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MODELING SMOG ALONG THE LOS ANGELES - PALM SPRINGS TRAJECTORY

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by

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Abstract

Observations of smog concentrations and wind patterns during the summer of 1973 in Los Angeles, Pomona, Riverside, Banning, and Palm Springs are presented which show that high oxidant concentrations at Banning and Palm Springs are often due to advection of smog from source regions in the more densely populated western part of the Los Angeles basin. At Pomona and Riverside, advection from upwind source regions combines with the effects of local emissions to cause long durations of high oxidant concentrations with peak times in the mid afternoon. An empirical model for the diurnal oxidant variation is suggested which satisfactorily simulates observed concentrations. More complex models which include chemical kinetics systems do not perform very satisfactorily at the rural stations of Banning and Palm Springs, especially at night when observed oxidant concentrations remain high.

I. Introduction

The problem of photochemical smog in the Los Angeles basin has been recognized for many years (U.S. D.H.E.W. Consultation Report¹) and has been the subject of many research and observation programs. As a result of these studies, various kinds of emissions controls have been suggested and implemented, and smog concentrations in the basin have been observed to decrease significantly (Altsuller²). It has been recognized that, while oxidant concentrations have decreased in the central areas of the basin characterized by high emissions, oxidant concentrations are increasing in the areas of Southern California that do not have very high emissions (Gloria et al.,³ Drivas and Shair,⁴Metronics,⁵ Altshuller,²). In this paper, measurements along a trajectory from Los Angeles to Palm Springs are presented which show that as the smoggy air is advected towards the east, the time of peak oxidant concentration is delayed towards evening, and the duration of high oxidant concentrations increases. The roles of advection, diffusion, and chemical reactions are discussed.

Observations are reported as either ozone or oxidant. While ozone is the chief oxidant in the air, small amounts of other substances such as PAN (peroxyacetyl nitrate) are represented in the oxidant observation. The presence of ozone or oxidant in regions outside primary source areas has been observed in several regions of this country. Stasiuk and Coffee⁶ reported ozone concentrations of 8 pphm (parts per hundred million) in rural New York State. The typical background concentration reported by the U. S. D.H.E.W. ⁷ is 3 pphm. Although at any given time,

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local sources or infusions of stratospheric ozone can cause variations in the background. The National Air Quality Criterion⁸ for oxidant states that an hourly average concentration of 8 pphm may be exceeded no more than once a year. Cleveland and Kleiner⁹ discuss observations of ozone concentrations exceeding the Air Quality Criterion in small towns about 50 km from Philadelphia, and show that the highest concentrations occur when the wind is blowing in a direction from Philadelphia to the towns. Richter¹⁰ and Research Triangle Institute¹¹ report high values of oxidant measured in mountainous regions in the eastern U. S. This may be partly due to hydrocarbon emissions from the forests. The occurrence of high ozone concentrations in Livermore Valley, east of San Francisco, is shown by Ludwig and Kealoha¹² to be caused by chemical reactions in air advected from the more populated areas of San Francisco and San Jose.

Many studies have been made of the three dimensional distribution of ozone or oxidant in Southern California (e.g. Gloria et al.,³Miller and Ahrens,¹³ Lea,¹⁴ Edinger,¹⁵). The studies all find that layers of ozone exist, and that often the highest ozone concentrations occur near the top of the mixed layer. These elevated layers of ozone can stretch with little variation across the Los Angeles basin, and impact upon the forested slopes of the mountains to the east and north of the basin. Ozone concentrations in these elevated layers do not vary much with time of day.

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A tracer study by Drivas and Shair shows that pollutants emitted in the more populous western part of the Los Angeles basin can be advected through the passes in the hills into the eastern part of the basin. Another tracer study by Metronics found that considerable transport of material from Los Angeles to Riverside took place, but suggested that the main cause of high pollutant concentrations in Riverside is local emissions. The Los Angeles Reactive Pollutant Program, which took place in late summer, 1973, also used tracer techniques to follow air parcels across the basin (see Angeli, et al. 16). Constant level balloons were flown, as on other occasions (e.g., Angell et al. 17) in order to more accurately determine air trajectories. The tetroon flights verify that the sea breeze regime often dominates the air flow (DeMarrais et al, 18), causing pollutants to drift inland during the day and out to sea at night. 19 These patterns were also confirmed by the study by Edinger et al. Mountain valley breezes dominate the flow near the large mountain ranges to the east of the basin (U.S., 1). It will be shown later. in this paper that the sea breeze and mountain breeze interact to form a smog front which flows to the east during the afternoon and reaches Palm Springs in the early evening. Climatological summaries show that this air can have its origins either in Los Angeles or Orange Counties. For the episode analyzed here, the origin is Los Angeles.

Occasionally, the smog front is a very striking visible phenomenon. Stephens²⁰ provides photographs and documentation for a smog front on 16 March, 1972, as it passes Riverside. He states that such extremely

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sharp demarcations between the polluted marine air and the clean desert air occur about a dozen times per year, and are most common during October.

