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# ANALYSIS OF HISTORICAL OZONE TRENDS IN LOS ANGELES SORTED BY THE NMHC/$NO_x$ RATIO

FINAL REPORT

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by

John Trijonis

Santa Fe Research Corporation
Route 7, Box 124K
Santa Fe, New Mexico 87501

California Air Resources Board
P.O. Box 2815
Sacramento, California 95812

Mr. Chuck Unger, Project Officer

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## ABSTRACT

The EPA EKMA ozone model suggests that the Los Angeles atmosphere is currently in a condition, with respect to the ambient $NMHC/NO_x$ ratio, where ozone levels should be extremely sensitive to future reductions in hydrocarbon emissions. A method is devised to test this hypothesis by investigating historical ozone trends grouped according to percentiles in the daily 6-9 AM $NMHC/NO_x$ ratio. In essence, the days of lowest $NMHC/NO_x$ ratio in the middle 1960's are used to represent current conditions, and future hydrocarbon reductions are simulated by examining the effect of historical control strategies on the low ratio days.

The method is applied to two ozone receptor sites, Azusa and Downtown LA, using historical trend data from 1964 to 1978. Special attention is paid to choosing or determining the best ozone air quality indices, source/receptor transport restrictions, historical precursor trends, and EKMA modeling parameters. The historical trend data do not confirm the EKMA hypothesis; contrary to EKMA predictions, historical ozone trends are nearly identical on low, medium, and high ratio days. This finding is inconclusive in the sense that we cannot be sure whether the EKMA hypothesis is erroneous or whether the study has been undermined by errors in the data base (e.g. in the routine data for the ambient $NMHC/NO_x$ ratio).

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# 1. INTRODUCTION AND EXECUTIVE SUMMARY

The Los Angeles basin experiences the highest levels of ozone and other photochemical pollutants found anywhere in the nation. Planning and monitoring control strategies for photochemical smog in Los Angeles has been problematical and frustrating. Much of the difficulty in managing photochemical air quality stems from the complex, nonlinear nature of the relationship between photochemical pollutants (e.g. ozone) and the precursor emissions (hydrocarbons and nitrogen oxides). Various predictive methodologies -- based on smog chamber experiments, empirical analyses of monitoring data, and physicochemical simulation models -- often disagree concerning the dependence of ozone on precursor emissions. Furthermore, historical trends for ozone have been rather puzzling. Over the past 15 to 20 years, control strategies have been producing a continual reduction in hydrocarbon emissions. In response, ozone levels over most of the Los Angeles basin decreased from the early 1960's to the middle 1970's, increased from the middle 1970's to the late 1970's, and decreased again in recent years. The cause for the inconsistent response of ozone trends, whether it be meteorology, temporary failure of control strategies, or the complexities of hydrocarbon and $NO_x$ interactions, is still not understood.

At least one ozone predictive technique, the EPA EKMA model (Dimitriades 1977; EPA 1977, 1978, 1980; Trijonis and Mortimer 1981) gives some cause for optimism regarding future photochemical smog control in Los Angeles. Specifically, the EKMA model suggests that the control strategies of the last 15 years have taken the Los Angeles atmosphere to a condition (in terms of the ambient $NMHC/NO_x$ ratio*) where ozone levels should be extremely sensitive to future reductions in hydrocarbon emissions. In fact, according to the EKMA model, a 50% reduction in hydrocarbon emissions from current levels should nearly eradicate the ozone problem in Los Angeles.

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*Throughout this report we will use the abbreviations HC for hydrocarbons, NMHC for nonmethane hydrocarbons, and $NO_x$ for nitrogen oxides.

Considering uncertainties regarding photochemical relationships in general and the EKMA model in particular, the above noted implications of EKMA should be viewed with some skepticism. The EKMA conclusions need confirmation before they can be accepted. We recently came up with an idea for checking the EKMA hypothesis concerning future hydrocarbon control through an analysis of historical trend data. Specifically, a certain subset of days in the middle 1960's -- those days with low NMHC/$NO_x$ ratios -- should approximate the current situation regarding the ambient NMHC/$NO_x$ ratio. The effect of future hydrocarbon reductions on ozone can be tested by examining the effect of past hydrocarbon reductions on this particular subset of days. The purpose of this report is to conduct such a trend analysis designed to test the EKMA hypothesis concerning future hydrocarbon control.

We did not undertake this project wthout some trepidation. The planned analysis faces difficulties due to the spatial/temporal coarseness of the historical data base and due to potentially serious errors in the data base. Nevertheless, the analysis seems definitely worthy of pursuit because, if it does work, it would validate the EKMA model for future hydrocarbon reductions, and it would provide strong justification for pursuing hydrocarbon controls. It would demonstrate that we are indeed near a steep downward slope on Haagen-Smit's "ozone hill", and that the photochemical smog problem in Los Angeles could be solved by further stringent but feasible hydrocarbon controls.

For those readers who are not interested in the technical details, we should note immediately that the historical trend data did <u>not</u> confirm the EKMA prediction. Also, whereas a positive finding would have been a definitive check on EKMA, our negative finding is inconclusive. We cannot be sure whether the failure to confirm the EKMA hypothesis implies that the EKMA implications are wrong, or that the EKMA implications are correct but our analysis suffers from data quality problems.

The remainder of this chapter describes the concept and design for the study and summarizes our technical analyses and results. The details of the technical analyses are presented in the main body of the report, Chapters 2 through 4.

## 1.1 STUDY CONCEPT

Recently, Santa Fe Research Corporation completed an EKMA validation study for Los Angeles under contract to EPA (Trijonis and Mortimer 1981). Based on the results of that study, we conceived a new idea for using historical data to check the effects of future hydrocarbon reductions in Los Angeles. To indicate the framework for the idea, let us start by discussing Figure 1.1, an EKMA diagram for yearly maximum ozone at Azusa. Our current best estimate for the EKMA-equivalent median summertime NMHC/$NO_x$ ratio in the Los Angeles basin in 1965 is 12:1.* The 1965 point in Figure 1.1 is the intersect of the 12:1 ratio line with the .49 ppm ozone isopleth (.49 ppm is the yearly maximum ozone at Azusa, averaged over 1964-66). The subsequent points reflect historical precursor changes from 1965 to 1968, to 1971, to 1974, and to 1977. The precursor changes are based on an average of emission trend data and ambient trend data compiled in our EPA report.

Figure 1.1 shows that by 1977 Los Angeles had reached a median NMHC/$NO_x$ ratio of 7:1. Also, as noted above, Figure 1.1 indicates that -- starting from the 1977 point -- a 50% NMHC reduction, decreasing the ratio to less than 4:1, would virtually eradicate the ozone problem at Azusa. How can this possibility be tested with historical data? Our idea is that the effects of the historical hydrocarbon reductions can be tested under low ratio conditions (in the 7:1 to 4:1 range) as well as under average ratio conditions (in the 12:1 to 7:1 range). This can be done by sorting the days each year according to groups defined by percentiles of the daily NMHC/$NO_x$ ratio. In 1965, the group corresponding to the lowest 20th percentile of the NMHC/$NO_x$ ratio would have had an average ratio of about 6:1. Due to the historical control strategy, the average NMHC/$NO_x$ ratio for this low ratio group should have been reduced to less than

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*One must use extreme care in selecting an EKMA-equivalent NMHC/$NO_x$ ratio because of differences in monitoring techniques (Dimitriades 1970, 1972; Crowe 1980; Kinosian 1981), differences in hydrocarbon reactivity (Dimitriades 1980; Trijonis and Mortimer 1981), and potential inadequacies in the chemical-kinetic mechanism used in EKMA (Carter et al. 1981). In choosing our best estimate for the EKMA-equivalent NMHC/$NO_x$ ratio, we have considered all of these factors as well as the ratio that we have found works best in explaining historical ozone trends (Trijonis and Mortimer 1981).

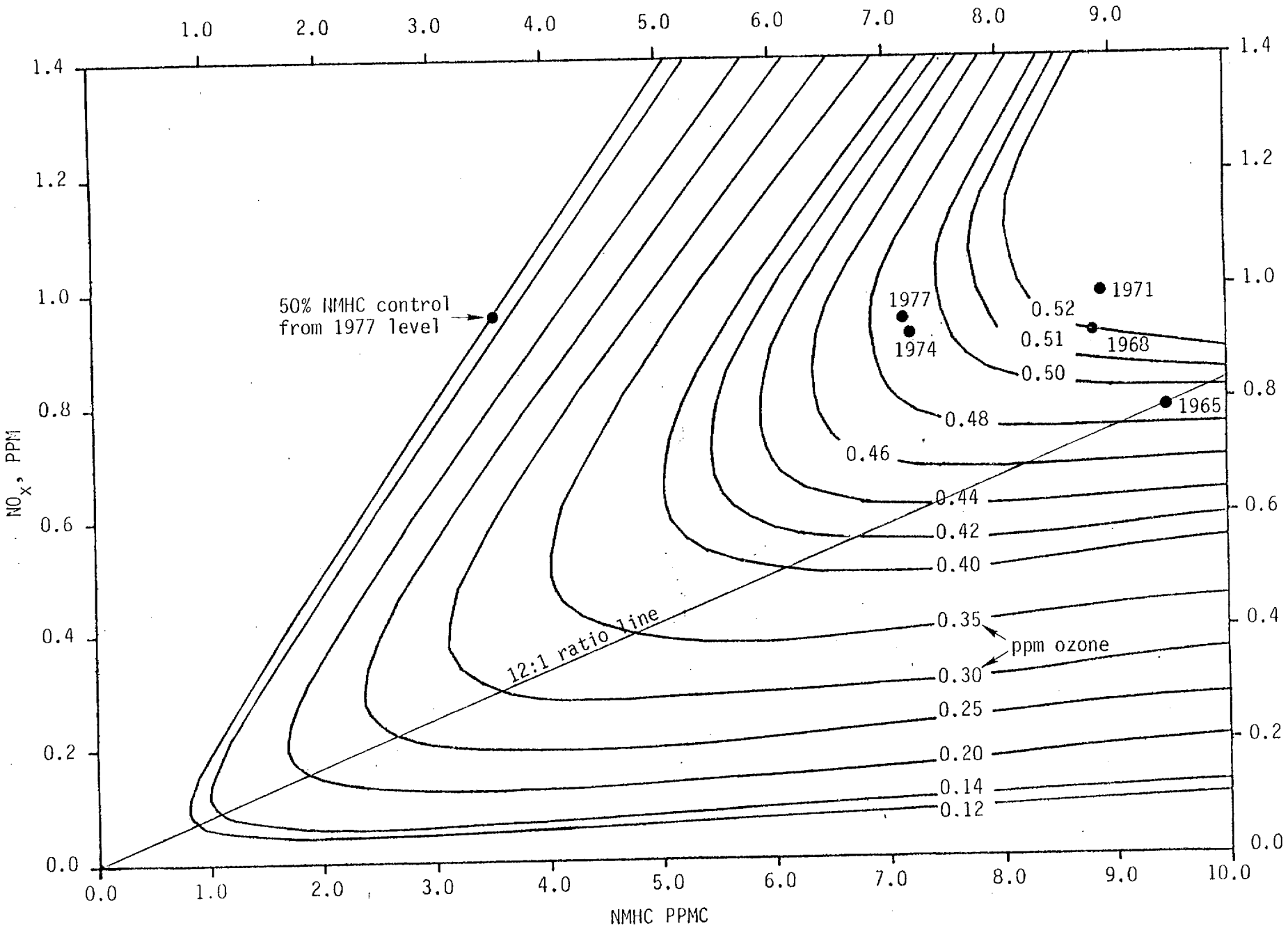


Figure 1.1 EKMA isopleth diagram for yearly maximum ozone at Azusa.

4:1 by the middle 1970's, and according to the EKMA diagram, ozone levels on such days should have decreased by more than a factor of two by the middle 1970's. In essence, our idea is to use the days of lowest NMHC/$NO_x$ ratios in 1965 to represent where we are now, and to simulate future NMHC reductions by examining the effect of historical control strategies on the low NMHC/$NO_x$ ratio days.

## 1.2 STUDY DESIGN

Following the precedence of Trijonis and Hunsaker (1978) and Trijonis and Mortimer (1981), the data base for the historical trend test is organized into 3-year periods: 1964-66, 1967-69, 1970-72, 1973-75, and 1976-78. Organizing the data into 3-year periods provides good robustness in the air quality statistics. The data are separated into three basic groups defined by the daily 6-9 AM NMHC/$NO_x$ ratio measured at a "source" site. The groups are the low 20% of ratio days (below the 20th percentile ratio for each individual 3-year period), middle 60% of ratio days (between the 20th and 80th percentiles for each period), and high 20% of ratio days (above the 80th percentile for each period). For each ratio group, the EKMA model predictions are tested as follows. The base period for the test is 1964-66. Using the necessary base period inputs for the EKMA model as well as information on historical precursor changes (from both emissions data and ambient data), predictions are made of ozone levels at "receptor" sites for each subsequent 3-year period. The EKMA predicted ozone trends for each ratio group are then compared to actual ozone trends for that ratio group.

Before the test can be carried out, the study design must be made more specific. In particular, we must choose or determine the following:

- The source and receptor sites.
- Receptor ozone averaging times.
- Wind restrictions for source/receptor transport.
- Historical precursor trends (based on both emission estimates and ambient data).
- Characteristic base year NMHC/$NO_x$ ratios for the EKMA model.
- EKMA simulation conditions (irradiation times, dilution patterns, etc.)

The above specifications are made in Chapters 2 and 3 of this report. Chapter 4 provides the results of the EKMA historical trend test.

## 1.3 SUMMARY

The following section summarizes our findings and conclusions. For convenient referral, the summary is organized according to the order of the chapters.

### 1.3.1 Preliminary Considerations (Chapter 2)

The most restrictive data constraint on this study is the availability of continuous measurements of the ambient NMHC/$NO_x$ ratio covering a 15-year period. In fact, the only feasible choice of a data base is the long-term AQMD data set for THC (total hydrocarbons) and $NO_x$, with the THC measurements converted to NMHC using an empirical formula.

A crucial initial step in our analysis is to examine the spatial uniformity of daily fluctuations in the 6-9 AM NMHC/$NO_x$ ratio. Essentially, we need to study the correlation of the daily NMHC/$NO_x$ ratio between monitoring stations. If the interstation correlations are high, it would imply (1) that the ambient data for the NMHC/$NO_x$ ratio are of good quality, (2) that we could define rather broad source and receptor areas, and our study would not require daily wind data to keep track of exact transport patterns, and (3) that we could be assured of a definitive test of our historical trend hypothesis.

