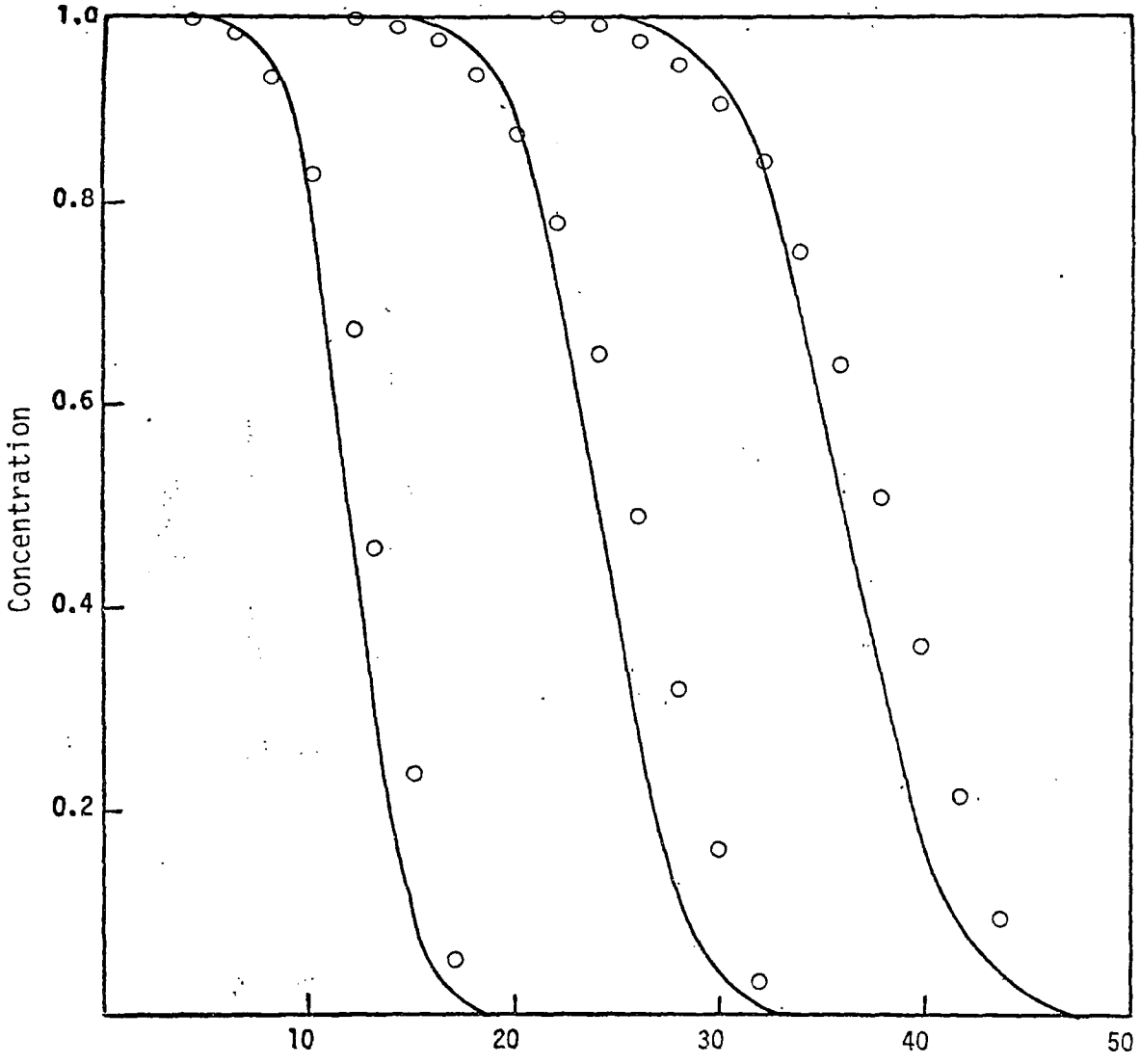


FIGURE 23. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE IMPLICIT PRICE SCHEME



(b) Pec = 206, k = 0 sec^{-1}

FIGURE 23. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE IMPLICIT PRICE SCHEME (Continued)

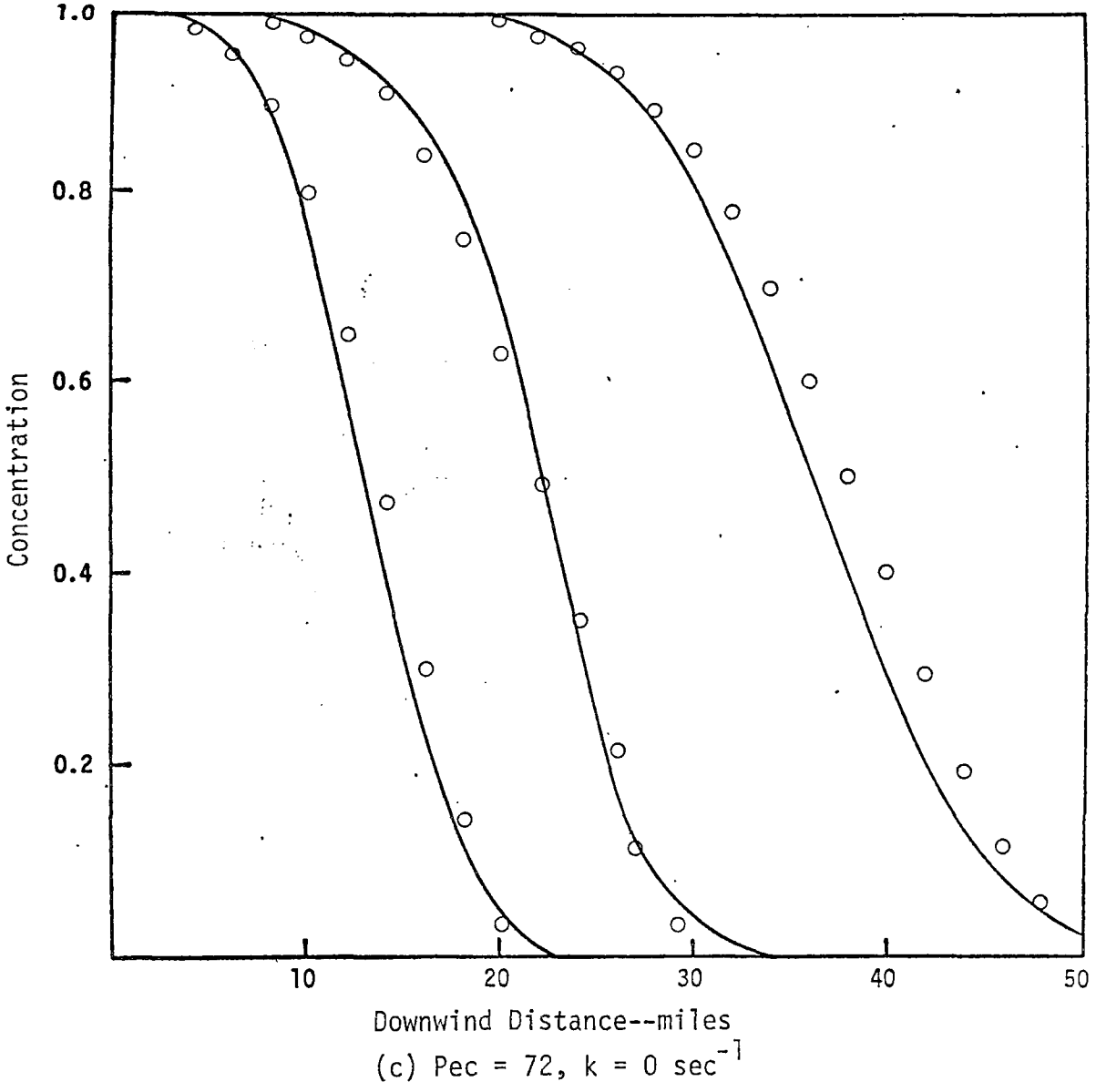
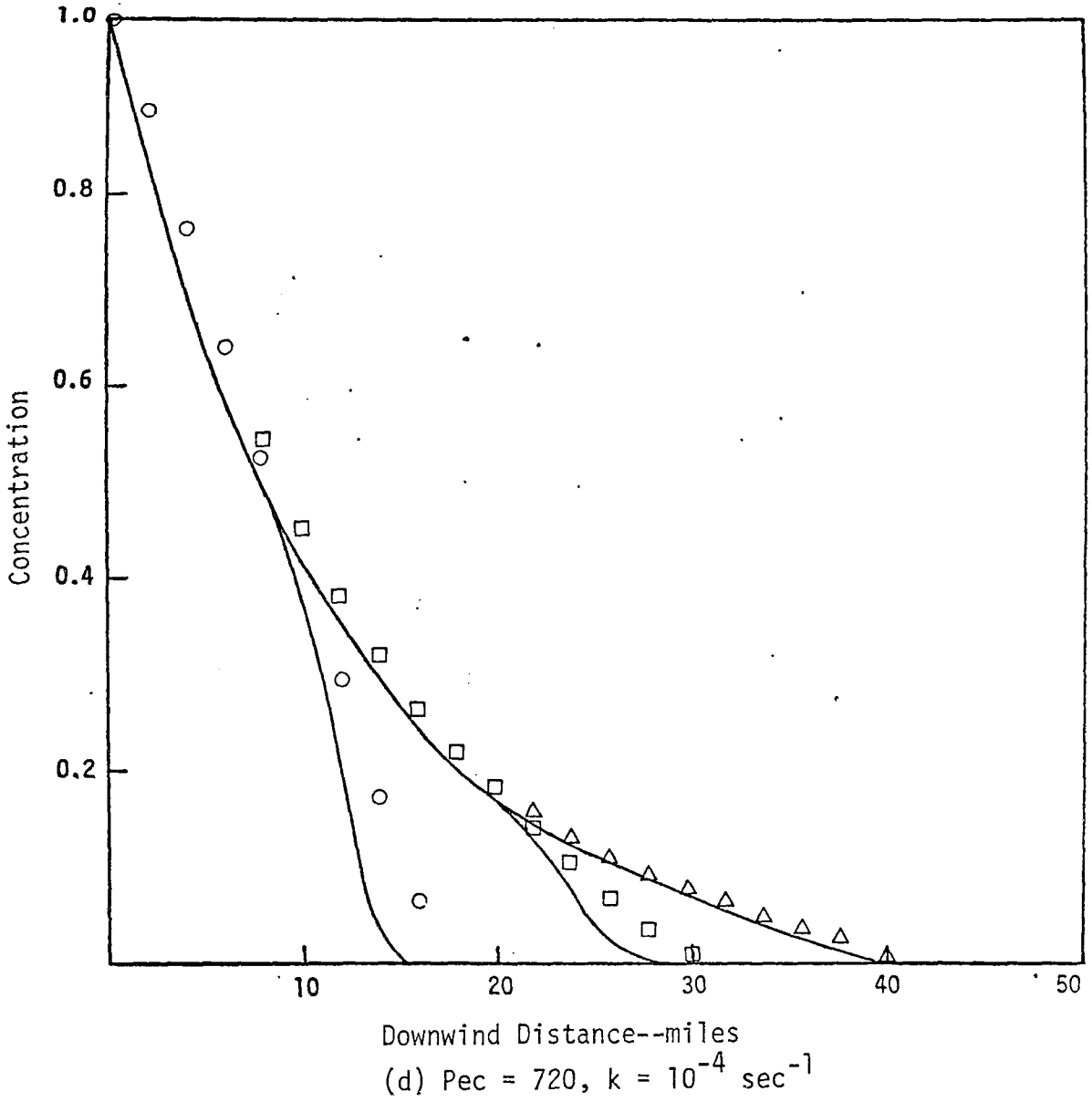
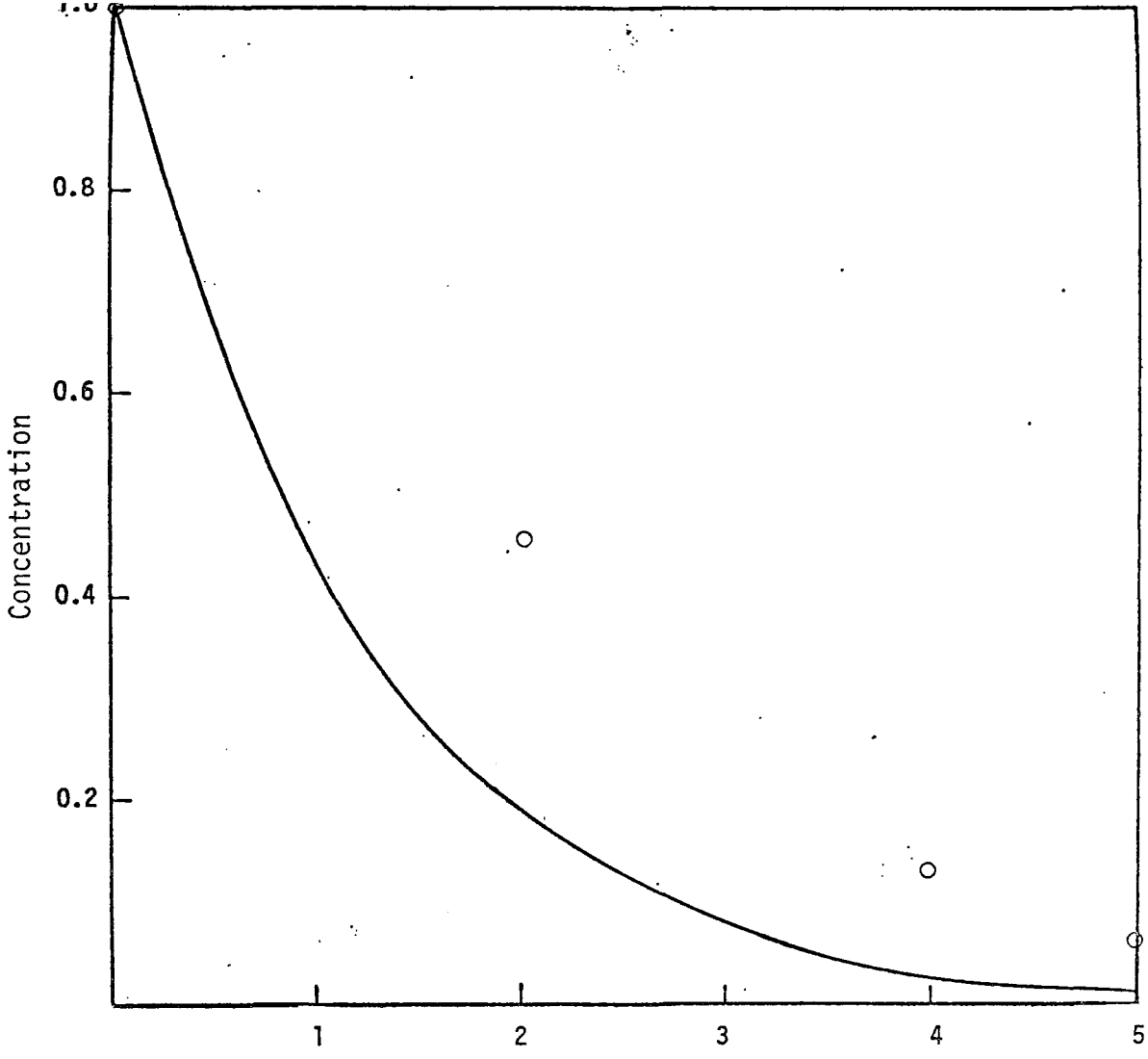


FIGURE 23. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE IMPLICIT PRICE SCHEME (Continued)



(d) Pec = 720, k = 10^{-4} sec^{-1}

FIGURE 23. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE IMPLICIT PRICE SCHEME (Continued)



(e) Pec = 720, k = 10^{-3} sec^{-1}

FIGURE 23. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE IMPLICIT PRICE SCHEME (Concluded)

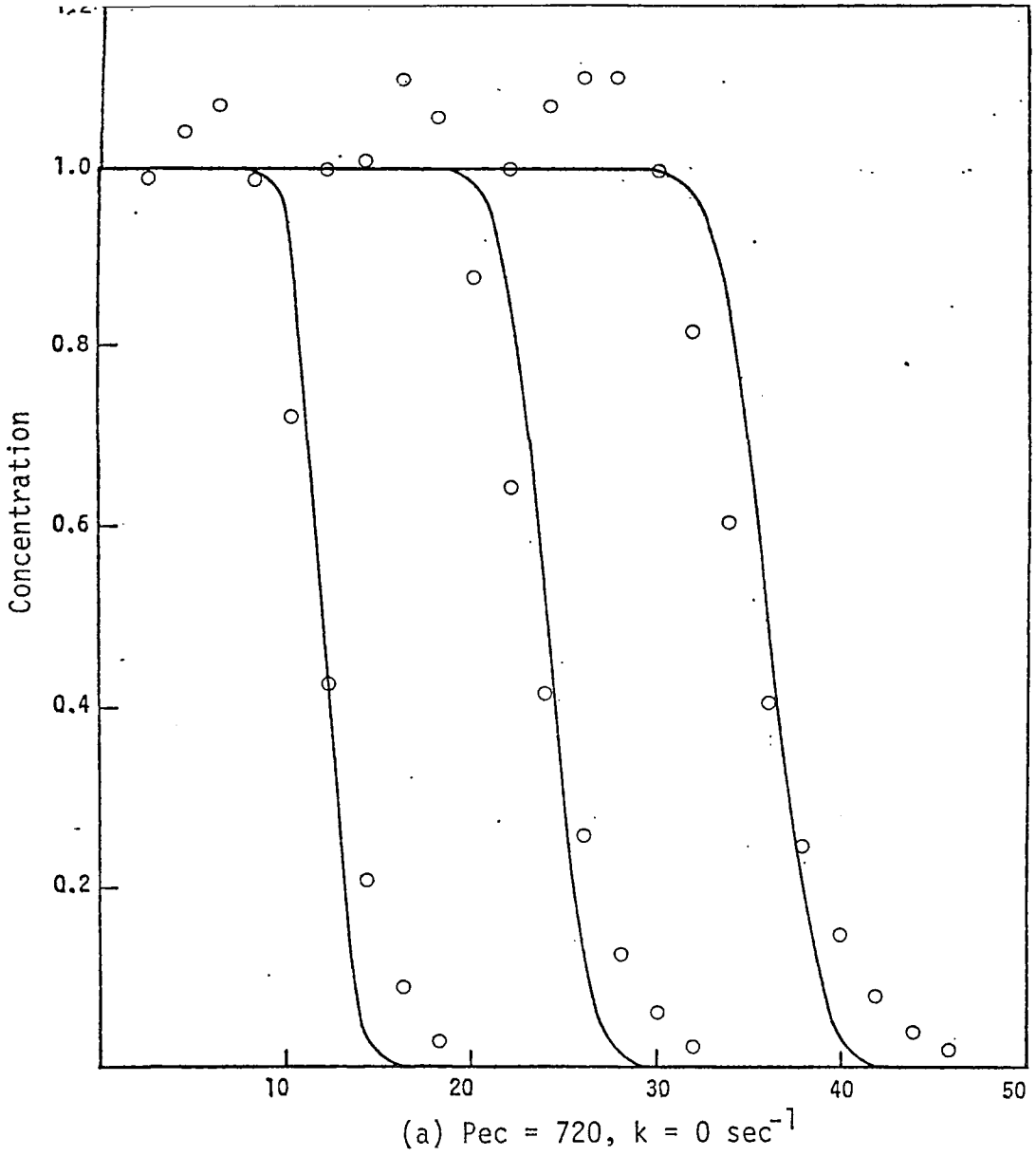


FIGURE 24. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE CROWLEY SECOND-ORDER SCHEME

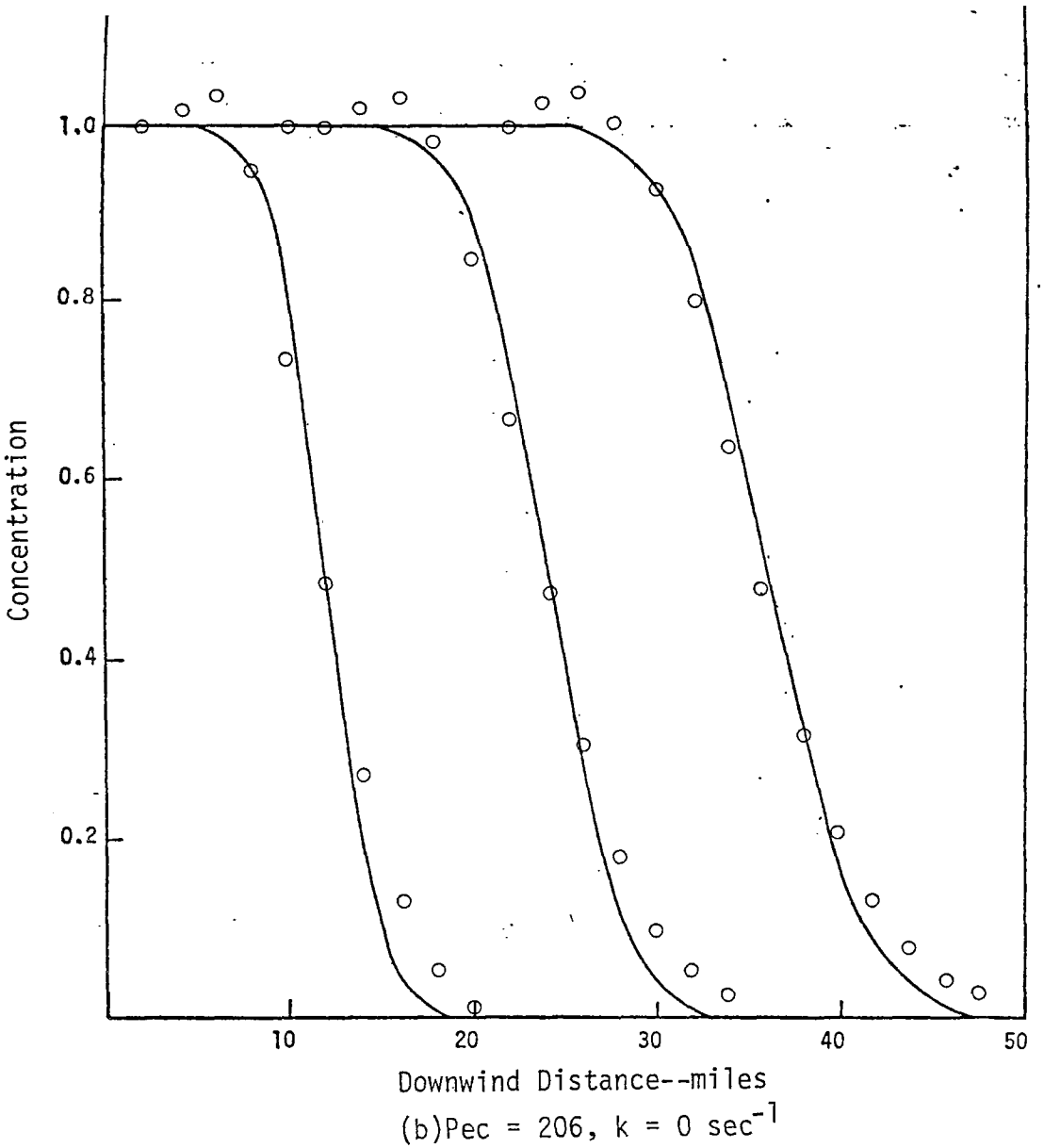


FIGURE 24. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE CROWLEY SECOND-ORDER SCHEME (Continued)

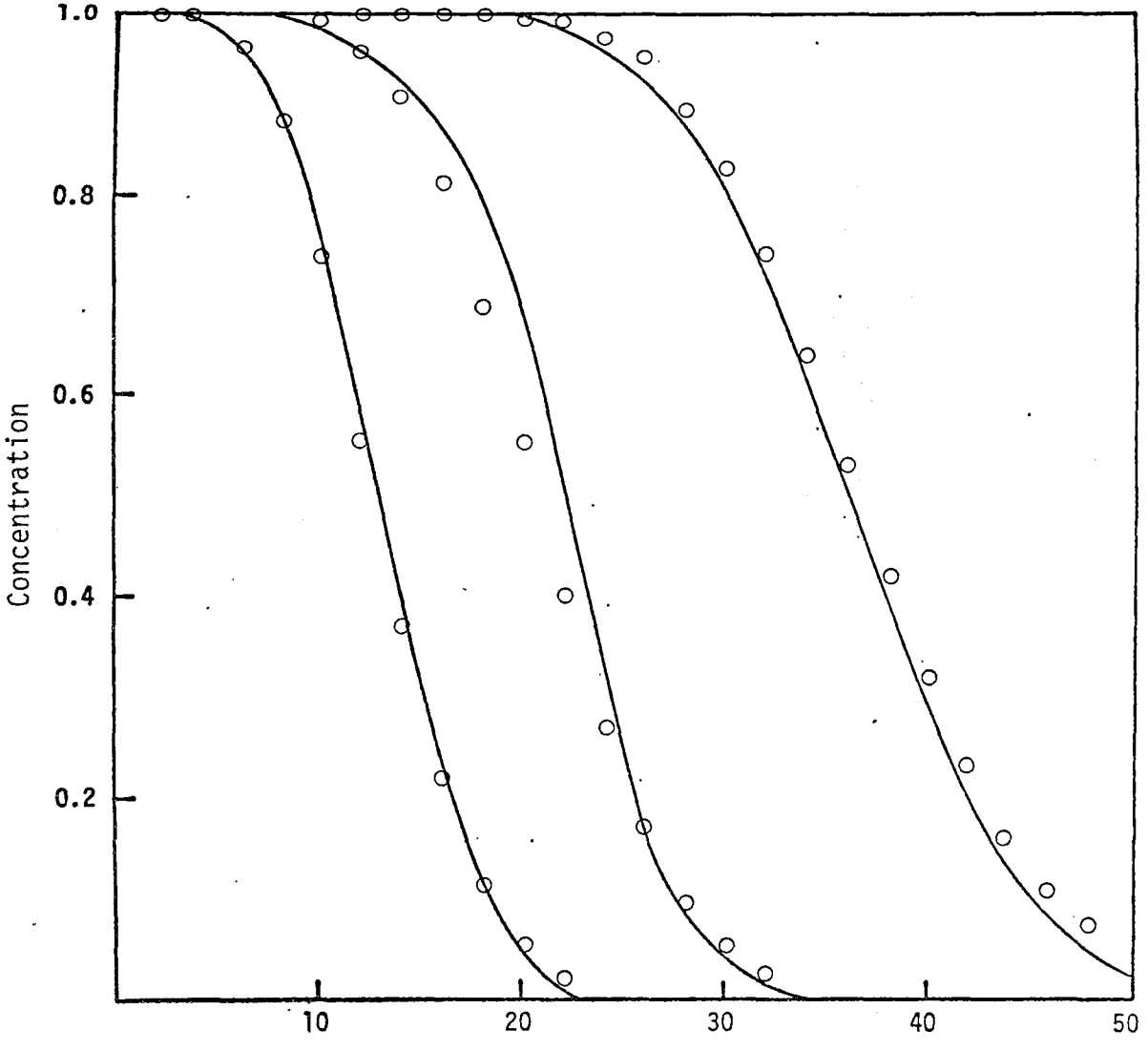


FIGURE 24. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE CROWLEY SECOND-ORDER SCHEME (Continued)

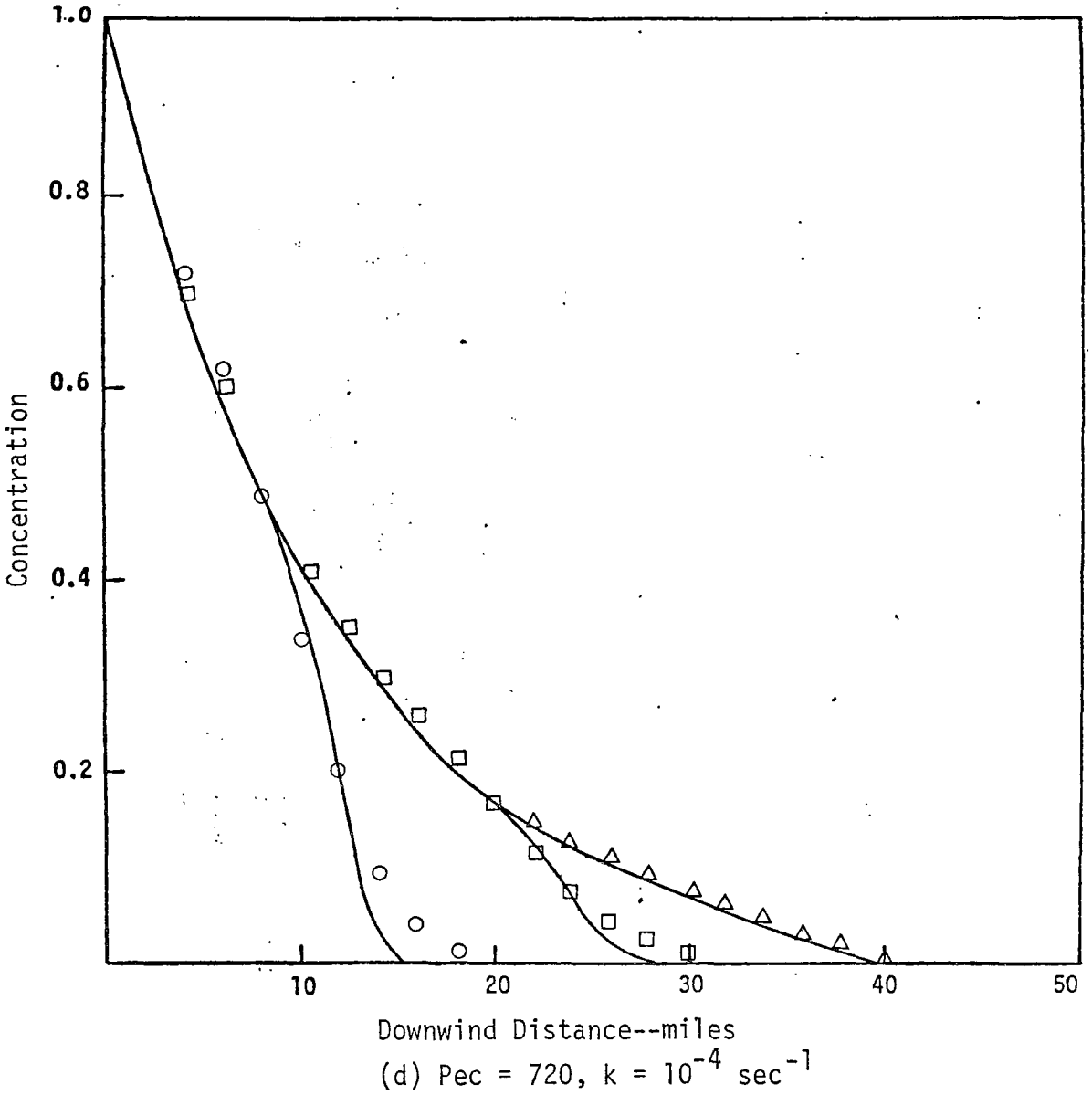


FIGURE 24. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE CROWLEY SECOND-ORDER SCHEME (Continued)

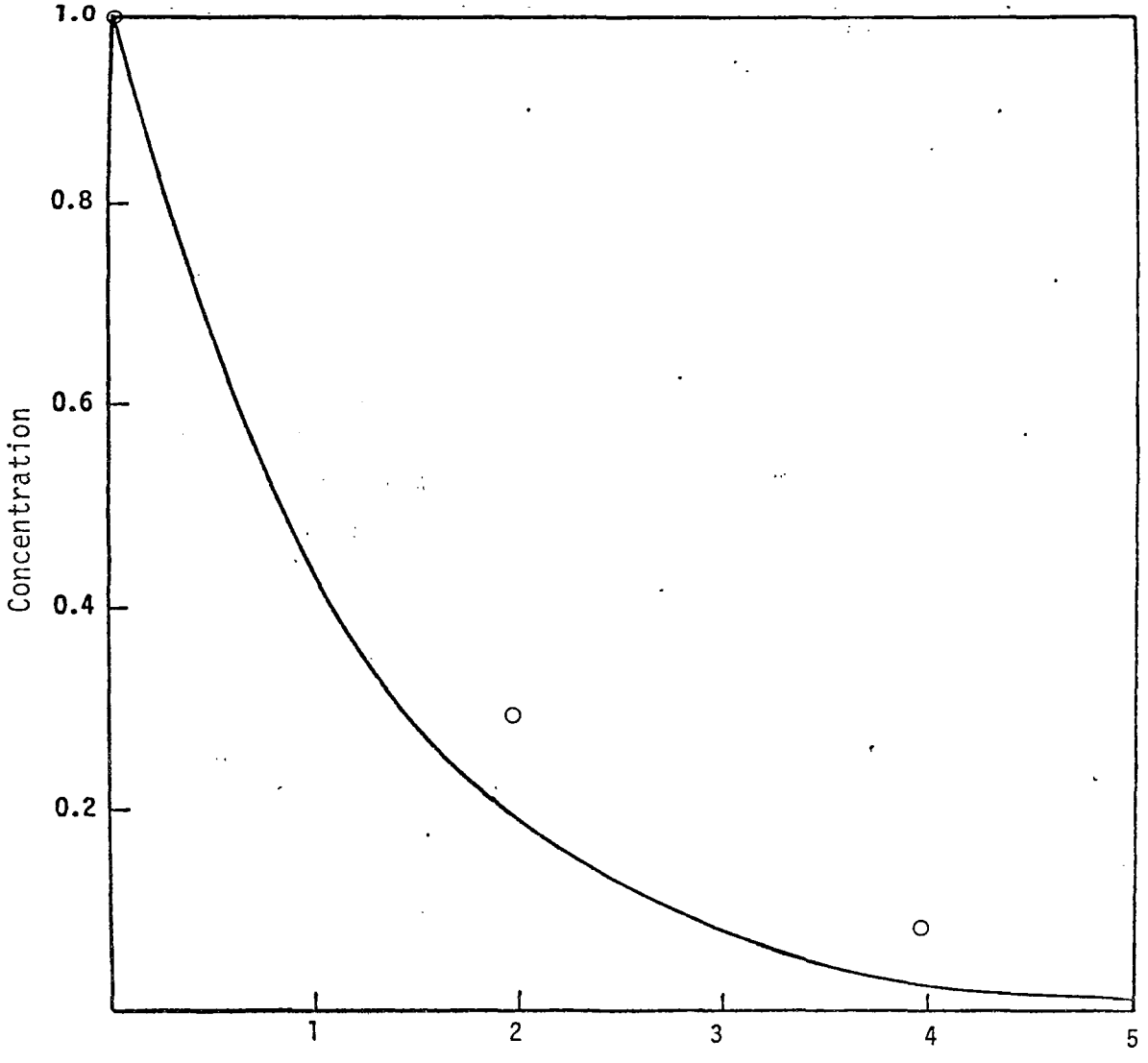


FIGURE 24. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE CROWLEY SECOND-ORDER SCHEME (Concluded)

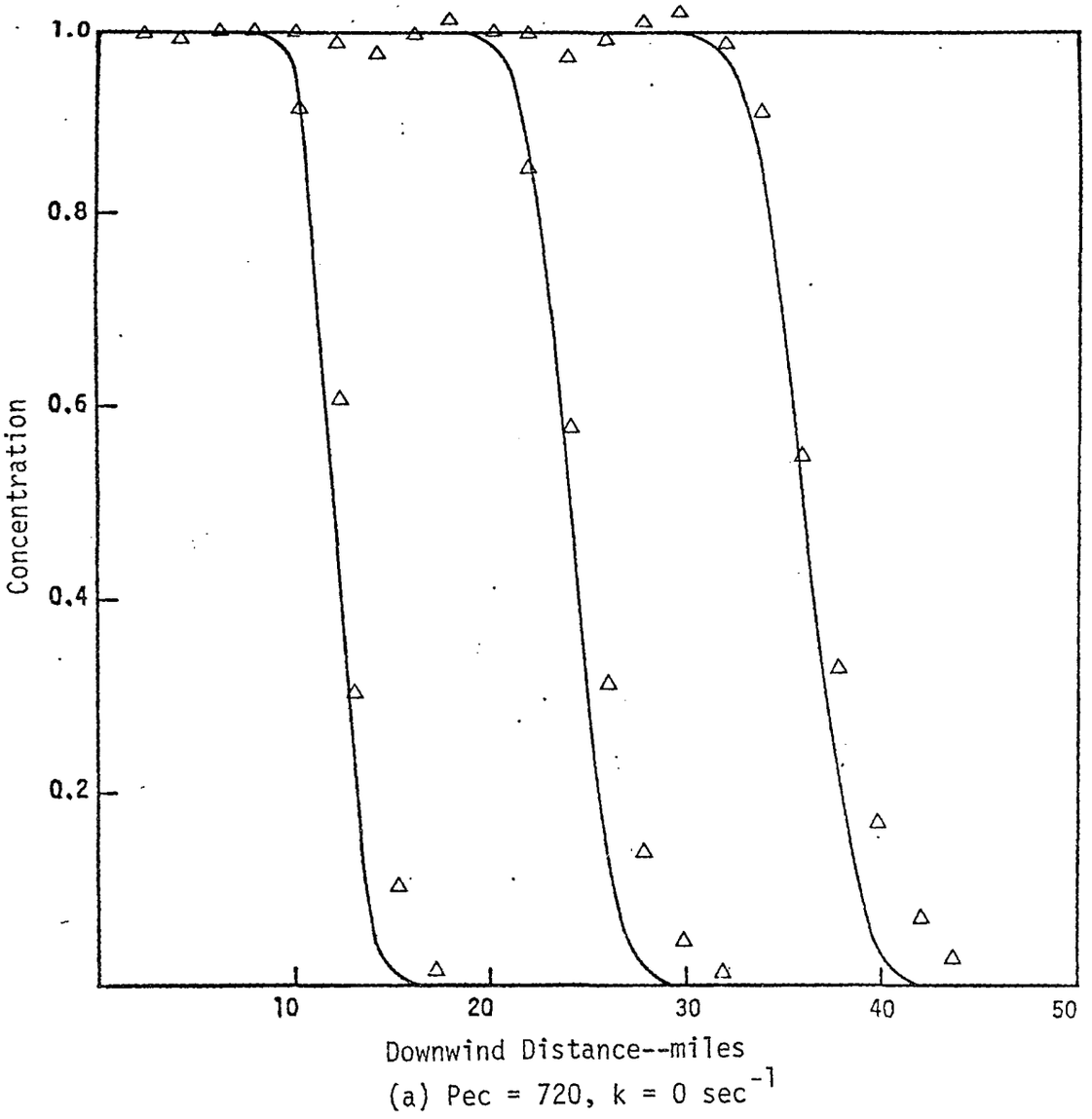


FIGURE 25. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE CROWLEY FOURTH-ORDER SCHEME

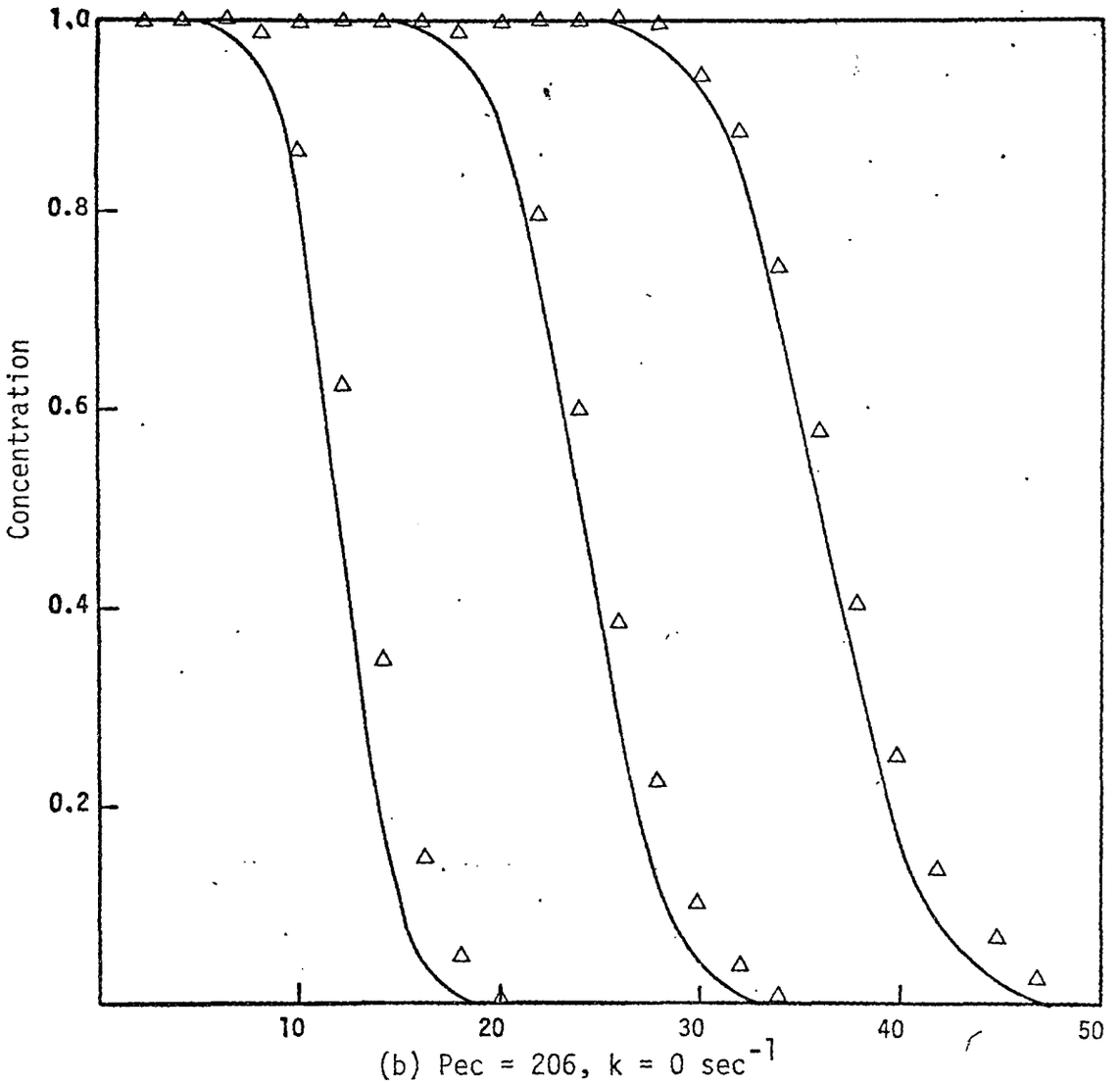


FIGURE 25. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE CROWLEY FOURTH-ORDER SCHEME (Continued)

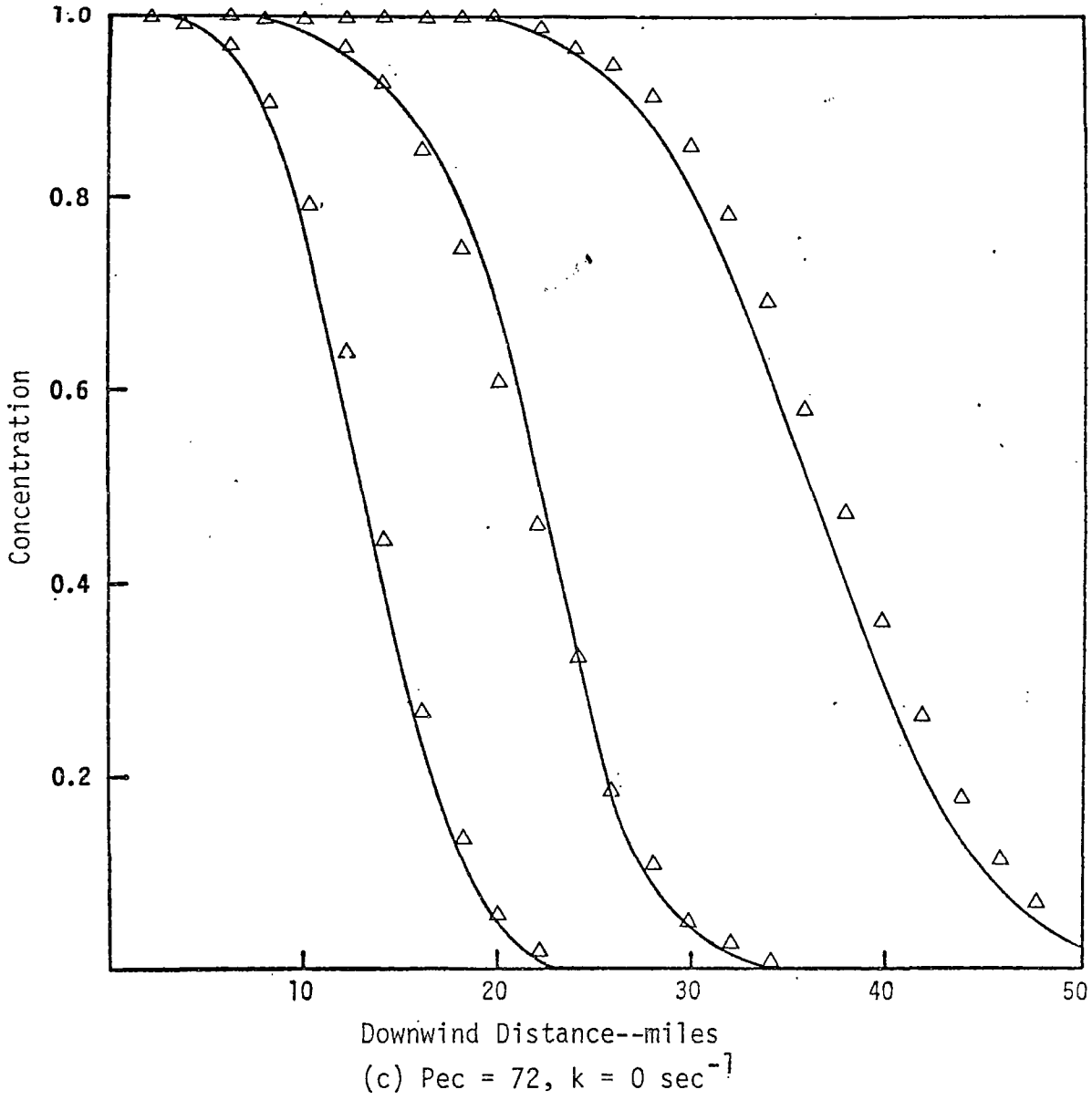


FIGURE 25. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE CROWLEY FOURTH-ORDER SCHEME (Continued)