Once the phenomenon of smog advection is documented, the next question is whether it can be modeled. Urban diffusion modeling of Los Angeles has progressed from Frenkiel's ²¹ simple model to the complex models of, for example, Pandolfo and Jacobs,²² Reynolds et al,^{23,24} and Roth.²⁵ These simple models have been validated so far only in the parts of the basin where local emissions are significant. A simple model developed by Hanna²⁶ was found to yield useful results where local emissions and meteorological conditions do not vary by more than an order of magnitude over time periods of several hours and distances of several kilometers. But the pollution episodes discussed here occur over regions where local emissions are insignificant and when meteorological conditions are changeable. In the model developed here, several chemical kinetic schemes are tried, in an attempt to simulate the observed smog patterns.

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2. Observations during the Summer of 1973.

To illustrate the variations in smog concentrations across Southern California, the five stations shown in Figure 1 were used. The distances between Downtown Los Angeles, Pomona, Riverside, Banning, and Palm Springs are 46, 29, 51, and 26 km, respectively. These stations are along the trajectory of an air parcel flowing eastward from Los Angeles, through the San Gorgonio Pass (near Banning) to Palm Springs. The San Gorgonio Pass (el 500m), which is about 3 km wide, is the only low passage through the steep San Bernardino, San Jacinto, and Santa Rosa Mountains on the north and east sides of the Los Angeles basin.

Emissions characteristics of the areas around the five stations are listed in-Table 1. These emissions represent an average over about 100 km²

Table 1

Emissions Characteristics in Southern California

		Average	Daily Emissio	ns (cm^3/m^2)	sec)
Station	City Population	<u>co</u>	Reactive Hydrocarbons	NO	$\frac{NO}{2}$
Los Angeles	2,816,000	.11	.021	.004	3×10^{-4}
Pomona	87,000	.014	2.7×10^{-3}	1.7×10^{-3}	10-4
Riverside	140,000	.014	2.7×10^{-3}	1.7×10^{-3}	10-4
Banning	12,000	1.4×10^{-3}	2.7×10^{-4}	1.7::10-4	10 ⁻⁵
Palm Springs	21,000	1.4×10^{-3}	2.7×10^{-4}	1.7×10^{-4}	10-5

The emissions for the first three stations are estimated from the data published by Weisburd et al.²⁷ Emissions were estimated for Banning and Palm Springs on the basis of population, compared with Riverside, since there were no published emission data available.

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Based on emissions data analyzed by Roth et al (1974), the average daily emissions reported in Table 1 must be multiplied by the following factors to obtain hourly values:

hr	0-5	.173;	hr	9	1.56;	hr	16-18	1.92;
hr	6	.295;	hr	10	1.24;	hr	19	1.36;
hr	7	1.06 ;	hr	11-14	1.31;	hr	20-22	.73;
hr	8	1.70 ;	hr	15	1.41;	hr	23-24	.173.

The most severe smog episode during 1973 occurred during the four day period from 23 July through 26 July. The hourly oxidant concentrations, averaged over the four days, are plotted in Figure 2. The Los Angeles, Pomona, and Riverside curves are all typical for an urban location with strong local emissions, increasing from near zero during the night to a peak near mid-day. However, the time of the peak oxidant concentration occurs later in the afternoon for the more easterly stations, due to advection of smog from Los Angeles. Furthermore, the duration of high oxidant concentrations is longer for the more easterly stations. This is also evident in the oxidant summary in Table 2.

Table 2

Time, Magnitude, and Duration of Observed Oxidant Peaks along the Los Angeles-Palm Springs Trajectory for 23-26 July 1973*

Date	Time (hr.) and Magnitude (pphm, in parentheses) of Oxidant Peak					Duration (hr.) of Ox. Conc. > 10 pphm				
	LA	POM	RIV	BAN	PS	LA	POM	RIV	BAN	PS
23 July 73	12(10)	14(23)	13(26)	17(30)	18(25)	4	8	12	23	23
24 July 73	12(27)	15(31)	14(37)	22(25)	24(19)	6	10	14	14	11
25 July 73	11(31)	12(26)	16(33)	19(37)	21(24)	5	8	11	15	9
26 July 73	13(17)	13(16)	12(26)	15(21)	19(15)	5	6	10	15	15
Average	12(21)	14(23)	14(30)	18(28)	20(21)	5	8	12	17	14

*Data supplied by the California Air Resources Board and the Riverside County Air Pollution Control District. The observation that the oxidant concentration begins its rise later in the morning at the Los Angeles station is probably due to the persistence of low level clouds close to the coast in the early morning. At the rural stations in Banning and Palm Springs, in contrast, the oxidant concentrations remain above the National Air Quality Criterion,⁸ 8 pphm, at night. There are not enough nitrogen oxides in the advected air or local emissions of nitrogen oxides to scavenge the oxidant. The oxidant concentrations in Banning and Palm Springs rise sharply at 4 pm and 8 pm, respectively, as the smog front passes through.