As it turns out, the interstation correlations of the daily NMHC/$NO_x$ ratio are rather low, basically less than 0.20. These low interstation correlations can be explained by either or both of two factors: (1) measurement errors in the data for the NMHC/$NO_x$ ratio, or (2) spatial inhomogeneity of daily fluctuations in the ratio. If the first factor predominates (a distinct possibility), then our study cannot be successful because grouping the ozone trends by daily ratio values means we are sorting by measurement errors rather than by a real effect.

After discussions with various experts familiar with the problem, we decide that the second explanation is likely enough to warrant continuation of

the study. However, continuing the study under the assumption that observed ratio fluctuations are real but spatially nonuniform requires an additional constraint on our analysis. Specifically, if the ambient NMHC/$NO_x$ ratio is spatially nonuniform on a daily basis, we must use wind data to try to preserve equivalent air masses between source and receptor monitoring sites.

The source site selected for monitoring the NMHC/$NO_x$ ratio is Downtown LA, which has the best historical data and is conveniently situated. Two separate receptor sites are chosen for the ozone trend data, Azusa and Downtown LA. The receptor ozone data best correspond to the source ratio data if we use 12-3 PM ozone averages at Azusa and 10 AM-1 PM ozone averages at Downtown LA and we restrict the study at each receptor site to only those days with appropriate wind transport conditions.

### 1.3.2 Data Base for the Historical Trend Test (Chapter 3)

One of the necessary inputs to the historical test of the EKMA hypothesis is trend information for the ozone precursors, hydrocarbons and nitrogen oxides. Precursor trend information for the source areas affecting the two receptor sites is developed herein using both emissions data and ambient data. Both the emissions data and the ambient data indicate that, in entirety, the Los Angeles basin has undergone a moderate (15-30%) decrease in NMHC and a moderate (20-35%) increase in $NO_x$ from the middle 1960's to the late 1970's.

The base year NMHC/$NO_x$ ratio and the EKMA simulation conditions are key parameters that must be specified in setting up the EKMA prediction model. We find that the base period (1964-66), EKMA equivalent, 6-9 AM, ambient NMHC/$NO_x$ ratios for the low, medium, and high ratio groups are 6:1, 12:1, and 24:1, respectively. The EKMA simulation conditions selected are the standard EKMA conditions except for specifying fixed irradiation times (representative of fixed receptor sites), using special dilution rates, and adding post 8 AM emissions.

Historical ozone trends at each receptor site are determined using five basic programming steps: (1) grouping the data into 3-year periods, (2) calculating the 3-hour ozone averages each day, (3) eliminating days at each site without the appropriate wind transport conditions, (4) sorting and grouping the remaining daily data for each site by the 6-9 AM NMHC/$NO_x$ ratio at Downtown LA, and (5) computing various ozone air quality indices for each site, each

3-hour period, and each ratio group. We find that historical ozone changes for various air quality indices (e.g. 90th percentile versus average, or summer versus annual) are nearly identical. The air quality index chosen for the study is the summertime 90th percentile of the daily 3-hour averages.

### 1.3.3 Historical Test of Ozone Trends Sorted by the NMHC/$NO_x$ Ratio (Chapter 4)

The principal hypothesis to be tested in this study is whether historical ozone trends in Los Angeles differ significantly for data sets sorted by daily values of the 6-9 AM NMHC/$NO_x$ ratio. Most importantly, we want to investigate if days with low NMHC/$NO_x$ ratios experienced dramatic (>50%) reductions in ozone from the middle 1960's to the late 1970's.

Figures 1.2 and 1.3 summarize the results of the historical trend test. The top halves of the figures indicate EKMA predicted ozone trends for the three ratio groups (predictions based on averages of emission trend data and ambient precursor trend data), while the bottom halves of the figures show actual ozone trends for the three ratio groups. It is obvious that the actual ozone trend data at Azusa and Downtown LA do not confirm the EKMA hypothesis. The predicted ozone trends are widely divergent among the ratio groups, but the actual trends are about the same among the ratio groups (nearly identical in terms of the overall net change from 1964-66 to 1976-78). Most notably, actual ozone for the low ratio group did not exhibit especially large reductions historically.

If the actual ozone trend data had confirmed the EKMA predictions, the results would have been a definitive validation of the EKMA hypothesis. The only plausible explanation would have been that the data for this study are indeed of good quality (i.e. with respect to the ambient NMHC/$NO_x$ ratio), and that the EKMA model is correct concerning extreme sensitivity of ozone to hydrocarbon control at the current NMHC/$NO_x$ ratio.

That the actual ozone trend data did not confirm the EKMA hypothesis is not only disappointing but also ambiguous. One potential explanation is that the EKMA implications are erroneous, i.e. that ozone levels in Los Angeles are not currently in a very sensitive position with respect to the NMHC/$NO_x$

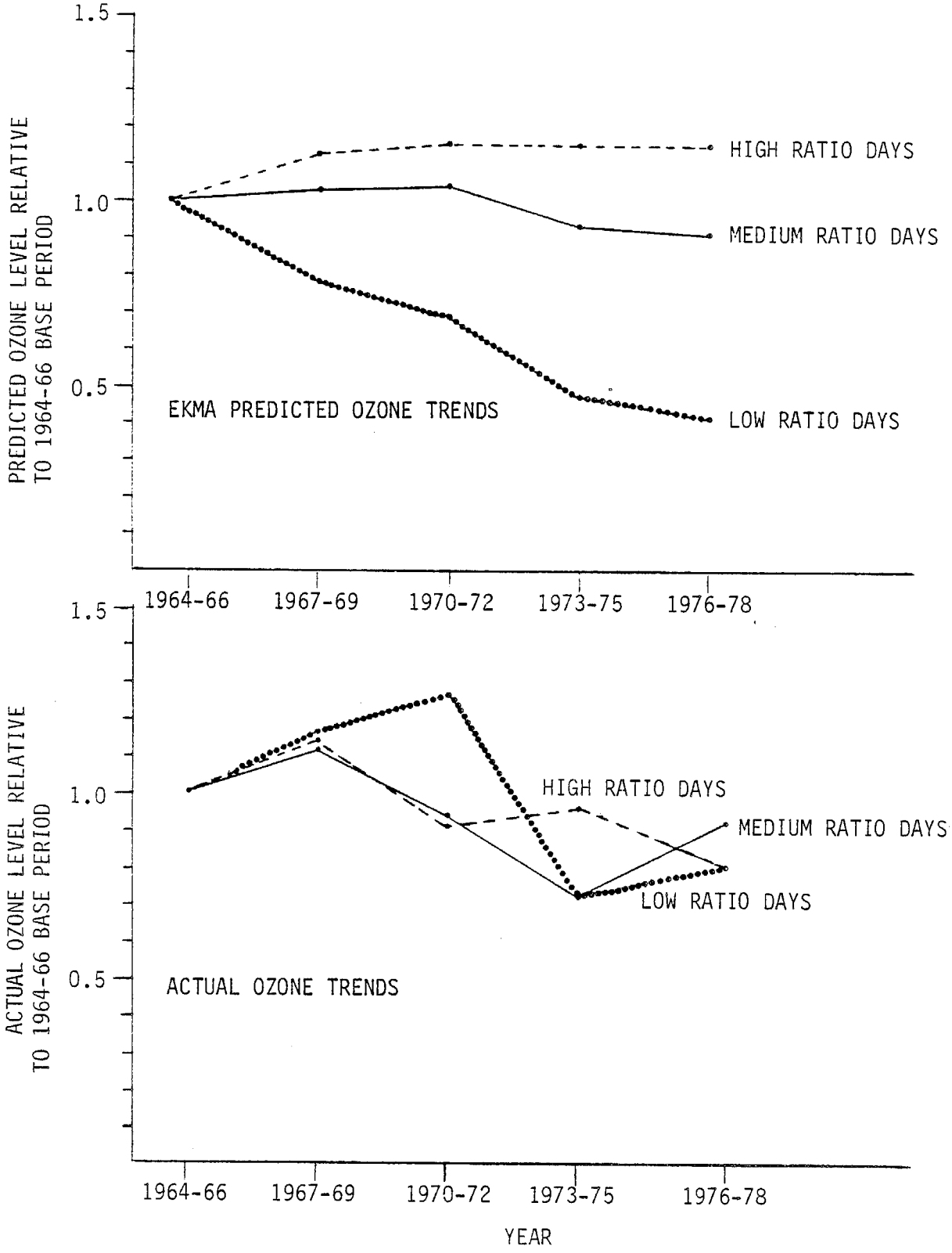


Figure 1.2 EKMA-predicted ozone trends for the three ratio groups and actual ozone trends for the three ratio groups at Azusa.

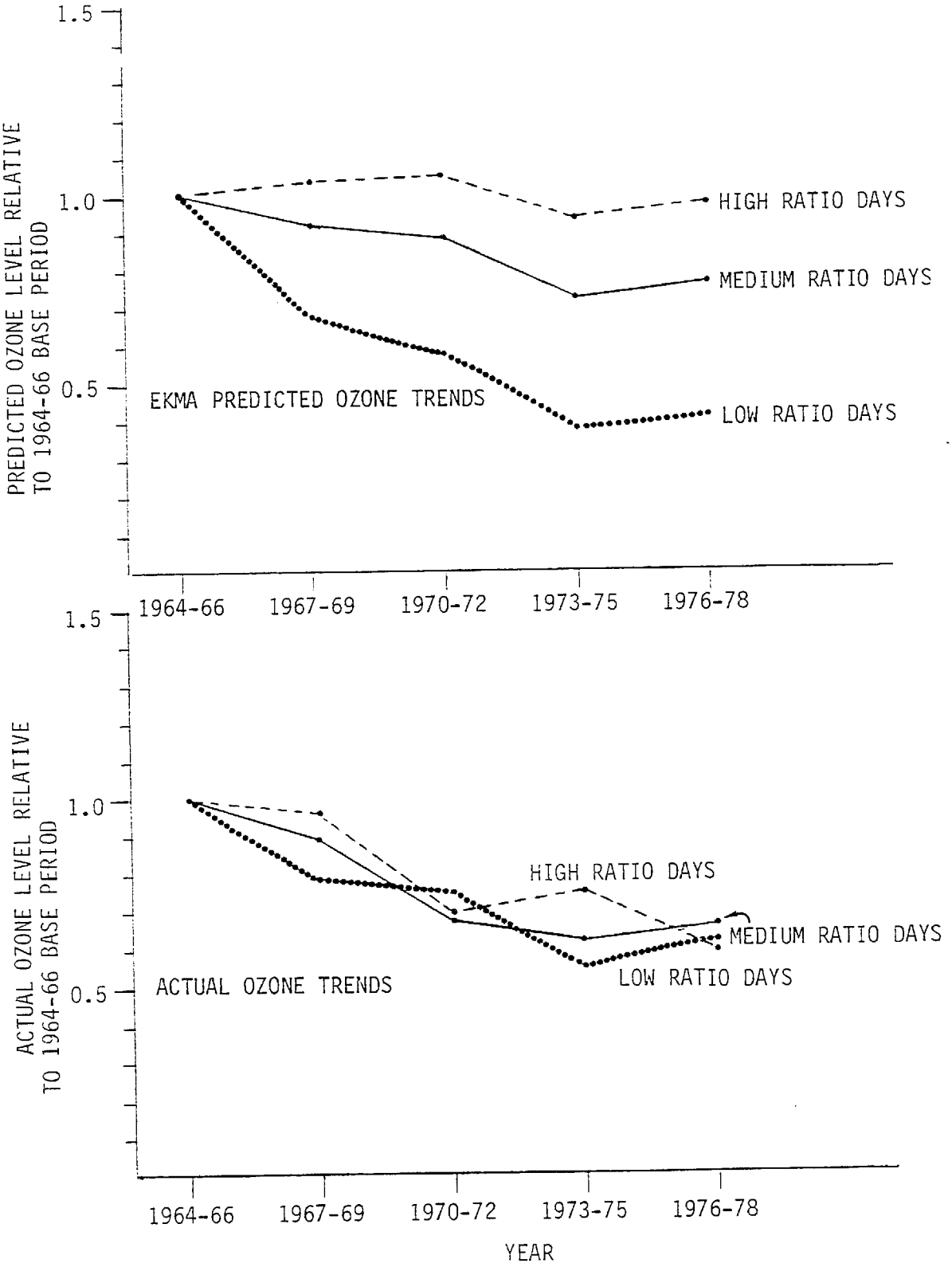


Figure 1.3 EKMA-predicted ozone trends for the three ratio groups and actual ozone trends for the three ratio groups at Downtown LA.

ratio. The second potential explanation concerns inadequacies in the data base; this study may be undermined by errors in the routine data for the $NMHC/NO_x$ ratio or by imprecision in the wind transport specifications.

# 2. PRELIMINARY CONSIDERATIONS

This chapter deals with several preliminary issues that need to be resolved before we assemble the data base for the historical trend test. Among the preliminary issues are selection of study sites, an initial feasibility analysis of the approach, and specification of study conditions. Section 2.1 discusses potential "source" sites (sites with long-term monitoring data for the ambient NMHC/$NO_x$ ratio). Section 2.2 investigates the spatial consistency of daily variations in the 6-9 AM NMHC/$NO_x$ ratio; this issue is important with respect to the feasibility of the approach and with respect to requirements regarding wind transport data. Section 2.3 selects the final "source-receptor" site pairs and specifies the averaging times and wind transport conditions.

## 2.1 LONG TERM DATA FOR THE AMBIENT NMHC/$NO_x$ RATIO

The most restrictive data constraint on this study is the availability of continuous long-term data for the ambient NMHC/$NO_x$ ratio, in particular for the hydrocarbon part of the ratio. Although several agencies have performed continuous hydrocarbon monitoring in the Los Angeles basin, long-term data (for $\approx$ 15 years) are available only from the AQMD. Most of the AQMD hydrocarbon data pertain to total hydrocarbons (THC), although some AQMD data also exist for nonmethane hydrocarbons (NMHC).

