THE RELATIONSHIP BETWEEN URBAN OZONE AND METEOROLOGY WITH APPLICATION TO AIR QUALITY DATA FROM THE PORTLAND AREA

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ABSTRACT

The primary explanation of the variability of urban ozone concentrations is variable meteorology. In order to develop a better understanding of this relationship, the physics and chemistry of urban ozone formation is considered from a theoretical point of view. If it is assumed that the ratios of the emission rates among the precursors to ozone formation are constants and that the formation of reactive radicals (i.e. those species that convert NO to NO_2 without the destruction of O_3) is proportional to initial hydrocarbon concentration, then a simple six step reaction model for ozone formation can be solved analytically. Expressing this solution in terms of meteorological parameters results in an equation giving a rough estimate of the sensitivity of O_3 concentration to wind speed, mixing height, intensity of solar radiation, precursor emission rate, background O_3 concentration and location downwind of an urban center.

A computer simulation of ozone formation for the Portland, Oregon area was also developed as a more realistic model. The model is characterized by a photochemical reaction mechanism of 33 specific reactions that takes into account the effect of variations in solar intensity, dilution due to lifting of the mixing height, and a non-impulsive schedule for precursor injection. This computer program gives an estimate of O_3 concentration in the Portland area as a function of wind speed, mixing height, precursor emission rate, background O_3 concen-

tration, time of day, time of year, and location downwind.

Computer simulation results indicate that immediately downwind of an urban center the size of Portland, O_3 concentration on sunny days depends most strongly on wind speed and less strongly upon mixing height, precursor emission rate and time of year as long as the time of year is the months of April through September. In addition it appears that O_3 due to precursors from Portland and upwind ozone levels cannot be simply summed to give O_3 at a downwind location; that is, the relationship is more complex than additive. These results are consistent with the results derived analytically.

Analysis of air quality data for sunny days from two locations in the Portland area sustains these conclusions. The two locations are relatively near (10 km) and relatively far (30 km) from city center. For the near location, wind speed and upwind O_3 concentration are clearly the most important determinants, while wind direction and upwind O_3 concentration appear to be more important for the more distant location. Background O_3 levels appear to be related to the degree of stagnation of the high pressure system that characterizes the meteorology of the region on days with elevated O_3 levels. This effect results in a correlation between background O_3 and temperature. In addition the data give some evidence for the existence of a second order positive coupling between precursor emissions and upwind ozone concentration.

A practical result of this work is a procedure for forecasting O_3 levels in the Portland area. The procedure is the result of regression analysis of air quality and meteorological data using equations

suggested by computer simulation results. The forecasting methodology is also based in part upon a time series analysis of the residuals of the regression analysis. The forecast appears to be fairly successful for the near location but only moderately successful for the far location.

CHAPTER I

INTRODUCTION

Of the six atmospheric pollutants for which federal standards exist, probably the most complex from a scientific point of view is ozone. The formation, transport and dispersion of this gas in association with man's activities has been studied fairly intensively for the past 10 to 15 years. Most of the scientific investigation has been with respect to the situation in the Los Angeles area where the problem is generally recognized to be the worst. At this point in time, a fairly clear picture is beginning to emerge of the physical and chemical basis of the problem. There can be no doubt that the primary source of the problem is the combined effect of oxides of nitrogen and reactive hydrocarbons of anthropogenic origin and sunlight. Because of the role of solar insolation, ozone levels follow a complex diurnal pattern with maximum concentrations in the afternoon hours. Further complicating the situation is the fact that one of the precursors to ozone formation, NO, actually reacts with this pollutant in the absence of sunlight. The result is very low levels of O_3 in urban areas at night.

Because a time period of the order of a few hours is required for ozone formation, the problem tends to be worse downwind of an urban center rather than at the point of maximum emissions. This fact explains why elevated ozone levels are often most common in lightly populated rural areas immediately downwind of cities. In addition to short range transport, it became apparent in the mid 1970's that elevated O_3 levels were related to air mass stagnation associated with slowly moving anticyclones. This fact is evidence for the phenomenon of long range transport of ozone and its precursors. It is conjectured that this mechanism may affect air quality as much as 1000 km from the precursor source (Dimitriades and Altshuller, 1978).

For some time it was conjectured that the stratosphere was a major source of the urban ozone problem. It now appears that stratospheric O_3 is not important, at least during time periods characterized by warm, sunny weather when the problem is the most serious.

In response to the increasing evidence of adverse health effects from ozone as well as from five other atmospheric pollutants, the 1970 amendments to the Clean Air Act established national ambient air quality standards. The amendments also mandated that control agencies enact contingency plans when it is expected that pollutant concentrations will be above these levels. It, therefore, became necessary for air pollution control agencies to forecast as accurately as possible during periods of stagnant meteorology at the very least. Obviously such contingency plans can have severe economic consequences and can result in inconvenience to a large number of people. At the same time, control agencies were required to implement emission control programs so as to be in compliance with ambient air quality standards. Their measures are often controversial both at the time of enactment and during subsequent enforcement. It is, therefore, of interest to determine if air quality data indicate the control measures are producing the desired effect. A direct analysis of pollutant concentration data by itself can be deceiving because of the variability in the data that is due to meteorology.

Both of these requirements, that is, the need for accurate forecasts and the need for better procedures for trend determination in air quality data, indicate that a better understanding of the relationship of meteorology to air quality is necessary. Particularly complex is the case of ozone. Because strong solar insolation is required for the reaction $NO_2 \xrightarrow{h\nu} NO + O$, ozone production is minimal on cloudy or mostly cloudy days. Even on sunny days that differ only in time of year, it is to be expected that significant differences in O_3 production will occur due to differences in the degree to which the atmosphere attenuates solar radiation. This fact has been indicated by the computer studies of Schjoldager (1977), Peterson and Demerjian (1976), and Nieboer et al. (1976). In addition, there is the obvious variability in the diluting effects of wind and mixing height. Finally the work of Ludwick et al. (1976), Cox (1977), and Chatfield and Rasmussen (1977) among others indicate considerable variability in background ozone concentrations.

Historically, the problem of relating photochemical air pollution to meteorology has been approached from two directions. The most obvious is to develop a computer model of the physical and chemical processes that occur in the polluted atmosphere. The models developed by Reynolds et al. (1974), Eschenroeder and Martinez (1972), MacCracken and Sauter (1975) and Graedel et al. (1976) are examples. Such models suffer from the lack of complete understanding of the processes involved and require considerable input data, place severe requirements on computer storage, and use large amounts of computer execution time. Historically, the accuracy of such models has been somewhat disappointing. Graedel et al. (1976), for example, report agreement with actual air quality data only to a factor of two.

A second approach exemplified by the work of Bruntz et al. (1974), Karl and DeMarrais (1977), and Revlett (1978) involves regressing actual ozone data upon such parameters as solar radiation, wind speed, temperature and mixing height. For the most part, this approach ignores the physics and chemistry involved and is dependent upon a guess for the functional form of the relationship between the dependent and independent variables. The agreement between predicted and actual ozone concentrations using this method has been considerably better. Revlett (1978), for example, reports agreement to 25%. It should be noted that this approach is site specific and lacks the generality of the first approach.

It is the objective of this thesis to investigate the relationship between ozone levels and meteorology as applied to air quality data from the Portland area. The analysis incorporates features of both approaches described above. The discussion begins with a theoretical consideration of the basic physics and chemistry involved in a simplified version of the problem of urban ozone formation (Chapter II). Computer simulation results for a more complex version of the problem are presented in Chapter III. These results suggest a fairly simple relationship between urban ozone levels and meteorology and emission parameters. The degree to which the data fit this relationship is then discussed in Chapters IV-VI. In these chapters regression analysis is performed on actual air quality and meteorology data to determine the most sensitive parameters of the functional relation suggested by computer simulation results. The discussion of Chapter IV centers on data collected during the summers of 1974-76 by the State of Oregon Department of Environmental Quality (DEQ) relatively near the center of Portland in the city of Milwaukie. A practical application of this effort is the development of a method to forecast O_3 levels at Milwaukie (Chapter V). The forecast is based upon the results of the regression analysis supplemented by a time series analysis of the residuals of this analysis. It was determined that autocorrelation existed in the residuals and this fact indicated the forecast could be improved using a time series analysis of the type formulated by Box and Jenkins (1975). The result is a forecast that is based in part upon the extent that the forecast for the previous day is in error. The degree to which the forecasted and actual concentrations are in agreement during the 1977 season is presented in Chapter V along with a discussion of an ozone episode that occurred during the first 17 days of August of that summer. Chapter VI is devoted to a discussion of data collected at a more distant location relative to Portland in Carus. The discussion is necessarily brief as the historical record consists of the 1976 and 1977 seasons only. The concluding chapter (VII) summarizes the principal conclusions of the effort, presents recommendation for additional monitoring, and suggests additional data analysis tasks.

The Portland area is a particularly interesting area to investigate the urban ozone phenomenon because of the complex interplay of meteorology and topography. The location of Portland near the confluence of the Willamette and Columbia Rivers results in a very complex wind field pattern. This in turn produces a complicated urban ozone pattern as indicated by surface and aircraft measurements (Huntzicker _et al_., 1977).

That meteorology is an extremely important determinant of ozone concentration in the Portland area can be seen in Figures 1 and 2. The first of these figures depicts a number of parameters to indicate frequency distributions for maximum ozone concentration at the Milwaukie location for the summers of 1974-1977. The data used are maximum hourly [O_3] on days that had the potential for elevation ozone levels; that is, warm, sunny days in the late spring and summer. Considerable variability can be seen in the distributions from one year to the next. Even greater variability is seen in Figure 2 which indicates the number of days in these same years that the federal standard for oxidants of .08 ppm as an hourly average was violated at Milwaukie. The cause of the high degree of variability from year to year is either variable emissions or variable meteorology. It is hard to imagine precursor emission fluctuating to such an extent. If emissions have changed during this period, then the change is somewhere between a slight increase as seen in increased traffic counts or a slight decrease due to the hydrocarbon emission control program initiated in 1975. Clearly the more important factor that explains the variability of Figures 1 and 2 is meteorology.

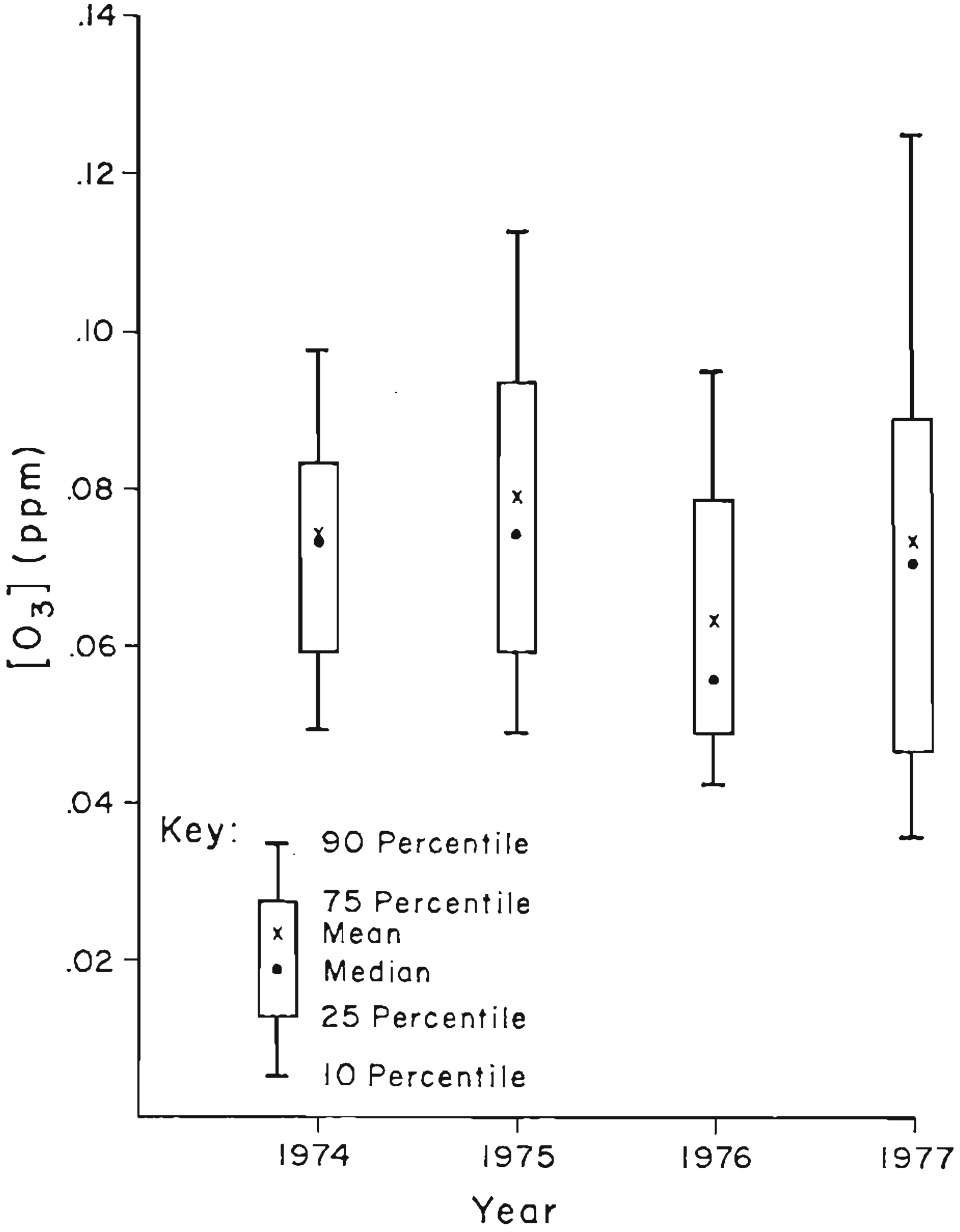

Figure 1 Frequency distributions for maximum hourly average $[O_3]$ at Milwaukie

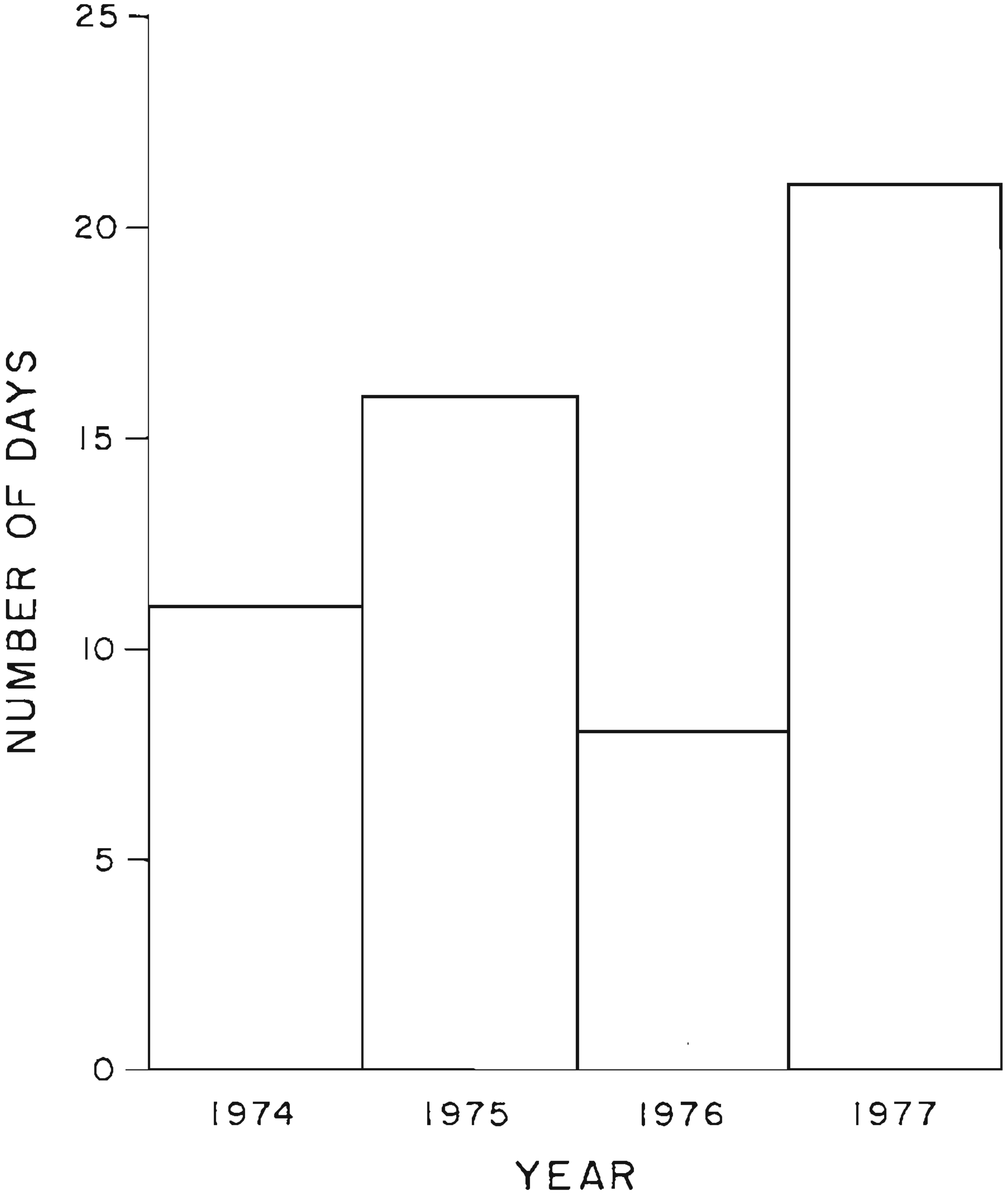

Figure 2 Violations of the federal oxidant standard of .08 ppm at Milwaukie

CHAPTER II

THEORETICAL CONSIDERATIONS

The formation of ozone in a photochemical environment is a very complex process, incorporating physical and chemical processes that are not completely understood in some instances. Any attempt to develop an analytic solution to the real world problem of ozone formation is probably doomed to failure; however, it is possible to solve explicitly for the time dependence of ozone concentration using an approximate model, and thereby develop a rough understanding of the effect of meteorology on ozone formation. If it is assumed that the ratios of the emission rates among the precursors to ozone formation are constants, then some progress can be made. Limited data that is discussed in Section III.2.2 indicate that this is only approximately true for the Portland area; therefore, this assumption constitutes a first approximation to urban ozone formation. What is presented here is a theoretical development for ozone formation. The development makes use of computer simulation results and is in some sense a combination of the two approaches to modeling urban ozone production. The development is based upon several simplifying assumptions that have the effect of limiting the applicability of the results to the first two or three hours of the photochemical cycle.

Consider the following simplified photochemical smog model:

$$O_2 + NO_2 + h\nu \xrightarrow{k_1} NO + O_3$$

$NO + O_3 \xrightarrow{k_3} NO_2 + O_2$

$HC \xrightarrow{k_4}$ Radicals

Radicals + $NO \xrightarrow{k_5} NO_2$ + Radicals

Radicals + $NO_2 \xrightarrow{k_6}$ Stable Products

where HC signifies reactive hydrocarbons.

In addition assume that:

1) $[O_3] = \frac{k_1 [NO_2]}{k_3 [NO]}$ at all times. This relationship follows if it is assumed that the rate of formation of ozone is exactly equal to the rate of disappearance so that $\frac{d[O_3]}{dt} = 0$. This does not mean that $[O_3]$ = constant; rather, it implies that ozone concentration adjusts to changes in k_1, $[NO_2]$ and $[NO]$ much faster than any of these three parameters change. The assumption is well known in photochemical smog work as the photostationary state (O'Brien, 1972).

2) The effect of dilution and fresh emissions can be ignored. Ozone formation for an urban center is thus modeled by a single injection of precursors into a box defined by wind speed and mixing height. The effect of ignoring dilution is to limit the applicability of the results to the first two or three hours of the photochemical smog process.

3) The photodissociation constant (k_1) does not vary during the time period of O_3 formation. Values for k_1 as a function of time of day and time of year as computed for the Portland area can be found in Table 1. Since no claim is made for realistic modeling beyond the first two to three hours, it can be seen that this assumption introduced an error no greater than 10%. It should be pointed

Table 1 Values for the photodissociation constant k_1

Day / Time (PDT)	June 21	July 21	August 21	Sept. 21
11:00	.561	.550	.520	.454
12:00	.584	.572	.549	.491
13:00	.592	.580	.558	.502
14:00	.584	.572	.549	.491
15:00	.561	.550	.520	.454
16:00	.522	.512	.466	.386

out that the assumption is not that k_1 is a constant throughout. Thus variations in this parameter are allowed to model photochemistry at different times of the day and times of the year.

4) [Radicals] = $K[HC]_0^{\beta} f(t)$ where $[HC]_0$ is the initial concentration of reactive hydrocarbons and f(t) is an unknown function of time. Examination of detailed computer simulation results indicate that this is a reasonably accurate representation of the time dependence of the radical species provided the ratios among the initial precursor concentrations are fixed. That is,

$$\frac{[HC]_0}{[NO_x]_0} = C_1 \quad \frac{[NO]_0}{[NO_2]_0} = C_2$$

In reality, processes 4-6 represent several specific reactions. Differences among the numerous computer models of the chemistry of ozone formation are to a great extent differences in the way in which these three processes are modeled. Computer simulation results based upon the photochemical smog model developed by Hecht, Seinfeld and Dodge (1974) indicate that the concentration of each of the important radical species can be represented by:

$$[Rad] = K[HC]_0^{\beta}\ f(t) \qquad (II.1)$$

The Hecht, Seinfeld and Dodge model contains 3 reactive species that participate either in the conversion of NO to NO_2 or in the removal of NO_2 to a significant extent. They are RO_2, RCO_3 and NO_3. The first two species are composites that represent all peroxyalkyl and peroxyacyl radicals. The radical HO_2 does participate in the conversion of NO to NO_2 via

$$HO_2 + NO \longrightarrow NO_2 + OH$$

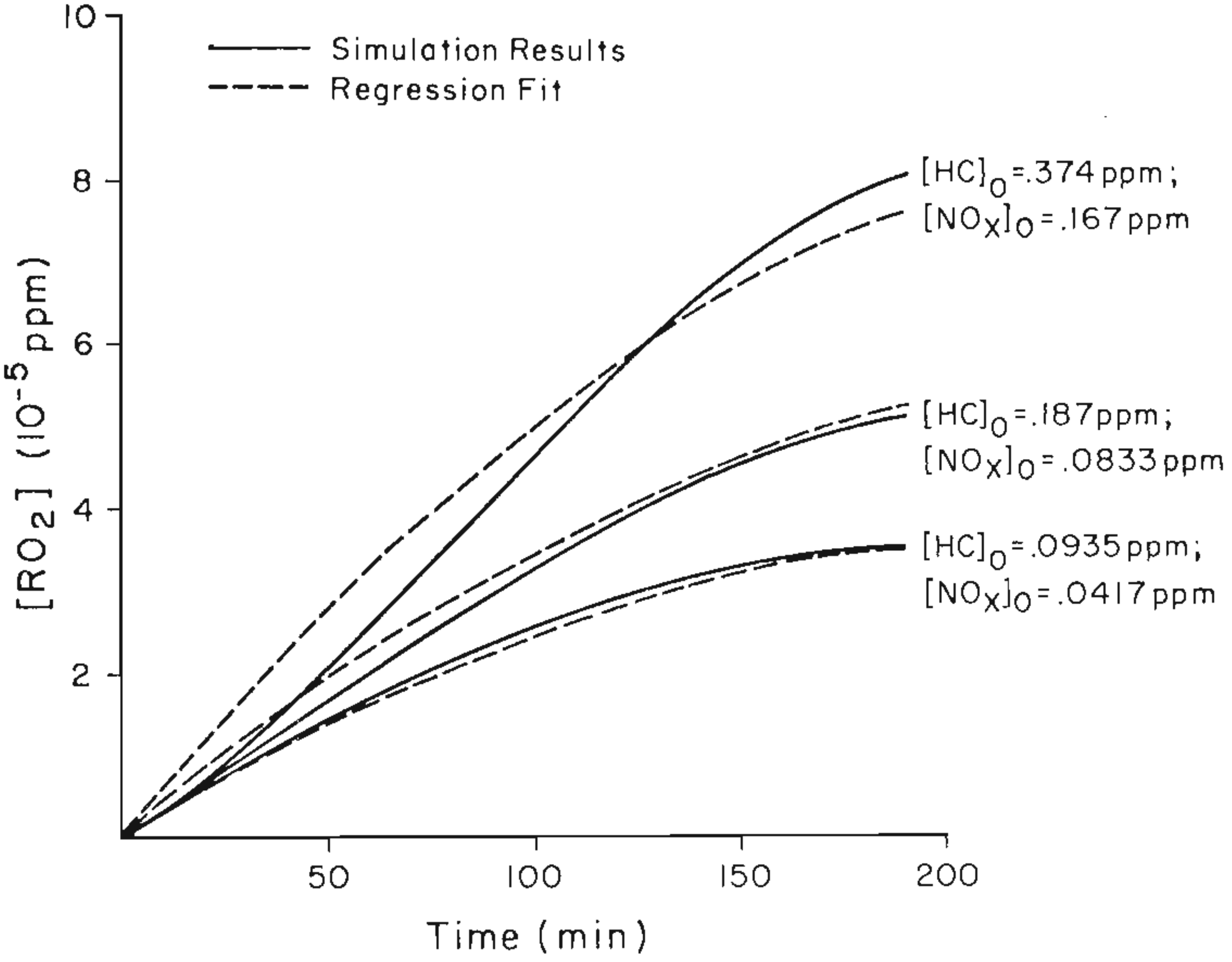

Figure 3 Concentration of RO_2 radical

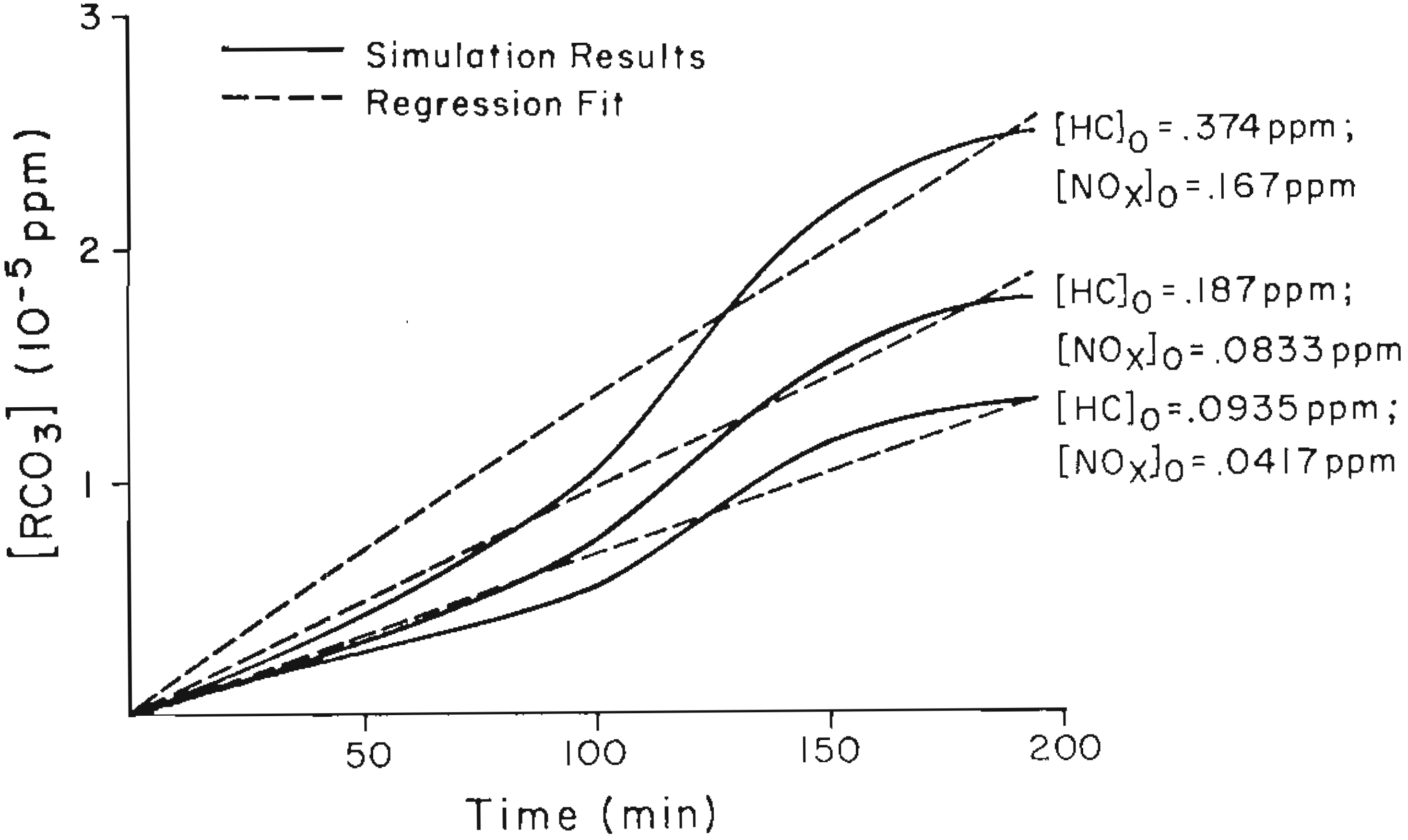

Figure 4 Concentration of RCO_3 radical

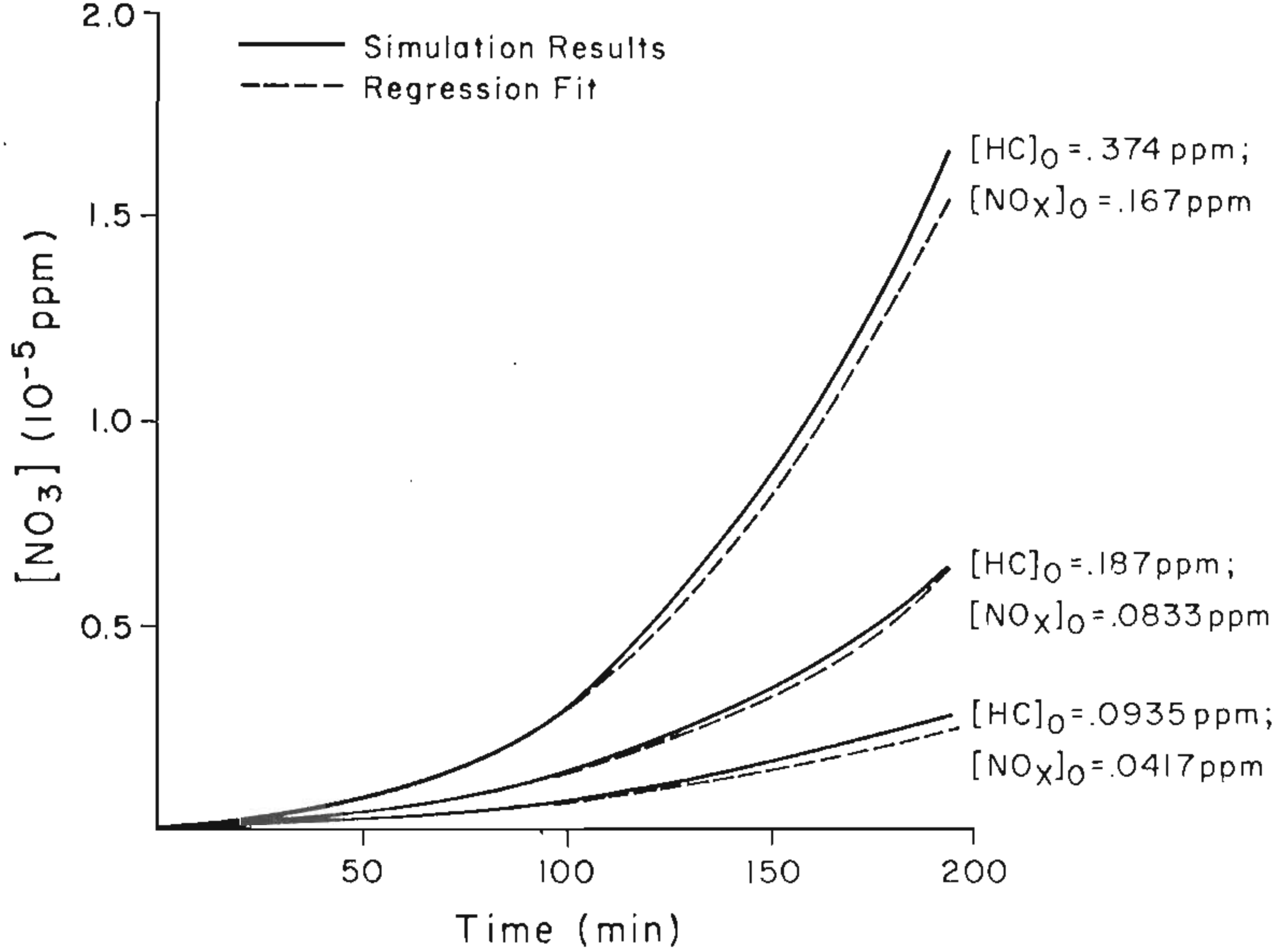

Figure 5 Concentration of NO_3 radical

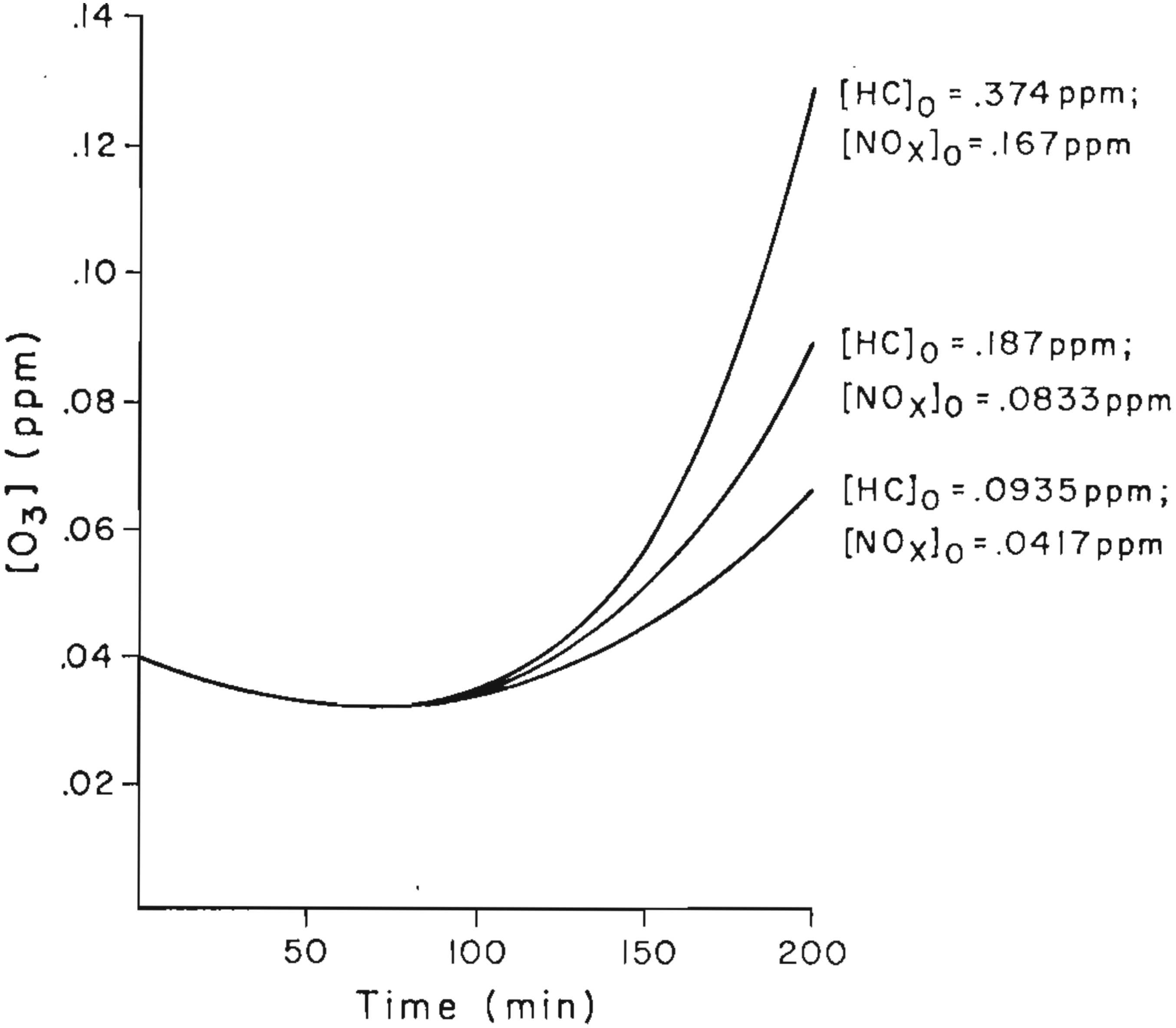

Figure 6 Simulated $[O_3]$ for different precursor injections (Initial $[O_3]$ = .04 ppm)

However, the subsequent reaction

$$NO_2 + OH \longrightarrow HNO_3$$

has a rate constant that is larger by a factor of five so that this radical does not appear to be especially effective in converting NO to NO_2. Plots of the concentration of these radicals as functions of time for three different initial precursor concentration are depicted in Figures 3, 4, and 5. The resulting $[O_3]$ for these initial precursor concentration can be found in Figure 6. It should be pointed out that the results depicted in Figures 3-6 are based upon an initial $[O_3]$ of .04 ppm and upon an injection schedule spread out over the entire 200 sec. (The actual injection schedule can be found in Figure 10 of Section III.2.4). These results are based upon the following set of ratios among the precursors

$$C_1 = 8.8 \text{ ppmC/ppm and } C_2 = 3$$

Also plotted in Figure 3-5 are regression fits that are based upon the following equations

$$[RO_2] = 4.4 \times 10^{-6}[HC]_0^{.54}t^{.64}$$

$$[RCO_3] = 2.5 \times 10^{-7}[HC]_0^{.43}t^{.95}$$

$$[NO_3] = 2.8 \times 10^{-10}[HC]_0^{1.3}t^{2.3}$$

From these equations, it can be seen that the Eq.(II.1) is a realistic representation for all species where the parameter β is in the interval .43 to 1.3.