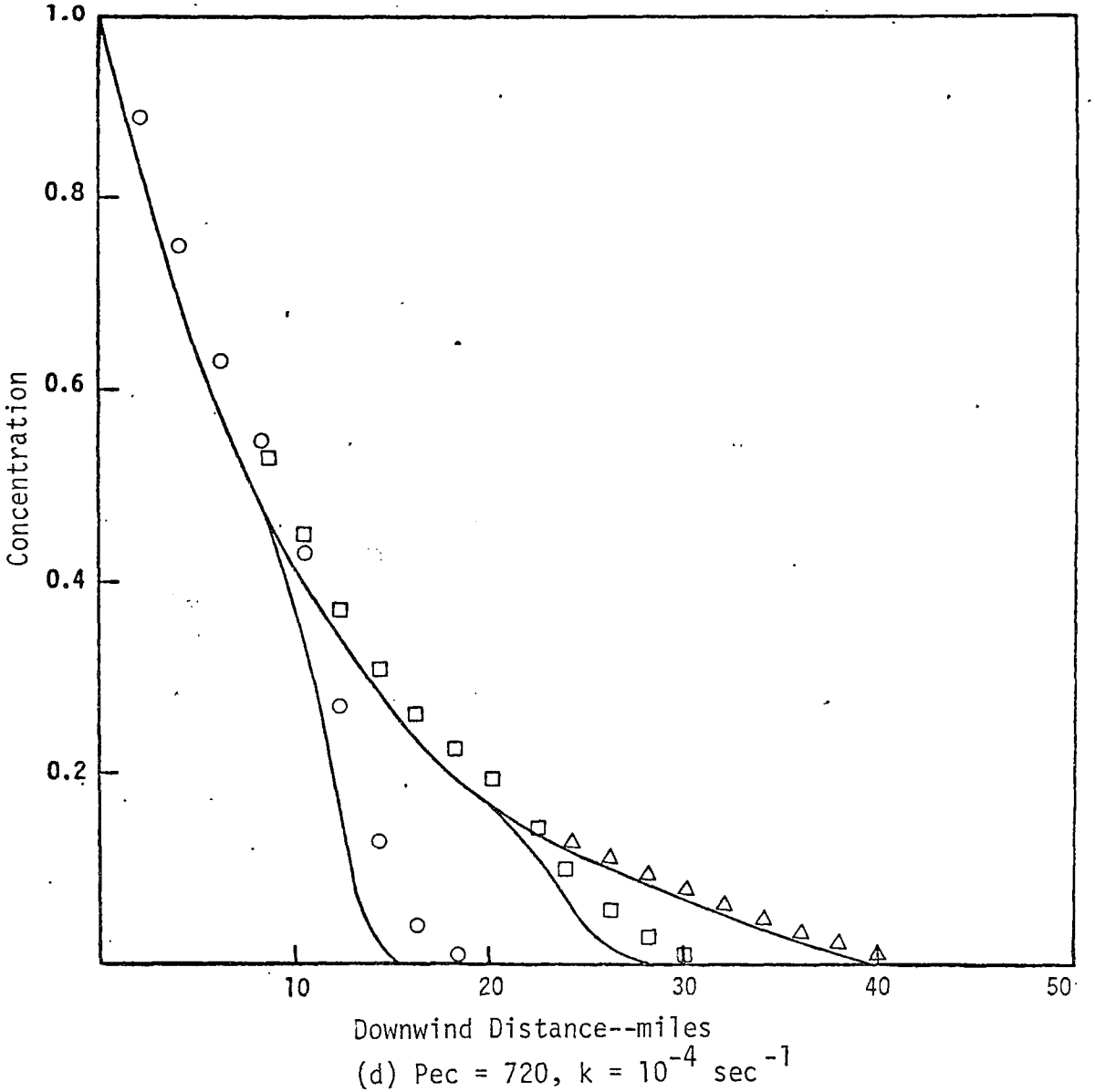
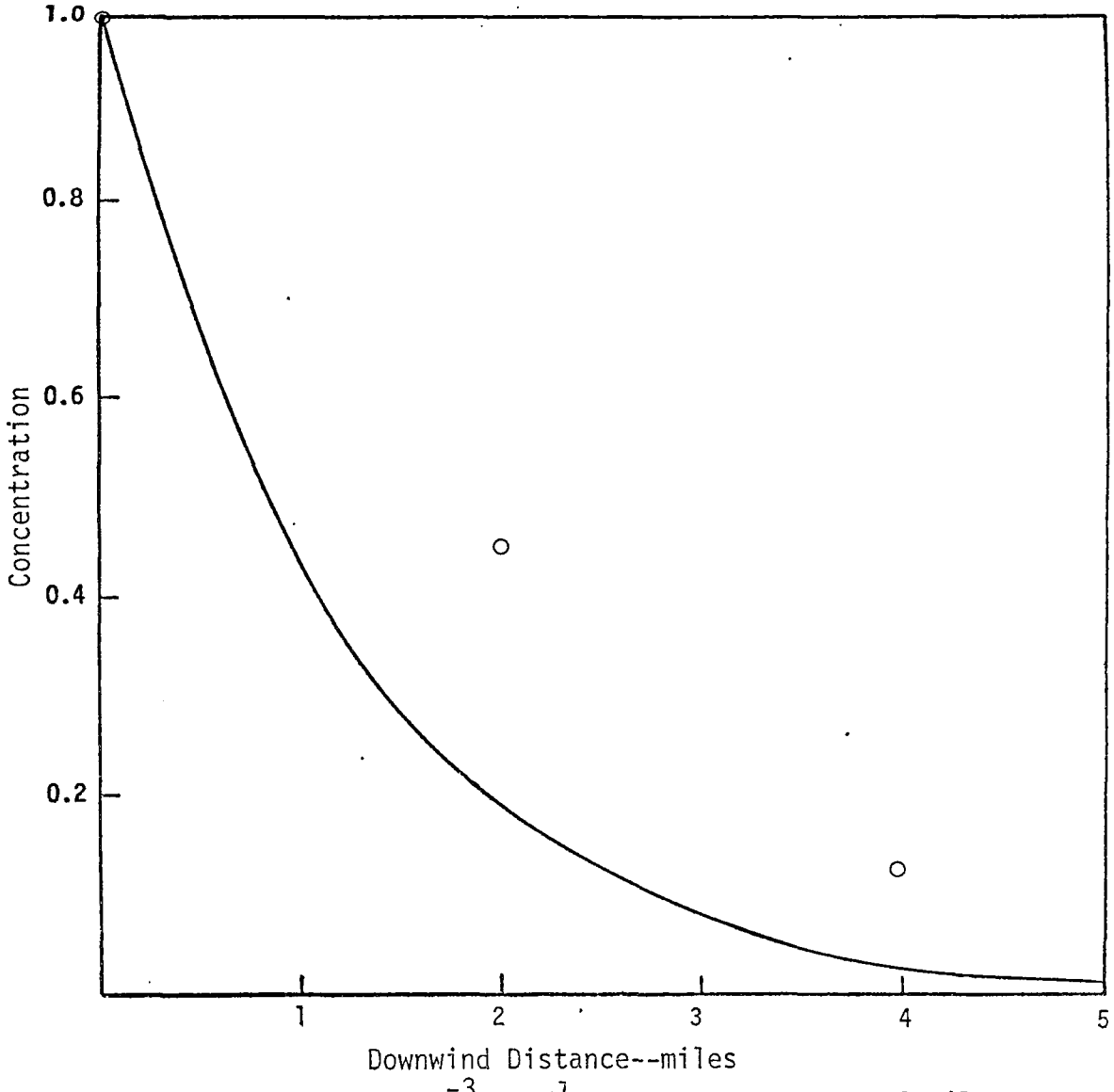


FIGURE 25. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE CROWLEY FOURTH-ORDER SCHEME (Continued)



(e) Pec = 720, $k = 10^{-3}$ sec^{-1}, δt = 300 sec, δx = 2 miles

FIGURE 25. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE CROWLEY FOURTH-ORDER SCHEME (Concluded)

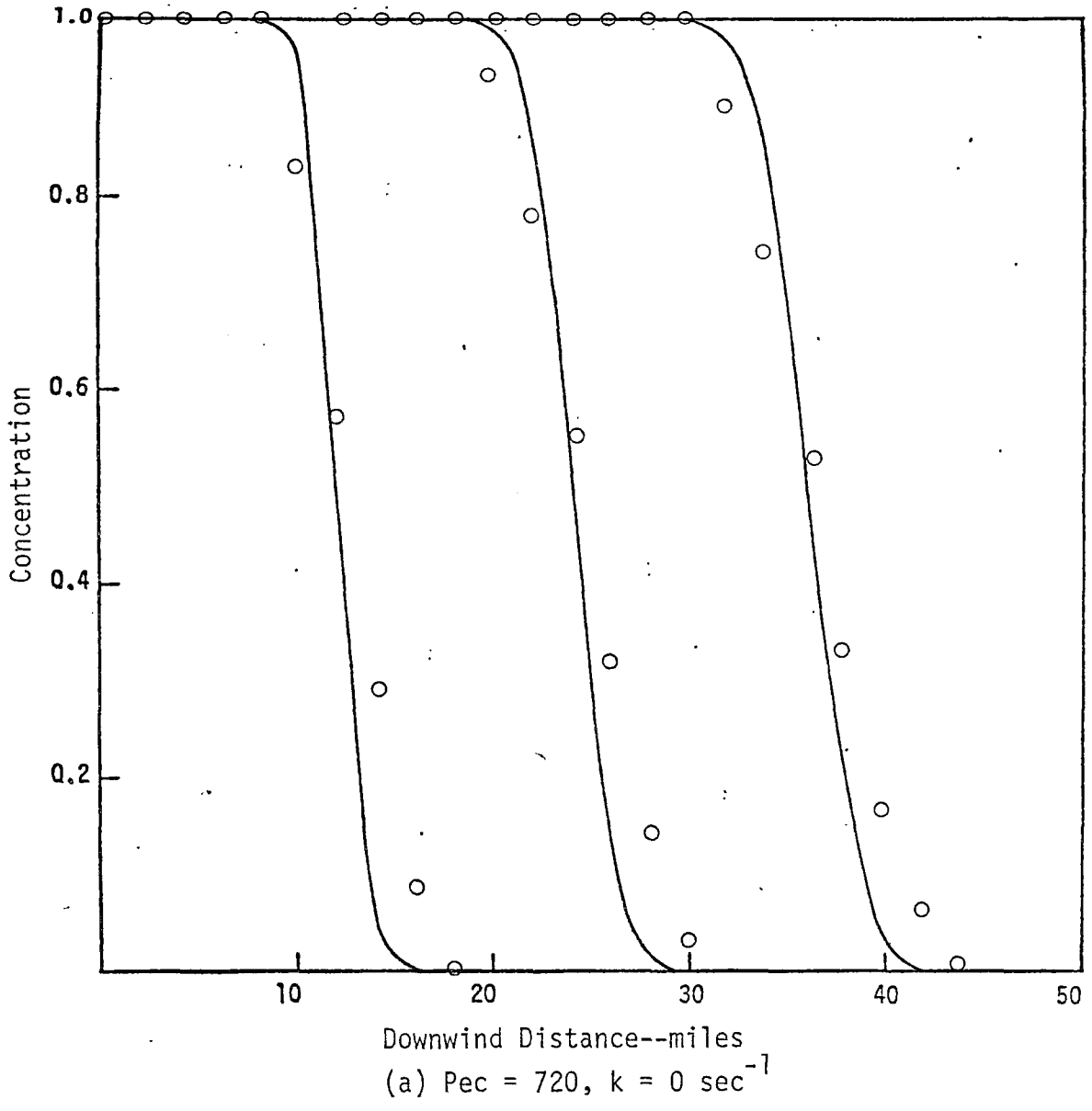


FIGURE 26. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE SHASTA METHOD

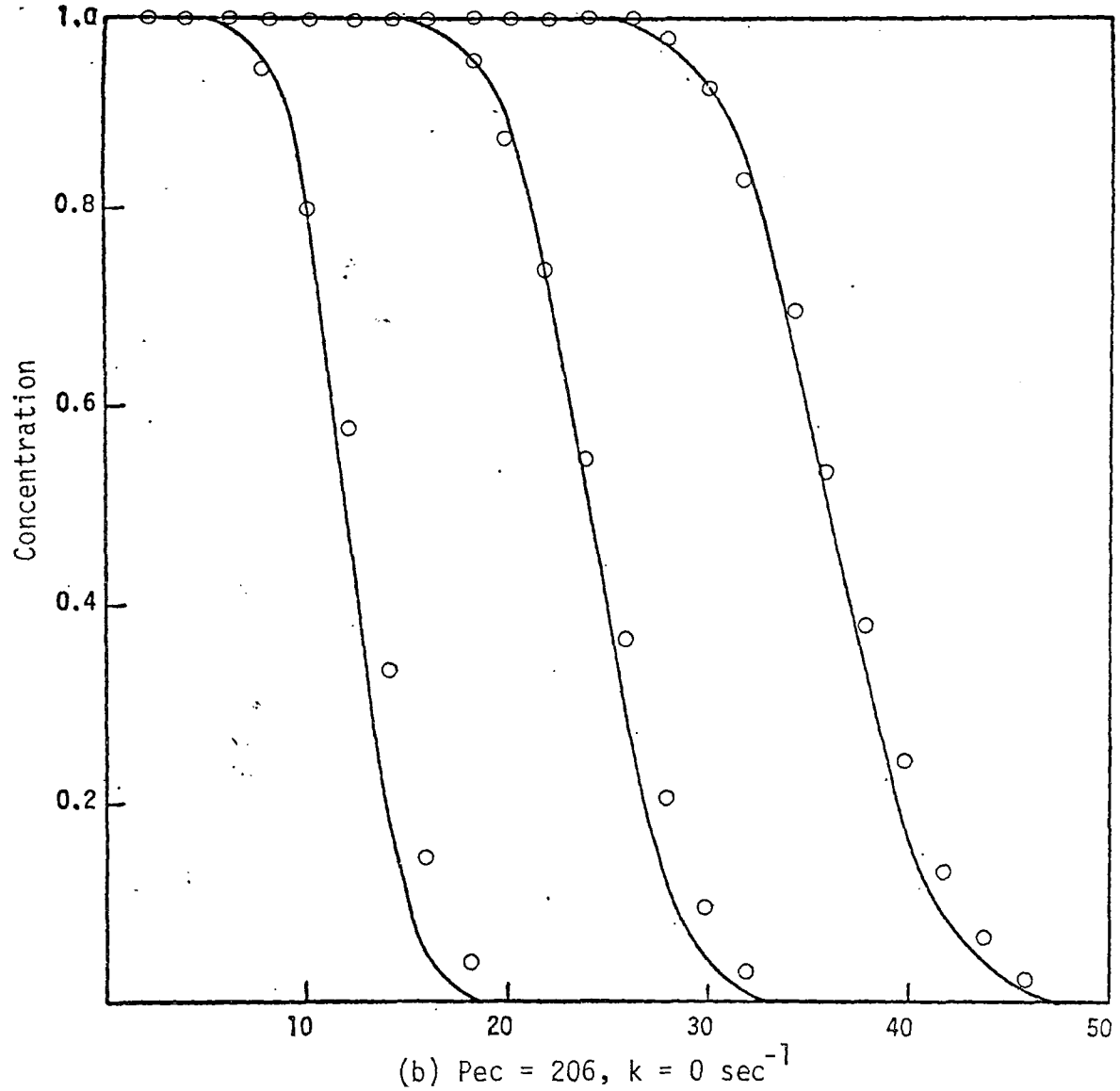
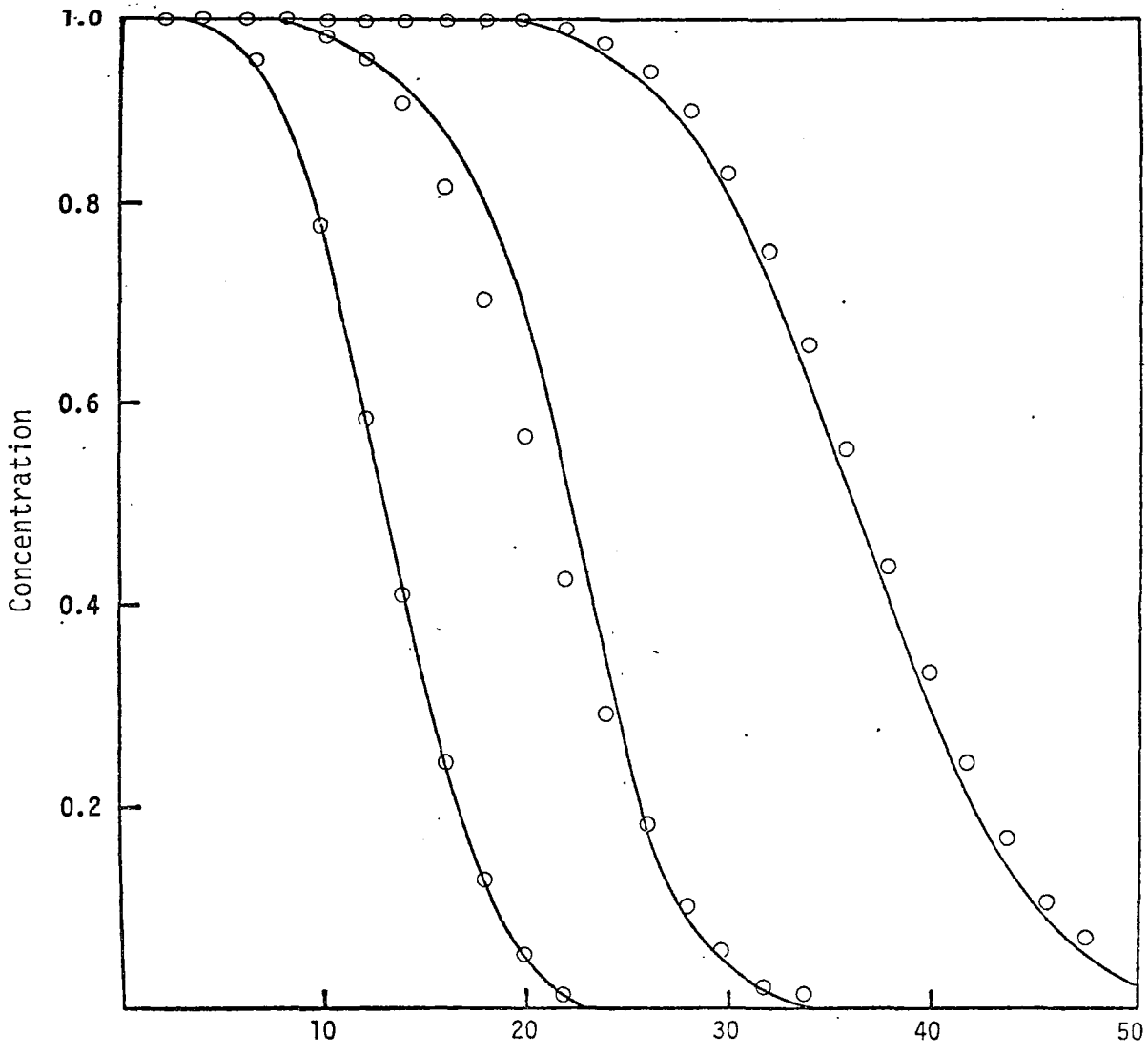
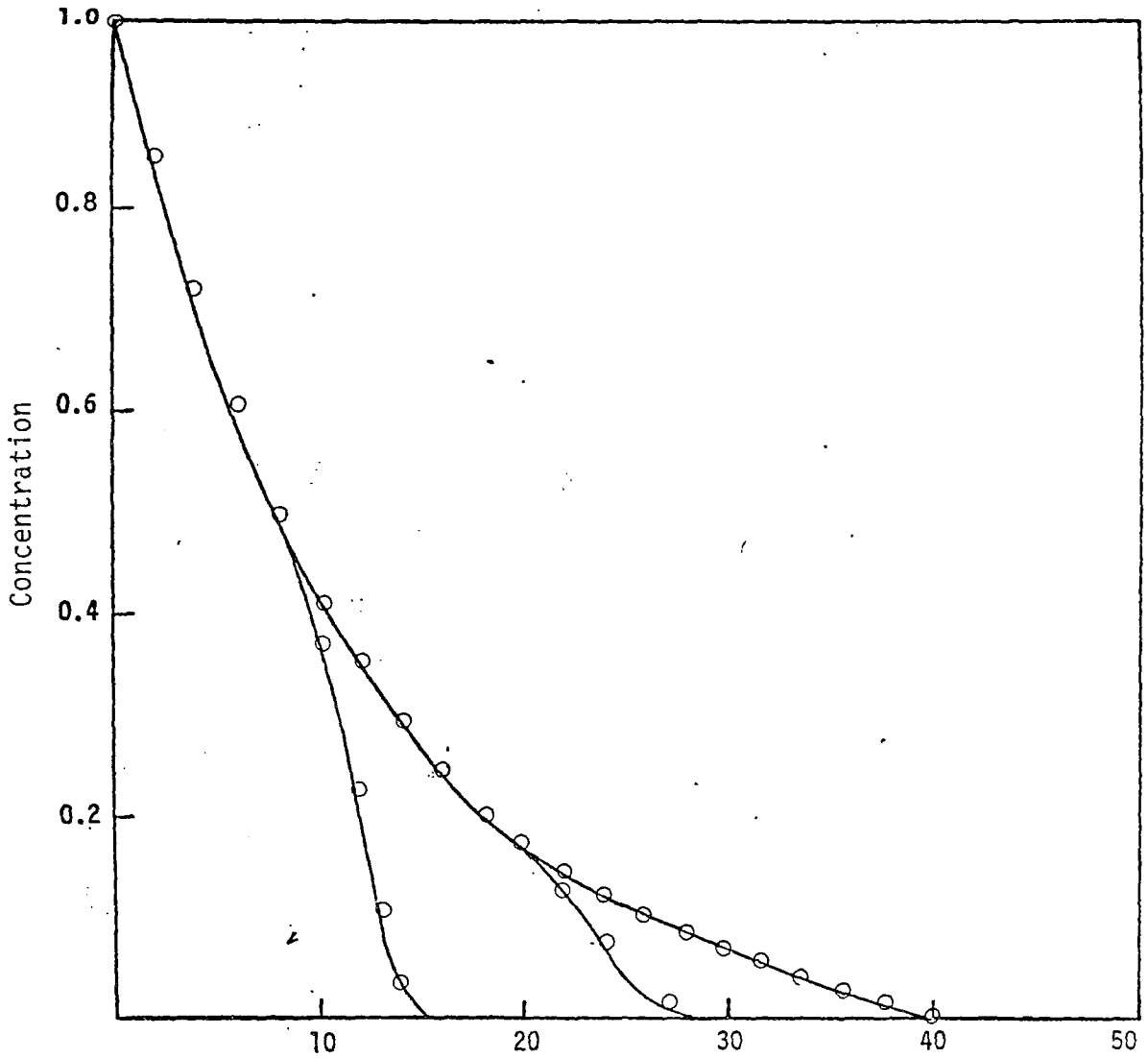


FIGURE 26. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE SHASTA METHOD (Continued)



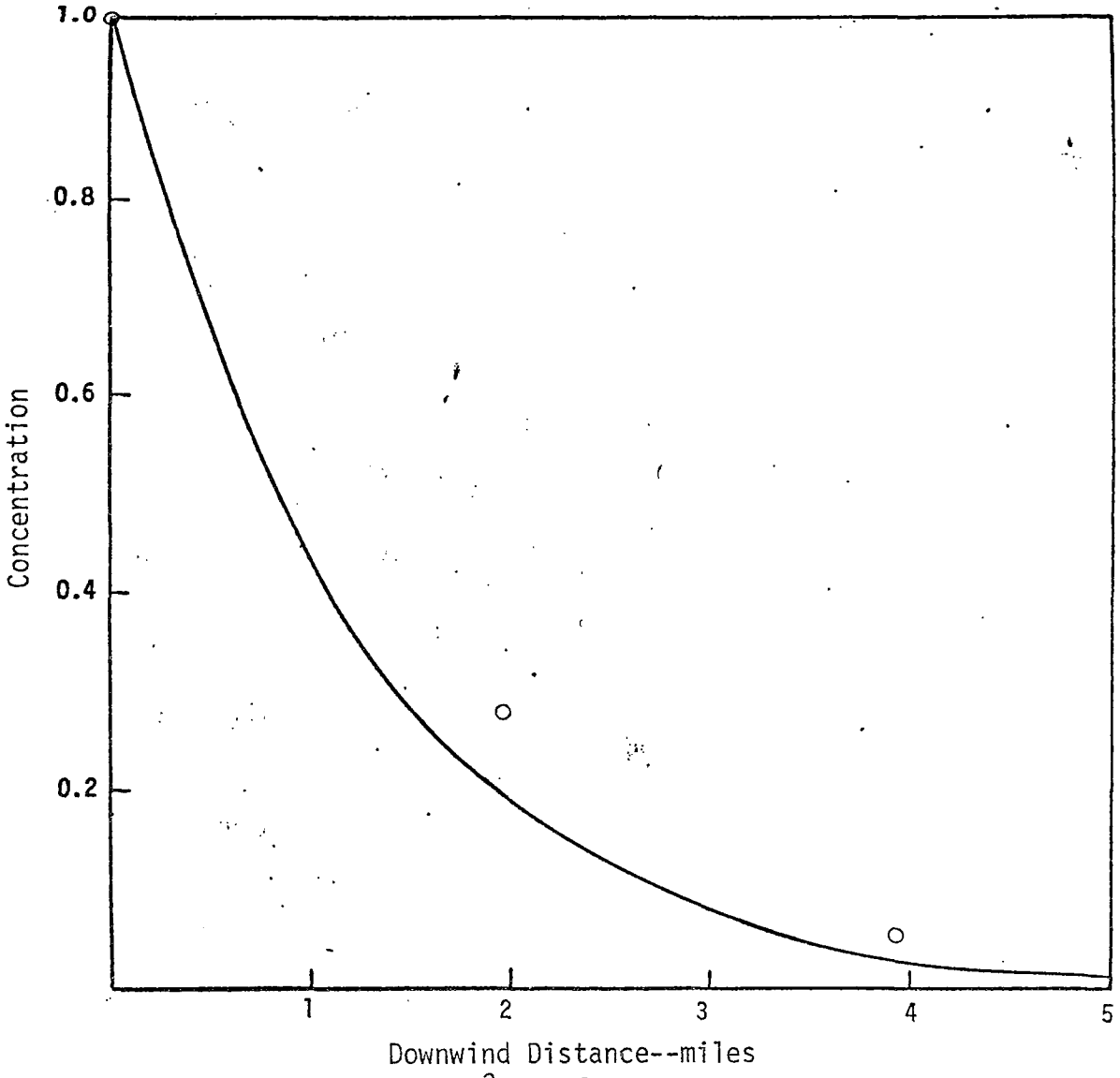
(c) Pec = 72, k = 0 sec^{-1}

FIGURE 26. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE SHASTA METHOD (Continued)



(d) Pec = 720, $k = 10^{-4}$ sec^{-1}

FIGURE 26. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE SHASTA METHOD (Continued)



(e) Pec = 720, $k = 10^{-3}$ sec^{-1}, δt = 300 sec, δx = 2 miles

FIGURE 26. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE SHASTA METHOD (Concluded)

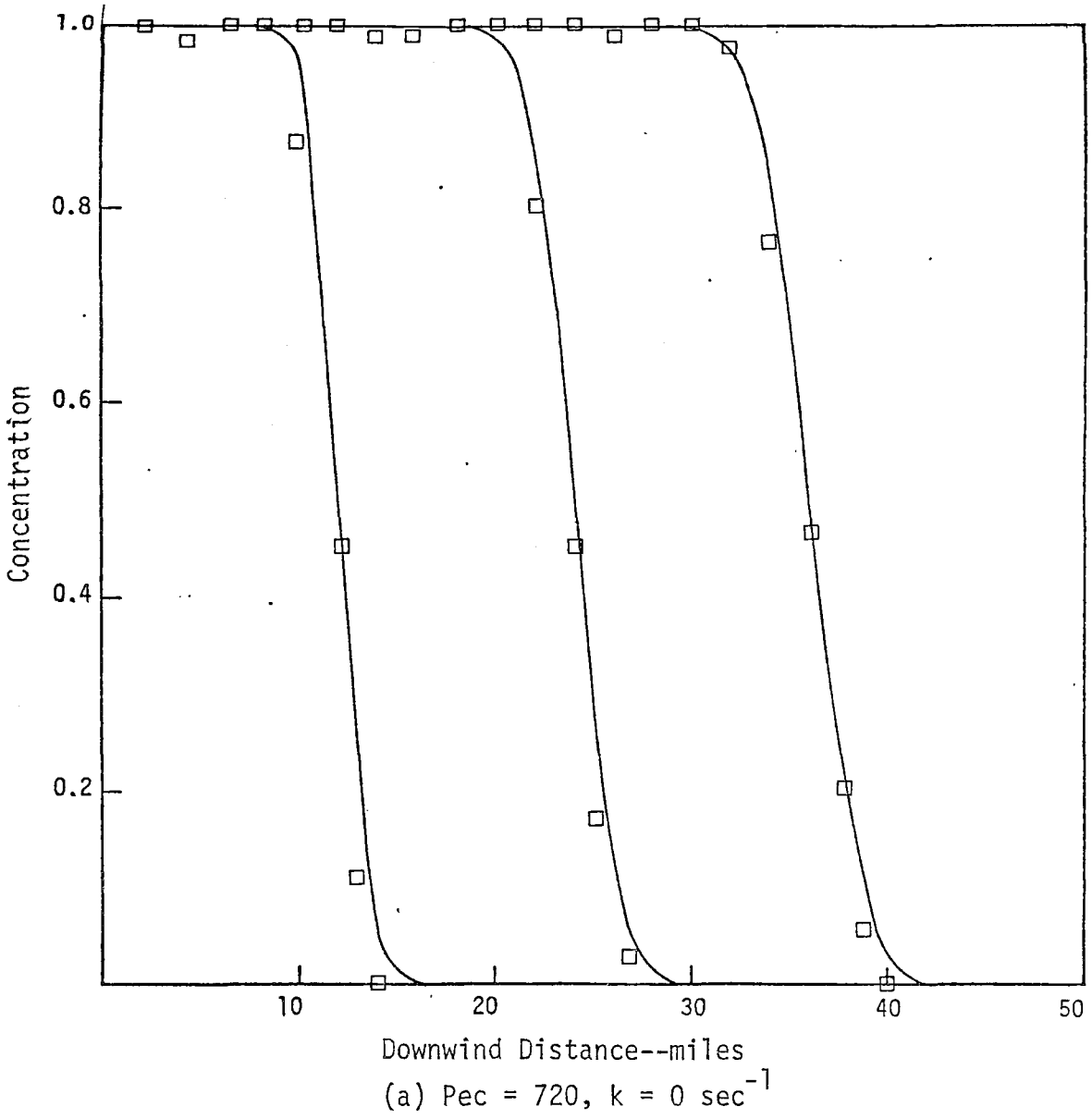


FIGURE 27. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE GALERKIN METHOD

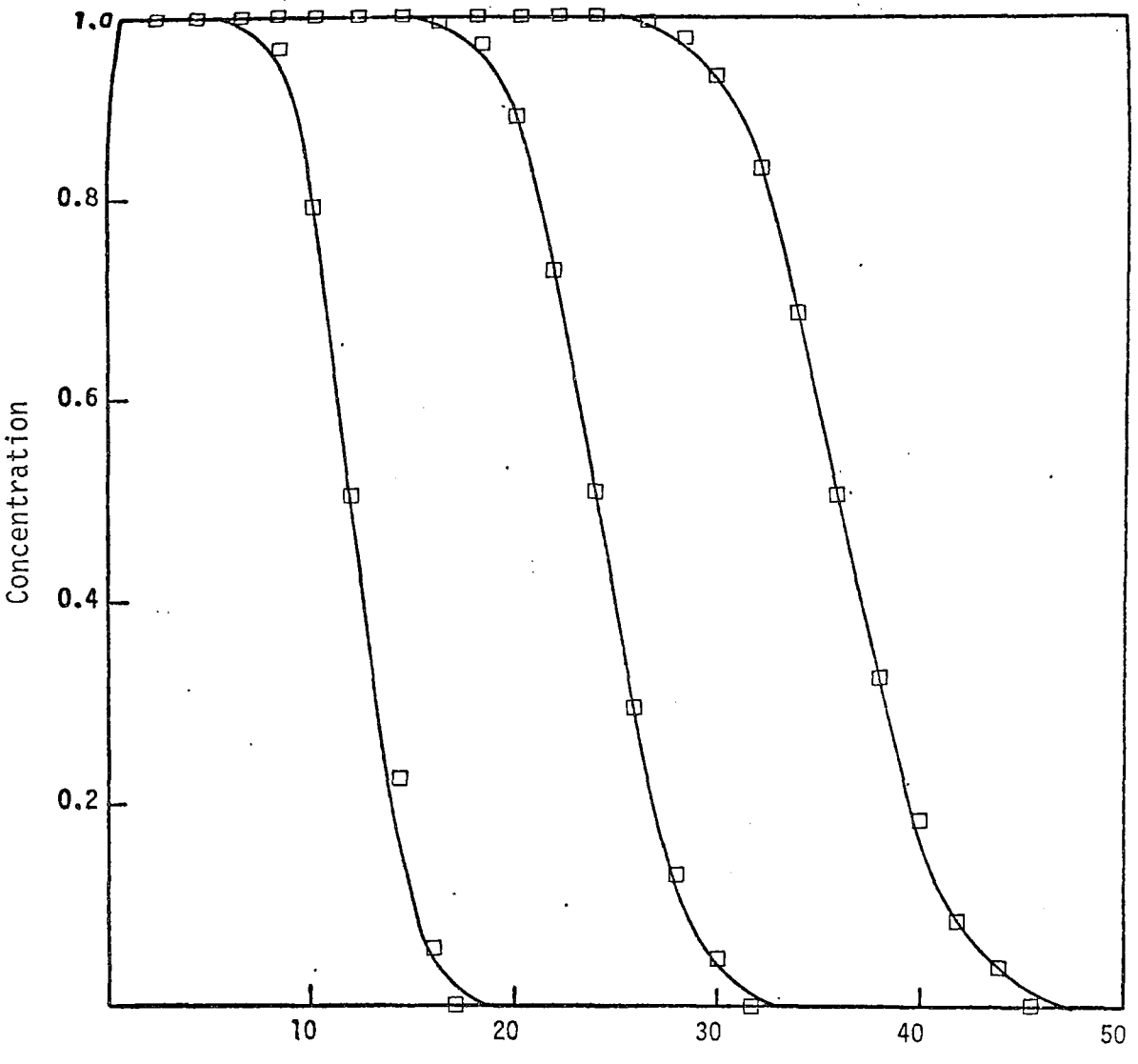


FIGURE 27. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE GALERKIN METHOD (Continued)

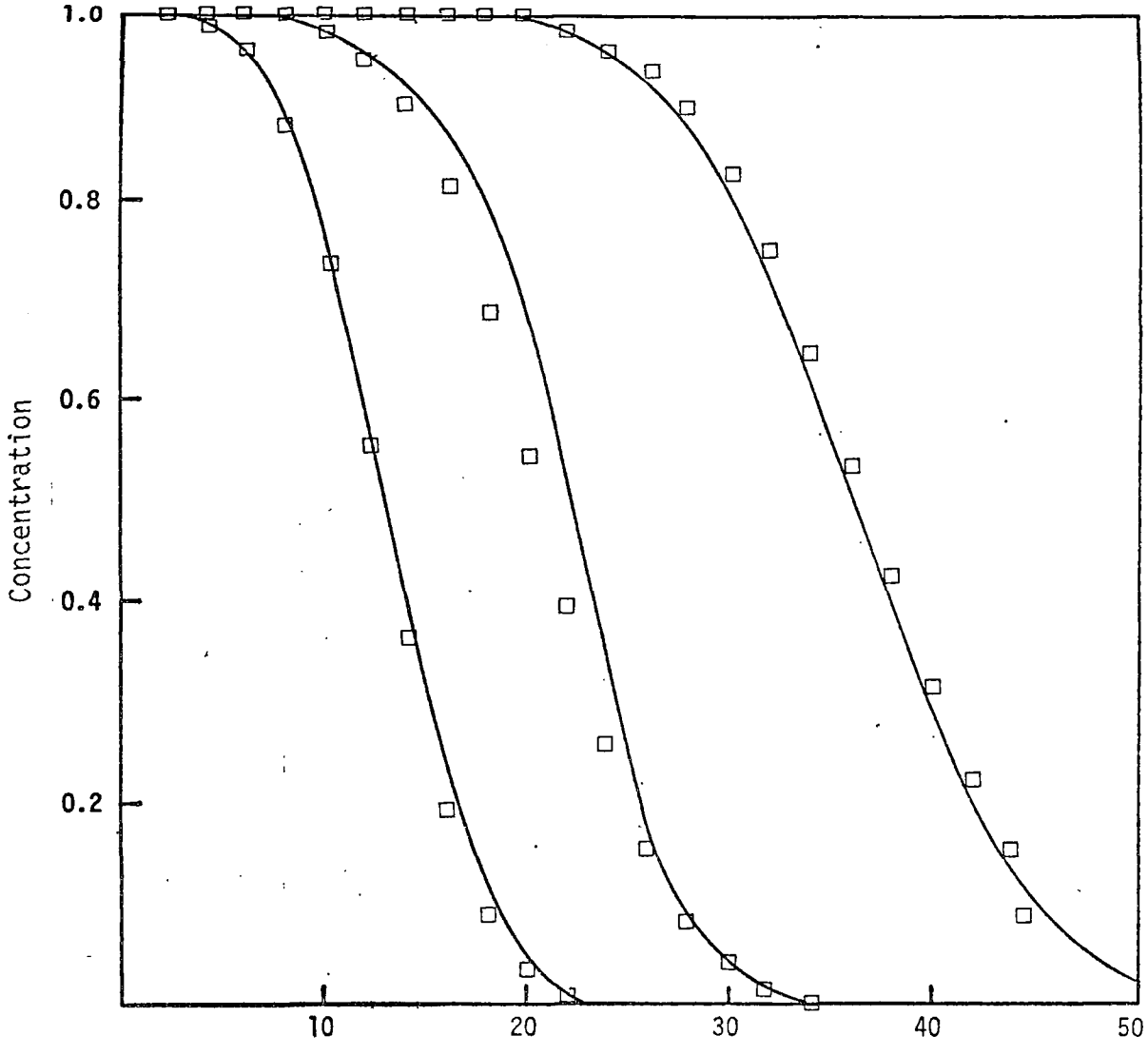


FIGURE 27. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE GALERKIN METHOD (Continued)