Eldon and Trijonis (1977a) performed extensive studies regarding the quality of routine monitoring data for photochemical pollutants in the Los Angeles basin. They concluded that estimating NMHC concentrations from THC measurements yields significantly better quality data than using AQMD NMHC measurements directly. In the present study, we will estimate NMHC concentrations from THC data according to the equation, NMHC = 0.7(THC-1.5), with units of ppm; this equation is approximately the same as the formula derived statistically by Paskind and Kinosian (1974). Trijonis and Hunsaker (1978) and Trijonis and Mortimer (1981) have shown that this equation leads to NMHC/$NO_x$ ratio values that are consistent in overall magnitude with the most recent and highest quality data for the NMHC/$NO_x$ ratio.

In order to summarize the availability of long-term data for the 6-9 AM NMHC/$NO_x$ ratio, we have compiled Table 2.1 from ARB computer tapes of AQMD measurements. Table 2.1 lists the number of nonmissing daily values for the ratio, grouped according to our three-year study periods. For the purpose of this table, a ratio value is defined as "nonmissing" if at least two hours of data are available for both THC and $NO_x$ during the 6-9 AM period.

Considering the compilations of Table 2.1 as well as the typical daily dynamics of photochemical smog in Los Angeles, it is obvious that Downtown LA represents the best candidate as a "source site" for our historical trend test. Downtown LA provides, by far, the most complete historical record for the NMHC/$NO_x$ ratio. Also, Downtown LA represents a dense emission source area (especially for traffic), and it lies upwind of the highest ozone stations (in the San Gabriel, Pomona, and San Bernardino Valleys). Azusa and Anaheim might also be useful as source sites for the morning NMHC/$NO_x$ ratio, if receptor sites were chosen in the San Bernardino and La Habra/Riverside areas, respectively. Some of the other stations in Table 2.1 are potentially useful for studies over shorter time spans, e.g. 9 years rather than 15 years.

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TABLE 2.1 AVAILABILITY OF ROUTINE AQMD MONITORING DATA FOR THE AMBIENT NMHC/$NO_x$ RATIO

| YEARS | NUMBER OF DAILY OBSERVATIONS FOR 6-9 AM NMHC/$NO_x$ RATIO | | | | | |
|---|---|---|---|---|---|---|
| | Downtown LA | Azusa | Anaheim | Burbank | Lennox | Pomona |
| 1964-66 | 917 | 332 | 383 | 449 | 41 | 0 |
| 1967-69 | 924 | 770 | 747 | 0 | 0 | 0 |
| 1970-72 | 986 | 976 | 918 | 859 | 914 | 924 |
| 1973-75 | 975 | 1033 | 913 | 1026 | 841 | 1073 |
| 1976-78 | 966 | 966 | 862 | 1008 | 716 | 1047 |

Notes: An observation is defined as nonmissing if at least two THC and at least two $NO_x$ measurements are available for the 6-9 AM period. See later Figure 3.5 (page 29) for a map showing the locations of these monitoring sites.

## 2.2 SPATIAL CONSISTENCY OF FLUCTUATIONS IN THE NMHC/$NO_X$ RATIO

A crucial initial step in our analysis is to investigate the spatial homogeneity of daily fluctuations in the 6-9 AM NMHC/$NO_X$ ratio. Basically, we need to examine the correlation of the daily NMHC/$NO_X$ ratio between monitoring stations. In this correlation analysis, the data must be divided into rather short historical periods (e.g. three year spans), because otherwise the daily spatial fluctuations of the ratio would be confounded with long-term trends of the ratio.

If the daily variations in the 6-9 AM NMHC/$NO_X$ ratio correlate fairly well among the monitoring stations, it would mean that the ambient data for the NMHC/$NO_X$ ratio are of good quality (with respect to differentiating high ratio values from low ratio values at a particular location). Specifically, because the ratio fluctuations at a given site are confirmed independently at other sites, it would imply that the daily ratio fluctuations are real and are not just produced by measurement errors. Also, if the correlations among stations are fairly high, then we might be able to define rather broad source areas (possibly containing two or more correlated monitoring sites), so that, in the analysis, we would not have to keep track of detailed daily transport conditions. In essence, if the interstation correlations are good, we can be assured of a rather definitive test of our historical trend hypothesis, and we can omit daily wind data from our analysis.

Using the data summarized previously in Table 2.1, we have determined interstation correlations among daily values of the 6-9 AM NMHC/$NO_X$ ratio for each of the 3-year periods. The results for 1976-78, presented in Table 2.2, are generally representative of our findings for all of the 3-year periods. Table 2.2 shows that, although the interstation correlations are usually statistically significant, they are rather low, basically less than 0.20.* A correlation level of less than 0.20 means that the relationship between stations explains less than 4% of the variance in the observed daily fluctuations

*Note that, because of the large sample sizes (typically a few hundred data points), fairly low correlation levels can still be statistically quite significant.

TABLE 2.2 INTERSTATION CORRELATION COEFFICIENTS FOR THE 6-9 AM NMHC/$NO_x$ RATIO, 1976-1978.

| | Downtown LA | Azusa | Anaheim | Burbank | Lennox | Pomona |
|---|---|---|---|---|---|---|
| Downtown LA | 1.00 | .16•• | .08• | .14•• | .19•• | .17•• |
| Azusa | | 1.00 | .14•• | .10•• | -.04 | .04 |
| Anaheim | | | 1.00 | .21•• | .07• | .12•• |
| Burbank | | | | 1.00 | .08 | .01 |
| Lennox | | | | | 1.00 | .12•• |
| Pomona | | | | | | 1.00 |

•Statistically significant at 95% confidence level

••Statistically significant at 99% confidence level

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of the ratio.* This disappointing result caused us to reevaluate and reformulate our study plan.

The low interstation correlations for the ratio can be produced by either or both of two factors: (1) measurement errors in the data for the NMHC/$NO_x$ ratio, and (2) spatial inhomogeneity of daily fluctuations in the ratio. If the first factor predominates, then our study cannot be successful, because grouping the ozone trends by daily ratio values means that we are sorting by measurement errors rather than by a real atmospheric variation. If the second factor predominates, the study still could be planned and carried out successfully.

That the first explanation, measurement errors, basically accounts for the daily fluctuations in the NMHC/$NO_x$ ratio is a distinct possibility. ELdon and Trijonis (1977a) concluded that the qualities of routine monitoring

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*One of the likely reasons for the low correlations is imprecision in the ambient hydrocarbon data (Eldon and Trijonis 1977a). Thinking that the hydrocarbon data might be more precise at higher hydrocarbon levels, we redid the correlation analysis restricting the data to days when THC concentrations exceeded 2.5 ppm. This restriction, however, did not improve the correlations significantly.

data for $NO_x$ and THC are only good and fair, respectively, as compared to excellent for $O_3$. The observed fluctuations in the NMHC/$NO_x$ ratio could very possibly be due to a compounding of separate errors in the $NO_x$ and THC data. In fact, if upwind emissions of hydrocarbons and $NO_x$ affecting each monitoring site were constant every day, and if transport patterns were the same each day, there would be no reason for the ambient ratio of hydrocarbons to $NO_x$ to fluctuate (both hydrocarbons and $NO_x$ would vary up and down together with dispersion conditions), and all of the observed ratio fluctuations would have to be measurement errors.

However, after discussing this issue at length with various experts on Los Angeles photochemical smog (G. Cass, A. Davidson, J. Holmes, J. Kinosian, G. McRae, C. Unger 1981), we decided that the second explanation -- real variations in the NMHC/$NO_x$ ratio that are spatially nonuniform -- was likely enough to warrant continuation of the study. There are two major considerations in this decision. First, although Eldon and Trijonis (1977a) concluded that routine THC and $NO_x$ data were only of fair to good quality, they did find nevertheless that the ambient precursor data, including fluctuations in the NMHC/$NO_x$ ratio, yielded reasonable and useful results as part of a statistical ozone modeling analysis. Several other investigators (Merz et al. 1972; Kinosian and Paskind 1973; Trijonis 1974, 1978) have also found that variations in the ambient ratio make sense when used in statistical photochemical models. Second, it is physically reasonable for the NMHC/$NO_x$ ratio to fluctuate spatially in a nonuniform way. Three basic phenomena exist that should cause the NMHC/$NO_x$ ratio to vary from day to day: (1) temperature and relative humidity can affect the NMHC/$NO_x$ emission ratios from sources (e.g. automobiles); (2) the NMHC/$NO_x$ ratio should depend on the amount of carry-over pollution from the previous day, with the ratio being higher when carry-over is greater (Kinosian 1981; Horie et al. 1979); and (3) the daily ratio at a given site should depend on whether the upwind trajectory was nearer hydrocarbon rich stationary sources or $NO_x$ rich stationary sources. The second and especially the third of these factors should produce spatially inhomogeneous variations in the ratio.

Continuing the study under the assumption that observed ratio fluctuations are real but spatially inhomogeneous requires an additional constraint in our analysis. Specifically, if the ratio is spatially nonuniform on a daily basis, then we must use wind data each day to track the air mass from the source (precursor) site to the receptor (ozone) site. That is -- we must try to maintain the same air mass in connecting the 6-9 AM NMHC/$NO_x$ ratio to subsequent ozone measurements. The next section presents source/receptor pairs and wind specifications that should meet this constraint.

## 2.3 SOURCE/RECEPTOR SPECIFICATIONS

In the original study plan for this project, we intended to analyze about three or four pairings of source/receptor areas. Some of these areas would be rather broad geographically and would contain two or more monitoring sites. Furthermore, hoping that the variations in the daily NMHC/$NO_x$ ratio would be spatially uniform, we planned to omit daily wind data from the study. The findings of the previous section, however, caused us to change our study plan. With the concurrence of the ARB staff, we made two alterations. First, we added daily wind trajectory constraints to the analysis in an attempt to maintain equivalent air masses on the study days. Second, we limited the analysis to only the two most promising pairings of individual source/receptor sites.

For both source/receptor pairings, we selected Downtown LA as the source monitoring site. There were three strong reasons for this selection. First, as noted previously, Downtown LA provides by far the most extensive historical data record for the ambient NMHC/$NO_x$ ratio (see previous Table 2.1). Second, Table 2.2 suggests that the NMHC/$NO_x$ data might be of better quality at Downtown LA than at the other sites because the interstation correlations are slightly better for pairings involving Downtown LA. It would not be unreasonable for Downtown LA to have better quality data historically, considering that the Downtown station was operated at the Los Angeles APCD headquarters. Third, Eldon and Trijonis (1977b) concluded that Downtown LA provides the best source site for statistical ozone modeling studies in Los Angeles, because Downtown LA yields the best overall correlations between morning precursor levels and downwind afternoon ozone levels.

Based on the study of source/receptor relationships conducted by Eldon and Trijonis (1977b), the two most obvious receptor sites to use in our historical trend test are Azusa and Downtown LA.* Eldon and Trijonis determined ozone averaging times and wind conditions for these sites that maximize the correlation between daily ozone concentrations and morning precursor concentrations. For example, they found that it was best to use 3-hour ozone averages, to use earlier ozone hours at Downtown LA than at Azusa, and to restrict Downtown LA studies to low wind speeds and Azusa studies to higher southwesterly winds. The exact specifications that we will use in this study are as follows:

| | Azusa Study Days | Downtown LA Study Days |
|---|---|---|
| Ozone averaging time | 12-3 PM PDT | 10 AM-1 PM PDT |
| Vector-averaged 7 AM-2 PM Downtown LA wind velocity | speed $\geq$4 mph | speed $\leq$ 5 mph |
| | direction from southwest quadrant | |

The study plan now is as follows. A separate historical trend test will be conducted for the Azusa/Downtown LA and the Downtown LA/Downtown LA source-receptor pairings. For each pairing, the study will be restricted to days with nonmissing ratio values (at least two of the three hours complete), to days with nonmissing ozone values (at least two of the three hours complete), and to days satisfying the appropriate wind constraints. For each 3-year study period, the receptor-site ozone data will be sorted into 3 groups according to the daily source-site NMHC/$NO_x$ ratio -- lowest 20th percent of the ratio, middle 20th to 80th percentile of the ratio, and highest 20th percent of the ratio. Ozone trend indices will be computed for each of the three ratio groups and each source/receptor pairing. The actual ratio sorted ozone trends will then be compared to ratio-sorted ozone trends predicted by the EKMA model.

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*A third potential choice, Pasadena, is inappropriate for historical trend studies because of two significant site relocations during the period of interest. Some readers might argue with the choice of Downtown LA as a receptor site paired with itself as a source site. However, previous studies (Trijonis 1974; Eldon and Trijonis 1978) have shown that this is a useful source/receptor pairing as long as ozone is measured early (i.e. in the late morning) and as long as wind speeds are low.

# 3. DATA BASE FOR THE HISTORICAL TREND TEST

This chapter describes the data bases and specifies the parameters for the historical trend test. Section 3.1 presents data concerning historical precursor changes; these include both emission trends and ambient precursor trends for the source areas affecting the two study sites (Azusa and Downtown LA). Section 3.2 specifies the parameters for the EKMA ozone prediction model; the key parameters being the base year NMHC/$NO_x$ ratio and the EKMA simulation conditions. Section 3.3 presents the actual ozone trends, sorted by daily NMHC/$NO_x$ ratio and restricted to days with the appropriate transport patterns.

## 3.1 HISTORICAL PRECURSOR TRENDS

One of the critical inputs to our historical test is trend information for the ozone precursors, hydrocarbons and nitrogen oxides. Below, we develop the precursor trend information using both emissions data and ambient data. The emission trends and the ambient precursor trends will later be used individually in the historical tests with the EKMA model. As indicated by the discussions below, this section basically relies on data compiled in a previous Los Angeles study performed for EPA by Trijonis and Mortimer (1981).

Because the historical test will be conducted grouping data by three year periods -- 1964-1966, 1967-1969, 1970-1972, 1973-1975, 1976-1978 -- the precursor data presented herein will be put into a tri-yearly format. Also, the precursor trend information will be compiled individually for the two areas of interest -- the source area affecting Azusa ozone and the source area affecting Downtown LA ozone.

### 3.1.1 Emission Trends

Trijonis and Mortimer (1981) have conducted a very extensive analysis of historical emission trends for reactive hydrocarbons (RHC) and $NO_x$ in the Los Angeles basin from 1965 to 1978. They compiled emission trends for various source categories based on an analysis of three basic factors: uncontrolled emission levels, source growth/attrition rates, and source control schedules. They

documented these factors on a consistent basis using the latest information available from research firms, trade associations, and numerous federal/state/local agencies. Below, we will only summarize the results that are most pertinent to the present study. For more detailed discussions of the methodology and results, the reader is referred to the final report for EPA (Trijonis and Mortimer 1981).