From the four assumptions listed above

$$\frac{d[NO]}{dt} = k_1[NO_2] - k_3[NO][O_3] - k_5[Rads][NO]$$

$$= -k_5K[HC]_0^{\beta}[NO]\ f(t) \qquad (II.2)$$

and $$\frac{d[NO_2]}{dt} = -k_1[NO_2] + k_3[NO][O_3] + k_5[Rads][NO] - k_6[Rads][NO_2]$$

$$= K[HC]_0^\beta f(t)\{k_5[NO]-k_6[NO_2]\} \qquad \text{(II.3)}$$

Solving the first equation gives

$$[NO] = [NO]_0 \exp(-k_5 K[HC]_0^\beta \int_0^t f(\tau)d\tau)$$

Let $u = K[HC]_0^\beta \int_0^t f(\tau)d\tau$

then $du = K[HC]_0^\beta f(t)dt$

Eq.(II.3) can be solved using the integrating factor $\exp(k_6 u)$

$$[NO_2] = [NO_2]_0 \exp(-k_6 u) + \frac{k_5[NO]_0}{k_6-k_5}\{\exp(-k_5 u)-\exp(-k_6 u)\}$$

From the first assumption

$$[O_3] = \frac{k_1[NO_2]_0}{k_3[NO]_0}\exp(u\{k_5-k_6\}) - \frac{k_1 k_5}{k_3(k_5-k_6)}\{1-\exp(u\{k_5-k_6\})\} \qquad \text{(II.4)}$$

II.1 Case with $[NO_2]_0 = 0$

In the special case when the $[NO_x]_0$ is entirely in the form of NO

$$[O_3] = \frac{k_1 k_5}{k_3(k_5-k_6)}\{\exp(u\{k_5-k_6\})-1\} \qquad \text{(II.5)}$$

If t is sufficiently short, the approximation $\exp(x) = 1 + x$ can be used

$$[O_3] = \frac{k_1 k_5}{k_3}u$$

$$= \frac{k_1 k_5}{k_3} K[HC]_0^\beta \int_0^t f(\tau)d\tau \qquad \text{(II.6)}$$

The validity of this approximation is discussed in Section II.2.

The regression equations listed above indicate that for the initial phases of O_3 formation $f(t) = Ct^\alpha$ where α is in the interval .64 to 2.3.

Integration of Eq.(II.6) yields

$$[O_3] = \frac{k_1 k_5}{k_3}\frac{KC}{\alpha+1}[HC]_0^{\beta} t^{\alpha+1}$$

This equation can now be applied to the specific problem of interest, the effect of meteorology upon urban ozone concentrations. If it is assumed that all pollutants are well mixed within a box defined by the mixing height and wind velocity, then $[HC]_0 = \frac{EF}{HV_w}$ where EF is an emission factor, H is the mixing height and V_w is the wind speed. In addition, time can be related to wind speed via $t = \frac{D}{V_w}$ where D is the distance the air parcel has traveled from precursor injection to the point of interest. Thus

$$[O_3] = \frac{k_1 K'(EF)^{\beta}}{H^{\beta} V_w^{\alpha+\beta+1}}$$

with $K' = \frac{k_5 KCD^{\alpha+1}}{k_3(\alpha+1)}$. The results in Table 1 indicate that k_1 depends upon time of day and time of year. That is, $k_1 = g$ (HR,N) where HR is the hour of the day and N is some measure of time of year as, for example, Julian day.

$$[O_3] = \frac{K'(EF)^{\beta}}{H^{\beta} V_w^{\alpha+\beta+1}} g(HR,N)$$

Since the results in Figure 3 , 4 , and 5 indicate that α and $\beta \leq 1$ for most of the specific reactions represented by the fifth and sixth processes, this equation suggests that urban ozone levels at a location fixed relative to an urban center vary somewhat less strongly than linearly with emission factor and the inverse of mixing height while varying much more strongly with wind speed.

II.2 Validity of approximation for exponential

Consider the validity of the approximation

$$\exp(u\{k_5-k_6\}) \simeq 1 + u(k_5-k_6) \qquad \text{(II.7)}$$

In reality the fifth reaction represents all radical reactions that convert NO to NO_2 while the sixth reaction represents all reactions involving radicals that remove NO_2. A list of all these reactions for the Hecht, Seinfeld and Dodge model can be found in Table 2. The data of Figure 3, 4 and 5 along with the rate constants of the table indicate that RO_2 is the most important radical that participates in the conversion of NO to NO_2 without the destruction of O_3. Assume for the moment this is the only radical that participates in this process. If this is the case,

$$g(t) \equiv u(k_5-k_6) = 4.4 \times 10^{-6}[HC]_0^{.54} \int^{t} t^{.64}(800)$$

$$= 2.15 \times 10^{-3}[HC]_0^{.54} t^{1.64}$$

Air quality data indicate that reactive hydrocarbon concentration in the Portland area is of the order of .05 to .1 ppm. If the larger value is used

$$g(t) = 6.2 \times 10^{-4} t^{1.64}$$

Comparison of Figure 4 with Figure 3 indicates that this expression should be scaled by a factor of 1.3 to account for the effect of RCO_3. The effect of NO_3 can be ignored because the concentration is an order of magnitude less. With this assumption

$$g(t) = 8 \times 10^{-4} t^{1.64}$$

Table 2 Reactions involving radicals

$NO \longrightarrow NO_2$ reactions	Rate constant k $(ppm^{-1}min^{-1})$
$RO_2 + NO \longrightarrow RO + NO_2$	800
$RCO_3 + NO \longrightarrow RO_2 + NO_2 + CO_2$	800
$NO_3 + NO \longrightarrow 2NO_2$	13000
$NO_2 \longrightarrow$ Stable product reaction	
$RCO_3 + NO_2 \longrightarrow RCO_3NO_2$	100

Tabulated values are as follows:

Table 3 Evaluation of exponential approximation

Time (min.)	g(t)	exp g(t)-1
30	.21	.23
60	.66	.94
90	1.29	2.64

These results suggest that Eq.(II.7) is a satisfactory approximation for the first hour of photochemical activity in the Portland area. The approximation is probably good for somewhat more than the first hour since the effect of dilution has been ignored. Assuming a dilution factor of 2, then Eq.(II.7) is probably good for the first two hours. For longer periods of time Eq.(II.5) is more appropriate.

II.3 Effect of variations in background ozone

The discussion up to this point has been based on the assumption that background concentrations for all pollutants are zero. In reality non-zero concentrations for O_3, NO, NO_2 and reactive hydrocarbons have been measured at even the most remote areas of the world. Consider the problem of the impact of urban emissions upon non-zero background levels. Assume that background conditions correspond to the photostationary state. That is,

$$[O_3]_b = \frac{k_1[NO_2]_b}{k_3[NO]_b}$$

where the subscript (b) refers to background levels. Since there is a one for one relationship between destruction of O_3 and NO and creation of NO_2, the concentration of three primary pollutants immediately after emission would be

$$[NO]_0 = [NO]_b + [NO]_{ur} - x$$

$$[NO_2]_0 = [NO_2]_b + [NO_2]_{ur} + x$$

$$[O_3]_0 = [O_3]_b - x = \frac{k_1}{k_3}\,\frac{[NO_2]_b + [NO_2]_{ur} + x}{[NO]_b + [NO]_{ur} - x} \qquad \text{(II.8)}$$

where the subscript (ur) refers to the urban contribution.

Eq.(II.4) now becomes

$$[O_3] = [O_3]_b \frac{1+\frac{[NO_2]_{ur}+x}{[NO_2]_b}}{1+\frac{[NO]_{ur}-x}{[NO]_b}} \exp(u\{k_5-k_6\}) + \frac{k_1k_5}{k_3(k_5-k_6)}\{\exp(u\{k_5-k_6\})-1\} \qquad \text{(II.9)}$$

where x is determined from Eq.(II.8) to be

$$x = \frac{A + B + \frac{k_1}{k_3} - \{(A + B + \frac{k_1}{k_3})^2 - 4(AB - \frac{k_1}{k_3}C)\}^{1/2}}{2}$$

with

$$A = [O_3]_b$$

$$B = [NO]_b + [NO]_{ur}$$

$$C = [NO_2]_b + [NO_2]_{ur}$$

Consider two cases that are identical except for differences in $[O_3]_b$. Thus,

$$[O_3]_2 - [O_3]_1 = \exp(u\{k_5 - k_6\}) \left\{ [O_3]_{b_2} \frac{1 + \frac{[NO_2]_{ur} + x_2}{[NO_2]_{b_2}}}{1 + \frac{[NO]_{ur} - x_2}{[NO]_{b_2}}} - [O_3]_{b_1} \frac{1 + \frac{[NO_2]_{ur} + x_1}{[NO_2]_{b_1}}}{1 + \frac{[NO]_{ur} - x_1}{[NO]_{b_1}}} \right\}$$

This equation indicates a coupling between background and urban contributions to O_3 levels. Comparison of NO data collected by the Portland General Electric Company upwind of Portland with NO data collected by the DEQ in the central business area of Portland indicates that $\frac{[NO]_{ur}}{[NO]_b} \doteq 2$ as an average for the late morning and afternoon hours on sunny days. The data also indicate an average value for $[NO_b/[NO_2]_b \doteq 1$. Occasionally $[NO]_{ur}/[NO]_b$ is as large as 10 in the early morning hours; however, it appears that elevated photochemical O_3 levels in the Portland area arise from emissions prior to 10:00 PDT only very rarely (Huntzicker et al., 1977). Thus, it is possible because of the exponential that

$$[O_3]_2 - [O_3]_1 > [O_3]_{b_2} - [O_3]_{b_1}$$

for t sufficiently large. This result suggests that it is not correct simply to subtract background to obtain the contribution to O_3

concentration from the urban center immediately upwind. The relationship to be used should be based upon Eq.(II.9).

Consider now the effect of meteorology on Eq.(II.9). It is reasonable to assume that $[NO]_b = C_1$

$$[NO]_{ur} = \frac{C_2}{H\ V_w}$$

It can be shown that

$$[O_3] = [O_3]_b \frac{K_1 H V_w}{H V_w + K_2} \exp(u\{k_5 - k_6\}) + \frac{k_1 k_5}{k_3(k_5 - k_6)} \left\{\exp(u\{k_5 - k_6\}) - 1\right\} \quad \text{(II.10)}$$

where K_1 and K_2 are constants. This equation suggests that background and urban ozone can be added directly only in the limit of high wind speed and small reaction time. When wind speed and reaction time are both sufficiently small that

$$\frac{K_1 H V_w}{H V_w + K_2} \exp(u\{k_5 - k_6\}) < 1, \text{ then it is possible for } [O_3] < [O_3]_b.$$

This is, of course, the well known effect of fresh NO emissions from an urban center reducing O_3 concentrations below upwind levels. Finally, precursor emissions and background ozone levels are positively coupled. That is, the amount of ozone observed downwind of an urban center for a particular background level would be greater than the sum of the background level and the amount of ozone observed under the same meteorology conditions with $[O_3]_b = 0$.

CHAPTER III

COMPUTER SIMULATION FOR OZONE FORMATION IN THE PORTLAND AREA

The results of the previous section are based upon a very much simplified model for urban ozone formation. Considerably more realism is added with the use of a computer simulation that takes into account variations in solar intensity, the effect of fresh emissions and a chemical model more complex than the five reaction scheme previously described. The computer program described in this chapter simulates photochemistry for air masses that pass over Portland and are exposed to solar radiation for up to four hours. The program is not a generalized model for O_3 formation in the Portland area; rather, it was developed to investigate the relationship between O_3 and meteorology as seen in air quality data from Milwaukie and Carus.

III.1 Application of a photochemical smog model to the Portland area

The meteorology of the Portland area is known to be both complex and variable (Mathews, 1971); nonetheless, definite patterns exist. Examination of Figure 7 indicates that a pattern exists for surface winds. Plotted are composite wind roses based on hourly average wind data for 1975 from two locations, downtown Portland and the Portland Airport. Data were restricted to the afternoon and early evening (12:00-19:00 PDT) on those days when meteorology was conducive to O_3 production; that is, days from May 1 to September 30 for which the sun

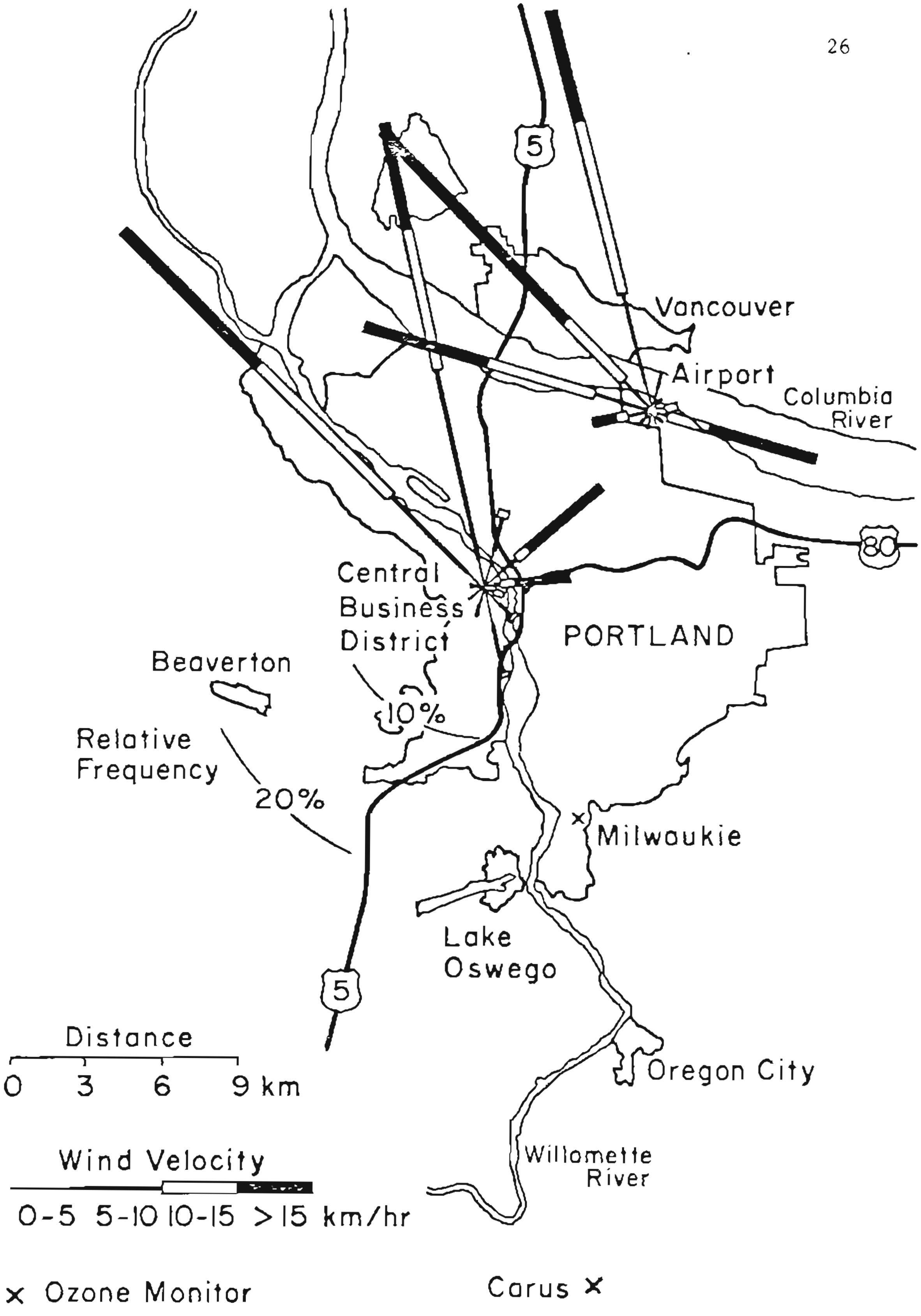

Figure 7 Frequency wind roses for the Portland area during the ozone season

was out at least 70% of the time possible and the maximum temperature was at least 23°C. Represented in the figure are 64 of the 153 days in the five month interval.

The major peak at 345° corresponds to air being channeled up the Willamette River by the effect of the West Hills. This pattern places the city of Milwaukie downwind of Portland. In fact this location is almost exactly downwind of the area of maximum precursor emissions for Portland. This can be seen in Figure 8 which depicts normalized emission density isopleths for NO_x as determined by the emission inventory of Pitter (1976). The pattern for hydrocarbons is much the same.

The secondary peak of Figure 7 in the northeast and east directions represents winds out of the Columbia River gorge. This pattern is fairly common during the month of September.

What is of importance for pollutant transport is the average wind within the mixing layer, that is, the transport wind. Unfortunately, soundings are not made in the Portland area on a regular basis. Data from the 17:00 PDT sounding at Salem, Oregon (80 km to the south) indicate that alignment of the surface and transport winds occurs most of the time. Examination of the days upon which the wind roses are based indicated that the two winds were within 45° for 81% of the days. Those days on which misalignment was observed were characterized by very light winds as would be expected.

The meteorology of the greater Portland area during the ozone season indicates that a fairly simple model can be used to simulate O_3 production. The Portland-Milwaukie-Carus area can be considered a "reaction pipeline" where the direction of the pipeline runs from Portland to

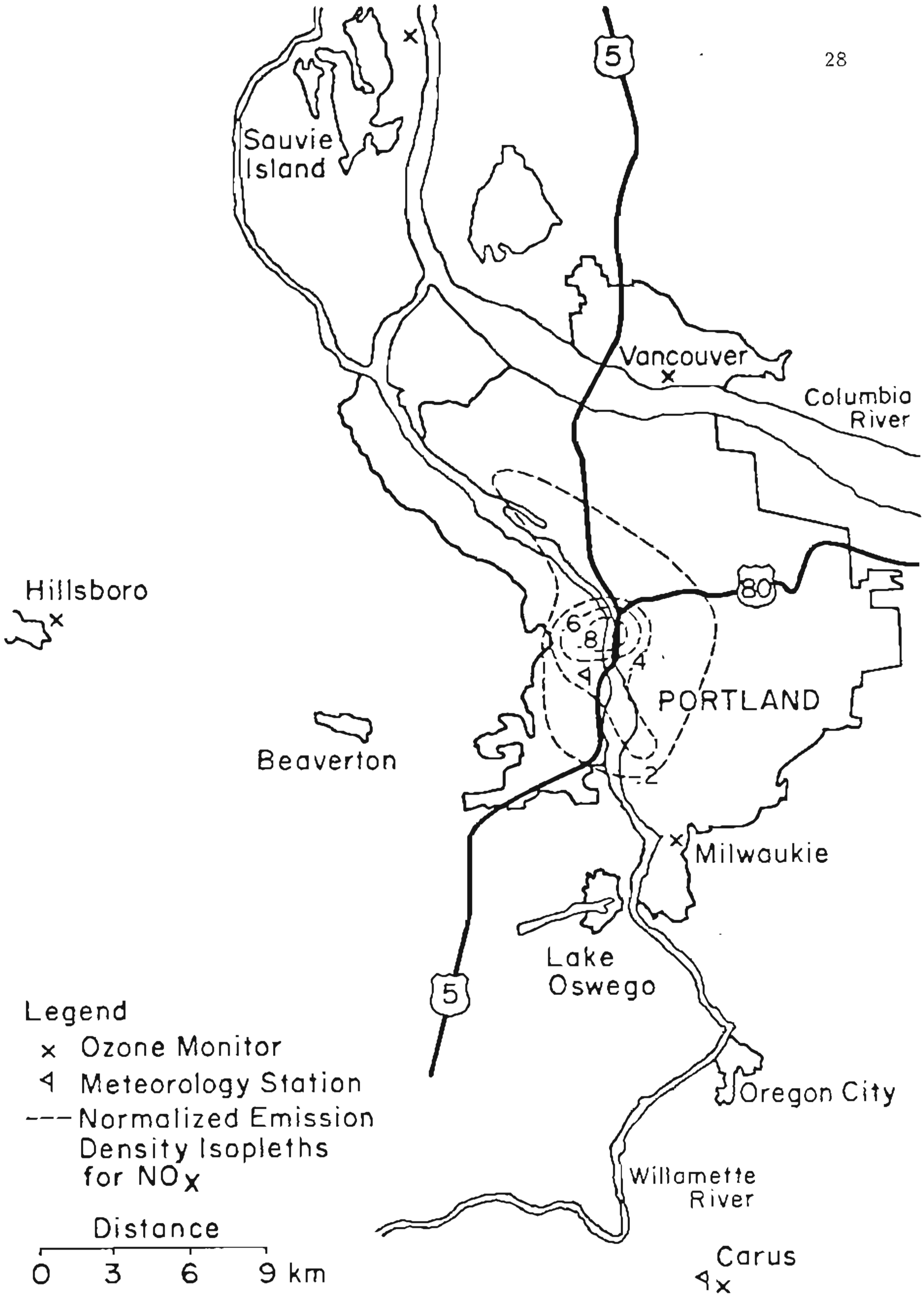

Figure 8 Emission density isopleths for NO_x

Carus and the concentration of all gases is homogeneous in a plane perpendicular to the pipeline. Concentration variations can occur only in the direction of the pipeline and are determined by the combined effects of photochemistry and wind. In this model precursors are emitted in the downtown Portland area and are transported by the prevailing northwest winds to Milwaukie. Photochemistry results in O_3 production within the air parcel for the length of time it takes to travel to Carus. Such a pipeline is defined at the top by the base of the temperature inversion, on the west side by the West Hills, and on the bottom by the ground. The pipeline is open on the east side; however, the assumption of homogeneity in an east-west direction is probably still valid since the emission inventory of Figure 8 indicates that precursor emissions drop off fairly slowly in a direction east of downtown Portland. The assumption of homogeneity in the vertical is probably incorrect since vertical gradients of NO_x have been observed above areas characterized by large precursor emissions (Blumenthal et al., 1974). Unfortunately such measurements have not been made in the Portland area. In Appendix A it is shown that the time for ground level emissions to become well mixed on sunny days is significantly less than the time of transport of an air parcel from the central business area of Portland to Milwaukie. This implies that the assumption of homogeneity for precursors is not necessary to model ozone production. This assumption is substantiated for areas outside the central business area by measurements for the 1976 season (Huntzicker et al., 1977) which indicate that ozone concentration is constant within the mixing layer provided the mixing height is less than 1000 m.

The meteorology of the Portland area indicates that a very simple model for dilution is adequate: a model in which the only mechanism for dilution is the lifting of the mixing height in the time required for the air parcel to be transported from Portland to Carus. It is felt that the effect of variations in wind direction can be ignored. The data of Figure 7 indicate that the variation in wind direction to the west would be fairly small because of the funneling effect of the West Hills. Variations in wind direction to the east would be higher; however, the effect on dilution would be small because emissions drop off fairly slowly to the east.

A simulation based upon the "pipeline" model consequently was developed by modifying a standard photochemical smog model to incorporate the effects of dilution and fresh emission. It must be pointed out that the purpose of this effort was not to model accurately ozone production but rather to develop an understanding of the effects of meteorology on O_3 levels. Because the model is relatively crude, some restrictions must be placed upon the historical data to be analyzed. This point is discussed in detail in Chapter IV.

III.2 Description of program

The photochemical portion of the program is based upon the work of Hecht, Seinfeld and Dodge (1974) as modified by Schjoldager (1977). Thirty reactions among eighteen compounds are included with five of the reactions being photolytic. Hydrocarbon reactivity is simulated by assuming a mixture of n-butane and propylene. The photochemistry of the model is described in detail in the references.

III.2.1 Rate constants

The program simulates the effect of solar radiation in a relatively sophisticated fashion. Photolytic rate constants are computed as a function of solar zenith angle as described by Leighton (1961), taking into account the effects of molecular scattering, particle diffusion and absorption due to atmospheric ozone. The effect of clouds is not considered so the results described below apply to clear days only.

Recent work by Peterson (1977) indicates that the effect of altitude on the photodissociation constant for NO_2 is significant. The program was therefore modified so that this constant was computed corresponding to an altitude of 300 m which is an approximate value for average elevation within the mixing layer.

Thermal rate constants were assumed to be temperature independent as the more detailed simulation work of Hecht _et al_. (1973), Peterson (1976), and Bottenheim _et al_. (1977) indicate that the rate of O_3 formation is insensitive to temperature above 17°C.

III.2.2 Relative precursor concentrations

Relative precursor concentrations were set to simulate conditions specific to Portland. Data collected by the State of Oregon Highway Department in southeast Portland during the summer of 1976 indicated that the ratio of non-methane hydrocarbons to NO_x is of the order of 8.8 ppmC/ppm NO_x (standard deviation = 3.7). It was assumed that most of the NO_x was emitted as NO (75% NO, 25% NO_2) and that

$$[\text{n-butane}]/[\text{propylene}] = 3$$

Because hydrocarbon data of greater detail than the methane and non-methane portions do not exist for the Portland area, conditions analogous to Los Angeles were assumed (Hecht, et al., 1974).

III.2.3 Dilution capability

A dilution capability was incorporated into the program in order to simulate the effect of the diurnal increase in mixing height. The amount of dilution was in direct proportion to the increase in mixing height under simulation. Baseline values for pollutant concentrations for background air are as follows:

$$[O_3]_b = .04 \text{ ppm}$$

$$[NO_2]_b = .014 \text{ ppm}$$

$$[NO]_b = \frac{k_1[NO_2]_b}{k_3[O_3]_b}$$

The values for $[O_3]_b$ and $[NO_2]_b$ are reasonable approximations for average background levels upwind of Portland as measured by the DEQ and the Portland General Electric Company. The concentration of NO assumes conditions corresponding to the photostationary state exist among the three pollutants.

A comparison study was undertaken to determine the accuracy of the Schjoldager model as modified for dilution. A number of runs were made in an attempt to duplicate results reported by Dodge (1977). This exercise was primarily a verification of the level of detail of photochemistry. The Dodge model is considerably more sophisticated as it consists of 75 reactions among 34 species. Dodge also compared model predictions with actual smog chamber data and got fairly good results (14% average discrepancy for 17 comparisons).

The degree to which the two models agreed was very much a function of precursor ratio as indicated in Figure 9. Along the "reactive ridge" ($[NMHC]/[NO_x]$ = 5.6 ppmC/ppm) the Schjoldager model was 12% low, while at a ratio of 11.2 it was 21% high relative to the results of Dodge. At a ratio of 2.8 the agreement was quite poor as the Schjoldager model was low by 60%. Since non-methane hydrocarbon data indicate that the Portland atmosphere corresponds to a ratio of the order of 8.8, the two programs are in good agreement in the region of interest.