Meteorological conditions during the period 23-26 July 1973 were typical of those occurring in Los Angeles during the summer. The winds were generally from the west during this period at all stations except Banning and Palm Springs, where easterly winds during the afternoon were replaced by westerly winds at night. Detailed data are given in Figures 8 and 9. With the switch to westerly winds, the "smog front" arrived and oxidant concentration increased noticeably. An analysis of 24 days during June and July when the "smog front" was noticeable shows that the peak at Banning occurs an average of 3 1/4 hours later than that at Riverside, and the peak at Palm Springs occurs an average of 2 1/4 later than that at Banning. These times are nearly equal to the distance between the stations divided by the average wind speed at the two stations. Wind measurements refer to anemometer height and averages are taken over three hour periods and for the two stations at either end of the trajectory. In Figure 3, the time delay between peak oxidant at Riverside and Banning is plotted against wind speed, illustrating the good agreement.

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In Table 2, it is seen that the peak oxidant concentration in the 23-26 July 1973 period does not decrease much between the urban source areas and Palm Springs. If diffusion were the dominant mechanism affecting the oxidant concentration, then it would be expected that the oxidant concentration would decrease as the smog front flowed towards Palm Springs. Perhaps the oxidant concentrations remain high because the peak occurs in the evening when atmospheric stability is higher and diffusion rates are low. Or, as suggested by the USDHEW ¹ in its consultation report, the continual chemical production of oxidant proceeds at a greater rate than the diffusion.

In order to broaden the data base for these conclusions, data from each day of June and July 1973 were also analyzed. The results are summarized in Table 3.

Table 3

Time, Magnitude, and Duration of Observed Oxidant Peaks along the Los Angeles-Palm Springs Trajectory for June-July 1973.

Month	Time (hr.) an in parenthese	Buration Ox. Conc	Duration (hrs) of Ox. Conc. > 10 pphm			
	LA	RIV	PS	LA	RIV	PS
June 1973	not available	14(21)	17(15)	not available	7	. 8
July 1973	12(12)	14(22)	18(18)	2.5	8	12

On some days included in this analysis, the smog front never reached Palm Springs, and a local oxidant peak occurred at noon. However, the general results in Table 3 support the conclusions based on the smog episode data in Table 2. Peak oxidant concentrations occur six hours later at Palm Springs than at Los Angeles, and the duration of high oxidant concentrations is greater at Palm Springs.

Figures 4 through 9 contain hourly measurements of wind speed and direction, and concentrations of oxidants, CO, NO, and NO₂ for the five stations during the period from 23 July through 26 July, 1973. Hydrocarbon concentrations were also measured at the Los Angeles and Pomona stations, but are not plotted because they generally were about one half the magnitude of the CO concentrations. The main purpose of including all of these data is to provide a comprehensive set of measurements for others to use in validating models. Also, it is interesting to follow the concentration curves and compare curves for different stations.

For example, the CO and NO concentrations at Los Angeles and Pomona are nearly the same, even though the emissions at Los Angeles are reported to be almost an order of magnitude greater than those at Pomona. This inconsistency could be due to advection of CO from Los Angeles

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to Pomona, errors in reported emissions rates, or unrepresentative placement of the measuring stations. The CO concentration at Palm Springs tends to increase in the evening, as does the oxidant concentration, when the smog frontarrives. However, the NO₂ peak at Palm Springs tends to occur in early morning, suggesting that it is a local phenomenon due to local emissions. The low NO₂ concentration at the time of the passage of the smog front verifies the hypothesis that the smoggy air contains much oxidant but very little nitrogen oxide. Otherwise the oxidant would disappear.

There is an inconsistency in that carbon monoxide, a nearly inert gas, is not present in significant amounts in the air accompanying the smog front in Palm Springs, whereas the oxidant arrives virtually undepleted from its value in Los Angeles. We can conclude that oxidant arriving at Palm Springs is the result of chemical reactions in the presence of diffusion. Diffusion is sufficient to dilute the CO, but evidently the production of oxidant by chemical reactions balances the dilution by diffusion.

The relation between oxidant peak at Banning and Palm Springs and wind direction is strikingly illustrated by Figures 4 and 9. For example, in Banning on July 23, when the wind direction switched sharply to WNW at 3 pm, the oxidant concentration jumped to 30 pphm. The wind then shifted to SW at 5pm, and oxidant concentration fell.

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From the wind speed traces in Figure 8, it is seen that relatively strong winds usually mark the passage of the smog front at Banning and Palm Springs. This is normally followed by a gradual decrease in both wind speed and oxidant concentration.

It is evident from figures 4 through 9 that the daily cycles of pollutant concentrations and meteorological variables are fairly regular. The regularity of wind patterns in the Los Angeles basin is mentioned by Anderson ²⁸ and De Marrais et al.¹⁸ On this basis the simplified wind speed record in Table 4 has been developed from the data in Figure 8, for use in an empirical model.

Table 4

Smoothed Component towards the East of the Wind Speed along a Trajectory Connecting the Five Stations in Figure 1, for the Period 23-26 July 1973.