Trijonis and Mortimer first estimated basinwide emission trends for RHC and $NO_x$ on a yearly basis from 1965 to 1978. Figures 3.1 and 3.2 summarize the results. The top line in each figure represents total emission trends, while the distances between lines represent contributions from individual source categories. The points for 1978 are connected with dashed lines because only data for 1965 to 1977 are required for our historical test.

As shown in Figure 3.1, estimated basinwide emissions of RHC decreased continually during the study period, with a net reduction of 20% from 1965 to 1977. The predominant part of this reduction was due to decreases in emissions from light/medium duty vehicles (the largest source category); light/medium duty vehicle RHC emissions decreased 40% from 1965 to 1977 despite a 54% increase in traffic levels. Organic solvent emissions also underwent a significant (30%) decrease, with this reduction basically occurring between 1965 and 1974.

As shown in Figure 3.2, estimated basinwide $NO_x$ emissions rose rapidly from 1965 to 1973 and then basically leveled off. The net increase over the entire study period, 1965 to 1977, was 34%. The predominant part of this rise was due to a 55% increase in $NO_x$ emissions from light/medium duty vehicles (the largest source category). The net increase in light/medium duty vehicle $NO_x$ from 1965 to 1977 basically represented traffic growth. Light/medium duty vehicle $NO_x$ emission factors for new cars jumped upward in the late 1960's, but by 1977 the fleet-averaged $NO_x$ emission factor was reduced back to the 1965 level due to the new car $NO_x$ emission standards of the 1970's. $NO_x$ emissions from heavy duty vehicles and residential/commercial/industrial fuel burning also increased significantly from 1965 to 1977, reflecting growth in traffic and natural gas usage, respectively. Power plant $NO_x$ emissions decreased slightly from 1965 to 1977.

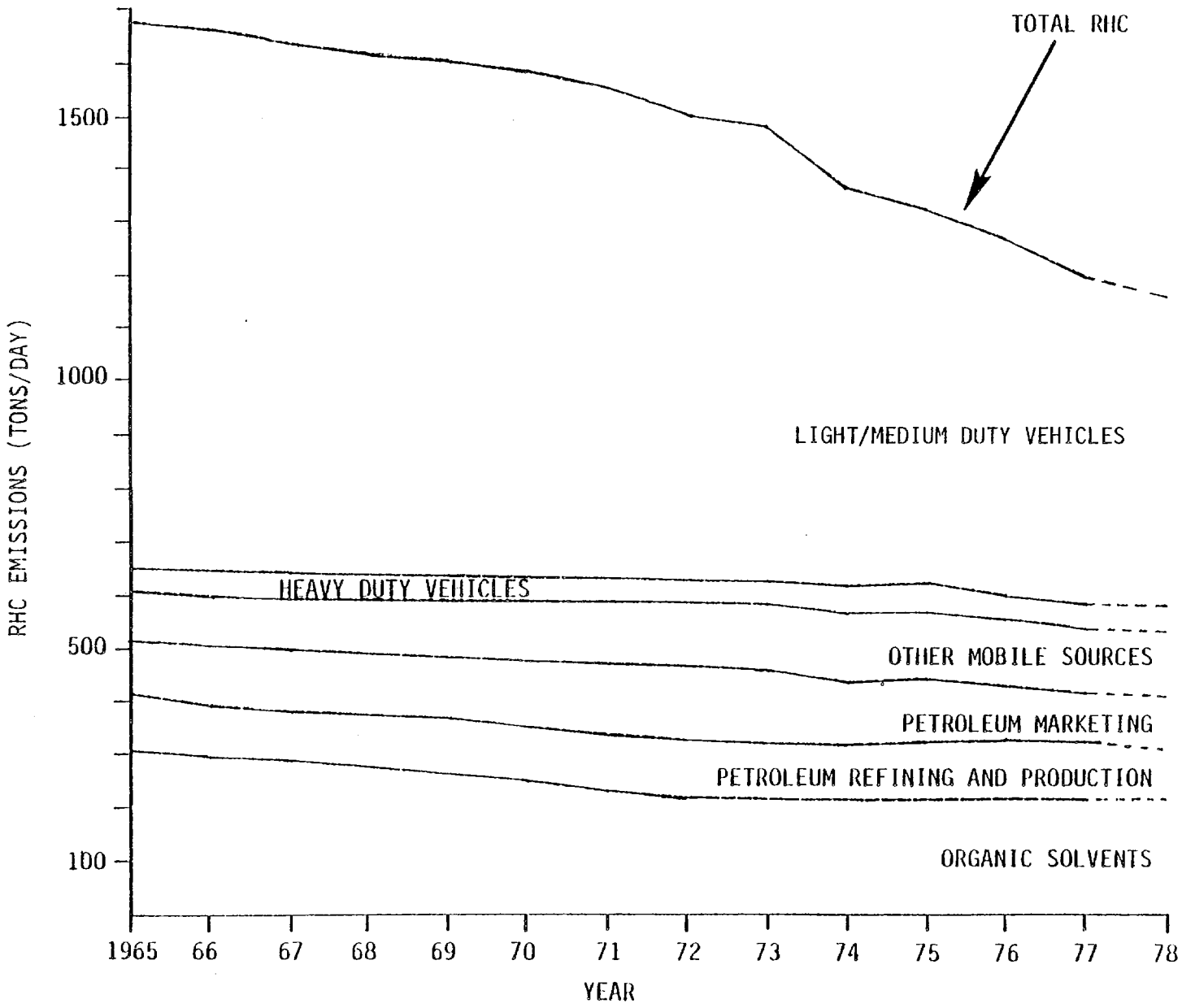


Figure 3.1 Historical RHC emission trends in the Los Angeles basin (Trijonis and Mortimer 1981).

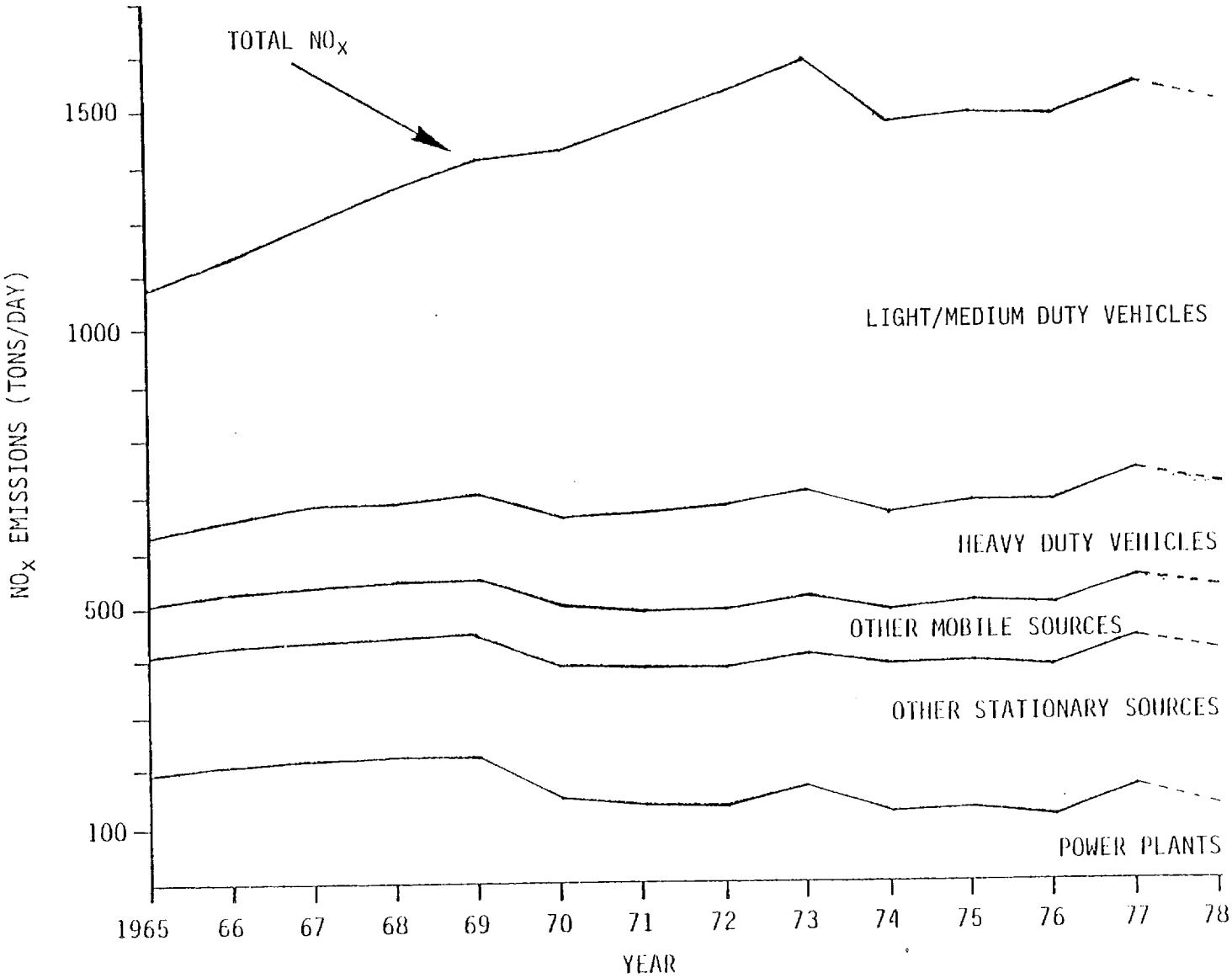


Figure 3.2 Historical $NO_X$ emission trends in the Los Angeles basin (Trijonis and Mortimer 1981).

The emission trends relevant to this study are emission trends for the specific source areas affecting noon-3 PM ozone at Azusa and 10 AM-1 PM ozone at Downtown LA under typical transport conditions. The selection of ozone source areas in Los Angeles has been discussed extensively in previous reports (Trijonis and Hunsaker 1978; Eldon and Trijonis 1977b). Those reports identified source areas for ozone at given monitoring sites based on a review of various wind trajectory and wind streamline studies. Using the results of those reports, Trijonis and Mortimer (1981) selected source areas for ozone at Azusa and Downtown LA (under typical transport conditions) as shown in Figures 3.3 and 3.4.

Data on historical source growth rates (e.g. traffic growth rates) are not available with sufficient spatial detail to conduct a rigorous, quantitative analysis of emission trends for the individual source areas. To estimate emission trends for the specific source areas, Trijonis and Mortimer made approximate adjustments to the basinwide emission trends, taking into account the detailed spatial distribution of population growth in the Los Angeles region (Trijonis and Hunsaker 1978), the county-by-county distribution of traffic growth (Trijonis et al. 1978), and the spatial distribution of various source types (Trijonis et al. 1975; ARB 1980). The resulting estimates of emission trends for the Azusa and Downtown LA source areas are listed in Table 3.1. As required by the

TABLE 3.1 ESTIMATES OF EMISSION TRENDS FOR THE AZUSA AND DOWNTOWN LA SOURCE AREAS.

| YEARS | RHC Emission Changes Relative to Base Period | | $NO_x$ Emission Changes Relative to Base Period | |
|---|---|---|---|---|
| | Azusa | DOLA | Azusa | DOLA |
| 1964-1966 | 0% | 0% | 0% | 0% |
| 1967-1969 | -5% | -5% | +15% | +13% |
| 1970-1972 | -11% | -12% | +21% | +18% |
| 1973-1975 | -24% | -26% | +22% | +18% |
| 1976-1978 | -34% | -36% | +20% | +16% |

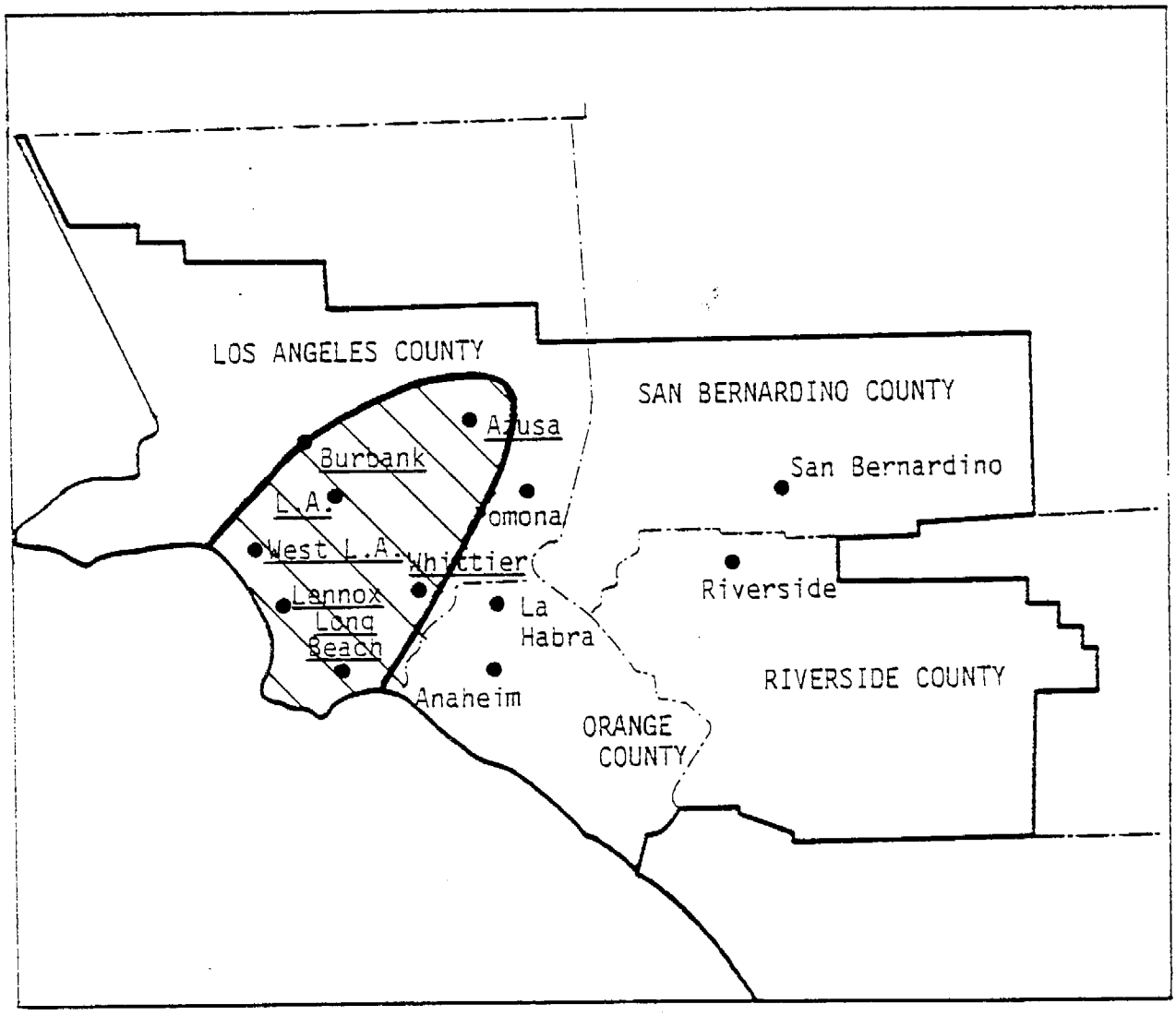


Figure 3.3 Approximate source area affecting ozone at Azusa.