III.2.4 Precursor injection capability

In order to represent ozone production in the Portland area more accurately, the photochemical smog model was also modified to incorporate the effects of fresh emissions. As described in Section III.1, ozone production is simulated from the point of view of an air parcel that enters the Portland airshed and is transported up the Willamette River by the prevailing northwesterly winds. The effect of fresh emissions is simulated via periodic injections of precursors corresponding to emissions at various locations in the Portland area. The injection schedule is based upon the concentration isopleths of Figure 8 as determined from the emission inventory developed by Pitter (1976). Since this inventory determined that vehicular traffic is the primary sources of oxides of nitrogen (76%) and hydrocarbons (60%), it was decided to use the same

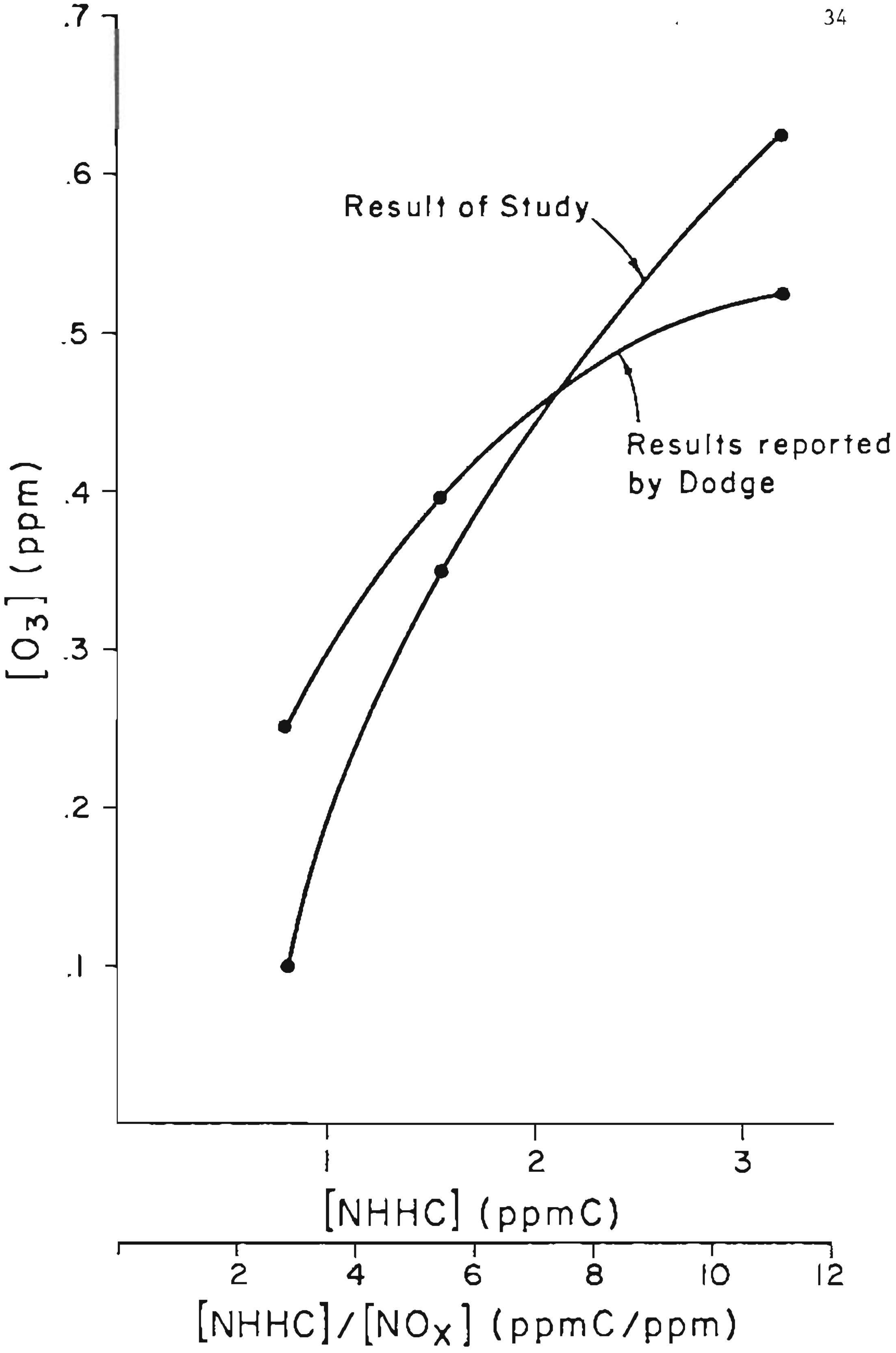

Figure 9 Comparison of computer simulation results with results reported by Dodge

injection schedule for both pollutants. The primary difference in the inventories is the presence of point sources of hydrocarbons from industrial activity in northwest Portland. The fraction of hydrocarbons from these sources was determined to be 25% greater than the fraction of NO_x. It was decided that the effect of this difference would not justify a more complex injection schedule. The injection schedule for both pollutants was developed by averaging emission densities for the region bordering the Willamette River and is depicted in Figure 10. Plotted in the figure is the relative size of each injection as a function of location along the Willamette River. For locations north of the area of maximum emissions corresponding to the central business district, averaging was over a somewhat larger area than for locations nearer to Milwaukie. Points corresponding to actual locations in the Portland area are identified in the figure. It was determined that 20 injections were sufficient; that is, little change was observed in pollutant concentrations once beyond the central business district using a more frequent injection schedule.

The injection of precursors into an air parcel is simulated as follows. At t=0, the air parcel enters the Portland area with the concentration of all pollutants at background levels. As time increases, precursors are injected to represent pollutants picked up by the parcel as it moves toward Milwaukie. The peak of Figure 10 corresponds to the central business area; its exact time depends upon the particular wind speed being simulated. The size of each injection then decreases as the parcel moves in a southerly direction up the Willamette River.

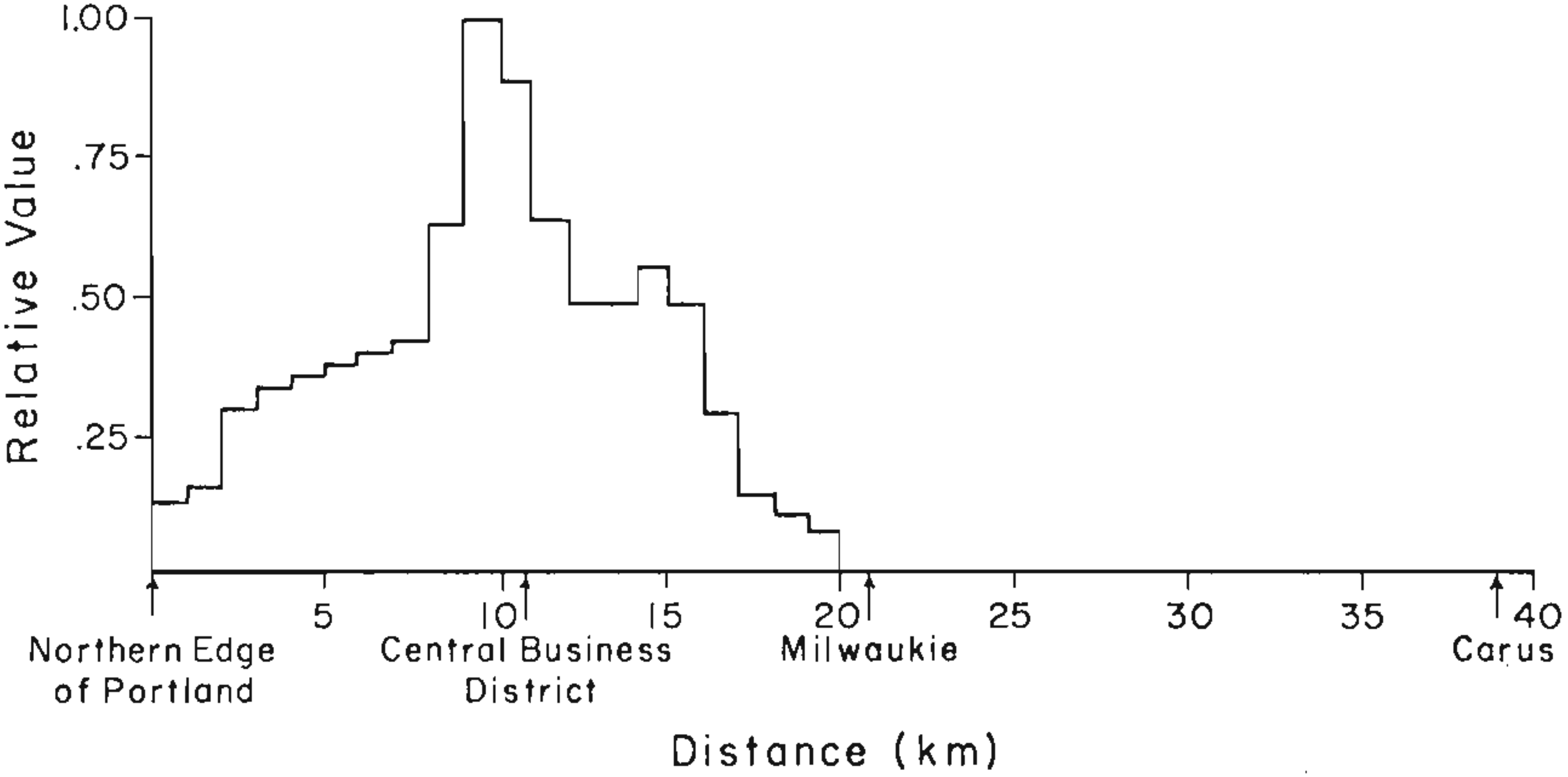

Figure 10 Precursor injection schedule

The schedule of Figure 10 specifies the relative size of each injection (i.e., ratios rather than actual values in ppm). The actual values will depend upon meteorology and precursor emission rates. This gap was bridged using NO_x and meteorology data. A data survey identified 9 days during the summers of 1975-76 for which simultaneous data existed for $[NO_x]$, wind speed, and mixing height. The reason that the data base is so limited is the lack of mixing height data for Portland. The NO_x data used were the 8:00-9:00 hourly averages from the CAM station in downtown Portland. None of the 9 days were on the weekend, so that the variability in the data is due almost entirely to meteorology.

Data from 8:00-9:00 were used because that time is late enough to show the effects of early morning rush hour traffic yet not so late that photochemistry can convert the NO_x to other species.

Conservation of mass considerations suggest that the concentration of NO_x should be inversely proportional to mixing height and wind speed. Figure 11 is a plot of NO_x concentration against the inverse of the product of mixing height and wind speed. Although there is considerable scatter in the data, proportionality is observed. A comparison of NO_x values as predicted by the computer program for the central business area under specific meteorology conditions with the data of Figure 11 makes it possible to calibrate the emission ratios to actual values in ppm. This was accomplished by selecting a set of values for wind speed and mixing height such that their product was equal to 10^3 m km/hr. Since Figure 11 indicates a resulting $[NO_x]$ of .18 ppm, the size of each injection of precursors in the simulation was scaled

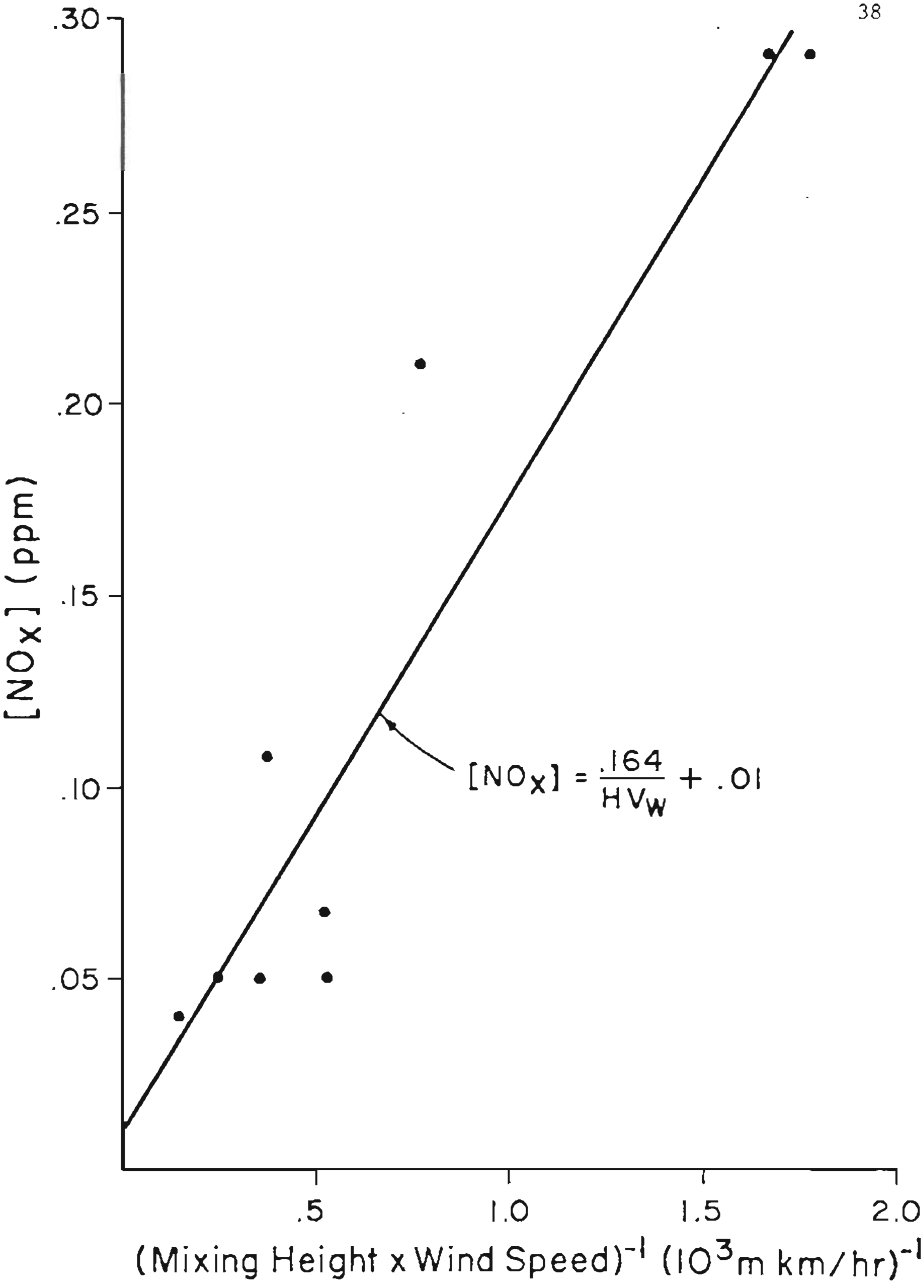

Figure 11 Early morning $[NO_x]$ as a function of dispersion factor

up until the program produced this concentration for the central business district.

III.2.5 Application of the program to the problem of determining the relationship between ozone and meteorology

As a summary of the computer simulation that was used in the study, an explicit description will be given of the method used to incorporate each meteorology and emission parameter. The effect of wind speed is to dilute precursors and to reduce the time for photochemistry to produce ozone. Thus the absolute size of each injection in ppm was set to be inversely proportional to wind speed. Since the purpose of the simulation is to analyze ozone data for a fixed location, a second effect of wind speed variations is to determine the time when the parcel passes over Milwaukie. For example, doubling wind speed means that time of passage is reduced by one-half. The increase in mixing height as the day progresses is simulated by a proportionate dilution of all reactants. The well mixed assumption again implies that the absolute size of each injection should be inversely proportional to mixing height. Variations in precursor emission rates are simulated by simply scaling each injection by an emission factor (EF) with the ratios given in Section III.2.2. The effect of variations in solar radiation is to produce a time of day effect and a seasonal effect. Variations in background pollutant concentrations are modeled by scaling the values listed in Section III.2.3. Finally the effect of temperature on reaction rates is ignored as more detailed photochemical models indicate that the effect is minor above 17°C (Section III.2.2).

III.3 Simulation results

A large number of computer simulations were made to determine the sensitivity of $[O_3]$ downwind of Portland to 7 different meteorology and emission parameters. A particular run is determined by specifying values for each of the following:

- Initial mixing height (H_I)
- Final mixing height (H_F)
- Wind speed (V_w)
- Emission Factor (EF)
- Hour of the day (HR)
- Day of year (N)
- Background ozone concentration $[O_3]_b$

In this section each of these parameters will be discussed individually. The discussion will be with reference to $[O_3]$ as predicted at the Milwaukie location. The results of this sensitivity analysis are summarized in Table 4. The extent to which the conclusions are different for the Carus location is discussed in Section III.3.6.

Table 4 Summary of computer simulation results as applied to Milwaukie

Parameter	Nature of relationship between ozone level and parameter
Initial mixing height	Insensitive
Final mixing height	Inverse relationship between urban ozone term and H_F
Wind speed	Very strong relationship between urban ozone term and V_w
Emission factor	Relationship slightly less strong than linear between urban ozone term and EF
Hour of day	Maximum $[O_3]$ at 14:30 PDT
Day of year	Maximum $[O_3]$ on June 21
Background $[O_3]$	Additive with a slight coupling between the background and urban terms

III.3.1 Sensitivity to mixing height

Attention was first focused on the effect of mixing height variations. For unreactive pollutants, conservation of mass considerations together with the well mixed assumption imply that concentration should be inversely proportional to mixing height. Since O_3 is a secondary pollutant, it is not obvious that this relationship should hold. Ozone may, in fact, depend upon mixing height history as well as current value. To investigate this question, a series of runs were made with values for all parameters fixed except for H_I. The results presented in Figure 12 indicate that $[O_3]$ is insensitive to mixing height history. The wind speed that was used, 4.8 km/hr, resulted in a time of travel from the point of maximum precursor emissions to run termination (average transport time) of 2.5 hours. It can be seen that the variability in initial mixing height produced a 5 to 10% difference in final $[O_3]$ for both values of final mixing height. The fact that a higher initial mixing height resulted in slightly greater O_3 levels compared with a lower initial mixing height when both cases terminate at the same final value is probably a consequence of

$$[\text{Rads}] = k\ [\text{HC}]_0^{\beta}\ f(t)$$

with $\beta < 1$. If $\beta = 1$ then the two cases would probably give the same results, while for $\beta < 1$ the inequality would probably be reversed. That this is a plausible explanation can be seen from the following calculation. Consider the dynamic process of O_3 formation where mixing height increases by a factor of two during the time t.

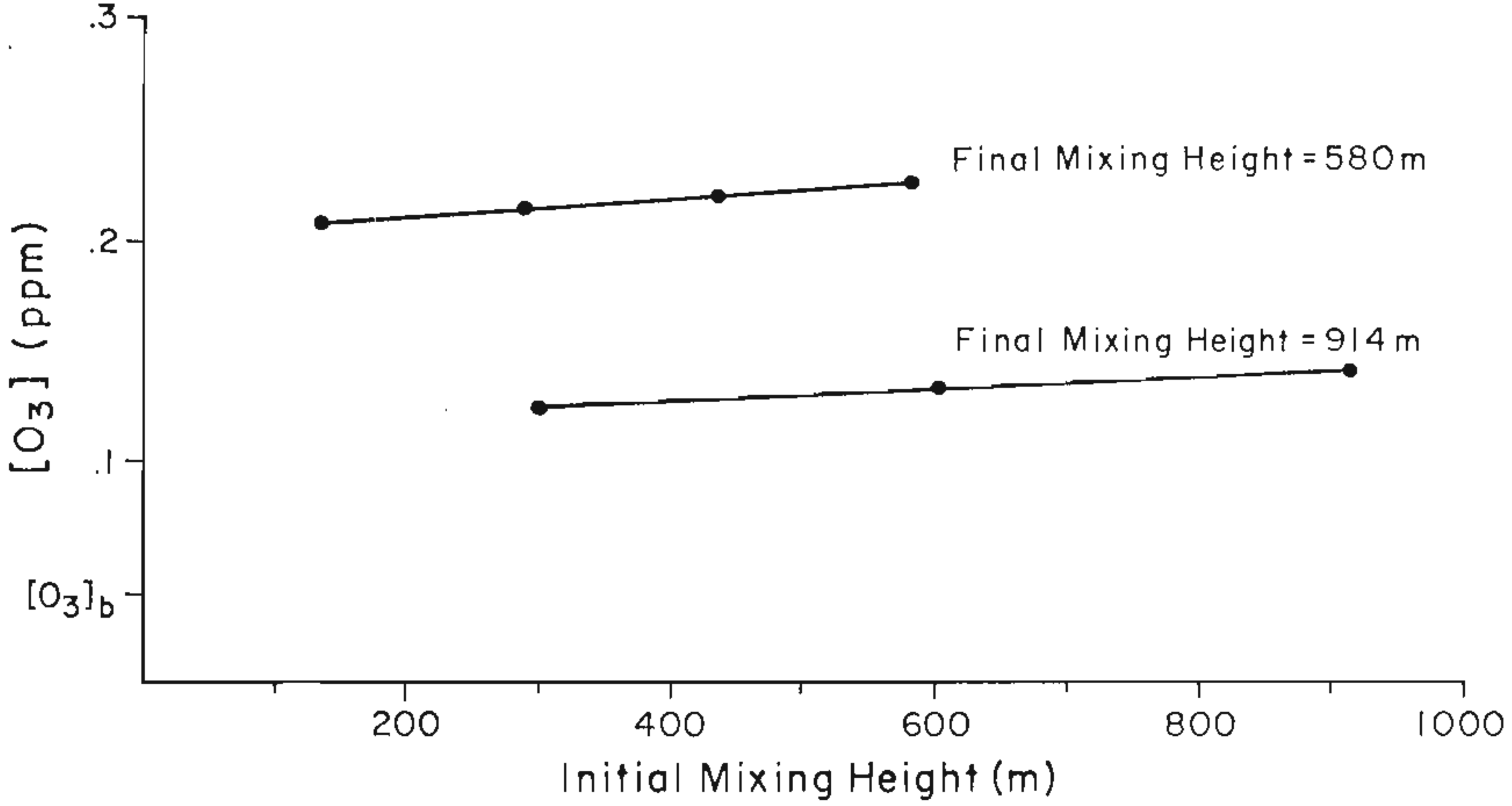

Figure 12 Sensitivity of [O$_3$] to initial mixing height (Total amount of precursors for the case with $H_I = H_F$ = 580m: [HC] = .29 ppm, [NO] = .099 ppm, [NO$_2$] = .033 ppm)

There are an infinite number of ways in which the dilution process can take place. At one extreme, dilution in its entirety occurs at time = 0 with no dilution for

$$0 < \text{time} \leq t$$

At the other extreme, no dilution occurs until time = t when all species are diluted by a factor of two. For these two situations

$$[\text{Rads}]_1 = K[\frac{HC}{2}]^{\beta}_{0}\ f(t)$$

$$[\text{Rads}]_2 = \frac{K}{2}[HC]^{\beta}_{0}\ f(t)$$

Clearly $[\text{Rads}]_1 > [\text{Rads}]_2$ if $\beta < 1$, which implies $[O_3] > [O_3]_2$ if $\beta < 1$. The variation implied in Figure 12 was deemed insignificant and in all subsequent work it was assumed that urban $[O_3]$ is independent of mixing height history. This result is in agreement with the smog chamber results of Jeffries et al. (1977) which indicate that $[O_3]$ depends upon the amount of dilution but not upon dilution history.

Results presented in Figure 13 indicate that an inverse relationship between urban O_3 and current mixing height is adequate. Presented are results for average transport times of 2.5 and 1.8 hrs. These results indicate that the dependence of ozone levels upon mixing height is analogous to that for primary pollutants. This dependence can be summarized as

$$[O_3] = \frac{K}{H} + [O_3]_b$$

ignoring as a first approximation the possibility of a coupling between the two terms.

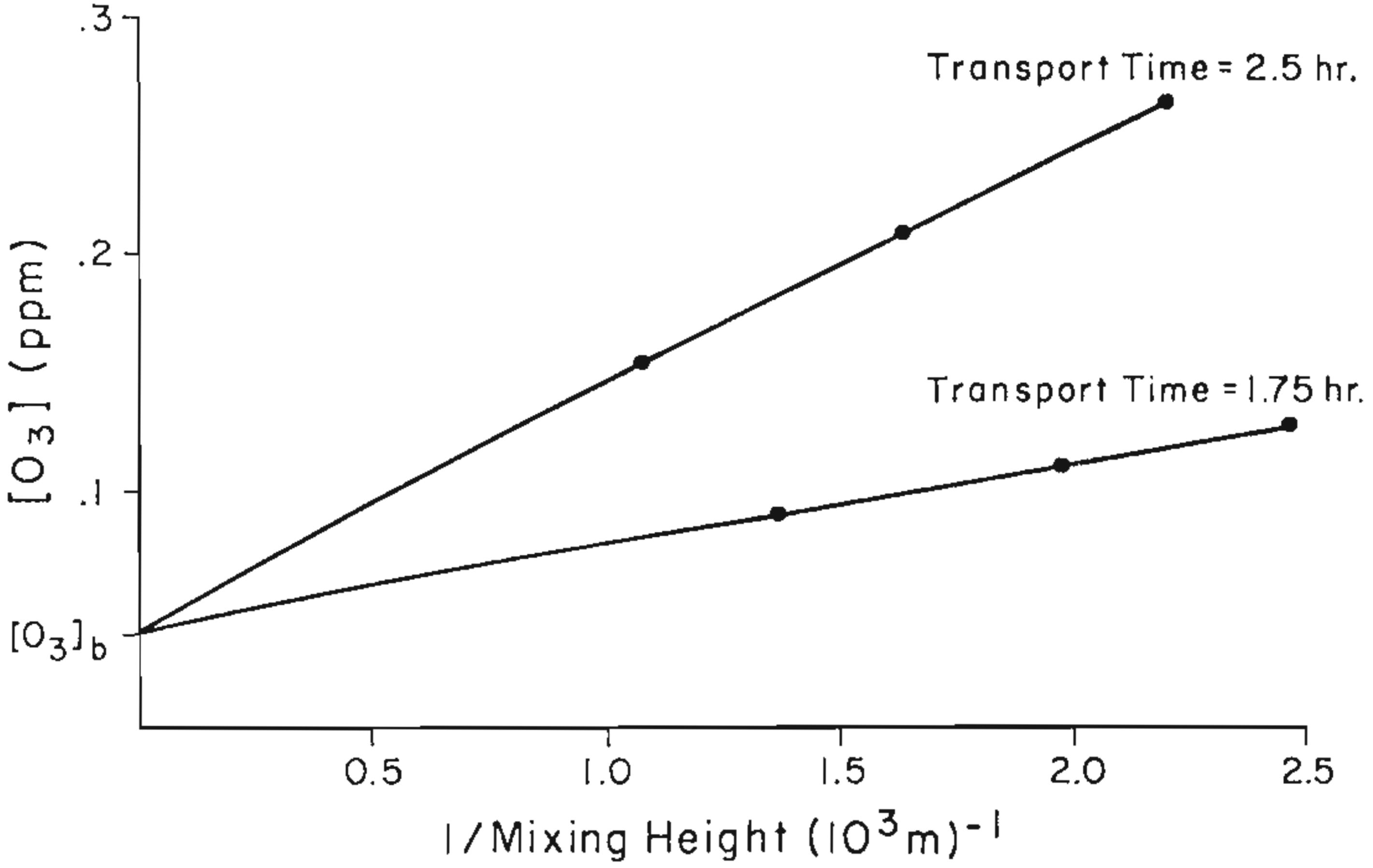

Figure 13 Sensitivity of $[O_3]$ to the inverse of mixing height

Elimination of initial inversion height reduces the number of meteorology and emission parameter by one. For all subsequent work the sensitivity analysis is with respect to the following baseline set of values:

- H = 510 m
- V_w = 4.8 km/hr
- EF = 1
- Time of day = 15:00 PDT
- Day of year = June 21
- $[O_3]_b$ = .04 ppm

Unless specified otherwise these values will be used throughout the remainder of this chapter.

III.3.2 Sensitivity to wind speed

Data presented in Figure 14 indicate a very strong relationship between $[O_3]$ and wind speed. Five values were used to generate the plot and the starting time for each simulation was adjusted such that the air parcel arrived at Milwaukie at 3:00 in the afternoon. Non-linear regression was performed on these results with the objective of finding a functional relationship between the two parameters. It was determined to a first approximation that an exponential relationship of the form

$$[O_3] = \frac{K}{V_w^{\alpha}} + [O_3]_b$$

fit fairly well (Correlation coefficient: $r = .95$) where α was of the order of 2.5.

This evidence for a strong dependence of urban ozone on wind speed is reasonable since the effect of wind speed is two-fold. In addition to diluting precursors initially, a strong wind reduces the time for photochemistry to produce O_3 relative to a light wind. Additional results indicated that the relationship held for other values for time of day and time of year, although the values for α were variable. In particular, values for α tended to increase with increased solar zenith angle. For example, $\alpha = 4.2$ on September 21 at 3:00 PDT.

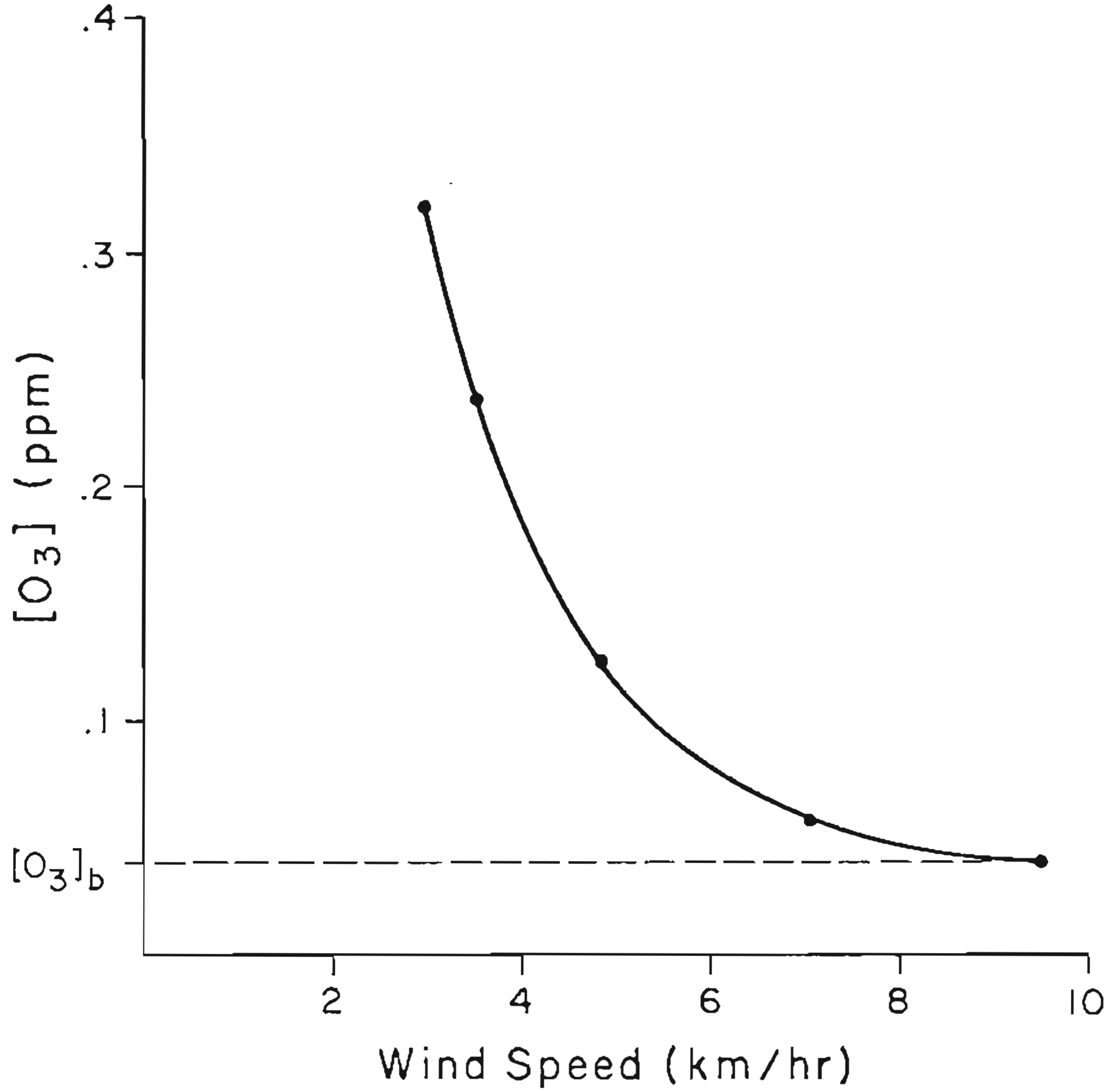

Figure 14 Sensitivity of $[O_3]$ to wind speed

III.3.3 Sensitivity to emission factor

Simulation results in Figure 15 indicate that the relationship between urban O_3 and precursor emission factor is less sensitive than for wind speed. A least square curve fit to the data corresponding to an average time of transit of 2.5 hr gave a relationship of the form

$$[O_3] = K\ (EF)^{.89} + [O_3]_b$$

with r = .9997. This result is consistent with the ozone isopleth curves developed by Dodge (1977) (Figure 16). Regression analysis of her results indicated a similar functional relationship except that the exponent has a value of .70. A possible explanation of this difference is the increased irradiation time as her results are for 9 hours. In either case the assumption of linearity between emission factor and urban ozone is probably sufficient.