Los Angeles	Pomona	Riverside	Banning	Palm Springs
7 pm-8 am 1 m/s;	7 pm-9 am .5 m/s;	7 pm-9 am .5 m/s;	2 am-7 am 2 m/s;	8 am-7 pm -2.5 m/s;
8 am-7 pm 3.5 m/s;	9 am-7 pm 2.5 m/s;	9 am-7 pm 4 m/s;	7 am-2 pm -1 m/s;	7 pm-1 am 3 m/s;
			2 pm-2 am 2.5 m/s;	1 am-8 am 1 m/s.
				and show a sub-state of the second

Station

The use of a smoothed wind record is justified by experience with the application of the ATDL simple urban dispersion model (Hanna,²⁹ and Gifford and Hanna^{30,31}). Individual station wind records are generally not truly representative of the integrated air flow across a region. We find (Nappo,³² Gifford³³) that when wind speeds are averaged somewhat over time and space in order to smooth unrepresentative observations, better agreement between concentrations and those calculated by means of a simple urban pollution model is obtained.

3. A Simple Empirical Model for Oxidants

The oxidant patterns in Figure 2 appear so smooth and regular that it should be possible to reproduce the curves through a simple empirical formula. The empirical model should account for oxidant production due to local emissions and due to advection from upwind regions. Based on the results reported in the earlier articles by Hanna^{26,34} the local contribution to oxidant concentration, OX_1 (pphm), is assumed to be directly proportional to the rate constant for photochemical dissociation of NO₂ (denoted by r_1 (sec⁻¹) in most reports) and to the square root of emissions of reactive hydrocarbons, $Q_{\rm RH}$ (cm³/m²sec), but is inversely proportional to the wind speed, U (m/s).

$$0X_{1}(x,t) = \frac{cr_{1} Q_{RH}^{1/2}(x,t)}{U(x,t)}; \qquad (1)$$

where c is a dimensional constant, determined by comparisons with data to be equal to about 150 m²s^{1/2} cm^{-3/2}, x is location on the trajectory, and t is time. The constant r_1 is assumed to be proportional to the sine of the sun's elevation angle.

The advection contribution, $0X_a$ (pphm), should account for dilution and chemical reactions. It has been shown that horizontal diffusion is not important in most urban regions (e.g., Gifford and Hanna,³⁰).

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Therefore only vertical dispersion need be accounted for, and it is assumed that the pollutant is well mixed up to a lid at height Z(m). Furthermore, the expression to be proposed should satisfy the conditions that during the night and at the eastern end of the trajectory, chemical reactions are insignificant. The following expression is proposed for the contribution of advection to oxidant concentrations, OX_b (pphm):

$$0X_{a}(x,t) = \frac{0X(x_{o}, t-(x-x_{o})/U)}{Z(x,t)/Z(x_{o},t_{o})} \left[1 - \left(1 - \frac{r_{1}(t)}{r_{1}(noon)}\right) \frac{Q_{RH}^{-1im}}{Q_{RH}}\right]$$
(2)

where U is wind speed, $x-x_0$ is the distance from one station (position x_0) to the next downwind station (position x), and lim is the reactive hydrocarbon source strength at Banning and Palm Springs. The total oxidant concentration is given by adding equations (1) and (2) to the background oxidant concentration, $0X_b$ (pphm):

$$OX(x,t) = OX_{b} + \frac{cr_{1} Q_{RH}^{1/2}(x,t)}{U(x,t)} + \frac{OX(x_{o},t-(x-x_{o})/U)}{Z(x,t)/Z(x_{o},t_{o})} \left[1 - \left(1 - \frac{r_{1}(t)}{r_{1}(noon)}\right) \frac{Q_{RH}^{-1im}}{Q_{RH}}\right] (3)$$

This empirical equation was applied to the five stations in Southern California which are studied in this report, in an attempt to simulate the four day average diurnal oxidant curves drawn in Figure 2. Emissions given in Table 1, a sinusoidal variation of r_1 with time (with r_1 (noon) = .006 sec⁻¹), and wind speeds given in Table 4 were assumed. The mixing height Z was assumed to equal 200m, 300m, 450m, 900m, and 1800m

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over Los Angeles, Pomona, Riverside, Banning, and Palm Springs, respectively (Holzworth, 35 and U.S.D.H.E.W.¹). Furthermore a background oxidant concentration of 10 pphm was assumed for Banning and Palm Springs, and zero for the other stations, as suggested by the observations at these stations during smog episodes. The calculated oxidant concentration at the upwind station at time t-(x-x_o)/U, beginning with Los Angeles, was used as input to the advective portion of equation (3). The results of applying this model at each of the five stations are presented in Figures 10a through 10e (the dashed curves).