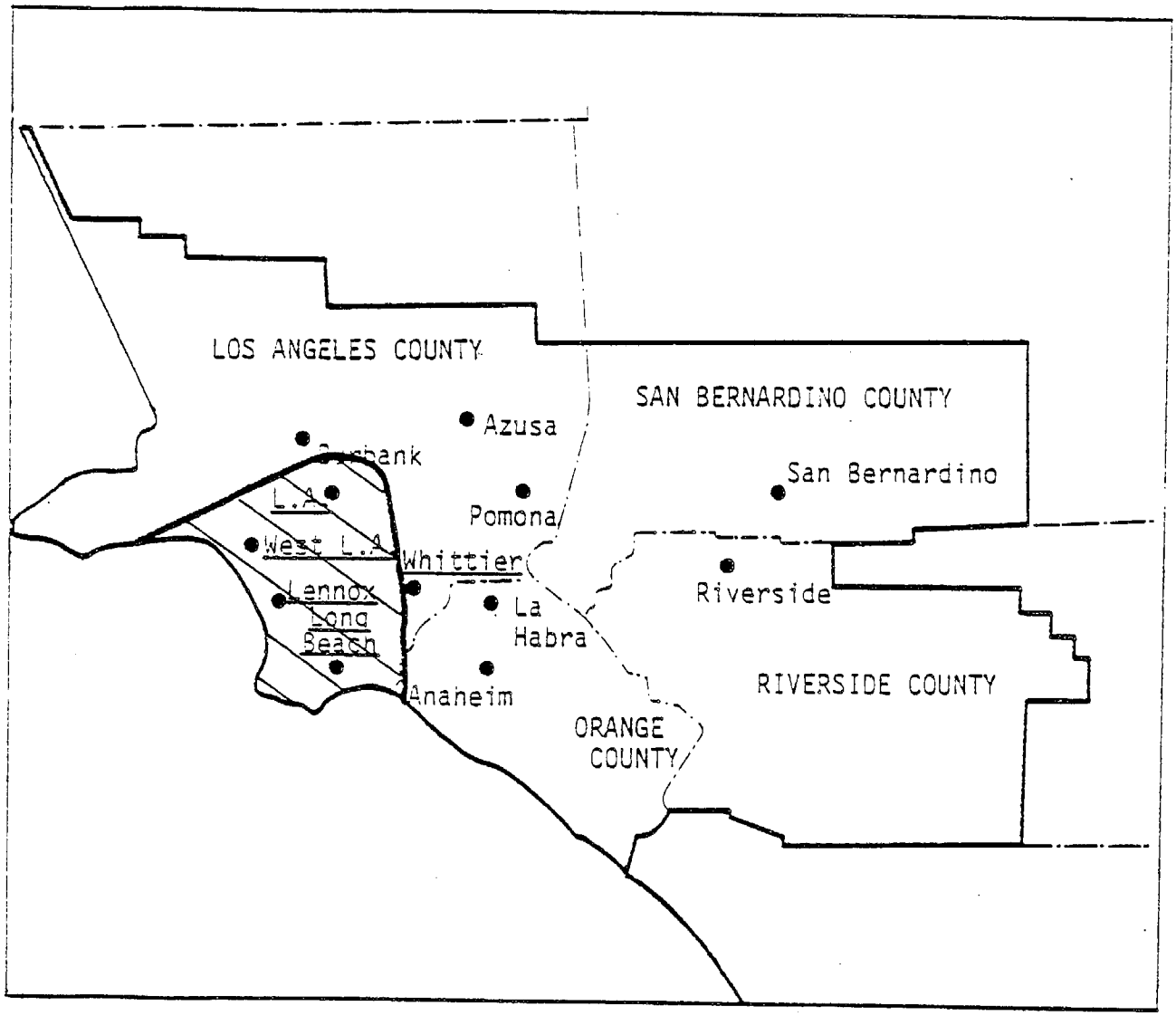


Figure 3.4 Approximate source area affecting ozone at Downtown Los Angeles.

EKMA model, the trends are specified in terms of the net percent change in emissions from the base period (1964-1966) to each subsequent 3-year period.

### 3.1.2 Ambient Precursor Trends

Trijonis and Mortimer (1981) also made a compendium of ambient trend data for NMHC and $NO_x$ at the monitoring sites shown in Figure 3.5. The NMHC trends were computed from data for total hydrocarbons (THC) using an empirical formula developed by Paskind and Kinosian (1974). Also, interpolations and extrapolations were made for certain sites with incomplete or missing years data. The final trend analysis was based on a single air quality index -- the yearly average of daily maximum hourly concentrations -- which was shown to be equivalent to other indices (e.g. to the annual mean of all hours). For a complete discussion of the trend methodology, the reader should consult the previously referenced EPA report.

The underlined monitoring sites in Figures 3.3 and 3.4 were used to determine ambient precursor trends for the Azusa and Downtown LA source areas. Tables 3.2 and 3.3 summarize the ambient trends, expressed as net percent changes in precursor concentrations from the 1964-66 base period. The individual monitoring sites sometimes differ considerably with respect to historical precursor trends; the differences are due to spatial variations in emission trends, statistical variance in the ambient trend data, and, possibly, to inconsistencies (errors) in the historical trend data at individual sites. The average (over the monitoring sites) of the percent changes will be used to represent the ambient precursor trends for the entire source area.

### 3.1.3 Comparison of Emission Trends and Ambient Precursor Trends

Figure 3.6 compares the ambient precursor trends with estimated emission trends in each of the two source areas. The agreement between emission trends and ambient trends is generally good, especially when the data are viewed in an overall sense from 1965 to 1977. In fact, considering the agreement between the emissions and ambient data, we can state -- with a high degree of confidence -- that there has been a moderate decrease in hydrocarbons and a moderate increase in $NO_x$ within the Los Angeles basin from 1965 to 1977.

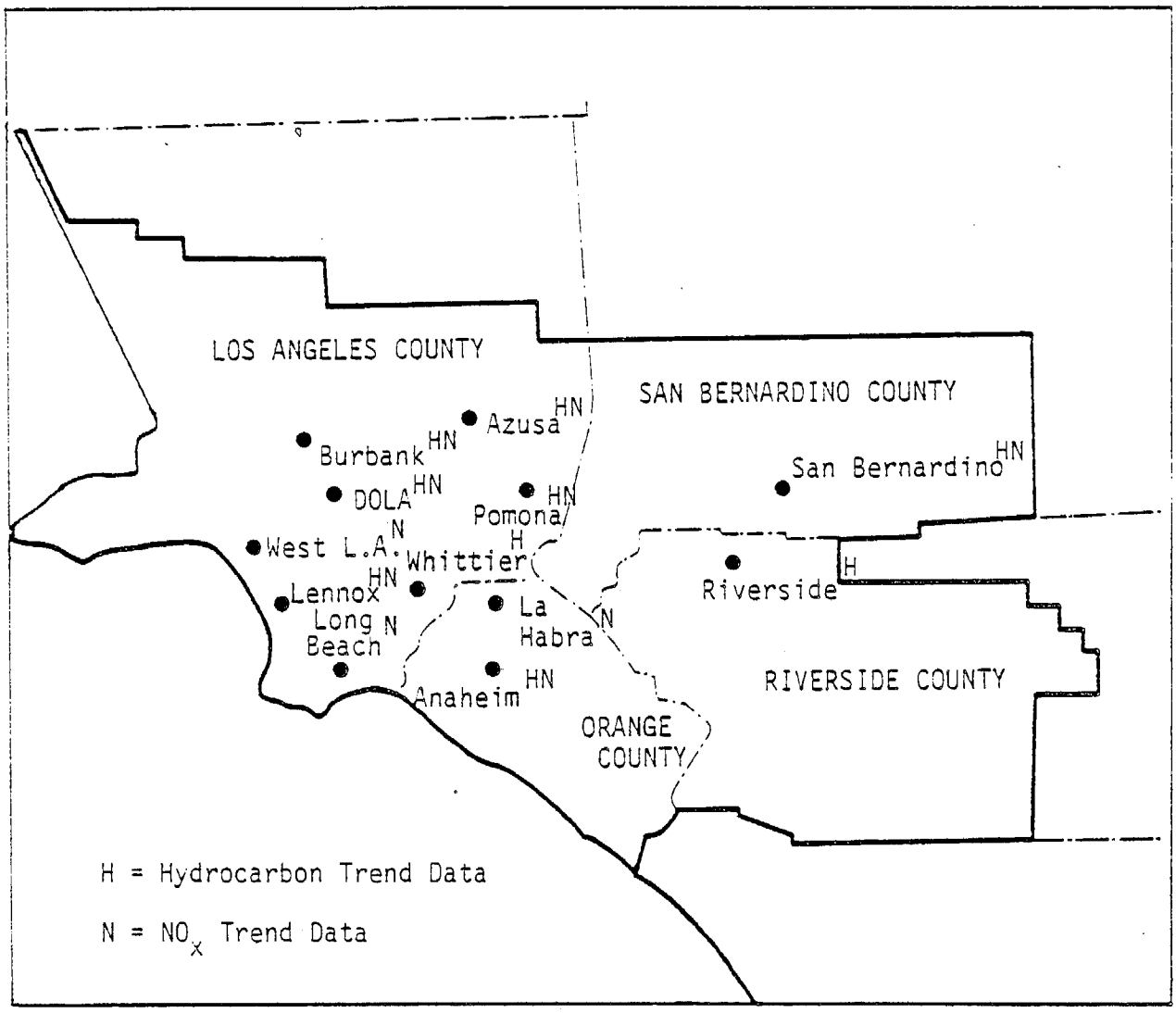


Figure 3.5 Monitoring sites used to characterize ambient precursor trends in the Los Angeles basin.

TABLE 3.2 AMBIENT PRECURSOR TRENDS FOR THE SOURCE AREA AFFECTING AZUSA OZONE.

Table 3.2a Percent Changes in Yearly Average of Daily One-Hour Maximum NMHC Relative to 1964-1966.

| YEARS | STATION | | | | | AVERAGE OF PERCENT CHANGES |
|---|---|---|---|---|---|---|
| | DOLA | Lennox | Whittier | Burbank | Azusa | |
| 1964-66 | 0% | 0% | 0% | 0% | 0% | 0% |
| 1967-69 | -25% | -25% | -17% | +8% | +17% | -8% |
| 1970-72 | -25% | -25% | -13% | +11% | +51% | 0% |
| 1973-75 | -49% | -43% | -36% | -8% | +21% | -23% |
| 1976-78 | -42% | -28% | -3% | -1% | +6% | -14% |

Table 3.2b Percent Changes in Yearly Average of Daily One-Hour Maximum $NO_x$ Relative to 1964-1966.

| YEARS | STATION | | | | | | AVERAGE OF PERCENT CHANGES |
|---|---|---|---|---|---|---|---|
| | DOLA | Lennox | Burbank | Azusa | Long Beach | West L.A. | |
| 1964-66 | 0% | 0% | 0% | 0% | 0% | 0% | 0% |
| 1967-69 | +7% | +25% | +34% | +16% | +19% | +8% | +18% |
| 1970-72 | +22% | +33% | +36% | +56% | +20% | +17% | +31% |
| 1973-75 | 0% | +16% | +7% | +47% | -8% | +10% | +12% |
| 1976-78 | +14% | +22% | +19% | +63% | 0% | +13% | +22% |

TABLE 3.3 AMBIENT PRECURSOR TRENDS FOR THE SOURCE AREA AFFECTING DOWNTOWN LOS ANGELES OZONE.