III.3.4 Sensitivity to solar radiation

The role played by solar radiation in ozone formation leads to time of day and time of year effects. A large number of computer runs was made in order to characterize the relationship. Results are summarized in Figure 17 in which $[O_3]$ at Milwaukie is plotted as a function of time of day for the months of June through September. For each month the day simulated was actually the 21st. It can be seen that the time of occurence of maximum ozone was near 14:30 PDT with the function falling off in a more or less symmetric fashion on either side of the

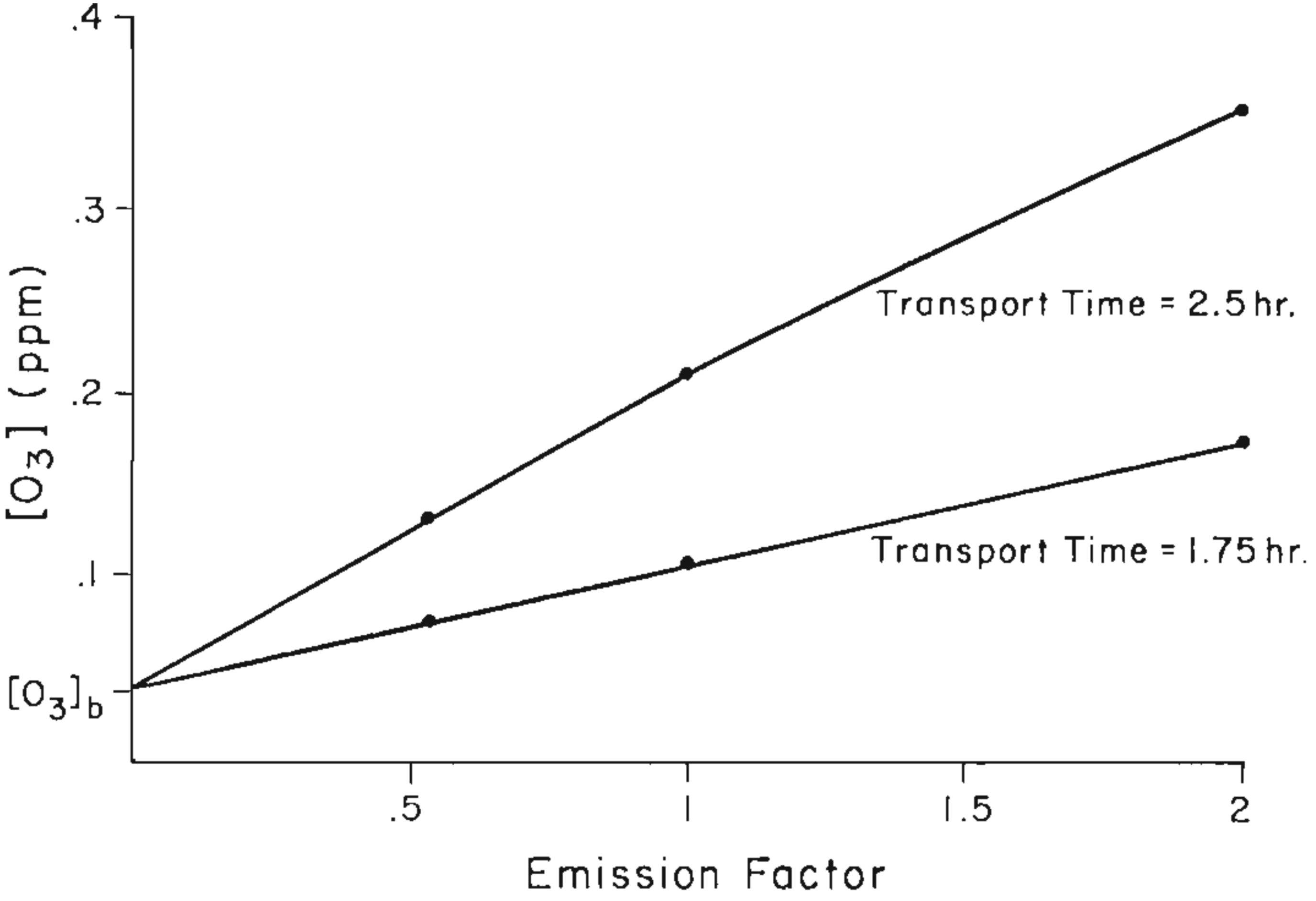

Figure 15 Sensitivity of $[O_3]$ to emission factor

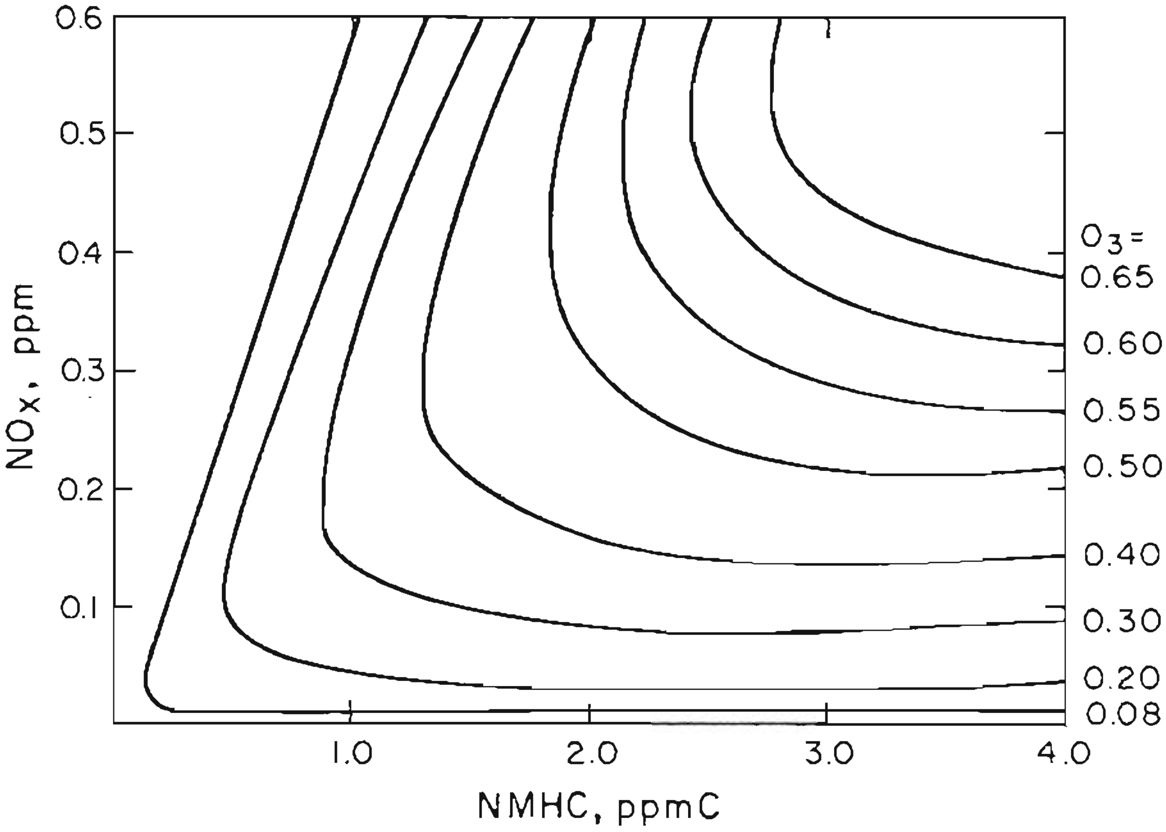

Figure 16 Ozone isopleths corresponding to maximum one hour O_3 concentrations. Source: Dodge (1977)

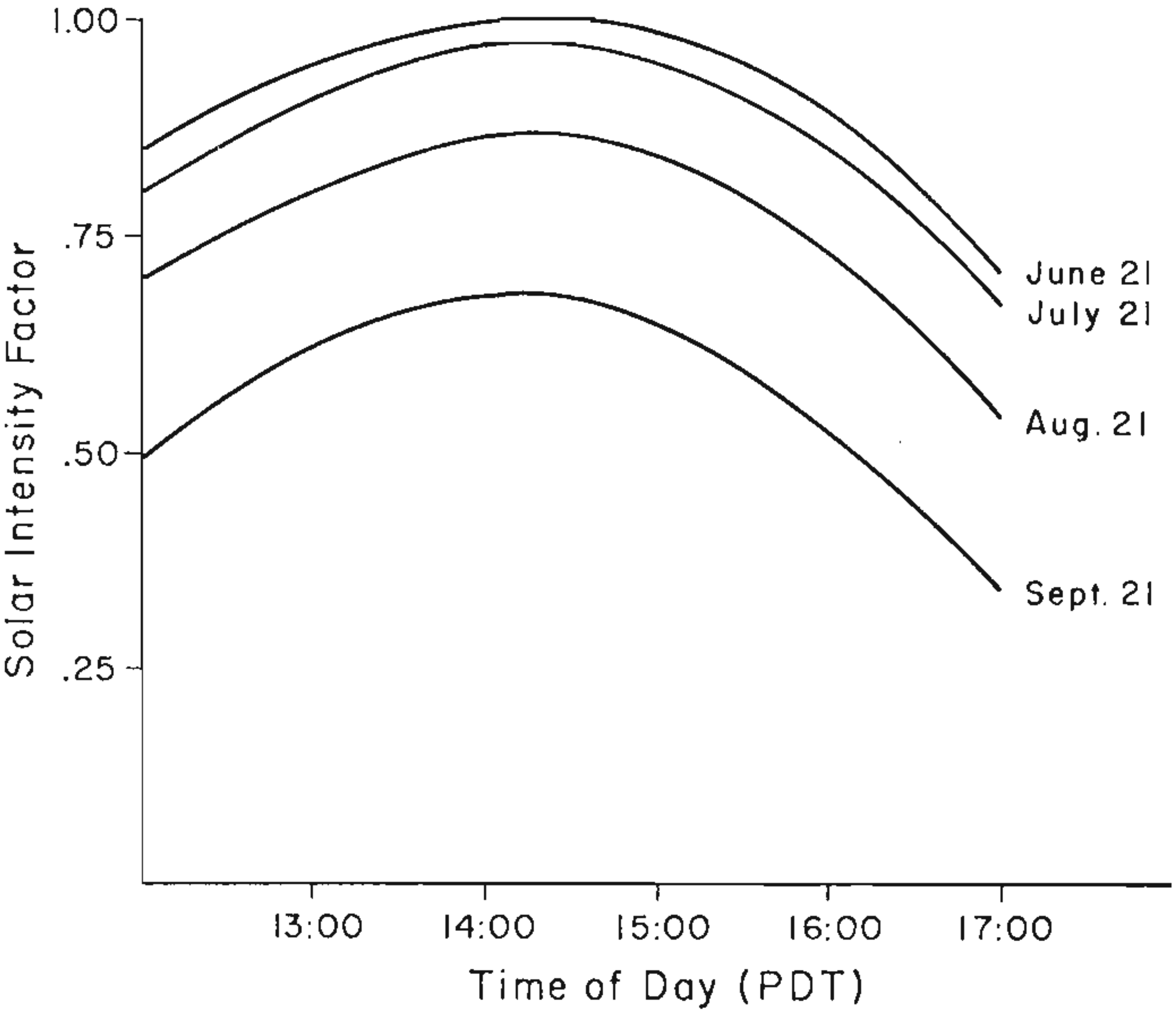

Figure 17 Solar intensity factor

maximum. It must be pointed out that emission factor was constant so that the variation is due solely to variation in solar intensity.

Multiple regression was performed on these results and an equation that is quadratic in both variables produced an adequate fit. The result is a solar radiation factor of the form

$$\begin{aligned} f(HR,N) = & -8.66 + .22 \times 10^{-1}N - .105 \times 10^{-3}N^2 + 1.326HR \\ & - .251 \times 10^{-2}HRN + .112 \times 10^{-4}HRN^2 - .467 \times 10^{-1}HR^2 \\ & + .978 \times 10^{-4}HR^2N - .454 \times 10^{-6}HR^2N^2 \end{aligned} \qquad \text{(III.1)}$$

where HR is the hour of the day and N is the number of the day in the year with N = 1 corresponding to April 1. In this formulation

$$f(HR,N) \lesssim 1$$

always, and

$$f(HR,N) = 1$$

at 14:30 on June 21.

Additional runs were made to determine the extent to which this equation held for other wind speeds. Surprisingly the time of occurence of maximum O_3 concentration was only weakly dependent upon wind speed (Figure 18). Although a comprehensive study was not undertaken, it is estimated that Eq. (III.1) is good to 15% for other wind speeds. The sensitivity of f(HR,N) to variations in emission factor and mixing height was not undertaken. Because Eq. (III.1) is reasonably accurate for the wind speeds normally encountered, and because variation in wind speed is a more sensitive determinant of O_3 concentration than variations in emission factor and mixing height, it was felt that the degree to which f(HR,N) varies with changes in these other two parameters was too small to be of concern.

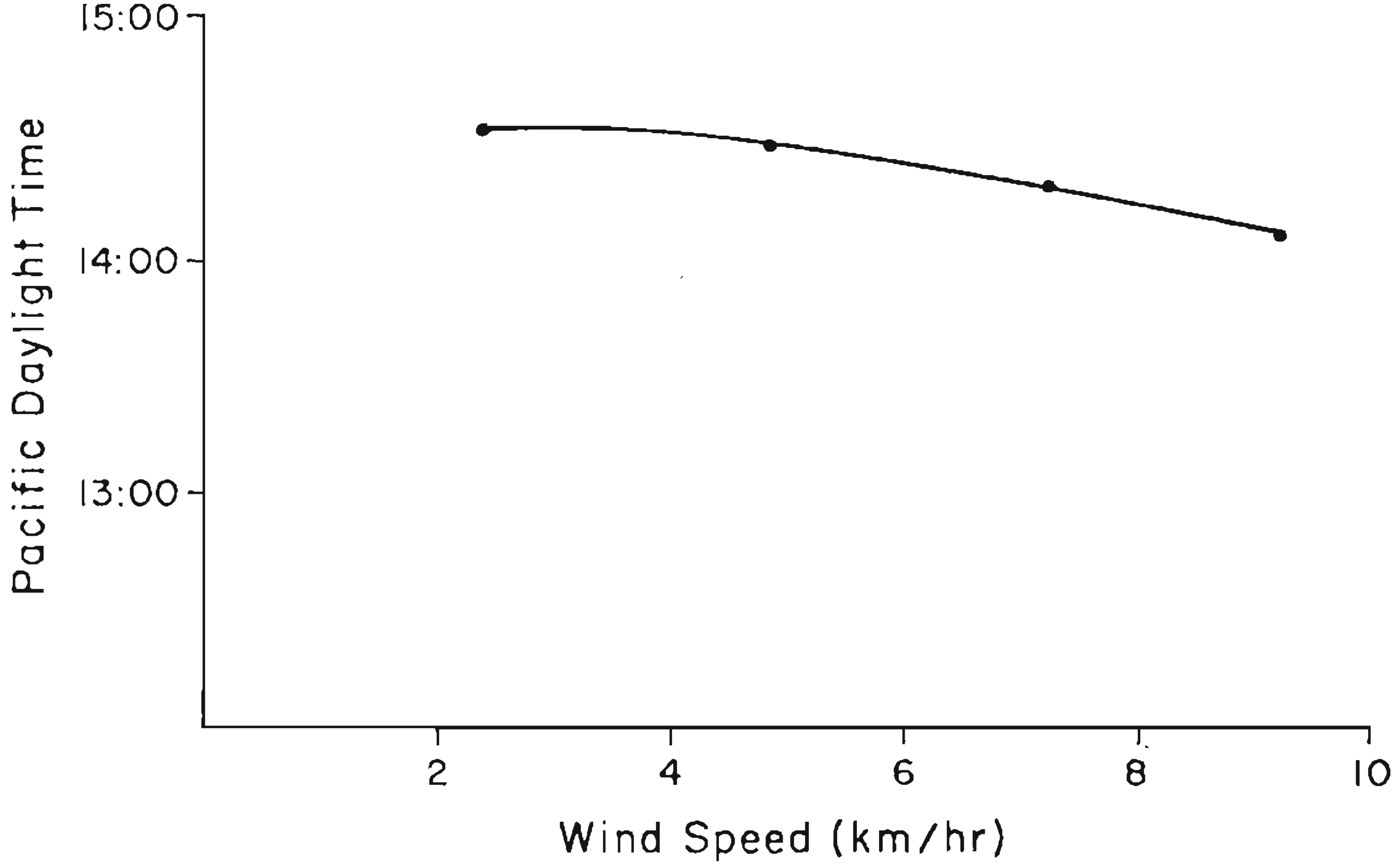

Figure 18 Time of maximum $[O_3]$ at Milwaukie

III.3.5 Sensitivity to background ozone concentration

Computer simulation results depicted in Figures 19 - 21 indicate the effect of variations in background O_3 levels. Each figure shows O_3 concentration as a function of time for low (.01 ppm), average (.04 ppm) and high (.08 ppm) background levels. Each figure corresponds to a different value for wind speed, and the corresponding time of passage over Milwaukie and Carus is identified on each. A close examination of each figure reveals that the three lines converge initially and then slowly diverge. This result is consistent with the analysis presented in Section II.3. Table 5 presents the change in O_3 concentration at Milwaukie as a function of change in background for the three wind speed values. The numbers were obtained from Figure 19 - 21 using the case with

$$[O_3]_b = .01$$

as baseline.

Table 5 The effect of variations in $[O_3]_b$ on O_3 levels at Milwaukie

Wind Speed (km/hr)	$\Delta[O_3]_b$ (ppm)	$\Delta[O_3]$ at Milwaukie (ppm)
4.8	.07	.095
4.8	.03	.045
7.2	.07	.085
7.2	.03	.034
9.6	.07	.072
9.6	.03	.031

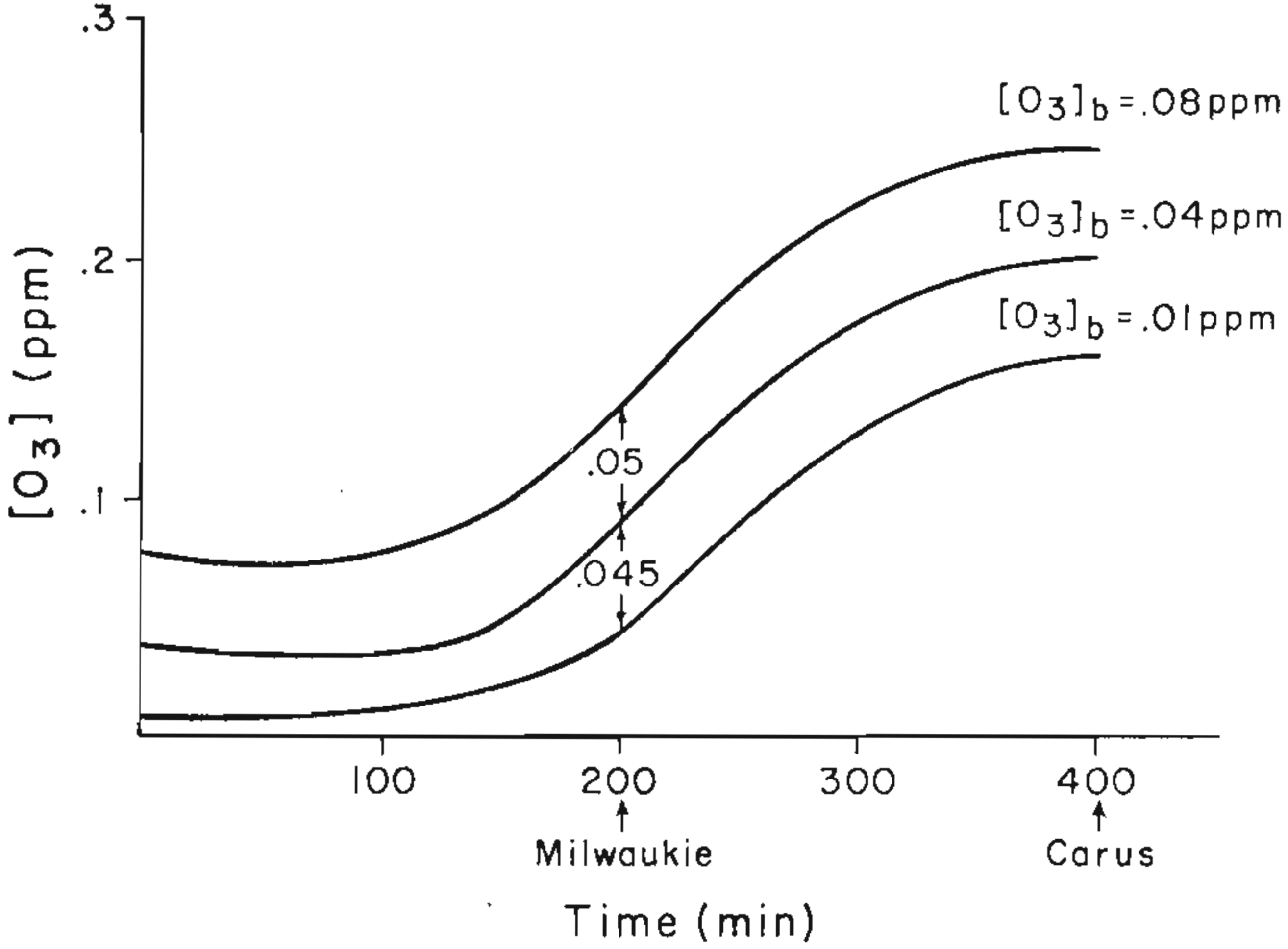

Figure 19 Sensitivity of [O$_3$] to background level for V_w = 4.8 km/hr

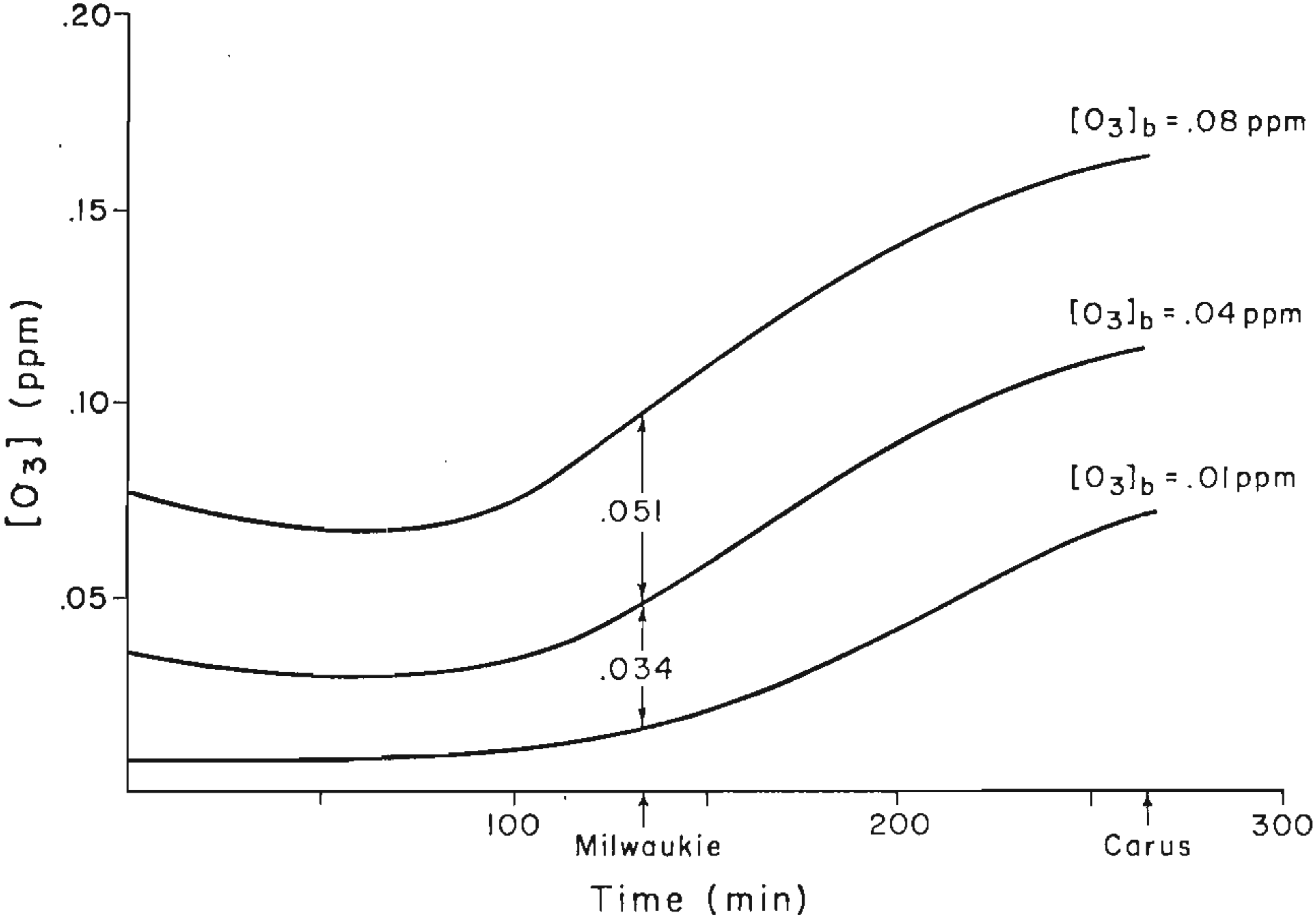

Figure 20 Sensitivity of $[O_3]$ to background level for V_w = 7.2 km/hr

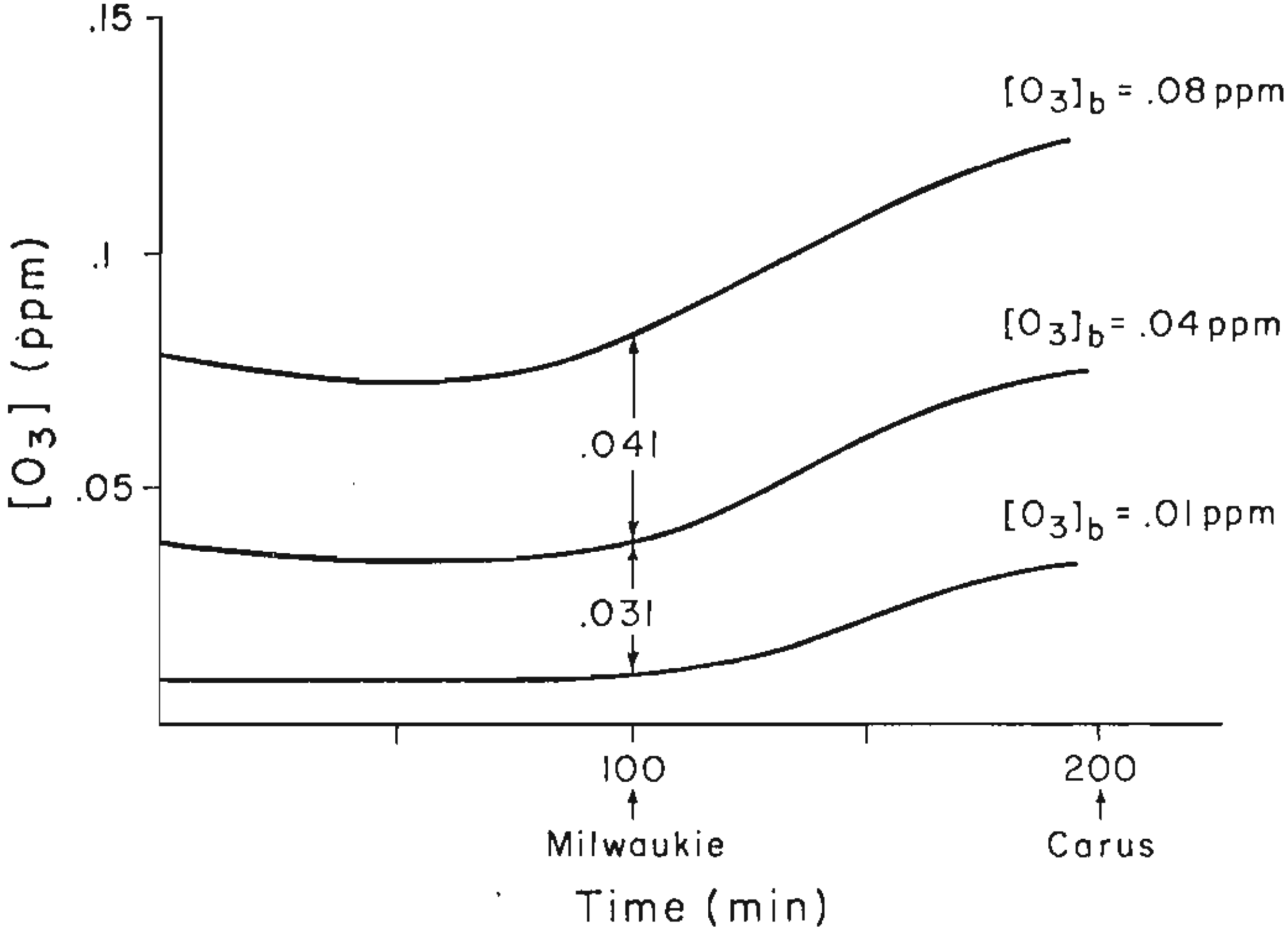

Figure 21 Sensitivity of $[O_3]$ to background level for V_w = 9.6 km/hr

It can be seen that the difference in $[O_3]$ at Milwaukie approaches the difference in background O_3 as wind velocity increases. A reasonably close fit for O_3 concentration at Milwaukie that incorporates variations in background levels is as

$$[O_3]_{Mil} = \frac{V_w}{V_w - 1}[O_3]_b + [O_3]_{Mil,0} \qquad (III.2)$$

where $[O_3]_{Mil,0}$ is the concentration of O_3 which would result if $[O_3]_b = 0$. It should be pointed out that the coupling between the urban and background terms is quite small and constitutes a second order effect.

III.3.6 Concluding remarks

In summary, computer simulation results indicate the following relationships between meteorology/emission parameters and O_3 concentration at Milwaukie:

•O_3 concentration can be decomposed into two terms, where the first term (urban O_3) is the effect of precursors emitted by the urban center in the immediate vicinity, while the second is the concentration of O_3 upwind of the urban center.

•Urban O_3 should be inversely proportional to mixing height at the time of interest but independent of the way in which mixing height reached its final value.

•Urban O_3 should depend very strongly upon wind speed (inversely as the second to third power).

•Urban O_3 should vary somewhat less strongly than linearly with emission factor.

•Total O_3 should depend upon time of day and time of year in the fashion of Eq. (III.1).

•Background and urban O_3 cannot be added directly to give a total. Eq. (III.2) is a more realistic relationship.

These results can be combined in an equation that is applicable to the Milwaukie data of the form

$$[O_3] = \frac{KEF}{HV_w^{\alpha}} f(HR,N) + \frac{V_w}{V_w - 1} [O_3]_b \qquad (III.3)$$

where f(HR,N) is given by Eq. (III.2).

Additional computer simulation results indicate that the relationship for the Carus location would be the same except for the following modifications,

•The value of the proportionality constant for the urban O_3 term (K) is larger to correspond to the more ideal location of Carus relative to Portland for maximizing O_3 concentration

•The value of α is significantly smaller, of the order of 1.5 to 2 depending upon solar zenith angle.

•The form of Eq. (III.2) is modified to give a time of maximum O_3 an hour and a half later at 16:00 PDT. The time of year variation remains unchanged.

CHAPTER IV

ANALYSIS OF OZONE DATA FROM MILWAUKIE

Data collected by the State of Oregon Department of Environmental Quality were analyzed using the results of the previous two chapters to indicate possible functional relationships between [O_3] and meteorology parameters. Daily values for maximum hourly average oxidant concentration as measured at the Milwaukie location were selected for detailed investigation. The station was set up in June of 1974 and has been in operation ever since. The location of this site relative to Portland can be found in Figure 8. As described in Section III.1, the Milwaukie location is almost always downwind of the area of maximum precursor emissions during the ozone season.

Figure 17 indicates that maximum hourly average ozone concentration should occur during the hour 14:00-15:00 PDT. This result is based upon solar intensity considerations only; that is, if emission rate, wind speed and mixing height are constant, then maximum ozone should occur at this time. Preliminary examination of the data indicated that ozone concentration peaked during this hour only 50% of the time. While average time of maximum ozone was very near 15:00, the data showed great variability. The cause of this variability is undoubtedly the variability in the meteorological parameters. Increasing winds during the afternoon would, for example, explain a very early peak, while dying or shifting winds would explain a peak later than 15:00. Because variability in meteorology dominates over solar intensity considerations in determining the time of maximum ozone, the time of day variation was dropped for Eq.(III.3).

Emission factor was also eliminated as a dependent variable because of a lack of hourly precursor emission data of sufficient detail. It should be pointed out that some relevant time dependent emission factors do exist, in particular, hourly emission rates for NO_x due to vehicular traffic (DEQ, 1975). This very limited data suggest that NO_x emissions in the Portland area vary by about 40% from an average value during the hours 10:00-16:00. Huntzicker _et al._ (1977) determined that emissions prior to 10:00 result in maximum $[O_3]$ only very rarely in the Portland area. It is estimated that the daily variation in hydrocarbon emissions would be about the same. This variability is significantly smaller than the variability due to meteorology. Wind speed, for example, varies by an order of magnitude while background ozone varies by a factor of three. Therefore, the error introduced by assuming that emission factor is a constant is probably not significant.

The result of these two simplifications is to reduce the equation relating ozone to meteorology to

$$[O_3] = \frac{K\ f(N)}{H\ V_w^{\alpha}} + [O_3]_b \qquad \text{(IV.1)}$$

with $$f(N) = .758 + .60 \times 10^{-2}N - .371 \times 10^{-4}N^2 \qquad \text{(IV.2)}$$

where N is the number of the day beginning on April 1. Eq.(IV.1) as a first approximation ignores the coupling between the urban and background terms.

IV.1 Restrictions on data

Because of the importance of solar insolation in ozone production, data analysis was restricted to those days that were sunny (> 70% of the time possible) and warm (< 23°C). This restriction reduced the number of days to 141 for the 1974-76 seasons. The ozone season for the Portland area begins in April with the occasional day in the months April-June with many more days in July-September. Another 23 days were eliminated because the wind patterns were such that Milwaukie was not downwind of Portland. Almost all of these days corresponded to east wind conditions; a pattern fairly common during September. Finally, another 20 days were eliminated because of a lack of ozone, wind or mixing height data. The resulting data set contained 98 days with mean of .073 ppm and standard deviation of .023 ppm.

Wind data from the central business location were used for the analysis. For each day the vector average for the two hours preceeding and the hour of maximum ozone at Milwaukie was used as measure of wind speed. Because of poor instrumentation response at very low wind speeds, a minimum value of 3.6 km/hr was placed on all wind data.

Temperature soundings are not taken at Portland; therefore, data from the U.S. Weather Bureau station at Salem, 80 km to the south, were used. Mixing height as determined by the 17:00 sounding was determined for each of the 98 days of the data base. Huntzicker _et al._, (1977) determined that ozone concentration tends to be homogeneous in the mixing layer downwind of Portland as long as the mixing height is less than 1000 m. For mixing heights greater than this, ozone concentration tends to decrease with altitude. Because Eq.(IV.1) is based on the assumption of homogeneity, a maximum value of 1000 m was placed on the mixing height data. Finally it should be pointed out that an error of undetermined magnitude is introduced in using mixing height as determined at 17:00. What should actually be used are values at the time of maximum ozone concentration. This error may be of importance on those days when maximum ozone occurs in the early afternoon.