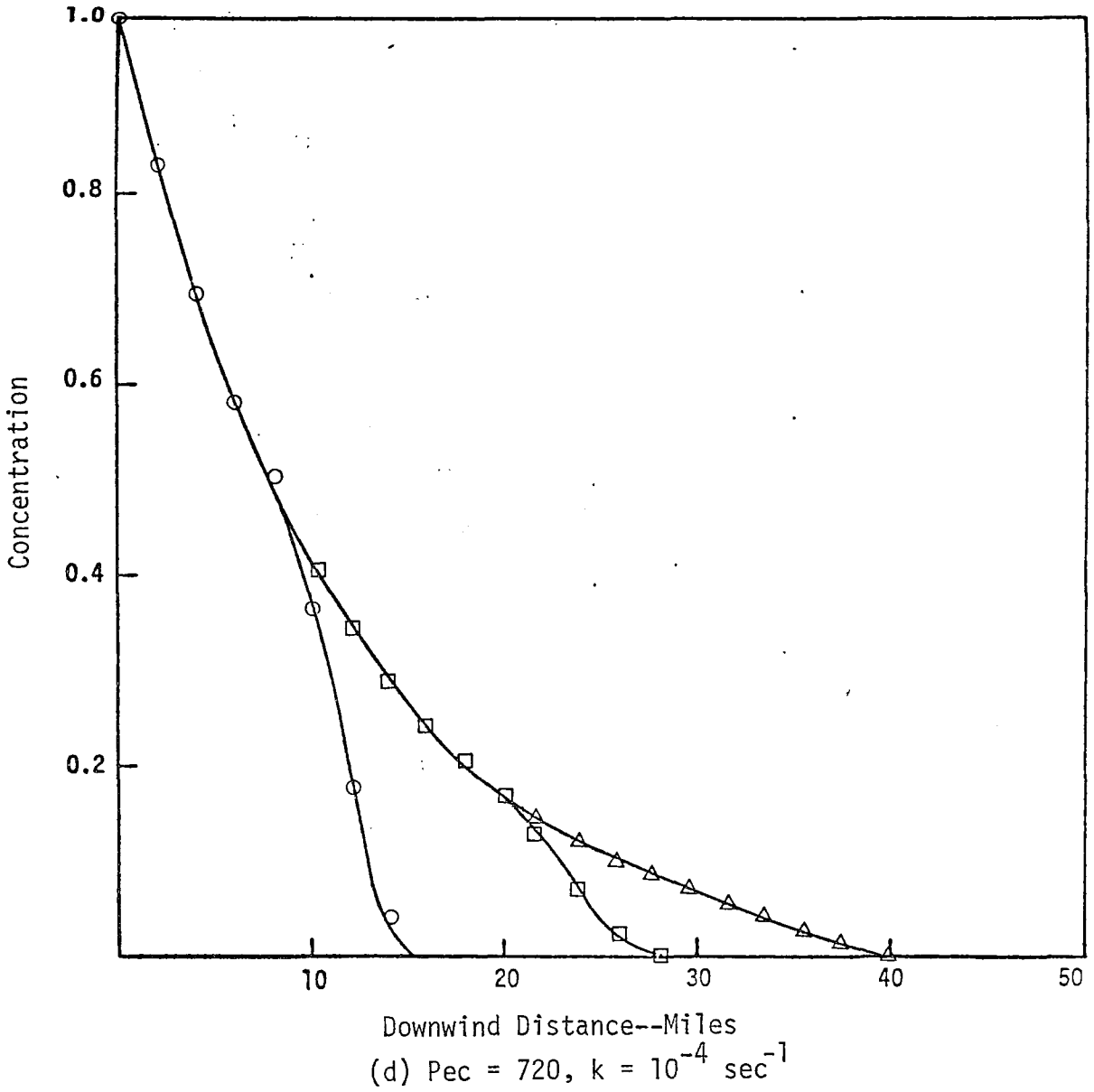
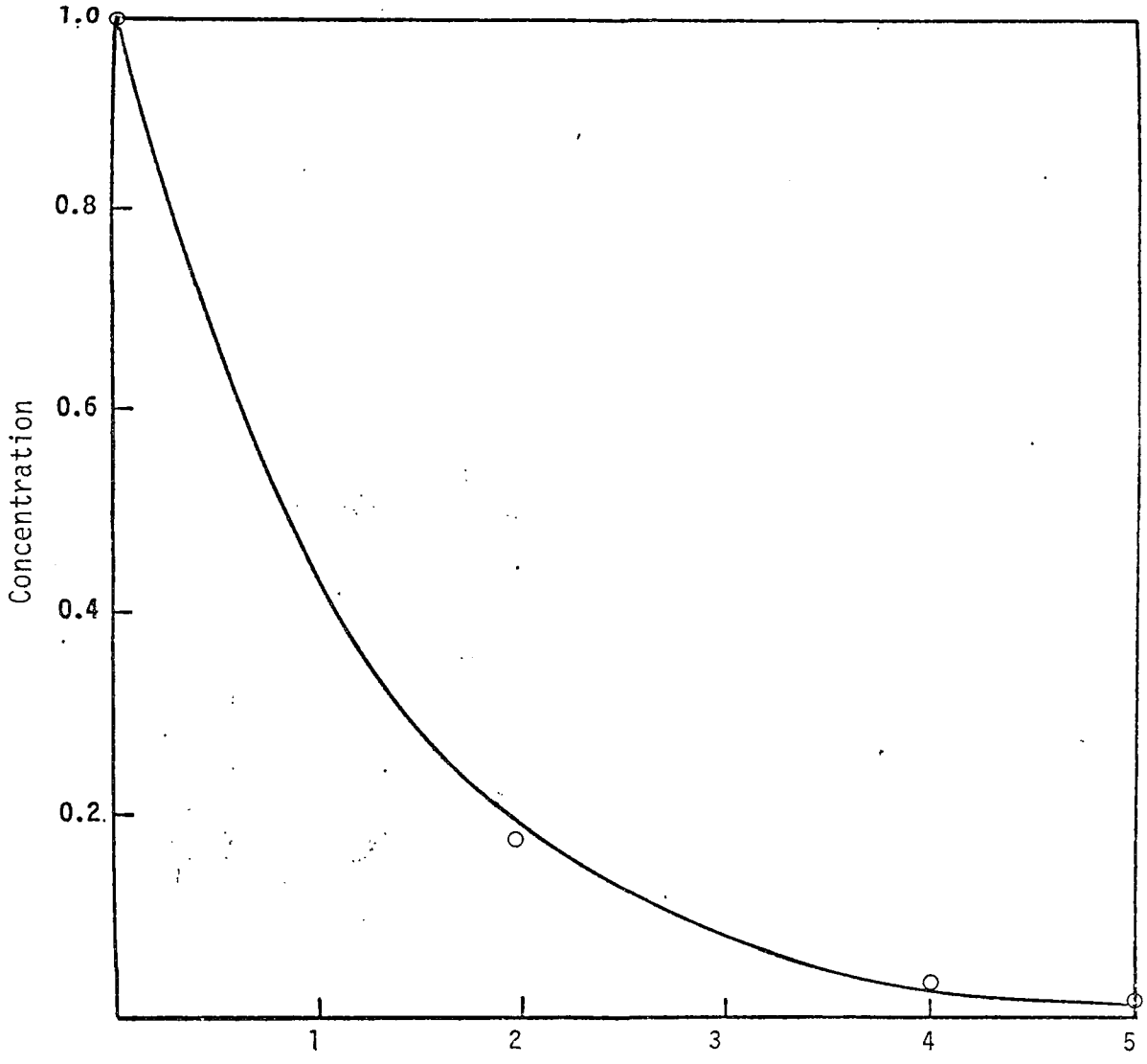
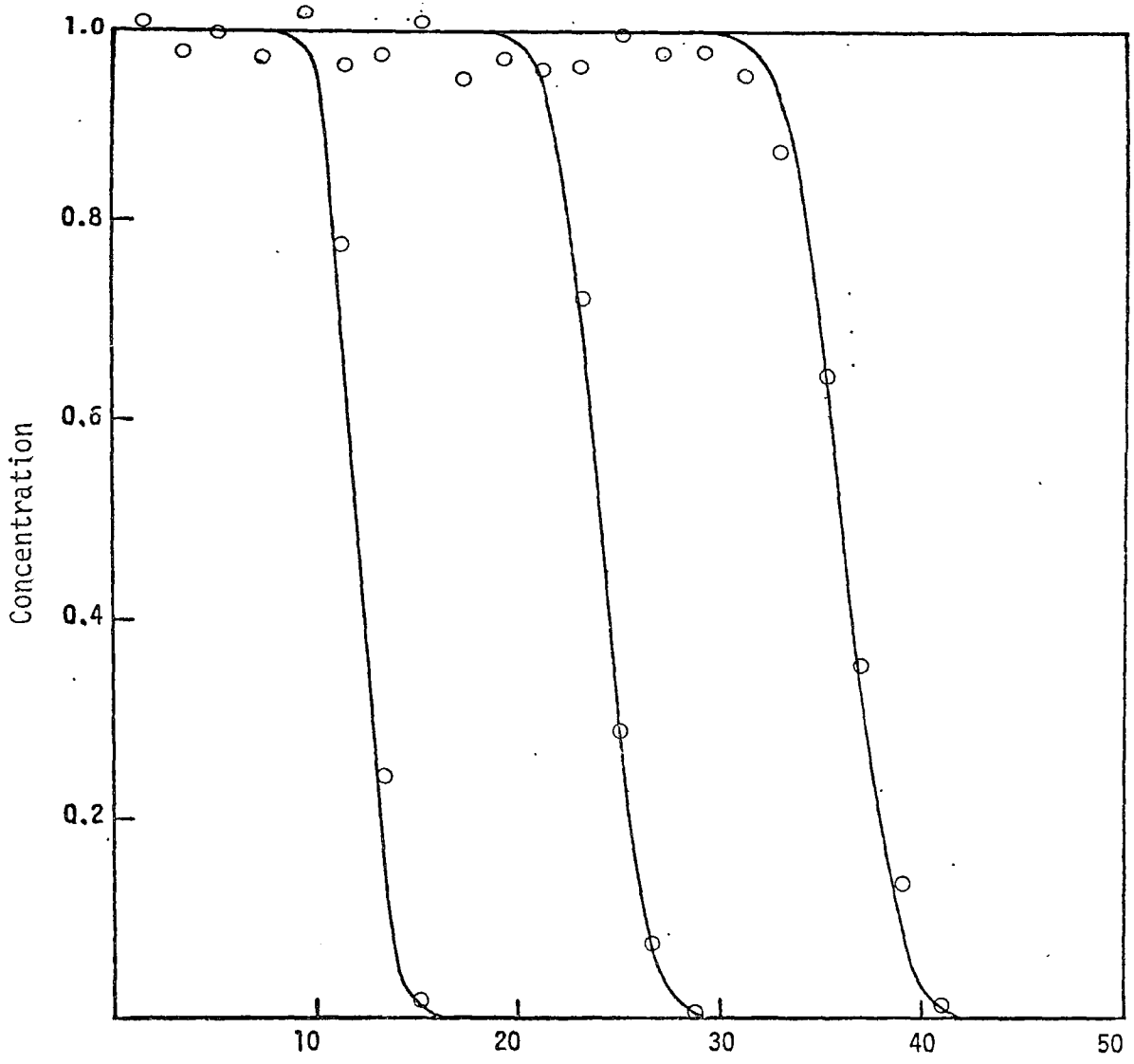


FIGURE 27. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE GALERKIN METHOD (Continued)



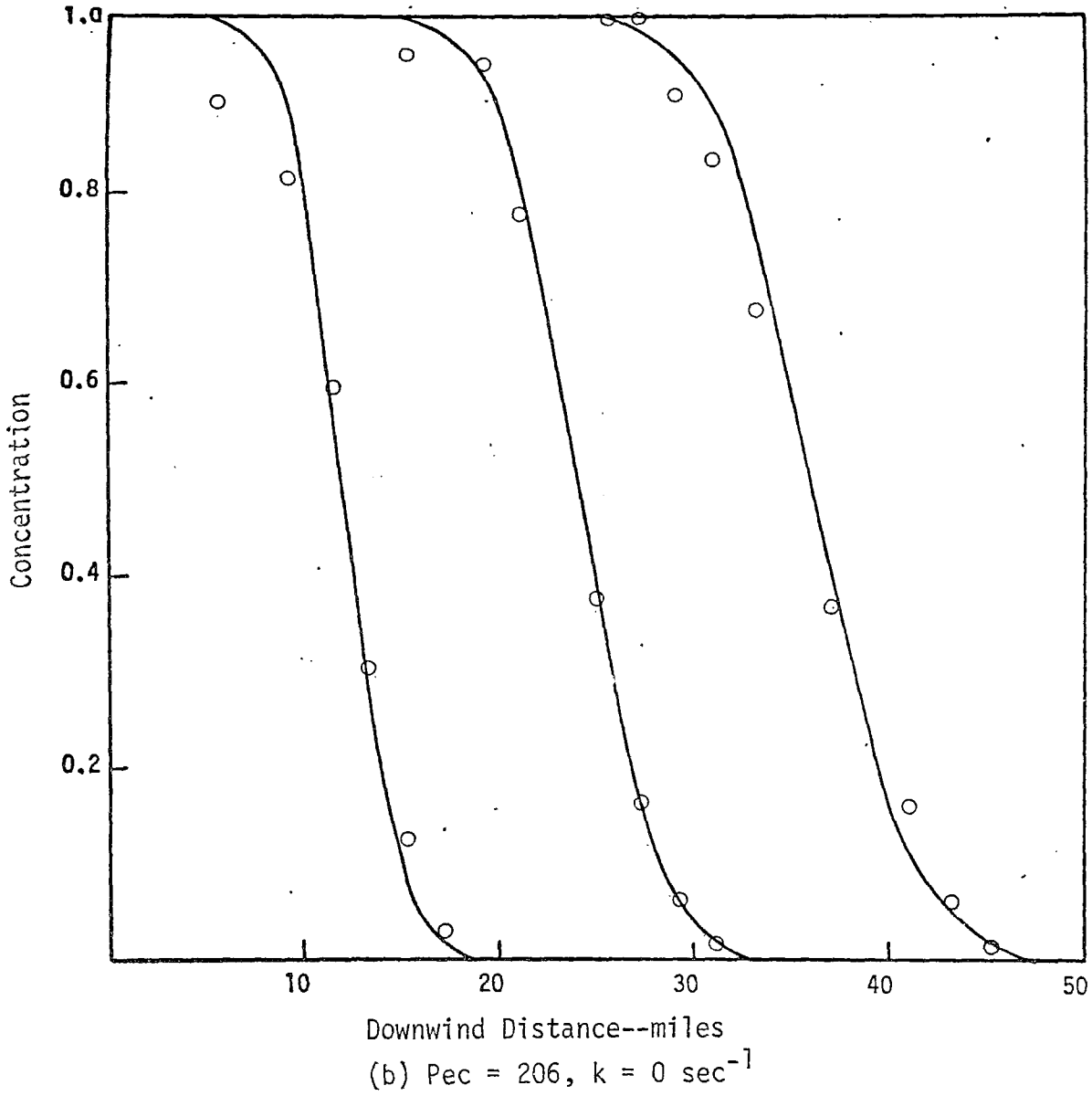
(e) Pec = 720, $k = 10^{-3}$ sec^{-1}

FIGURE 27. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE GALERKIN METHOD (Continued)



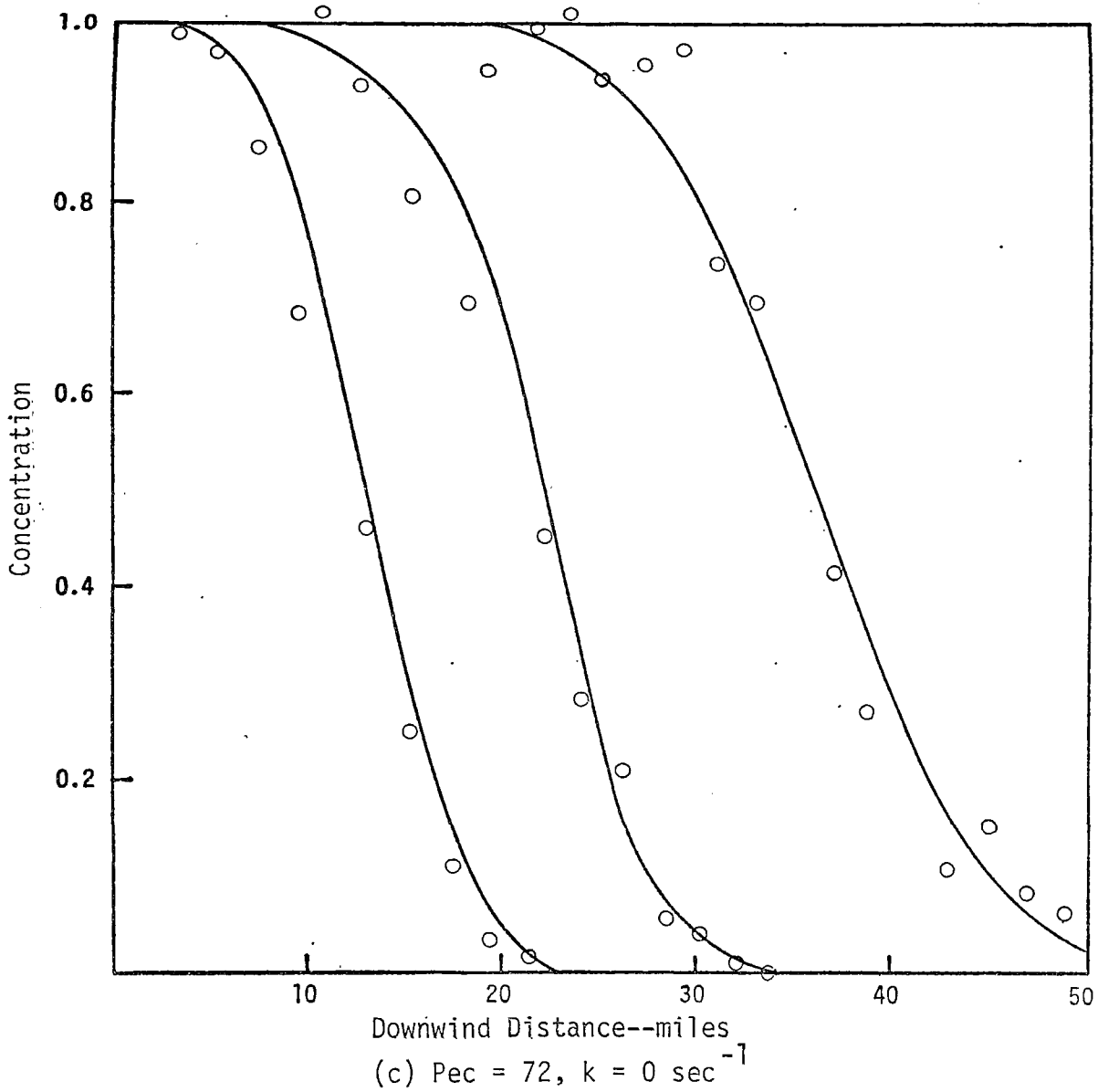
(a) Pec = 720, k = 0 sec^{-1}

FIGURE 28. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE PARTICLE-IN-CELL (SMOOTHED) METHODS



(b) Pec = 206, k = 0 sec^{-1}

FIGURE 28. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE PARTICLE-IN-CELL (SMOOTHED) METHODS (Continued)



(c) Pec = 72, k = 0 sec^{-1}

FIGURE 28. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE PARTICLE-IN-CELL (SMOOTHED) METHODS (Continued)

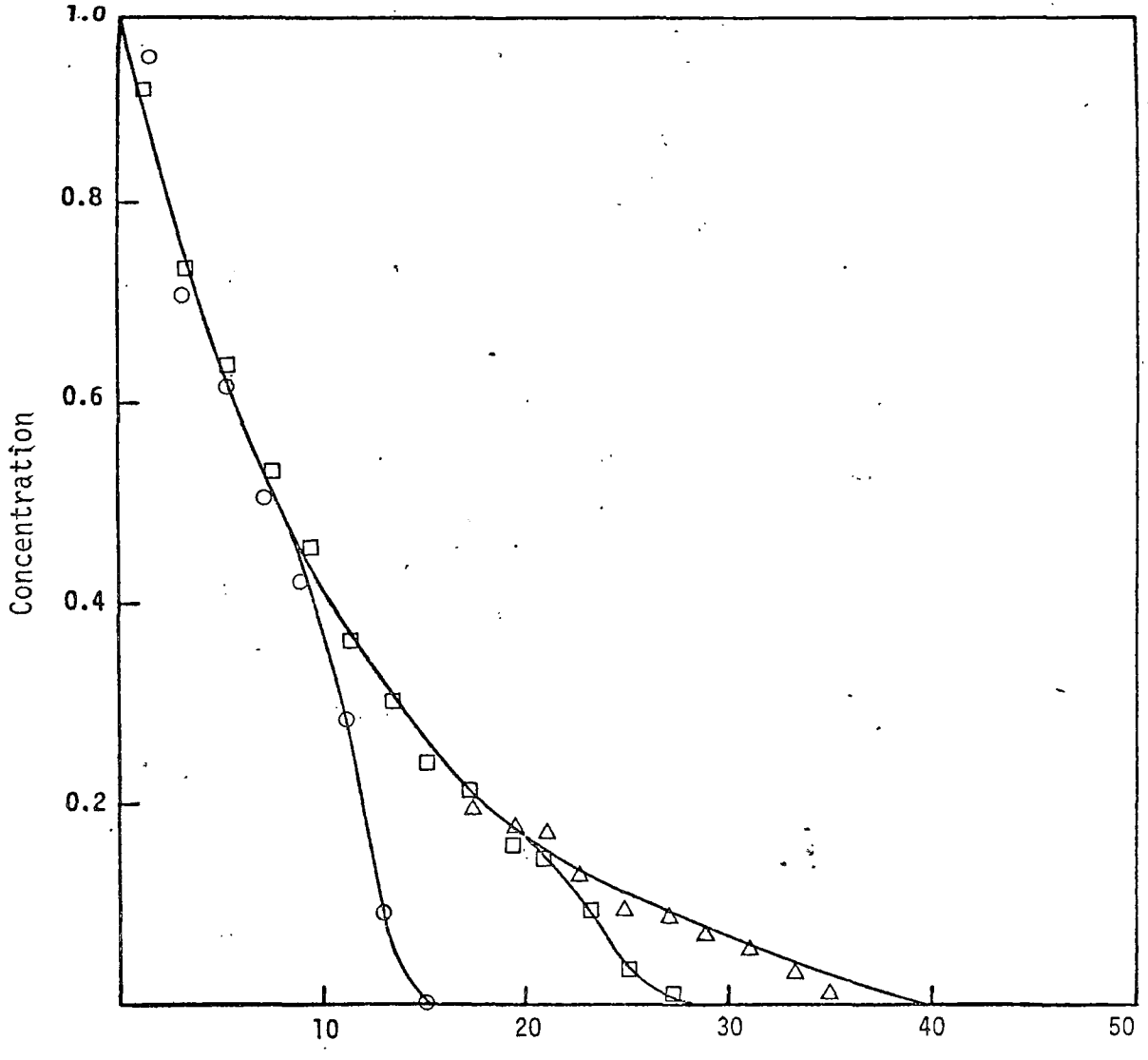


FIGURE 28. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE PARTICLE-IN-CELL (SMOOTHED) METHODS (Continued)

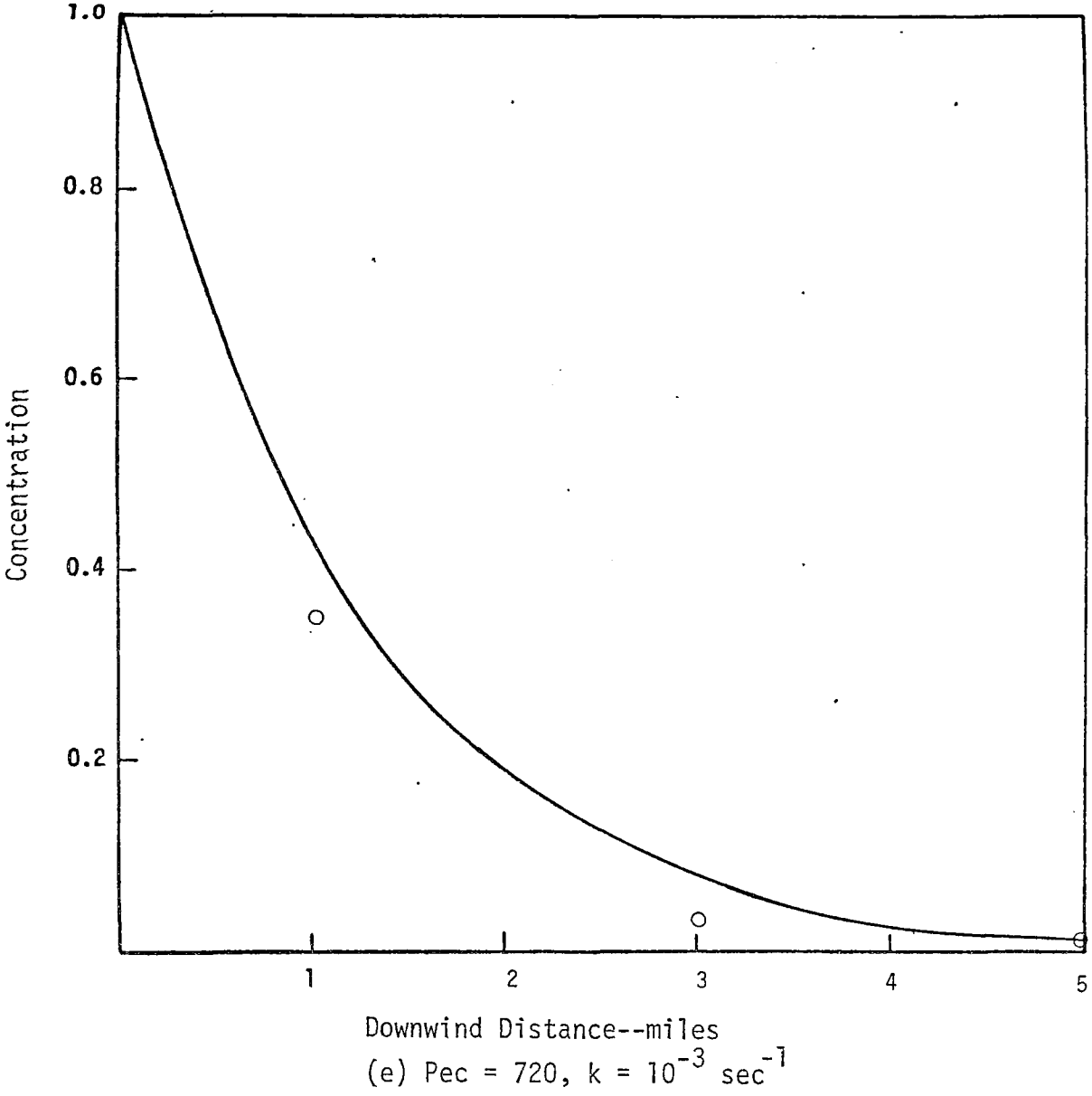


FIGURE 28. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE PARTICLE-IN-CELL (SMOOTHED) METHODS (Concluded)

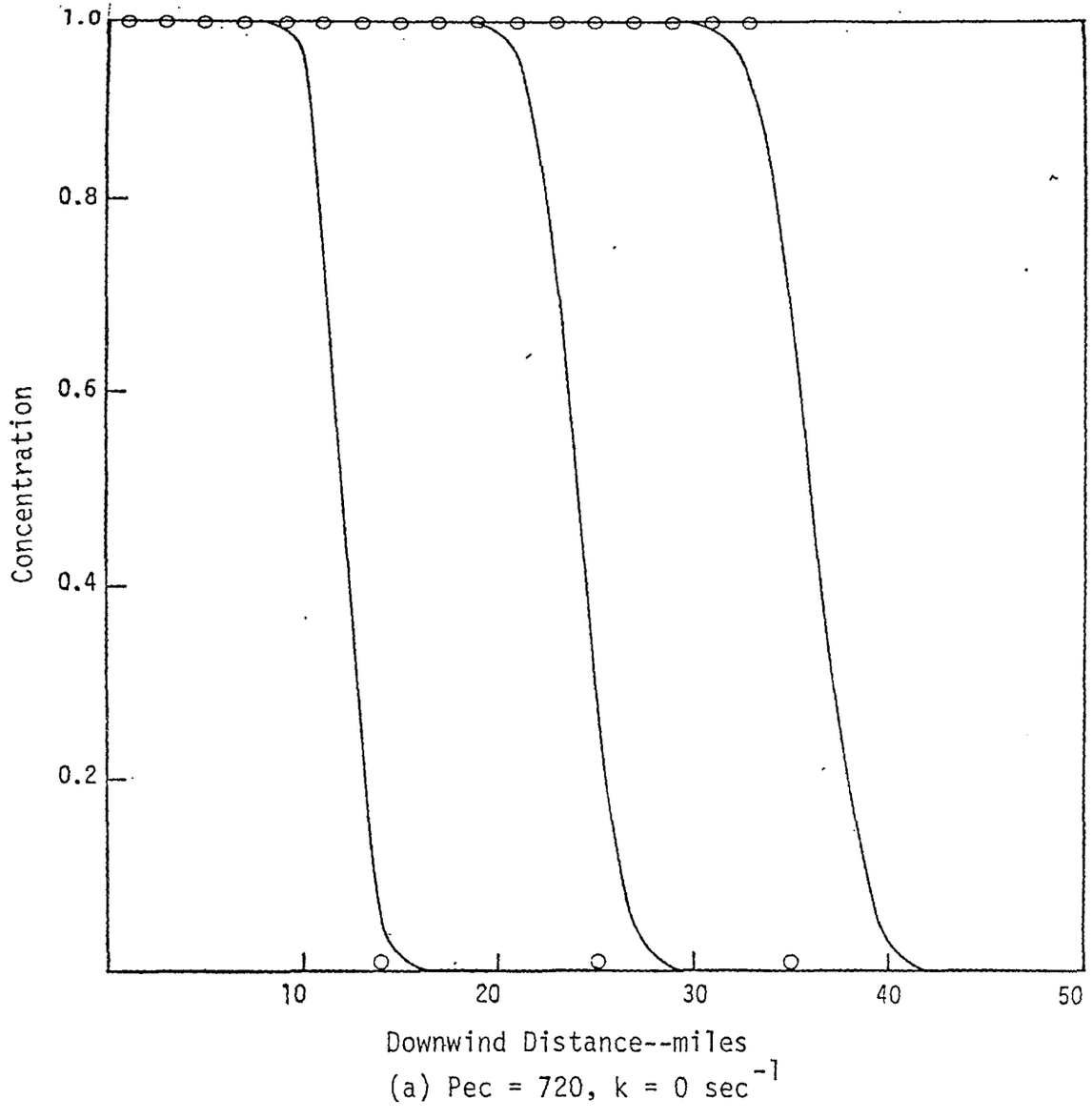


FIGURE 29. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE EGAN AND MAHONEY METHOD

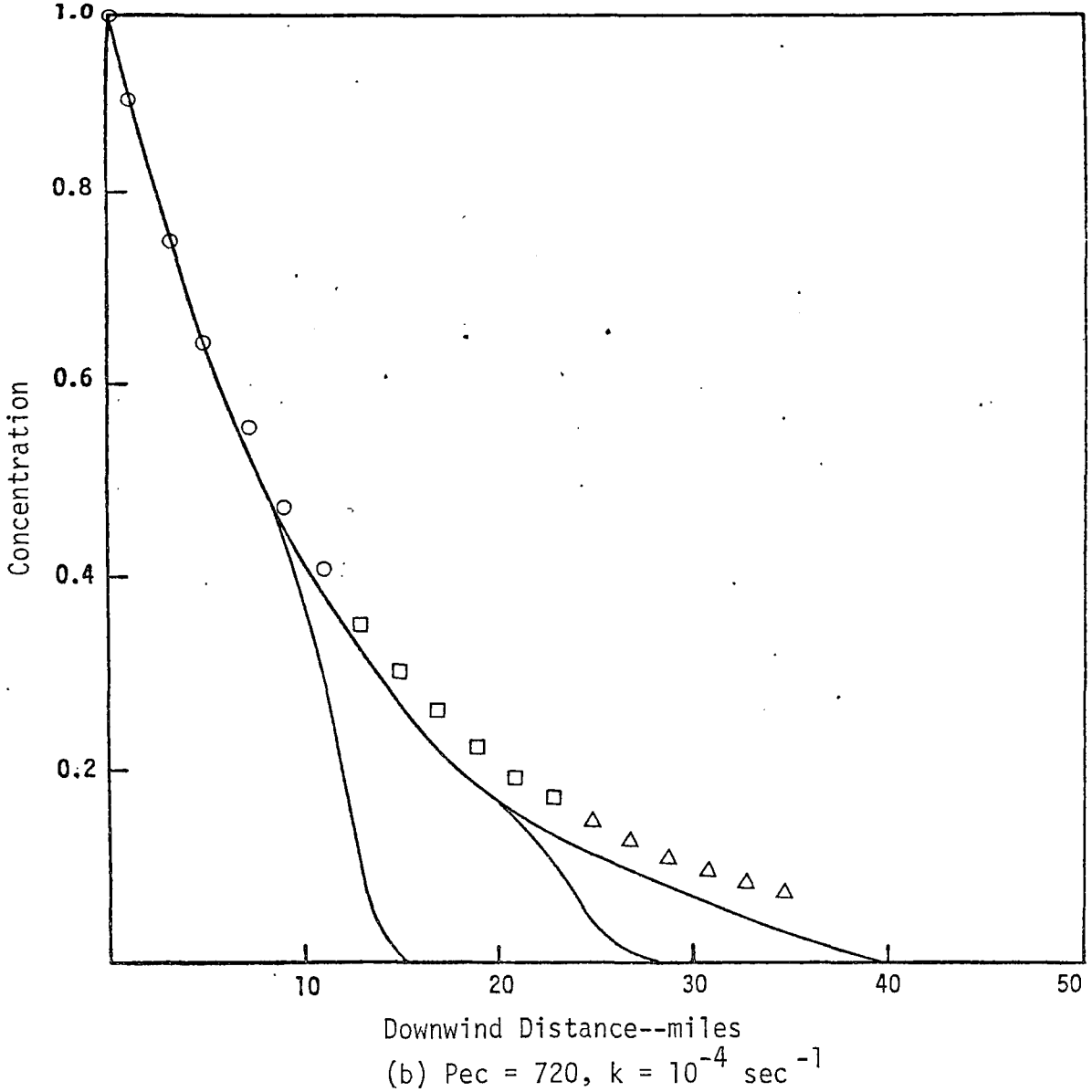


FIGURE 29. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE EGAN AND MAHONEY METHOD (Continued)

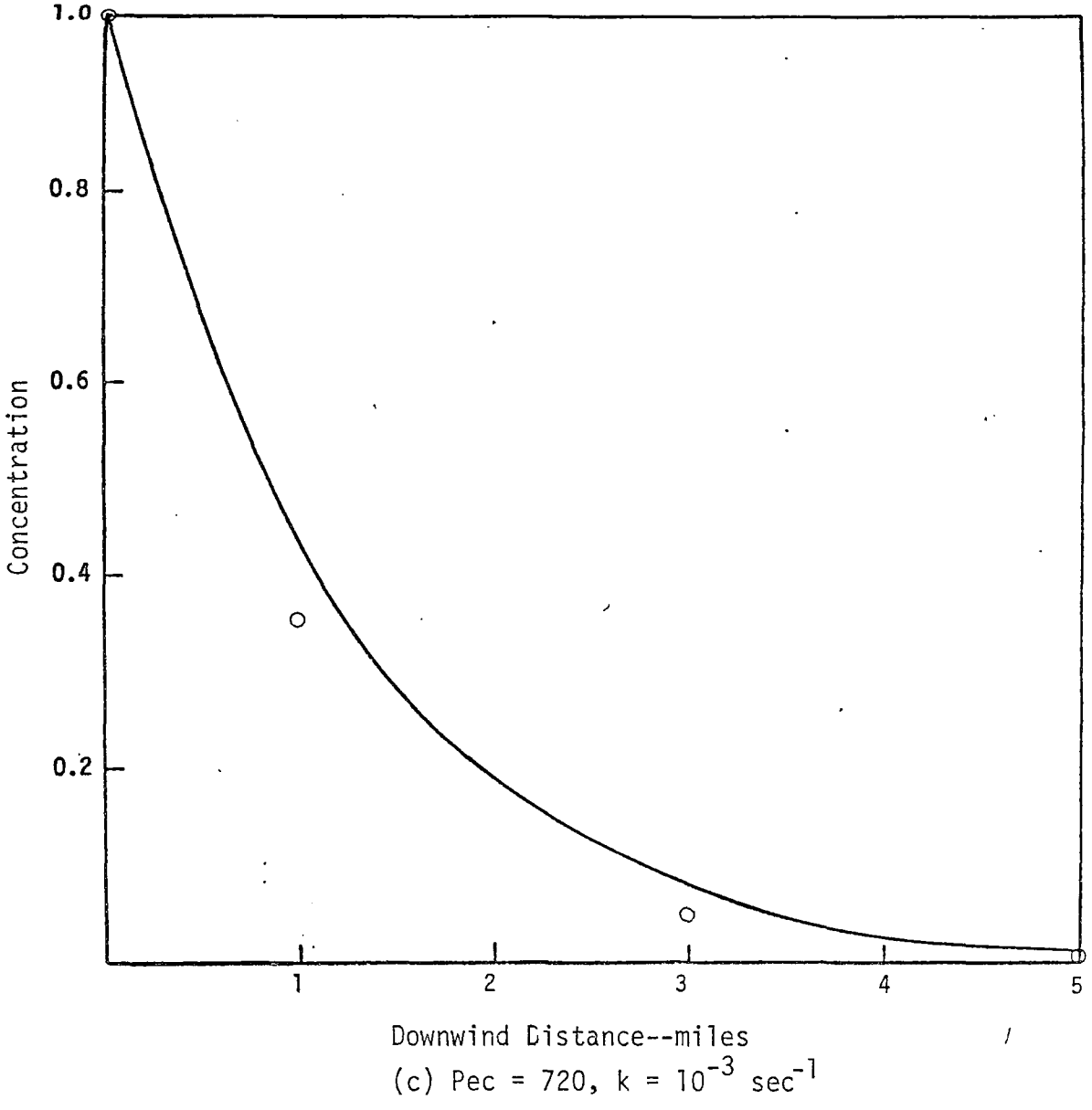


FIGURE 29. CONCENTRATION AS A FUNCTION OF DOWNWIND DISTANCE FOR THE EGAN AND MAHONEY METHOD (Concluded)

7. Computational Time

Concurrent with any appraisal of the accuracy associated with alternative solution techniques must be a comparison of the computing times required for these methods. Although a particular method may be extremely accurate, the computational time it requires may be so large that a less accurate, more efficient algorithm would be a better choice. Table 27 lists the computing times for the various methods surveyed in this study.

Table 27

COMPUTING TIME REQUIRED FOR ALTERNATIVE SOLUTION METHODS

Method	Computing Time (sec)
Price--explicit	7.50
Price--implicit	11.10
Crowley--second order	7.40
Crowley--fourth order	7.40
SHASTA	7.95
Galerkin	13.2
Egan and Mahoney	1.10
Particle-in-cell	68.2

Note that all of the explicit finite difference methods use approximately the same amount of computing time (approximately 7.5 seconds). Of the implicit schemes, only a slight difference exists between the Galerkin and the Price methods. Obviously, the accuracy more than compensates for the larger computational time. Finally, the particle-in-cell methods are extremely costly in computing time and should be used only as a last resort.

E. CONCLUSIONS

The selection of a solution algorithm for a set of partial differential equations should be based on considerations of both speed and accuracy. For the methods surveyed in this analysis, we drew the following conclusions:

- For a rapid explicit scheme, the SHASTA technique should be chosen. Not only is the method accurate and efficient, but also it is guaranteed not to predict negative concentrations in areas having steep concentration gradients. This latter quality greatly enhances the appeal of the SHASTA method over competing schemes.
- In those cases in which extremely high resolution is desirable, it is advisable to develop a Galerkin algorithm for the transport equation. The increase in accuracy, stability, and ease of modeling irregularly spaced regimes more than offsets the increased cost in computational time.
- As more information becomes available in the open literature, the Egan and Mahoney method should be explored as a possible supplement or replacement for either the SHASTA or the Galerkin scheme.
- Finite difference techniques introduce a considerable amount of numerical diffusion into the calculation, producing an overprediction of pollutant concentrations downwind from the source. The effect is most pronounced using the Price scheme and is somewhat smaller using the Crowley second- and fourth-order systems. The Crowley fourth-order scheme tends to be more accurate than the corresponding second-order scheme in regions having a steep concentration gradient, though the fourth-order scheme frequently predicts negative concentrations in regions in which complex flow fields exist. Regardless of the technique used, finite difference methods are inaccurate for systems in which extremely fast reactions occur.

> The particle-in-cell technique developed by Sklarew (1971) is accurate for both reactive and nonreactive systems, provided that a sufficient number of particles is used in the simulation. However, the time required for the simulation for a given accuracy can be prohitively excessive and can thus invalidate the use of the technique.

In conclusion, we wish to caution the reader about interpreting the results obtained in this study: These results were developed for a simple one-dimensional, time-dependent problem in which a simple first-order reaction occurs. In a real situation, this idealized model can easily be invalidated by a complex flow field, a set of nonlinear reactions, or a complicated source emissions pattern. In essence, this analysis focused on one aspect of the complete problem: the identification and assessment of the errors associated with the solution of the one-dimensional advection-diffusion equation. The study did not treat problems that are associated with the method of fractional steps, nor did it consider systems in which nonlinearities occur (as they frequently do in the real world). Yet, since the numerical diffusion associated with finite difference techniques is considerable, the results of this study serve as a benchmark for identifying those schemes that are the most accurate in a one-dimensional sense. If one can assume that this accuracy is maintained throughout the entire solution, then the application of the most promising of these techniques to the current SAI model will most likely produce--but cannot guarantee--an improvement in the results.

V AIRSHED MODEL MODIFICATION FOR MULTIDAY SIMULATION

Steven D. Reynolds
Jody Ames

A. INTRODUCTION

In the past, the application of the SAI airshed model has been limited to the simulation of one daytime period (usually 5 a.m. to 3 p.m.). During the present study, we adapted the model for multiday runs. The two most important benefits to be derived from multiday simulations are the following:

> Treatment of multiday episodes. A primary objective of adapting models to perform multiday computations is to provide the basis for evaluating the effectiveness of air pollution control strategies. For example, difficulties in specifying initial conditions for some future year can be averted by performing a multiday run, since the predictions on the second and subsequent days are generally less sensitive to the choice of the initial concentration distribution input to the model. Also of interest is the short range prediction of the ground-level pollutant concentrations for strategies such as those that might be put into effect when meteorological conditions conducive to severe pollution episodes occur.

> Identification of errors. Multiday simulations will be instrumental in establishing possible sources of error in the airshed model. Errors incurred in a short term simulation (say, less than 12 hours) would not accumulate to the extent that they would over a two- or three-day period. As an example, suppose that the predicted concentrations of total nitrogen oxides were much higher than measured values after a simulation of several days. This might suggest that either NO_x emissions are too high or sinks of NO_x have not been properly accounted for in the model.

One obvious difficulty that might preclude usage of the model for multiday runs is the accumulation of errors introduced by the numerical integration scheme. But as noted in the previous chapter, several promising numerical techniques are available that--if implemented in the model--should reduce numerical error propagation significantly.

In modifying the SAI model, we considered the following aspects of multiday usage:

- Treatment of photochemistry at night.
- Definition of the modeling region.
- Use of a grid with variable resolution.
- Generalization of the finite difference solution technique for use on a grid with variable vertical resolution.
- Modification of the computer codes.

Furthermore, to obtain some experience in the performance of multiday runs, we prepared a set of emissions, meteorological, and air quality inputs applicable to the Los Angeles basin on 29 and 30 September 1969. These are two days that we studied under a previous EPA contract (68-02-0339). Using these days, we were able to compare results from the multiday simulation with those obtained from the corresponding 5 a.m. to 3 p.m. runs made previously. Of particular interest is the comparison of the two sets of predictions at 3 p.m. on 30 September to determine to what extent the two sets of predictions agree.

In the following sections, we summarize our efforts in each of the pursuits listed above.

B. MODEL REFINEMENTS

1. Treatment of Photochemistry at Night

The primary objectives of this study were to examine the suitability of the kinetic mechanism employed in the airshed model for performing nighttime simulations and to determine whether chemical reaction effects can be ignored during a portion of the nighttime period to reduce computing costs. In addition, we wished to obtain some experience in running the model at night, since previous efforts were limited to the simulation of single daytime periods of 10 hours in duration. Because of the difficulties we experienced in incorporating the expanded 36-step mechanism in the airshed model, we decided to try to use the original version of the airshed model, which treats the kinetics using a 15-step mechanism.

To determine the applicability of the original 15-step kinetic mechanism employed in the airshed model (see Hecht, 1972) for use at night, we performed several "numerical" smog chamber simulations with photolysis rate constants set to only a small fraction of their nominal values. Since sunlight is one of the most important driving forces in the mechanism, we expected the photochemical processes to be slowed considerably after sunset. We set k_1 (the NO_2 photolysis rate constant) equal to 0.01 min^{-1} [the remaining rate constants and stoichiometric coefficients were assumed to be equal to those employed in the 29 September 1969 validation study (see Reynolds et al., 1973)] and employed the following initial conditions:

Species	Initial Concentration (ppm)
RHC	0.4
NO	0.5
NO_2	0.15
CO	15.0

The model predicted the following concentrations after eight hours:

Species	Concentration (ppm)
RHC	0.30
NO	0.32
NO_2	0.32

These results clearly indicate that substantial chemical conversion is predicted in the absence of strong sunlight.

Since we expected the predicted concentrations to change only slightly from the initial conditions, we hypothesized that the HNO_2 steady-state assumption was responsible for the large change in concentrations. The RHC, NO, NO_2, and O_3 concentrations predicted by the mechanism are independent of the value of k_7 (the HNO_2 photolysis rate constant) used when HNO_2 is assumed to be in a pseudo-steady state. We then carried out a second simulation, which was similar in all respects to the first except that HNO_2 was <u>not</u> assumed to be in a steady state. The results of this simulation after eight hours were as follows:

Species	Concentration (ppm)
RHC	0.38
NO	0.45
NO_2	0.17

These results indicate that considerably less chemical conversion is realized when it is assumed that $d(HNO_2)/dt \neq 0$.

As a final check on the old SAI mechanism employed above, we performed an eight-hour simulation using the new SAI mechanism currently being validated. The purpose of this test was to use the best available kinetic mechanism to obtain an estimate of how much chemical reaction takes place in the absence of intense sunlight. Assuming RHC to be entirely propylene, k_1 to be equal to 0.01 min^{-1} (other photolysis rate constants were scaled accordingly), and initial conditions to be the same as those cited previously, the new mechanism predicted the following concentrations after eight hours:

Species	Concentration (ppm)
RHC	0.38
NO	0.45
NO_2	0.18

These results reinforce our initial belief that the HNO_2 steady-state assumption is responsible for the observed conversion of NO to NO_2 in the 15-step mechanism.

It appears from the results of these tests that the 15-step kinetic mechanism previously employed in the airshed model with HNO_2 in a steady state will not be suitable for carrying out photochemical calculations at night. Since considerable effort would be required to remove the HNO_2 steady-state constraint from the old airshed model and, furthermore, since we are replacing the 15-step mechanism with the new expanded mechanism (in which HNO_2 is not assumed to be in a steady state), we decided to defer further study of the treatment of photochemistry at night. This effort should be resumed, however, when further experience is obtained in using the new mechanism in actual airshed simulations.

After reviewing the results of the smog chamber runs cited above, we found that we may be able to drop some, or perhaps all, of the reaction terms in the governing equations during a portion of the nighttime period. If this is possible, then computing requirements can be reduced significantly. And since we are concerned with multiday runs, it is especially important to find ways of reducing the costs of such simulations. To study further the possibility of modifying the treatment of chemistry at night, we need to perform appropriate nighttime simulations, both with and without chemistry in the model, to determine whether and when chemical reaction effects can be ignored. If the chemistry cannot be completely omitted from the model, perhaps the mechanism can be simplified.

2. Definition of the Modeling Region

To minimize errors resulting from the need to specify pollutant concentrations at points of transport into the modeling area, one should choose boundaries of the region such that either background levels or actual measurements can be

used to estimate the boundary conditions. In previous simulations of pollutants in the Los Angeles basin, we exercised particular care to account properly for pollutants transported into the region from areas over the ocean and aloft (i.e., contaminants originally residing in the inversion layer and subsequently injected into the mixed layer as the inversion was eroded by convective heating). Although significant amounts of pollutants are often carried out over the ocean at night, it is usually difficult to estimate the concentration levels in the returning off-shore air mass because of the absence of appropriate measurements. To employ background concentrations as the boundary conditions, one must model both the urban area of interest and a portion of the surrounding environs (suburban, rural, and ocean areas). In addition, the upper boundary of the modeling region should be defined at that elevation where background levels generally exist (1 to 2 kilometers should be sufficient). Thus, we modified our original treatment of the vertical extent of the model from the region between the ground and the inversion base to the region between the ground and a user-specified surface aloft. As an example, one could define the top of the region to correspond to the top of the inversion layer. The trapping effect of an elevated inversion layer within the model is treated through the z-dependence of the vertical diffusivity.