In Figure 10a, for Los Angeles, the calculated OX curve is a sine curve which agrees fairly well with observations at midday but exceeds the observations in the early morning and late afternoon. The error in the early morning may be due to the presence of stratus clouds which are not accounted for in the model. The error in the late afternoon is probably due to failure of the model to account satisfactorily for scavenging of oxidants by nitrogen oxides, which are emitted in large quantities in the area around this station. The agreement between observed and calculated curves in Pomona in Figure 10b is remarkable and probably somewhat fortuitous. The forms of the curves for Riverside in Figure 10c are similar, but the magnitude of the calculated concentrations is only about 50 to 60 percent of the observations. The calculated curves for Banning and Palm Springs in Figures 10d and 10e are in good agreement with the observed curves. The times of peak oxidant concentration are calculated to be within about one hour of the observed times.

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We can conclude that the simple empirical model given by equation (3) is a good predictor of oxidant concentrations for these data. The model should of course be tested with other independent observations (as should those of all smog models). However, we can state with some confidence, based on the present study, that oxidant episodes in Los Angeles are due to local emissions, those at Pomona and Riverside are due partly to local emissions and partly to advection from upwind areas, and those at Banning and Palm Springs are almost entirely due to advection from upwind areas. 4. Numerical Models of Photochemical Smog.

Modeling of photochemical smog in Los Angeles has recently received a great deal of attention, mainly due to the encouragement of the Environmental Protection Agency. The characteristics of the models depend upon the needs for which they were developed, EPA needs are related to environmental legislation, implementation, planning, impact assessment, transportation planning, and episode controls. Photochemical diffusion models were developed independently by Sklarew et al., Roth et al., ²⁵ Reynolds et al., ^{23,24} Weisburd etal., ²⁷ and Eschen+ roeder et al. 37 Each of thes models uses a slightly different system of approximate chemical kinetic equations. The number of chemical reactions accounted for ranges from about ten to about thirty. The diffusion methods and meteorological input to these models are relatively crude when compared to the methods used in the models for inert substances developed by, for example, Pandolfo and Jacobs²² and the very detailed model presented by Hilst et al. 38 In the first group of models listed above, grid squares which either move with the air or are stationary are used, and atmospheric diffusion enters the problem only through a vertical diffusivity coefficient, K, and fluctuations After considerable "tuning" of these models in wind velocity. with the observations, these investigators generally can show rather good agreement between calculated and observed concentrations of CO, OX, NO, NO, and reactive hydrocarbons.

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A simpler model of diffusion of photochemical smog was suggested by Hanna (1973a, 1973b). In this model, the pollutants are assumed to be well mixed throughout the volume of air passing over a grid square, and the basic simple model for inert pollutants,

$$X_{i} = C \frac{Q_{i}}{U}$$
(4)

is used as a normalizing factor in the model (see Hanna,²⁹ and Gifford and Hanna³¹). In equation (4), X_i is concentration of species i, in ppm or cm^3/m^3 , C is a dimensionless constant found to equal about 200 on the average, and Q, is the area source emissions of species i, in cm^3/m^2 sec. When the equation for the time rate of change of pollutant concentrations is normalized by the factor on the right hand side of (4), several dimensionless numbers are produced which describe the relative influence of chemical reactions, advection, and emissions on the change of pollutant concentration. The chemical reactions used are those suggested by Friedlander and Seinfeld. 39 although other reactive schemes could be used. From these dimensionless numbers, which are functions of emissions rate, wind speed, mixing depth, and chemical rate constants, it is possible to estimate the deviation of the actual concentration given by the equation for the time rate of change of pollutant concentrantions from the equilibrium inert concentration given by equation (4).

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One valid objection to the original model by Hanna²⁶ for photochemical smog is that it can not be used for situations in which local emissions are not strong and advection from upwind polluted areas is important, which is exactly the type of situation described in Section 2. The original model is accordingly modified in the following manner to account for these processes. As before, it is assumed that horizontal diffusion is insignificant, due to the broad extent of the emissions region. Concentrations within boxes of length 40 km, centered nearly over each station, are assumed uniform. A schematic drawing of the location of the boxes is given in Figure 11. The continuity equation for the time rate of change of concentration of pollutant X_i (cm³/m³ or ppm) in one of the boxes is

$$\overline{Z}DX \frac{\partial X_{i}}{\partial t} = -DX \frac{\partial}{\partial x} \overline{Z}UX_{i} + Q_{i}DX + \overline{Z}DX\SigmaR_{j}$$
 (5)

where \overline{Z} is the average height of the mixing layer over the grid block, and R_j is the rate of change of concentration of pollutant X_i due to reaction j. Written in the finite difference form used in the numerical solution, and assuming positive U for the purpose of illustration, equation (5) becomes:

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$$X_{i}(k,t_{0}+DT) = X_{i}(k,t_{0}) + DT \left[\frac{Q_{ik}}{\overline{z}_{k}} + U_{k-1} X_{i}(k-t_{0}) \frac{Z_{k-1}}{DX\overline{z}_{k}} - U_{k} X_{i}(k,t_{0}) \frac{Z_{k}}{DX\overline{z}_{k}} + \Sigma_{j}R_{j}, \right]$$
(6)

where DT is the time step, k is the grid block number, and t_C is an initial time at which all quantities are assumed to be known. As an example, to calculate the CO concentration in grid block 3, with all wind speeds U constant, the following equation would be used:

$$X_{CO}(3,t_{0} + DT) = X_{CO}(3,t_{0}) + DT \left[\frac{Q_{CO3}}{\overline{z}_{3}} + U X_{CO}(2,t_{0}) \frac{z_{2}}{DX\overline{z}_{3}} - U X_{CO}(3,t_{0}) \frac{z_{3}}{DX\overline{z}_{3}} \right]$$
(7)

Note that for steady-state conditions with no upwind sources, this equation reduces to the Gifford-Hanna simple model, $X_{CO} = CQ/U$, where C is equivalent to the ratio DX/\overline{Z} .

In this study, the differential equation (6) is solved for the variable pollutants CO, NO, NO₂, oxidant, and reactive hydrocarbons. For more detailed chemical kinetics systems, additional differential equations would be required for other chemical substances. Many important chemical substances can simply be assumed to be in steady-state equilibrium. The chemical kinetics systems used is that proposed by Friedlander and Seinfeld ³⁹, which is based on the work by Leighton⁴⁰. In Friedlander and Seinfeld's seven step scheme, oxidants are assumed to be in steady-state equilibrium. In the present study this restriction is removed during the night, because it is not valid then. The partial differential equation for oxidant concentration will, I hope, permit advection but not much chemical conversion at these stations at night. The reader should refer to Friedlander and Seinfeld's ³⁹ paper for details of the chemical kinetics systems.

Additonal specific conditions are imposed as follows. Noon mixing heights of 200m, 400m, 800m, 1600m, and 1600m are used for the five stations; at night the mixing depth is then assumed to fluctuate as a sine curve between sunrise and sunset. A time step, DT, equal to 60 seconds, is used. To prevent computational instabilities in solving equation (6) for the concentration X_i at time (t_0 + 60 sec), values of X_i at time t_0 and values of all other species concentration^S X_j at time (t_0 - 60 sec) are used in R_j on the right hand side of equation (6). Observed initial concentration values are those for midnight on June 22-23, 1973.

Resulting concentrations for Pomona on 23 July are shown in Figure 12a through 12d. It is seen that agreement is fair for all pollutants, considering that no adjustments have yet been made in the "tunable parameters" such as mixing depth and rate constants. Unfortunately, the calculated oxidant curve misses the observed curve significantly, both in terms of magnitude and time of peak.

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For the stations at Banning and Palm Springs, the model results differ significantly from observations. With an initial oxidant concentration of 12pphm and initial NO and NO₂ concentrations of 1 pphm, the oxidant concentration rapidly decreases with a half life of about two hours. In contrast to observations, the calculated oxidant is almost completely eliminated by sunrise. Thus this system is not satisfactory for modeling smog at night in rural areas.

Since the Friedlander and Seinfeld seven-step kinetic mechanism has been criticized for being too short, and it does not yield very satisfactory results in this application, the Systems Applications, Inc. 15 step (Roth et al, ⁴¹) and 19 step (Reynolds et al, ²³) kinetic mechanisms were tested. The difference between these two mechanisms is that the 15 step mechanism uses only a single hydrocarbon class, while the 19-step mechanism uses two hydrocarbon classes, based on reactivity. It is assumed here that hydrocarbon emissions are divided equally between the two classes. The result of both of these applications, using equation (6), is, perhaps, a slight improvement over the results using the Friedlander and Seinfeld scheme. But the most important observations from our point of view, namely the high background oxidant and smog front at Banning and

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Palm Springs, are poorly simulated even by these more comprehensive chemical kinetics systems. In all cases the observed background oxidant concentration is whittled away at night to near zero in a few hours. Furthermore, the high oxidant concentrations associated with the smog front are not evident in the model, even though the front does arrive at the proper time, as insured by the input wind observations. Further research on chemical reactions in smoggy atmospheres during the night is necessary.

We plan to continue testing variations of this model. The next step will be to use the Lagrangian or trajectory approach suggested by 37 Eschenroeder and Martinez and applied to the San Francisco basin by Ludwig and Kealoha ¹². The more recent chemical kinetic scheme proposed by Hecht et al. 42 may be used, since this scheme divides the hydrocarbons into classes according to their chemical composition, rather than according to their reactivity. However, since the first three equations in the chemical kinetics system are nearly the same in all the models, we do not foresee much improvement over the results of the other models. It is wise not to spend too much time cross-checking each model with the same set of observations. The more this is done, the more "tuning," with the large number of adjustable parameters in these models, is involved. The end result is a model which is not independent of the data set used in its validation.