IV.2 Background ozone

Typically about 50% of a particular ozone measurement at Milwaukie is simply background; that is, ozone levels at the Milwaukie site are about double the values upwind of Portland. It should be pointed out that the term "background ozone" as used here refers to ozone concentration upwind of Portland. It does not necessarily imply air that is free from anthropogenic influences. This point is discussed in more detail below.

In order to develop a better understanding of the relationship between background ozone and meteorology, data from three locations that are usually upwind of Portland were analyzed. The locations are in the cities of Hillsboro, Oregon and Vancouver, Washington and on Sauvie Island on the Columbia River (Figure 8). Ozone monitors have been located at these sites for varying lengths of time, beginning in August 1974 and continuing through the 1975 and 1976 seasons. Background data exist for 62 of the 98 days of the data set. Eight of the 62 days are represented by data from two locations while data from all three locations exist for 13 additional days. For those days with more than one measurement, the average difference between maximum hourly concentrations was .012 ppm which indicates reasonably good inter-site consistency.

The maximum hourly concentrations at these sites show considerable variability extending from a minimum of .02 ppm to a maximum of .07 ppm. The most obvious correlation was with maximum temperature as depicted in Figure 22 (r = .57). Plotted in the figure are data for the 62 days where averaging was done on those days with multiple measurements. A possible explanation of this correlation relates to the degree of stagnation of the air mass over the Northwest. As a high pressure system moves in from the Pacific, both ozone concentration and air temperature are relatively low. It is well known that maximum temperatures tend to increase as a high stagnates over the continent during the summer months. A concurrent increase in ozone concentration with air mass stagnation has been observed throughout the midwest and east coast of the United States (Vukovick *et al*., 1977; Husar *et al*., 1977; Wolff *et al*., 1977). A similar mechanism undoubtedly exists for the Pacific Northwest. With respect to the Portland area, long range transport of anthropogenic ozone from the Puget Sound region of Washington by the prevailing northerly winds to give elevated background levels is a possibility. Unfortunately insufficient data exist for the time period of interest to investigate this question.

It should be pointed out that this explanation for the correlation

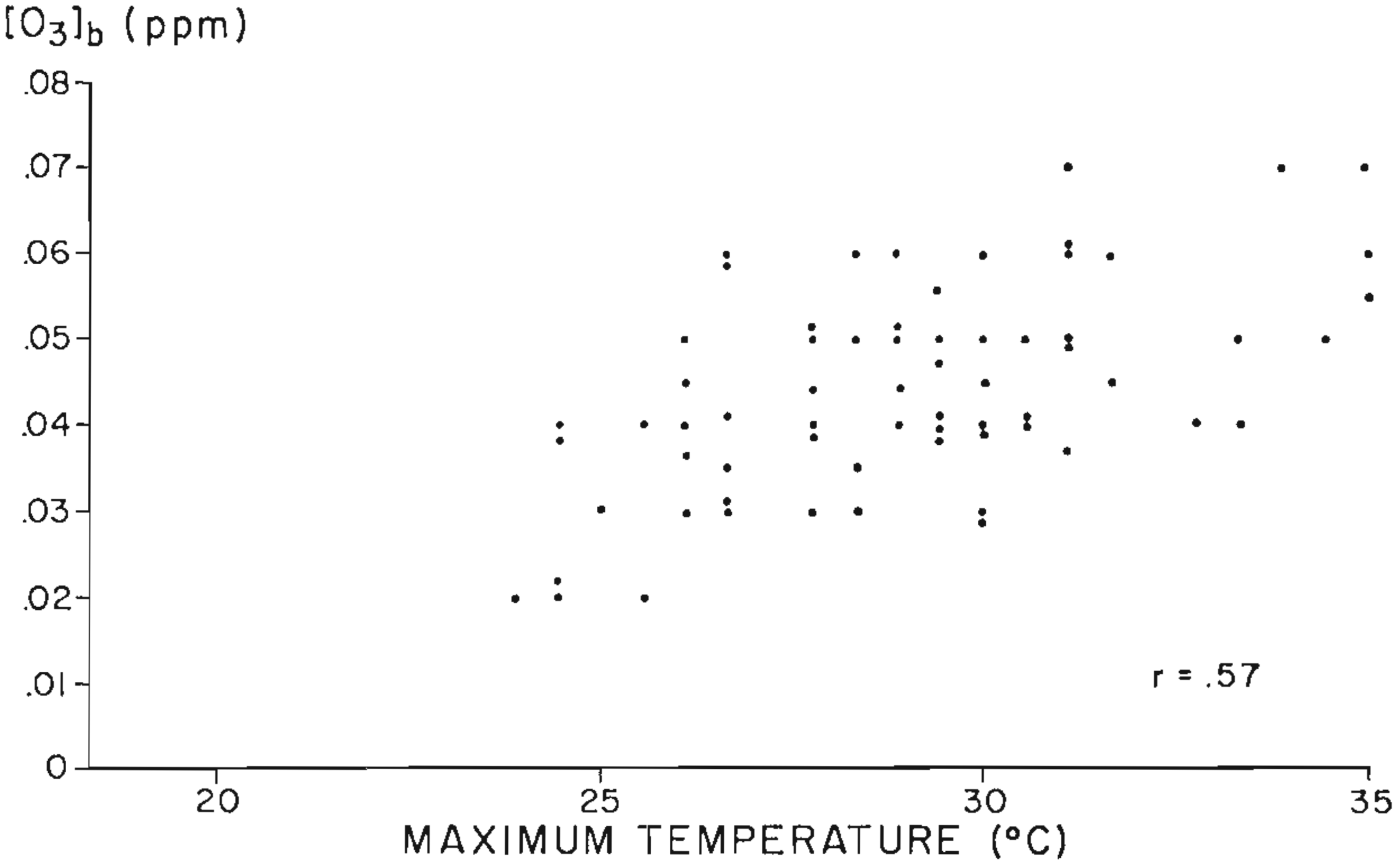

Figure 22 Background [O$_3$]

between background O_3 and temperature may be reinforced by another phenomenon. Measurements made by Rasmussen (1972) indicate that natural emissions of reactive hydrocarbons in forested areas increase with temperature. Since it is well known that these compounds can produce O_3 in the presence of NO_x and sunlight, elevated background ozone during hot weather may be due, in part, to increased natural emissions. Additional investigation must be done to determine if this effect is important. Very recent work by Sandberg *et al*. (1978) gives some indication that this effect may be important for the San Francisco Bay area. Its importance for the Pacific Northwest is an open question.

A slightly better correlation (r = .60) is obtained if the ozone data of Figure 22 are adjusted for the time of year effect. Division by the appropriate time of year factor (Eq.IV.2) was performed on each point of this figure to obtain the scatter of points of Figure 23. A least squares linear regression was performed on this data to give the following model for background ozone:

$$[O_3]_b = (.00297T_{Max} - .0392)\ f(N) \qquad \text{(IV.3)}$$

where T_{Max} is the maximum temperature (°C) and f(N) is given by Eq.(IV.2). Examination of the figure indicates a 1σ uncertainty associated with this equation of the order of .01 ppm.

It is of interest to consider the extent to which seasonally adjusted ozone varies with temperature under east wind conditions. Figure 24 gives maximum hourly concentrations as measured on 19 days during the 1975-1976 seasons when winds were out of the Columbia River gorge. Comparison with Figure 23 indicates that background

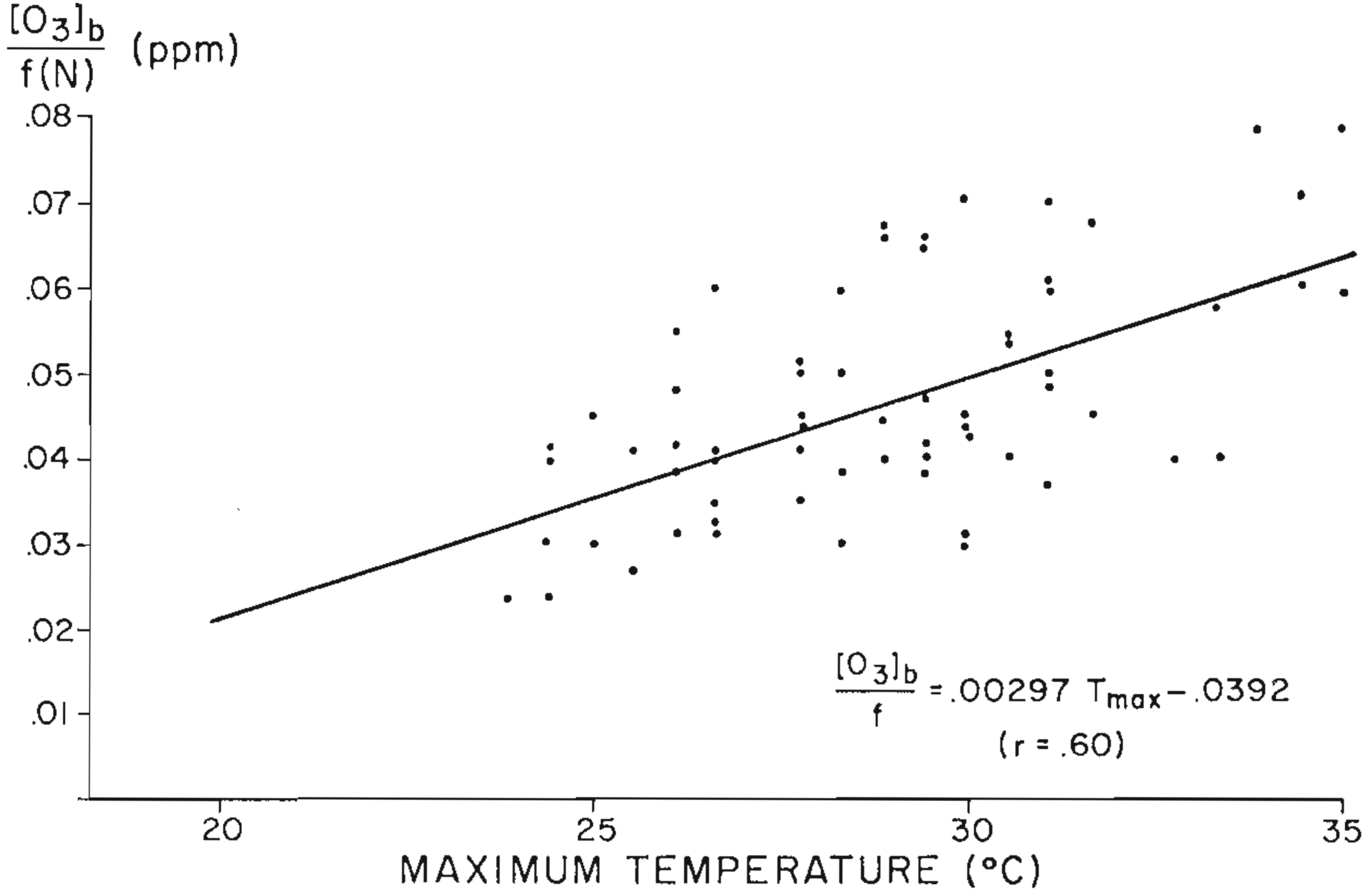

Figure 23 Seasonally adjusted background $[O_3]$

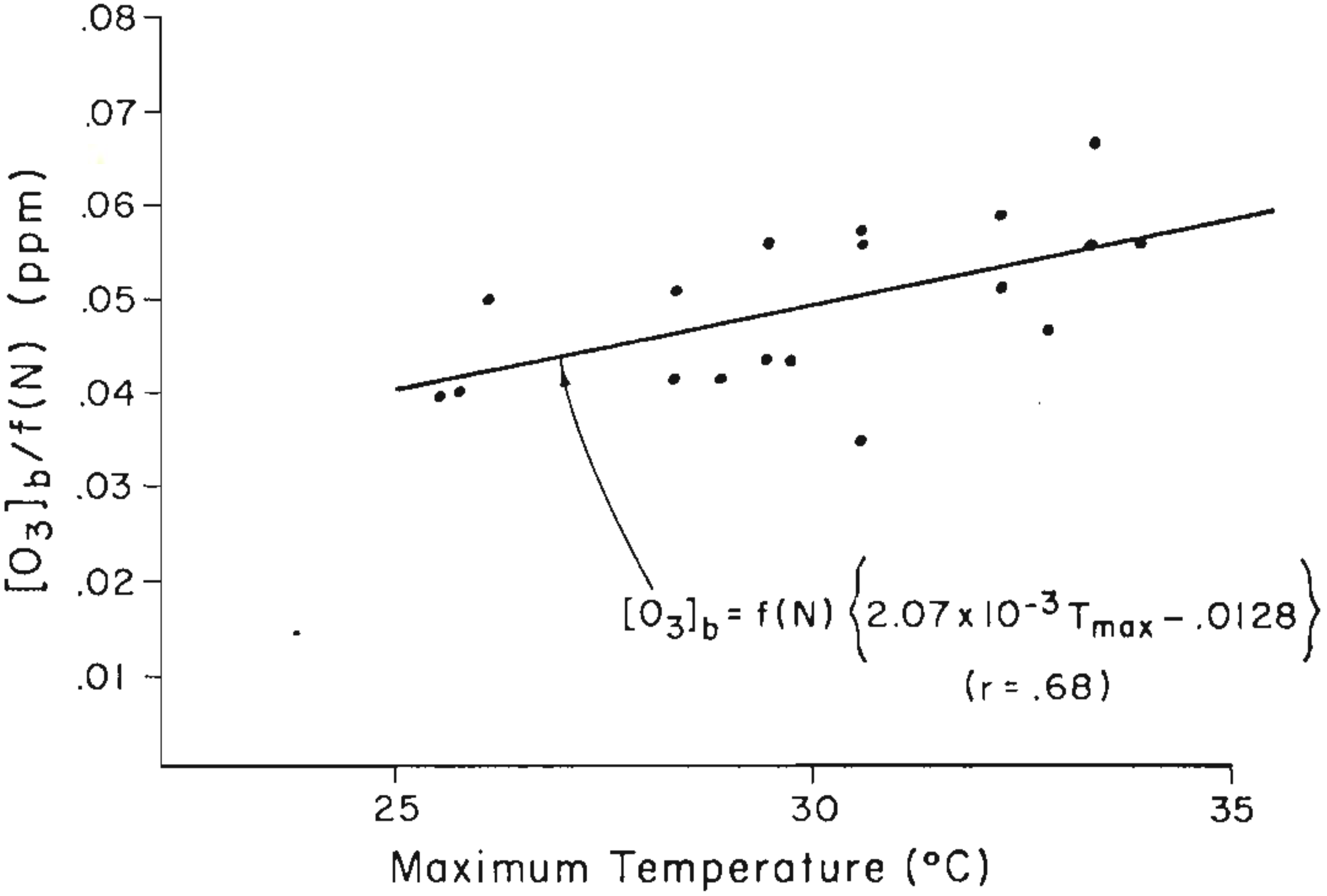

Figure 24 Background $[O_3]$ under east wind conditions

O_3 tends to be smaller with east winds compared with north winds for the same temperature. Because the region east of Portland is sparsely populated, the possibility of long range transport of anthropogenic O_3 is small. Thus, the fact that background $[O_3]$ is higher with north winds is evidence that the air out of the north is more polluted. More polluted air, in turn, can be explained by long range transport from the Puget Sound area.

IV.3 Regression analysis of basic equation

The general approach that was taken in order to determine the extent to which the ozone and meteorological data agree with the results of Chapter III was to perform a regression analysis using equations (IV.1)-(IV.3). The regression was on the most sensitive parameters of Eq.(IV.1), the constant of proportionality (K) and the exponent to which wind speed is raised (α). The determination of K and α in Eq.(IV.1) constitute a non-linear regression problem. If logarithms are taken the problem is linearized.

$$\ln \left\{\frac{[O_3]-[O_3]_b}{f(N)}\right\} = \alpha \ln \frac{1}{V_w} + \ln K$$

A standard least square method was used to obtain estimates for K and α. The resulting values were then used as first guesses for the real problem of interest, the determination of a best fit for Eq.(IV.1). An iterative procedure based upon the method of steepest descent as described by Bevington (1969) was utilized. In all cases four iterations were sufficient to estimate the two parameters.

Results of the regression analysis in the form of least square fits for K and α together with the resulting RMS error for each fit are summarized in Table 6. The six sets of values correspond to six different models of increasing complexity and are designed to show the relative importance of the meteorology parameters. The first case shows that results were quite poor when ozone was modeled simply as a function of wind speed. Considerably better results were obtained for case 2 for which a distinction is made between urban ozone as dependent upon wind speed and background ozone as a constant. The RMS error was reduced further by incorporating the background model as given by Eq.(IV.3) (Case 3). Cases 4 and 5 indicate no improvement if variations in mixing height and the time of year effect are incorporated into the model.

The final entry of Table 6 shows a slight improvement in results using the fact that the residuals of the fit were correlated. These residuals constitute a time series with autocorrelation and were analyzed using the method developed by Box and Jenkins (1976) and implemented by Tiao et al. (1976). Detailed time series analysis indicated optimum results if the basic equation relating ozone to meteorology were modified as follows:

$$[O_3] = \frac{Kf(N)}{V_w{}^{\alpha}H} + [O_3]_b - .107\ \varepsilon_{-1} \qquad \text{(IV.4)}$$

where ε_{-1} = the error in the previous fit.

The previous fit is defined to be the fit for the day in the data base previous to the day of interest, as long as the two are no more than three days apart. A distinction must be made between the previous fit and the previous day to account for the fact that the time series has a large number of vacancies that represent days not in the

Table 6 Results of regression analysis of 1974-1976 data

	Regression Equation for $[\hat{O}_3]$	K	α	RMS Error (ppm)
1	$\frac{K}{V_w^{\alpha}}$	.0919	.16	.0234
2	$\frac{K}{V_w^{\alpha}} + .045$	.0944	.648	.0194
3	$\frac{K}{V_w^{\alpha}} + [O_3]_b$	.150	.851	.0169
4	$\frac{K}{V_w^{\alpha}H} + [O_3]_b$	156.4	.803	.0169
5	$\frac{Kf(N)}{V_w^{\alpha}H} + [O_3]_b$	160.3	.784	.0169
6	$\frac{Kf(N)}{V_w^{\alpha}H} + [O_3]_b -$ $.107([\hat{O}_3]_{-1}-[O_3]_{-1})$	160.3	.784	.0167

data base, either because of meteorology not conducive to ozone formation or because of missing data. A maximum separation of three days in the determination of the error in the previous fit was used because it minimized the RMS error.

The physical basis for the use of this additional term is that it partially accounts for bias error sources within the data base. If a bias error source is present, then the estimated $[O_3]$ for two consecutive days will be correlated. The autocorrelation function for the time series of residuals for Case 5 had a value of .17 which indicates a small but significant amount of correlation. The time series analysis makes use of this fact to improve the estimates. The particular bias error sources of relevancy are probably uncertainties associated with the O_3 data and errors in the values computed for background O_3.

It should be pointed out that an inconsistency exists in the regression analysis, as no attempt was made to optimize the exponent of mixing height as was done with wind speed. Cases 3 and 4 of the table indicate that essentially the same results were obtained with exponential values of zero and one. The optimum value would undoubtedly be between these extremes. Since the two values gave the same result, this additional optimization was not performed. The fact that the data for $[O_3]$ at Milwaukie are insensitive to mixing height variation is a consequence of the poor quality of the data.

The results of Table 6 indicate that α is of the order of .8, a value significantly less than the value of 2.5 anticipated in Section III.3.2. In order to determine the sensitivity of the RMS error to variations in α, a regression was performed with α frozen at the theoretical value of 2.5. The resulting RMS error for Case 4 was .0211 ppm which indicates a sizable decrease in the quality of the fit. Two different factors explain the discrepancy in values for α from theory vis-a-vis data analysis. The first is the fact that the regression equations of Table 6 are based upon a number of simplifying assumptions. The most important of these is undoubtedly the fact that variations in both the relative and absolute precursor emission rates as well as the time of day effect were ignored. The effect of these modeling assumptions is to add noise to the system and decrease sensitivity. In addition, measurement uncertainties for those parameters that were modeled effectively decrease sensitivity. Obviously as measurements of a relationship that is fairly sensitive become more and more dominated by noise, regression upon those measurements will indicate a relationship that becomes progressively weaker. In the limit of a measurement set completely dominated by noise, power law regression will indicate $\alpha = 0$. Monte Carlo simulation results discussed in Appendix B shows that the quality of the wind and ozone data used in the study severely limits the size of α obtained from regression analysis, even in the absence of modeling assumptions.

A number of additional regressions were performed on equations more complex than those of Table 6 with the object of generating a better fit; however, none of them met with any success. Theoretical results described in Chapter II indicate an exponential relationship between $[O_3]$ and meteorological parameters. With Eq.(II.5) as a guide, regression analysis was performed on

$$[O_3] = \exp\left(\frac{Kf(N)}{H\ V_w^{\alpha}}\right) - 1) + [O_3]_b$$

The resulting RMS error was slightly larger (< 1%) than that of Case 5, which indicates no advantage with the use of this more complex relationship.

Results discussed in Sections II.3, and III.3.5 indicate that a coupling exists between urban and background sources of ozone. Regression was performed upon

$$[O_3] = \frac{Kf(N)}{H\ V_w^{\alpha}} + K'[O_3]_b$$

with the value of K' varied to optimize results. Again, no improvement was observed. It should be pointed out that a slight improvement in the quality of the fit was observed in the analysis of the 1977 data with K' = 1.1. The fact that a coupling was observed in the analysis of the 1977 data is explained by the better quality of the meteorology data for that season. This point is discussed in detail in Section V.3.

Finally an attempt was made to incorporate the wind data obtained from the 17:00 sounding at Salem. Up to this point the analysis has been based upon surface winds from the central business area of Portland. Its use can be criticized on the grounds that surface data may not be a good measure of pollutant transport throughout the mixing layer. Use of average wind speed throughout the mixing layer as calculated from sounding data is certainly a better measure of pollutant transport. Unfortunately, the Salem soundings suffer from the fact that they were taken at a location 80 km from Portland and at a fixed time rather than at the time of maximum $[O_3]$. Case 5 was reanalyzed using average wind speed values as computed from the 17:00 sounding at Salem. The result was an increase in the RMS error of 20%. Evidently the improvement to be expected using a wind data base representative of transport throughout the mixing layer was more than cancelled by the degradation due to measuring at the wrong place and at the wrong time.

CHAPTER V

FORECASTING OZONE CONCENTRATION

A problem of interest to all air pollution control agencies is the requirement to forecast photochemical smog episodes as accurately as possible. The State of Oregon DEQ bases their forecast upon persistence; that is, an episode is forecast when field monitoring indicates that the concentration of ozone is above a specified level. The forecast remains in effect until the concentration falls below this level. Probably the most sophisticated procedure actually used by an agency is that of the Los Angeles County Air Pollution Control District. They use a combination of weather forecast and past air quality statistics to predict maximum O_3 as well as visibility and eye irritation. Such a forecast is made using a weather forecast along with knowledge of air quality in the past under similar meteorological conditions. This forecast is then translated into an alert if certain limits are exceeded. Finally very recent work on this problem has been in the application of time series analysis to forecasting. McCollister and Wilson (1975) and Tiao et al. (1976) developed forecasting algorithms based upon time series analysis as developed by Box and Jenkins (1976). These procedures use the high degree of correlation in air quality data, both on a daily and on a seasonal basis, to forecast O_3 concentration from historic data.

V.1 Forecasting results for the 1977 season

A practical application of the results of the previous chapter is the development of a forecasting scheme for maximum $[O_3]$ at Milwaukie. Case 6 of Table 6 was selected for investigation. The relationship between O_3 concentration and meteorology for this case is given by

$$[\hat{O}_3] = \frac{160.3\ f(N)}{V_w^{.784}H} + [O_3]_b - .107([\hat{O}_3]_{-1} - [O_3]_{-1}) \tag{V.1}$$

This equation is based upon data for the 1974-76 seasons, and its utility as a forecasting tool was tested by analyzing data for the 1977 season. The choice of years was fortuitous from the point of view of data analysis, as the 1977 season turned out to be the worst since O_3 has been monitored at Milwaukie. The total number of days that the federal standard of .08 ppm as an hourly average was violated exceeded the number for each of the previous years by a significant amount (Figure 2), and violations were the earliest ever recorded with 6 violations in the month of April. It was determined that 60 of the 153 days in the time period April 1 - Sept. 30 had the potential for urban ozone formation. Because of instrumentation malfunction on 8 of these days, the actual data base consisted of 52 days.

Forecasting results are depicted in Figure 25. Presented are actual and predicted concentrations at Milwaukie for the 33 days of the data base when the actual concentrations were > .06 ppm. The 19 days excluded from the figure were characterized by relatively low ozone levels, both predicted and actual, and they represent

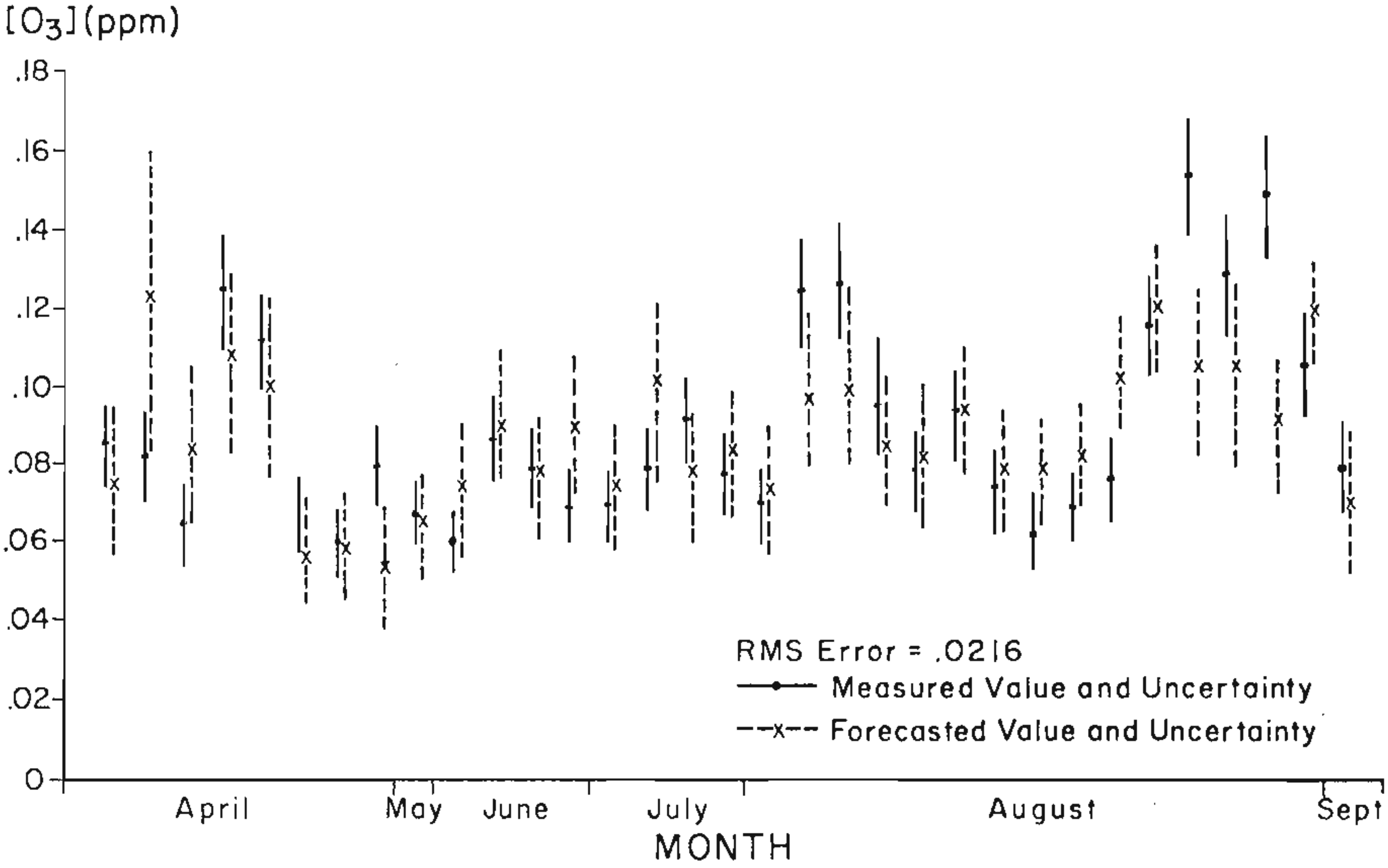

Figure 25 Forecasting results for Milwaukie

the least interesting portion of the data base.

Actual values were used for all meteorological parameters; that is, O_3 was forecast with Eq.(V.1) using values for mixing height, wind speed and maximum temperature as measured at the time of occurrence of maximum ozone. Thus these results correspond to the idealized case of perfect prediction of meteorology.

Uncertainties in the actual values are based upon the error model for ozone measurements that is described in Appendix B. This error analysis indicated an uncertainty of the order of .01 ppm. Uncertainties in the predicted values are based upon the following set of measurement uncertainties.

$\Delta[O_3]_b$ = .01 ppm

ΔH = 50 m

ΔV_W = 2 km/hr

ΔEq.(V.1) = .01 ppm

The effect of each of these error sources on the forecasted concentrations was determined using the standard method for compounding uncorrelated error sources. That is,

$$\Delta[\hat{O}_3] = \left[\left(\frac{\partial[\hat{O}_3]}{\partial V_W}\,\Delta V_W\right)^2 + \left(\frac{\partial[\hat{O}_3]}{\partial H}\Delta H\right)^2 + \left(\frac{\partial[O_3]}{\partial[O_3]_b}\,[O_3]_b\right)^2 + .0001\right]^{1/2} \qquad (V.2)$$

It can be seen that the quality of the forecast is reasonably good but hardly spectacular. Part of the problem is explained by the fact that the meteorology station that is the source of the wind data was moved between the 1976 and 1977 seasons. A fire in February of 1977 destroyed the Hughes Building where the meteorology equipment had been installed. Subsequently a new site was selected on top of the Federal Building. An attempt was made to select a site that duplicates conditions as closely as possible to those at the Hughes Building. The Hughes site was 32 m above street level, while the site on the Federal Building is 34 m above the street and approximately 1.5 km to the northwest. Although the two sites are quite similar, the possibility exists that they would have given significantly different measurements if they had been in operation simultaneously. This is particularly important on those days when small differences in wind velocity produce sizeable differences in O_3 levels at Milwaukie; that is, those days characterized by very light winds.

Apart from the problem associated with the wind data, probably the single greatest source of error in the results of Figure 25 is the error in predicting background O_3. Comparison of predicted concentrations, using Eq.(IV.3) with actual concentrations indicated sizable differences, particularly during a major photochemical smog episode that occurred during the first 17 days of August 1977. Because of its importance, it is discussed in some detail in Section V.2. Suffice it to note at this point that the severity of the episode exceeded that at any other time in the four years there has been a monitoring program at Milwaukie. Discrepancies between predicted and actual background O_3 as great as .025 ppm were noted during this period. Figure 26 presents forecasting results based on the use of actual, rather than predicted, values for background. It can be seen that there is significant improvement in the quality of the forecast. In particular, the root-mean-square discrepancy decreased by approximately 20% from .0216 ppm to .0174 ppm.