3. Use of a Grid with Variable Resolution

For efficient modeling of an urban area and a portion of its surroundings, a grid with variable resolution should be used. Choosing the appropriate degree of resolution in a particular area of the airshed depends primarily on the spatial characteristics of gradients in the concentration field. In areas where gradients are large, a relatively fine grid should be used; where gradients are small, a relatively coarse mesh spacing may be adequate. With respect to horizontal grid resolution, the mesh spacing in the outlying areas could be, say, two to four times that used over the urban center. Because many sources are located at "ground level," the vertical concentration gradient is often greatest near the surface. Thus, it may be advantageous to use fine vertical spacing near the ground and coarse spacing aloft. Since the numerical technique currently employed in the model is not readily adaptable for variable horizontal grid resolution, we developed only variable vertical grid resolution capabilities during this study.

However, inclusion of a variable horizontal mesh in the model, possibly using a nested grid approach, should be considered in future efforts to incorporate improved numerical solution techniques in the model.

4. Modification of the Finite Difference Equations

Because the finite difference equations previously employed in the model were derived for an equally spaced grid, it was necessary to modify the difference expressions involving derivatives of the concentration field in the z (or ρ) direction. [See Reynolds (1973) for a discussion of the numerical integration procedure.] In particular, changes were required in the advective and diffusive flux terms in Step III of the numerical integration technique. As an illustration of the nature of the changes made, Eqs. (44) through (54) in Reynolds (1973) become:

$$
\begin{aligned}
{}_{\ell}C^{n+1}_{i,j,k} = {}_{\ell}C^{**}_{i,j,k} \frac{\Delta H^{n}_{i,j}}{\Delta H^{n+1}_{i,j}} + \frac{\Delta\tau}{2\Delta\rho_k \Delta H^{n+1}_{i,j}} \Bigg({}_{\ell}F^{n+1}_{i,j,k-\frac{1}{2}} + {}_{\ell}F^{**}_{i,j,k-\frac{1}{2}} \\
- {}_{\ell}F^{n+1}_{i,j,k+\frac{1}{2}} - {}_{\ell}F^{**}_{i,j,k+\frac{1}{2}} \Bigg) + \frac{\Delta\tau}{2\Delta H^{n+1}_{i,j}} \Bigg({}_{\ell}R^{n+1}_{i,j,k} \, \Delta H^{n+1}_{i,j} \\
+ {}_{\ell}R^{**}_{i,j,k} \, \Delta H^{n}_{i,j} \Bigg) + \frac{\Delta\tau}{2\Delta H^{n+1}_{i,j}} \Bigg({}_{\ell}S^{n+1}_{i,j,k} \, \Delta H^{n+1}_{i,j} + {}_{\ell}S^{n}_{i,j,k} \, \Delta H^{n}_{i,j} \Bigg) \quad , \qquad (104)
\end{aligned}
$$

where

$$
\begin{aligned}
{}_{\ell}F^{n+1}_{i,j,k-\frac{1}{2}} = \frac{\phi^{n+1}_{i,j,k-\frac{1}{2}}}{2} \Bigg(\lambda_k \, {}_{\ell}C^{n+1}_{i,j,k-1} + (1 - \lambda_k) \, {}_{\ell}C^{n+1}_{i,j,k} \Bigg) \\
+ \mu^{n+1}_{i,j,k-\frac{1}{2}} \Bigg({}_{\ell}C^{n+1}_{i,j,k-1} - {}_{\ell}C^{n+1}_{i,j,k} \Bigg) \quad , \quad k = 2, 3, \ldots, K \quad . \qquad (105)
\end{aligned}
$$

$$ {}_{\ell}F^{**}_{i,j,k-\frac{1}{2}} = \frac{\phi^{n}_{i,j,k-\frac{1}{2}}}{2}\left(\lambda_k \, {}_{\ell}C^{**}_{i,j,k-1} + (1 - \lambda_k) \, {}_{\ell}C^{**}_{i,j,k}\right) $$

$$ + \mu^{n}_{i,j,k-\frac{1}{2}}\left({}_{\ell}C^{**}_{i,j,k-1} - {}_{\ell}C^{**}_{i,j,k}\right) \quad , \quad k = 2, 3, \ldots, K \tag{106} $$

$$ \phi^{n}_{i,j,k-\frac{1}{2}} = W^{n}_{i,j,k-\frac{1}{2}} \quad . \tag{107} $$

$$ \mu^{n}_{i,j,k-\frac{1}{2}} = \frac{V^{Kn}_{i,j,k-\frac{1}{2}}}{0.5\,(\Delta\rho_{k-1} + \Delta\rho_k)\,\Delta H^{n}_{i,j}} \quad . \tag{108} $$

$$ \lambda_k = \frac{\Delta\rho_k}{\Delta\rho_{k-1} + \Delta\rho_k} \quad . $$

In view of the discussion given in the previous section, ρ is now defined by the following relationship:

$$ \rho = \frac{z - h(x,y)}{H(x,y,t) - h(x,y)} \quad , $$

where

$h(x,y)$ = terrain elevation,
$H(x,y,t)$ = elevation of the upper boundary of the modeling region,
$\Delta\rho_k$ = the dimensionless height of the k-th level grid cell.

The boundary conditions at the ground and aloft are the following:

(1) $\rho = 0$

$$ {}_{\ell}F^{n+1}_{i,j,\frac{1}{2}} = {}_{\ell}Q^{n+1}_{i,j} \quad , \tag{109} $$

$$ {}_{\ell}F^{**}_{i,j,\frac{1}{2}} = {}_{\ell}Q^{n}_{i,j} \quad , \tag{110} $$

where $k = 1/2$ is equivalent to $\rho = 0$.

(2) $\rho = 1$

$$F^{n+1}_{i,j,K+\frac{1}{2}} = \phi^{n+1}_{i,j,K+\frac{1}{2}}\, \ell g^{n+1}_{i,j,K+\frac{1}{2}} \quad \text{if} \quad \phi^{n+1}_{i,j,K+\frac{1}{2}} \leq 0 \quad ,, \qquad (111)$$

$$\ell F^{n+1}_{i,j,K+\frac{1}{2}} = \phi^{n+1}_{i,j,K+\frac{1}{2}}\, \ell C^{n+1}_{i,j,K} \quad \text{if} \quad \phi^{n+1}_{i,j,K+\frac{1}{2}} > 0 \quad , \qquad (112)$$

$$\ell F^{**}_{i,j,K+\frac{1}{2}} = \phi^{n}_{i,j,K+\frac{1}{2}}\, \ell g^{n}_{i,j,K+\frac{1}{2}} \quad \text{if} \quad \phi^{n}_{i,j,K+\frac{1}{2}} \leq 0 \quad , \qquad (113)$$

$$\ell F^{**}_{i,j,K+\frac{1}{2}} = {}^{n}_{i,j,K+\frac{1}{2}}\, \ell C^{**}_{i,j,K} \quad \text{if} \quad \phi^{n}_{i,j,K+\frac{1}{2}} > 0 \quad , \qquad (114)$$

where $k = K + \frac{1}{2}$ is equivalent to $\rho = 1$.

Changes in the matrix expressions given in Eqs. (55) through (70) of Reynolds (1973) follow directly from the difference equations given above.

5. Modification of the Computer Codes

To carry out multiday simulations, we modified several portions of the computer programs. These changes essentially make the codes more general. Furthermore, the main code now allows the user to use a grid with variable vertical resolution, where the spacing interval is treated as a model input. As an example, in the Los Angeles simulation, which is discussed in the next section, we used a grid with 10 vertical levels and the following mesh spacing:

Level	Grid Spacing (feet)
10 (top)	1625
9	825
8	425
7	225
6	125
5	75
4	50
3	50
2	50
1 (ground level)	50

Thus, the modeling region is assumed to extend from the ground to an elevation of 3500 feet above the terrain. In addition, we implemented appropriate changes, corresponding to the discussion given in the previous section, in the coding of the finite difference equations.

In addition to the above-mentioned changes, we restructured the input data deck setup to operate in the following manner. First, all parameters global to the run--i.e., those parameters that would not be expected to vary from day to day--are input. Then, the remaining inputs are arranged in daily packets, one packet for each day to be simulated. When the simulation reaches midnight, the input packet for the next day is read from the input file. After the first day, some daily parameters can be omitted from the input packet, and the values used on the previous day can be used again.

We also included provisions that allow the user to establish multiple emission files for the input of emissions data to the program. For example, one might establish two sets of emissions, one applicable to weekdays and the other suitable for weekends. Once such a set of files is established for an urban area, multiday runs consisting of any pattern of weekdays and weekends can be simulated. Table 28 illustrates the deck setup and lists some of the main parameters included as part of the global and daily inputs.

C. MULTIDAY SIMULATION OF THE LOS ANGELES BASIN

1. Preparation of Emissions and Meteorological Inputs

Since previous applications of the airshed model were limited to the simulation of a 10-hour daylight portion of each of six days in 1969, little consideration was given to the definition of emissions and meteorological inputs for use at night. Thus, to gain experience in the performance of multiday runs with the SAI model, we carried out a necessarily limited effort to estimate meteorological and emission inputs that would apply during the period from 3 p.m. on 29 September to 5 a.m. on 30 September 1969 (previous simulations were carried out for the 5 a.m. to 3 p.m. period on both 29 and 30 September 1969). In particular, we performed the following tasks:

Table 28

ORGANIZATION OF MULTIDAY INPUT

Global data

- Run heading
- Simulation options and grid definition
- Start and stop times and dates
- I/O units
- Print options for maps
- Region definition
- Stations and landmarks
- Integration parameters and stoichiometric coefficients
- Activation energies
- Initial Conditions

Day 1 packet

- Date, emissions type, input controls
- Rate constants
- Light intensity factors
- Deposition velocities
- Concentrations aloft
- Point source emissions
- Boundary conditions

Day 2 packet

- Date, emissions type, input controls
- Rate constants*
- Light intensity factors*
- Deposition velocities*
- Concentrations aloft*
- Point source emissions*
- Boundary conditions*

Day 3 packet

.
.
.

* Can be omitted after Day 1.

- We used the SAI automated wind field analysis package to generate hourly wind speed and direction maps spanning the period from 5 a.m. on 29 September to 3 p.m. on 30 September 1969.
- We employed the SAI automated inversion analysis program to estimate hourly mixing depth maps, using actual observed mixing depths available for the daytime periods to the extent possible. We examined nighttime temperature profiles measured by Meteorological Research, Incorporated in the Los Angeles basin during the summer of 1973 and estimated that pollutants would typically be mixed throughout a depth of about 60 to 70 meters at night.
- We prepared a set of fixed-source emission maps for hydrocarbons and NO_x that are applicable from 6 p.m. to 6 a.m. the following morning; the original SAI fixed-source maps were dervied for the complementary 12-hour period. Using data presented in Appendix A of Roth et al. (1971), we estimated that about 25.5 tons of NO_x and 30 tons of low reactivity hydrocarbons are emitted in the modeling region between 6 p.m. and 6 a.m.
- We specified boundary conditions at points of horizontal inflow into the model between 3 p.m. on 29 September and 5 a.m. on 30 September. Boundary conditions at other hours were available from the model validation studies reported in Reynolds et al. (1973).

At this point, it is appropriate to note that the paucity of meteorological and emissions data applicable specifically during the nighttime hours makes the estimation of mixing depths and emission rates highly uncertain. The primary objective of our present effort was simply to assemble a set of "reasonable" inputs that can be used in tests of the multiday version of the SAI airshed model. Further efforts should be made to refine the temporal distribution of surface street and freeway traffic activity and the spatial and temporal distributions of the HC and NO_x emissions from stationary sources at night [see Roberts et al., (1971)].

2. Discussion of the Multiday Simulation Results

To test the various modifications made in both the structure of the model and the computer codes, we performed a multiday simulation of pollutant concen-

trations in the Los Angeles basin. As noted in Section B-1, we decided that the 15-step chemical kinetic mechanism employed in the model is inappropriate for use at night. Thus, the simulation reported here was carried out for CO alone. When an appropriate set of emissions inputs suitable for usage with the new mechanism can be developed, multiday photochemical simulations should be undertaken.

Plots of predicted and measured CO concentrations at the downtown Los Angeles, Long Beach, West Los Angeles, Burbank, Reseda, Whittier, and Azusa stations are given in Figures 30 through 36, respectively. The simulation extends from 5 a.m. PST on 29 September to 3 p.m. PST on 30 September 1969. The results for the 5 a.m. to 3 p.m. period on 29 September are very similar to those obtained in the previously reported SAI validation effort. (Discrepancies in the two sets of predicted results are due to the manner in which the meteorological variables were specified--automatically in the former case and manually in the latter.) Of greater interest is an examination of the remaining results, which are best approached by considering the 5 p.m. to 5 a.m. nighttime period and the following 5 a.m. to 3 p.m. daytime period separately.

In general, the nighttime predictions are reasonably accurate considering the fact that neither vertical temperature measurements nor refined temporal distributions for motor vehicle activity were available to estimate the corresponding meteorological and emissions inputs. Results at the end of this period (5 a.m.) often fell within a few parts per million of the measured concentrations, as shown in Table 29. Two notable exceptions, however, are illustrated in the downtown Los Angeles and Burbank predictions (Figures 30 and 33, respectively). Upon further examination of the results for these two stations, we made the following observations:

> Downtown Los Angeles. A rather substantial build-up in the CO concentration was observed to occur from 9 p.m. to midnight, but it was predicted to take place two hours earlier, from 7 p.m. to 10 p.m. Since the magnitudes of predicted and measured concentrations during the early morning hours of 30 September agree

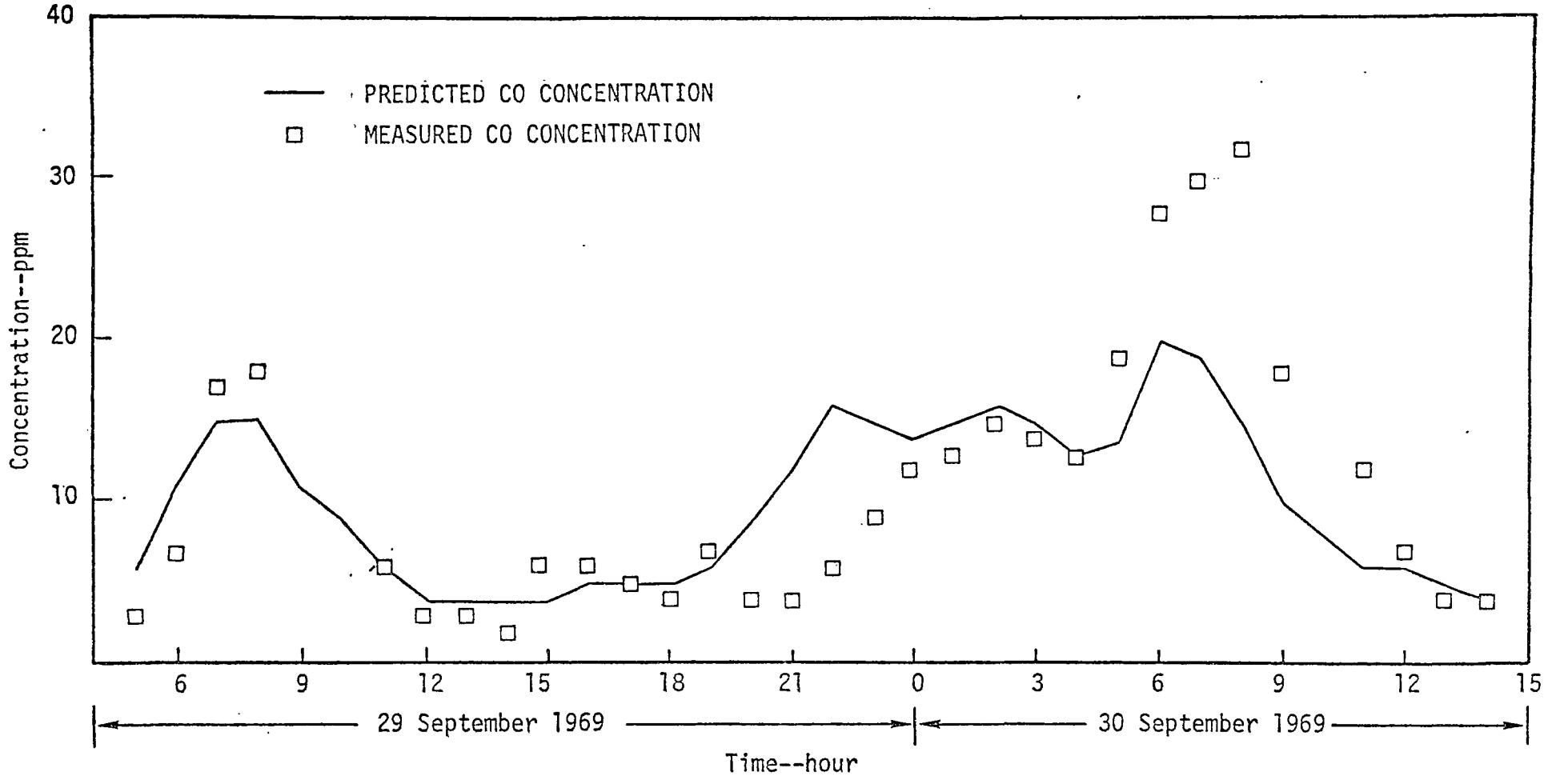


FIGURE 30. COMPARISON OF PREDICTED AND MEASURED HOURLY AVERAGED CO CONCENTRATIONS AT DOWNTOWN LOS ANGELES

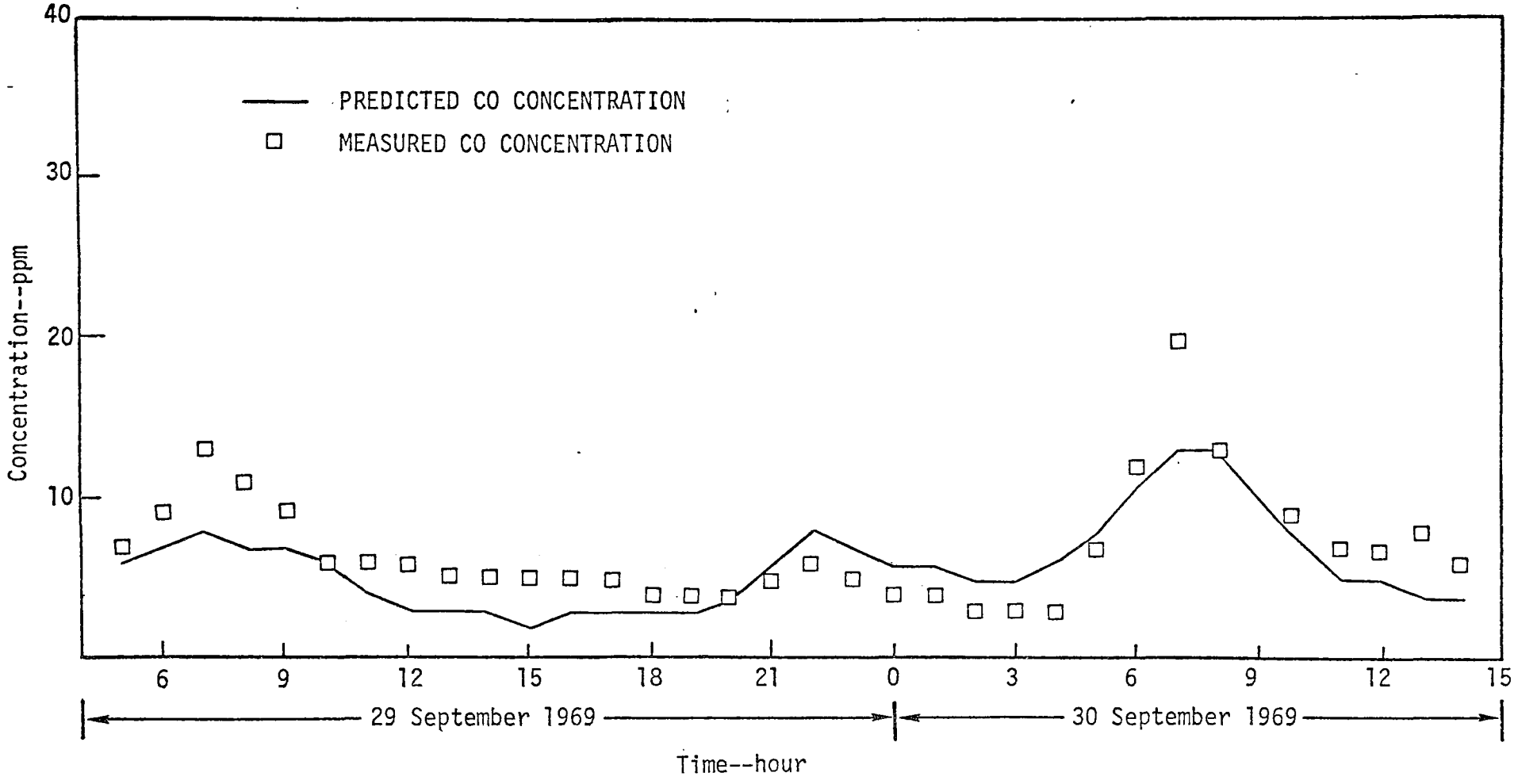


FIGURE 31. COMPARISON OF PREDICTED AND MEASURED HOURLY AVERAGED CO CONCENTRATIONS AT LONG BEACH

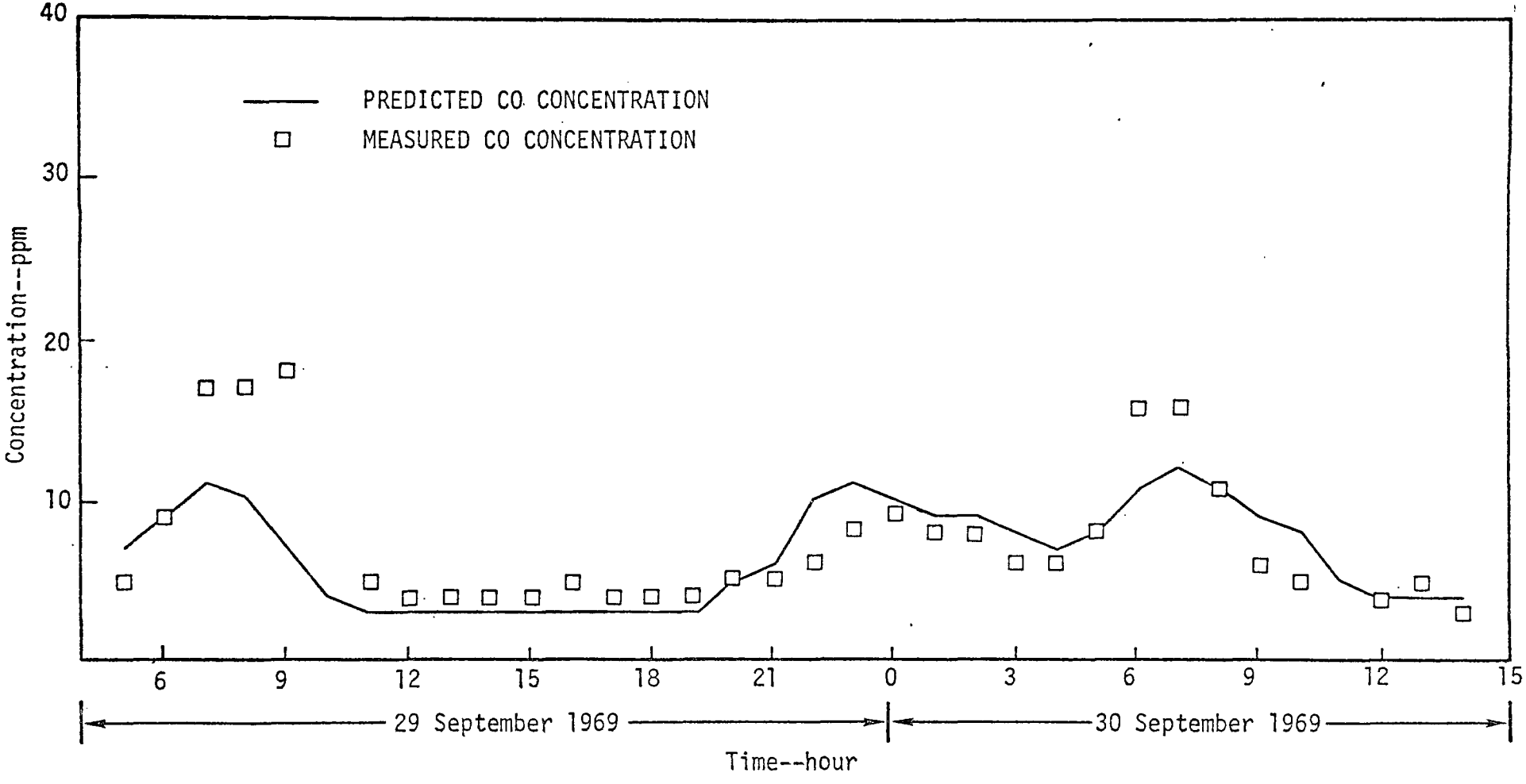


FIGURE 32. COMPARISON OF PREDICTED AND MEASURED HOURLY AVERAGED CO CONCENTRATIONS AT WEST LOS ANGELES

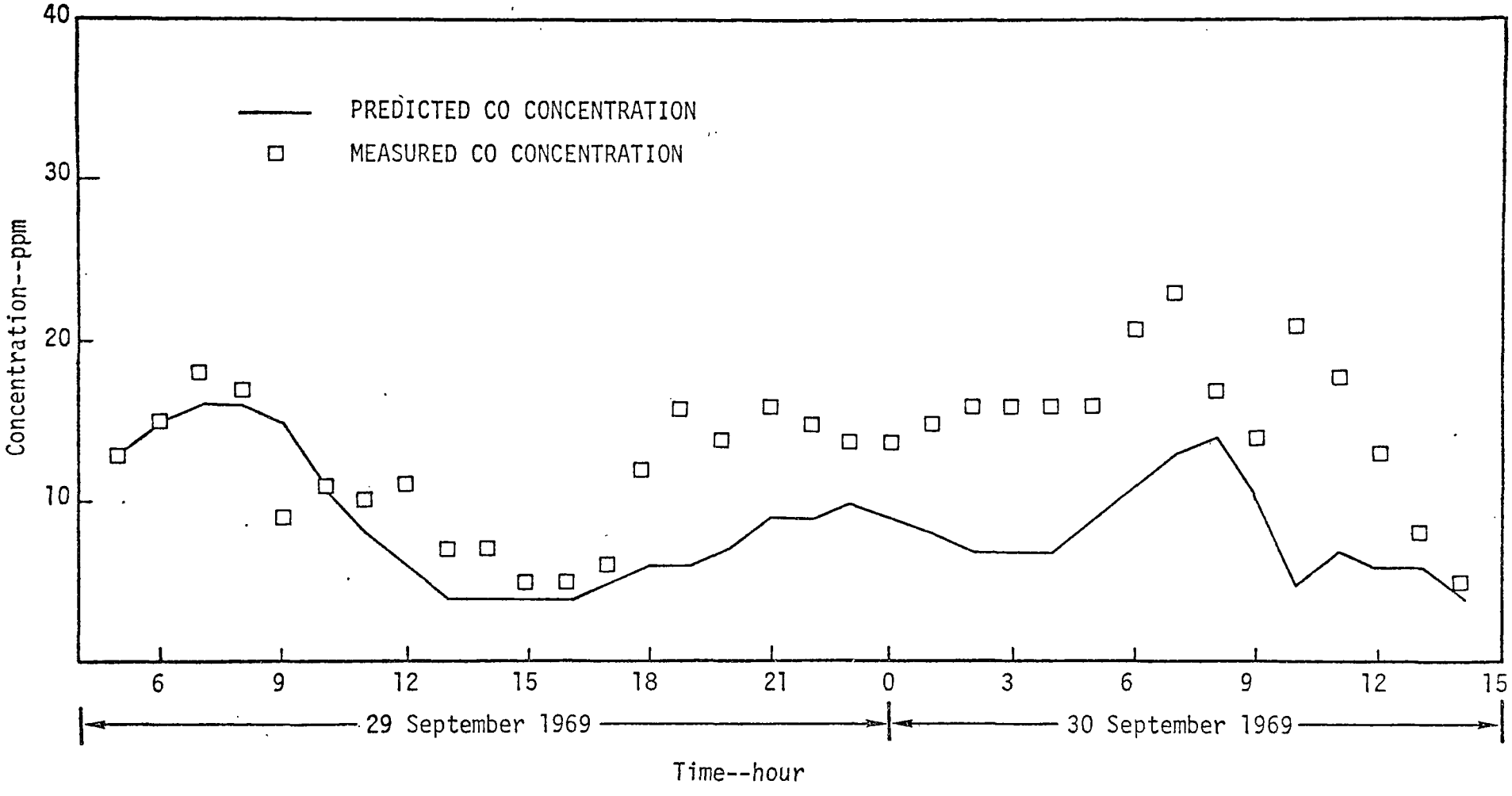


FIGURE 33. COMPARISON OF PREDICTED AND MEASURED HOURLY AVERAGED CO CONCENTRATIONS AT BURBANK

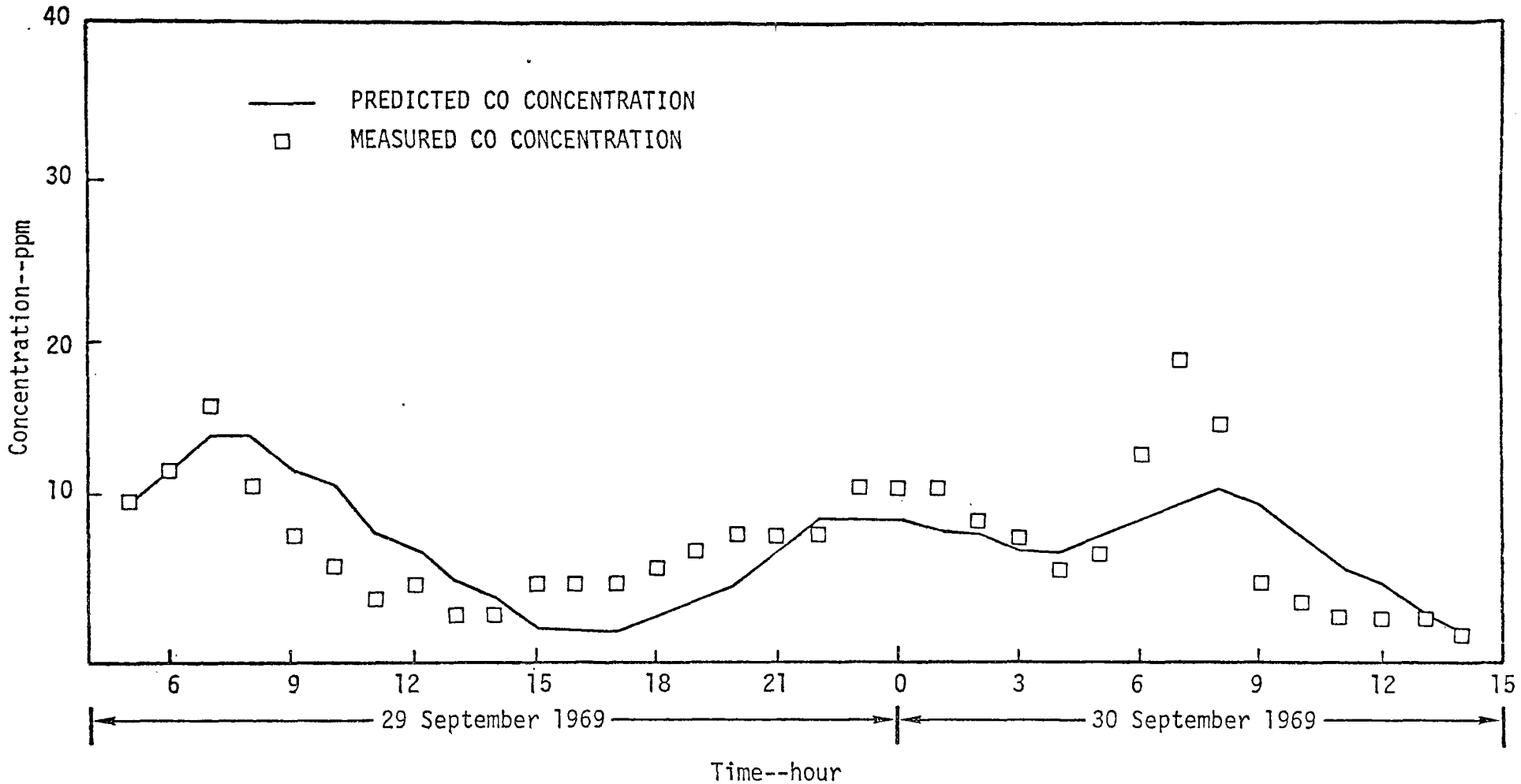


FIGURE 34. COMPARISON OF PREDICTED AND MEASURED HOURLY AVERAGED CO CONCENTRATIONS AT RESEDA

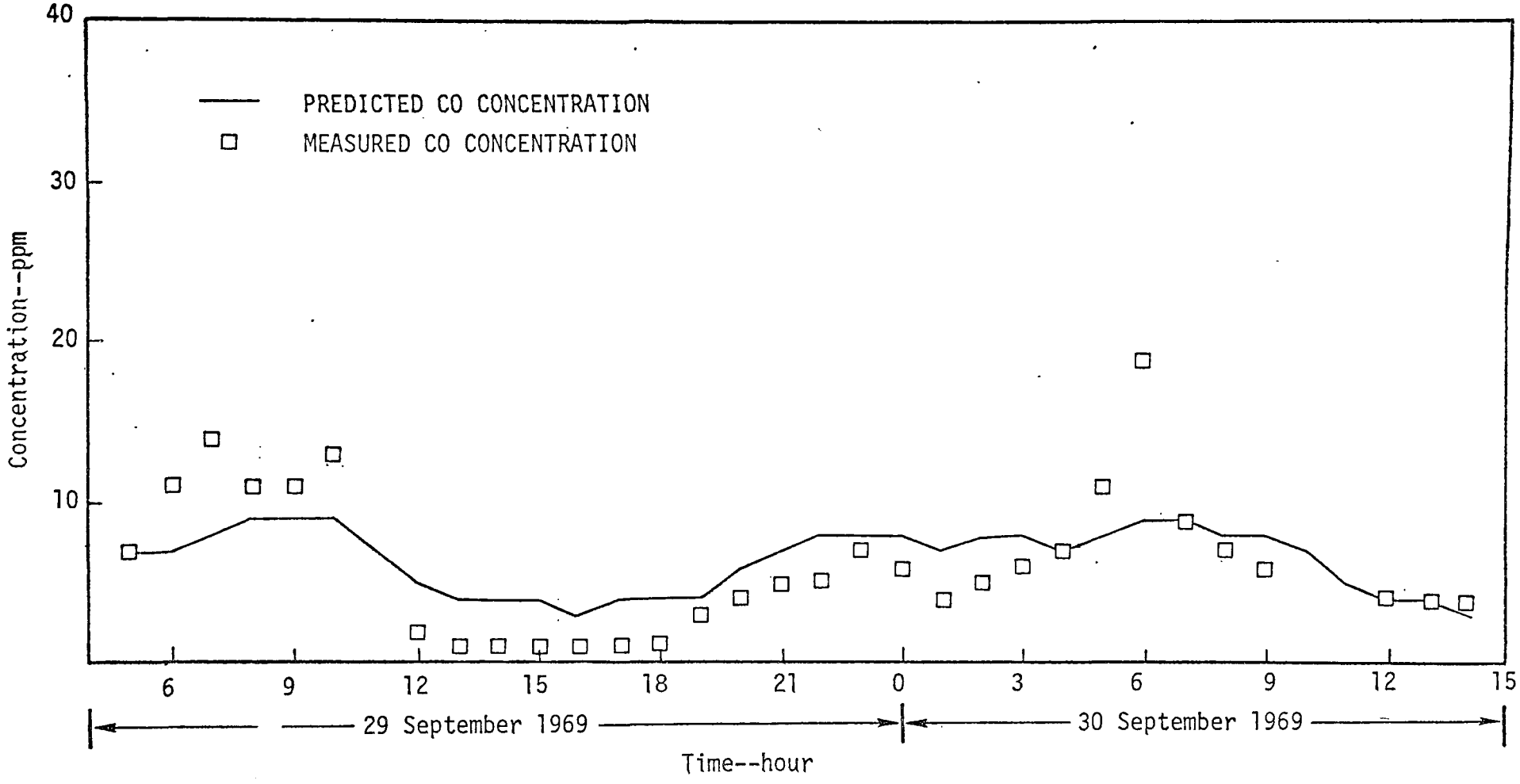


FIGURE 35. COMPARISON OF PREDICTED AND MEASURED HOURLY AVERAGED CO CONCENTRATIONS AT WHITTIER

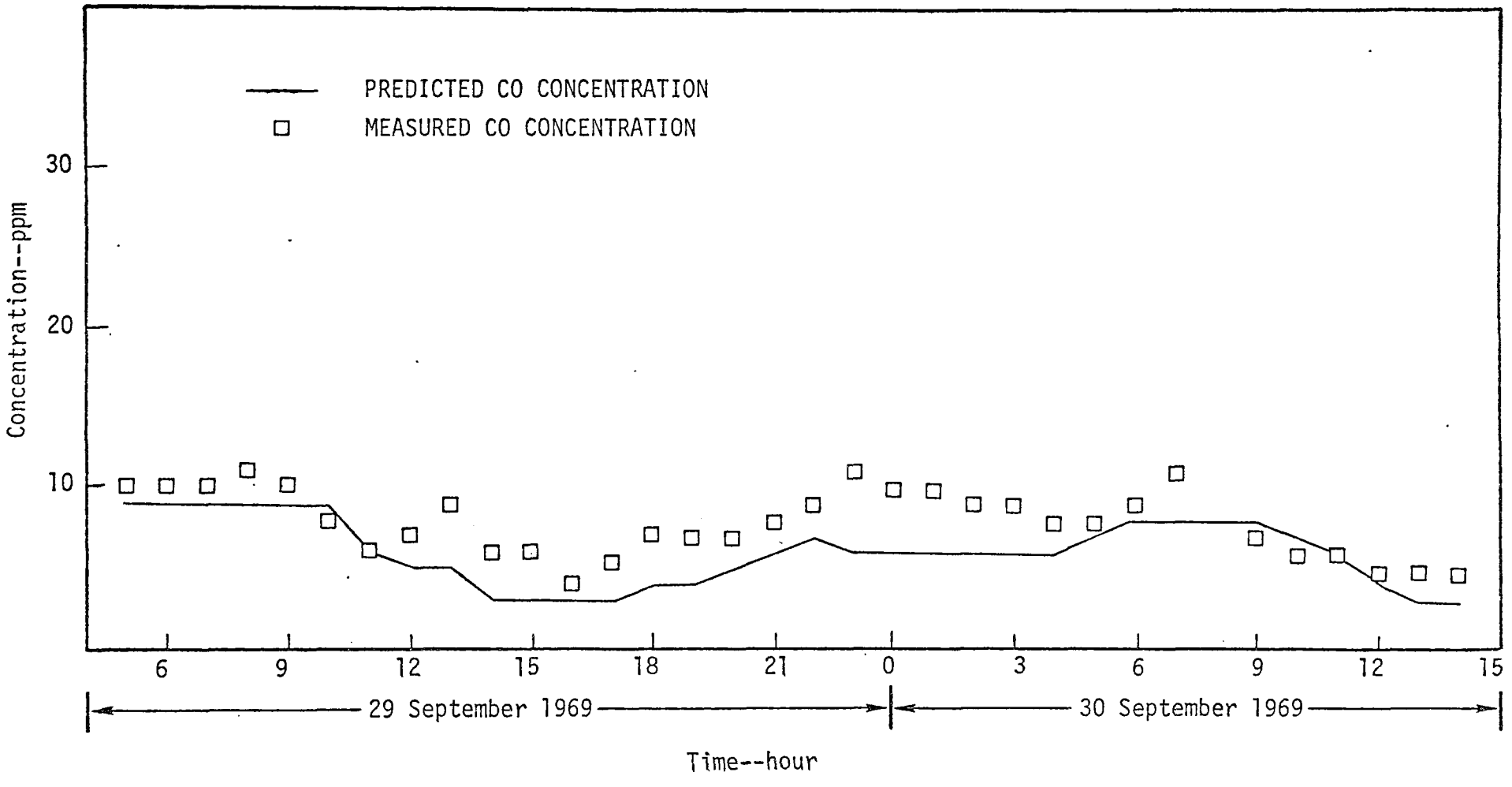


FIGURE 36. COMPARISON OF PREDICTED AND MEASURED HOURLY AVERAGED CO CONCENTRATIONS AT AZUSA

fairly well, the discrepancy in the time of occurrence of the build-up may well be the result of inaccuracies in the temporal distribution of motor vehicle emissions (the only source of CO in the model) during the period from 7 p.m. to midnight. Thus, the total loading seems correct, but the temporal distribution appears to be in error by about two hours. Traffic activity at 5 a.m. also seems to be greater than that predicted by the SAI emissions model.

> Burbank. Of all the results presented in Figures 30 through 36, those calculated for the Burbank station are the poorest. Predicted concentrations after 5 p.m. on 29 September are consistently low by as much as 10 ppm. Upon examining the results for Reseda (also located in the San Fernando Valley), we noted that, although predictions are often low, the discrepancy in the predicted and measured concentrations is at most only 3 ppm. Meteorological data for Burbank indicate very light winds (1 mph) from the north. The high concentrations at this station may thus be the results of local emissions from the major interstate freeway situated to the north of the station. A shallow mixing layer coupled with near-calm conditions would certainly limit the extent to which local freeway emissions would be dispersed.

Basically, the nighttime predictions do not indicate any systematic errant behavior in the model. In fact, considering the absence of key meteorological and emissions data, the 5 p.m. to 5 a.m. results are about as good as might be expected under the circumstances.

Turning now to an examination of the daytime results for 30 September, we note that at many stations the multiday predictions are very similar to those previously reported in the single-day test of the model. Since the meteorological and emission inputs for these two runs were not significantly different, discrepancies in the two sets of predictions can be attributed primarily to differences between the multiday and single-day CO concentration distributions at 5 a.m. PST on 30 September 1969. In the single-day run, which began at 5 a.m., the initial CO concentration field, shown in

Table 29

PREDICTED AND MEASURED HOURLY AVERAGED CO CONCENTRATIONS AT THE END OF THE 29 TO 30 SEPTEMBER NIGHTTIME PERIOD*

Station	Predicted Concentration (ppm)	Measured Concentration (ppm)
Downtown Los Angeles	13	13
Azusa	6	8
Burbank	7	16
West Los Angeles	7	6
Long Beach	6	3
Reseda	7	6
Pomona	3	3
Lennox	7	8
Whittier	7	7

*The figures presented in this table were averaged from 4 a.m. to 5 a.m. PST on 30 September 1969.

Table 30, was estimated from the appropriate measurements reported by the Los Angeles and Orange County Air Pollution Control Districts. The concentration field on the grid at 5 a.m. in the multiday run is, of course, the result of a continuous simulation started at 5 a.m. on the previous morning. The ground-level concentration map for this case is illustrated in Table 31. Over much of the modeling region, the two sets of predictions agree within 2 or 3 ppm. However, the discrepancies are much higher in the Pasadena, downtown Los Angeles, and Burbank areas. The high CO levels in these areas given in Table 30 are the result of manual interpolation of the measured values reported at downtown Los Angeles and Burbank (the Pasadena station did not report CO levels on 30 September). In general, the single-day results for downtown Los Angeles and Burbank are better than the corresponding multiday predictions. At other stations, the model predicted CO levels reasonably well, especially in view of the significant impact that local roadways may have on measured concentrations during the peak traffic hours in the morning.