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5. Conclusions

Observations of smog concentrations during the summer of 1973 in Los Angeles, Pomona, Riverside, Banning, and Palm Springs show that smoggy air is often advected eastward from its source region in Los Angeles and Orange counties towards the more rural areas of Banning and Palm Springs. As a result of the interaction of sea breeze and mountain breeze effects, a smog front is formed which causes abrupt increases in oxidant concentration as it passes the rural stations. On the average, the time of peak oxidant concentration occurs six hours later at Palm Springs than at Los Angles. Oxidant episodes at Palm Springs and Banning are almost entirely due to advection from the urban area, while episodes at Los Angeles are almost entirely due to strong local emissions. At Pomona and Riverside, both local emissions and advection play an important role, often resulting in days with a long duration of high oxidant concentrations, having a peak during mid-afternoon.

An empirical model of the diurnal oxidant variation is shown to agree fairly well with the observations. This model accounts both for local emissions and advection from upwind areas. In contrast, solutions to the partial differential equations for the time rate of change of pollutant concentrations due to emissions, advection, vertical mixing, and chemical reactions, could not satisfactorily simulate the observed high oxidant concentrations in Banning and Palm Springs at night.

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After this work was completed, a report entitled "Comparison of Oxidant Calibration Procedures" by the Ad hoc Oxidant Measurement Committee of the California Air Resources Board (Feb. 3, 1975) was sent to me. This committee believes that the oxidant measurement reported from Riverside, Banning and Palm Springs are consistently 25 to 30% too high. These errors do not affect the basic conclusions of this paper. In future work using these data, however, the oxidant concentrations at Riverside, Banning, and Palm Springs should be reduced by 25%.

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References

- 1. U. S. Dept. of Health, Ed., and Welfare, Report for Consultation on the Metropolitan Los Angeles Air Quality Control Region. Pub. Health Serv., 79pp, Nov. 1968.
- 2. A. P. Altshuller, J. Air Poll. Cont. Assoc., 25, 19 (1975).
- H. R. Gloria, J. N. Pitts, G. Bradburn, R. F. Reinisch and L. Zafonte, J. Air Poll. Cont. Assoc., 24, 645 (1974).
- 4. P. J. Drivas and F. H. Shair, Atmos. Environ. 8, 1155 (1974).
- 5. Metronics Assoc., Inc., Field Study of Air Pollution Transport in the South Coast Basin, Tech. Rept. No. 186 (May 1973).
- W. N. Stasiuk and P. E. Coffey, J. Air Poll. Cont. Assoc., <u>24</u>, 564 (1974).
- U. S. Dept. of Health Ed., and Welfare. Air Quality Criteria for Photochemical Oxidants. NAPCA Publ. AP-G3 (\$1.75), Pub. Health Serv., (March, 1970).
- Nat. Primary and Secondary Ambient Air Quality Standard for Photochemical Oxidants. .08ppm maximum one hour concentration not to be exceeded more than once per year. Fed. Reg., 36(84), 8187 (Jan. 1973).
- 9. W. S. Cleveland and B. Kleiner, The Transport of Photochemical Air Pollution from the Camden-Philadelphia Urban Complex. Report from Bell Laboratories, Murray Hill, N.J. 07974, 12 pp. (1975).
- H. G. Richter, Special Ozone and Oxidant Measurements in Vicinity of Mount Storm, West Virginia. Res. Tri. Inst., N.C. (1970).
- Research Triangle Institute, Investigation of High Ozone Concentration in the Vicinity of Garrett County, Maryland and Preston County, West Virginia. Res. Tri. Inst. publ. NTIS-PB-218540 (1973).
- 12. F. L. Ludwig and J. H. Koeloha, Present and Prospective San Francisco Ray Area Air Quality, SRI project 3274 Final Report, by Stanford Research Institute, Menlo Park, Cal. 94025, for Wallace, McHarg, Roberts, and Todd and Metropolitan Transportation Commission, 110p. (1974).
- 13. A. Miller and C. P. Ahrens, Tellus, 22, 328 (1970).
- 14. D. A. Lea, J. Appl. Meteorol., 7, 252 (1968).