Table 3.3a Percent Changes in Yearly Average of Daily One-Hour Maximum NMHC Relative to 1964-1966.

| YEARS | Downtown Los Angeles | Lennox | Whittier | AVERAGE OF PERCENT CHANGES |
|---|---|---|---|---|
| 1964-66 | 0% | 0% | 0% | 0% |
| 1967-69 | -25% | -25% | -17% | -22% |
| 1970-72 | -25% | -25% | -13% | -21% |
| 1973-75 | -49% | -43% | -36% | -43% |
| 1976-78 | -42% | -28% | -3% | -24% |

Table 3.3b Percent Changes in Yearly Average of Daily One-Hour Maximum $NO_x$ Relative to 1964-1966.

| YEARS | STATION | | | | AVERAGE OF PERCENT CHANGES |
|---|---|---|---|---|---|
| | Downtown Los Angeles | Lennox | West L.A. | Long Beach | |
| 1964-66 | 0% | 0% | 0% | 0% | 0% |
| 1967-69 | +7% | +25% | +8% | +19% | +15% |
| 1970-72 | +22% | +33% | +17% | +20% | +23% |
| 1973-75 | 0% | +16% | +10% | -8% | +5% |
| 1976-78 | +14% | +22% | +13% | 0% | +12% |

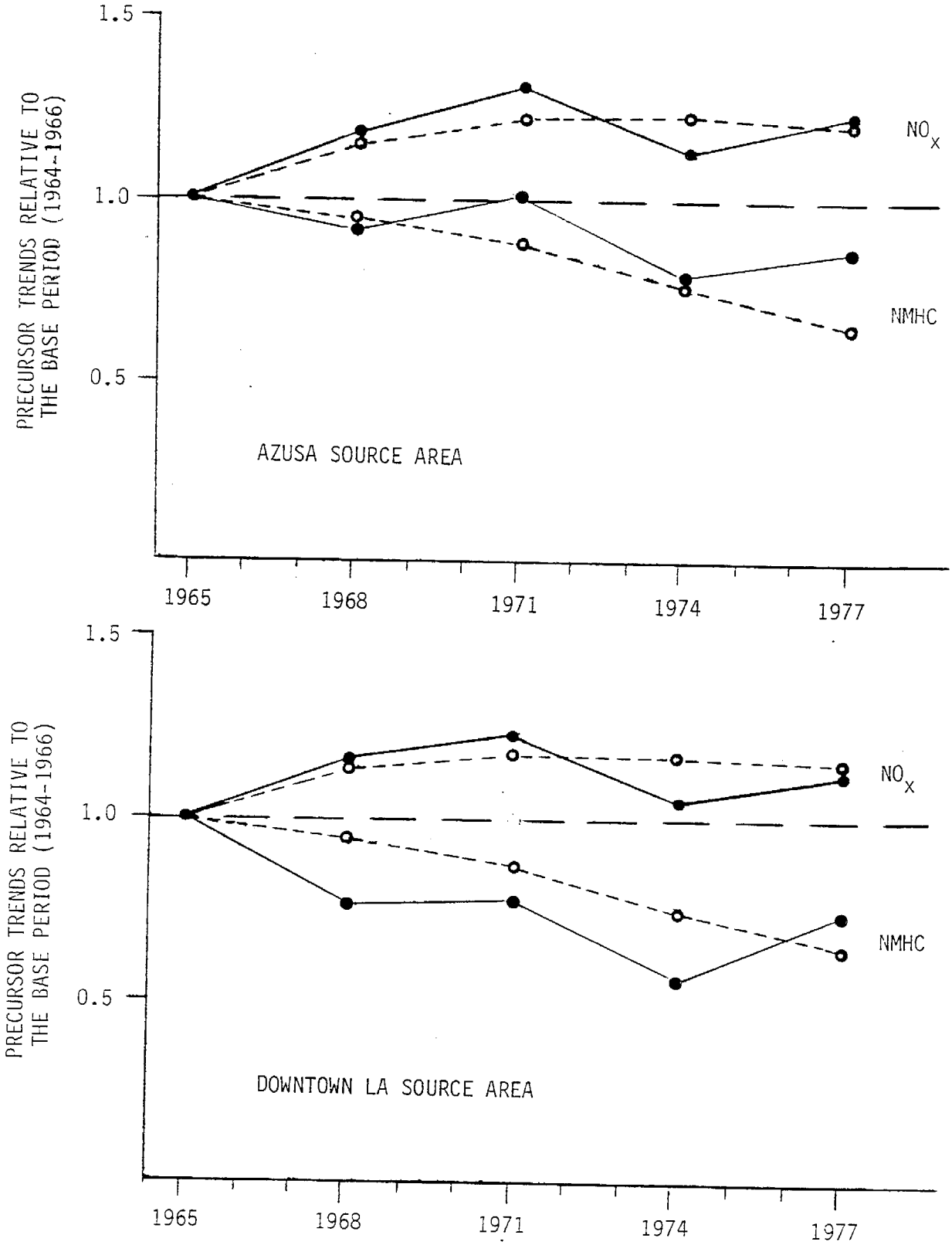


Figure 3.6 Comparison of emission trends (o---o) with ambient trends (•—•) for the two source areas.

Another significant feature of Figure 3.6 is that the agreement between emissions and ambient trends is somewhat better for $NO_x$ than it is for hydrocarbons. This makes good sense. The ambient trend data are better for $NO_x$ because $NO_x$ monitoring instruments are more reliable than NMHC monitoring instruments (Eldon and Trijonis 1977a), and because there are more trend monitoring sites for $NO_x$ than for NMHC. Furthermore, the stationary source emission trend data should be more accurate for $NO_x$ than for RHC. For $NO_x$, there are only two significant stationary source categories (power plants and natural gas usage in the residential/commercial/industrial sectors), and historical growth/control levels for these categories can be documented rather accurately. For RHC, there are numerous individual types of source categories with individual growth/control levels that are sometimes hard to estimate with good precision.

It is not obvious whether the emission data or the ambient data more accurately reflect historical precursor changes. In fact, an error analysis by Trijonis and Mortimer (1981) suggests that the uncertainties in the emission trends are about the same magnitude as the uncertainties in the ambient trends. In the historical trend tests of the next chapter, we will use the emission changes and ambient precursor changes individually to arrive at two sets of predicted ozone trends.

## 3.2 EKMA MODELING PARAMETERS

This section specifies the parameters for the EKMA modeling analysis. Section 3.2.1 deals with the base year NMHC/$NO_x$ ratio. Section 3.2.2 discusses the simulation conditions used to generate EKMA ozone isopleths.

### 3.2.1 Base Year NMHC/$NO_x$ Ratio

In many EKMA applications, the base period, median, 6-9 AM, NMHC/$NO_x$ ratio is the most critical modeling parameter. For our 1964-66 base period in Los Angeles, Trijonis and Mortimer (1981) performed an extensive study of EKMA-equivalent NMHC/$NO_x$ ratios. They started by examining 6-9 AM NMHC/$NO_x$ ratios during the early 1970's from several monitoring programs (Statewide Air Pollution Research Center, Los Angeles Reactive Pollutant Program, ARB El Monte Laboratory monitoring, routine ARB monitoring, and routine AQMD monitoring). In an attempt to make the atmospheric NMHC concentrations more nearly equivalent to

EKMA NMHC concentrations, all the ambient NMHC data were adjusted to correspond to measurements made with propane calibration. Also, the contributions from the nearly unreactive compounds ethane and propane (about 10% of total NMHC) were subtracted from the ambient NMHC data. After resolving discrepancies among the monitoring programs to arrive at a consensus ratio value for the early 1970's, they extrapolated this value back to 1964-66 based on historical trends in ambient precursor levels. From a review of the findings by Trijonis and Mortimer, we select 12:1 as the overall median, EKMA equivalent, NMHC/$NO_x$ ratio for the Los Angeles basin in 1964-66.*

The historical trend tests in this report will be conducted for three groups of data: days with lowest 20% of NMHC/$NO_x$ ratio, days with middle 20th-80th percentile of NMHC/$NO_x$ ratio, and days with highest 20% of NMHC/$NO_x$ ratio. For the EKMA modeling analysis of each group, we require the median NMHC/$NO_x$ ratio <u>within</u> each group. The medians within the three groups are obviously the 10th, 50th, and 90th percentiles of the overall distribution of NMHC/$NO_x$ ratios. As noted above, the overall 50th percentile NMHC/$NO_x$ ratio for 1964-66 is 12:1. From ambient monitoring data for the NMHC/$NO_x$ ratio, we find that the 10th percentile is about one-half the median and that the 90th percentile is about twice the median. Thus, the three, base period, EKMA equivalent, NMHC/$NO_x$ ratios to be used in this study are as follows:

low ratio days . . . 6:1
medium ratio days . . .12:1
high ratio days . . .24:1

### 3.2.2 EKMA Simulation Conditions

Isopleth diagrams of ozone versus initial NMHC and $NO_x$ can be generated by the EKMA model under a variety of simulation conditions. The "standard" EKMA isopleths represent the following conditions:

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*Actually, in their initial review of the data, Trijonis and Mortimer chose a 13:1 NMHC/$NO_x$ ratio for 1964-66. However, based on historical EKMA validation tests in Los Angeles, they concluded that the true "EKMA-equivalent" NMHC/$NO_x$ ratio might be lower, possibly as low as 10:1. The 12:1 ratio seems to be a reasonable choice based on the findings of Trijonis and Mortimer.

- A 10 hour irradiation with diurnal sunlight intensity corresponding to 8 AM-6 PM LDT for the summer solstice at 34°N latitude (the latitude of Los Angeles).
- A dilution rate of 3% per hour for the first 7 hours and zero dilution thereafter (corresponding to a mixing height change from 510 meters at 8 AM to 630 meters at 3 PM).
- No emissions after 8 AM.
- No transported or advected ozone.
- A hydrocarbon mix of 25% propylene and 75% n-butane with aldehydes of 5% the initial NMHC.
- An initial $NO_2/NO_x$ ratio of 0.25.
- Ozone value defined as maximum ozone during the 10 hour irradiation.

In this study, we have modified the EKMA simulation conditions in three ways. The first refinement is to use isopleths that represent ozone values at fixed irradiation times rather than maximum ozone values over the entire irradiation period. Such isopleths should provide a better simulation of ozone trends at fixed monitoring stations. Because they were readily available from EPA, we chose 5 hour isopleths for Downtown LA and 6 hour isopleths for Azusa. The second refinement is to use a special dilution curve that is characteristic of the highest ozone days in Los Angeles (Meyer 1980). The third and most significant refinement is to add post 8 AM emissions to the model (using emission data specific to the Los Angeles region).

Trijonis and Mortimer (1981) performed sensitivity analyses relating predicted ozone trends in Los Angeles to variations in EKMA simulation conditions. They concluded that predicted ozone trends are moderately sensitive to the specific simulation conditions. Their study shows that the simulation conditions adopted in the present study produce better overall agreement between predicted and actual ozone trends throughout the Los Angeles basin than do the "standard" simulation conditions. The addition of post 8 AM emissions is particularly important in improving the performance of EKMA (evaluated against overall Los Angeles ozone trends).

## 3.3 HISTORICAL OZONE TRENDS

As indicated in Chapter 1, the basic purpose of this study is to investigate historical ozone trends, with the data sorted into groups according to percentiles in the daily, 6-9 AM, $NMHC/NO_x$ ratio. For both receptor ozone sites -- Azusa and Downtown LA -- the daily, 6-9 AM, $NMHC/NO_x$ ratio data are taken at Downtown LA. The specific grouping of the data is as follows: lowest 20th percentile of daily $NMHC/NO_x$ ratios, middle 20th to 80th percentile of daily ratios, and upper 20th percentile of daily ratios. As indicated in Chapter 2, in order for our analysis to have a reasonable chance of success, the ozone trend data should represent noon-3 PM averages at Azusa and 10 AM-1 PM averages at Downtown LA under the appropriate transport patterns (vector averaged 7 AM-2 PM wind at Downtown LA being greater than 4 mph and from the south to west for Azusa study days, and being less than 5 mph for Downtown LA study days).

Table 3.4 summarizes the historical ozone trend data under the appropriate conditions -- sorted by percentiles in the daily $NMHC/NO_x$ ratio, and restricted to days with the correct wind patterns. The table includes values for four reasonable air quality trend indices: the average of the daily 3-hour concentrations for each group and the 90th percentile of the daily 3-hour concentrations for each group, each considered for the entire year as well as for the summer only. We have compiled Table 3.4 from ARB computer tapes with five basic programming steps: (1) grouping the data into three-year periods, (2) calculating the three-hour ozone averages each day (allowing at most one missing hourly value), (3) eliminating days at each site without the appropriate wind conditions for that site, (4) sorting and grouping the remaining daily data at each site by the 6-9 AM $NMHC/NO_x$ ratio at Downtown LA, and (5) computing the ozone air quality indices for each site, each three-year period, and each ratio group.

The question arises as to whether the trends in the four air quality indices for each group are divergent or are nearly equivalent. If the ozone trends differ significantly according to which air quality index is used, then separate EKMA modeling analyses should be performed for each index. Figure 3.7 compares the ozone trends for the four air quality indices, with each index normalized according to the base period (1964-66) value. It is obvious that

# TABLE 3.4 HISTORICAL TRENDS IN OZONE AIR QUALITY, SORTED BY PERCENTILES of the 6-9 AM NMHC/$NO_X$ RATIO, AND RESTRICTED TO DAYS WITH APPROPRIATE TRANSPORT PATTERNS

## Table 3.4a 12-3 PM Ozone at Azusa, Annual

| YEARS | LOWEST 20% RATIO DAYS | | | MIDDLE 60% RATIO DAYS | | | HIGHEST 20% RATIO DAYS | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sample Size | Average Ozone, pphm | 90th Percentile Ozone, pphm | Sample Size | Average Ozone, pphm | 90th Percentile Ozone, pphm | Sample Size | Average Ozone, pphm | 90th Percentile Ozone, pphm |
| 1964-66 | 36 | 12.3 | 27.0 | 109 | 17.8 | 29.3 | 36 | 18.0 | 30.3 |
| 1967-69 | 38 | 10.6 | 25.2 | 113 | 18.7 | 33.0 | 38 | 21.5 | 34.1 |
| 1970-72 | 56 | 14.7 | 28.2 | 168 | 16.9 | 28.2 | 56 | 18.0 | 27.5 |
| 1973-75 | 45 | 6.4 | 14.4 | 138 | 12.9 | 21.7 | 45 | 17.5 | 27.0 |
| 1976-78 | 22 | 8.1 | 18.9 | 66 | 15.2 | 27.0 | 22 | 13.8 | 25.1 |

## Table 3.4b 12-3 PM Ozone at Azusa, Summer

| YEARS | LOWEST 20% RATIO DAYS | | | MIDDLE 60% RATIO DAYS | | | HIGHEST 20% RATIO DAYS | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sample Size | Average Ozone, pphm | 90th Percentile Ozone, pphm | Sample Size | Average Ozone, pphm | 90th Percentile Ozone, pphm | Sample Size | Average Ozone, pphm | 90th Percentile Ozone, pphm |
| 1964-66 | 24 | 13.1 | 25.4 | 72 | 21.8 | 31.2 | 24 | 21.2 | 30.4 |
| 1967-69 | 27 | 16.2 | 29.6 | 83 | 22.7 | 34.7 | 28 | 23.2 | 34.7 |
| 1970-72 | 43 | 19.1 | 31.9 | 129 | 19.5 | 29.4 | 43 | 17.6 | 27.6 |
| 1973-75 | 34 | 8.5 | 18.3 | 102 | 15.0 | 22.7 | 34 | 19.5 | 29.3 |
| 1976-78 | 15 | 13.2 | 20.2 | 45 | 19.1 | 28.7 | 15 | 14.0 | 24.2 |