It is also interesting to note the extent to which errors have accumulated throughout the multiday run. In Table 32, we give both the predicted and mea-

Table 30

MULTIDAY GROUND-LEVEL CO CONCENTRATION MAP
AT 5 a.m. PST ON 30 SEPTEMBER 1969

CO GROUND LEVEL CONCENTRATIONS (PPM) AT 500.00 PST

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	7.0	7.0	7.0	7.0	7.0	8.0	9.0	10.0	11.0	11.0	11.0														
24	7.0	7.0	7.0	7.0	8.0	9.0	11.0	12.0	13.0	13.0	12.0														
23	7.0	7.0	7.0	7.0	8.0	10.0	12.0	14.0	15.0	15.0	14.0	12.0	10.0												
22	7.0	7.0	7.0	7.0	8.0	10.0	12.0	14.0	16.0	16.0	16.0	14.0	12.0	11.0	10.0	9.0									
21	6.0	7.0	7.0	7.0	8.0	10.0	12.0	14.0	16.0	16.0	16.0	15.0	14.0	13.0	12.0	11.0	8.0	8.0	8.0	8.0	8.0	7.0	6.0	5.0	4.0
20	5.0	6.0	7.0	7.0	7.0	9.0	11.0	13.0	15.0	16.0	16.0	16.0	16.0	15.0	14.0	12.0	10.0	8.0	8.0	8.0	8.0	7.0	6.0	5.0	4.0
19	5.0	6.0	7.0	7.0	7.0	8.0	9.0	11.0	13.0	15.0	16.0	16.0	16.0	16.0	15.0	12.0	11.0	8.0	8.0	8.0	8.0	7.0	6.0	5.0	4.0
18	5.0	6.0	7.0	7.0	7.0	7.0	8.0	9.0	11.0	13.0	15.0	16.0	16.0	16.0	16.0	13.0	11.0	8.0	8.0	8.0	8.0	7.0	6.0	5.0	4.0
17	5.0	5.0	6.0	6.0	6.0	7.0	7.0	8.0	10.0	12.0	15.0	16.0	16.0	16.0	13.0	11.0	8.0	8.0	8.0	8.0	7.0	6.0	5.0	4.0	
16				5.0	6.0	7.0	7.0	8.0	10.0	12.0	14.0	16.0	16.0	16.0	16.0	13.0	11.0	8.0	8.0	8.0	8.0	7.0	6.0	5.0	4.0
15					5.0	6.0	7.0	8.0	10.0	12.0	14.0	15.0	16.0	16.0	15.0	12.0	10.0	8.0	8.0	8.0	8.0	7.0	6.0	5.0	4.0
14						6.0	7.0	9.0	10.0	12.0	12.0	12.0	12.0	12.0	11.0	11.0	10.0	8.0	8.0	8.0	8.0	7.0	6.0	5.0	4.0
13						6.0	8.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	9.0	8.0	8.0	7.0	6.0	5.0	5.0	5.0	5.0
12							5.0	7.0	7.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	7.0	7.0	7.0	6.0	6.0	5.0	5.0	5.0	5.0
11							3.0	4.0	5.0	5.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	5.0	5.0	5.0	5.0	5.0	5.0
10							3.0	3.0	4.0	4.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
9							3.0	3.0	4.0	4.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
8							3.0	3.0	3.0	4.0	4.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
7							3.0	3.0	3.0	3.0	3.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	5.0	5.0	5.0	5.0	5.0
6							3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	4.0	4.0	4.0	5.0	5.0	5.0	5.0	5.0
5																	3.0	3.0	4.0	4.0	5.0	5.0	5.0	5.0	5.0
4																		3.0	3.0	4.0	4.0	5.0	5.0	5.0	5.0
3																			3.0	3.0	3.0	4.0	4.0	5.0	5.0
2																				3.0	3.0	4.0	4.0	5.0	5.0
1																					3.0	3.0	4.0	4.0	4.0

RESEDA
BURBANK
SAN GABRIEL MTNS
PASADENA
AZUSA
SANTA MONICA MTNS
EL MONTE
DOWNTOWN LA
POMONA
WEST LA
COMMERCE
LENNOX
WHITTIER
LA HABRA
LONG BEACH
ANAHEIM
PALOS VERDES
PACIFIC OCEAN
SANTA ANA

Table 31

SINGLE-DAY GROUND-LEVEL CO CONCENTRATION MAP
AT 5 a.m. PST ON 30 SEPTEMBER 1969

CO GROUND LEVEL CONCENTRATIONS (PPM) AT 500.00 ON 690930

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
25	5.2	4.9	4.8	5.2	6.1	6.7	7.1	7.6	7.9	7.9	8.0														
24	6.1	5.2	5.2	5.5	6.7	7.2	7.4	7.2	7.4	7.7	7.9														
23	6.4	5.8	5.9	6.5	8.4	8.5	8.6	8.0	7.2	7.0	7.4	8.0	8.1												
22	5.8	6.3	6.9	7.9	9.6	10.3	10.2	8.9	7.6	7.1	6.7	7.6	8.0	8.2	8.2	8.0									
21	6.0	6.5	7.0	6.7	8.1	9.7	10.8	10.8	8.8	7.7	6.8	7.3	7.7	8.4	8.7	8.5	8.5	9.2	9.0	8.1	6.6	5.1	4.1	3.5	3.1
20	4.6	4.7	4.6	4.0	4.6	5.5	7.9	9.9	8.4	7.4	7.5	6.8	7.5	8.3	9.0	9.1	9.1	9.5	8.9	7.1	6.2	5.5	4.5	3.6	3.1
19	3.7	3.6	3.3	3.0	3.8	4.0	5.9	8.7	10.2	8.8	8.4	7.7	7.6	8.2	8.8	9.1	9.3	9.2	8.0	6.6	6.5	6.2	4.8	3.6	3.2
18	2.8	2.8	2.8	3.0	3.9	4.5	5.9	8.4	10.0	10.6	10.7	10.0	9.0	8.9	9.4	10.0	10.4	10.1	8.8	8.1	8.3	7.6	6.7	4.1	3.5
17	2.1	2.6	3.1	3.7	4.7	6.5	6.3	8.5	10.7	12.5	14.0	12.5	11.8	11.0	10.0	9.8	10.7	10.6	9.1	8.1	7.8	7.3	5.9	4.2	3.3
16				4.7	6.2	6.9	7.6	7.8	10.0	12.6	15.4	14.2	14.0	13.6	11.1	10.5	11.0	10.5	9.1	7.9	7.2	7.2	6.2	4.4	3.3
15					5.8	6.6	7.5	7.8	9.1	11.6	14.1	13.0	12.3	13.4	12.7	11.0	10.9	9.4	7.9	6.5	6.3	6.9	5.9	4.3	3.3
14						5.7	6.8	7.9	8.0	9.3	11.2	10.4	10.7	12.3	12.1	11.4	9.7	8.5	6.5	5.0	4.9	5.8	5.6	4.3	3.3
13							4.3	6.0	7.1	6.9	7.2	8.3	8.1	9.0	10.5	11.0	11.2	8.8	7.4	5.8	4.8	4.6	5.4	5.3	4.2	3.3
12								4.4	5.8	5.8	6.0	6.3	6.5	7.6	8.5	9.5	10.3	9.1	7.2	5.7	4.9	5.0	5.5	5.4	4.3	3.3
11								2.7	4.0	5.6	5.6	5.4	5.4	6.5	7.0	8.4	9.3	8.7	8.4	7.9	6.6	6.6	6.2	5.4	4.2	3.4
10								1.7	3.0	3.9	4.5	5.4	4.9	5.9	6.4	7.7	8.6	8.2	8.6	9.3	9.7	9.2	7.8	6.1	4.7	3.4
9								1.4	2.2	2.9	3.7	4.5	5.2	6.5	6.7	7.8	7.8	7.5	8.1	9.3	10.1	10.1	8.3	6.3	4.7	3.3
8								1.4	1.7	2.3	3.2	4.1	4.8	6.2	6.7	7.6	8.5	7.8	7.9	9.0	9.9	10.4	10.0	7.6	5.5	3.4
7								1.4	1.4	1.7	2.4	3.1	3.8	4.9	5.8	6.7	6.9	6.5	7.2	8.2	9.4	10.0	9.4	8.5	5.6	3.5
6								1.2	1.1	1.4	2.0	2.2	2.6	3.4	4.2	4.7	4.8	4.9	5.8	7.1	7.4	7.6	7.2	6.1	4.9	3.7
5																	3.3	4.2	5.3	5.9	5.6	5.0	4.4	3.7	3.4
4																		3.0	4.0	4.4	4.4	4.0	3.5	3.3	3.2
3																			3.1	3.5	3.6	2.8	2.6	2.7	2.9
2																				2.2	2.3	2.1	2.2	2.5	2.9
1																					1.6	1.6	2.0	2.3	2.6

RESEDA
BURBANK
PASADENA
AZUSA
SAN GABRIEL MTNS
SANTA MONICA MTNS
EL MONTE
DOWNTOWN LA
POMONA
WEST L.A.
COMMERCE
LENNOX
WHITTIER
LA HABRA
LONG BEACH
ANAHEIM
PALOS VERDES
PACIFIC OCEAN
SANTA ANA

sured hourly averaged concentrations over the last hour of the simulation. Overall, the predicted results tend to be lower than the measurements by 1 to 2 ppm; in only one instance is the discrepancy greater than 2 ppm. Since we expect the model to predict concentrations somewhat lower than those measured at stations situated on heavily traveled streets, it is difficult to assess the cumulative effect of meteorological, emissions, and numerical errors in this simulation. Thus, it appears that we may have to carry out longer runs (three or four days) to observe the build-up of modeling errors clearly.

Table 32

PREDICTED AND MEASURED HOURLY AVERAGED CO CONCENTRATIONS FOR THE LAST HOUR OF THE MULTIDAY SIMULATION

Station	Predicted Concentration (ppm)	Measured Concentration (ppm)
Downtown Los Angeles	5	4
Azusa	3	5
Burbank	4	5
West Los Angeles	4	3
Long Beach	4	6
Reseda	2	3
Pomona	3	6
Lennox	3	5
Whittier	3	4

D. RECOMMENDATIONS FOR FUTURE WORK

During this study, we adapted the SAI airshed model for use in the prediction of inert pollutant concentrations over multiday periods. The prediction of photochemical contaminant concentrations should be undertaken when the program containing the new kinetic mechanism is fully operational and suitable hydrocarbon emission inputs are developed. To gain experience in multiday usage, we simulated pollutant concentrations in the Los Angeles basin for the

34-hour period extending from 5 a.m. on 29 September to 3 p.m. on 30 September 1969. In general, the results obtained from this run agree reasonably well with available measured pollutant concentration data.

We recommend that the following tasks be undertaken in the future:

> Assembly of an accurate data base for both meteorological and emissions inputs for a multiple-day period.

> Performance of photochemical simulations as soon as possible.

> Performance of CO (and eventually photochemical) runs over several consecutive days (say, four or more) to obtain a better understanding of the cumulative effects of meteorological, emission, and numerical errors on our ability to exercise the model on a multiday basis.

Our present experience indicates that, given a suitable input data base, the model should be capable of producing reasonably good predictions of inert species concentrations for at least two consecutive days. However, further testing will be required to establish guidelines regarding the total number of days that can be simulated before errors accumulate to unacceptable levels.

APPENDIX
A USER'S GUIDE TO MODKIN

David C. Whitney

APPENDIX
A USER'S GUIDE TO MODKIN

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1. INTRODUCTION

Quantitative description of the rates of chemical reaction of atmospheric contaminants is a vital ingredient in the formulation of a model capable of accurately predicting ground-level concentrations of gaseous pollutants. The formulation of a kinetic mechanism having general validity is, however, an endeavor beset by several inherent difficulties. First, many stable chemical species are present in the atmosphere. Most of these exist at very low concentrations, thereby creating major problems of detection and analysis. In fact, a number of atmospheric constituents remain unidentified. Second, the large variety of highly reactive, short-lived intermediate species and free radicals further complicates the picture. Finally, the enormous number of individual chemical reactions that these species undergo creates an even greater barrier to understanding. Nevertheless, despite our limited knowledge of atmospheric reaction processes, it is essential that we attempt to formulate quantitative descriptions of the processes that are suitable for inclusion in an overall simulation model.

The formulation and development of a kinetic mechanism that is to be incorporated in any airshed model is both delicate and exacting, an undertaking requiring a blend of science, craftsmanship, and art. On one hand, such a mechanism must not be overly complex because the computation times for integration of the continuity equations in which the mechanism is to be imbedded are likely to be excessive. On the other hand, too simplified a mechanism may omit important reaction steps and may thus be inadequate for describing atmospheric reaction processes. Therefore, one major issue is the requirement that the mechanism predict the chemical behavior of a complex mixture of many

hydrocarbons, and yet do so with a paucity of detail. Thus, in postulating a mechanism, the formulator must strike a careful balance between compactness of form and accuracy in prediction.

As an aid in the development of a kinetic mechanism for atmospheric photochemical reactions, we prepared a computer program that allows the user to present his proposed mechanism via data input cards in the same manner as he would formulate it on paper--i.e., as a series of chemical equations and their associated rate constants. Moreover, he can select the method of calculation for determining the concentration of each chemical species in the mechanism from among the following choices: the integration of coupled or uncoupled differential equations, the solution of algebraic equations for species in a steady-state, or the assumption of a constant concentration. Either static or dynamic smog chamber observations can be simulated, and plots of species concentration as a function of time are provided as part of the printed output. Reactions of similar species can be combined into a single "lumped" reaction. Changes in the reaction mechanism, rate constants, or species type designation can be effected by simple input card replacement; recoding or recompilation of the program is not necessary.

Since descriptions of the solution techniques and the development of the chemical mechanisms have appeared elsewhere (Seinfeld et al., 1971; Hecht, 1972), we do not repeat them here beyond the degree necessary for an understanding of the computer program. This appendix is designed to serve primarily as a user's guide to program operation and as a programmer's guide for such program maintenance and modification as may be needed in the future.

2. USE OF THE PROGRAM

The input to MODKIN consists of two control cards, a set of reaction cards, a set of species cards, a set of flow cards, and a set of plot cards. The card formats are described in Table A-1, and additional comments regarding program input are given below.

Table A-1

INPUT CARD FORMAT FOR MODKIN

Card No.	Column No.	Variable Name	Item Format	Units of Measure	Comments
1	1-12	NTIT(J)	3A4	--	Twelve-character title for run heading
1	16-20	NRXN	I5	--	Number of reactions in the mechanism (maximum 99)
1	21-25	NLMP	I5	--	Number of reactions that contain species to be be replaced, i.e., are lumped (maximum 10)
1	26-30	NDIF	I5	--	Number of species to be solved in a coupled differential equation (maximum 40)
1	31-35	NSTS	I5	--	Number of species to be solved in a steady-state approximation
1	36-40	NUNC	I5	--	Number of species to be solved via uncoupled differential equations
1	41-45	NREP	I5	--	Number of species that are replacements for lumped species
1	46-50	NINT	I5	--	Number of inert (constant concentration) species (the total count of the above five species types cannot exceed 50)
1	51-55	NFLW	I5	--	Number of species flowing into the reaction chamber
1	56-60	NRAT	I5	--	If nonzero, reaction rates will be printed
2	1-10	TINCR	F10.0	min	Time increment for printing and plotting results
2	11-20	TEND	F10.0	min	Ending time for run
2	21-30	HSTART	F10.0	min	Initial time step size

Table A-1 (Continued)

Card No.	Column No.	Variable Name	Item Format	Units of Measure	Comments
2	31-40	HMINF	F10.0	min	Minimum time step size
2	41-50	HMAXF	F10.0	min	Maximum time step size
2	51-60	EPSF	F10.0	--	Fractional allowable error for iterative solutions
2	61-70	Q	F10.0	min^{-1}	Dilution or flow rate (sampling and leakage compensation)
3	1-20	NMRC(J,K)	4(A4,1X)	--	Reactant names, up to four per reaction (if lumped reaction, species to be replaced must appear first)
3	21-50	COEFF(J,K)/ NMPD(J,K)	3(F6.0, A4)	--	Species coefficients and product names, up to three per reaction
3	51-60	RK(K)	F10.0	ppm^{1-n}_{-1} min^{-1}	Rate constant; n is the number of reacting species
4	1-4	NTEST	A4	--	Name of species to be replaced in the lumped reaction
4	6-10	NLOC	I5	--	Number of reactions contributing to the lumped reaction (maximum 10)
5	1-20	NMRC(J,K)	4(A4,1X)	--	Reactant names, up to four per reaction (the first species name must be the replacement for the lumped species)
5	21-50	COEFF(J,K)/ NMPD(J,K)	3(F6.0, A4)	--	Species coefficient and product names, up to three per reaction
5	51-60	RK(K)	F10.0	ppm^{1-n}_{-1} min^{-1}	Rate constant; n is the number of reacting species

Table A-1 (Continued)

Card No.	Column No.	Variable Name	Item Format	Units of Measure	Comments
6	1-4	NAME(L)	A4	--	Species name
6	11-20	YAX(L)	E10.0	ppm	Species initial concentration
7	1-4	NTEST	A4	--	Flowing species name
7	6-10	NTIM	I5	--	Number of flow points (maximum 10)
8	1-80	FTIME(J,L)/ FLOW(J,L)	4(2F10.0)	min ppm^{-1}	Time of measurement and concentration of flowing species
9	1-4	NTEST	A4	--	Name of species to be plotted
9	6-7	NDAT	I2	--	Number of input data for the plot (maximum 80)
9	9	JSYMB	A1	--	Symbol to be used for the calculated data
9	11-14	JFACT	A4	--	Conversion factor for the label
9	16-40	JCONC(J)	5(A4,1X)	--	Concentration labels for the y-axix
9	41-50	CLOW	F10.0	ppm	Minimum concentration value to be considered for plotting
9	51-60	CHIGH	F10.0	ppm	Maximum concentration value to be considered for plotting
9	61-70	TLOW	F10.0	min	Minimum time value to be considered for plotting

Table A-1 (Concluded)

Card No.	Column No.	Variable Time	Item Format	Units of Measure	Comments
9	71-80	THIGH	F10.0	min	Maximum time value to be considered for plotting
10	1-80	TIME(J)/ DATA(J)	4(2F10.0)	min ppm^{-1}	Time and concentration input data to be plotted
11	1-4	JBLANK	A4	--	Blank in Columns 1-4 stops plotting

The first control card contains title and parameter information for the run. The first field on this card is a 12-character title; the contents of this field will be printed following "MODULAR KINETICS RUN NO." on the first page of the printout. The number of reactions is given next; the program expects this number of reaction cards to follow the control card. The next entry specifies how many of these reactions represent lumped reactions and thus need to be recalculated from sets of contributing reactions. The following five entries are the counts of each of the different types of species: differential, steady state, uncoupled, replacement, and inert. Note that there are limits on both the number of differential species and the total number of species. The program expects to find one species card for every species named on the reaction cards; they must be ordered as shown above (i.e., all differential species first, then all steady-state species, and so forth). The next-to-last entry on the control card is the number of species that are flowing into the reaction chamber; there must be a set of flow cards for each of these species. The final entry is a request flag governing the printout of the reaction rates.

The first two entries on the second control card are printout parameters. The first one determines the time increments (e.g., every five minutes) for which the current concentration of all species are to be printed and plotted; the second specifies the time at which the kinetics run is to be terminated. The next four values are control parameters for the differential equation solution routine. In order, these parameters are the initial time step (normally on the order of 10^{-4} min), the minimum allowable time step (normally about 10^{-5} min), the maximum time step (about 1 to 10 min), and the fractional error acceptable for iterative solutions. The final entry on the second control card is the rate at which each species concentration would be reduced in the absence of reaction. This "dilution rate" primarily reflects the loss of material through sampling; if there is an inflow, it is presumed to occur at this same rate.

The set of reaction cards provides all the reactions and rate constants, one per card. Each card begins with a list of reactants, which must appear in consecutive fields, since a blank stops the scan. For a lumped reaction, the

name of the species to be replaced must appear first; otherwise, the order of reactant names is immaterial. Note, incidentally, that the reactants appear in the printed output in reverse order. If a species reacts with itself, it must appear twice in the list of reactants. The products, along with their coefficients, follow. Coefficients can be whole numbers or fractions; the printout is rounded to two decimal places. Again, products must appear consecutively, since a blank stops the scan, but their order is unimportant. The final entry on the card is the rate constant. The order of the reaction cards does not matter, except that lumped reactions must follow nonlumped reactions.

A set of contributing reactions consists of an identification card containing the name of the lumped reactant (the species being replaced) and the number of contributing reactions, followed by the list of contributing reactions. All of the comments offered above regarding reaction cards apply to these contributing reactions, except that these reactions cannot themselves be lumped ones. The contributing reaction must have its reactants and products in the same relative location on the card as they are on the lumped reaction card; i.e., the replacement species must appear first, and all products must be shown, even those that have zero coefficients. However, the order of the reactions within a set does not matter. The order of the sets of contributing reactions must be the same as the order of the lumped reactions in the set of reaction cards described above, and there must be one set of contributing reactions for each lumped reaction.

The set of species cards is used to identify the species by type and to initialize the species concentrations. Each card contains a species name and concentration. The following is the order of the species types: differential, steady state, uncoupled, replacement, and inert. Within a given type, no particular order is necessary; in fact, some orderings of steady-state species are clearly preferable to others in terms of elapsed computing time.

A set of flow cards consists of an identification card containing the species name and the number of input points, followed by cards specifying the data points themselves. The data are not interpolated; instead, the inflowing concentration is changed to a new value whenever the progression of time in the mechanism passes an input time. Note particularly that the concentration for the inflowing species is zero until its first input time is passed.

The plot cards control the pictorial representation of concentration as a function of time for each species. Instead of processing the output using a plotter, the plot cards map the concentration-time profile onto a page-size grid of the printout. The first card, which is the plot control card, contains the species name, the number of experimental data points to be read, the symbol to be used to represent the calculated data (an asterisk is used for experimental points), the conversion factor, the concentration labels, and the grid limits. These last three items require comment.

The grid has been divided into four vertical sections and eight horizontal sections. Aesthetically, therefore, the time (horizontal) limits should be chosen to give a span divisible evenly by eight (e.g., a limit of 0 to 400 will result in the printing of a label every 50 minutes). Similarly, the concentration (vertical) limits should be divisible evenly by four, and they should be the true rather than the scaled concentrations. The labels for the vertical axis are not calculated from the concentration span, but rather are read in from the control card. They can be any multiple of the true concentrations. The scale factor, which appears in the figure caption along with the run title and species values, indicates what multiplier was used. For example, if the data prints were expected to range between 0.08 and 0.16 ppm, a scale factor of "10+1"; concentration labels of "0.75", "1.00", "1.25", "1.50", and "1.75"; and concentration limits of "0.075" and "0.175" would give a plot containing all the points. Note that no check is made among the labels, scale factor, and limits to insure consistency. Also, the limit values themselves will not appear on the plot; plotted points must fall within the grid boundaries.

Experimental data cards, if any, come after the control card. If desired, sets of plot cards can be stacked. The end of the plot deck is denoted by a card with a blank species name; the program will then expect another MODKIN run control card.

3. PROGRAM DESCRIPTION

The modular kinetics program consists of a main routine labeled MODKIN, the subroutines LMPCAL, DIFSUB, and PLOT, which are called by MODKIN, and the subroutines DIFFUN, MATINV, and PEDERV, which are called by DIFSUB. Each routine is treated in detail below. Listings and samples of program inputs and outputs appear at the end of this appendix. Symbol glossaries are included within each routine that was written especially for this program.

a. MODKIN

The program begins by declaring a number of variables used by DIFSUB as being DOUBLE PRECISION. All arrays are identified in DIMENSION statements and variables needed by LMPCAL and DIFFUN are placed in COMMON. The DATA declarations include the input and output units, a blank word, and the maximum sizes of the various arrays used for holding user inputs.

The control cards are read (note that this is a return point for stacked data decks). An initial page is written listing all the control card parameters. The number of reactions is checked, and the set of reaction cards is read. The number of lumped reactions is checked, and the contributing sets are read. For each set, the number of contributing reactions and the lumped species name are checked, the reaction counter is incremented and checked, and the contributing reactions are read. The number of differential species is checked, the total number of species is calculated and checked, and the set of species cards is read. The number of flowing species is checked, the flow variables are cleared to zero, and the flow cards are checked and read.

The numerical identifiers for each species and the uncoupled species reaction rates are cleared to zero. The initial concentrations of the differential species are set to their input values, and the input errors and initial maxima are set. The numerical species indentifiers for the reactants and products of each reaction are cleared to zero.

The counters for the lumped reactions are set. The reactions are analyzed, and each species is identified; if it does not match a species list name, a flag is set. Numerical identifiers are placed in the reaction and species matrices to allow reference by reaction and location within the reaction expression. If this is the first of a set of replacement reactions, a message is printed. The order of the reactants is reversed, and the list of chemical reactions and rate constants is printed. LMPCAL is called to adjust the lumped reactions and species concentrations, and the list of initial species concentrations, broken down by type, is printed. If the name flag is set, processing halts. A number of computation parameters are initialized. Initial concentrations are saved, and the incoming concentrations of any flowing species are initialized.

A call is made to the differential equation solution routine DIFSUB (which in turn calls DIFFUN for solution of the steady-state equations); note that this is a return point from the calculation loop. The time values are updated, and the concentration values are saved and checked for negative values. If a negative value is found, the time step is reset to one-tenth of its former value (note that this is done only once and that the time step must be greater than the user-specified minimum value), the concentrations from the previous time step are restored, and the call to DIFSUB is repeated.

The replacement species concentrations are calculated using the following algorithm:

$$Y_{i(n)} = Y_{i(o)} \exp\left[-\Delta T \sum_{J=1}^{J} \left(RK_j \prod_{K=2}^{K} Y_k \right) \right] (1 - Q\Delta T) \quad ,$$

where

$Y_{i(n)}$ = the new concentration of replacement species i,

$Y_{i(o)}$ = the old concentration of replacement species i,

ΔT = the change in time since the previous calculation,

RK_j = the rate constant of the j-th reaction of the set of J contributing reactions that have species i as the first reactant,

Y_k = the concentration of the K-th reactant species in the set of K reactants in contributing reaction j,

Q = the dilution rate.

LMPCAL is then called to adjust the lumped reactions and species concentrations to reflect the changes in the replacement species concentrations.

The uncoupled species concentrations are calculated using the algorithm described below under DIFFUN. Note that the uncoupled species reaction rates are averaged with those derived during the previous time step. The current uncoupled species reaction rates are saved.

The time is checked against having passed the user-provided limit, in which case no plot points are saved. The incremental time since the last printout is checked against the user-specified value. If appropriate, the current concentration values are saved for plotting, unless the maximum number of plot points has been exceeded. The current concentrations are then printed, regardless of whether the plot points have been saved. If the user has indicated that the reaction rates are to be printed, they are sorted from largest to smallest and are listed five per line.

If the time limit has been passed, if a repeated negative concentration has been encountered, or if an error has occurred in DIFSUB, the error flag is printed and the PLOT routine is called. Control then passes back to the beginning of the program, where another set of input cards can be processed Otherwise, the inflowing species are checked to determine whether any concentrations should be updated; if any updates are made, an appropriate message is printed. Finally, the current time and concentrations are saved (in case it is necessary to restart the calculation with a smaller time step), and control returns to the call of DIFSUB for calculation of the next time step.

b. LMPCAL

This subroutine is called by MODKIN to calculate the rate constants and product species coefficients for the lumped reactions. Two arguments are provided to this routine by MODKIN: the number of lumped reactions and the number of contributing reactions for each lumped reaction. COMMON is defined as in MODKIN, array sizes are set with DIMENSION statements, and parameters are defined via DATA statements.

The location and number of the current set of contributing reactions are established, and the corresponding lumped reaction is identified. The rate constants, product coefficients, and replacement species concentrations for each contributing reaction are transferred to local arrays, and the replacement species concentration is summed. The concentration of the lumped species is set to the sum of all the replacement concentrations, and the mole fraction of each replacement species is calculated. The rate constant of the lumped reaction is calculated as the sum of the rate constants for the contributing reactions multiplied by the replacement species mole fraction. The product species coefficients are calculated as the sum of the coefficients for the product species multiplied by the replacement species mole fraction for each contributing reaction, weighted by the ratio of the rate constant for the contributing reaction to that of the lumped reaction. Note that as a final step any product species coefficient below a minimum value is reset to zero to avoid underflow problems in later computations.

c. DIFSUB

This subroutine, which is called by MODKIN, is a copy of the program for the integration of coupled first-order ordinary differential equations that was presented in the Collected Algorithms of the Association for Computing Machinery (Gear, 1971). Since the algorithm and program are described in detail in the cited reference, they are not discussed further here. The only change likely to be needed is the alteration of the DIMENSION statement near the beginning.

d. DIFFUN

This subroutine is called by DIFSUB to calculate the rates of change of the differential species. It also includes, however, the algorithm for the steady-state calculations, since the reactions involving species in a steady state are presumed to be fast relative to the time steps in DIFSUB and must therefore be updated at every time trial. The three arguments provided to this subroutine by DIFSUB are the time, the differential species concentrations, and the rates of change of these concentrations; these are all DOUBLE PRECISION. The arguments are sized in a DIMENSION statement, COMMON is defined as in MODKIN, and several parameters are defined via DATA statements.

The concentrations are transferred to a local array, and the convergence loop is begun. The reaction rate for each reaction is calculated by using the following algorithm:

$$R_i = RK_i \prod_{j=1}^{J} Y_j \quad ,$$

where R_i is the reaction rate and RK_i is the rate constant of the i-th reaction, and Y_j is the concentration of the j-th reactant species in the set of J reactants in reaction i.

The steady-state concentrations are calculated by using the following dynamic mass-balance algorithm:

$$Y_j = \frac{\sum_{i=1}^{I} R_i C_{ij}}{Q + \sum_{m=1}^{M} RK_m \sum_{k=1}^{K} Y_k} \quad , \quad k \neq j \quad ,$$

where

Y_j = the concentration of the j-th steady-state species,

R_i and C_{ij} = the reaction rate of the i-th reaction and the coefficient of species j in the i-th reaction, respectively, of the set of I reactions in which species j is a product,

Q = the dilution rate,

RK_m = the rate constant for the m-th reaction in the set of M reactions in which species j is a reactant,

Y_k = the concentration of the k-th reactant (except when k = j) in the set of K reactants in reaction m.

Note that in the case of a species reacting with itself, Y_j may be the same as Y_k even though $k \neq j$; this case has been explicitly programmed.

If the old and new steady-state values agree within the requisite tolerance, a convergence counter is incremented; in any event, the new value is saved. If the value registered on the convergence counter equals the number of steady-state species, the loop is completed; otherwise, another pass is made. If the steady-state concentrations do not converge, a warning message is written and processing continues.

As a final step, the differentials are calculated according to the following algorithm:

$$\Delta Y_j = \sum_{i=1}^{I} R_i C_{ij} - \sum_{m=1}^{M} R_m + Q(YF_j - Y_j) \quad ,$$

where

ΔY_j = the change in concentration of the j-th species with time,

R_i and C_{ij} = the reaction rate of the i-th reaction and the coefficient of species j in the i-th reaction, respectively, of the set of I reactions in which species j is a product,

R_m = the reaction rate of the m-th reaction in the set of M reactions in which species j is a reactant,

Q = the dilution rate,

YF_j = the inflowing concentration of species j,

Y_j = the concentration of species j.

These differential values are returned to the calling program.

e. MATINV

This subroutine is called by DIFSUB to perform matrix inversions. Since it is a standard matrix inversion routine taken from the utility subroutine library at the California Institute of Technology, it is not described here. The only change likely to be needed is the alteration of the DIMENSION statement near the beginning.

f. PEDERV

This subroutine, which is called by DIFSUB, is used to provide a Jacobian matrix for the calculation of partial derivatives and is not necessary in this application. Nevertheless, to preserve the integrity of the Gear routine and to allow for possible future use of partial derivatives, we retained the routine in the program as a dummy subroutine. It does contain, however, a DIMENSION statement; thus, any alteration of array sizes in DIFSUB should also be made in PEDERV.

g. PLOT

This subroutine is called by MODKIN following completion of the time-concentration calculations. It maps the results, along with any user input data, onto a page-sized grid of concentration as a function of time cells for as many species as the user wishes.

The routine begins by providing DIMENSION statements for some of the arguments and the local arrays. The vertical axis and vertical label are established via DATA statements, as are the I/O units, some symbols, and the maximum array sizes.

The grid is cleared to blanks, and the control card is read. If the name is blank, control returns to MODKIN. If there are input data, the number is checked and the data are read. The normalization factors are calculated, and the numerical labels are placed on the axes. The species is identified; if it is misspelled, the plot is skipped.

The data points, if any, are scaled to the grid; the points are checked; and, if they are acceptable, the appropriate symbol is placed on the grid. The same procedure is used for the calculated points. A page is skipped, and the vertical labels and axis and the grid itself are printed. The horizontal axis and labels and the figure caption are printed, and the routine returns control to MODKIN.

4. LISTINGS AND SAMPLE REPORT AND OUTPUT

The following pages contain a complete listing of the computer program, including the main routine MODKIN (Exhibit A-1) and the subroutines LMPCAL, DIFSUB, DIFFUN, MATINV, PEDERV, and PLOT (Exhibits A-2 through A-7). These routines are all written in ASA FORTRAN and should be acceptable without changes for any computer system that supports FORTRAN.

Following the program listings is an input deck describing a typical kinetics mechanism (Exhibit A-8) and selected printout from the computer run using this input deck (Exhibit A-9). We note that, except for the plot (which uses an entire 11 x 15 inch computer printout page), the output is contained on a standard 8½ x 11 inch page. With relatively minor changes in the PLOT routine, the plot can also be reduced to this size.