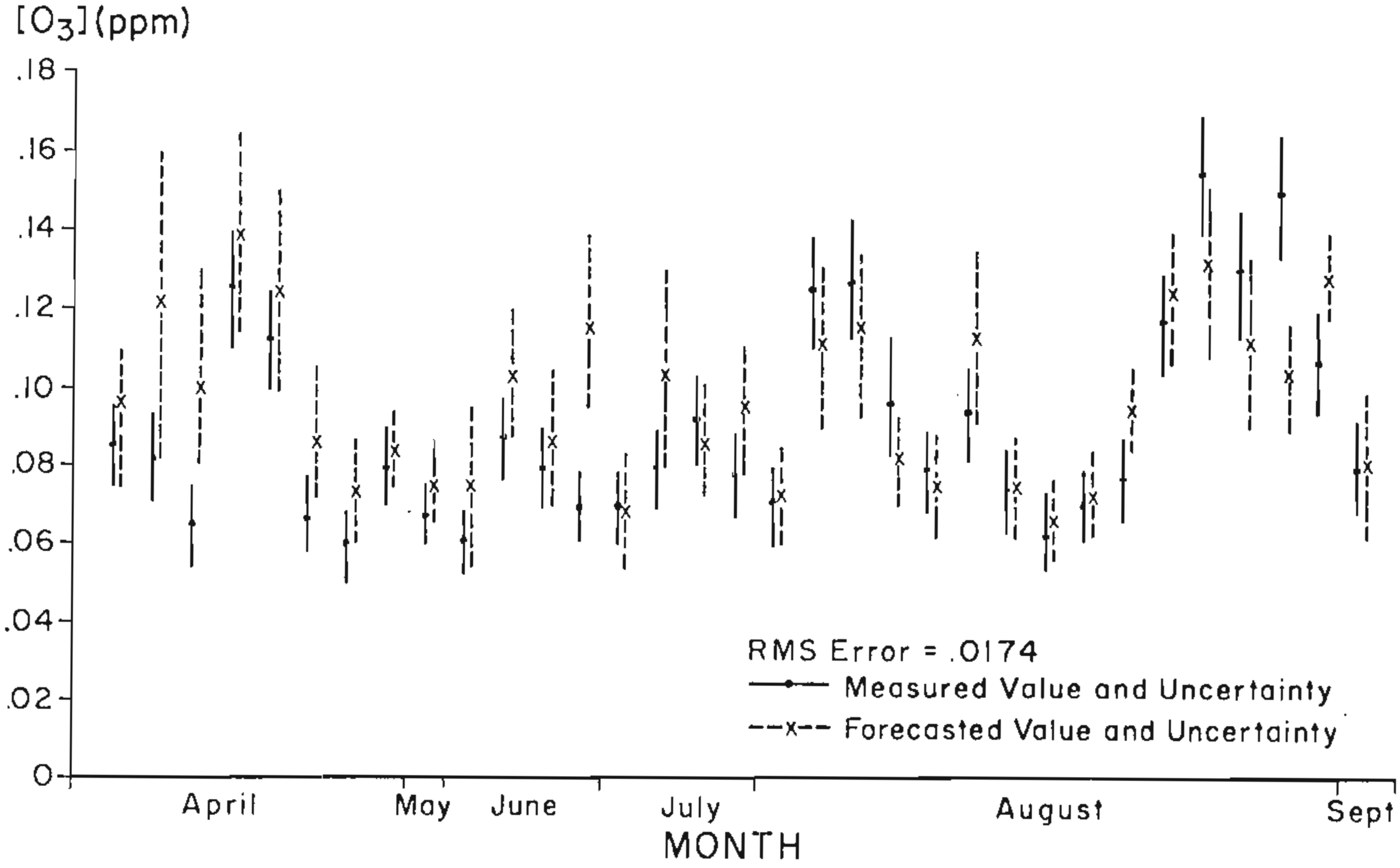

Figure 26 Forecasting results assuming perfect prediction of background [O_3]

Forecasting results up to this point have been based upon actual, rather than predicted, values for meteorology parameters; hence, they assume perfect weather prediction. It would be of interest to compare actual with predicted concentrations that are based on predicted meteorology. The precedure for forecasting maximum hourly average O_3 would be to use Eq.(V.1) together with forecasted values for mixing height, wind speed, and temperature at several times during the afternoon, and then select the largest value as the forecasted maximum. Unfortunately the forecast of the United States Weather Bureau is not of sufficient detail to perform this operation. In particular, forecasted winds are in terms of very general categories, rather than actual values, and only occasionally is an attempt made to anticipate changes in wind conditions in the course of a day.

Some measure of the effect of using forecasted meteorology was determined by using Eq.(V.2) and the following set of forecasting uncertainties:

$\Delta[O_3]_b = .01$ ppm

$\Delta H = 100$ m

$\Delta V_w = 4$ km/hr

ΔEq.(V.2) = .01 ppm

These values represent fairly good accuracy and they are meant to correspond to prediction after the 5:00 AM sounding on the day of the forecast. Uncertainties corresponding to a forecast at an earlier time would, of course, be greater. These uncertainties produce error bars somewhat larger than those of Figures 25 and 26. The degree of increase depended almost entirely upon wind velocity. On days with very light winds (< 5 km/hr), increases were as great as 85%, while on days with fairly strong winds (>10 km/hr), the uncertainties were essentially the same as those of the two figures. The average increase in the error bars was 30%.

V.2 August 1977 photochemical smog episode

From Figure 26 it can be seen that very high O_3 concentrations were recorded at Milwaukie during the month of August. Elevated ozone levels were not restricted to Milwaukie, as violations of the federal standard were recorded throughout the Pacific Northwest. Ozone levels at various locations in western Oregon and the portion of western Washington south of Seattle are listed in Table 7. The table gives concentrations for the first 17 days of the month when the episode was in effect along with data on the 18th to indicate the end of the episode. The location of these sites can be found in Figure 27. It can be seen that a high degree of spatial correlation exists in this data; that is, the very highest levels tended to occur at the same time. Note, for example, that very high levels were recorded on the 16th at each site in Oregon and on the 17th at each site in Washington.

The meteorology of this period is summarized in Table 8. The data are with respect to Portland and they indicate the development and stagnation of a high pressure system off the coast. The information on the location of the high (Column 2) refers to the pressure pattern at the 500 mbar level. It can be seen that the high developed off

Table 7 Ozone concentrations during the August episode

Date	Maximum Ozone Concentration (ppm)								
	Locations in Western Oregon						Locations in Western Washington		
	Milwaukie	Carus	Port.Cam	Salem	Eugene	Medford	Vancouver	Sumner	Lakewood
1	.06	--	--	.06	.04	.11	.06	.06	.04
2	.06	--	.03	.06	.03	.10	.04	.05	.07
3	.13	.08	.09	.08	.05	.10	.10	.09	.06
4	.13	.08	.04	.05	.02	.08	.05	.08	.06
5	.10	.13	.03	.09	.04	.06	.05	.14	.09
6	.08	.13	.04	.08	.03	.06	.04	.07	.05
7	.09	.13	.06	.09	.03	.08	.06	.08	.06
8	.07	.13	.02	.10	.03	.09	.04	.08	.07
9	.06	.11	.02	.08	--	.08	.05	.09	.05
10	.07	.11	--	.07	--	.11	.05	.12	--
11	.08	.13	.04	.11	.08	.10	.05	.13	--
12	.12	--	.03	.13	.09	.09	.06	.07	.05
13	.16	.09	.08	.07	.04	.11	.07	.07	.04
14	.13	.10	.06	.06	.05	.11	.05	.07	.05
15	.06	.13	.04	.08	.08	.10	.04	.11	.09
16	.15	.22	.06	.16	.11	.14	.07	.10	.10
17	.11	.17	.07	.15	.05	.13	.08	.15	.10
18	.05	.07	.01	.05	.03	.07	.05	.04	.04

Figure 27 Monitoring sites during August 1977 photochemical smog episode

Table 8 Meteorology during the August episode

Date	Location of High Relative to Portland	Maximum Temperature (°C)	Percent Sunshine	Afternoon Surface Winds (km/hr)	Background $[O_3]$*(ppm)
1	1540 km SE	33	98	23.0	.06
2	1500 km SW	35	87	14.1	.04
3	580 km W	33	95	4.7	--
4	960 km NW	30	62	5.8	.05
5	1440 km NW	34	66	9.4	.05
6	1500 km W	32	85	8.0	.04
7	670 km W	31	73	4.7	.06
8	1150 km SW	32	72	8.3	.04
9	380 km NW	37	100	21.2	.05
10	480 km W	38	100	13.7	.05
11	580 km NW	39	97	14.4	.05
12	770 km W	40	100	9.4	.06
13	960 km W	33	94	5.8	.07
14	1060 km NW	30	80	5.4	.05
15	1130 km NW	34	69	11.5	.04
16	740 km NW	39	100	9.7	.07
17	1500 km NW	40	100	13.7	.08
18	2100 km NW	27	60	10.5	.05

*Data are from the Vancouver location

the coast on the 2nd, remained more or less stationary for 15 days, and then drifted to the northwest on the 18th.

As noted in Section IV.2, elevated O_3 levels that are regional in scope have been observed throughout the midwest and east coast of the United States. There can be no question that such a phenomenon developed in the Pacific Northwest in August of 1977. Of particular interest in understanding the Milwaukie data is background O_3 during this period. The last column of Table 8 gives background levels assuming the data from Vancouver is a reasonable measure of concentrations upwind of Portland. Since both surface and transport winds were out of the north to northwest almost exclusively, this is a reasonable assumption. The missing data on the 3rd corresponds to a very light wind situation where the possibility exists for transport from Portland. It would have been of great value to incorporate data from the Sauvie Island site into this investigation. Unfortunately, the site was in the process of relocation and no measurements were taken.

An attempt was made to gather additional data on this episode; in particular, to determine the extent of long range transport of photochemical ozone and its precursors from the Puget Sound area to Portland. Contacts were made with a large number of individuals involved in air pollution work in the Pacific Northwest with the goal of gathering additional air quality and meteorological information. A list of individuals and agencies contacted can be found in Appendix C. This effort proved fruitless as no additional O_3 data were located. This fact indicates a substantial gap in the monitoring program in the Northwest. Because of the possibility of long range transport from the Puget Sound area, additional monitoring should be conducted between Portland and Seattle. The problem with the Vancouver data is that it may be influenced by local emissions and not be representative of conditions upwind of Portland. It is conjectured that this influence, if anything, is a negative influence arising from the effect of local NO emissions lowering ozone below upwind levels. The problem with the Sauvie Island location as a measure of background is that transport down the Columbia River from Portland is an occasional occurence. Probably the best location for measuring background is either north of Vancouver near, for example, the community of Battle Ground or west of Portland in Washington County. Either site would be free from the influences of local emissions and far enough from the Columbia River to be unaffected by funneling of emissions from Portland down the gorge.

A procedure that has been used to investigate the possibility of long range transport of ozone in the midwest and east coast of the United States (Wolff _et_ _al_., 1977) is to compute air parcel "back trajectories" and thereby determine the history of the air that passes over a monitoring site. The procedure involves interpolation between locations where surface or transport wind data have been collected to trace back air parcels 24 to 48 hours in time. Because of complex terrain effects, a determination of back trajectories based on surface winds would be of dubious value for the Pacific Northwest. A calculation based on transport wind data would be reasonable; unfortunately, daily soundings are taken at only three locations, Salem and Medford in Oregon and Quillayute near the northwest corner of the Olympic

Peninsula in Washington. A much denser sampling program to determine upper level winds would be essential before reasonably accurate back trajectories can be determined.

V.3 Updated forecasting algorithm for Milwaukie

For completeness, the air quality and meteorology data for the 1977 season was incorporated in the forecasting equations for Milwaukie. The first step was to update Eq.(IV.3) for background ozone so that it reflects these additional data. It was determined that a linear regression of seasonally adjusted background O_3 on the deviation of maximum temperature from the normal for the date rather than on maximum temperature gave better results. Data for 105 days from the 1974-1977 seasons are presented in Figure 28. A correlation coefficient of .59 resulted with the regression equation

$$[O_3]_b = f(N)\{.00244\ \Delta T_{max} + .0362\}$$

where ΔT_{max} is the departure of maximum temperature from the normal for the date in °C and f(N) is given by Eq.(IV.2). The correlation coefficient for a fit based upon maximum temperature was significantly smaller (r=.44). The explanation for the better fit using ΔT_{max} rather than T_{max} is that the former is a more accurate measure of degree of stagnation of an air mass over continental areas when considering the entire span of time from April through September. Until the 1977 season the data base consisted of days almost entirely in the months of June-September when both parameters gave essentially the same results. The 1977 season included 8 days in April with background O_3 as large as .06 ppm. Although maximum temperatures were unseasonably high because

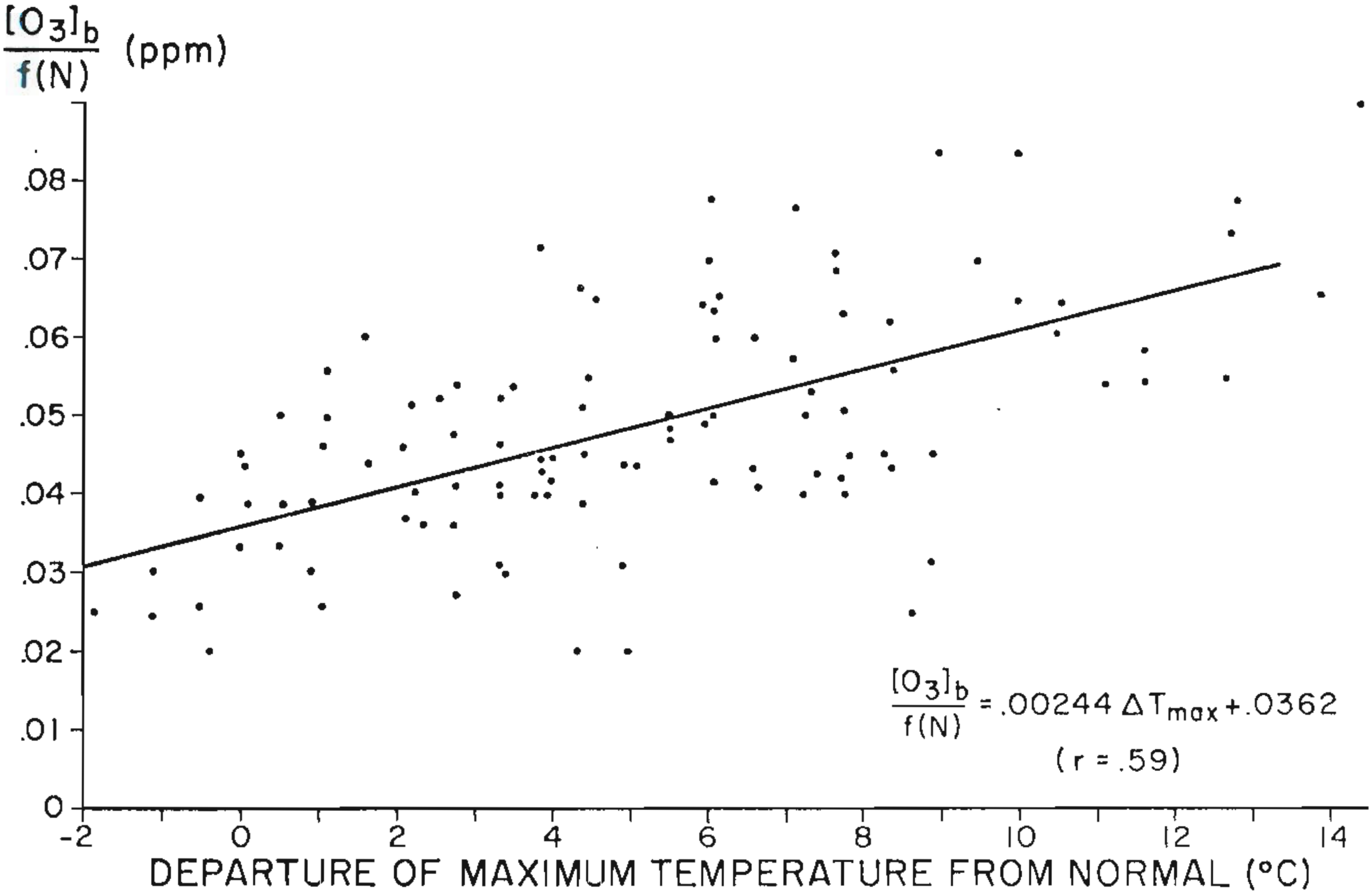

Figure 28 Seasonally adjusted background $[O_3]$ for the 1974-1977 seasons

of air mass stagnation, the actual temperatures were relatively low compared with the rest of the data base. This problem was eliminated by basing the regression on the departure of maximum temperature from the normal.

An improvement in the 1977 data base over that for the years 1974-76 is in the quality of the mixing height data. As part of the Portland Aerosol Characterization Study (ERT, 1977), a program to obtain temperature profiles was initiated in April of 1977. The program resulted in a fairly accurate determination of mixing height in the Portland area at the time of maximum ozone for approximately half the days of 1977. For those days in which soundings were not taken, mixing heights as measured at Salem at 17:00 were used.

In Section V.1 it was noted that an inconsistency exists in the surface wind data because the monitoring equipment was moved to a new location in February of 1977. Because of this inconsistency, it was decided to update the regression analysis using 1977 data rather than 1974-1977 data.

Regression results are summarized in Table 9 . The first entry indicates that the data set has a mean of .071 ppm and standard deviation of .032 ppm. The second entry indicates a very significant reduction in the RMS error if a distinction is made between urban and background ozone, where the former depends upon wind speed while the latter depends on deviation of temperature from the normal. A similar reduction was obtained from the 1974-76 data. The third entry indicates further reduction if the effect of time of year and variability in

Table 9 Results of regression analysis of

1977 Milwaukie data

Case	Equation for $[O_3]$	RMS Error (ppm)	α
1	$\overline{[O_3]} = .071$ ppm	.0319	
2	$\frac{K}{V_w^{\alpha}} + [O_3]_b$	.0212	1.21
3	$\frac{KF(N)}{HV_w^{\alpha}} + [O_3]_b$	.0192	1.19
4	$\frac{KF(N)}{HV_w^{\alpha}} + 1.1[O_3]b$	.0190	1.18
5	$\frac{KF(N)}{HV_w^{\alpha}} + \frac{V_w}{V_w-.6}[O_3]_b$	.0189	.88
6	$\frac{KF(N)}{HV_w^{\alpha}} + \frac{V_w}{V_w-.6}[O_3]_b-.22\varepsilon_{-1}$	.0182	.88

mixing height is acknowledged. This reduction was not seen in the 1974-76 data and is probably a result of the more accurate determination of mixing heights for 1977. The fourth and fifth entries support the results of Sections II.3 and III.3.5 that indicate that urban emissions augment the background term. The fourth equation was obtained by assuming local emissions effectively scale the background term by a constant. Under this assumption it was determined that a value of 1.1 minimized the RMS error. The basis for the fifth entry is Eq.(II.9) which indicates that background should be scaled by a function of the form

$$\frac{V_w}{V_w - C}$$

It was determined that results were optimized with

$$C = .6$$

The final entry in Table 9 indicates additional improvement using the fact that there is correlation in the residuals of the fit.

To summarize, the updated forecasting algorithm for the Milwaukie location consists of the following equations

$$f(N) = .758 + .60 \times 10^{-2}N - .371 \times 10^{-4}N^2$$

$$[O_3]_b = f(N)\left\{.000244\ \Delta T_{max} + .0362\right\}$$

$$[\hat{O}_3] = \frac{151\ f(N)}{V_w^{.88}H} + \frac{V_w}{V_w - .6}[O_3]_b - .22\ [\hat{O}_3]_{-1} - [O_3]_{-1})$$

From Table 9 it can be seen that these equations reduced the variability in the O_3 data by about 43% for the 1977 season.

CHAPTER VI

ANALYSIS OF OZONE DATA FROM CARUS

In October of 1975 the Department of Environmental Quality initiated an ozone monitoring program at Carus. The location of this site can be found in Figure 3 and it is seen to be approximately 30 km. south of the center of Portland. The site is in rolling farmland and is uneffected by local emissions. Ozone levels at Carus have been consistently higher than at Milwaukie. This can be seen in Figure 29 which gives concentrations for the two sites on 66 days with simultaneous measurements during the 1976 and 1977 seasons. The data indicate that Carus is nearer the optimum location for measuring urban ozone from Portland. The problem with the Milwaukie location is that on windy days the time of transport from Portland to Milwaukie is insufficient for significant O_3 production. The Carus station is far enough from Portland to allow sufficient time for photochemistry yet not so far that dispersion dilutes to background levels.

Regression analysis was performed on the Carus data in order to determine a functional relationship between O_3 concentration and meteorology. The data set consisted of 80 days that have the potential for significant ozone formation using the criteria described in Section IV.1. Results of this analysis are summarized in Table 10. The first entry indicates that the data set had a mean of .095 ppm and standard deviation of .0295 ppm. The second entry indicates a

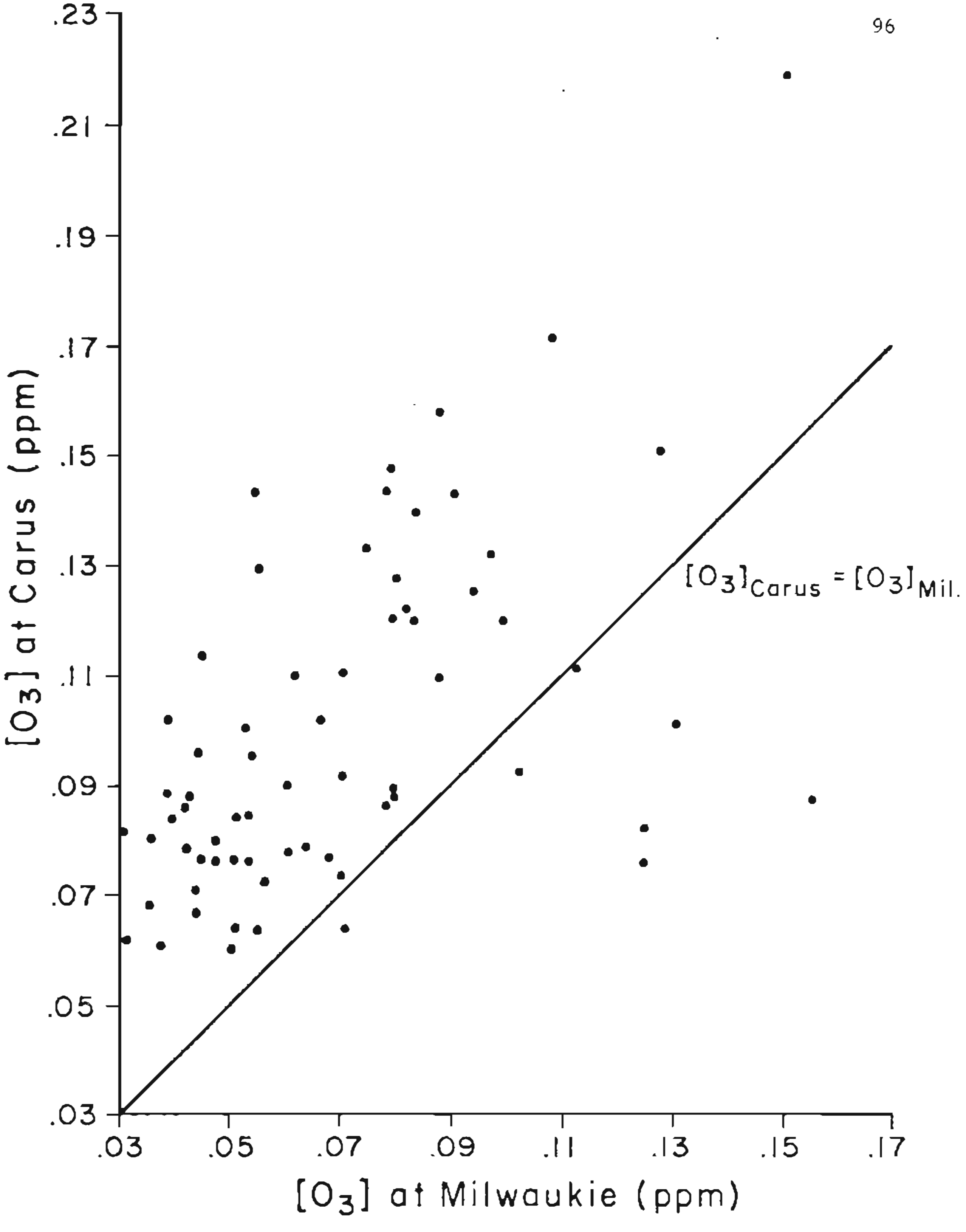

Figure 29 Comparison of ozone levels at Carus and Milwaukie

Table 10 Results of regression analysis of Carus data

Equation for $[\hat{O}_3]$	Size of Data Set (Days)	K_1	α or K_2	RMS Error (ppm)
$[\bar{O}_3] = .095$	80			.0295
$\frac{K_1}{V_w^{\alpha}} + [O_3]_b$	80	.045	.01	.0246
$\frac{K_1 f(N)}{V_w^{\alpha} H} + [O_3]_b$	80	48.1	-.01	.0246
$\frac{K_1 f(N)}{V_w^{\alpha} H} + [O_3]_b$ Carus Wind Data	80	70.3	.19	.0252
$K_1 + K_2[O_3]_b$	80	.0269	1.59	.0237
$K_1 + K_2[O_3]_b$	76	.0249	1.65	.0231
$K_1 + K_2[O_3]_b - .125([\hat{O}_3]_{-1} - [O_3]_{-1})$	76	.0249	1.65	.0227

sizable reduction in the estimation error when account is taken of the variability of wind speed and background O_3. The next entry shows no observable improvement in the quality of the fit when the time of year effect and variability of mixing height are acknowledged.

Both the second and third equations contain wind speed as an independent variable. The actual values used were the three hour vector averages as measured in the central business district of Portland. The time period included the two hours preceeding and the hour of maximum O_3. Meteorological data are also available for the Carus site, and its effectiveness as a regression parameter was tested with the last case in the top half of Table 10. It can be seen that wind data from Carus produced a fit of slightly poorer quality.

The values for α in the top half of the table indicate a very weak relationship between O_3 at Carus and wind speed. This result is in marked contrast to results for the Milwaukie site. The explanation of this discrepancy lies in the fact that the variability due to wind direction is of much greater importance for Carus. Because wind direction is not an independent variable in any of the regression equations, the analysis can only be applied to data collected at locations corresponding to maximum O_3 along the axis of the Portland plume. Because of the prevailing north to northwest winds, this maximum almost surely passes close to the Milwaukie site. On the other hand, the greater distance from Portland to Carus means that the point of maximum ozone 30 km downwind of Portland may be well to the east or to the west of Carus, even with north to northwest winds. In Figure 30 are plots at three different times of O_3 concentration along a west to east line passing through Carus. These plots are based on aircraft measurements taken during the 1976 Survey of Ozone and Light Scattering Particles in Western Oregon (Huntzicker et al., 1977). The plot at the top of the figure gives conditions on a day when maximum O_3 was very near Carus while the middle and bottom portions indicate days when maximum O_3 is to the west and to the east.

Surface winds at Carus for these three days are presented in Table 11. Although there are some gaps in the data due to instrumentation malfunction, what is presented in the table indicates no obvious relationship with the results of Figure 30 that is general enough to apply to all days. It was hoped that it might be possible to use wind direction to make a rough assignment of each of the 80 days of the data base to one of the three categories of Figure 30.

The effect of ignoring the variability in wind direction is to blur the sensitivity of O_3 concentration at Carus to wind speed, mixing height and time of year. For this reason it was decided to eliminate these three parameters and to investigate a very simple two term model, where the first term is a constant that gives the effect of precursors from Portland and the second term is a measure of the extent to which urban emissions augment background levels. The bottom portion of Table 10 gives results for three such models. The first set of results are based upon the entire set of 80 days, while the second gives results after eliminating four days when transport of O_3 and its precursors from Portland to Carus was extremely doubtful. These four days are represented by the four points of

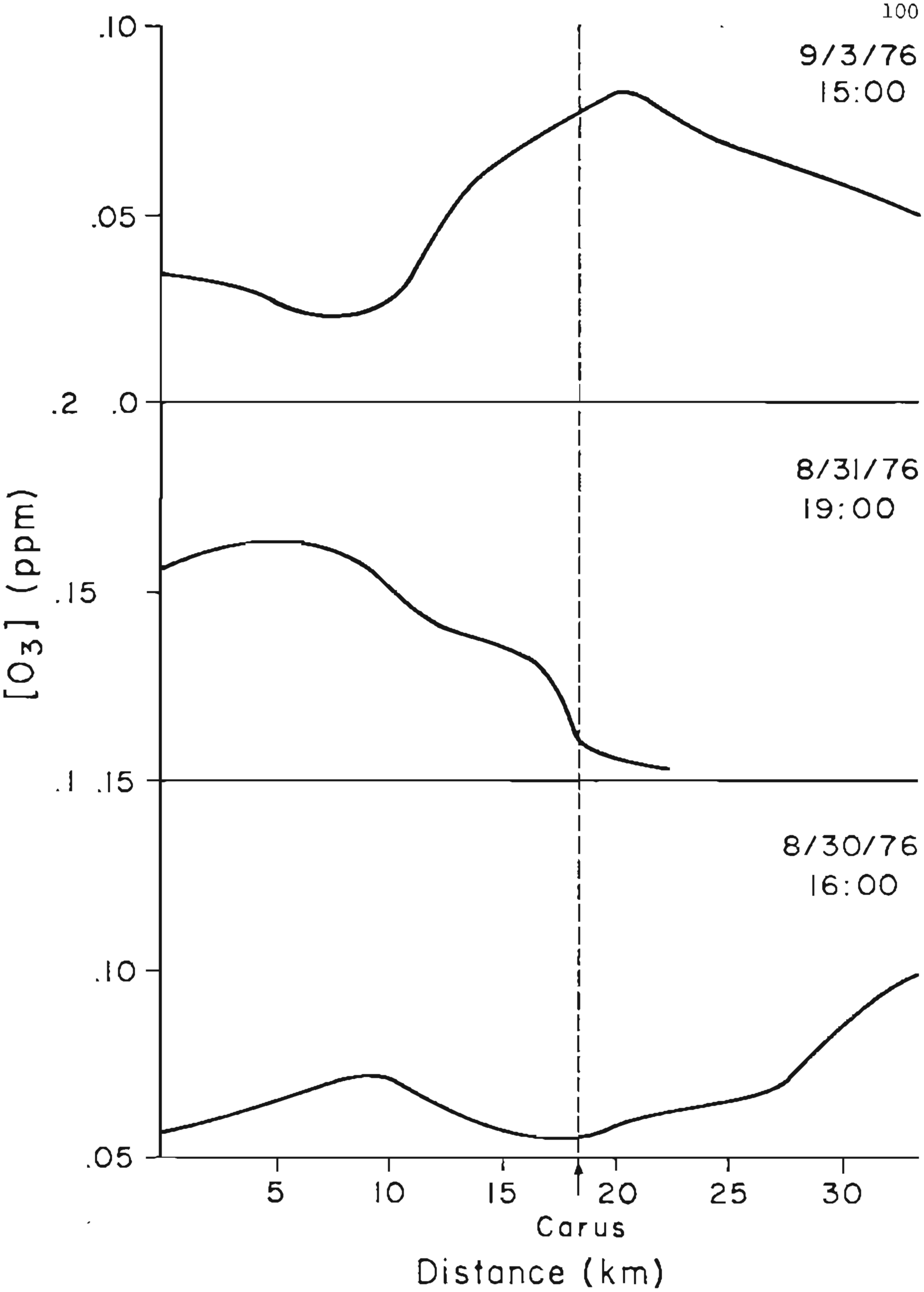

Figure 30 Ozone concentrations in the Carus area

Table 11 Surface winds at Carus

Date - Time	Wind Speed (km/hr)	Wind Direction (deg)
9/3/76; 13:00	--	--
14:00	--	--
15:00	16.5	321
8/31/76; 17:00	4.4	360
18:00	1.6	346
19:00	--	--
8/30/76; 14:00	12.4	360
15:00	12.2	1
16:00	12.1	9

Figure 29 with

$$[O_3]_{Mil.} > [O_3]_{Carus}$$

by a significant amount. Detailed examination of meteorology data indicates the same pattern for all four; that is, very light winds in Portland with westerly winds at Carus. It is postulated that on these days the Portland plume passed over Milwaukie and then moved in a southeast direction so that at a distance of 30 km it was well to the east of Carus. From the table it can be seen that there was a slight improvement in the quality of the fit with the elimination of these days. The final entry in the table indicates some additional improvement using the autocorrelation in the residuals of the fit to trim successive estimates.

A forecasting scheme for ozone at Carus that is analogous to that for Milwaukie would be given by

$$[\hat{O}_3] = .0249 + 1.65\ [O_3]_b - .125([\hat{O}_3]_{-1} - [O_3]_{-1})$$

where $[O_3]_b$ is given by Eq.(IV.3). Because of the problem associated with variability in wind direction, it is anticipated that this model would not be as accurate as that for Milwaukie. It would be possible to develop a more accurate model if O_3 data were available for several other locations 30 km south of Portland. An intensive monitoring program of this sort would guarantee data from a location near the O_3 maximum of the Portland plume. Such a model would not be site specific as it would apply to the site closest to the 30 km O_3 maximum on the day of the forecast. The model would undoubtedly show a dependence upon wind speed, mixing height and time of year.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

This study indicates that the relationship between ozone levels in the vicinity of an urban center and meteorology is quite complex. Theoretical considerations along with computer simulation results indicate that variations in O_3 concentration are due to two very general effects, the variability in the effect of meteorology upon precursors emitted by the urban center and the variability in background O_3 concentration. These results predict that urban ozone in turn should vary slightly less strongly than linearly with both emission factor and the inverse of mixing height. The dependence upon wind speed is much stronger, particularly for locations very near the urban center. Also predicted is a time of year effect of the order of 35% for the Portland area. Theoretical and computer simulation results also indicate a coupling between background and urban ozone levels that is of second order. It is well known that locally emitted NO can decrease O_3 concentration below background levels within an urban center. What is new here is an indication that urban emissions have the apparent effect of augmenting the background term downwind of the urban center.

These conclusions are sustained by an analysis of air quality and meteorological data from two locations in the Portland area. On cloudless days, O_3 concentration at Milwaukie depends most strongly upon wind speed and background level. The sensitivity to mixing height, precursor emission factor and time of year is weaker so long as the time of year is within the months of April-September. For the Carus location, O_3 concentration on sunny days depends most strongly upon wind direction and background concentration. Finally the data give some evidence for the coupling between the background and urban terms that was predicted from theoretical and computer simulation results. Variations in background ozone appear in turn to be related to the degree of stagnation of the high pressure system that determines the meteorology at the time of interest.

A practical application of the results of the regression analysis is an algorithm for forecasting maximum hourly average $[O_3]$. Using 1974-76 data, a simple procedure was developed for the Milwaukie location. The algorithm requires values for those parameters usually associated with a detailed weather forecast; that is, wind speed, maximum temperature and mixing height. The procedure was tested for the 1977 season and fairly good results were obtained (rms error = .0174 ppm). It should be pointed out that the prediction was based upon actual rather than forecasted meteorology, so that the effect of errors in forecasting the meteorology parameters was not evaluated. For the Milwaukie location it is conjectured that the only parameter that would cause a problem would be wind speed, particularly if winds are anticipated to be relatively light. If winds are expected to be less than 7 km/hr, then a forecast should be within 2 km/hr. For winds greater than 7 km/hr, accurate prediction is not necessary. It is conjectured that predicting winds to an accuracy of 2 km/hr 12 to 24 hours in advance may be a problem.