- 15. J. G. Edinger, Environ. Sci. and Tech., 7, 247 (1973).
- J. K. Angell, C. R. Dickson, and W. H. Hoecker, Relative Dispersion within the Los Angeles Basin as Estimated from Tetroon Triads. NOAA Tech. Memo. ERL ARL-46, 34 pp. (1974).
- J. K. Angell, D. H. Pack, L. Machta, C. R. Dickson, and W. H. Hoecker, J. Appl. Meteorol., 11, 451 (1972).
- G. DeMarrais, G. C. Holzworth, and C. R. Hosler, Meteorological Summaries Pertinent to Atmospheric Transport and Dispersion over Southern California. Tech. Paper No. 54, Weather Bureau, U. S. Dept. of Comm. (1965),
- J. G. Edinger, M. H. McCutchan, P. R. Miller, B. C. Ryan, M. J. Schroeder, and J. V. Behar, J. Air Poll. Cont. Assoc., 22, 882 (1972).
- 20. E. R. Stephens, J. Air Poll. Cont. Assoc., 24, 521 (1975).
- 21. F. Frenkiel, Smithsonian Inst. Report for 1956, 269 (1957).
- 22. J. P. Pandolfo and C. A. Jacobs, Tests of an Urban Meteorological-Pollutant Model using CO Validation Data in the Los Angeles Metropolitan Area, Vol. I, CEM Rept. 490a, Cont. No. 68-02-0223 by The Center for the Environment and Man, Inc., 275 Windsor St., Hartford, Conn. 06120, prepared for U. S. EPA, 176pp. (1973).
- 23. S. D. Reynolds and P. M. Roth, Atmos. Environ., 7, 1033 (1973).
- 24. S. D. Reynolds, M. K. Liu, T. A. Hecht, P. M. Roth, and J. H. Seinfeld, Atmos. Environ., 8, 563 (1974).
- 25. P. M. Roth, P. J. Roberts, M. K. Liu, S. D. Reynolds and J. H. Seinfeld, Atmos. Environ., 8, 97 (1974).
- 26. S. R. Hanna, Atmos. Environ., 7, 803 (1973).
- 27. M. I. Weisburd, L. G. Wayne, R. Danchick, and A. Kokin, Development of a Simulation Model for Estimating Ground Level Concentrations of Photochemical Pollutants, Final Report NAPCA Contract CPA 70-151. System Development Corporation, Santa Monica, Cal. (Jan. 1971).
- G. E. Anderson, A. Mesoscale Windfield Analysis of the Los Angeles Basin, Cont. No. 68-02-0223 by the Center for The Environment and Man, Inc., 275 Windsor St., Hartford, Conn. 06120, for the U.S.E.P.A., 113 pp., (1973).

- 29. S. R. Hanna, J. Air Poll. Control Assoc., 21, 774 (1971).
- 30. F. A. Gifford and S. R. Hanna, Urban Air Pollution Modeling, 1970 Meeting of the Int. Union of Air Poll. Prev. Assoc., Washington, 11 Dec., 17 pp + 7 figs. (1970).
- 31. F. A. Gifford and S. R. Hanna, Atmos. Environ., 7, 131 (1973).
- 32. C. J. Nappo, A Method for Evaluating the Accuracy of Air Pollution Prediction Models, Proceedings of the Symposium on Atmospheric Diffusion and Air Pollution, held 9-13 Sept. 1974 in Santa Barbara, Cal., Am. Meteorol. Soc., 325 (1974).
- F. A. Gifford, Further Comparison of Urban Air Pollution Models. Report to the 5th Meeting of NATO/CCMS Expert Panel on Air Pollution Modeling, Roskilde, Denmark, 8 pp. (1974).
- 34. S. R. Hanna, Application of a Simple Model of Photochemical Smog. Proceedings of 3rd Clean Air Congress, Dusseldorf, Germ., (1973)
- 35. G. Holzworth, Mixing Depths., Wind Speeds and Potential for Urban Air Pollution throughout the Contiguous United States. Environ. Prot. Agency Pub. No. AP-101, 118 p. (1972).
- R. C. Sklarew, A. J. Fabrick, and J. E. Prager, <u>J. Air Poll. Cont.</u> <u>Assoc.</u>, <u>22</u>, 865 (1972).
- 37. A. Q. Eschenroeder, J. R. Martinez, and R. A. Nordsieck, Evaluation of a Diffusion Model for Photochemical Smog Simulation, Final Rept. Cont. No. 68-02-0336 by Gen. Res. Corp., P. O. Box 3587, Santa Barbara, Calif. 93105, for Environ. Prot. Ag., 212 pp. (1972).
- G. R. Hilst, C. duP. Donaldson, M. Teske, R. Contiliano, and J. Freiberg, A Coupled 2-D Diffusion and Chemistry Model. EPA Cont. Rept. EPA-R4-73-016C (1973).
- S. K. Friedlander and J. H. Seinfeld, <u>Environ. Res. and Tech. 3</u>, 1175 (1969).
- 40. P. A. Leighton, <u>Photochemistry of Air Pollution</u>, Academic Press, New York (1961).
- 41. P. M. Roth, S. D. Reynolds, P. J. Roberts, and J. H. Seinfeld, Development of a Simulation Model for Estimating Ground Level Concentrations of Photochemical Pollutants. Final Report, Cont. No. CPA 70-148 by Systems Appl. Inc., Beverly Hills, Cal. 90212 for the Environ. Prot. Ag., 55 pp + 6 Appen. (May 1971).
- 42. T. A. Hecht, J. H. Seinfeld, and M. C. Dodge, Environ. Sci. and Tech., <u>8</u>, 327 (1974).



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Ine time between peak oxidant concentrations at banning and Riverside, as a function of the average wind speed at the two stations. The curve given by the time = distance/ wind speed is also shown.





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ORNL-DWG 75-2685





Hourly wind speeds for the period 23 through 26 July 1973. Figure 8.









Figure 10e







23 July 1973, compared with calculated (dashed line) con-Friedlander and Seinfeld (1969) chemical kinetics system. Observed (solid line) hourly concentrations at Pomona on centrations, made using the numerical model with the Figure 12.