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN

```
C MAIN PROGRAM ****** M O D K I N ******                                    00000010
C                                                                           00000020
C THIS PROGRAM READS AND ANALYZES INPUT FOR MODULAR KINETICS PROGRAM.       00000030
C  SETS INITIAL VALUES, CONTROLS ITERATION PRINTOUT, AND CALLS THE          00000040
C DIFFERENTIAL EQUATION SOLVING AND PLOT ROUTINES.                          00000050
C                                                                           00000060
C WRITTEN BY D. C. WHITNEY FOR SYSTEMS APPLICATIONS, INC.                   00000070
C ORIGINAL DATE 31 AUGUST 1973, LATEST MODIFICATION 25 OCTOBER 1973.        00000080
C THIS PROGRAM AND ALL SUBROUTINES (EXCEPT DIFSUB AND MATINV) ARE THE       00000090
C PROPERTY OF AND COPYRIGHT BY SYSTEMS APPLICATIONS. INC.                   00000100
C 950 NORTHGATE DRIVE; SAN RAFAEL, CALIFORNIA 94903.                        00000110
C                                                                           00000120
C SYMBOL DESCRIPTIONS --                                                    00000130
C                                                                           00000140
C COEFF    NUMBER OF PARTICLES, ONE PER PRODUCT SPECIES PER REACTION        00000150
C DELT     DIFFERENCE BETWEEN TWO CONSECUTIVE TIME STEPS                    00000160
C EPS      CONVERGENCE CRITERION, DOUBLE PRECISION, FOR DIFSUB              00000170
C EPSF     CONVERGENCE CRITERION                                            00000180
C ERROR    ESTIMATE OF ERROR IN CONCENTRATIONS, PPM, ONE PER SPECIES.       00000190
C              DOUBLE PRECISION, FOR DIFSUB                                 00000200
C ESUM     SUM OF THE EXPONENTIAL TERMS FOR THE REPLACEMENT SPECIES         00000210
C ETERM    TERM IN THE EXPONENTIAL CALCULATION OF THE REPLACEMENT SPEC.     00000220
C FLOW     SPECIES INFLOWS, PPM/MIN, 10 PER SPECIES                         00000230
C FTEST    TEMPORARY FLOW TIME OR CONCENTRATION FOR TESTING, MIN OR PPM     00000240
C FTIME    TIMES AT WHICH INFLOW IS MEASURED, MIN, 10 PER SPECIES           00000250
C H        NEXT STEP SIZE, MIN, DOUBLE PRECISION, FOR DIFSUB                00000260
C HMAX     MAXIMUM TIME STEP, MIN, DOUBLE PRECISION, FOR DIFSUB             00000270
C HMAXF    MAXIMUM TIME STEP, MIN                                           00000280
C HMIN     MINIMUM TIME STEP, MIN, DOUBLE PRECISION, FOR DIFSUB             00000290
C HMIN     MINIMUM TIME STEP, MIN                                           00000300
C HSTART   INITIAL STEP SIZE FOR DIFSUB                                     00000310
C J        DO-LOOP INDICES OR LOCAL POINTERS                                00000320
C JBLANK   A HOLLERITH WORD OF FOUR BLANK CHARACTERS                        00000330
C JFLAG    INDICATES NEGATIVE SPECIES FOUND IN DIFFERENTIAL CALCULATION     00000340
C JSTART   INPUT FLAG, FOR DIFSUB                                           00000350
C K        DO-LOOP INDICES OR LOCAL POINTERS                                00000360
C KCOF     COEFFICIENT POINTERS, ONE PER REACTION PRODUCT PER SPECIES.       00000370
C KFLAG    PERFORMANCE FLAG FOR DIFSUB                                      00000380
C KLMP     NUMBER OF CONTRIBUTING REACTIONS TO EACH LUMPED REACTION         00000390
C KLOC     LOCAL POINTER TO CONTRIBUTING REACTION                           00000400
C KPRD     PRODUCT POINTERS, ONE PER PRODUCT SPECIES PER REACTION           00000410
C KRCT     REACTANT POINTERS, ONE PER REACTANT SPECIES PER REACTION         00000420
C KRXN     REACTION POINTERS, ONE PER REACTION PER SPECIES                  00000430
C L        DO-LOOP INDICES OR LOCAL POINTERS                                00000440
C LFLAG    INDICATES INCORRECT SPECIES NAME IN REACTION -- STOPS JOB        00000450
C LRXN     POINTER TO FIRST OF A SERIES OF REPLACEMENT REACTIONS            00000460
C M        DO-LOOP INDICES OR LOCAL POINTERS                                00000470
C MAXDER   MAXIMUM ORDER FOR DERIVATIVES, FOR DIFSUB                        00000480
C MAXDIF   MAXIMUM NUMBER OF DIFFERENTIAL SPECIES                           00000490
C MAXFLW   MAXIMUM NUMBER OF FLOW TIMES                                     00000500
C MAXLMP   MAXIMUM NUMBER OF LUMPED REACTIONS                               00000510
C MAXPNT   MAXIMUM NUMBER OF SAVED TIME AND CONCENTRATION POINTS            00000520
C MAXPRD   MAXIMUM NUMBER OF PRODUCTS                                       00000530
C MAXPRT   MAXIMUM NUMBER OF ENTRIES ON PRINT LINE FOR RATES                00000540
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EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

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C MAXRCT   MAXIMUM NUMBER OF REACTANTS                                          00000550
C MAXREP   MAXIMUM NUMBER OF REPLACEMENT REACTIONS PER LUMPED REACTION          00000560
C MAXRXN   MAXIMUM NUMBER OF REACTIONS                                          00000570
C MAXSPC   MAXIMUM NUMBER OF SPECIES                                            00000580
C MF       METHOD INDICATOR, FOR DIFSUB                                         00000590
C MRXN     TOTAL NUMBER OF REACTIONS, INCLUDING REPLACEMENTS                    00000600
C N        DO-LOOP INDICES OR LOCAL POINTERS                                    00000610
C NAME     SPECIES NAMES, ONE PER SPECIES                                       00000620
C NDIF     NUMBER OF DIFFERENTIAL SPECIES                                       00000630
C NFLW     NUMBER OF FLOWING SPECIES                                            00000640
C NIN      THE FORTRAN INPUT UNIT (NORMALLY 5)                                  00000650
C NINT     NUMBER OF INERT/CONSTANT SPECIES                                     00000660
C NLMP     NUMBER OF LUMPED REACTIONS                                           00000670
C NLOC     NUMBER OF CONTIBUTING REACTIONS PERTAINING TO LUMPED REACTION        00000680
C NMPD     PRODUCT NAMES, ONE PER PRODUCT SPECIES PER REACTION                  00000690
C NMRC     REACTANT NAMES, ONE PER REACTANT SPECIES PER REACTION                00000700
C NOUT     THE FORTRAN OUTPUT UNIT NUMBER (NORMALLY 6)                          00000710
C NP       LOCAL POINTER TO REACTION RATE TO BE PRINTED                         00000720
C NPNT     NUMBER OF SAVED TIMES AND CONCENTRATIONS                             00000730
C NPRT     HOLDING AREA TO PRINT OUT A LINE OF NAMES OR NUMBERS                 00000740
C NR       POINTER TO REPLACEMENT SPECIES                                       00000750
C NRAT     USER INPUT FLAG REQUESTING PRINT OF REACTION RATES                   00000760
C NREP     NUMBER OF REPLACEMENT SPECIES                                        00000770
C NRESET   COUNTER FOR NUMBER OF TIMES STEP,SIZE IS RESET SMALLER               00000780
C NRXN     NUMBER OF REACTIONS                                                  00000790
C NS       POINTER TO REACTING SPECIES                                          00000800
C NSTS     NUMBER OF STEADY-STATE SPECIES                                       00000810
C NTEST    SPECIES NAME FOR TESTING                                             00000820
C NTIM     NUMBER OF TIMES AND FLOWS FOR A SPECIES                              00000830
C NTIT     USER-INPUT TITLE FOR PRINTOUT, 3 FOUR-CHARACTER WORDS                00000840
C NTOT     TOTAL NUMBER OF SPECIES                                              00000850
C NU       LOCAL POINTER TO UNCOUPLED SPECIES                                   00000860
C NUNC     NUMBER OF UNCOUPLED SPECIES                                          00000870
C PSAVE    BLOCK STORAGE, NUMBER OF SPECIES SQUARED, FOR DIFSUB                 00000880
C Q        DEGRADATION RATE, /MIN                                               00000890
C R        REACTION RATES, SEC, ONE PER REACTION                                00000900
C RATE     LOCAL REPRESENTATION OF R, THE REACTION RATE                         00000910
C RK       REACTION RATE CONSTANTS, PPM-MIN, ONE PER REACTION                   00000920
C RPRT     HOLDING AREA TO PRINT OUT A LINE OF REACTION RATES                   00000930
C SAVE     BLOCK STORAGE, 12 PER SPECIES, DOUBLE PRECISION, FOR DIFSUB          00000940
C SAVCON   SPECIES CONCENTRATIONS, PPM, ONE PER SPECIES AT 80 TIMES             00000950
C SAVTIM   TIMES THAT CONCENTRATIONS ARE SAVED, MIN, UP TO 80 VALUES            00000960
C T        CURRENT REACTION TIME, SEC, DOUBLE PRECISION,                        00000970
C              FOR AND FROM DIFSUB                                              00000980
C TCOUNT   NEXT TIME FOR OUTPUT, MIN                                            00000990
C TEND     ENDING TIME, MIN                                                     00001000
C TF       PREVIOUS TIME OF DIFSUB CALL, MIN                                    00001010
C TINCR    TIME INCREMENT FOR OUTPUT, MIN                                       00001020
C TOL      CONVERGENCE TOLERANCE ON STEADY-STATE ITERATION, PPM                 00001030
C UNCOLD   PREVIOUS VALUES OF RATE OF CHANGE, PPM/MIN, ONE PER SPECIES          00001040
C TOLD     TIME OF PREVIOUS CALL TO DIFSUB                                      00001050
C Y        SPECIES CONCENTRATIONS, 8 PER SPECIES, DOUBLE PRECISION,             00001060
C              FOR AND FROM DIFSUB                                              00001070
C YAX      SPECIES CONCENTRATIONS, PPM, ONE PER SPECIES                         00001080
C YCALC    LOCAL REPRESENTATION OF YDOT, THE RATE OF CHANGE                     00001090
C YIN      SPECIES INFLOW RATES, PPM/MIN, ONE PER SPECIES                       00001100
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
C YMAX      CURRENT MAXIMUM CONCENTRATION VALUES, PPM, ONE-PER SPECIES,   00001110
C               DOUBLE PRECISION, FOR AND FROM DIFSUB                     00001120
C YOLD      CONCENTRATIONS AT PREVIOUS CALL TO DIFSUB, ONE PER SPECIES    00001130
C YUNC      RATE OF CHANGE OF UNCOUPLED SPECIES, PPM/MIN                  00001140
C                                                                         00001150
C BEGINNING OF PROGRAM.                                                   00001160
C                                                                         00001170
C DECLARE VARIABLES FOR DIFSUB AS DOUBLE PRECISION                        00001180
C                                                                         00001190
      DOUBLE PRECISION HMIN, HMAX, EPS, YMAX, ERROR, H, SAVE, T, Y        00001200
C                                                                         00001210
C DEFINE VARIABLES AND DIMENSIONS OF COMMON STORAGE WITH DIFFUN           00001220
C                                                                         00001230
      COMMON RK(99), R(99), YAX(50), YIN(50), COEFF(3,99)                 00001240
      COMMON KRCT(4,99), KPRD(3,99), KRXN(99,50), KCOF(99,50)             00001250
      COMMON Q, TOL, NRXN, NDIF, NSTS                                     00001260
C                                                                         00001270
C DEFINE DIMENSIONS OF LOCAL ARRAYS                                       00001280
C                                                                         00001290
      DIMENSION Y(8,40), YMAX(40), SAVE(12,40), ERROR(40), PSAVE(1600)    00001300
      DIMENSION NMRC(4,99), NMPD(3,99), NTIT(3), NPRT(10), RPRT(10)       00001310
      DIMENSION FTIME(10,50), FLOW(10,50), SAVCON(50,80), SAVTIM(80)      00001320
      DIMENSION YOLD(50), NAME(50), UNCOLD(50), KLMP(10)                  00001330
C                                                                         00001340
C SET MISCELLANEOUS DATA VALUES                                           00001350
C                                                                         00001360
      DATA MAXRCT /4/, NIN /5/, NOUT /6/, MAXPRD /3/, JBLANK /4H    /    00001370
      DATA MAXRXN /99/, MAXDIF /40/, MAXFLW /10/, MAXPNT /80/             00001380
      DATA MAXSPC /50/, MAXLMP /10/, MAXREP /10/, MAXPRT /5/              00001390
C                                                                         00001400
C READ CONTROL CARDS -- NOTE THIS IS RETURN POINT FROM PLOT CALL          00001410
C                                                                         00001420
10    READ (NIN,2,END=900) NTIT, NRXN, NLMP, NDIF, NSTS, NUNC, NREP,     00001430
     &     NINT, NFLW, NRAT                                               00001440
      READ (NIN,4) TINCR, TEND, HSTART, HMINF, HMAXF, EPSF, Q             00001450
C                                                                         00001460
C PRINT HEADING PAGE AND CONTROL CARD INPUTS                              00001470
C                                                                         00001480
      WRITE (NOUT,1002) NTIT, NRXN, NLMP, NDIF, NSTS, NUNC, NREP, NINT,  00001490
     &     NFLW, NRAT, TINCR, TEND, HSTART, HMINF, HMAXF, EPSF, Q         00001500
C                                                                         00001510
C TEST REACTION COUNT                                                     00001520
C                                                                         00001530
      IF (NRXN .GT. 0 .AND. NRXN .LE. MAXRXN) GO TO 12                    00001540
      WRITE (NOUT,1001) MAXRXN                                            00001550
      GO TO 900                                                           00001560
C                                                                         00001570
C SET SPECIES NAME FLAG AND OVERALL REACTION COUNT AND READ REACTIONS     00001580
C                                                                         00001590
12    LFLAG = 0                                                           00001600
      MRXN = NRXN                                                         00001610
      DO 15 K = 1,NRXN                                                    00001620
      READ (NIN,1) (NMRC(J,K), J = 1,MAXRCT),                             00001630
     &     (COEFF(J,K), NMPD(J,K), J = 1,MAXPRD), RK(K)                   00001640
15    CONTINUE                                                            00001650
C                                                                         00001660
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
C TEST NUMBER OF LUMPED REACTIONS                                       00001670
C                                                                       00001680
      IF (NLMP .LE. 0) GO TO 22                                         00001690
      IF (NLMP .LE. MAXLMP) GO TO 16                                    00001700
      WRITE (NOUT,1027) MAXLMP                                          00001710
      GO TO 900                                                         00001720
C                                                                       00001730
C READ AND TEST LUMPED SPECIES NAME AND NUMBER OF REPLACEMENT SPECIES   00001740
C                                                                       00001750
   16 DO 21 L = 1,NLMP                                                  00001760
      READ (NIN,6) NTEST, NLOC                                          00001770
      IF (NTEST .EQ. NMRC(1,NRXN - NLMP + L)) GO TO 17                  00001780
      WRITE (NOUT,1028) NTEST                                           00001790
      LFLAG = 1                                                         00001800
   17 IF (NLOC .GT. 0 .AND. NLOC .LE. MAXREP) GO TO 18                  00001810
      WRITE (NOUT,1030) MAXREP                                          00001820
      GO TO 900                                                         00001830
C                                                                       00001840
C SAVE NUMBER OF REPLACEMENT REACTIONS AND UPDATE AND CHECK TOTAL       00001850
C                                                                       00001860
   18 KLMP(L) = NLOC                                                    00001870
      MRXN = MRXN + NLOC                                                00001880
      IF (MRXN .LE. MAXRXN) GO TO 19                                    00001890
      WRITE (NOUT,1001) MAXRXN                                          00001900
      GO TO 900                                                         00001910
C                                                                       00001920
C READ REPLACEMENT REACTIONS                                            00001930
C                                                                       00001940
   19 DO 20 K = 1,NLOC                                                  00001950
      KLOC = K + MRXN - NLOC                                            00001960
      READ (NIN,1) (NMRC(J,KLOC), J = 1,MAXRCT), (COEFF(J,KLOC),       00001970
     &     NMPD(J,KLOC), J = 1,MAXPRD), RK(KLOC)                        00001980
   20 CONTINUE                                                          00001990
   21 CONTINUE                                                          00002000
C                                                                       00002010
C TEST NUMBER OF DIFFERENTIAL SPECIES                                   00002020
C                                                                       00002030
   22 IF (NDIF .LE. MAXDIF) GO TO 23                                    00002040
      WRITE (NOUT,1012) MAXDIF                                          00002050
      GO TO 900                                                         00002060
C                                                                       00002070
C SET AND TEST TOTAL NUMBER OF SPECIES                                  00002080
C                                                                       00002090
   23 NTOT = NDIF + NSTS + NUNC + NREP + NINT                           00002100
      IF (NTOT .LE. MAXSPC) GO TO 25                                    00002110
      WRITE (NOUT,1011) MAXSPC                                          00002120
      GO TO 900                                                         00002130
      IF (NFLW .LE. 0) GO TO 50                                         00002210
      IF (NFLW .LE. NTOT) GO TO 30                                      00002220
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
      WRITE (NOUT, 1023) NTOT                                          00002230
      GO TO 900                                                        00002240
C                                                                      00002250
C SET FLOW RATES AND TIMES TO ZERO                                     00002260
      IF (NFLW .LE. 0) GO TO 50                                        00002210
      IF (NFLW .LE. NTOT) GO TO 30                                     00002220
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
      WRITE (NOUT, 1023) NTOT                                                  00002230
      GO TO 900                                                                00002240
C                                                                              00002250
C SET FLOW RATES AND TIMES TO ZERO                                             00002260
C                                                                              00002270
30    DO 33 K = 1,NTOT                                                         00002280
      DO 32 J = 1,MAXFLW                                                       00002290
      FTIME(J,K) = 0.0                                                         00002300
      FLOW(J,K) = 0.0                                                          00002310
32    CONTINUE                                                                 00002320
33    CONTINUE                                                                 00002330
C                                                                              00002340
C READ FLOW CONTROL CARD                                                       00002350
C                                                                              00002360
      DO 45 K = 1,NFLW                                                         00002370
      READ (NIN,6) NTEST, NTIM                                                 00002380
C                                                                              00002390
C IDENTIFY SPECIES NAME -- EXIT IF NOT FOUND                                   00002400
C                                                                              00002410
      DO 35 L = 1,NTOT                                                         00002420
      IF (NTEST .EQ. NAME(L)) GO TO 40                                         00002430
35    CONTINUE                                                                 00002440
      WRITE (NOUT,1003) NTEST                                                  00002450
      GO TO 900                                                                00002460
C                                                                              00002470
C CHECK NUMBER OF FLOW INPUTS                                                  00002480
C                                                                              00002490
40    IF (NTIM .LE. MAXFLW) GO TO 42                                           00002500
      WRITE (NOUT,1024) MAXFLW                                                 00002510
      GO TO 900                                                                00002520
C                                                                              00002530
C READ FLOW INPUTS                                                             00002540
C                                                                              00002550
42    READ (NIN,7) (FTIME(J,L), FLOW(J,L), J = 1,NTIM)                         00002560
45    CONTINUE                                                                 00002570
C                                                                              00002580
C CLEAR REACTION POINTERS, FLOWS, AND UNCOUPLED RATES                          00002590
C                                                                              00002600
50    DO 60 K = 1,NTOT                                                         00002610
      DO 55 J = 1,MRXN                                                         00002620
      KRXN(J,K) = 0                                                            00002630
      KCOF(J,K) = 0                                                            00002640
55    CONTINUE                                                                 00002650
      YIN(K) = 0.0                                                             00002660
      UNCOLD(K) = 0.0                                                          00002670
60    CONTINUE                                                                 00002680
C                                                                              00002690
C MOVE INITIAL DIFFERENTIAL CONCENTRATIONS AND SET ERRORS AND MAXIMA           00002700
C                                                                              00002710
      DO 65 J = 1,NDIF                                                         00002720
      Y(1,J) = YAX(J)                                                          00002730
      ERROR(J) = 0.0                                                           00002740
      YMAX(J) = 1.0                                                            00002750
65    CONTINUE                                                                 00002760
C                                                                              00002770
C CLEAR SPECIES POINTERS                                                       00002780
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
C                                                                       00002790
      DO 90 K = 1,MRXN                                                  00002800
      DO 70 J = 1,MAXRCT                                                00002810
      KRCT(J,K) = 0                                                     00002820
70    CONTINUE                                                          00002830
      DO 80 J = 1,MAXPRD                                                00002840
      KPRD(J,K) = 0                                                     00002850
80    CONTINUE                                                          00002860
90    CONTINUE                                                          00002870
C                                                                       00002880
C SET LUMPED REACTION COUNTERS                                          00002890
C                                                                       00002900
      LRXN = NRXN + 1                                                   00002910
      KLOC = 1                                                          00002920
      DO 190 M = 1,MRXN                                                 00002930
      DO 130 L = 1,MAXRCT                                               00002940
C                                                                       00002950
C IDENTIFY REACTANT SPECIES -- FLAG IF MISSING                          00002960
C                                                                       00002970
      NTEST = NMRC(L,M)                                                 00002980
      IF (NTEST .EQ. JBLANK) GO TO 140                                  00002990
      DO 110 K = 1,NTOT                                                 00003000
      IF (NTEST .EQ. NAME(K)) GO TO 115                                 00003010
110   CONTINUE                                                          00003020
      WRITE (NOUT,1003) NTEST                                           00003030
      LFLAG = 1                                                         00003040
      GO TO 130                                                         00003050
C                                                                       00003060
C FILL IN REACTION AND SPECIES POINTERS AND COUNTERS                    00003070
C                                                                       00003080
115   KRCT(L,M) = K                                                     00003090
      DO 120 J = 1,MAXRXN                                               00003100
      IF (KRXN(J,K) .EQ. 0) GO TO 125                                   00003110
120   CONTINUE                                                          00003120
125   KRXN(J,K) = M                                                     00003130
      KCOF(J,K) = -1                                                    00003140
130   CONTINUE                                                          00003150
C                                                                       00003160
C IDENTIFY PRODUCT SPECIES -- FLAG IF MISSING                           00003170
C                                                                       00003180
140   DO 170 L = 1,MAXPRD                                               00003190
      NTEST = NMPD(L,M)                                                 00003200
      IF (NTEST .EQ. JBLANK) GO TO 180                                  00003210
      DO 150 K = 1,NTOT                                                 00003220
      IF (NTEST .EQ. NAME(K)) GO TO 155                                 00003230
150   CONTINUE                                                          00003240
      WRITE (NOUT,1003) NTEST                                           00003250
      LFLAG = 1                                                         00003260
      GO TO 170                                                         00003270
C                                                                       00003280
C FILL IN REACTION AND SPECIES POINTERS AND COUNTERS                    00003290
C                                                                       00003300
155   KPRD(L,M) = K                                                     00003310
      DO 160 J = 1,MAXRXN                                               00003320
      IF (KRXN(J,K) .EQ. 0) GO TO 165                                   00003330
160   CONTINUE                                                          00003340
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
165   KRXN(J,K) = M                                                          00003350
      KCOF(J,K) = L                                                          00003360
170   CONTINUE                                                               00003370
C                                                                            00003380
C SAVE NUMBER OF PRODUCT SPECIES FOR THIS REACTION                           00003390
C                                                                            00003400
      L = MAXPRD + 1                                                         00003410
180   NPRD = L - 1                                                           00003420
C                                                                            00003430
C IF REPLACEMENT FOR LUMPED REACTION, PRINT MESSAGE AND UPDATE POINTERS      00003440
C                                                                            00003450
      IF (M .NE. LRXN) GO TO 183                                             00003460
      N = NRXN - NLMP + KLOC                                                 00003470
      WRITE (NOUT,1029) KLMP(KLOC), N                                        00003480
      LRXN = LRXN + KLMP(KLOC)                                               00003490
      KLOC = KLOC + 1                                                        00003500
C                                                                            00003510
C REVERSE ORDER OF REACTANTS FOR PRINTING                                    00003520
C                                                                            00003530
  183 DO 185 J = 1,MAXRCT                                                    00003540
      K = MAXRCT - J + 1                                                     00003550
      NPRT(J) = NMRC(K,M)                                                    00003560
185   CONTINUE                                                               00003570
C                                                                            00003580
C PRINT SET OF REACTIONS                                                     00003590
C                                                                            00003600
      WRITE (NOUT,1004) M, RK(M), (NPRT(J), J=1,MAXRCT),                     00003610
     &     (COEFF(J,M), NMPD(J,M), J = 1,NPRD)                               00003620
190   CONTINUE                                                               00003630
C                                                                            00003640
C GET INITIAL CONDITIONS FOR LUMPED REACTIONS AND SPECIES                    00003650
C                                                                            00003660
      IF (NLMP .GT. 0) CALL LMPCAL(NLMP, KLMP)                               00003670
C                                                                            00003680
C PRINT INITIAL SPECIES CONCENTRATIONS -- EXIT IF FLAG SET                   00003690
C                                                                            00003700
      WRITE (NOUT,1013)                                                      00003710
      WRITE (NOUT,1005)                                                      00003720
      WRITE (NOUT,1006) (NAME(J), YAX(J), J=1,NDIF)                          00003730
      IF (NSTS .GT. 0)                                                       00003740
     &WRITE (NOUT,1025) (NAME(J+NDIF), YAX(J+NDIF), J=1,NSTS)                00003750
      IF (NUNC .GT. 0)                                                       00003760
     &WRITE (NOUT,1007) (NAME(J+NDIF+NSTS),                                  00003770
     &     YAX(J+NDIF+NSTS), J = 1,NUNC)                                     00003780
      IF (NREP .GT. 0)                                                       00003790
     &WRITE (NOUT,1031) (NAME(J+NDIF+NSTS+NUNC),                             00003800
     &     YAX(J+NDIF+NSTS+NUNC), J = 1,NREP)                                00003810
      IF (NINT .GT. 0)                                                       00003820
     &WRITE (NOUT,1008) (NAME(J+NDIF+NSTS+NUNC+NREP),                        00003830
     &     YAX(J+NDIF+NSTS+NUNC+NREP), J = 1,NINT)                           00003840
      IF (LFLAG .EQ. 1) GO TO 900                                            00003850
C                                                                            00003860
C SET INITIAL CONDITIONS                                                     00003870
C                                                                            00003880
      HMAX = HMAXF                                                           00003890
      HMIN = HMINF                                                           00003900
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
      TCOUNT = TINCR                                                    00003910
      EPS = EPSF                                                        00003920
      TOL = EPSF                                                        00003930
      H = HSTART                                                        00003940
      MF = 2                                                            00003950
      JSTART = 0                                                        00003960
      NPNT = 0                                                          00003970
      TF = 0.0                                                          00003980
      T = 0.0                                                           00003990
      TOLD = 0.0                                                        00004000
      MAXDER = 6                                                        00004010
      JFLAG = 0                                                         00004020
      KFLAG = 1                                                         00004030
      NRESET = 0                                                        00004040
C                                                                       00004050
C SAVE INITIAL CONCENTRATIONS AND FLOWS                                 00004060
C                                                                       00004070
      DO 195 J = 1,NTOT                                                 00004080
      YOLD(J) = YAX(J)                                                  00004090
      IF (NFLW .EQ. 0) GO TO 195                                        00004100
      IF (FTIME(1,J) .GT. 0.0) GO TO 195                                00004110
      YIN(J) = FLOW(1,J)                                                00004120
  195 CONTINUE                                                          00004130
C                                                                       00004140
C CALL DIFFERENTIAL SPECIES SOLVER -- NOTE THIS IS A RETURN POINT       00004150
C                                                                       00004160
  200 CALL DIFSUB(NDIF, T, Y, SAVE, H, HMIN, HMAX, EPS, MF,             00004170
     &     YMAX, ERROR, KFLAG, JSTART, MAXDER, PSAVE)                   00004180
C                                                                       00004190
C UPDATE TIME AND SAVE CONCENTRATIONS, CHECKING FOR NEGATIVITY          00004200
C                                                                       00004210
      TF = T                                                            00004220
      DELT = TF - TOLD                                                  00004230
      DO 210 J = 1,NTOT                                                 00004240
      IF (J .LE. NDIF) YAX(J) = Y(1,J)                                  00004250
      IF (YAX(J) .LT. 0.0) JFLAG = 1                                    00004260
  210 CONTINUE                                                          00004270
      IF (JFLAG .EQ. 0) GO TO 230                                       00004280
      JFLAG = 0                                                         00004290
C                                                                       00004300
C NEGATIVE CONCENTRATION -- RESET AND TEST STEP SIZE                    00004310
C                                                                       00004320
      H = 0.1 * H                                                       00004330
      IF (H .LT. HMIN) KFLAG = 0                                        00004340
C                                                                       00004350
C TEST RESET COUNTER FOR RE-ENTRY, THEN SET TO PREVENT SAME--TEST FLAG  00004360
C                                                                       00004370
      IF (NRESET .GT. 0) KFLAG = 0                                      00004380
      NRESET = 1                                                        00004390
      IF (KFLAG .NE. 1) GO TO 330                                       00004400
C                                                                       00004410
C RESTORE OLD CONCENTRATIONS AND RECALL DIFSUB WITH SMALLER STEP SIZE   00004420
C                                                                       00004430
      DO 220 J = 1,NTOT                                                 00004440
      YAX(J) = YOLD(J)                                                  00004450
  220 CONTINUE                                                          00004460
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
      JSTART = -1                                                        00004470
      GO TO 200                                                          00004480
C                                                                        00004490
C TEST FOR AND SET POINTERS TO REPLACEMENT SPECIES                       00004500
C                                                                        00004510
  230 IF (NREP .LE. 0) GO TO 265                                         00004520
      LRXN = NRXN + 1                                                    00004530
      DO 260 M = 1,NREP                                                  00004540
      NR = NDIF + NSTS + NUNC + M                                        00004550
      ESUM = 0.0                                                         00004560
C                                                                        00004570
C FIND REACTIONS CONTAINING REPLACEMENT SPECIES                          00004580
C                                                                        00004590
      DO 250 L = LRXN, MRXN                                              00004600
      IF (KRCT(1,L) .NE. NR) GO TO 250                                   00004610
C                                                                        00004620
C MULTIPLY TOGETHER ALL OTHER REACTANT CONCENTRATIONS                    00004630
C                                                                        00004640
      ETERM = 1.0                                                        00004650
      DO 240 K = 2,MAXRCT                                                00004660
      NS = KRCT(K,L)                                                     00004670
      IF (NS .EQ. 0) GO TO 245                                           00004680
      ETERM = ETERM * YAX(NS)                                            00004690
  240 CONTINUE                                                           00004700
C                                                                        00004710
C MULTIPLY BY RATE CONSTANT AND ADD TO EXPONENTIAL SUM                   00004720
C                                                                        00004730
  245 ESUM = ESUM + RK(L) * ETERM                                        00004740
  250 CONTINUE                                                           00004750
C                                                                        00004760
C CALCULATE NEW SPECIES CONCENTRATIONS                                   00004770
C                                                                        00004780
      YAX(NR) = YAX(NR) * EXP(-ESUM * DELT) * (1.0 - DELT * Q)           00004790
  260 CONTINUE                                                           00004800
C                                                                        00004810
C UPDATE LUMPED REACTIONS AND SPECIES PARAMETERS                         00004820
C                                                                        00004830
      CALL LMPCAL(NLMP, KLMP)                                            00004840
C                                                                        00004850
C TEST FOR AND SET POINTERS TO UNCOUPLED SPECIES                         00004860
C                                                                        00004870
  265 IF (NUNC .LE. 0) GO TO 300                                         00004880
      DO 290 M = 1,NUNC                                                  00004890
      NU = NDIF + NSTS + M                                               00004900
      YUNC = 0.0                                                         00004910
      DO 270 L = 1,NRXN                                                  00004920
      J = KCOF(L,NU)                                                     00004930
      K = KRXN(L,NU)                                                     00004940
C                                                                        00004950
C CALCULATE THE RATE OF CHANGE OF THE UNCOUPLED SPECIES                  00004960
C                                                                        00004970
      IF (J) 267, 280, 268                                               00004980
  267 YUNC = YUNC - R(K)                                                 00004990
      GO TO 270                                                          00005000
  268 YUNC = YUNC + R(K) * COEFF(J,K)                                    00005010
  270 CONTINUE                                                           00005020
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
  280 YUNC = YUNC + Q * (YIN(NU) - YAX(NU))                          00005030
C                                                                    00005040
C CALCULATE UNCOUPLED SPECIES CONCENTRATION AND UPDATE OLD RATE      00005050
C                                                                    00005060
      YAX(NU) = YAX(NU) + (YUNC + UNCOLD(NU)) * DELT * 0.5           00005070
      UNCOLD(NU) = YUNC                                              00005080
  290 CONTINUE                                                       00005090
C                                                                    00005100
C CHECK TIME FOR END AND PRINTING AND SAVING OF PLOT POINTS          00005110
C                                                                    00005120
  300 IF (TF .GT. TEND) GO TO 330                                    00005130
      IF (TF .LE. TCOUNT) GO TO 340                                  00005140
C                                                                    00005150
C INCREMENT TIME AND PLOT POINT COUNTERS                             00005160
C                                                                    00005170
      TCOUNT = TCOUNT + TINCR                                        00005180
      NPNT = NPNT + 1                                                00005190
C                                                                    00005200
C CHECK PLOT POINT COUNTER FOR OVERFLOW                              00005210
C                                                                    00005220
      IF (NPNT .LE. MAXPNT) GO TO 310                                00005230
      WRITE (NOUT,1019) MAXPNT, TF                                   00005240
      NPNT = NPNT - 1                                                00005250
      GO TO 330                                                      00005260
C                                                                    00005270
C SAVE PLOT POINTS                                                   00005280
C                                                                    00005290
  310 SAVTIM(NPNT) = TF                                              00005300
      DO 320 J = 1,NTOT                                              00005310
      SAVCON(J,NPNT) = YAX(J)                                        00005320
  320 CONTINUE                                                       00005330
C                                                                    00005340
C PRINT INTERMEDIATE RESULTS                                         00005350
C                                                                    00005360
  330 WRITE (NOUT,1009) TF                                           00005370
      WRITE (NOUT,1005)                                              00005380
      WRITE (NOUT,1006) (NAME(J), YAX(J), J = 1,NDIF)                00005390
      IF (NSTS .GT. 0)                                               00005400
     &WRITE (NOUT,1025) (NAME(J+NDIF), YAX(J+NDIF), J=1,NSTS)        00005410
      IF (NUNC .GT. 0)                                               00005420
     &WRITE (NOUT,1007) (NAME(J+NDIF+NSTS),                          00005430
     &     YAX(J+NDIF+NSTS), J = 1,NUNC)                             00005440
      IF (NREP .GT. 0)                                               00005450
     &WRITE (NOUT,1031) (NAME(J+NDIF+NSTS+NUNC),                     00005460
     &     YAX(J+NDIF+NSTS+NUNC), J = 1,NREP)                        00005470
C                                                                    00005480
C CHECK RATE PRINT FLAG, PRINT HEADER, AND SET SORT PARAMETERS       00005490
C                                                                    00005500
      IF (NRAT .EQ. 0) GO TO 339                                     00005510
      WRITE (NOUT,1032)                                              00005520
      N = 0                                                          00005530
      RATE = -1.0                                                    00005540
      NP = 0                                                         00005550
      DO 338 M = 1,NRXN                                              00005560
C                                                                    00005570
C FIND LARGEST RATE                                                  00005580
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
C                                                                       00005590
      DO 336 L = 1,NRXN                                                 00005600
      IF (R(L) .LT. RATE) GO TO 336                                     00005610
      RATE = R(L)                                                       00005620
      NP = L                                                            00005630
  336 CONTINUE                                                          00005640
C                                                                       00005650
C SAVE AND FLAG THIS RATE AND RESET SORT PARAMETERS                     00005660
C                                                                       00005670
      N = N + 1                                                         00005680
      NPRT(N) = NP                                                      00005690
      RPRT(N) = RATE                                                    00005700
      R(NP) = -1.0                                                      00005710
      RATE = -1.0                                                       00005720
      NP = 0                                                            00005730
C                                                                       00005740
C CHECK PRINT COUNT AND PRINT IF FULL LINE OR END OF LOOP               00005750
C                                                                       00005760
  337 IF (N. LT. MAXPRT .AND. M .NE. NRXN) GO TO 338                    00005770
      WRITE (NOUT,1033) (NPRT(K), RPRT(K), K = 1,N)                     00005780
      N = 0                                                             00005790
  338 CONTINUE                                                          00005800
C                                                                       00005810
C CHECK FOR ERROR OR FINAL TIME PASSED, IF SO PLOT AND GET NEXT SET     00005820
C                                                                       00005830
  339 IF (TF .LT. TEND .AND. KFLAG .EQ. 1) GO TO 340                    00005840
      WRITE (NOUT,1010) KFLAG                                           00005850
      CALL PLOT(NTIT, NPNT, NTOT, NAME, SAVTIM, SAVCON)                 00005860
      GO TO 10                                                          00005870
C                                                                       00005880
C CHECK FOR INFLOW UPDATES                                              00005890
C                                                                       00005900
  340 IF (NFLW .LE. 0) GO TO 380                                        00005910
      DO 370 K = 1,NTOT                                                 00005920
      DO 350 J = 1,MAXFLW                                               00005930
      IF (J .EQ. MAXFLW) GO TO 360                                      00005940
      FTEST = FTIME(J+1,K)                                              00005950
      IF (FTEST .GT. TF) GO TO 360                                      00005960
      IF (FTEST .LE. 0.) GO TO 360                                      00005970
  350 CONTINUE                                                          00005980
C                                                                       00005990
C UPDATE INFLOWS AND WRITE MESSAGE                                      00006000
C                                                                       00006010
  360 FTEST = FLOW(J,K)                                                 00006020
      IF (YIN(K) .EQ. FTEST) GO TO 370                                  00006030
      YIN(K) = FTEST                                                    00006040
      WRITE (NOUT,1026) NAME(K), FTEST, TF                              00006050
  370 CONTINUE                                                          00006060
C                                                                       00006070
C UPDATE TIME AND CONCENTRATION AND TAKE NEXT TIME STEP                 00006080
C                                                                       00006090
  380 TOLD = TF                                                         00006100
      NRESET = 0                                                        00006110
      DO 390 J = 1,NTOT                                                 00006120
      YOLD(J) = YAX(J)                                                  00006130
  390 CONTINUE                                                          00006140
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Continued)

```
      GO TO 200                                                          00006150
C                                                                        00006160
C END OF PROGRAM                                                         00006170
C                                                                        00006180
900   STOP                                                               00006190
C                                                                        00006200
C LIST OF FORMAT STATEMENTS                                              00006210
C                                                                        00006220
1     FORMAT (4(A4, 1X), 3(F6.0, A4), F10.0)                             00006230
2     FORMAT (3A4, 3X, 9I5)                                              00006240
3     FORMAT (A4, 6X, F10.0)                                             00006250
    4 FORMAT (8F10.0)                                                    00006260
6     FORMAT (A4, 1X, I5)                                                00006270
7     FORMAT (8F10.0)                                                    00006280
 1001 FORMAT (33H PROGRAM CANNOT HANDLE MORE THAN , I4,                  00006290
     &      26H REACTIONS -- JOB ABORTED.)                              00006300
 1002 FORMAT (1H1, 20X, 25HMODULAR KINETICS RUN NO. , 3A4, ////,         00006310
     &      29H TOTAL NUMBER OF REACTIONS = , I3, //,                   00006320
     &      30H NUMBER OF LUMPED REACTIONS = , I3, //,                  00006330
     &      34H NUMBER OF DIFFERENTIAL SPECIES = , I3, //,              00006340
     &      34H NUMBER OF STEADY STATE SPECIES = , I3, //,              00006350
     &      31H NUMBER OF UNCOUPLED SPECIES = , I3, //,                 00006360
     &      33H NUMBER OF REPLACEMENT SPECIES = , I3, //,               00006370
     &      39H NUMBER OF INERT OR CONSTANT SPECIES = , I3, //,         00006380
     &      29H NUMBER OF FLOWING SPECIES = , I3, //,                   00006390
     &      36H REACTION RATE PRINT REQUEST FLAG = , I3, //,            00006400
     &      18H TIME INCREMENT = , 1PE12.3, 9H MINUTES , //,            00006410
     &      15H ENDING TIME = , 1PE12.3, 9H MINUTES , //,               00006420
     &      22H STARTING STEP SIZE = , 1PE12.3, 9H MINUTES , //,        00006430
     &      21H MINIMUM STEP SIZE = , 1PE12.3, 9H MINUTES , //,         00006440
     &      21H MAXIMUM STEP SIZE = , 1PE12.3, 9H MINUTES , //,         00006450
     &      25H CONVERGENCE TOLERANCE = , 1PE12.3, //,                  00006460
     &      17H DILUTION RATE = , 1PE12.3, 12H MINUTES(-1), //,         00006470
     &      1H1, 26X, 18H LIST OF REACTIONS, //,                        00006480
     &      14H     R. CONST., 8X, 9HREACTANTS, 12X, 8HPRODUCTS, /)     00006490
 1003 FORMAT (14H SPECIES NAME , A4, 21H NOT IN SPECIES LIST,            00006500
     &      21H JOB WILL BE ABORTED.)                                   00006510
 1004 FORMAT (I3, 1PE11.3, 4(1X, A4), 2H =,                              00006520
     &      3(0PF6.2, 1X, A4))                                          00006530
 1005 FORMAT (/, 4(18H SPECIES   VALUE  ))                               00006540
 1006 FORMAT (/, 18H DIFFERENTIAL(PPM), //, (4(3X, A4, 1PE11.3)))       00006550
 1007 FORMAT (/, 15H UNCOUPLED(PPM), //, (4(3X, A4, 1PE11.3)))          00006560
 1008 FORMAT (/, 20H INERT/CONSTANT(PPM), //, (4(3X, A4, 1PE11.3)))     00006570
 1009 FORMAT (//, 20X, 8H TIME = , 1PE12.3, 8H MINUTES, /)               00006580
 1010 FORMAT (/, 33H THIS RUN TERMINATED WITH KFLAG = , I3)              00006590
 1011 FORMAT (//, 33H PROGRAM CANNOT HANDLE MORE THAN , I4,              00006600
     &      24H SPECIES -- JOB ABORTED.)                                00006610
 1012 FORMAT (//, 33H PROGRAM CANNOT HANDLE MORE THAN , I4,              00006620
     &      30H DIFFERENTIALS -- JOB ABORTED.)                          00006630
 1013 FORMAT (/, 1H1, 20X, 30HINITIAL SPECIES CONCENTRATIONS, /)         00006640
 1019 FORMAT (/, 31H MAXIMUM NUMBER OF PLOT POINTS , I3,                 00006650
     &      19H HAS BEEN EXCEEDED., /, 15H POINT AT TIME , F8.2,        00006660
     &      21H WILL NOT BE PLOTTED.)                                   00006670
 1023 FORMAT (//, 33H PROGRAM CANNOT HANDLE MORE THAN , I4,              00006680
     &      22H FLOWS -- JOB ABORTED.)                                  00006690
 1024 FORMAT (//, 33H PROGRAM CANNOT HANDLE MORE THAN , I4,              00006700
```

EXHIBIT A-1. LISTING OF MAIN PROGRAM MODKIN (Concluded)

```
     &     27H FLOW TIMES -- JOB ABORTED.)                                  00006710
1025 FORMAT (/, 18H STEADY STATE(PPM), //, (4(3X, A4, 1PE11.3)))            00006720
1026 FORMAT (/, 10H INCOMING , A4, 26H CONCENTRATION CHANGED TO ,            00006730
     &     1PE11.3, 4H AT , 1PE11.3, 5H MIN.)                              00006740
1027 FORMAT (//, 33H PROGRAM CANNOT HANDLE MORE THAN , I4,                   00006750
     &     33H LUMPED REACTIONS -- JOB ABORTED.)                            00006760
1028 FORMAT (16H LUMPED SPECIES , A4, 24H IS NOT FIRST SPECIES IN,           00006770
     &     54H CORRESPONDING LUMPED REACTION -- JOB WILL BE ABORTED.)       00006780
1029 FORMAT (/, 21H THE FOLLOWING SET OF , I3,                               00006790
     &     42H REACTIONS CORRESPONDS TO REACTION NUMBER , I3, /)            00006800
1030 FORMAT (//, 33H PROGRAM CANNOT HANDLE MORE THAN , I4,                   00006810
     &     39H CONTRIBUTING REACTIONS -- JOB ABORTED.)                      00006820
1031 FORMAT (/, 17H REPLACEMENT(PPM), //, (4(3X, A4, 1PE11.3)))             00006830
1032 FORMAT (/, 15X, 44HREACTION RATES (SORTED INTO DECREASING SIZE),        00006840
     &     //, 5(15H   NO.   RATE  ), /)                                    00006850
1033 FORMAT (5(I5, 1PE10.2))                                                 00006860
     END                                                                     00006870
```

EXHIBIT A-2. LISTING OF SUBROUTINE LMPCAL

```
C SUBROUTINE ****** L M P C A L ******                                    00000010
C                                                                         00000020
C THIS SUBROUTINE CALCULATES THE CONCENTRATIONS OF LUMPED SPECIES AND     00000030
C THE COEFFICIENTS AND RATE CONSTANTS FOR THE CORRESPONDING REACTIONS     00000040
C                                                                         00000050
C SYMBOL DEFINITIONS --                                                   00000060
C                                                                         00000070
C ALPHA     LOCAL VALUES OF COEFF, THE PRODUCT COEFFICIENTS               00000080
C COEFF     NUMBER OF PARTICLES, ONE PER PRODUCT SPECIES PER REACTION     00000090
C COLOC     LOCAL VALUE OF PRODUCT COEFFCIENT                             00000100
C COMIN     MINIMUM ALLOWABLE COEFFICIENT SIZE                            00000110
C J         DO-LOOP INDICES OR LOCAL POINTERS                             00000120
C K         DO-LOOP INDICES OR LOCAL POINTERS                             00000130
C KCOF      COEFFICIENT POINTERS, ONE PER REACTION PRODUCT PER SPECIES     00000140
C KLMP      NUMBER OF CONTRIBUTING REACTIONS TO EACH LUMPED REACTION       00000150
C KPRD      PRODUCT POINTERS, ONE PER PRODUCT SPECIES PER REACTION        00000160
C KRCT      REACTANT POINTERS, ONE PER REACTANT SPECIES PER REACTION      00000170
C KRXN      REACTION POINTERS, ONE PER REACTION PER SPECIES               00000180
C L         DO-LOOP INDICES OR LOCAL POINTERS                             00000190
C LRXN      POINTER TO LUMPED REACTION                                    00000200
C M         DO-LOOP INDICES OR LOCAL POINTERS                             00000210
C MAXPRD    MAXIMUM NUMBER OF PRODUCTS                                    00000220
C N         DO-LOOP INDICES OR LOCAL POINTERS                             00000230
C NDIF      NUMBER OF DIFFERENTIAL SPECIES                                00000240
C NLMP      NUMBER OF LUMPED REACTIONS                                    00000250
C NLOC      NUMBER OF REPLACEMENT REACTIONS FOR THIS LUMPED REACTION      00000260
C NOUT      THE FORTRAN OUTPUT UNIT NUMBER (NORMALLY 6)                   00000270
C NR        POINTER TO REPLACEMENT REACTION                               00000280
C NRXN      NUMBER OF REACTIONS                                           00000290
C NS        POINTER TO REACTANT SPECIES                                   00000300
C NSTS      NUMBER OF STEADY-STATE SPECIES                                00000310
C Q         DEGRADATION RATE, /MIN                                        00000320
C R         REACTION RATES, SEC, ONE PER REACTION                         00000330
C RK        REACTION RATE CONSTANTS, PPM-MIN, ONE PER REACTION            00000340
C RKLMP     LOCAL VALUE OF LUMPED RATE CONSTANT                           00000350
C RKLOC     LOCAL VALUES OF RK, THE REACTION RATE CONSTANTS               00000360
C SUM       SUM OF CONCENTRATIONS OF ALL THE REPLACEMENT SPECIES          00000370
C TOL       CONVERGENCE TOLERANCE ON STEADY-STATE ITERATION, PPM          00000380
C YAX       SPECIES CONCENTRATIONS, PPM, ONE PER SPECIES                  00000390
C YF        THE MOLE FRACTIONS OF THE REPLACEMENT SPECIES                 00000400
C YIN       SPECIES INFLOW RATES. PPM/MIN, ONE PER SPECIES                00000410
C YLOC      LOCAL VALUES OF YAX, THE SPECIES CONCENTRATIONS               00000420
C                                                                         00000430
C SUBROUTINE ENTRY POINT                                                  00000440
C                                                                         00000450
      SUBROUTINE LMPCAL(NLMP, KLMP)                                       00000460
C                                                                         00000470
C DECLARE COMMON STORAGE                                                  00000480
C                                                                         00000490
      COMMON RK(99), R(99), YAX(50), YIN(50), COEFF(3,99)                 00000500
      COMMON KRCT(4,99), KPRD(3,99), KRXN(99,50), KCOF(99,50)             00000510
      COMMON Q, TOL, NRXN, NDIF, NSTS                                     00000520
C                                                                         00000530
C SET DIMENSIONS                                                          00000540
```

EXHIBIT A-2. LISTING OF SUBROUTINE LMPCAL (Continued)

```
C                                                                       00000550
      DIMENSION YLOC(10), RKLOC(10), ALPHA(3,10), YF(10), KLMP(NLMP)    00000560
C                                                                       00000570
C SET DATA STATEMENT PARAMETERS                                         00000580
C                                                                       00000590
      DATA MAXPRD /3/, COMIN /0.0001/                                   00000600
C                                                                       00000610
C SET CONTRIBUTING REACTION POINTER AND NUMBER OF CONTRIBUTING REACTIONS00000620
C                                                                       00000630
      NR = NRXN + 1                                                     00000640
      DO 70 N = 1,NLMP                                                  00000650
      NLOC = KLMP(N)                                                    00000660
      LRXN = NRXN - NLMP + N                                            00000670
C                                                                       00000680
C SAVE RATE CONSTANT AND SAVE AND SUM SPECIES CONCENTRATIONS            00000690
C                                                                       00000700
      SUM = 0.0                                                         00000710
      DO 20 K = 1,NLOC                                                  00000720
      NS = KRCT(1,NR)                                                   00000730
      RKLOC(K) = RK(NR)                                                 00000740
      YLOC(K) = YAX(NS)                                                 00000750
      SUM = SUM + YLOC(K)                                               00000760
C                                                                       00000770
C SAVE PRODUCT COEFFICIENTS                                             00000780
C                                                                       00000790
      DO 10 J = 1,MAXPRD                                                00000800
      ALPHA(J,K) = COEFF(J,NR)                                          00000810
   10 CONTINUE                                                          00000820
C                                                                       00000830
C ADVANCE REACTION POINTER AND SAVE OVERALL SUM                         00000840
C                                                                       00000850
      NR = NR + 1                                                       00000860
   20 CONTINUE                                                          00000870
      NS = KRCT(1,LRXN)                                                 00000880
      YAX(NS) = SUM                                                     00000890
C                                                                       00000900
C CALCULATE THE MOLE FRACTIONS                                          00000910
C                                                                       00000920
      DO 30 K = 1,NLOC                                                  00000930
      YF(K) = YLOC(K) / SUM                                             00000940
   30 CONTINUE                                                          00000950
C                                                                       00000960
C CALCULATE LUMPED RATE CONSTANT                                        00000970
C                                                                       00000980
      RKLMP = 0.0                                                       00000990
      DO 40 K = 1,NLOC                                                  00001000
      RKLMP = RKLMP + YF(K) * RKLOC(K)                                  00001010
   40 CONTINUE                                                          00001020
      RK(LRXN) = RKLMP                                                  00001030
C                                                                       00001040
C CALCULATE SPECIES COEFFICIENTS                                        00001050
C                                                                       00001060
      DO 60 J = 1,MAXPRD                                                00001070
      COLOC = 0.0                                                       00001080
      DO 50 K = 1,NLOC                                                  00001090
      COLOC = COLOC + ALPHA(J,K) * RKLOC(K) * YF(K)                     00001100
```

EXHIBIT A-2. LISTING OF SUBROUTINE LMPCAL (Concluded)

```
   50 CONTINUE                                                          00001110
C                                                                       00001120
C NORMALIZE COEFFICIENT AND CHECK FOR UNDERFLOW                         00001130
C                                                                       00001140
      COLOC = COLOC / RKLMP                                             00001150
      IF (COLOC .LT. COMIN) COLOC = 0.0                                 00001160
      COEFF(J,LRXN) = COLOC                                             00001170
   60 CONTINUE                                                          00001180
   70 CONTINUE                                                          00001190
C                                                                       00001200
C END OF PROGRAM -- RETURN TO CALLER                                    00001210
C                                                                       00001220
      RETURN                                                            00001230
      END                                                               00001240
```

EXHIBIT A-3. LISTING OF SUBROUTINE DIFSUB

```
C**********************************************************************00000010
C* THE PARAMETERS TO THE SUBROUTINE DIFSUB HAVE                         00000020
C* THE FOLLOWING MEANINGS:                                              00000030
C*                                                                      00000040
C*  N     THE NUMBER OF FIRST ORDER DIFFERENTIAL EQUATIONS.  N          00000050
C*          MAY BE DECREASED ON LATER CALLS IF THE NUMBER OF            00000060
C*          ACTIVE EQUATIONS REDUCES. BUT IT MUST NOT BE                00000070
C*          INCREASED WITHOUT CALLING WITH JSTART = 0                   00000080
C*  T     THE INDEPENDENT VARIABLE.                                     00000090
C*  Y     AN 8 BY N ARRAY CONTAINING THE DEPENDENT VARIABLES AND        00000100
C*          THEIR SCALED DERIVATIVES.  Y(J+1,I) CONTAINS                00000110
C*          THE J-TH DERIVATIVE OF Y(I) SCALED BY                       00000120
C*          H**J/FACTORIAL(J) WHERE H IS THE CURRENT                    00000130
C*          STEP SIZE. ONLY Y(1,I) NEED BE PROVIDED BY                  00000140
C*          THE CALLING PROGRAM ON THE FIRST ENTRY.                     00000150
C*            IF IT IS DESIRED TO INTERPOLATE TO NON MESH POINTS        00000160
C*          THESE VALUES CAN BE USED.  IF THE CURRENT STEP SIZE         00000170
C*          IS H AND THE VALUE AT T + E IS NEEDED, FORM                 00000180
C*          S = E/H, AND THEN COMPUTE                                   00000190
C*                          NQ                                          00000200
C*            Y(I)(T+E) = SUM  Y(J+1,I)*S**J                            00000210
C*                         J=0                                          00000220
C*  SAVE A BLOCK OF AT LEAST 12*N FLOATING POINT LOCATIONS              00000230
C*          USED BY THE SUBROUTINES.                                    00000240
C*  H     THE STEP SIZE TO BE ATTEMPTED ON THE NEXT STEP.               00000250
C*          H MAY BE ADJUSTED UP OR DOWN BY THE PROGRAM                 00000260
C*          IN ORDER TO ACHEIVE AN ECONOMICAL INTEGRATION.              00000270
C*          HOWEVER, IF THE H PROVIDED BY THE USER DOES                 00000280
C*          NOT CAUSE A LARGER ERROR THAN REQUESTED, IT                 00000290
C*          WILL BE USED.  TO SAVE COMPUTER TIME, THE USER IS           00000300
C*          ADVISED TO USE A FAIRLY SMALL STEP FOR THE FIRST            00000310
C*          CALL.  IT WILL BE AUTOMATICALLY INCREASED LATER.            00000320
C*  HMIN THE MINIMUM STEP SIZE THAT WILL BE USED FOR THE                00000330
C*          INTEGRATION.  NOTE THAT ON STARTING THIS MUST               00000340
C*          BE MUCH SMALLER THAN THE AVERAGE H EXPECTED SINCE           00000350
C*          A FIRST ORDER METHOD IS USED INITIALLY.                     00000360
C*  EPS   THE ERROR TEST CONSTANT.  SINGLE STEP ERROR ESTIMATES         00000370
C*          DIVIDED BY YMAX(I) MUST BE LESS THAN THIS                   00000380
C*          IN THE EUCLIDEAN NORM.  THE STEP AND/OR ORDER IS            00000390
C*          ADJUSTED TO ACHIEVE THIS.                                   00000400
C*  MF    THE METHOD INDICATOR.  THE FOLLOWING ARE ALLOWED:             00000410
C*                0    AN ADAMS PREDICTOR CORRECTOR IS USED.           00000420
C*                1    A MULTI-STEP METHOD SUITABLE FOR STIFF          00000430
C*                       SYSTEMS IS USED.  IT WILL ALSO WORK FOR       00000440
C*                       NON-STIFF SYSTEMS.  HOWEVER THE USER          00000450
C*                       MUST PROVIDE A SUBROUTINE PEDERV WHICH        00000460
C*                       EVALUATES THE PARTIAL DEVIVATIVES OF          00000470
C*                       THE DIFFERENTIAL EQUATIONS WITH RESPECT       00000480
C*                       Y'S.  THIS IS DONE BY CALLING                 00000490
C*                       PEDERV(T,Y,PW,M).  PW IS AN N BY N ARRAY      00000500
C*                       WHICH MUST BE SET TO THE PARTIAL OF           00000510
C*                       THE I-TH EQUATION WITH RESPECT                00000520
C*                       TO THE J DEPENDENT VARIABLE IN PW(I,J).       00000530
C*                       PW IS ACTUALLY STORED IN AN M BY M            00000540
```

EXHIBIT A-3. LISTING OF SUBROUTINE DIFSUB (Continued)