## Table 3.4c 10 AM-1 PM Ozone at Downtown LA, Annual

| YEARS | LOWEST 20% RATIO DAYS | | | MIDDLE 60% RATIO DAYS | | | HIGHEST 20% RATIO DAYS | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sample Size | Average Ozone, pphm | 90th Percentile Ozone, pphm | Sample Size | Average Ozone, pphm | 90th Percentile Ozone, pphm | Sample Size | Average Ozone pphm | 90th Percentile Ozone, pphm |
| 1964-66 | 151 | 5.8 | 12.8 | 453 | 8.3 | 17.0 | 151 | 8.7 | 17.2 |
| 1967-69 | 151 | 4.5 | 9.4 | 453 | 6.7 | 13.5 | 151 | 8.3 | 16.0 |
| 1970-72 | 152 | 3.6 | 7.0 | 455 | 5.4 | 11.5 | 151 | 5.9 | 11.9 |
| 1973-75 | 153 | 3.4 | 8.0 | 480 | 4.5 | 9.7 | 154 | 7.3 | 12.9 |
| 1976-78 | 168 | 3.5 | 7.0 | 507 | 5.5 | 10.7 | 168 | 5.5 | 9.5 |

## Table 3.4d 10 AM-1 PM Ozone at Downtown LA, Summer

| YEARS | LOWEST 20% RATIO DAYS | | | MIDDLE 60% RATIO DAYS | | | HIGHEST 20% RATIO DAYS | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sample Size | Average Ozone, pphm | 90th Percentile Ozone, pphm | Sample Size | Average Ozone, pphm | 90th Percentile Ozone, pphm | Sample Size | Average Ozone pphm | 90th Percentile Ozone, pphm |
| 1964-66 | 74 | 9.8 | 15.6 | 233 | 11.4 | 19.7 | 65 | 9.2 | 17.7 |
| 1967-69 | 73 | 6.4 | 12.3 | 220 | 9.5 | 17.6 | 74 | 8.9 | 17.0 |
| 1970-72 | 75 | 6.0 | 11.7 | 226 | 7.2 | 13.3 | 75 | 6.4 | 12.3 |
| 1973-75 | 75 | 4.5 | 8.6 | 226 | 7.0 | 12.3 | 75 | 8.2 | 13.3 |
| 1976-78 | 107 | 5.7 | 9.7 | 240 | 7.0 | 13.0 | 87 | 6.3 | 10.8 |

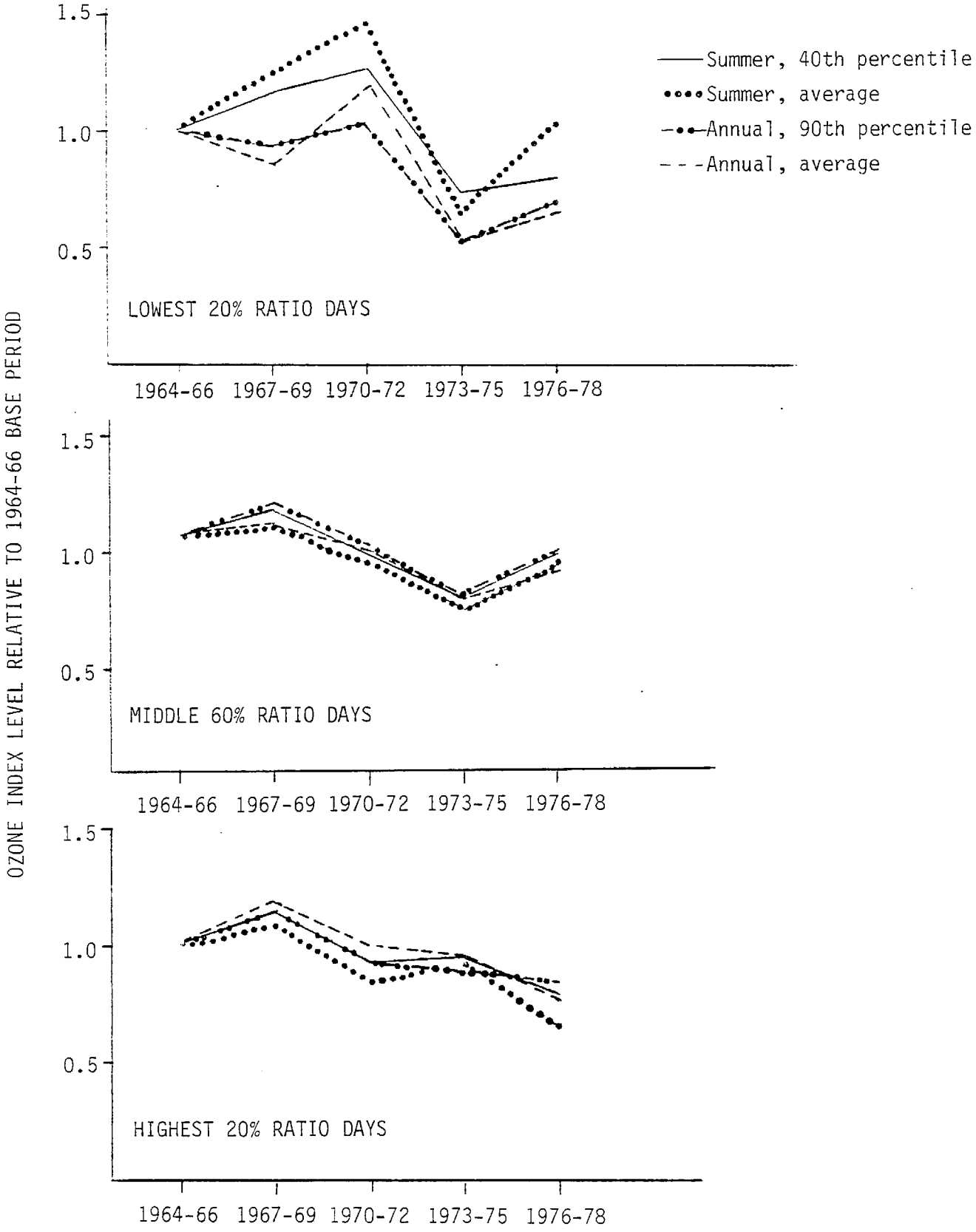


Figure 3.7a Comparison of alternative ozone trend indices for Azusa.

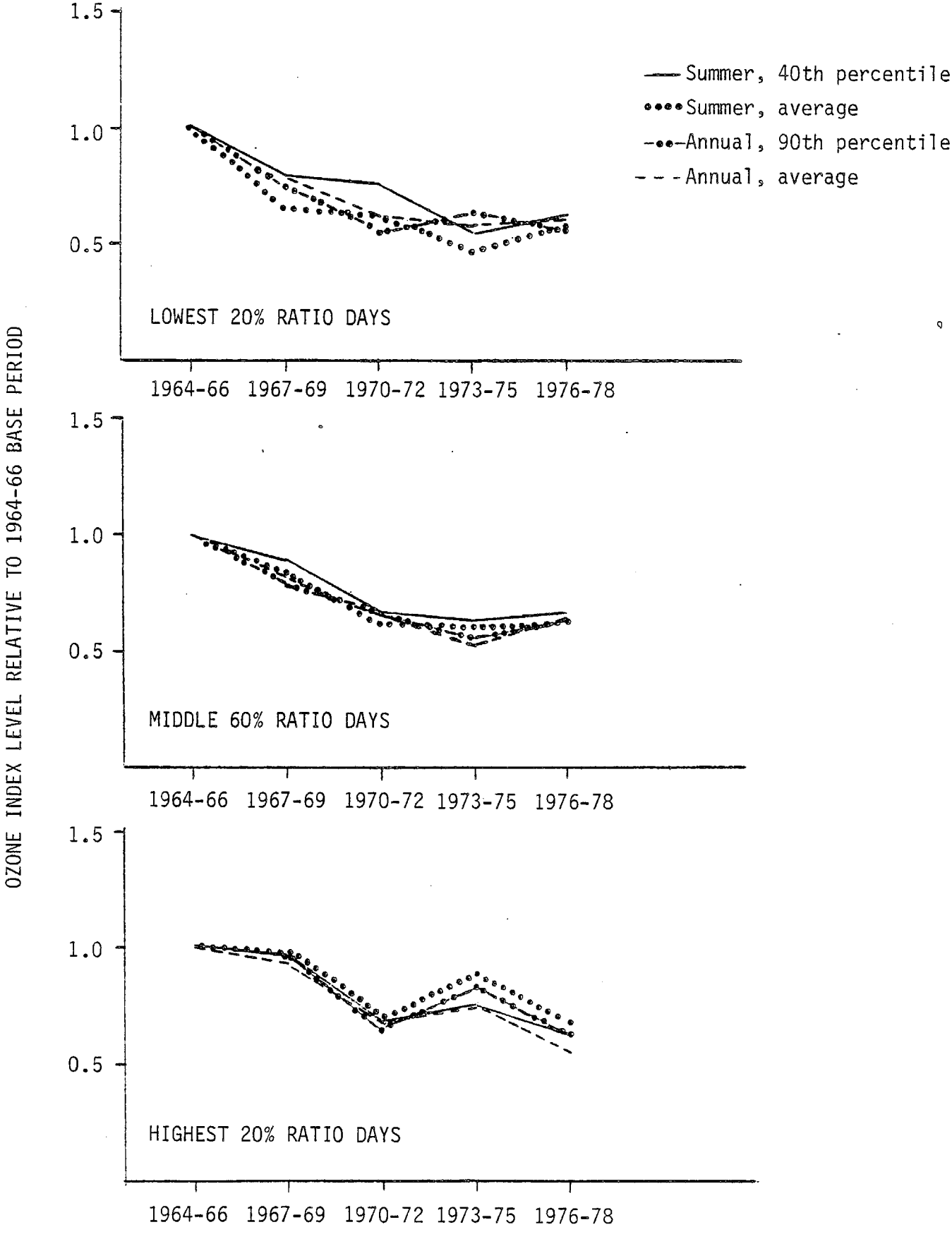


Figure 3.7b Comparison of alternative ozone trend indices for Downtown LA.

the four air quality indices are nearly equivalent, so that only one index needs to be considered in the EKMA modeling analysis. Because the EKMA isopleth diagrams are easier to use with high ozone values, we select the highest of the four ozone air quality indices -- the 90th percentile concentration during the summer -- as the index for this study.

Table 3.4 and Figure 3.7 indicate that historical ozone trends are somewhat different at Azusa and Downtown LA. As noted by Trijonis et al. (1978), the difference can be explained in terms of (1) the spatial inhomogeneity of source growth, and (2) the effects of historical changes in the NMHC/$NO_x$ ratio on early-day versus mid-day ozone.

It is worthwhile to note that Figure 3.7 already suggests that we will not find the effect we are searching for. Specifically, Figure 3.7 indicates that the ozone trends for the three ratio groups are not very different (i.e. not decreasing much more historically for low ratio days than for high ratio days). We will wait, however, for the next chapter before finalizing our conclusions.

# 4. HISTORICAL TEST OF OZONE TRENDS SORTED BY THE NMHC/$NO_x$ RATIO

As discussed in Chapter 1, the principal hypothesis to be tested in this study is whether historical ozone trends in Los Angeles differ significantly for data sets sorted by daily values of the 6-9 AM NMHC/$NO_x$ ratio. Most importantly, we want to determine if days with low NMHC/$NO_x$ ratios underwent dramatic (greater than 50%) reductions in ozone levels from the middle 1960's to the late 1970's. This chapter presents the results of our hypothesis test.

Section 4.1 derives predicted ozone trends by applying the EKMA ozone model to historical emission and ambient trend data for hydrocarbons and nitrogen oxides. The predicted trends are determined for three groups of ratio days -- lowest 20%, middle 60%, and highest 20%. Section 4.2 tests our basic hypothesis by comparing predicted ozone trends with actual ozone trends for each ratio group. Section 4.3 discusses the fundamental conclusions implied by our results.

## 4.1 EKMA PREDICTED OZONE TRENDS

The historical test involves six basic cases -- two source/receptor pairings (Downtown LA/Azusa and Downtown LA/Downtown LA) and three types of days (low, medium, and high days for the NMHC/$NO_x$ ratio). For each of these cases, an EKMA validation study is performed as follows. The base period for each validation study is 1964-66. The two base period inputs to the EKMA model are the 1964-66 summer ozone 90th percentile (see Table 3.4 page 37) and the 1964-66 NMHC/$NO_x$ ratio (values of 6:1, 12:1, and 24:1 for the three ratio groups, see page 34). Using the base period inputs and the historical precursor trends (either the emission trends in Table 3.1 on page 25 or the ambient precursor trends in Tables 3.2 and 3.3 on pages 30 and 31), predictions are made of historical ozone trends with the graphical EKMA technique for each subsequent three-year period -- 1967-69, 1970-72, 1973-75, and 1976-78. The predicted ozone trends for the summer 90th percentile are then compared to actual ozone trends (the latter are listed in Table 3.4 on page 37).

Figure 4.1 illustrates the graphical EKMA technique for the case of the Azusa receptor site, with historical precursor trends based on the emissions data. The base period points (1964-66, labeled "1965") are determined by the intersections of the NMHC/$NO_x$ ratio lines (6:1, 12:1, and 24:1 for the three ratio groups) with the ozone values for the base period (25.4, 31.2, and 30.4 pphm for the three ratio groups). The location of the points for the four subsequent three-year periods (labeled "1968", "1971", "1974", and "1977") are found by factoring the NMHC and $NO_x$ coordinates of the base period points according to the precursor changes relative to the base period. The isopleths then yield predicted ozone values for the subsequent periods.

Table 4.1 lists the predicted ozone trends. Values are presented for each of the two receptor sites, for each of the three ratio groups, and for predictions based on either emission trend data or ambient precursor trend data.

## 4.2 HYPOTHESIS TEST

Figures 4.2 and 4.3 compare predicted ozone trends to actual ozone trends for the Azusa and Downtown LA receptor sites, respectively. For each of the three ratio groups, actual trends are compared to two predicted trends, one based on EKMA analyses using historical emission changes and the other based on EKMA analyses using ambient precursor trends. As noted previously, the ozone values represent 90th percentiles of daily 3-hour averages, restricted to the summer (May-October) as well as to days with the appropriate wind transport conditions.

Figures 4.2 and 4.3 show that the actual ozone trends agree fairly well with EKMA predictions for the medium ratio group. The actual trends, however, do not corroborate the EKMA predictions for the low and high ratio groups. In particular, actual ozone levels have decreased more than EKMA predictions for the high ratio group, and actual ozone levels have <u>not</u> exhibited the $50^{+}$% reduction predicted by EKMA for the low ratio group.