Because the historical record for Carus extended over only two seasons at the time this study was undertaken, it was not possible to evaluate a forecasting procedure for this location. It is anticipated that this would be a somewhat more difficult problem because one of the principal determinants of $[O_3]$ at Carus, wind direction, is difficult to forecast with the necessary accuracy.

VII.1 Recommendations for additional monitoring

In working with the data it became apparent that additional monitoring should be undertaken to develop a more complete understanding of O_3 formation and transport in the Portland area. Because of the possibility of long range transport of ozone and its precursors from the Puget Sound area, additional monitoring should be undertaken between Seattle and Portland. Such data would indicate the extent to which violations of the federal standard in Oregon can be attributed to emissions from the state of Washington. In addition, at least one more monitor should be set up at a distance 30 km downwind of Portland to complement the Carus data. Detailed analysis on days when ozone levels were higher at Milwaukie than at Carus indicate a meteorological pattern that places the Portland plume well to the east of Carus. Thus, additional monitoring should be undertaken 30 km southeast of Portland near, for example, the community of Estacada.

Finally, additional soundings should be made in the Pacific Northwest to determine wind speed and direction throughout the mixing layer. Currently, United States Weather Bureau soundings are taken at three locations in the states of Oregon and Washington. Clearly, the density of sampling is insufficient to determine air parcel back trajectories. Additional soundings would allow for the determination of such trajectories and, thus, give some indication of the history of air parcels passing over Portland.

VII.2 Recommendations for additional studies

Probably the least understood aspect of this study is the variability in background ozone levels. Additional studies should be undertaken to determine why background levels vary from a low of .02 ppm to a high on the order of .08 ppm. Among the specific questions to be answered are the extent of long range transport of anthropogenic ozone from Puget Sound to Portland, the degree of carry over of urban ozone in the Portland area from one day to the next, and the relative importance of elevated ozone because of natural emissions of reactive hydrocarbons by plants. All three effects are associated with stagnation of a high pressure system, and it is essential from an air quality improvement point of view that the relative values of each be evaluated.

With the increased understanding of the relationship between urban ozone and meteorology, it is now possible to remove a sizable portion of the variability in the data that is due to weather. The resulting preprocessed data should be used as the basis for two different data analysis studies. The first would be an examination to determine if a weekday-weekend effect exists for the Portland area. Cleveland

and McRae (1977) determined a statistically significant difference in O_3 levels in the northeastern portion of the United States on weekends as compared with weekdays. Their work is based upon maximum hourly average ozone data uncorrected for the variability due to meteorology. It would be of interest to determine if such a difference can be seen in the Portland data; in particular, if it can be seen in the preprocessed data.

The second data analysis study would be to determine if long term trends can be seen in the data. Long term trends have been detected in the Los Angeles ozone data using a time series analysis approach by Merz et al. (1972) and Tiao et al. (1975). Both groups base their analysis upon air quality data that exhibits variability due to meteorology. It is doubtful that a trend could be discerned in the raw data from Portland both because the historical record is so short and because the variability due to meteorology is probably greater. It may be possible to determine a trend using data preprocessed to remove the variability due to weather. Such a study should be undertaken as the time period of interest, 1974-1977, corresponds to the establishment of a hydrocarbon emission control program for automobiles in the greater Portland area. It would be of interest to determine if the data indicate an improvement in air quality for this period.

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Wolff, G.T., Lioy, P.J. and Wight, G.D. (1977). "An Investigation of Long-Range Transport of Ozone across the Midwestern and Eastern United States". Atmos. Environ. 11, 797-802.

Appendix A Justification for the assumption that pollutant concentration is invariant in the vertical direction within the mixing layer.

A basic assumption of the computer program that was developed to simulate ozone production in the Portland area is that the concentration of all pollutants is independent of altitude from the ground up to the mixing height. This assumption is justified if it can be shown that the time for pollutants emitted at the ground to become well mixed is less than the time for photochemistry to produce significant amounts of ozone from NO_x and reactive hydrocarbons. The most obvious way to establish this fact is to develop a three dimensional computer simulation for O_3 formation that accounts for variations in wind speed and eddy diffusivity with altitude. This is a very difficult problem and is beyond the scope of this study. The approach taken here is to use a Gaussian plume model and to represent precursor emissions from Portland by a continuous point source. This simplification is equivalent to reducing the problem to two dimensions and to assuming that the wind and turbulent fields are independent of height. The procedure will be to assume that the precursors are unreactive, to compute a mixing time (t_{mix}), and to show that

$$t_{mix} < t_{re}$$

where t_{re} is the time required for significant O_3 production.

The Gaussian plume formula for a continuous point source is given by (Seinfeld, 1975)

$$c(x,z) = \frac{S}{\pi \sigma_y \sigma_z} \left[\exp(-\frac{z^2}{2\sigma_z^2} + \sum_{n=1}^{\infty} \left\{ \exp(-\frac{(z-2nH)^2}{2\sigma_z^2}) + \exp(-\frac{(z+2nH)^2}{2\sigma_z^2}) \right\} \right]$$

where S = source strength

σ_y = horizontal dispersion coefficient

σ_z = vertical dispersion coefficient

and the other quantities have been previously defined. Tabulated values for pollutant concentration as a function of distance downwind for various points in the vertical can be found in Table A1. Because urban O_3 formation occurs on warm sunny days, the stability class selected was Class B (moderately unstable). In addition, all values in the table are based on a mixing height of 1000m.

Table A1 _Pollutant concentration downwind of a continuous point source

Distance Downwind(km)	Height(m)	σ_y (m)	σ_z (m)	$c(x,z)/c(x,0)$
1	0	175	125	1.
1	500	175	125	3.4×10^{-4}
1	1000	175	125	2.5×10^{-14}
2	0	300	340	1.
2	500	300	340	.34
2	1000	300	340	.03
3	0	420	720	1.
3	500	420	720	.87
3	1000	420	720	.73
4	0	540	1200	1.
4	500	540	1200	1.
4	1000	540	1200	.99

From the table it can be seen that pollutant concentration becomes homogeneous at a distance of about 3 km downwind of the source. This value is the same as that reported by Ragland and Dennis (1975) for the location at which pollutant concentration becomes well mixed downwind of a point source under unstable atmospheric conditions. The basis for their conclusion is a numerical solution of the diffusion equation that accounts for variable wind and diffusivity profiles.

Assuming an average wind speed of 10 km/hr,

$$t_{mix} = 20 \text{ min.}$$

It is well known that the time constant for urban ozone formation is of the order of hours. Thus this calculation indicates that precursors become well mixed before there is time for any significant O_3 production.

Appendix B The effect of data uncertainties upon the regression analysis

The intent of this appendix is to present Monte Carlo simulation results to demonstrate that the effect of uncertainties in the ozone and meteorology data used for the regression analysis is to produce sensitivities significantly smaller than those predicted from theory. To simplify the analysis, it will be assumed that the basic equation relating ozone to meteorology is given by

$$[O_3]_{ur} = [O_3] - [O_3]_b = \frac{K}{V_w^{\alpha}} \tag{B.1}$$

The assumption is that variations in the urban contribution to ozone ($[O_3]_{ur}$) is due solely to variations in wind speed. Computer simulation results presented in Chapter III indicate that

$$\alpha \doteq 2.5$$

and $$K \doteq 1.3$$

if the units of ozone concentration and wind speed are ppm and km/hr respectively.

The basic procedure will be to treat V_w as a random variable and to assume that Eq.(B.1) gives urban O_3 concentration for a particular wind speed. If a data set of values for urban ozone and wind speed is constructed in Monte Carlo fashion, the regression procedure can be used to derive the values assumed for K and α. Adding measurement noise to the data set and repeating the regression procedure will then show the effect of uncertainties in the data upon the regressed values for these two parameters.

An examination of the wind data used in the study indicates an approximate log normal distribution with geometric mean of 9.11 km/hr and geometric standard deviation of .49. An array of 500 wind speed values with these statistical properties was constructed using standard Monte Carlo techniques. Associated ozone concentration were then generated using Eq.(B.1), and Gaussian distributed and uncorrelated noise was added to both the ozone and wind data.

B.1 Error analysis of ozone data

In order to determine the quality of the ozone data, an error analysis was performed on the DEQ monitoring program.

Although a number of different instruments have been used to measure O_3 at Milwaukie, all have been chemiluminescent devices. The primary calibration used by the DEQ is against the neutral buffered KI method. EPA claims that the KI method is good to 4% (1σ); that is, for an ensemble of measurement, 68% would be within 4% of the actual concentration, with 99.5% (3σ) within 12% (Smith, 1973). This seems too optimistic; looking at the DEQ calibration data, it is estimated that 8% accuracy is a more realistic 1σ value. The DEQ makes only one calibration for each setting of the O_3 generator unless they are calibrating a new instrument or there is an obvious discrepancy. If more than one measurement per setting were made and the results averaged, the uncertainty would be something less than that quoted above. Once a number of settings of an O_3 generator have been calibrated, a calibration curve is derived using a linear least square procedure. This procedure is repeated at least every 6 months.

Occasionally a monitor is directly calibrated against KI; however, the usual procedure is to calibrate an O_3 generator with KI and then perform a secondary calibration of the monitor with the generator at some later time. If a secondary calibration is performed, one must worry about generator drift. Both EPA and DEQ feel that 10% (3σ) is a reasonable value for generator drift provided a careful operating procedure is maintained. This value is an average for the interval zero to .25 ppm. Since ambient $[O_3]$ are almost always in the first half of this interval, a 10% uncertainty is too low; therefore, an 18% 3σ uncertainty was assumed. Secondary calibrations are performed about twice per month.

The most frequent checks are those associated with the span and zero modes of the monitor. They are performed about three times per week. The DEQ procedure for changing the span setting depends on the outcome of the check as follows:

$\text{Span drift} \leq 3\%$ - do nothing
$3\% < \text{Span drift} \leq 5\%$ - change span setting
$5\% < \text{Span drift}$ - disregard data

EPA and the DEQ both estimate zero drift to be a significant error source (0.01 ppm as a 3σ uncertainty).

The final error source that must be considered is the data processing error. The DEQ used a data acquisition system that averages reading every 20 sec. to determine an hourly average. The data are also recorded on a strip chart and occasional comparisons are made between automated and manually determined hourly average concentrations. The DEQ estimates that the data processing error is probably less than

.005 ppm for almost all cases. The author has had some experience in determining hourly average concentrations from continuous strip chart recording and would agree with this number. A reasonable 1σ value would thus be .0035 ppm.

The calibration and data processing procedure described above suggests a five term error model. The terms of the model and the associated uncertainties are listed in Table B1. Also listed in the table are estimates for the uncertainties that would be expected for O_3 concentrations of .08 and .16 ppm. If the assumption is made that the error sources are normally distributed and uncorrelated, then the total error would be found by root-sum-squaring the individual errors.

$$\sigma_T = \sqrt{\sum_{i=1}^{5} \sigma_i^2}$$

It appears that a reasonable value for the accuracy of the DEQ data is 12%; that is, 68% of the measurements would be within 12% of the true value while 99.5% would be within 36%. As is the usual case in error analysis work, these estimates are probably low since the listing of error sources is undoubtedly incomplete.

Table B1 Error estimate for ozone data

Error Source	1σ Uncertainty	Uncertainty for $[O_3]$=.08ppm	Uncertainty for $[O_3]$=.16ppm
Primary Calibration	8%	.0065	.0128
Generator Drift	6%	.0048	.0096
Zero Drift	.0033ppm	.0033	.0033
Span Drift	3%	.0024	.0048
Data Processing	.0035 ppm	.0035	.0035
σ_T		.0097 (12.1%)	.0174 (10.9%)

B.2 Monte Carlo simulation results

Monte Carlo simulation results are summarized in Table B2 which gives estimated values for the exponent ($\hat{\alpha}$) as a function of data quality. The ratio of 1σ values for the uncertainties in the ozone and wind data was set to .0067 ppm/km/hr as a rough measure of the relative quality of the two parameters. As expected, the assumed value was estimated for the error free case. It can also be seen that $\hat{\alpha}$ decreased very quickly with decreased data quality.

Table B2 Monte Carlo simulation results

1σ Uncertainty in $[O_3]_{ur}$ (ppm)	1σ Uncertainty in Wind Speed (km/hr)	$\hat{\alpha}$
0	0	2.50
.01	1.5	1.86
.02	3.0	1.20
.04	6.0	.62

It is estimated that the quality of the data used in the regression analysis roughly corresponds to the third case ($\hat{\alpha} = 1.20$). Uncertainties in calculated values for urban ozone are due to measurement errors in the Milwaukie data, as well as to errors in modeling background ozone. Measurement errors are of the order of .01 to .017 ppm as described above while uncertainties associated with calculated background levels are of the order of .01 ppm (Figure 23). Statistical combination gives an uncertainty of the order of .02 ppm. Uncertainties in the wind speed data are due to instrumentation error and to the fact that only one number was used to characterize wind speed each day. Undoubtedly, better results would have been obtained if data from a number of locations were used to compute an area wide average. It is estimated that 3 km/hr is a reasonable value for the 1σ uncertainties in the wind data.

In summary, these results indicate that the quality of the ozone and wind data have the effect of limiting the results of a sensitivity analysis between the two parameters to a significant extent. The discussion of this appendix ignores the effect of uncertainties in the other parameters in the model, as well as the effect of modeling assumptions. Uncertainties that were ignored include those associated with the determination of mixing height and the time of year effect. The most important modeling assumptions are undoubtedly that the ratios of the emission rates among the precursors are constants, that the overall emission rate is invariant and that the time of day effect can be ignored. All of these assumptions have the effect of adding noise to the total system. Thus it is not surprising that the value of α determined from regression analysis is even smaller than 1.2 as suggested here.

Appendix C Contacts established during investigation of August 1977 photochemical smog episode

A large number of individuals involved in air pollution work in the Pacific Northwest were contacted with the hope of obtaining additional ozone data during the August 1977 episode. The State of Washington Department of Ecology was able to supply data for the Lakewood School and Sumner locations. With this one exception, the search for additional data was unsuccessful. There appears to have been no monitoring in southwest Washington outside of the Southwest Washington APCA site in Vancouver. This fact indicates a serious deficiency in the O_3 monitoring program in this region. It is recommended that an expanded monitoring program be initiated in this area in order to determine the extent of long range transport of anthropogenic O_3 from the Puget Sound area to Northwest Oregon.

A complete list of contacts is as follows:

Name	Organization	City	Phone Number
Pat Thede	Dept. of Ecology	Olympia	206 753-2843
Bob Charlson	University of Washington	Seattle	206 543-2537
Tony George	Oregon Highway Dept.	Salem	503 378-8486
Roy Jones	EPA	Seattle	206 442-1223
Ray Weiss	University of Washington	Seattle	206 543-2044
Duane Goodman	SW Washington APCA	Vancouver	206 753-2827
Ted Phillips	PPL	Portland	503 243-1122

List of contacts (Cont.)

Name	Organization	City	Phone Number
Don Ludwick	Battelle NW	Richland	509 942-3431
Barry Townes	EPA	Seattle	206 442-1106
Jim Miller	Reynolds Metal	Longview	206 425-2800
Walt Wyss	Weyerhaeuser	Longview	206 425-2150
Dr. Hobbs	Atmos. Sciences/UW	Seattle	

Appendix D Computer programs developed in the study

Several computer programs were developed in the course of this study. The formation and transport of ozone in the Portland area was simulated using the program OZONE. The program is an outgrowth of the photochemical smog model developed by Schjoldager (1977). Modification made to the top level executive of the Schjoldager program can be found in this appendix. A listing of the remainder of OZONE can be found in the reference. Also contained in this appendix are listed four programs that constitute the data analysis software package. A functional flowchart for this package with short description of each program can be found in Figure D1. Listing for each program can be found below. Finally, two additional programs were developed. POLY performs least square polynomial regression for two independent variables. It fits data to an equation of the form

$$f(x,y) = a_0 + a_1x + a_2x^2 + a_3y + a_4 xy + a_5 x^2y + a_6y^2 + a_7 xy^2 + a_8 x^2y^2$$

MONTE is the Monte Carlo simulation program that was used to determine the effect of data uncertainties on the regression analysis.