```
C*                        ARRAY WHERE M IS THE VALUE OF N USED ON          00000550
C*                        THE FIRST CALL TO THIS PROGRAM.                  00000560
C*                2     THE SAME AS CASE 1, EXCEPT THAT THIS              00000570
C*                        SUBROUTINE COMPUTES THE PARTIAL                  00000580
C*                        DEVIVATIVES BY NUMERICAL DIFFERENCING            00000590
C*                        OF THE DEVIVATIVES.  HENCE PEDERV IS             00000600
C*                        NOT CALLED.                                      00000610
C*  YMAX AN ARRAY OF N LOCATIONS WHICH CONTAINS THE MAXIMUM                00000620
C*       OF EACH Y SEEN SO FAR.  IT SHOULD NORMALLY BE SET TO              00000630
C*       1 IN EACH COMPONENT BEFORE THE FIRST ENTRY.  (SEE THE             00000640
C*       DESCRIPTION OF EPS.)                                              00000650
C*  ERROR  AN ARRAY OF N ELEMENTS WHICH CONTAINS THE ESTIMATED             00000660
C*       ONE STEP ERROR IN EACH COMPONENT.                                 00000670
C*  KFLAG  A COMPLETION CODE WITH THE FOLLOWING MEANINGS:                  00000680
C*               +1    THE STEP WAS SUCCESSFUL.                          00000690
C*               -1    THE STEP WAS TAKEN WITH H = HMIN, BUT THE         00000700
C*                       REQUESTED ERROR WAS NOT ACHIEVED.                00000710
C*               -2    THE MAXIMUM ORDER SPECIFIED WAS FOUND TO          00000720
C*                       BE TOO LARGE.                                    00000730
C*               -3    CORRECTOR CONVERGENCE COULD NOT BE                00000740
C*                       ACHIEVED FOR H .GT. HMIN.                        00000750
C*               -4    THE REQUESTED ERROR IS SMALLER THAN CAN           00000760
C*                       BE HANDLED FOR THIS PROBLEM.                     00000770
C*  JSTART   AN INPUT INDICATOR WITH THE FOLLOWING MEANINGS:               00000780
C*               -1    REPEAT THE LAST STEP WITH A NEW H                 00000790
C*                0    PERFORM THE FIRST STEP.  THE FIRST STEP           00000800
C*                       MUST BE DONE WITH THIS VALUE OF JSTART           00000810
C*                       SO THAT THE SUBROUTINE CAN INITIALIZE            00000820
C*                       ITSELF.                                          00000830
C*               +1    TAKE A NEW STEP CONTINUING FROM THE LAST.         00000840
C*          JSTART IS SET TO NQ, THE CURRENT ORDER OF THE METHOD          00000850
C*          DERIVATIVE USED, THIS RESTRICTS THE ORDER.  IT MUST           00000900
C*          BE LESS THAN 8 FOR ADAMS AND 7 FOR STIFF METHODS.             00000910
C*  PSAVE  A BLOCK OF AT LEAST N**2 FLOATING POINT LOCATIONS.              00000920
C***********************************************************************00000930
C*          DERIVATIVE USED, THIS RESTRICTS THE ORDER.  IT MUST           00000900
C*          BE LESS THAN 8 FOR ADAMS AND 7 FOR STIFF METHODS.             00000910
C*  PSAVE  A BLOCK OF AT LEAST N**2 FLOATING POINT LOCATIONS.              00000920
C***********************************************************************00000930
      SUBROUTINE DIFSUB(N,T,Y,SAVE,H,HMIN,HMAX,EPS,MF,YMAX,ERROR,KFLAG,  00000940
     1  JSTART,MAXDER,PSAVE)                                             00000950
      DOUBLE PRECISION A,D,E,H,R,T,Y,R1,R2,BND,EPS,EUP,EDWN,ENQ1        00000960
     1 ,ENQ2,ENQ3,HMAX,HMIN,HNEW,HOLD,SAVE,TOLD,YMAX,ERROR,RACUM        00000970
     2,SDOT1,SDOT2                                                      00000980
      DIMENSION Y(8,40), YMAX(40), SAVE(12,40), ERROR(40), PSAVE(1600)  00000990
      DIMENSION A(8), PERTST(7,2,3), SDOT1(40), SDOT2(40)               00001000
C***********************************************************************00001010
C*  THE COEFFICIENTS IN PERTST ARE USED IN SELECTING THE STEP AND        00001020
C*  ORDER. THEREFORE ONLY ABOUT ONE PERCENT ACCURACY IS NEEDED.          00001030
C***********************************************************************00001040
      DATA PERTST /2.0,4.5,7.333,10.42,13.7,17.15,1.0,                  00001050
     1            2.0,12.0,24.0,37.89,53.33,70.08,87.97,                00001060
     1            3.0,6.0,9.167,12.5,15.98,1.0,1.0,                     00001070
     1            12.0,24.0,37.89,53.33,70.08,87.97,1.0,                00001080
     1            1.,1.,0.5,0.1667,0.04133,0.008267,1.0,                00001090
     1            1.0,1.0,2.0,1.0,.3157,.07407,.0139/                   00001100
```

EXHIBIT A-3. LISTING OF SUBROUTINE DIFSUB (Continued)

```
      A(2)=-1.                                                          00001110
      IRET = 1                                                          00001120
      KFLAG = 1                                                         00001130
      IF(JSTART.LE.0) GO TO 140                                         00001140
C*****************************************************************************00001150
C*  BEGIN BY SAVING INFORMATION FOR POSSIBLE RESTARTS AND CHANGING       00001160
C*  H BY THE FACTOR R IF THE CALLER HAS CHANGED H.  ALL VARIABLES        00001170
C*  DEPENDENT ON H MUST ALSO BE CHANGED.                                 00001180
C*  E IS A COMPARISON FOR ERRORS OF THE CURRENT ORDER NQ.  EUP IS        00001190
C*  TO TEST FOR INCREASING THE ORDER, EDWN FOR DECREASING THE ORDER.     00001200
C*  HNEW IS THE STEP SIZE THAT WAS USED ON THE LAST CALL.                00001210
C*****************************************************************************00001220
 100  DO 110 I = 1,N                                                    00001230
      DO 110 J = 1,K                                                    00001240
 110  SAVE(J,I) = Y(J,I)                                                00001250
      HOLD = HNEW                                                       00001260
      IF ( H.EQ.HOLD) GO TO 130                                         00001270
 120  RACUM = H/HOLD                                                    00001280
      IRET1 = 1                                                         00001290
      GO TO 750                                                         00001300
 130  NQOLD = NQ                                                        00001310
      TOLD = T                                                          00001320
      RACUM = 1.0                                                       00001330
      IF (JSTART.GT.0) GO TO 250                                        00001340
      GO TO 170                                                         00001350
 140  IF (JSTART.EQ.-1) GO TO 160                                       00001360
C*****************************************************************************00001370
C*  ON THE FIRST CALL, THE ORDER IS SET TO 1 AND THE INITIAL             00001380
C*  DERIVATIVES ARE CALCULATED.                                          00001390
C*****************************************************************************00001400
      NQ = 1                                                            00001410
      N3 = N                                                            00001420
      N1 = N*10                                                         00001430
      N2 = N1 + 1                                                       00001440
      N4 = N**2                                                         00001450
      N5 = N1 + N                                                       00001460
      N6 = N5 + 1                                                       00001470
      CALL DIFFUN(T,Y,SDOT1)                                            00001480
      DO 150 I = 1,N                                                    00001490
 150  Y(2,I) = SDOT1(I)*H                                               00001500
      HNEW = H                                                          00001510
      K = 2                                                             00001520
      GO TO 100                                                         00001530
C*****************************************************************************00001540
C*  REPEAT LAST STEP BY RESTORING SAVED INFORMATION.                     00001550
C*****************************************************************************00001560
 160  IF (NQ.EQ.NQOLD) JSTART = 1                                       00001570
      IF(KFLAG.GE.-1) T = T - HOLD                                      00001580
      NQ = NQOLD                                                        00001590
      K = NQ + 1                                                        00001600
      GO TO 120                                                         00001610
C*****************************************************************************00001620
C*  SET THE COEFFICIENTS THAT DETERMINE THE ORDER AND THE METHOD         00001630
C*  TYPE.  CHECK FOR EXCESSIVE ORDER.  THE LAST TWO STATEMENTS OF        00001640
C*  THIS SECTION SET IWEVAL.GT.0 IF PW IS TO BE RE-EVALUATED             00001650
C*  BECAUSE OF THE ORDER CHANGE, AND THEN REPEAT THE INTEGRATION         00001660
```

EXHIBIT A-3. LISTING OF SUBROUTINE DIFSUB (Continued)

```
C*  STEP IF IT HAS NOT YET BEEN DONE (IRET = 1) OR SKIP TO A FINAL       00001670
C*  SCALING BEFORE EXIT IF IT HAS BEEN COMPLETED (IRET = 2).             00001680
C*********************************************************************00001690
 170  IF(MF.EQ.0) GO TO 180                                             00001700
      IF (NQ.GT.6) GO TO 190                                            00001710
      GO TO (221,222,223,224,225,226),NQ                                00001720
 180  IF(NQ.GT.7) GO TO 190                                             00001730
      GO TO (211,212,213,214,215,216,217),NQ                            00001740
 190  KFLAG = -2                                                        00001750
      RETURN                                                            00001760
C*********************************************************************00001770
C*  THE FOLLOWING COEFFICIENTS SHOULD BE DEFINED TO THE MAXIMUM         00001780
C*  ACCURACY PERMITTED BY THE MACHINE.  THEY ARE IN THE ORDER USED:     00001790
C*                                                                      00001800
C*  -1                                                                  00001810
C*  -1/2,-1/2                                                           00001820
C*  -5/12,-3/4,-1/6                                                     00001830
C*  -3/8,-11/12,-1/3,-1/24                                              00001840
C*  -251/720,-25/24,-35/72,-5/48,-1/120                                 00001850
C*  -95/288,-137/120,-5/8,-17/96,-1/40,-1/720                           00001860
C*  -19087/60480,-49/40,-203/270,-49/192,-7/144,-7/1440,-1/5040         00001870
C*                                                                      00001880
C*  -1                                                                  00001890
C*  -2/3,-1/3                                                           00001900
C*  -6/11,-6/11,-1/11                                                   00001910
C*  -12/25,-7/10,-1/5,-1/50                                             00001920
C*  -120/274,-225/274,-85/274,-15/274,-1/274                            00001930
C*  -180/441,-58/63,-15/36,-25/252,-3/252,-1/1764                       00001940
C*********************************************************************00001950
 211  A(1) = -1.0                                                       00001960
      GO TO 230                                                         00001970
 212  A(1) = -0.500000000                                               00001980
      A(3) = -0.500000000                                               00001990
      GO TO 230                                                         00002000
 213  A(1) = -0.4166666666666667                                        00002010
      A(3) = -0.750000000                                               00002020
       A(4) = -0.166666666666667                                        00002030
      GO TO 230                                                         00002040
 214  A(1) = -0.375000000                                               00002050
      A(3) = -0.9166666666666667                                        00002060
      A(4) = -0.3333333333333333                                        00002070
      A(5) = -0.0416666666666667                                        00002080
      GO TO 230                                                         00002090
 215  A(1) = -0.34861111111111                                          00002100
      A(3) = -1.04166666666667                                          00002110
      A(4) = -0.48611111111111111                                       00002120
      A(5) = -0.10416666666666667                                       00002130
      A(6) = -0.00833333333333333                                       00002140
      GO TO 230                                                         00002150
 216  A(1) = -0.3298611111111111                                        00002160
      A(3) = -1.14166666666666667                                       00002170
      A(4) = -0.625000000                                               00002180
      A(5) = -0.1770833333333333333                                     00002190
      A(6) = -0.02500000000                                             00002200
      A(7) = -0.00138888888888889                                       00002210
      GO TO 230                                                         00002220
```

EXHIBIT A-3. LISTING OF SUBROUTINE DIFSUB (Continued)

```
 217  A(1) = -0.3155919312169312                                          00002230
      A(3) = -1.235000000                                                 00002240
      A(4) = -0.7518518518518519                                          00002250
      A(5) = -0.2552083333333333                                          00002260
      A(6) = -0.0486111111111111                                          00002270
      A(7) = -0.0048611111111111                                          00002280
      A(8) = -0.0001984126984126984                                       00002290
      GO TO 230                                                           00002300
 221  A(1) = -1.000000000                                                 00002310
      GO TO 230                                                           00002320
 222  A(1) = -0.6666666666666667                                          00002330
      A(3) = -0.3333333333333333                                          00002340
      GO TO 230                                                           00002350
 223  A(1) = -0.5454545454545455                                          00002360
      A(3) = A(1)                                                         00002370
      A(4) = -0.0909090909090911                                          00002380
      GO TO 230                                                           00002390
 224  A(1) = -0.480000000                                                 00002400
      A(3) = -0.7000000000                                                00002410
      A(4) = -0.2000000000                                                00002420
      A(5) = -0.0200000000                                                00002430
      GO TO 230                                                           00002440
 225  A(1) = -0.437956204379562                                           00002450
      A(3) = -0.8211678832116788                                          00002460
      A(4) = -0.3102189781021898                                          00002470
      A(5) = -0.0547445255474526                                          00002480
      A(6) = -0.0036496350364963504                                       00002490
      GO TO 230                                                           00002500
 226  A(1) = -0.4081632653061225                                          00002510
      A(3) = -0.9206349206349206                                          00002520
      A(4) = -0.4166666666666667                                          00002530
      A(5) = -0.0992063492063492                                          00002540
      A(6) = -0.0119047619047619                                          00002550
      A(7) = -0.00056689342403628 2                                       00002560
 230  K = NQ+1                                                            00002570
      IDOUB = K                                                           00002580
      MTYP = (4 -MF)/2                                                    00002590
      ENQ2 = .5/FLOAT(NQ + 1)                                             00002600
      ENQ3 = .5/FLOAT(NQ +2)                                              00002610
      ENQ1 = .5/FLOAT(NQ)                                                 00002620
      PEPSH = EPS                                                         00002630
      EUP = (PERTST(NQ,MTYP,2)*PEPSH)**2                                  00002640
      E = (PERTST(NQ,MTYP,1)*PEPSH)**2                                    00002650
      EDWN = (PERTST(NQ,MTYP,3)*PEPSH)**2                                 00002660
      IF (EDWN.EQ.0) GO TO 780                                            00002670
      BND = EPS*ENQ3/FLOAT(N)                                             00002680
 240  IWEVAL = MF                                                         00002690
      GO TO (250 ,680 ),IRET                                              00002700
C*************************************************************************00002710
C*  THIS SECTION COMPUTES THE PREDICTED VALUES BY EFFECTIVELY            00002720
C*  MULTIPLYING THE SAVED INFORMATION BY THE PASCAL TRIANGLE             00002730
C*  MATRIX.                                                              00002740
C*************************************************************************00002750
 250  T = T + H                                                           00002760
      DO 260 J = 2,K                                                      00002770
      DO 260 J1 = J,K                                                     00002780
```

EXHIBIT A-3. LISTING OF SUBROUTINE DIFSUB (Continued)

```
      J2 = K-J1 + J - 1                                                 00002790
      DO 260 I = 1,N                                                    00002800
 260  Y(J2,I) = Y(J2,I) + Y(J2+1,I)                                     00002810
C*******************************************************************00002820
C*  UP TO 3 CORRECTOR ITERATIONS ARE TAKEN.  CONVERGENCE IS TESTED     00002830
C*  BY REQUIRING CHANGES TO BE LESS THAN BND WHICH IS DEPENDENT ON     00002840
C*  THE ERROR TEST CONSTANT.                                          00002850
C*     THE SUM OF THE CORRECTIONS IS ACCUMULATED IN THE ARRAY         00002860
C*  ERROR(I).  IT IS EQUAL TO THE I-TH DERIVATIVE OF Y MULTIPLIED      00002870
C*  BY H**K/(FACTORIAL(K-1)*A(K)), AND IS THEREFORE PROPORTIONAL       00002880
C*  TO THE ACTUAL ERRORS TO THE LOWEST POWER OF H PRESENT.  (H**K)     00002890
C*******************************************************************00002900
      DO 270 I = 1,N                                                    00002910
 270  ERROR(I) = 0.0                                                    00002920
      DO 430 L = 1,3                                                    00002930
      CALL DIFFUN(T,Y,SDOT1)                                            00002940
C*******************************************************************00002950
C*  IF THERE HAS BEEN A CHANGE OF ORDER OR THERE HAS BEEN TROUBLE      00002960
C*  WITH CONVERGENCE, PW IS RE-EVALUATED PRIOR TO STARTING THE         00002970
C*  CORRECTOR ITERATION IN THE CASE OF STIFF METHODS.  IWEVAL IS       00002980
C*  THEN SET TO -1 AS AN INDICATOR THAT IT HAS BEEN DONE.             00002990
C*******************************************************************00003000
      IF (IWEVAL.LT.1) GO TO 350                                        00003010
      IF (MF.EQ.2) GO TO 310                                            00003020
      CALL PEDERV(T,Y,PSAVE,N3)                                         00003030
      R = A(1)*H                                                        00003040
      DO 280 I = 1,N4                                                   00003050
 280  PSAVE(I) = PSAVE(I)*R                                             00003060
 290  DO 300 I = 1,N                                                    00003070
 300  PSAVE(I*(N3+1)-N3) = 1.0 + PSAVE(I*(N3+1)-N3)                     00003080
      IWEVAL = -1                                                       00003090
      CALL MATINV(PSAVE,N3,N3,J1)                                       00003100
      IF(J1.GT.0) GO TO 350                                             00003110
      GO TO 440                                                         00003120
 310  DO 320 I = 1,N                                                    00003130
 320  SAVE(9,I) = Y(1,I)                                                00003140
      DO 340 J = 1,N                                                    00003150
      R = EPS*DMAX1(EPS,DABS(SAVE(9,J)))                                00003160
      Y(1,J) = Y(1,J) + R                                               00003170
      D = A(1)*H/R                                                      00003180
      CALL DIFFUN(T,Y,SDOT2)                                            00003190
      DO 330 I = 1,N                                                    00003200
 330  PSAVE(I+(J-1)*N3) = (SDOT2(I)-SDOT1(I))*D                         00003210
 340  Y(1,J) = SAVE(9,J)                                                00003220
      GO TO 290                                                         00003230
 350  IF (MF.NE.0) GO TO 370                                            00003240
      DO 360 I = 1,N                                                    00003250
 360  SAVE(9,I) = Y(2,I)-SDOT1(I)*H                                     00003260
      GO TO 410                                                         00003270
 370  DO 380 I = 1,N                                                    00003280
 380  SDOT2(I) = Y(2,I)-SDOT1(I)*H                                      00003290
      DO 400 I = 1,N                                                    00003300
      D = 0.0                                                           00003310
      DO 390 J = 1,N                                                    00003320
 390  D = D + PSAVE(I+(J-1)*N3)*SDOT2(J)                                00003330
 400  SAVE(9,I) = D                                                     00003340
```

EXHIBIT A-3. LISTING OF SUBROUTINE DIFSUB (Continued)

```
 410  NT = N                                                                    00003350
      DO 420 I = 1,N                                                           00003360
      Y(1,I) = Y(1,I) + A(1)*SAVE(9,I)                                         00003370
      Y(2,I) = Y(2,I) - SAVE(9,I)                                              00003380
      ERROR(I) = ERROR(I) + SAVE(9,I)                                          00003390
      IF (DABS(SAVE(9,I)).LE.(BND*YMAX(I))) NT = NT - 1                        00003400
 420  CONTINUE                                                                 00003410
      IF (NT.LE.0) GO TO 490                                                   00003420
 430  CONTINUE                                                                 00003430
C*************************************************************************** 00003440
C*  THE CORRECTOR ITERATION FAILED TO CONVERGE IN 3 TRIES.  VARIOUS          00003450
C*  POSSIBILITIES ARE CHECKED FOR.  IF H IS ALREADY HMIN AND                 00003460
C*  THIS IS EITHER ADAMS METHOD OR THE STIFF METHOD IN WHICH THE             00003470
C*  MATRIX PW HAS ALREADY BEEN RE-EVALUATED, A NO CONVERGENCE EXIT           00003480
C*  IS TAKEN.  OTHERWISE THE MATRIX PW IS RE-EVALUATED AND/OR THE            00003490
C*  STEP IS REDUCED TO TRY AND GET CONVERGENCE.                              00003500
C*************************************************************************** 00003510
 440  IF ((H.LE.(HMIN*1.00001)).AND.((IWEVAL - MTYP).LT.-1)) GO TO 460         00003520
      IF ((MF.EQ.0).OR.(IWEVAL.NE.0)) RACUM = RACUM**2*0.5                     00003530
      IWEVAL = MF                                                              00003540
      T = T - H                                                                00003550
      IRET1 = 2                                                                00003560
      GO TO 750                                                                00003570
 460  KFLAG = -3                                                               00003580
 470  DO 480 I = 1,N                                                           00003590
      DO 480 J = 1,K                                                           00003600
 480  Y(J,I) = SAVE(J,I)                                                       00003610
      H = HOLD                                                                 00003620
      NQ = NQOLD                                                               00003630
      JSTART = NQ                                                              00003640
      RETURN                                                                   00003650
C*************************************************************************** 00003660
C*  THE CORRECTOR CONVERGED AND CONTROL IS PASSED TO STATEMENT 520           00003670
C*  IF THE ERROR TEST IS O.K., AND TO 540 OTHERWISE.                         00003680
C*  IF THE STEP IS O.K. IT IS ACCEPTED.  IF IDOUB HAS BEEN REDUCED           00003690
C*  TO ONE, A TEST IS MADE TO SEE IF THE STEP CAN BE INCREASED               00003700
C*  AT THE CURRENT ORDER OR BY GOING TO ONE HIGHER OR ONE LOWER.             00003710
C*  SUCH A CHANGE IS ONLY MADE IF THE STEP CAN BE INCREASED BY AT            00003720
C*  LEAST 1.1.  IF NO CHANGE IS POSSIBLE IDOUB IS SET TO 10 TO               00003730
C*  PREVENT FUTHER TESTING FOR 10 STEPS                                      00003740
C*  IF A CHANGE IS POSSIBLE, IT IS MADE AND IDOUB IS SET TO                  00003750
C*  NQ + 1    TO PREVENT FURTHER TESTING FOR THAT NUMBER OF STEPS.           00003760
C*  IF THE ERROR WAS TOO LARGE, THE OPTIMUM STEP SIZE FOR THIS OR            00003770
C*  LOWER ORDER IS COMPUTED, AND THE STEP RETRIED.  IF IT SHOULD             00003780
C*  FAIL TWICE MORE IT IS AN INDICATION THAT THE DERIVATIVES THAT            00003790
C*  HAVE ACCUMULATED IN THE Y ARRAY HAVE ERRORS OF THE WRONG ORDER           00003800
C*  SO THE FIRST DERIVATIVES ARE RECOMPUTED AND THE ORDER IS SET             00003810
C*  TO 1.                                                                    00003820
C*************************************************************************** 00003830
 490  D = 0.0                                                                  00003840
      DO 500 I = 1,N                                                           00003850
 500  D = D + (ERROR(I)/YMAX(I))**2                                            00003860
      IWEVAL = 0                                                               00003870
      IF (D.GT.E) GO TO 540                                                    00003880
      IF (K.LT.3) GO TO 520                                                    00003890
      DO 510 J = 3,K                                                           00003900
```

EXHIBIT A-3. LISTING OF SUBROUTINE DIFSUB (Continued)

```
      DO 510 I = 1,N                                                    00003910
510   Y(J,I) = Y(J,I) + A(J)*ERROR(I)                                   00003920
520   KFLAG = +1                                                        00003930
      HNEW = H                                                          00003940
      IF (IDOUB.LE.1) GO TO 550                                         00003950
      IDOUB = IDOUB - 1                                                 00003960
      IF (IDOUB.GT.1) GO TO 700                                         00003970
      DO 530 I = 1,N                                                    00003980
530   SAVE(10,I) = ERROR(I)                                             00003990
      GO TO 700                                                         00004000
540   KFLAG = KFLAG - 2                                                 00004010
      T = TOLD                                                          00004020
      IF (H.LE.(HMIN*1.00001)) GO TO 740                                00004030
      IF (KFLAG.LE.-5) GO TO 720                                        00004040
550   PR2 = (D/E)**ENQ2*1.2                                             00004050
      PR3 = 1.E+20                                                      00004060
      IF ((NQ.GE.MAXDER).OR.(KFLAG.LE.-1)) GO TO 570                    00004070
      D = 0.0                                                           00004080
      DO 560 I = 1,N                                                    00004090
560   D = D + ((ERROR(I) - SAVE(10,I))/YMAX(I))**2                      00004100
      PR3 = (D/EUP)**ENQ3*1.4                                           00004110
570   PR1 = 1.E+20                                                      00004120
      IF (NQ.LE.1) GO TO 590                                            00004130
      D = 0.0                                                           00004140
      DO 580 I = 1,N                                                    00004150
580   D = D + (Y(K,I)/YMAX(I))**2                                       00004160
      PR1 = (D/EDWN)**ENQ1*1.3                                          00004170
590   CONTINUE                                                          00004180
      IF (PR2.LE.PR3) GO TO 650                                         00004190
      IF (PR3.LT.PR1) GO TO 660                                         00004200
600   R = 1.0/AMAX1(PR1,1.E-4)                                          00004210
      NEWQ = NQ - 1                                                     00004220
610   IDOUB = 10                                                        00004230
      IF ((KFLAG.EQ.1).AND.(R.LT.(1.1))) GO TO 700                      00004240
      IF (NEWQ.LE.NQ) GO TO 630                                         00004250
      DO 620 I = 1,N                                                    00004260
620   Y(NEWQ+1,I) = ERROR(I)*A(K)/FLOAT(K)                              00004270
630   K = NEWQ + 1                                                      00004280
      IF ( KFLAG.EQ. 1 ) GO TO 670                                      00004290
      RACUM = RACUM*R                                                   00004300
      IRET1 = 3                                                         00004310
      GO TO 750                                                         00004320
640   IDOUB = K                                                         00004330
      IF (NEWQ.EQ.NQ) GO TO 250                                         00004340
      NQ = NEWQ                                                         00004350
      GO TO 170                                                         00004360
650   IF (PR2.GT.PR1) GO TO 600                                         00004370
      NEWQ = NQ                                                         00004380
      R = 1.0/AMAX1(PR2,1.E-4)                                          00004390
      GO TO 610                                                         00004400
660   R = 1.0/AMAX1(PR3,1.E-4)                                          00004410
      NEWQ = NQ + 1                                                     00004420
      GO TO 610                                                         00004430
670   IRET = 2                                                          00004440
      R = DMIN1(R,HMAX/DABS(H))                                         00004450
      H=H*R                                                             00004460
```

EXHIBIT A-3. LISTING OF SUBROUTINE DIFSUB (Concluded)

```
      HNEW = H                                                          00004470
      IF (NQ.EQ.NEWQ) GO TO 680                                         00004480
      NQ = NEWQ                                                         00004490
      GO TO 170                                                         00004500
  680 R1 = 1.0                                                          00004510
      DO 690 J = 2,K                                                    00004520
      R1 = R1*R                                                         00004530
      DO 690 I = 1,N                                                    00004540
  690 Y(J,I) = Y(J,I)*R1                                                00004550
      IDOUB = K                                                         00004560
  700 DO 710 I = 1,N                                                    00004570
  710 YMAX(I) = DMAX1(YMAX(I),DABS(Y(1,I)))                             00004580
      JSTART = NQ                                                       00004590
      RETURN                                                            00004600
  720 IF (NQ.EQ.1) GO TO 780                                            00004610
      CALL DIFFUN(T,Y,SDOT1)                                            00004620
      R = H/HOLD                                                        00004630
      DO 730 I = 1,N                                                    00004640
      Y(1,I) = SAVE(1,I)                                                00004650
      SAVE(2,I) = HOLD*SDOT1(I)                                         00004660
  730 Y(2,I) = SAVE(2,I)*R                                              00004670
      NQ = 1                                                            00004680
      KFLAG = 1                                                         00004690
      GO TO 170                                                         00004700
  740 KFLAG = -1                                                        00004710
      HNEW = H                                                          00004720
      JSTART = NQ                                                       00004730
      RETURN                                                            00004740
C*************************************************************************00004750
C*  THIS SECTION SCALES ALL VARIABLES CONNECTED WITH H AND RETURNS       00004760
C*  TO THE ENTERING SECTION.                                             00004770
C*************************************************************************00004780
  750 RACUM = DMAX1(DABS(HMIN/HOLD),RACUM)                              00004790
      RACUM = DMIN1(RACUM,DABS(HMAX/HOLD))                              00004800
      R1 = 1.0                                                          00004810
      DO 760 J = 2,K                                                    00004820
      R1 = R1*RACUM                                                     00004830
      DO 760 I = 1,N                                                    00004840
  760 Y(J,I) = SAVE(J,I)*R1                                             00004850
      H = HOLD*RACUM                                                    00004860
      DO 770 I = 1,N                                                    00004870
  770 Y(1,I) = SAVE(1,I)                                                00004880
      GO TO (130,250,640),IRET1                                         00004890
  780 KFLAG = -4                                                        00004900
      GO TO 470                                                         00004910
      END                                                               00004920
```

EXHIBIT A-4. LISTING OF SUBROUTINE DIFFUN

```
C SUBROUTINE ****** D I F F U N ******                                    0000001
C                                                                         0000002
C THIS SUBROUTINE CALCULATES THE RATE OF CHANGE OF DIFFERENTIAL AND       0000003
C STEADY-STATE SPECIES CONCENTRATIONS -- CALLED BY DIFSUB.                0000004
C                                                                         0000005
C                                                                         0000006
C SYMBOL DESCRIPTIONS --                                                  0000007
C                                                                         0000008
C COEFF     NUMBER OF PARTICLES, ONE PER PRODUCT SPECIES PER REACTION      0000009
C J         DO-LOOP INDICES OR LOCAL POINTERS                             0000010
C JFLAG     INDICATES SPECIES HAS BEEN SEPARATED FROM SDEN CALCULATION    0000011
C K         DO-LOOP INDICES OR LOCAL POINTERS                             0000012
C KCOF      COEFFICIENT POINTERS, ONE PER REACTION PRODUCT PER SPECIES     0000013
C KPRD      PRODUCT POINTERS, ONE PER PRODUCT SPECIES PER REACTION        0000014
C KRCT      REACTANT POINTERS, ONE PER REACTANT SPECIES PER REACTION      0000015
C KRXN      REACTION POINTERS, ONE PER REACTION PER SPECIES               0000016
C L         DO-LOOP INDICES OR LOCAL POINTERS                             0000017
C M         DO-LOOP INDICES OR LOCAL POINTERS                             0000018
C MAXPRD    MAXIMUM NUMBER OF PRODUCTS                                    0000019
C MAXRCT    MAXIMUM NUMBER OF REACTANTS                                   0000020
C N         DO-LOOP INDICES OR LOCAL POINTERS                             0000021
C NCNV      NUMBER OF CONVERGED STEADY-STATES                             0000022
C NDIF      NUMBER OF DIFFERENTIAL SPECIES                                0000023
C NOUT      THE FORTRAN OUTPUT UNIT NUMBER (NORMALLY 6)                   0000024
C NRXN      NUMBER OF REACTIONS                                           0000025
C NS        LOCAL POINTER TO STEADY-STATE SPECIES                         0000026
C NSTS      NUMBER OF STEADY-STATE SPECIES                                0000027
C NTRY      NUMBER OF ITERATION ATTEMPTS FOR STEADY-STATE CONVERGENCE     0000028
C Q         DEGRADATION RATE, /MIN                                        0000029
C R         REACTION RATES, SEC, ONE PER REACTION                         0000030
C RATE      LOCAL REPRESENTATION OF R, THE REACTION RATE                  0000031
C RK        REACTION RATE CONSTANTS, PPM-MIN, ONE PER REACTION            0000032
C SDEN      DENOMINATOR IN STEADY-STATE CALCULATION, /MIN                 0000033
C SNUM      NUMERATOR IN STEADY-STATE CALCULATION, PPM/MIN                0000034
C STEST     TEST VALUE FOR STEADY-STATE CONVERGENCE, PPM                  0000035
C T         CURRENT REACTION TIME, SEC, DOUBLE PRECISION,                 0000036
C               FOR AND FROM DIFSUB                                       0000037
C TOL       CONVERGENCE TOLERANCE ON STEADY-STATE ITERATION, PPM          0000038
C Y         SPECIES CONCENTRATIONS, 8 PER SPECIES, DOUBLE PRECISION,      0000039
C               FOR AND FROM DIFSUB                                       0000040
C YAX       SPECIES CONCENTRATIONS, PPM, ONE PER SPECIES                  0000041
C YCALC     LOCAL REPRESENTATION OF YDOT, THE RATE OF CHANGE              0000042
C YDOT      RATES OF CHANGE OF SPECIES CONCENTRATION,  PPM/MIN, ONE PER   0000043
C               DIFFERENTIAL SPECIES, DOUBLE PRECISION, FOR DIFSUB        0000044
C YIN       SPECIES INFLOW RATES, PPM/MIN, ONE PER SPECIES                0000045
C                                                                         0000046
C BEGINNING OF PROGRAM.                                                   0000047
C                                                                         0000048
C ENTRY POINT                                                             0000049
C                                                                         0000050
      SUBROUTINE DIFFUN(T, Y, YDOT)                                       0000051
C                                                                         0000052
C DECLARE INPUTS FROM DIFSUR TO BE DOUBLE PRECISION WITH DIMENSIONS       0000053
C                                                                         0000054
```

EXHIBIT A-4. LISTING OF SUBROUTINE DIFFUN (Continued)

```
      DOUBLE PRECISION T, Y, YDOT                                          0000055
      DIMENSION Y(8,40), YDOT(40)                                          0000056
C                                                                          0000057
C DEFINE VARIABLES AND DIMENSIONS OF COMMON STORAGE WITH MODKIN            0000058
C                                                                          0000059
      COMMON RK(99), R(99), YAX(50), YIN(50), COEFF(3,99)                  0000060
      COMMON KRCT(4,99), KPRD(3,99), KRXN(99,50), KCOF(99,50)              0000061
      COMMON Q, TOL, NRXN, NDIF, NSTS                                      0000062
C                                                                          0000063
C DEFINE MISCELLANEOUS DATA VALUES                                         0000064
C                                                                          0000065
      DATA NTRY /25/, MAXRCT /4/, MAXPRD /3/, NOUT /6/, NWARN /0/          0000066
C                                                                          0000067
C MOVE DIFFERENTIAL CONCENTRATIONS TO LOCAL ARRAY                          0000068
C                                                                          0000069
      DO 110 J = 1,NDIF                                                    0000070
      YAX(J) = Y(1,J)                                                      0000071
110   CONTINUE                                                             0000072
C                                                                          0000073
C SET ITERATION LOOP AND CALCULATE REACTION RATES                          0000074
C                                                                          0000075
      DO 260 N = 1,NTRY                                                    0000076
      DO 140 L = 1,NRXN                                                    0000077
      RATE = RK(L)                                                         0000078
      DO 120 K = 1,MAXRCT                                                  0000079
      J = KRCT(K,L)                                                        0000080
      IF (J .EQ. 0) GO TO 130                                              0000081
      RATE = RATE * YAX(J)                                                 0000082
120   CONTINUE                                                             0000083
130   R(L) = RATE                                                          0000084
140   CONTINUE                                                             0000085
C                                                                          0000086
C SET CONVERGENCE COUNTER AND BEGIN STEADY-STATE CALCULATION LOOP          0000087
C                                                                          0000088
      NCNV = 0                                                             0000089
      IF (NSTS .LE. 0) GO TO 255                                           0000090
      DO 250 M = 1,NSTS                                                    0000091
      SDEN = 0                                                             0000092
      SNUM = 0.0                                                           0000093
      NS = NDIF + M                                                        0000094
      STEST = YAX(NS)                                                      0000095
C                                                                          0000096
C IDENTIFY STEADY STATE SPECIES IN REACTION                                0000097
C                                                                          0000098
      DO 230 L = 1,NRXN                                                    0000099
      J = KCOF(L,NS)                                                       0000100
      K = KRXN(L,NS)                                                       0000101
C                                                                          0000102
C SKIP OVER LUMPED MECHANISM REPLACEMENT SPECIES                           0000103
C                                                                          0000104
      IF (K .GT. NRXN) GO TO 230                                           0000105
      IF (J) 205, 235, 203                                                 0000106
C                                                                          0000107
C CALCULATE NUMERATOR OF STEADY STATE EQUATION                             0000108
C                                                                          0000109
203   SNUM = SNUM + R(K) * COEFF(J,K)                                      0000110
```

EXHIBIT A-4. LISTING OF SUBROUTINE DIFFUN (Continued)

```
      GO TO 230                                                          0000111
C                                                                        0000112
C START REACTION RATE CALCULATION AND SET SPECIES FLAG                   0000113
C                                                                        0000114
205   RATE = RK(K)                                                       0000115
      JFLAG = 0                                                          0000116
      DO 210 NR = 1,MAXRCT                                               0000117
      J = KRCT(NR,K)                                                     0000118
      IF (J .EQ. 0) GO TO 220                                            0000119
      IF (J .NE. NS) GO TO 208                                           0000120
C                                                                        0000121
C CALCULATE RATE, SKIPPING FIRST OCCURRENCE OF SPECIES IN REACTION       0000122
C                                                                        0000123
      IF (JFLAG .EQ. 1) GO TO 208                                        0000124
      JFLAG = 1                                                          0000125
      GO TO 210                                                          0000126
208   RATE = RATE * YAX(J)                                               0000127
210   CONTINUE                                                           0000128
C                                                                        0000129
C CALCULATE DENOMINATOR OF STEADY STATE EQUATION                         0000130
C                                                                        0000131
220   SDEN = SDEN + RATE                                                 0000132
230   CONTINUE                                                           0000133
C                                                                        0000134
C TEST VALUES FOR ZERO -- SKIP CONVERGENCE TEST IF SO                    0000135
C                                                                        0000136
235   IF (SDEN .LE. 0.0) GO TO 240                                       0000137
      IF (SNUM .LE. 0.0) GO TO 240                                       0000138
C                                                                        0000139
C CALCULATE STEADY-STATE CONCENTRATION AND CHECK FOR CONVERGENCE         0000140
C                                                                        0000141
      STEST = SNUM / SDEN                                                0000142
      IF (ABS((STEST - YAX(NS)) / STEST) .GT. TOL) GO TO 245             0000143
C                                                                        0000144
C UPDATE CONVERGENCE COUNTER AND SPECIES CONCENTRATION                   0000145
C                                                                        0000146
240   NCNV = NCNV + 1                                                    0000147
245   YAX(NS) = STEST                                                    0000148
250   CONTINUE                                                           0000149
C                                                                        0000150
C TEST FOR CONVERGENCE OF ALL STEADY-STATES -- WRITE MESSAGE IF FAILED   0000151
C                                                                        0000152
255   IF (NCNV .EQ. NSTS) GO TO 300                                      0000153
260   CONTINUE                                                           0000154
      WRITE (NOUT,1031) NTRY                                             0000155
1031  FORMAT (' STEADY STATE FAILED TO CONVERGE IN ', I3,                0000156
     &     ' ITERATIONS.')                                               0000157
C                                                                        0000158
C INCREMENT WARNING COUNTER AND STOP IF TOO MANY                         0000159
C                                                                        0000160
      NWARN = NWARN + 1                                                  0000161
      IF (NWARN .GT. NTRY) STOP                                          0000162
C                                                                        0000163
C CALCULATE RATE OF CHANGE OF CONCENTRATION FOR DIFFERENTIAL SPECIES      0000164
C                                                                        0000165
300   DO 330 M = 1,NDIF                                                 0000166
```

EXHIBIT A-4. LISTING OF SUBROUTINE DIFFUN (Concluded)

```
      YCALC = 0.0                                                    0000167
      DO 310 L = 1,NRXN                                              0000168
      J = KCOF(L,M)                                                  0000169
      K = KRXN(L,M)                                                  0000170
C                                                                    0000171
C SKIP OVER LUMPED MECHANISM REPLACEMENT SPECIES                     0000172
C                                                                    0000173
      IF (K .GT. NRXN) GO TO 310                                     0000174
      IF (J) 305, 320, 307                                           0000175
305   YCALC = YCALC - R(K)                                           0000176
      GO TO 310                                                      0000177
307   YCALC = YCALC + R(K) * COEFF(J,K)                              0000178
310   CONTINUE                                                       0000179
320   YDOT(M) = YCALC + Q * (YIN(M) - YAX(M))                        0000180
330   CONTINUE                                                       0000181
C                                                                    0000182
C END OF ROUTINE -- RETURN TO CALLER                                 0000183
C                                                                    0000184
      RETURN                                                         0000185
      END                                                            0000186
```

EXHIBIT A-5. LISTING OF SUBROUTINE MATINV

```
      SUBROUTINE MATINV(PSAVE,N,MM,J1)                                  00000010
      DIMENSION A(40,40), INDEX(40,2), PIVOT(40), IPIVOT(40)            00000020
      DIMENSION PSAVE(1600)                                             00000030
      EQUIVALENCE (IROW,JROW), (ICOLUM,JCOLUM), (AMAX, T, SWAP)         00000040
      KK = 0                                                            00000050
      DO 67 I = 1,N                                                     00000060
      DO 67 J = 1,N                                                     00000070
      KK = KK + 1                                                       00000080
67    A(J,I) = PSAVE(KK)                                                00000090
   10 DETERM=1.0                                                        00000100
   15 DO 20 J=1,N                                                       00000110
   20 IPIVOT(J)=0                                                       00000120
   30 DO 550 I=1,N                                                      00000130
   40 AMAX=0.0                                                          00000140
   45 DO 105 J=1,N                                                      00000150
   50 IF (IPIVOT(J)-1) 60, 105, 60                                      00000160
   60 DO 100 K=1,N                                                      00000170
   70 IF (IPIVOT(K)-1) 80, 100, 740                                     00000180
   80 IF (ABS (AMAX)-ABS (A(J,K))) 85, 100, 100                         00000190
   85 IROW=J                                                            00000200
   90 ICOLUM=K                                                          00000210
   95 AMAX=A(J,K)                                                       00000220
  100 CONTINUE                                                          00000230
  105 CONTINUE                                                          00000240
      IF(AMAX .EQ. 0.) GO TO 760                                        00000250
  110 IPIVOT(ICOLUM)=IPIVOT(ICOLUM)+1                                   00000260
  130 IF (IROW-ICOLUM) 140, 260, 140                                    00000270
  140 DETERM=-DETERM                                                    00000280
  150 DO 200 L=1,N                                                      00000290
  160 SWAP=A(IROW,L)                                                    00000300
  170 A(IROW,L)=A(ICOLUM,L)                                             00000310
  200 A(ICOLUM,L)=SWAP                                                  00000320
  260 INDEX(I,1)=IROW                                                   00000330
  270 INDEX(I,2)=ICOLUM                                                 00000340
  310 PIVOT(I)=A(ICOLUM,ICOLUM)                                         00000350
  320 DETERM=DETERM*PIVOT(I)                                            00000360
  330 A(ICOLUM,ICOLUM)=1.0                                              00000370
  340 DO 350 L= 1,N                                                     00000380
  350 A(ICOLUM,L)=A(ICOLUM,L)/PIVOT(I)                                  00000390
  380 DO 550 L1=1,N                                                     00000400
  390 IF(L1-ICOLUM) 400, 550, 400                                       00000410
  400 T=A(L1,ICOLUM)                                                    00000420
  420 A(L1,ICOLUM)=0.0                                                  00000430
  430 DO 450 L=1,N                                                      00000440
  450 A(L1,L)=A(L1,L)-A(ICOLUM,L)*T                                     00000450
  550 CONTINUE                                                          00000460
  600 DO 710 I=1,N                                                      00000470
  610 L=N+1-I                                                           00000480
  620 IF (INDEX(L,1)-INDEX(L,2)) 630, 710, 630                          00000490
  630 JROW=INDEX(L,1)                                                   00000500
  640 JCOLUM=INDEX(L,2)                                                 00000510
  650 DO 705 K=1,N                                                      00000520
  660 SWAP=A(K,JROW)                                                    00000530
  670 A(K,JROW)=A(K,JCOLUM)                                             00000540
```

EXHIBIT A-5. LISTING OF SUBROUTINE MATINV (Concluded)

```
 700 A(K,JCOLUM)=SWAP                                                00000550
 705 CONTINUE                                                        00000560
     J1 = 1                                                          00000570
 710 CONTINUE                                                        00000580
740  GO TO 780                                                      00000590
 760 DETERM = 0.                                                     00000600
     J1 = -1                                                         00000610
780  KK = 0                                                         00000620
     DO 68 I = 1,N                                                   00000630
     DO 68 J = 1,N                                                   00000640
     KK = KK + 1                                                     00000650
68   PSAVE(KK) = A(J,I)                                              00000660
     RETURN                                                          00000670
      END                                                            00000680
```

EXHIBIT A-6. LISTING OF SUBROUTINE PEDERV

```
SUBROUTINE PEDERV(T,Y,PSAVE,N)                                  00000010
DOUBLE PRECISION T, Y                                           00000020
DIMENSION Y(8,40), PSAVE(1600)                                  00000030
RETURN                                                          00000040
END                                                             00000050
```

EXHIBIT A-7. LISTING OF SUBROUTINE PLOT

```
C SUBROUTINE ****** P L O T ******                                          00000010
C                                                                          00000020
C THIS SUBROUTINE READS THE PLOT CARDS AND PLOTS THE RESULTS AS PART       00000030
C OF THE PRINTED OUTPUT -- IT DOES NOT DRIVE A PLOTTER.                    00000040
C                                                                          00000050
C SYMBOL DESCRIPTIONS --                                                   00000060
C                                                                          00000070
C CGRID     THE LENGTH OF THE VERTICAL AXIS, PPM                           00000080
C CHIGH     HIGHEST CONCENTRATION VALUE, PPM                               00000090
C CLOW      LOWEST CONCENTRATION VALUE, PPM                                00000100
C CSPAN     CONCENTRATION NORMALIZATION FACTOR                             00000110
C DATA      CONCENTRATION DATA POINTS, PPM, UP TO 80                       00000120
C J         DO-LOOP INDICES OR LOCAL POINTERS                              00000130
C JBLANK    A HOLLERITH WORD OF FOUR BLANK CHARACTERS                      00000140
C JCONC     CONCENTRATION LABELS                                           00000150
C JFACT     CONVERSION FACTOR FOR LABEL                                    00000160
C JGRID     THE PLOTTING GRID                                              00000170
C JSTAR     THE CHARACTER '*'                                              00000180
C JSYMB     SYMBOL TO BE USED FOR PLOTTING SAVED POINTS                    00000190
C JVERT     VERTICAL LEGEND                                                00000200
C K         DO-LOOP INDICES OR LOCAL POINTERS                              00000210
C KCON      CONCENTRATION COORDINATE ON GRID                               00000220
C KTIM      TIME COORDINATE ON GRID                                        00000230
C L         DO-LOOP INDICES OR LOCAL POINTERS                              00000240
C M         DO-LOOP INDICES OR LOCAL POINTERS                              00000250
C MAXCON    LIMIT ON NUMBER OF VERTICAL POINTS                             00000260
C MAXPNT    MAXIMUM NUMBER OF SAVED TIME AND CONCENTRATION POINTS          00000270
C MAXTIM    LIMIT ON NUMBER OF HORIZONTAL POINTS                           00000280
C N         DO-LOOP INDICES OR LOCAL POINTERS                              00000290
C NAME      SPECIES NAMES, ONE PER SPECIES                                 00000300
C NDAT      NUMBER OF CONCENTRATION DATA POINTS                            00000310
C NIN       THE FORTRAN INPUT UNIT (NORMALLY 5)                            00000320
C NOUT      THE FORTRAN OUTPUT UNIT NUMBER (NORMALLY 6)                    00000330
C NPNT      NUMBER OF SAVED TIMES AND CONCENTRATIONS                       00000340
C NTEST     SPECIES NAME FOR TESTING                                       00000350
C NTIT      USER-INPUT TITLE FOR PRINTOUT, 3 FOUR-CHARACTER WORDS          00000360
C NTOT      TOTAL NUMBER OF SPECIES                                        00000370
C SAVCON    SPECIES CONCENTRATIONS, PPM, ONE PER SPECIES AT 80 TIMES       00000380
C SAVTIM    TIMES THAT CONCENTRATIONS ARE SAVED, MIN, UP TO 80 VALUES      00000390
C TGRID     THE LENGTH OF THE HORIZONTAL AXIS, MIN                         00000400
C THIGH     HIGHEST TIME VALUE, MIN                                        00000410
C TIME      TIMES AT WHICH CONCENTRATIONS ARE INPUT, MIN, UP TO 80         00000420
C TLOW      LOWEST TIME VALUE, MIN                                         00000430
C TPRINT    TIMES FOR PRINTOUT ON HORIZONTAL AXIS, MIN                     00000440
C TSPAN     TIME NORMALIZATION FACTOR                                      00000450
C                                                                          00000460
C BEGINNING OF PROGRAM.                                                    00000470
C                                                                          00000480
C ENTRY POINT                                                              00000490
      SUBROUTINE PLOT(NTIT, NPNT, NTOT, NAME, SAVTIM, SAVCON)              00000500
C                                                                          00000510
C SET DIMENSIONS OF INCOMING ARRAYS                                        00000520
C                                                                          00000530
      DIMENSION SAVCON(50,80), SAVTIM(80), NTIT(3), NAME(50)               00000540
```

EXHIBIT A-7. LISTING OF SUBROUTINE PLOT (Continued)

```
C                                                                       0000055(
C SET DIMENSIONS OF LOCAL ARRAYS                                        0000056(
C                                                                       0000057(
      DIMENSION JVERT(52,2), JCONC(5), TIME(80), DATA(80)               0000058(
      DIMENSION JGRID(121,52), TPRINT(9)                                0000059(
C                                                                       0000060(
C DEFINE THE VERTICAL AXIS VIA DATA STATEMENTS                          0000061(
C                                                                       0000062(
      DATA JGRID(1,1)/1H-/,JGRID(1,2)/1H|/,JGRID(1,3)/1H|/              0000063(
      DATA JGRID(1,4)/1H|/,JGRID(1,5)/1H|/,JGRID(1,6)/1H|/              0000064(
      DATA JGRID(1,7)/1H|/,JGRID(1,8)/1H|/,JGRID(1,9)/1H|/              0000065(
      DATA JGRID(1,10)/1H|/,JGRID(1,11)/1H|/,JGRID(1,12)/1H|/           0000066(
      DATA JGRID(1,13)/1H|/,JGRID(1,14)/1H-/,JGRID(1,15)/1H|/           0000067(
      DATA JGRID(1,16)/1H|/,JGRID(1,17)/1H|/,JGRID(1,18)/1H|/           0000068(
      DATA JGRID(1,19)/1H|/,JGRID(1,20)/1H|/,JGRID(1,21)/1H|/           0000069(
      DATA JGRID(1,22)/1H|/,JGRID(1,23)/1H|/,JGRID(1,24)/1H|/           0000070(
      DATA JGRID(1,25)/1H|/,JGRID(1,26)/1H|/,JGRID(1,27)/1H-/           0000071(
      DATA JGRID(1,28)/1H|/,JGRID(1,29)/1H|/,JGRID(1,30)/1H|/           0000072(
      DATA JGRID(1,31)/1H|/,JGRID(1,32)/1H|/,JGRID(1,33)/1H|/           0000073(
      DATA JGRID(1,34)/1H|/,JGRID(1,35)/1H|/,JGRID(1,36)/1H|/           0000074(
      DATA JGRID(1,37)/1H|/,JGRID(1,38)/1H|/,JGRID(1,39)/1H|/           0000075(
      DATA JGRID(1,40)/1H-/,JGRID(1,41)/1H|/,JGRID(1,42)/1H|/           0000076(
      DATA JGRID(1,43)/1H|/,JGRID(1,44)/1H|/,JGRID(1,45)/1H|/           0000077(
      DATA JGRID(1,46)/1H|/,JGRID(1,47)/1H|/,JGRID(1,48)/1H|/           0000078(
      DATA JGRID(1,49)/1H|/,JGRID(1,50)/1H|/,JGRID(1,51)/1H|/           0000079(
      DATA JGRID(1,52)/1H|/                                             0000080(
C                                                                       0000081(
C DEFINE THE VERTICAL LABEL                                             0000082(
C                                                                       0000083(
      DATA JVERT /18 * 4H    , 4H C  , 4H O  , 4H N  ,                  0000084(
     &     4H C  , 4H E  , 4H N  , 4H T  , 4H R  , 4H A  ,              0000085(
     &     4H T  , 4H I  , 4H O  , 4H N  , 4H    , 4H P  ,              0000086(
     &     4H P  , 4H M  , 69 * 4H    /                               0000087(
C                                                                       0000088(
C DEFINE MISCELLANEOUS DATA VALUES                                      0000089(
C                                                                       0000090(
      DATA NIN /5/, NOUT /6/, JBLANK /4H    /                         0000091(
      DATA MAXTIM /121/, MAXCON /52/, MAXPNT /80/                       0000092(
      DATA JSTAR /1H*/, TGRID /120./, CGRID /52./                       0000093(
C                                                                       0000094(
C SET LOOP FOR ALL SPECIES AND CLEAR GRID                               0000095(
C                                                                       0000096(
      DO 360 N = 1,NTOT                                                 0000097(
      DO 250 K = 1,MAXCON                                               0000098(
      DO 240 J = 2,MAXTIM                                               0000099(
      JGRID(J,K) = JBLANK                                               0000100(
240   CONTINUE                                                          0000101(
250   CONTINUE                                                          0000102(
C                                                                       0000103(
C READ PLOT CONTROL CARD                                                0000104(
C                                                                       0000105(
      READ (NIN,4,END=900) NTEST, NDAT, JSYMB, JFACT, JCONC,            0000106(
     &     CLOW, CHIGH, TLOW, THIGH                                     0000107(
C                                                                       0000108(
C TEST FOR END OF PLOTTING                                              0000109(
C                                                                       0000110(
```

EXHIBIT A-7. LISTING OF SUBROUTINE PLOT (Continued)

```
      IF (NTEST .EQ. JBLANK) GO TO 800                                  00001110
C                                                                       00001120
C TEST NUMBER OF DATA POINTS AND READ DATA                              00001130
C                                                                       00001140
      IF (NDAT .LE. 0) GO TO 308                                        00001150
      IF (NDAT .LE. MAXPNT) GO TO 305                                   00001160
      WRITE (NOUT,1020) MAXPNT                                          00001170
      GO TO 900                                                         00001180
C                                                                       00001190
C READ DATA POINTS                                                      00001200
C                                                                       00001210
305   READ (NIN,5) (TIME(J), DATA(J), J = 1,NDAT)                       00001220
C                                                                       00001230
C SET NORMALIZATION FACTORS AND VERTICAL CONCENTRATION LABELS           00001240
C                                                                       00001250
308   CSPAN = CGRID / (CHIGH - CLOW)                                    00001260
      TSPAN = TGRID / (THIGH - TLOW)                                    00001270
      JVERT(1,2) = JCONC(5)                                             00001280
      JVERT(14,2) = JCONC(4)                                            00001290
      JVERT(27,2) = JCONC(3)                                            00001300
      JVERT(40,2) = JCONC(2)                                            00001310
C                                                                       00001320
C SET HORIZONTAL TIME LABELS                                            00001330
C                                                                       00001340
      DO 310 J = 1,9                                                    00001350
      TPRINT(J) = FLOAT(J - 1) / 8. * (THIGH - TLOW) + TLOW             00001360
310   CONTINUE                                                          00001370
C                                                                       00001380
C TEST FOR CORRECT SPECIES NAME                                         00001390
C                                                                       00001400
      DO 320 L = 1,NTOT                                                 00001410
      IF (NTEST .EQ. NAME(L)) GO TO 325                                 00001420
320   CONTINUE                                                          00001430
      WRITE (NOUT,1021) NTEST                                           00001440
      GO TO 360                                                         00001450
C                                                                       00001460
C IF THERE ARE DATA POINTS, GET THEIR COORDINATES                       00001470
C                                                                       00001480
325   IF (NDAT .LE. 0) GO TO 335                                        00001490
      DO 330 J = 1,NDAT                                                 00001500
      KTIM = IFIX((TIME(J) - TLOW) * TSPAN + 1.5)                       00001510
      KCON = IFIX((DATA(J) - CLOW) * CSPAN - 1.5)                       00001520
      KCON = MAXCON - KCON                                              00001530
C                                                                       00001540
C CHECK FOR BEING WITHIN GRID, THEN PLACE ON GRID                       00001550
C                                                                       00001560
      IF (KTIM .LT. 2) GO TO 330                                        00001570
      IF (KCON .LT. 1) GO TO 330                                        00001580
      IF (KTIM .GT. MAXTIM) GO TO 330                                   00001590
      IF (KCON.GT. MAXCON) GO TO 330                                    00001600
      JGRID(KTIM,KCON) = JSTAR                                          00001610
330   CONTINUE                                                          00001620
C                                                                       00001630
C IF THERE ARE CALCULATED POINTS, GET THEIR COORDINATES                 00001640
C                                                                       00001650
335   IF (NPNT .LE. 0) GO TO 345                                        00001660
```

EXHIBIT A-7. LISTING OF SUBROUTINE PLOT (Concluded)

```
      DO 340 J = 1,NPNT                                                 00001670
      KTIM = IFIX((SAVTIM(J) - TLOW) * TSPAN + 1.5)                     00001680
      KCON = IFIX((SAVCON(L,J) - CLOW) * CSPAN - 1.5)                   00001690
      KCON = MAXCON - KCON                                              00001700
C                                                                       00001710
C CHECK FOR BEING WITHIN GRID, THEN PLACE ON GRID                       00001720
C                                                                       00001730
      IF (KTIM .LT. 2) GO TO 340                                        00001740
      IF (KCON .LT. 1) GO TO 340                                        00001750
      IF (KTIM .GT. MAXTIM) GO TO 340                                   00001760
      IF (KCON .GT. MAXCON) GO TO 340                                   00001770
      JGRID(KTIM,KCON) = JSYMB                                          00001780
340   CONTINUE                                                          00001790
C                                                                       00001800
C SKIP A PAGE, THEN PRINT THE VERTICAL AXIS AND GRID                    00001810
C                                                                       00001820
345   WRITE (NOUT,1014)                                                 00001830
      DO 350 K = 1,MAXCON                                               00001840
      WRITE (NOUT,1015) JVERT(K,1), JVERT(K,2),                         00001850
     &     (JGRID(J,K), J = 1,MAXTIM)                                   00001860
350   CONTINUE                                                          00001870
C                                                                       00001880
C PRINT THE HORIZONTAL AXIS AND LABELS                                  00001890
C                                                                       00001900
      WRITE (NOUT, 1016) JCONC(1)                                       00001910
      WRITE (NOUT,1017) TPRINT                                          00001920
      WRITE (NOUT,1018) NTIT, NAME(L), JFACT                            00001930
360   CONTINUE                                                          00001940
C                                                                       00001950
C END OF SUBROUTINE -- RETURN TO CALLER                                 00001960
C                                                                       00001970
800   RETURN                                                            00001980
900   STOP                                                              00001990
C                                                                       00002000
C LIST OF FORMAT STATEMENTS                                             00002010
C                                                                       00002020
4     FORMAT (A4, 1X, I2, 1X, A1, 1X, 6(A4, 1X), 4F10.0)                00002030
5     FORMAT (8F10.0)                                                   00002040
 1014 FORMAT (1H1)                                                      00002050
1015  FORMAT(1X, 2A4, 121A1)                                            00002060
 1016 FORMAT (5X, A4, 1H+, 8(15H---------------|))                      00002070
 1017 FORMAT (F12.2, 8F15.2, /, 62X, 14HTIME (MINUTES), /)              00002080
 1018 FORMAT (27X, 11HFIGURE   . , 3A4, 12H.  SPECIES: , A4,            00002090
     &     5X, 28HCONCENTRATION SCALE FACTOR: , A4)                     00002100
 1020 FORMAT (33H PROGRAM CANNOT HANDLE MORE THAN , I4,                 00002110
     &     28H PLOT POINTS -- JOB ABORTED.)                             00002120
 1021 FORMAT (14HISPECIES NAME , A4, 21H NOT IN SPECIES LIST.,          00002130
     &     23H SKIPPING TO NEXT PLOT.)                                  00002140
      END                                                               00002150
```

EXHIBIT A-8. SAMPLE MODKIN INPUT

```
SAMPLE DECK        38    3   13    4    4    2    4    5    1
5.0        375.0      0.0001     0.00001    5.0         0.001      0.00835
NO2                          1NO         1O                    2.66E-1
O     O2    M                1O3         1M                    2.00E-5
O3    NO                     1NO2        1O2                   2.08E+1
O3    NO2                    1NO3        1O2                   4.65E-2
NO3   NO                     2NO2                              1.50E+4
NO3   NO2                    1N2O5                             4.50E+3
N2O5                         1NO2        1NO3                  2.70E+1
N2O5  H2O                    2HNO3                             1.00E-5
NO    NO2   H2O              2HNO2                             2.10E-6
HNO2  HNO2                   1NO         1NO2        1H2O      4.50E00
HNO2                         1OH         1NO                   1.30E-2
OH    NO2                    1HNO3                             1.50E+4
HO2   NO                     1OH         1NO2                  7.00E+2
HO2   HO2                    1H2O2       1O2                   5.30E+3
H2O2                         2OH                               1.06E-3
ALD                    0.63RO2    1.37HO2                     2.50E-3
ALD   OH               0.63RCO3   0.37HO2        1H2O         2.30E+4
RO2   NO                     1RO         1NO2                  9.10E+2
OH    NO                     1HNO2                             1.20E+4
RCO3  NO                     1RO2        1NO2        1CO2      9.10E+2
RCO3  NO2                    1PAN                              1.00E+2
RO    O2                     1HO2        1ALD                  2.40E-2
RO    NO                     1RNO2                             2.50E+2
RO    NO2                    1RNO3                             4.90E+2
RO2   RO2                    2RO
RO2   HO2                    1RO         1OH
O     NO                     1NO2
O     NO2                    1NO         1O2                   1.38E+4
O     NO2                    1NO3
NO    HNO3                   1HNO2       1NO2
HNO2  HNO3                   1H2O        2NO2
HO2   SO2                    1SO3        1OH               4.5000E-1
RO2   SO2                    1SO3        1RO               6.0000E-1
NO3   SO2                    1SO3        1NO2              1.5000E+4
N2O5  SO2                    1SO3        2NO2              4.0000E-1
OLEF  O                      1RO2     0.5RCO3    0.5HO2    1.9776E+3
OLEF  O3                     1RCO3       1RO         1ALD     0.64E-2
OLEF  OH                     1RO2        1ALD                 0.70E+4
OLEF      2
PROP  O                      1RO2     0.5RCO3    0.5HO2       6.80E+3
ETHY  O                      1RO2        0RCO3      1HO2       7.72E+2
OLEF      2
PROP  O3                     1RCO3       1RO         1ALD     1.60E-2
ETHY  O3                     1RCO3       1RO         1ALD     4.00E-3
OLEF      2
PROP  OH                     1RO2        1ALD                 2.50E+4
ETHY  OH                     1RO2        1ALD                 2.50E+3
NO2          0.08
NO           0.27
O3           0.022
N2O5
HO2
RO2
RCO3
HNO2
```

EXHIBIT A-8. SAMPLE MODKIN INPUT (Concluded)

```
H2O2
ALD       0.10
SO2       0.334
OLEF      1.90
HNO3
O            1.0E-9
NO3         1.0E-10
OH          5.0E-10
RO        0.0
PAN
RNO2
RNO3
SO3
ETHY      0.19
PROP      1.71
M         1000000.0
O2        210000.0
H2O       20000.0
CO2       10000.0
SO2     5
          0      0.291        49      0.241       108      0.396       173      0.409
        231      0.328
NO2     7
          0      0.035        29      0.039        64      0.040       117      0.048
        157      0.040       187      0.043       297      0.034
NO      7
          0      0.35         29      0.36         64      0.36        117      0.43
        157      0.36        187      0.39        297      0.31
ETHY    7
          0      0.184        35      0.193        91      0.201       121      0.202
        177      0.197       271      0.200       330      0.204
PROP    7
          0      1.656        35      1.737        91      1.809       121      1.818
        177      1.773       271      1.800       330      1.836
NO2   9 0 10+0 0.00 0.15 0.30 0.45 0.60          0.0        0.6         0.0      400.0
          8      0.09         29      0.27         44      0.40         64      0.33
        117      0.26        157      0.12        187      0.14        228      0.12
        297      0.090
NO    7 0 10+0 0.00 0.15 0.30 0.45 0.60          0.0        0.60        0.0      400.0
          8      0.26         29      0.16         44      0.05         64      0.00
        117      0.00        157      0.010       187      0.00
O3   10 0 10+0 0.00 0.15 0.30 0.45 0.60          0.0        0.6         0.0      400.0
         11      0.025        32      0.036        47      0.314        67      0.496
        118      0.54        158      0.46        188      0.41        229      0.41
        298      0.45        298      0.43
SO2  10 0 10+0 0.00 0.15 0.30 0.45 0.60          0.0        0.6         0.0      400.0
         11      0.353        11      0.384        47      0.285       108      0.186
        108      0.136       173      0.291       231      0.173       231      0.080
        305      0.241       305      0.415
PAN   7 0 10+0 0.00 0.15 0.30 0.45 0.60          0.0        0.6         0.0      400.0
         30      0.000       101      0.054       162      0.109       185      0.197
        225      0.211       266      0.220       311      0.213
OLEF 16 0 10+0 0.00 0.50 1.00 1.50 2.00          0.0        2.0         0.0      400.0
         16      1.85         31      1.78         42      1.63         51      1.56
         66      1.16         71      1.09         86      0.88        102      0.72
        116      0.71        132      0.69        151      0.70        191      0.69
        237      0.69        261      0.70        301      0.68        323      0.65
```

EXHIBIT A-9. SAMPLE MODKIN OUTPUT--SELECTED PAGES

MODULAR KINETICS RUN NO. SAMPLE DECK

TOTAL NUMBER OF REACTIONS = 38

NUMBER OF LUMPED REACTIONS = 3

NUMBER OF DIFFERENTIAL SPECIES = 13

NUMBER OF STEADY STATE SPECIES = 4

NUMBER OF UNCOUPLED SPECIES = 4

NUMBER OF REPLACEMENT SPECIES = 2

NUMBER OF INERT OR CONSTANT SPECIES = 4

NUMBER OF FLOWING SPECIES = 5

REACTION RATE PRINT REQUEST FLAG = 1

TIME INCREMENT = 5.000E 00 MINUTES

ENDING TIME = 3.750E 02 MINUTES

STARTING STEP SIZE = 1.000E-04 MINUTES

MINIMUM STEP SIZE = 1.000E-05 MINUTES

MAXIMUM STEP SIZE = 5.000E 00 MINUTES

CONVERGENCE TOLERANCE = 1.000E-03

DILUTION RATE = 8.350E-03 MINUTES(-1)

EXHIBIT A-9. SAMPLE MODKIN OUTPUT--SELECTED PAGES (Continued)

LIST OF REACTIONS

	R. CONST.	REACTANTS			PRODUCTS					
1	2.660E-01		NO2	=	1.00 NO	1.00 O				
2	2.000E-05	M O2	O	=	1.00 O3	1.00 M				
3	2.080E 01	NO	O3	=	1.00 NO2	1.00 O2				
4	4.650E-02	NO2	O3	=	1.00 NO3	1.00 O2				
5	1.500E 04	NO	NO3	=	2.00 NO2					
6	4.500E 03	NO2	NO3	=	1.00 N2O5					
7	2.700E 01		N2O5	=	1.00 NO2	1.00 NO3				
8	1.000E-05	H2O	N2O5	=	2.00 HNO3					
9	2.100E-06	H2O NO2	NO	=	2.00 HNO2					
10	4.500E 00	HNO2	HNO2	=	1.00 NO	1.00 NO2	1.00 H2O			
11	1.300E-02		HNO2	=	1.00 OH	1.00 NO				
12	1.500E 04	NO2	OH	=	1.00 HNO3					
13	7.000E 02	NO	HO2	=	1.00 OH	1.00 NO2				
14	5.300E 03	HO2	HO2	=	1.00 H2O2	1.00 O2				
15	1.060E-03		H2O2	=	2.00 OH					
16	2.500E-03		ALD	=	0.63 RO2	1.37 HO2				
17	2.300E 04	OH	ALD	=	0.63 RCO3	0.37 HO2	1.00 H2O			
18	9.100E 02	NO	RO2	=	1.00 RO	1.00 NO2				
19	1.200E 04	NO	OH	=	1.00 HNO2					
20	9.100E 02	NO	RCO3	=	1.00 RO2	1.00 NO2	1.00 CO2			
21	1.000E 02	NO2	RCO3	=	1.00 PAN					
22	2.400E-02	O2	RO	=	1.00 HO2	1.00 ALD				
23	2.500E 02	NO	RO	=	1.00 RNO2					
24	4.900E 02	NO2	RO	=	1.00 RNO3					
25	0.0	RO2	RO2	=	2.00 RO					
26	0.0	HO2	RO2	=	1.00 RO	1.00 OH				
27	0.0	NO	O	=	1.00 NO2					
28	1.380E 04	NO2	O	=	1.00 NO	1.00 O2				
29	0.0	NO2	O	=	1.00 NO3					
30	0.0	HNO3	NO	=	1.00 HNO2	1.00 NO2				
31	0.0	HNO3	HNO2	=	1.00 H2O	2.00 NO2				
32	4.500E-01	SO2	HO2	=	1.00 SO3	1.00 OH				
33	6.000E-01	SO2	RO2	=	1.00 SO3	1.00 RO				
34	1.500E 04	SO2	NO3	=	1.00 SO3	1.00 NO2				
35	4.000E-01	SO2	N2O5	=	1.00 SO3	2.00 NO2				
36	1.978E 03	O	OLEF	=	1.00 RO2	0.50 RCO3	0.50 HO2			
37	6.400E-03	O3	OLEF	=	1.00 RCO3	1.00 RO	1.00 ALD			
38	7.000E 03	OH	OLEF	=	1.00 RO2	1.00 ALD				
THE FOLLOWING SET OF 2 REACTIONS CORRESPONDS TO REACTION NUMBER 36										
39	6.800E 03	O	PROP	=	1.00 RO2	0.50 RCO3	0.50 HO2			
40	7.720E 02	O	ETHY	=	1.00 RO2	0.0 RCO3	1.00 HO2			
THE FOLLOWING SET OF 2 REACTIONS CORRESPONDS TO REACTION NUMBER 37										
41	1.600E-02	O3	PROP	=	1.00 RCO3	1.00 RO	1.00 ALD			
42	4.000E-03	O3	ETHY	=	1.00 RCO3	1.00 RO	1.00 ALD			
THE FOLLOWING SET OF 2 REACTIONS CORRESPONDS TO REACTION NUMBER 38										
43	2.500E 04	OH	PROP	=	1.00 RO2	1.00 ALD				
44	2.500E 03	OH	ETHY	=	1.00 RO2	1.00 ALD				

EXHIBIT A-9. SAMPLE MODKIN OUTPUT--SELECTED PAGES (Continued)

INITIAL SPECIES CONCENTRATIONS

SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE
DIFFERENTIAL(PPM)							
NO2	8.000E-02	NO	2.700E-01	O3	2.200E-02	N2O5	0.0
HO2	0.0	RO2	0.0	RCO3	0.0	HNO2	0.0
H2O2	0.0	ALD	1.000E-01	SO2	3.340E-01	OLEF	1.900E 00
HNO3	0.0						
STEADY STATE(PPM)							
O	1.000E-09	NO3	1.000E-10	OH	5.000E-10	RO	0.0
UNCOUPLED(PPM)							
PAN	0.0	RNO2	0.0	RNO3	0.0	SO3	0.0
REPLACEMENT(PPM)							
ETHY	1.900E-01	PROP	1.710E 00				
INERT/CONSTANT(PPM)							
M	1.000E 06	O2	2.100E 05	H2O	2.000E 04	CO2	1.000E 04

TIME = 5.021E 00 MINUTES

SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE
DIFFERENTIAL(PPM)							
NO2	1.856E-01	NO	1.505E-01	O3	1.436E-02	N2O5	5.113E-07
HO2	1.367E-04	RO2	9.789E-05	RCO3	8.061E-06	HNO2	1.142E-02
H2O2	1.937E-04	ALD	1.904E-01	SO2	3.319E-01	OLEF	1.773E 00
HNO3	2.405E-03						
STEADY STATE(PPM)							
O	1.172E-08	NO3	1.706E-08	OH	2.960E-07	RO	2.670E-06
UNCOUPLED(PPM)							
PAN	2.988E-04	RNO2	5.147E-04	RNO3	7.154E-04	SO3	3.069E-04
REPLACEMENT(PPM)							
ETHY	1.816E-01	PROP	1.591E 00				

EXHIBIT A-9. SAMPLE MODKIN OUTPUT--SELECTED PAGES (Continued)

REACTION RATES (SORTED INTO DECREASING SIZE)

NO.	RATE	NO.	RATE	NO.	RATE	NO.	RATE	NO.	RATE
1	4.94E-02	2	4.92E-02	3	4.49E-02	13	1.44E-02	22	1.35E-02
18	1.34E-02	38	1.19E-02	17	1.30E-03	9	1.17E-03	20	1.10E-03
12	8.24E-04	10	5.87E-04	19	5.34E-04	16	4.76E-04	37	3.76E-04
24	2.43E-04	21	1.50E-04	11	1.48E-04	36	1.28E-04	4	1.24E-04
23	1.00E-04	14	9.91E-05	34	8.50E-05	5	3.85E-05	28	3.00E-05
32	2.04E-05	33	1.95E-05	6	1.43E-05	7	1.38E-05	15	2.05E-07
8	1.02E-07	35	6.79E-08	31	0.0	30	0.0	29	0.0
27	0.0	26	0.0	25	0.0				

TIME = 1.007E 01 MINUTES

SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE
DIFFERENTIAL(PPM)							
NO2	2.753E-01	NO	5.053E-02	O3	5.492E-02	N2O5	5.508E-06
HO2	4.046E-04	RO2	2.890E-04	RCO3	3.710E-05	HNO2	1.311E-02
H2O2	2.104E-03	ALD	3.073E-01	SO2	3.285E-01	OLEF	1.634E 00
HNO3	7.896E-03						
STEADY STATE(PPM)							
O	1.738E-08	NO3	1.230E-07	OH	2.982E-07	RO	2.827E-06
UNCOUPLED(PPM)							
PAN	2.737E-03	RNO2	8.319E-04	RNO3	2.355E-03	SO3	2.064E-03
REPLACEMENT(PPM)							
ETHY	1.733E-01	PROP	1.461E 00				

REACTION RATES (SORTED INTO DECREASING SIZE)

NO.	RATE	NO.	RATE	NO.	RATE	NO.	RATE	NO.	RATE
1	7.32E-02	2	7.30E-02	3	5.77E-02	13	1.43E-02	22	1.43E-02
18	1.33E-02	38	1.10E-02	17	2.11E-03	20	1.71E-03	37	1.32E-03
12	1.23E-03	21	1.02E-03	14	8.68E-04	10	7.74E-04	16	7.68E-04
4	7.03E-04	34	6.06E-04	9	5.84E-04	24	3.81E-04	19	1.81E-04
36	1.75E-04	11	1.70E-04	6	1.52E-04	7	1.49E-04	5	9.32E-05
28	6.60E-05	32	5.98E-05	33	5.70E-05	23	3.57E-05	15	2.23E-06
8	1.10E-06	35	7.24E-07	31	0.0	30	0.0	29	0.0
27	0.0	26	0.0	25	0.0				

EXHIBIT A-9. SAMPLE MODKIN OUTPUT--SELECTED PAGES (Continued)

INCOMING SO2 CONCENTRATION CHANGED TO 3.960E-01 AT 1.103E 02 MIN.

TIME = 1.160E 02 MINUTES

SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE
DIFFERENTIAL(PPM)							
NO2	1.451E-01	NO	7.451E-03	O3	2.239E-01	N2O5	1.497E-05
HO2	5.998E-04	RO2	4.193E-04	RCO3	1.155E-04	HNO2	2.416E-03
H2O2	1.795E-01	ALD	6.646E-01	SO2	1.532E-01	OLEF	3.383E-01
HNO3	3.199E-02						
STEADY STATE(PPM)							
O	9.179E-09	NO3	6.252E-07	OH	1.454E-07	RO	7.696E-07
UNCOUPLED(PPM)							
PAN	1.826E-01	RNO2	6.014E-04	RNO3	1.037E-02	SO3	1.405E-01
REPLACEMENT(PPM)							
ETHY	6.209E-02	PROP	2.762E-01				

REACTION RATES (SORTED INTO DECREASING SIZE)

NO.	RATE	NO.	RATE	NO.	RATE	NO.	RATE	NO.	RATE
1	3.86E-02	2	3.86E-02	3	3.47E-02	22	3.88E-03	13	3.13E-03
18	2.84E-03	17	2.22E-03	14	1.91E-03	21	1.68E-03	16	1.66E-03
4	1.51E-03	34	1.44E-03	37	1.05E-03	38	1.03E-03	20	7.84E-04
6	4.08E-04	7	4.04E-04	12	3.16E-04	15	1.90E-04	5	6.99E-05
24	5.47E-05	9	4.54E-05	32	4.14E-05	33	3.86E-05	11	3.14E-05
10	2.63E-05	28	1.84E-05	36	1.78E-05	19	1.30E-05	8	2.99E-06
23	1.43E-06	35	9.17E-07	31	0.0	30	0.0	29	0.0
27	0.0	26	0.0	25	0.0				

INCOMING NO2 CONCENTRATION CHANGED TO 4.800E-02 AT 1.185E 02 MIN.

INCOMING NO CONCENTRATION CHANGED TO 4.300E-01 AT 1.185E 02 MIN.

TIME = 1.204E 02 MINUTES

SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE
DIFFERENTIAL(PPM)							
NO2	1.458E-01	NO	7.718E-03	O3	2.208E-01	N2O5	1.468E-05
HO2	5.840E-04	RO2	3.974E-04	RCO3	1.112E-04	HNO2	2.422E-03
H2O2	1.802E-01	ALD	6.492E-01	SO2	1.554E-01	OLEF	3.173E-01
HNO3	3.225E-02						

EXHIBIT A-9. SAMPLE MODKIN OUTPUT--SELECTED PAGES (Continued)

```
STEADY STATE(PPM)

  O      9.225E-09   NO3   6.102E-07   OH    1.514E-07   RO    7.428E-07

UNCOUPLED(PPM)

  PAN    1.831E-01   RNO2  5.857E-04   RNO3  1.023E-02   SO3   1.420E-01

REPLACEMENT(PPM)

  ETHY   5.951E-02   PROP  2.578E-01

              REACTION RATES (SORTED INTO DECREASING SIZE)

  NO.   RATE      NO.   RATE      NO.   RATE      NO.   RATE      NO.   RATE
   1  3.88E-02     2  3.87E-02     3  3.54E-02    22  3.74E-03    13  3.16E-03
  18  2.79E-03    17  2.26E-03    14  1.81E-03    16  1.62E-03    21  1.62E-03
   4  1.50E-03    34  1.42E-03    38  1.00E-03    37  9.70E-04    20  7.81E-04
   6  4.00E-04     7  3.96E-04    12  3.31E-04    15  1.91E-04     5  7.06E-05
  24  5.31E-05     9  4.73E-05    32  4.08E-05    33  3.71E-05    11  3.15E-05
  10  2.64E-05    28  1.86E-05    36  1.67E-05    19  1.40E-05     8  2.93E-06
  23  1.43E-06    35  9.12E-07    31  0.0         30  0.0         29  0.0
  27  0.0         26  0.0         25  0.0

INCOMING ETHY CONCENTRATION CHANGED TO   2.020E-01 AT   1.226E 02 MIN.

INCOMING PROP CONCENTRATION CHANGED TO   1.818E 00 AT   1.226E 02 MIN.

                    TIME =    1.298E 02 MINUTES

SPECIES   VALUE   SPECIES   VALUE   SPECIES   VALUE   SPECIES   VALUE

DIFFERENTIAL(PPM)

  NO2   1.514E-01   NO    8.386E-03   O3    2.122E-01   N2O5  1.474E-05
  HO2   5.474E-04   RO2   3.493E-04   RCO3  1.003E-04   HNO2  2.508E-03
  H2O2  1.801E-01   ALD   6.146E-01   SO2   1.600E-01   OLEF  2.763E-01
  HNO3  3.307E-02

STEADY STATE(PPM)

  O      9.581E-09   NO3   5.899E-07   OH    1.647E-07   RO    6.859E-07
```

EXHIBIT A-9. SAMPLE MODKIN OUTPUT--SELECTED PAGES (Continued)

TIME = 3.760E 02 MINUTES

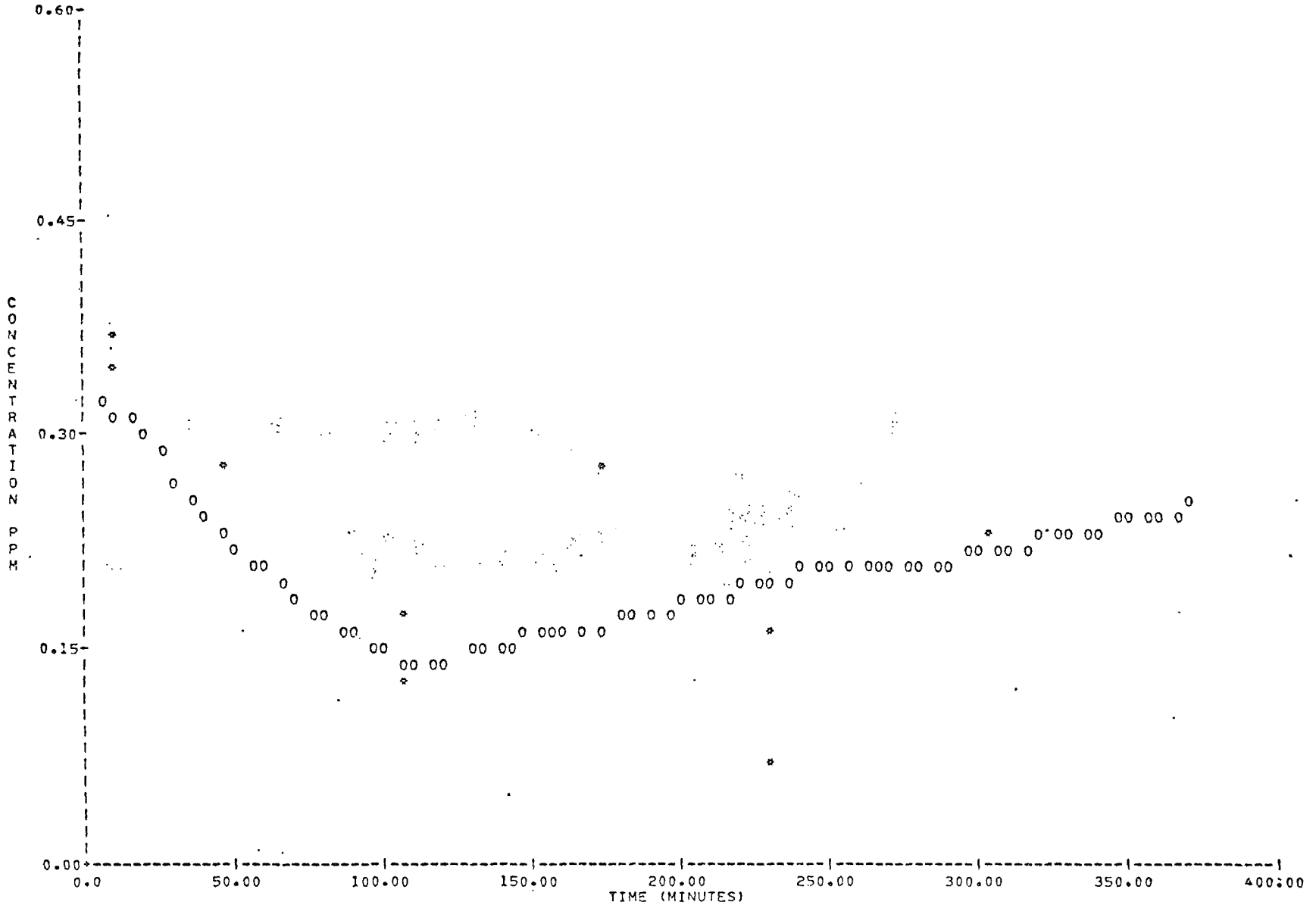
SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE	SPECIES	VALUE
DIFFERENTIAL(PPM)							
NO2	1.518E-01	NO	1.044E-01	O3	1.856E-02	N2O5	5.930E-07
HO2	6.287E-06	RO2	2.154E-06	RCO3	1.025E-06	HNO2	1.166E-02
H2O2	3.019E-02	ALD	5.619E-02	SO2	2.635E-01	OLEF	1.002E-02
HNO3	6.088E-02						
STEADY STATE(PPM)							
O	9.607E-09	NO3	2.370E-08	OH	1.367E-07	RO	4.048E-08
UNCOUPLED(PPM)							
PAN	5.204E-02	RNO2	1.897E-04	RNO3	2.607E-03	SO3	7.403E-02
REPLACEMENT(PPM)							
ETHY	5.277E-03	PROP	4.743E-03				

REACTION RATES (SORTED INTO DECREASING SIZE)

NO.	RATE	NO.	RATE	NO.	RATE	NO.	RATE	NO.	RATE
1	4.04E-02	2	4.03E-02	3	4.03E-02	9	6.66E-04	10	6.11E-04
13	4.62E-04	12	3.11E-04	18	2.06E-04	22	2.04E-04	17	1.77E-04
19	1.71E-04	11	1.52E-04	16	1.40E-04	4	1.31E-04	20	9.80E-05
34	9.37E-05	5	3.71E-05	15	3.20E-05	28	2.01E-05	38	1.88E-05
6	1.62E-05	7	1.60E-05	21	1.57E-05	24	3.01E-06	37	1.88E-06
23	1.06E-06	32	7.49E-07	36	3.65E-07	33	3.42E-07	14	2.11E-07
8	1.19E-07	35	6.25E-08	31	0.0	30	0.0	29	0.0
27	0.0	26	0.0	25	0.0				

THIS RUN TERMINATED WITH KFLAG = 1

EXHIBIT A-9. SAMPLE MODKIN OUTPUT--SELECTED PAGES (Concluded)



• SAMPLE DECK • SPECIES: SO2 CONCENTRATION SCALE FACTOR: 10+0

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16. ABSTRACT

This report describes the refinement of a mesoscale photochemical air quality simulation model through studies of selected chemical and meteorological phenomena that contribute to air pollution. The chemistry activities focused on the design of an automatic computer program for evaluating kinetic mechanisms, the improvement of a photochemical mechanism for incorporation in mesoscale models, and the development of a chemical mechanism for describing SO_2 oxidation. The meteorology studies examined the sensitivity of the model to the inclusion of wind shear, algorithms for deriving mass-consistent wind fields, and the treatment of turbulent diffusivities and elevated inversion layers. Alternative numerical techniques for solving the advection/diffusion equation in grid models are evaluated, including various finite difference, particle-in-cell, and finite element methods, in an attempt to find a suitable methodology for accurately calculating the horizontal transport of pollutants. Finally, the report considers the problem of multiday model usage and presents results from a two-day CO simulation for the Los Angeles basin.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air Pollution		13B
*Photochemical Reactions		07E
*Reaction Kinetics		07D
*Numerical Analysis		12A
*Mathematical Models		14B
*Meteorological Data		04B

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