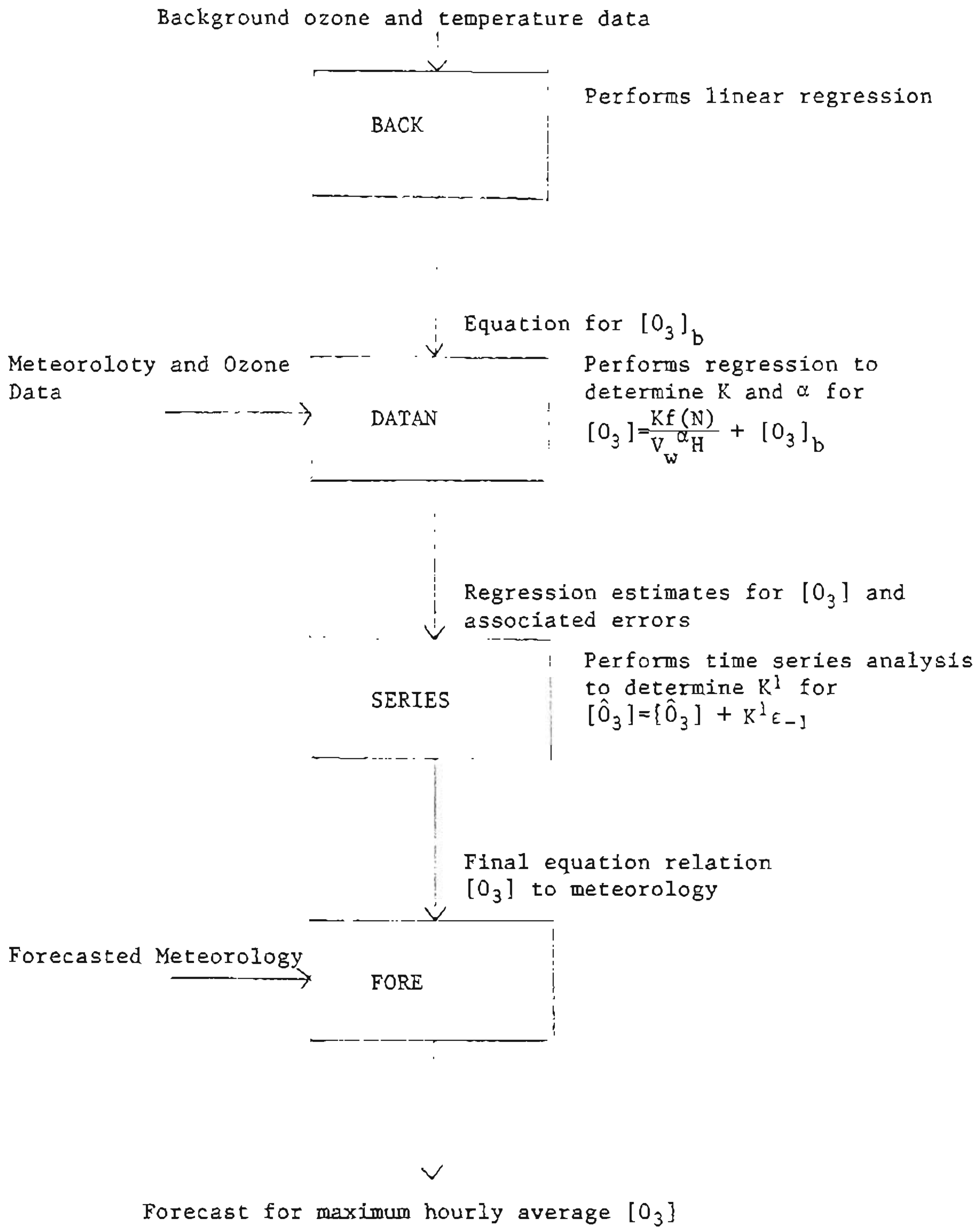

Figure D1 Functional flowchart of data analysis software package

```
C             OZONE


C             OZONE
C   FURTHER MODIFIED 33 STEP HECHT ET AL. PHOTOCHEMICAL MECHANISM
C   REACTIONS NO. 4, 6, 12, 13, 38 AND 39 HAS BEEN ELIMINATED FROM
C   THE ORIGINAL HECHT, SEINFELD AND DODGE MODEL, PUBLISHED IN
C   ENV. SCI. & TECHNOL., VOL. 8, NO. 4, PP. 327-339, (1974)
C
C   THE FOLLOWING RATE CONSTANTS HAVE BEEN UPDATED:
C   1,2,3,5,7,8,9,10,11,14,15,16,17,18,19,20,21,24,28,29,37.
C
C   A MODIFIED HAMMING'S PREDICTOR-CORRECTOR CODE WITH VARIABLE
C   STEP LENGTH IS USED FOR THE INTEGRATION.
C   THE FOLLOWING COMPONENTS ARE STEADY-STATED:
C   O, NO3, HO2, OH, RO, ROO, RCOOO.
C
      DIMENSION Y(13),DERY(13),AUX(16,13),PRMT(5),YIN(13)
      DOUBLE PRECISION Y,DERY,AUX,PRMT,FAC,YIN
      DOUBLE PRECISION DIL, WIN, DTIM, INVHT
      DOUBLE PRECISION ALFA,BETA,C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,
     &    C13,C14,C15,C16,C17,C18,C19,C20,C21,C22,C23,C24,C25,C26,C27,
     &    C28,C29,C30,C31,C32,C33,C34,C35,C36,C37,C38,C39
      COMMON ALFA,BETA,C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,C13,C14,
     &    C15,C16,C17,C18,C19,C20,C21,C22,C23,C24,C25,C26,C27,C28,
     &    C29,C30,C31,C32,C33,C34,C35,C36,C37,C38,C39
      DOUBLE PRECISION O, NO3, HO2, OH, RO, ROO, RCOOO
      COMMON /ST/ IOUT, O, NO3, HO2, OH, RO, ROO, RCOOO
      COMMON /OUT/ STEP, DSTEP, TINT
      DOUBLE PRECISION O2,M,H2O
      COMMON /CON/ ISW,IFLAG, N
      COMMON /LYS/ AZEN,BZEN,TSTART,RAD,FACT,OZONEC
      EXTERNAL FCT, OUTP
C
C   VALIDATION VALUES FOR RATE CONSTANTS AND STOCHIOMETRIC COEFFICIENTS.
C   STOCHIOMETRIC COEFFICIENTS ARE FOR PROPYLENE/N-BUTHANE
C
      DATA C1,C2,C3,C4,C5/0.26600,2.1D-5,25.200,3.5D-3,1.34D+4/,
     &    C6,C7,C8,C9,C10/2.2D-3,5.0D-2,1.3D+4,5.6D+3,2.4D+1/,
     &    C11,C12,C13,C14,C15/5.0D-6,2.5D-4,0.200,2.2D-9,1.3D-3/,
     &    C16,C17,C18,C19,C20/1.3D-2,9.2D+3,9.0D+3,2.1D+2,2.0D+3/,
     &    C21,C22,C23,C24,C25/1.864D-3,6.8D+3,1.6D-2,4.2D+4,1.07D+2/,
     &    C26,C27,C28,C29,C30/8.0D+3,6.5D+1,4.3D+3,2.5D-3,2.3D+4/,
     &    C31,C32,C33,C34,C35/9.1D+2,9.1D+2,1.0D+2,2.4D-2,4.9D+2/,
     &    C36,C37,C38,C39/2.5D+2,4.0D+3,1.0D+2,1.0D+2/
      DATA ALFA,BETA/0.500,0.6300/
C
      DATA O2,M,H2O/20.9D+4,1.0D+6,20.0D+3/
      DATA PI/3.141592653/, AVOGAD/6.024E+23/
C
      FACT = 2.303 * 1000.0 * 60.0 / AVOGAD
      RAD = PI / 180.0
      TINT = -1.0
      STEP = 0.0
C
C   CONTROL PARAMETERS AND INITIALIZATION.
      INVHT =15.00D0
      WIN = 4.0D0
      DIL = 2.333
```

```
C              OZONE


      DTIM = 48.0D0/WIN
C
      NDIM = 13
      DSTEP =  5.0
      PRMT(1) = 0.0D0
      PRMT(2) = DTIM
      PRMT(3) = 0.1D0
      PRMT(4) = 0.001D0
      TTOT = 48*DTIM
C
      AMONTH = 6.0
      XLAT = 45.5
      TSTART =10.00
      TIMIL = TSTART+1.2+.333*DTIM
C
      XDIM = NDIM
      DO 4 I = 1,NDIM
      DERY(I) = 1.0D0/XDIM
      YIN(I) = 0.0D0
    4 Y(I) = 0.0D0
C
C  MULTIPLICATION OF RATE CONSTANTS BY CONSTANT CONCENTRATIONS.
C
      C2 = C2 * O2 * M
      C4 = C4 * M
      C6 = C6 * M
      C11 = C11 * H2O
      C14 = C14 * H2O
      C34 = C34 * O2
C
C  CALCULATION OF DECLINATION (DEC) AND ATMOSPHERIC OZONE CONTENT
C  (OZONEC) AS A FUNCTION OF MONTH (AMONTH).
C
      DEC = 23.5 * SIN((30.0*AMONTH-90.0)*RAD)
      DEC = DEC*RAD
      CALL TOZONE(XLAT,AMONTH,OZONEC,RAD)
      XLAT = XLAT * RAD
      AZEN = COS(XLAT) * COS(DEC)
      BZEN = SIN(XLAT) * SIN(DEC)
C
C  ASSIGNMENT OF INITIAL CONCENTRATIONS
C  BACKGROUND CONCENTRATIONS ASSUMING PHOTOSTATIONARY STATE
C  BACKGROUND O3 DEPENDS ON TIME OF DAY
      CALL PHOTO(0)
      Y(1) = .02D0*(1.0D0+ SIN(.2244*TSTART-1.5708))
      Y(3) = .00667D0
      Y(2) = C1*Y(3)/(Y(1)*C3)
      Y(9) =  .00370D0
      Y(11) = .0112D0
      YIN(3) = .00667D0
C
C
      CALL SEARCH(2,'OUTPUT',2,0)
      WRITE(6,2101) INVHT, DIL, WIN, AMONTH, TIMIL
      WRITE(1,2101) INVHT, DIL, WIN, AMONTH, TIMIL
      WRITE(6,2102)
```

```
C              OZONE


      DO 100 J=1,40
      CALL DHPCG(PRMT,Y,DERY,NDIM,IHLF,FCT,OUTP,AUX)
C   DILUTION
      A=1+(DIL-1)*PRMT(2)/TTOT
      B=1+(DIL-1)*(PRMT(2)-DTIM)/TTOT
      FAC=A/B
      WRITE(1,2100) J,Y(1),FAC,YIN(1)
      X1=PRMT(2)
      YIN(1)= .020D0*(1.0D0+SIN(.2244*(TSTART + X1   /60)-1.5708))
      YIN(2)=C1*YIN(3)/(YIN(1)*C3)
      DO 9 I=1,NDIM
      Y(I)=(Y(I)+(FAC-1)*YIN(I))/FAC
    9 DERY(I)=1.0D0/XDIM
C   FRESH EMISSIONS
      IF (J.GT.10) GO TO 60
      GO TO (10,15,20,25,30,35,40,45,50,55),J
   10 FRESH=.032D0
      GO TO 92
   15 FRESH=.047D0
      GO TO 92
   20 FRESH=.072D0
      GO TO 92
   25 FRESH=.082D0
      GO TO 92
   30 FRESH= .036D0
      GO TO 92
   35 FRESH=.091D0
      GO TO 92
   40 FRESH=.094D0
      GO TO 92
   45 FRESH=.101D0
      GO TO 92
   50 FRESH=.154D0
      GO TO 92
   55 FRESH=.241D0
      GO TO 92
   60 IF (J.GT.20) GO TO 95
   70 GO TO (72,74,76,78,80,82,84,86,88,90),J-10
   72 FRESH= .215D0
      GO TO 92
   74 FRESH= .154D0
      GO TO 92
   76 FRESH=.116D0
      GO TO 92
   78 FRESH=.116D0
      GO TO 92
   80 FRESH=.135D0
      GO TO 92
   82 FRESH=.117D0
      GO TO 92
   84 FRESH=.078D0
      GO TO 92
   86 FRESH=.033D0
      GO TO 92
   88 FRESH=.025D0
      GO TO 92
```

```
C                 OZONE


   90 FRESH= 819D0
   92 DILF=WIN*A*INVHT
      Y(2)=Y(2)+FRESH*4 50D0/DILF
      Y(3)=Y(3)+FRESH*1.58D0/DILF
      Y(9)=Y(9)-FRESH*3.37D0/DILF
      Y(11)=Y(11)+FRESH*10.12D0/DILF
   95 PRMT(2)=PRMT(2)+DTIM
      PRMT(1)=PRMT(1)+DTIM
  100 PRMT(3)=0.1D0
      WRITE(6,2000) IHLF
 2000 FORMAT(1H ,5X,5HIHLF=,I2)
 2100 FORMAT(I2,5X,D13.4,5X,D13.4,5X,D13.4)
 2101 FORMAT(15HIHIT. INV. HT.=,D10.3,2X,4HDIL=,F5.2,2X,5HWIND=,D10 3,
     &    2X,6HMONTH=,I2,2X,7HTIMIL =,F6.2)
 2102 FORMAT(1H )
      CALL SEARCH(4,8,2,0)
      CALL EXIT
      END
```

```
C          BACK


C          BACK
C  THIS PROGRAM PERFORMS A LINEAR REGRESSION ON BACKGROUND OZONE DATA
      REAL MAXT

      DIMENSION DAY(114),HT(114),MAXT(114),OZE(114),WIND(114),OZEB(114)
      CALL SEARCH(3,'OUTPUT',2,0)
      CALL SEARCH(3,'DATA77',1,0)
      CALL SEARCH(3,'DATA76',3,0)
      M=114
      DO 50 I=1,62
      READ(7,500) DAY(I),MAXT(I),OZEB(I)
50    CONTINUE
      DO 60 I=63,M
      READ(5,510) DAY(I),HT(I),MAXT(I),OZE(I),WIND(I),OZEB(I)
60    CONTINUE
      DO 100 I=1,M
      IF(OZEB(I).LT.1.) GO TO 100
      WK=(DAY(I)-33.)/7.
      OZEB(I)=OZEB(I)/(.8942+WK*(.02766-.0018*WK))
      IF(DAY(I)-106.) 70,70,75
70    NOTEMP=58.1+DAY(I)*(.1610+.0034*DAY(I))
      GO TO 80
75    NOTEMP=53.6+DAY(I)*(.4871-.00218*DAY(I))
80    NOTEMP= 0
      TEMP1=.5555*(MAXT(I)-NOTEMP)
      TEMP9=TEMP9+TEMP1
      TEMP2=TEMP2+TEMP1*TEMP1
      TEMP3=OZEB(I)/2000
      TEMP4=TEMP4+TEMP3*TEMP1
      TEMP7=TEMP7+TEMP3*TEMP3
      TEMP5=TEMP5+TEMP3
      TEMP10=TEMP10+1
      WRITE(6,530) TEMP1,TEMP3
100   CONTINUE
      TEMP6=TEMP9*TEMP9-TEMP2*TEMP10
      SLO=(TEMP9*TEMP5-TEMP10*TEMP4)/TEMP6
      CONST=(TEMP9*TEMP4-TEMP2*TEMP5)/TEMP6
      R2=-SLO*(TEMP9*TEMP5-TEMP10*TEMP4)/(TEMP7*TEMP10-TEMP5*TEMP5)
      WRITE(6,520) SLO,CONST,R2
      CALL SEARCH(4,0,1,0)
      CALL SEARCH(4,0,2,0)
      CALL SEARCH(4,0,3,0)
500   FORMAT(F4.0,1X,F3.0,1X,F4.0)
510   FORMAT(F4.0,1X,F3.0,1X,2(F4.0,1X),F3.1,1X,F4.0)
520   FORMAT(6HSLOPE=,F8.5,5X,9HCONSTANT=,F8.5,5X,3HR2=,F7.4)
530   FORMAT(F6.2,5X,F6.4)
      CALL EXIT
      END
```

```
C          DATAN


C          DATAN
C  THIS PORTION OF THE PROGRAM COMPUTES LEAST SQUARE VALUES FOR
C  THE CONSTANT(CON) AND EXPONENT(ALF) FOR THE TRANSPORT WIND
      REAL   M0,M1,M2,M3,M4,M5,M6,M7,M8,M9
      DIMENSION WD(80),HT(80),WK(80),OZONE(80)
      DIMENSION OZE(80),WINDD(90),OZCAL(80)
      DIMENSION OZPOR(80),DEG(90),BACK(80)
      DIMENSION DAY(80),WINDCA(80),DIRWD(80)
      DATA DELHT,DELOZ,DELWIN,DELBAC/100.,.12,2.,.0075/
C  INITIALIZATION
      L=1
      M=0
      N=80
      DALF=-.01
      DCON=.4
C
      CALL SEARCH(2,'OUTPUT',2,0)
      CALL SEARCH(1,'DATACA',3,0)
      CALL SEARCH(2,'RESIDA',1,0)
      WRITE(6,1001)
      DO 2 I=1,N
      READ(7,985) DAY(I),HT(I),DEG(I),OZONE(I),WD(I),BACK(I),
     1  WINDCA(I),DIRWD(I)
      WK(I)=(DAY(I)-30.)/7.
      HT(I)=HT(I)/3.28
2     CONTINUE
      DO 40 I=L,N
      BACK(I)=BACK(I)/2000.
      FWEEK=-.0018*WK(I)*WK(I)+.02766*WK(I)+.8942
      WINDD(I)=3.600*WD(I)
      IF(WINDD(I).LT.3.6) WINDD(I)=3.6
      IF(BACK(I).GT..001) GO TO 8
      IF(DAY(I)-106.) 4,4,6
4     NOTEMP=58.1+DAY(I)*(.1618+.0004*DAY(I))
      GO TO 7
6     NOTEMP=53.6+DAY(I)*(.4871-.00218*DAY(I))
7     BACK(I)=FWEEK*(.0362+.00136*(DEG(I)-NOTEMP))
8     OZE(I)=OZONE(I)*.0005
      HT(I)=100*HT(I)
      IF (HT(I).GT.1000) HT(I)=1000
      X1=OZE(I)-1.0*BACK(I)
      OZPOR(I)=X1/FWEEK
      TEMP0=OZPOR(I)
      IF (TEMP0.LT..001) GO TO 40
      IF(TEMP0.GT..01) GO TO 10
      M0=M0+1
      GO TO 40
10    IF(TEMP0.GT..02) GO TO 15
      M1=M1+1
      GO TO 40
15    IF(TEMP0.GT..03) GO TO 20
      M2=M2+1
      GO TO 40
20    IF(TEMP0.GT..04) GO TO 25
      M3=M3+1
      GO TO 40
```

```
C            DATAN


25     IF(TEMP0.GT..05) GO TO 30
       M4=M4+1
       GO TO 48
30     IF(TEMP0.GT..06) GO TO 35
       M5=M5+1
       GO TO 48
35     IF(TEMP0.GT..07) GO TO 40
       M6=M6+1
       GO TO 48
40     IF(TEMP0.GT..08) GO TO 42
       M7=M7+1
       GO TO 48
42     IF(TEMP0.GT..09) GO TO 48
       M8=M8+1
48     CONTINUE
       WRITE(6,995) M0,M1,M2,M3,M4
       WRITE(6,995) M5,M6,M7,M8,M9
       WRITE(6,1002)
       WRITE(6,1006)
       DO 100 I=L,N
       IF(OZPOR(I).LT..001) GO TO 90
       WRITE(6,1004) OZPOR(I),HT(I), OZE(I),I
       TOTOZ=TOTOZ+OZE(I)
       TTEMP=TTEMP+DEG(I)
       TEMP1=ALOG(WINOD(I))
       TEMP9=TEMP9+TEMP1
       TEMP2=TEMP2+TEMP1*TEMP1
       TEMP3=ALOG(HT(I)*OZPOR(I))
       TEMP4=TEMP4+TEMP3*TEMP1
       TEMP7=TEMP7+TEMP3*TEMP3
       TEMP5=TEMP5+TEMP3
       TEMP10=TEMP10+1.
       GO TO 100
90     TOTOZ=TOTOZ+OZE(I)
       TTEMP=TTEMP+DEG(I)
       WRITE(6,990)
100    CONTINUE
C    THIS PORTION COMPUTES INITIAL VALUES FOR ALF AND CON
       AVEOZ=TOTOZ/(N-M-L+1)
       AVTEMP=TTEMP/(N-M-L+1)
       TEMP6=TEMP9*TEMP9-TEMP2*TEMP10
       ALF=(TEMP9*TEMP5-TEMP10*TEMP4)/TEMP6
       TEMP8=(TEMP9*TEMP4-TEMP2*TEMP5)/TEMP6
       CON=EXP(TEMP8)
       WRITE(1,1010) ALF,CON,R
       WRITE(6,1006)
       WRITE(6,1010)ALF,CON,R
       WRITE(6,1020)
       DO 200 I=L,N
       SCATOZ=SCATOZ+(OZE(I)-AVEOZ)**2
       COVAR=(OZE(I)-AVEOZ)*(DEG(I)-AVTEMP)+COVAR
       VART=VART+(DEG(I)-AVTEMP)**2
       CALL EVAL(ALF ,CON,WK(I),WINDD(I),OZE(I),RES,HT(I),
      1  BACK(I))
       CHI2=CHI2+RES*RES
200    CONTINUE
```

```
C           DATAH


      SCATOZ=SQRT(SCATOZ/(N-M-L+1))
      SMOOZ=SQRT(CHI2/(N-M-L+1))
      COVAR=COVAR/(N-M-L+1)
      VART=SQRT(VART/(N-M-L+1))
      R=COVAR/(VART*SCATOZ)
      WRITE(6,1040) AVEOZ,SCATOZ,SMOOZ ,SUMRES
      WRITE(6,1045)SUMRES,R
C   THIS PORTION COMPUTES FINAL VALUES USING A STEEPEST DECENT METHOD
      ALF1=ALF+DALF
      CON1=CON+DCON
      DO 500 J=1,5
      CHI3=0.
      CHI4=0
      DO 300 I=L,N
      CALL EVAL(ALF1,CON,WK(I),WINDO(I),OZE(I),RES,HT(I),
     &  BACK(I))
      CHI3=CHI3+RES*RES
      CALL EVAL(ALF,CON1,WK(I),WINDO(I),OZE(I),RES,HT(I),
     &  BACK(I))
      CHI4=CHI4+RES*RES
300   CONTINUE
      DCHI3=(CHI3-CHI2)/DALF
      DCHI4=(CHI4-CHI2)/DCON
      TEMP=(DCHI3*DALF)**2+(DCHI4*DCON)**2
      DELALF=-DCHI3*DALF*DALF/SQRT(TEMP)
      DELCON=-DCHI4*DCON*DCON/SQRT(TEMP)
      ALF=ALF+DELALF
      CON=CON+DELCON
      DCON=.5*DELCON
      DALF=.5*DELALF
      CHI0=.0
      CHI2=0.
      OZCALT=0.
      DO 400 I=L,N
      CALL EVAL(ALF ,CON,WK(I),WINDO(I),OZE(I),RES,HT(I),
     &  BACK(I))
      CHI2=CHI2+RES*RES
      CHI0=CHI0+RES*RES
      OZCALT=OZCALT+RES*OZE(I)
400   CONTINUE
      SMOOZ=SQRT(CHI0/(N-M-L+1))
      OZCALT=OZCALT/(N-M-L+1)
      WRITE(6,1810) ALF,CON,SMOOZ
      WRITE(1,1810) ALF,CON,SMOOZ
500   CONTINUE
      WRITE(6,1055)
      CHI0=0
      DO 550 I=L,N
      CALL EVAL(ALF ,CON,WK(I),WINDO(I),OZE(I),RES,HT(I),
     &  BACK(I))
530   OZCAL(I)=OZE(I)-RES
      CHI0=CHI0+RES*RES
      SUMRES=SUMRES+RES
      WRITE(6,1260) RES,OZE(I),OZCAL(I),I,DAY(I)
      WRITE(5,1290) RES,OZE(I)
550   CONTINUE
```

```
C           DATAN


      SUMRES=SUMRES/(N-M-L+1)
      SMOOZ=SQRT(CHI0/(N-M-L+1))
      DO 570 I=L,N
      TEMRES=TEMRES+(DEG(I)-AVTEMP)*(OZCAL(I)-OZE(I)-SUMRES)
570   CONTINUE
      TEMRES=TEMRES/(N-M-L+1)
      R=TEMRES/(VART*SMOOZ)
      WRITE(1,1010) ALF,CON,SMOOZ
      WRITE(6,1010) ALF,CON,SMOOZ
      WRITE(6,1045)SUMRES,R
985   FORMAT(F4.0,1X,F3.0,1X,2(F4.0,1X),F3.1,1X,F4.0,1X,F3.1,1X,F3.0)
990   FORMAT(39HOZONE CONCENTRATION AT BACKGROUND LEVEL)
995   FORMAT(5(F7.4,3X))
999   FORMAT(4(5X,F7.4))
1000  FORMAT(5X,F5.4,5X,F7.4,5X,F7.6)
1001  FORMAT(22HFREQUENCY DISTRIBUTION)
1002  FORMAT(33H        OZONE FROM PORT  INV HT.    OZONE)
1004  FORMAT(7X,F7.4,9X,F6.1,3X,F6.4,3X,I3)
1006  FORMAT(1H.)
1010  FORMAT(6HALPHA=,F6.3,5X,9HCONSTANT=,F7.3,5X,12HRESIDUAL SD=,F10.7)
1020  FORMAT(15HNO.      RESIDUAL)
1030  FORMAT(I3,5X,F7.4)
1040  FORMAT(11HAVE  OZONE=,F6.4,3X,9HVARIENCE=,F6.4,
     &    3X,23HSTD. DEV. OF RESIDUALS=,F6.4,3X,7HAV.RES=,F6.4)
1045  FORMAT(9HAVE. RES=,F7.4,3X,13HCOR. OZ.TEMP=,F6.3)
1055  FORMAT(35HRESIDUALS MEASURED O3 CALCULATED O3)
1060  FORMAT(3(F7.4,4X),I3,3X,F5.0)
1200  FORMAT(F7.4,4X,F7.4)
      CALL SEARCH(4,0,3,0)
      CALL SEARCH(4,0,2,0)
      CALL SEARCH(4,0,1,0)
      CALL EXIT
      END
C
C
      SUBROUTINE EVAL(ALF,CON    ,WK    ,WINDD       ,
     &  OZE    ,RES,HT,BACK)
      FWEEK=-.0018*WK    *WK    +.02766*WK    +.8942
      TEMP=HT               *WINDD    **(-ALF)
      RES=FWEEK*CON/TEMP+1.0*BACK-OZE
      RETURN
      END
```

```
C          SERIES


C          SERIES
C   THIS PROGRAM PERFORMS TIME SERIES ANALYSIS AS
C   FORMULATED BY BOX AND JENKINS
      DIMENSION RES(80),OZE(80),DAYBAC(80),OZCAL(80),RESP(80)
      DIMENSION RESPP(80),DAY(80)
      INTEGER DAYBAC,DAY
C   INITIALIZATION
      PHI1=-.2
      M=50
      DAYBAC(I)=100
      CALL SEARCH(3,'DATACA',3,0)
      CALL SEARCH(3,'OUTPUT',2,0)
      CALL SEARCH(3,'RESIDA',1,0)
      DO 50 I=1,M
      READ(5,500) RES(I), OZE(I)
      READ(7,510) DAY(I),TEMP,TEMP,TEMP,TEMP,TEMP,TEMP,TEMP
      RESP(I)=0.
      IF(I.EQ.1) GO TO 50
      DAYBAC(I)=DAY(I)-DAY(I-1)
50    CONTINUE
      CALL COMPR(OZE,RES,M,AVRES)
      CALL AUCOR(RES,AVRES)
      WRITE(6,535)
      CALL CONCOR(DAYBAC,M,OZE,RES,RESP,PHI1,RESPP)
      CALL AUCOR(RESPP,AVRES)
      WRITE(6,535)
      CALL SEARCH(4,0,2,0)
      CALL SEARCH(4,0,1,0)
500   FORMAT(F7.4,4X,F7.4)
505   FORMAT(F8.4)
510   FORMAT(I3,2X,F3.0,1X,2(F4.0,1X),F3.1,1X,F4.0,1X,F3.1,1X,F3.0)
535   FORMAT(28HST.DEV.    AUTOCOR1  AUTOCOR2)
      CALL EXIT
      END
C
      SUBROUTINE COMPR(OZE,RES,M,AVRES)
      DIMENSION OZE(80),RES(80)
      AVRES=.0
      AVOZE=.0
      VARX=.0
      VARY=.0
      VARXY=.0
      DO 50 I=1,M
      AVRES=AVRES+RES(I)
      AVOZE=AVOZE+OZE(I)
50    CONTINUE
      AVRES=AVRES/M
      AVOZE=AVOZE/M
      A=AVRES+AVOZE
      DO 100 I=1,M
      VARX=VARX+(OZE(I)-AVOZE)**2
      VARY=VARY+(OZE(I)+RES(I)-A)**2
      VARXY=VARXY+(OZE(I)-AVOZE)*(OZE(I)+RES(I)-A)
100   CONTINUE
      SIGX=SQRT(VARX/M)
      SIGY=SQRT(VARY/M)
```

```
C          SERIES


      R=VARXY/(SIGX*SIGY*M)
      WRITE(6,500) SIGX,SIGY,R
      WRITE(6,510) AVRES,AVOZE
500   FORMAT(15HSIGMA O3 MEAS.=,F7.4,2X,15HSIGMA O3 CALC.=F7.4,2X,
     1  2HR=,F7.4)
510   FORMAT(F7.4,2X,F7.4)
      RETURN
      END
C
      SUBROUTINE AUCOR(RES,AVRES)
      DIMENSION RES(80)
      SUMN=0.0
      SUMC1=0.0
      SUMC2=0.0
      SUMVAR=0.0
      CALL AUTO( 3,4,RES,AVRES,C1,C2,VAR,N)
      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      CALL AUTO(13,14,RES,AVRES,C1,C2,VAR,N)
      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      CALL AUTO(16,19,RES,AVRES,C1,C2,VAR,N)
      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      CALL AUTO(21,26,RES,AVRES,C1,C2,VAR,N)
      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      CALL AUTO(37,38,RES,AVRES,C1,C2,VAR,N)
      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      CALL AUTO(40,43,RES,AVRES,C1,C2,VAR,N)
      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      CALL AUTO(45,46,RES,AVRES,C1,C2,VAR,N)
      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      CALL AUTO(48,50,RES,AVRES,C1,C2,VAR,N)
      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      CALL AUTO(57,60,RES,AVRES,C1,C2,VAR,N)
```

```
C          SERIES


      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      CALL AUTO(62,74,RES,AVRES,C1,C2,VAR,N)
      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      CALL AUTO(77,80,RES,AVRES,C1,C2,VAR,N)
      SUMC1=SUMC1+C1
      SUMC2=SUMC2+C2
      SUMVAR=SUMVAR+VAR
      SUMN=SUMN+N
      A1=SUMC1/SUMVAR
      A2=SUMC2/SUMVAR
      SIG=SQRT(SUMVAR/SUMN)
      WRITE(6,520) SIG,A1,A2,SUMN
520   FORMAT(3(F7.4,3X),I3)
      RETURN
      END
C
C
      SUBROUTINE AUTO(K,L,RES,AVRES,C1,C2,VAR,N)
      DIMENSION RES(80)
      INTEGER K,L
      VAR=0.
      C1=0.0
      C2=0.
      N=0
      DO 50 I=K,L
      N=N+1
      VAR=VAR+(RES(I)-AVRES)**2
      C1=C1+(RES(I)-AVRES)*(RES(I-1)-AVRES)
      IF(I-K) 10,10,20
10    C2=C2-(RES(I)-AVRES)*AVRES
      GO TO 50
20    C2=C2+(RES(I)-AVRES)*(RES(I-2)-AVRES)
50    CONTINUE
      A1=C1/VAR
      A2=C2/VAR
      SIG=SQRT(VAR/N)
      WRITE(6,520) SIG,A1,A2,N
520   FORMAT(3(F7.4,3X),I3)
      RETURN
      END
C
C
      SUBROUTINE COMCOR(DAYBAC,M,OZE,RES,RESP,PHI1,RESPP)
      DIMENSION RES(80),OZE(80),DAYBAC(80),OZCAL(80),RESP(81)
      DIMENSION RESPP(80)
      INTEGER DAYBAC
      DELK= 05
      WRITE(6,540)
      DO 200 J=1,10
      DO 100 I=1,M
```

```
C          SERIES


      IF(DAYBAC(I).GE.3) GO TO 90
      IF(DAYBAC(I).LT.0) GO TO 90
      OZCAL(I)=OZE(I)+RES(I)+PHI1*RESP(I-1)
      RESP(I)  =OZCAL(I)-OZE(I)
      RESPP(I)=RESP(I)
      RESP(I-1)=0.0
      A=A+RESP(I)**2
      IF(J.LT.10)GO TO 100
      WRITE(6,530) RESP(I)  ,OZCAL(I),I
      GO TO 100
90    A=A+RES(I)**2
      RESPP(I)=RES(I)
      RESP(I)=RES(I)
      IF(J.LT.10)GO TO 100
      OZCAL(I)=OZE(I)+RES(I)
      WRITE(6,530) RES(I),OZCAL(I),I
100   CONTINUE
      V=SQRT(A/M)
      WRITE(6,510) V,PHI1
      DO 190 I=1,M
      IF(DAYBAC(I).GE.3) GO TO 150
      IF(DAYBAC(I).LT.0) GO TO 150
      OZCAL(I)=OZE(I)+RES(I)+(PHI1+DELK)*RESP(I-1)
      RESP(I)  =OZCAL(I)-OZE(I)
      RESP(I-1)=0.0
      B=B+RESP(I)**2
      GO TO 190
150   B=B+RES(I)**2
      RESP(I)=RES(I)
190   CONTINUE
      PAR=(A-B)/DELK
      PHI1=PHI1+SIGN(DELK,PAR)
      DELK=.5*DELK
      A=0.0
      B=0.0
200   CONTINUE
510   FORMAT(8HST DEV =,F9.6,3X,9HCONSTANT=,F7.4)
530   FORMAT(2(F7.4,3X),3X,I3)
540   FORMAT(17HRESIDUALS  CAL.O3)
      RETURN
      END
```

```
C        FORE
C  THIS PROGRAM FORECASTS OZONE CONCENTRATIONS FROM METEOROLOGY
C  DATA  (TIME OF TEMP, INVERSION HEIGHT, MAX  TEMPERATURE, WIND SPEED)
C       INITIALIZATION
        REAL MAXT
        DIMENSION HT(52),OZE(52),WIND(52),DAY(52),MAXT(52)
        DIMENSION OZEP(52),ERR(52),OZEB(52),OZEBP(53)
        DATA E1,E2,E3/.00214    ,.000025,.01060/
        DATA DELHT,DELV/30.,2./
        DATA CON,ALF/160.3,.704/
        CALL SEARCH(3,'OUTPUT',2,0)
        CALL SEARCH(3,'DATA77',1,0)
        M=52
        DO 50 I=1,M
        READ(5,500) DAY(I),HT(I),MAXT(I),OZE(I),WIND(I),OZEB(I)
50      CONTINUE
        WRITE(6,490)
        DO 100 I=1,M
        TEMP1=(DAY(I)-30)/7
        FWEEK=-.0010*TEMP1**2+.02766*TEMP1-.3942
        IF(OZEB(I).GT.1.) GO TO 60
        IF(DAY(I).LT.40) MAXT(I)=MAXT(I)+5
        OZEB(I)=FWEEK*(.00165*MAXT(I)-.092)
        GO TO 65
60      OZEB(I)= OZEB(I)/2000.
65      WIND(I)=2.30*WIND(I)
        IF(WIND(I).LT.3.60) WIND(I)=3.60
        HT(I)=30.48*HT(I)
        IF(HT(I).GT.1000. ) HT(I)=1000
        OZE(I)=OZE(I)*.0005
        TEMP2=HT(I)*WIND(I)**ALF
        OZEP(I)=FWEEK*(EXP(CON  /TEMP2)-1)+OZEB(I)
        IF(I.LT.2) GO TO 70
70      TEMP3=(OZEP(I)-OZEB(I))**2
        TEMP4=(DELHT/HT(I))**2+(ALF*DELV/WIND(I))**2
        TEMP5=SQRT(E1                    +TEMP3*TEMP4)
        ERR(I)=OZEP(I)-OZE(I)
        TEMP3=SQRT(    E2+E3*OZE(I)**2)
        WRITE(6,510) OZEP(I),TEMP5,OZE(I),TEMP3,ERR(I),DAY(I)
100     CONTINUE
        DO 150 I=1,M
        TERR=TERR+ERR(I)
        OZET=OZET+OZE(I)
150     CONTINUE
        AVERR=TERR/M
        AVOZE=OZET/M
        DO 200 I=1,M
        VAR=VAR+(ERR(I)-AVERR)**2
        VAROZ=VAROZ+(OZE(I)-AVOZE)**2
200     CONTINUE
        SDT=SQRT(VAR/M)
        SDOZ=SQRT(VAROZ/M)
        WRITE(6,520)
        WRITE(6,530) AVOZE,SDOZ,AVERR,SDT
        CALL EXIT
490     FORMAT(55HPREDICTED O3  UNCERTAINTY MEAS  O3   UNCERTAINTY     ERR)
500     FORMAT(F4.0,1X,F3.0,1X,2(F4.0,1X),F3.1,1X,F4.0)
510     FORMAT(2X,5(F7.4,5X),F4.0)
520     FORMAT(46HAVERAGE O3    STD DEV.    AVE. ERROR   STD  DEV.)
530     FORMAT(2X,F7.4,3(5X,F7.4))
        END
```

```
C          MONTE


C          MONTE
C  THIS PROGRAM  CHECKS THE EFFECT OF NOISE ON THE REGRESSION
C  ANALYSIS USING A MONTE CARLO APPROACH
      DIMENSION VW(500),OZ(500),ERRV(500),ERROZ(500)
      DATA E1,E2/1.5,.02000/
      CALL SEARCH(2,'OUTPUT',2,0)
      N=500
      CALL GAUSS(2.000,12,51,-.26,.26,N,VW)
      DO 50 I=1,N
      VW(I)=EXP(VW(I))
      OZ(I)=1.300*VW(I)**-2.5
50    CONTINUE
      CALL STAT(N,VW,VBAR,VVAR)
      CALL STAT(N,OZ,OZBAR,OZVAR)
      CALL REGRES(N,VW,OZ,CON,ALF)
C  NOW ADD NOISE
      E1=E1/2
      E2=E2/2
      CALL GAUSS(0,12,53,-E1,E1,N,ERRV)
      CALL GAUSS(0,12,57,-E2,E2,N,ERROZ)
      CALL STAT(N,ERRV,EVBAR,EVVAR)
      CALL STAT(N,ERROZ,EOZBAR,EOZVAR)
      CALL COR(N,VW,ERRV,VBAR,VVAR,EVBAR,EVVAR)
      CALL COR(N,VW,ERROZ,VBAR,VVAR,EOZBAR,EOZVAR)
      DO 100 I=1,N
      VW(I)=VW(I)+ERRV(I)
      IF(VW(I).LT.3.6) VW(I)=3.6
      OZ(I)=OZ(I)+ERROZ(I)
      IF(OZ(I).LT..001)OZ(I)=.001
100   CONTINUE
      CALL STAT(N,VW,VBAR,VVAR)
      CALL STAT(N,OZ,OZBAR,OZVAR)
      CALL REGRES(N,VW,OZ,CON,ALF)
      CALL SEARCH(4,0,2,0)
      CALL EXIT
      END
C
C
      SUBROUTINE STAT(J,XG,MEAN,VAR)
      DIMENSION XG(J)
      REAL MEAN
      TEMP=0
      DO 1 I=1,J
1     TEMP=TEMP+XG(I)
      MEAN=TEMP/J
      TEMP=0
      DO 5 I=1,J
5     TEMP=TEMP+(XG(I)-MEAN)**2
      VAR=SQRT(TEMP/J)
      WRITE(6,500) MEAN,VAR
500   FORMAT(F9.5,5X,F9.5)
      RETURN
      END
C
C
      SUBROUTINE REGRES(N,WIND,OZPOR,CON,ALF)
```

```
C          MONTE


       DIMENSION WIND(N),OZPOR(N)
       TEMP9=0
       TEMP2=0
       TEMP4=0
       TEMP7=0
       TEMP5=0
       TEMP10=0
       DO 1 I=1,N
       TEMP1=ALOG(WIND(I))
       TEMP9=TEMP9+TEMP1
       TEMP2=TEMP2+TEMP1*TEMP1
       TEMP3=ALOG(OZPOR(I))
       TEMP4=TEMP4+TEMP3*TEMP1
       TEMP7=TEMP7+TEMP3*TEMP3
       TEMP5=TEMP5+TEMP3
1      TEMP10=TEMP10+1
       TEMP6=TEMP9*TEMP9-TEMP2*TEMP10
       ALF=(TEMP9*TEMP5-TEMP10*TEMP4)/TEMP6
       TEMP8=(TEMP9*TEMP4-TEMP2*TEMP5)/TEMP6
       CON=EXP(TEMP8)
       DO 150 I=1,N
       SUM=SUM+(ALOG(OZPOR(I))-TEMP8-ALF*ALOG(WIND(I)))**2
       TEMP11=TEMP11+(ALOG(WIND(I))-TEMP9/N)**2
150    DALF=SUM/(N*TEMP11)
       WRITE(6,1010) ALF,CON,DALF
1010   FORMAT(6HALPHA=,F6.3,5X,9HCONSTANT=,F7.3,5X,F8.4)
       RETURN
       END
C
C
       SUBROUTINE COR(N,VW,ERRV,VBAR,VVAR,EVBAR,EVVAR)
       DIMENSION VW(N),ERRV(N)
       TEMP=0
       DO 1 I=1,N
1      TEMP=TEMP+(VW(I)-VBAR)*(ERRV(I)-EVBAR)
       R=TEMP/(VVAR*EVVAR*N)
       WRITE(6,500) R
500    FORMAT(F8.5)
       RETURN
       END


       SUBROUTINE GAUSS(XMEAN,NU,N,XMIN,XMAX,J,XG)
       DIMENSION XG(J)
       DO 10 I=1,J
       XG(I)=0.0
             DO 1 K=1,NU
             R=ODNAR(N,XMIN,XMAX)
1            XG(I)=XG(I)+R
10     XG(I)=XG(I)+XMEAN
       RETURN
       END
       FUNCTION ODNAR(N,XMIN,XMAX)
       N=N*253
       X=N
       X=X/32768.
       SPAN=XMAX-XMIN
       X=X*SPAN
       ODNAR=X+XMIN
       RETURN
       END
```

```
C         POLY


C         POLY
C   THIS PROGRAM GENERATES A LEAST SQUARE FIT OF THE FORM
C   Z=B0+B1X+B2X**2+B3Y+B4XY+B5X**2Y+B6Y**2+B7XY**2+B8X**2Y**2
      DIMENSION X(29,9),TEM(8),M(8,8),V(8)
      DIMENSION MATO(8,8),WORK(9,16),B(8),D(8,8)
      DOUBLE PRECISION M,MATO,D,WORK,B,V
      CALL SEARCH(3,'OUTPUT',2,0)
      CALL SEARCH(3,'DATT  ',1,0)
      N=29
      B0=0.0
      TEM0=0.0
      DO 20 I=1,8
      TEM(I)=0.0
      V(I)=0.0
      DO 20 J=1,8
      M(I,J)=0.0
20    CONTINUE
      DO 50 I=1,N
      READ(5,1000)X(I,1),X(I,3),X(I,9)
      X(I,2)=X(I,1)**2
      X(I,4)=X(I,1)*X(I,3)
      X(I,5)=X(I,2)*X(I,3)
      X(I,6)=X(I,3)**2
      X(I,7)=X(I,6)*X(I,1)
      X(I,8)=X(I,2)*X(I,6)
      DO 40 J=1,8
      TEM(J)=TEM(J)+X(I,J)
40    CONTINUE
      WRITE(6,1000)X(I,1),X(I,3),X(I,9)
      TEM0=TEM0+X(I,9)
50    CONTINUE
      DO 70 J=1,8
      TEM(J)=TEM(J)/N
70    CONTINUE
      TEM0=TEM0/N
      DO 90 I=1,8
      WRITE(6,1040)TEM(I)
90    CONTINUE
      DO 100 I=1,8
      DO 100 J=1,8
      DO 100 K=1,N
      M(I,J)=M(I,J)+(X(K,I)-TEM(I))*(X(K,J)-TEM(J))
      IF(J.LT.8) GO TO 100
      V(I)=V(I)+(X(K,9)-TEM0)*(X(K,I)-TEM(I))
100   CONTINUE
      WRITE(6,1010)V(1),V(2),V(3),V(4),V(5),V(6),V(7),V(8)
      DO 150 I=1,8
      WRITE(6,1010)M(I,1),M(I,2),M(I,3),M(I,4),M(I,5),M(I,6),M(I,7),
     &  M(I,8)
150   CONTINUE
      CALL MINV(MATO,M,8,WORK,9,16,IERR)
      WRITE(6,1015)IERR
      CALL MMLT(D,M,MATO,8,8,8)
      CALL MMLT(B,MATO,V,8,8,1)
      DO 200 I=1,8
      B0=B0-B(I)*TEM(I)
```

```
C        POLY


C        POLY
C   THIS PROGRAM GENERATES A LEAST SQUARE FIT OF THE FORM
C   Z=B0+B1X+B2X**2+B3Y+B4XY+B5X**2Y+B6Y**2+B7XY**2+B8X**2Y**2
      DIMENSION X(29,9),TEM(8),M(8,8),V(8)
      DIMENSION MATO(8,8),WORK(9,16),B(8),D(8,8)
      DOUBLE PRECISION M,MATO,D,WORK,B,V
      CALL SEARCH(3,'OUTPUT',2,0)
      CALL SEARCH(3,'DATT  ',1,0)
      N=29
      B0=0.0
      TEM0=0.0
      DO 20 I=1,8
      TEM(I)=0.0
      V(I)=0.0
      DO 20 J=1,8
      M(I,J)=0.0
20    CONTINUE
      DO 50 I=1,N
      READ(5,1000)X(I,1),X(I,3),X(I,9)
      X(I,2)=X(I,1)**2
      X(I,4)=X(I,1)*X(I,3)
      X(I,5)=X(I,2)*X(I,3)
      X(I,6)=X(I,3)**2
      X(I,7)=X(I,6)*X(I,1)
      X(I,8)=X(I,2)*X(I,6)
      DO 40 J=1,8
      TEM(J)=TEM(J)+X(I,J)
40    CONTINUE
      WRITE(6,1000)X(I,1),X(I,3),X(I,9)
      TEM0=TEM0+X(I,9)
50    CONTINUE
      DO 70 J=1,8
      TEM(J)=TEM(J)/N
70    CONTINUE
      TEM0=TEM0/N
      DO 90 I=1,8
      WRITE(6,1040)TEM(I)
90    CONTINUE
      DO 100 I=1,8
      DO 100 J=1,8
      DO 100 K=1,N
      M(I,J)=M(I,J)+(X(K,I)-TEM(I))*(X(K,J)-TEM(J))
      IF(J.LT.8) GO TO 100
      V(I)=V(I)+(X(K,9)-TEM0)*(X(K,I)-TEM(I))
100   CONTINUE
      WRITE(6,1030)V(1),V(2),V(3),V(4),V(5),V(6),V(7),V(8)
      DO 150 I=1,8
      WRITE(6,1010)M(I,1),M(I,2),M(I,3),M(I,4),M(I,5),M(I,6),M(I,7),
     &  M(I,8)
150   CONTINUE
      CALL MINV(MATO,M,8,WORK,9,16,IERR)
      WRITE(6,1015)IERR
      CALL MMLT(D,M,MATO,8,8,8)
      CALL MMLT(B,MATO,V,8,8,1)
      DO 200 I=1,8
      B0=B0-B(I)*TEM(I)
```

```
C        POLY


      WRITE(6,1020)D(I,1),D(I,2),D(I,3),D(I,4),D(I,5),D(I,6),D(I,7),
     1  D(I,8)
200   CONTINUE
      B0=B0+TEM0
      WRITE(6,1040) B0
      DO 300 I=1,N
      TEMP=0
      DO 250 J=1,8
      IF(I GT.1) GO TO 270
      WRITE(6,1030)J,B(J)
      IF(J.LT.8) GO TO 270
      WRITE(6,1035)
270   TEMP=TEMP+B(J)*X(I,J)
250   CONTINUE
      RES=X(I,9)-B0-TEMP
      ERR=RES*100/X(I,9)
      WRITE(6,1050) RES,ERR
300   CONTINUE
1000  FORMAT(F4 0,2X,F4.1,1X,F4.2)
1010  FORMAT(5(D10 3,1X))
1015  FORMAT(5HFLAG=,I1)
1018  FORMAT(12HDETERMINANT=,F10.2)
1020  FORMAT(8(D10.3,1X))
1030  FORMAT(5HTERM=,I1,3X,5HCOEF=,D12.5)
1035  FORMAT(17HRESIDUALS  %ERROR)
1040  FORMAT(F11.2)
1050  FORMAT(2(F7 4,4X))
      CALL SEARCH(4,0,2,0)
      CALL SEARCH(4,0,2,0)
      CALL EXIT
      END
      SUBROUTINE MMLT(MATP,MATL,MATR,N1,N2,N3)
      DOUBLE PRECISION MATP(N1,N3),MATL(N1,N2),MATR(N2,N3)
      DO 1 I=1,N1
      DO 1 J=1,N3
      MATP(I,J)=0 0
      DO 1 K=1,N2
1     MATP(I,J)=MATP(I,J)+ MATL(I,K)*MATR(K,J)
      RETURN
      END
```

Vita

Ed Kushner was born on April 22, 1942 in Portland, Oregon. He received a B.A. degree in Physics from the University of Oregon in 1964. He then entered the University of California and received an M.S. degree in Physics in 1966. From 1966 through 1974 he was a member of the technical staff of Logicon Inc. in Los Angeles. This work was primarily classified engineering research for the Air Force. It involved the formulation of mathematical models relating to ballistic missiles and the development of computer simulations based on such models. In 1975 he began graduate work at the Oregon Graduate Center. Presently, his primary technical interests are in the area of application of computer technology to environmental and energy problems.