The failure of the ozone trend data to confirm the EKMA hypothesis can be made even more evident by plotting the results as shown in Figures 4.4 and 4.5.

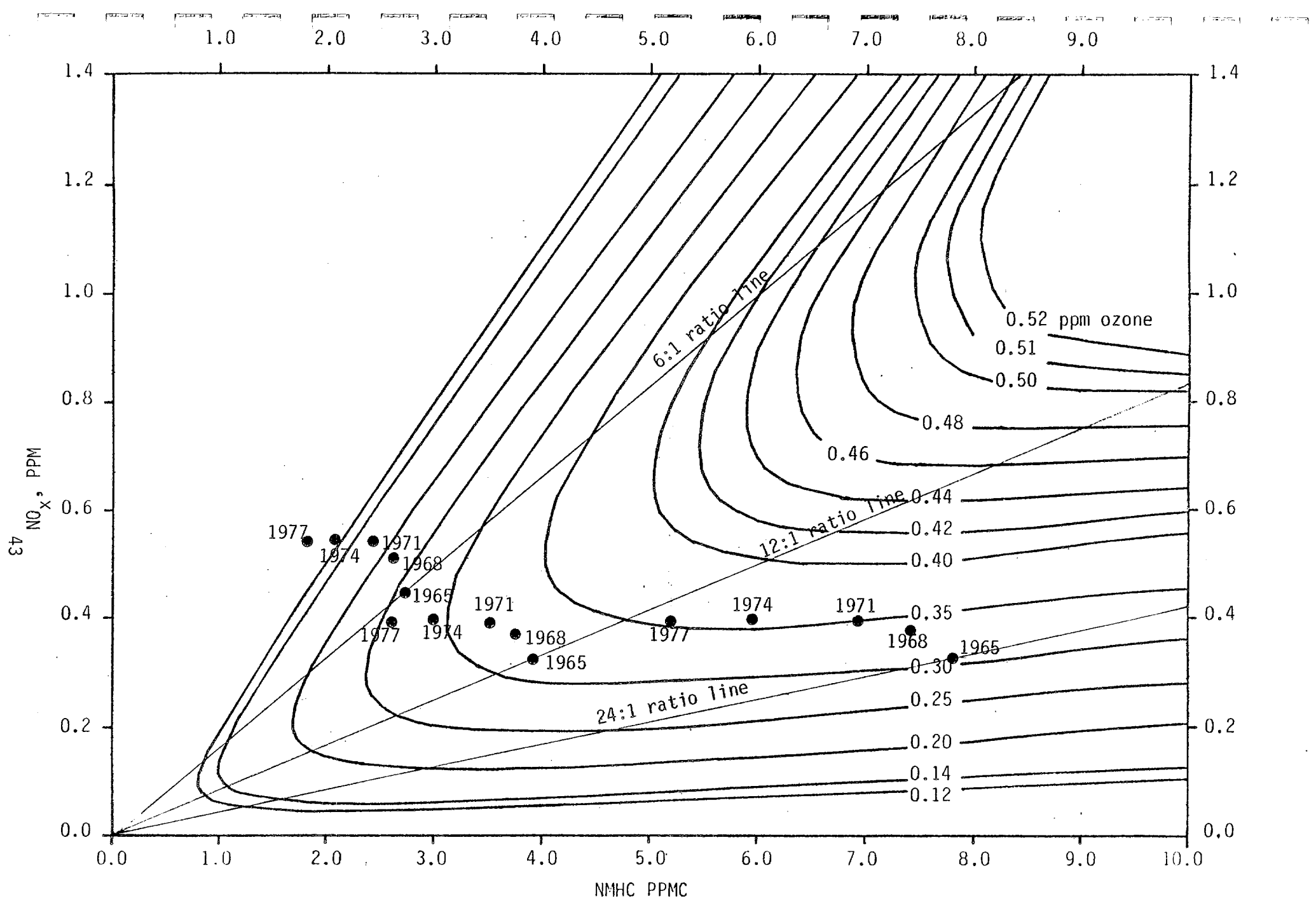


Figure 4.1 EKMA diagram for historical ozone trends at Azusa, using three ratio values, with precursor trends based on emissions data.

TABLE 4.1 HISTORICAL OZONE TRENDS PREDICTED BY THE EKMA MODEL

Table 4.1a Azusa

| YEAR | PREDICTED OZONE (PPHM) BASED ON EMISSION TRENDS FOR PRECURSORS | | |
|---|---|---|---|
| | Low Ratio Days | Medium Ratio Days | High Ratio Days |
| 1964-66 | 25.4 | 31.2 | 30.4 |
| 1967-69 | 18.8 | 31.9 | 34.3 |
| 1970-72 | 18.5 | 33.4 | 36.0 |
| 1973-75 | 13.2 | 29.0 | 33.9 |
| 1976-78 | 15.0 | 31.1 | 35.1 |

| YEAR | PREDICTED OZONE (PPHM) BASED ON AMBIENT TRENDS FOR PRECURSORS | | |
|---|---|---|---|
| | Low Ratio Days | Medium Ratio Days | High Ratio Days |
| 1964-66 | 25.4 | 31.2 | 30.4 |
| 1967-69 | 21.0 | 32.3 | 33.5 |
| 1970-72 | 16.3 | 31.4 | 34.7 |
| 1973-75 | 10.5 | 28.8 | 35.8 |
| 1976-78 | 6.0 | 25.8 | 35.2 |

Table 4.1b Downtown LA

| YEAR | PREDICTED OZONE (PPHM) BASED ON EMISSION TRENDS FOR PRECURSORS | | |
|---|---|---|---|
| | Low Ratio Days | Medium Ratio Days | High Ratio Days |
| 1964-66 | 15.6 | 19.8 | 17.7 |
| 1967-69 | 8.4 | 16.5 | 18.1 |
| 1970-72 | 7.2 | 16.5 | 18.6 |
| 1973-75 | 5.1 | 12.8 | 15.8 |
| 1976-78 | 7.8 | 16.3 | 17.8 |

| YEAR | PREDICTED OZONE (PPHM) BASED ON AMBIENT TRENDS FOR PRECURSORS | | |
|---|---|---|---|
| | Low Ratio Days | Medium Ratio Days | High Ratio Days |
| 1964-66 | 15.6 | 19.8 | 17.7 |
| 1967-69 | 12.8 | 19.7 | 18.8 |
| 1970-72 | 10.9 | 18.5 | 19.7 |
| 1973-75 | 7.0 | 15.8 | 17.6 |
| 1976-78 | 5.1 | 14.0 | 16.7 |

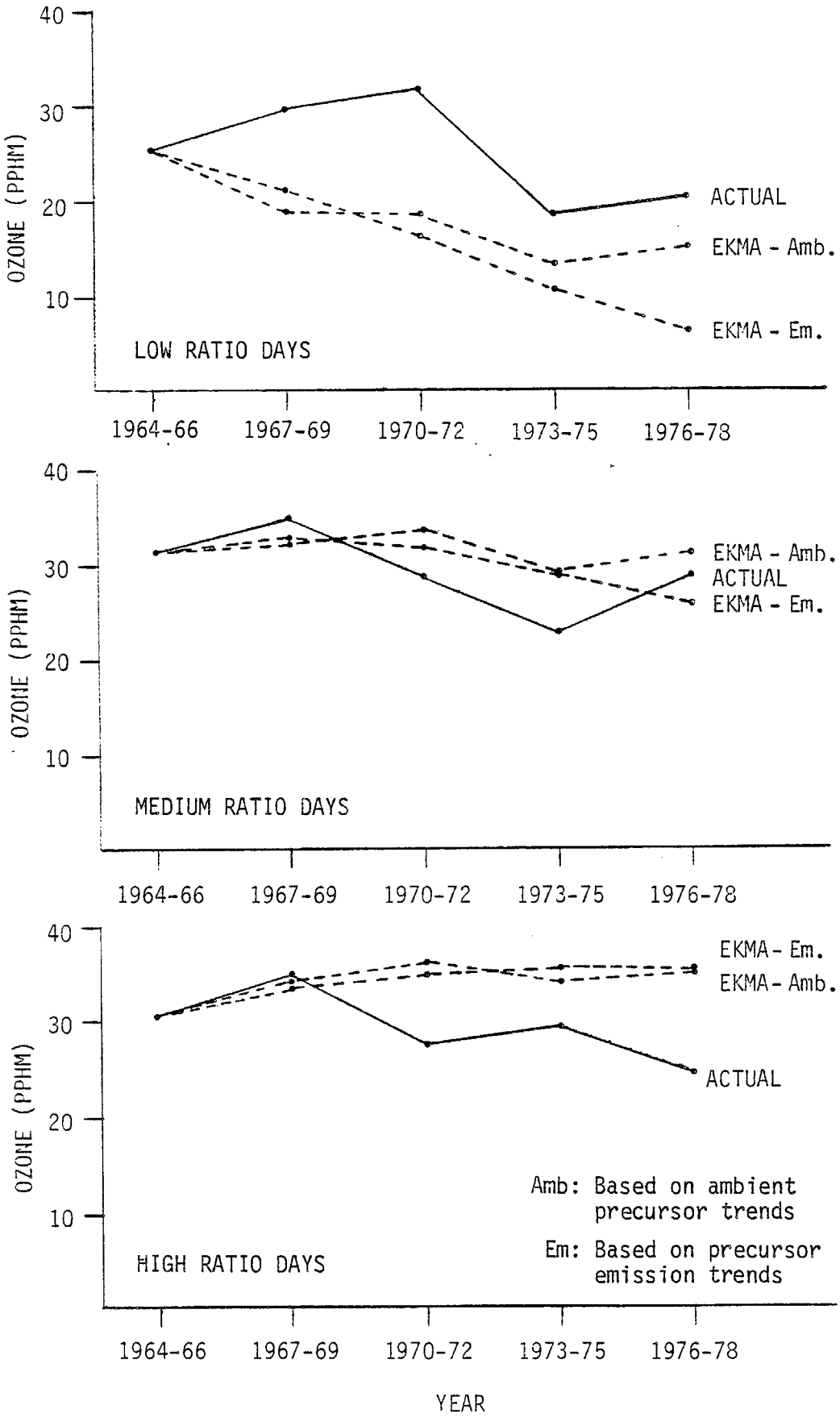


Figure 4.2 Comparison of actual and EKMA-predicted ozone trends at Azusa for the three ratio groups.

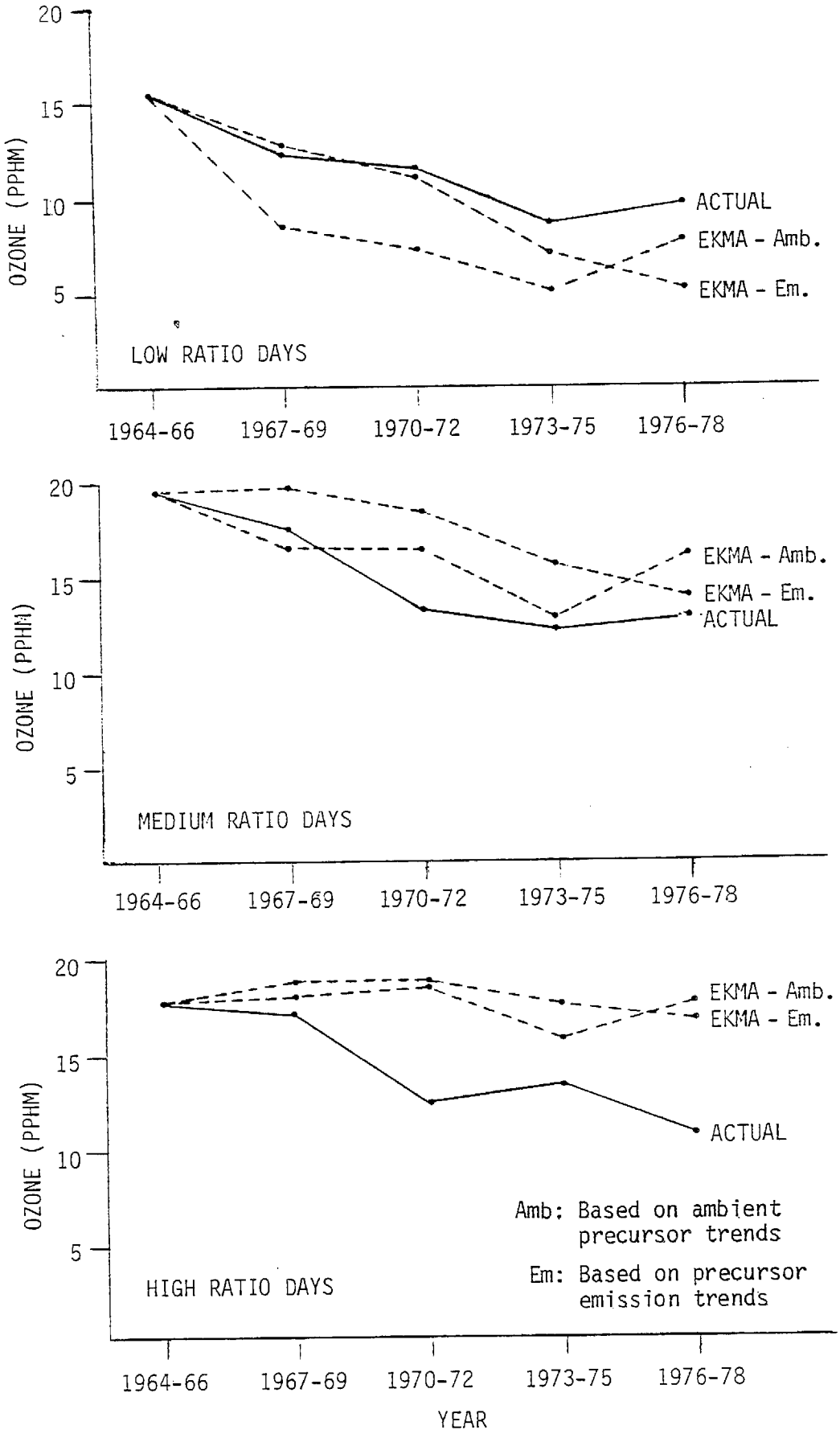


Figure 4.3 Comparison of actual and Ekma-predicted ozone trends at Downtown LA for the three ratio groups.

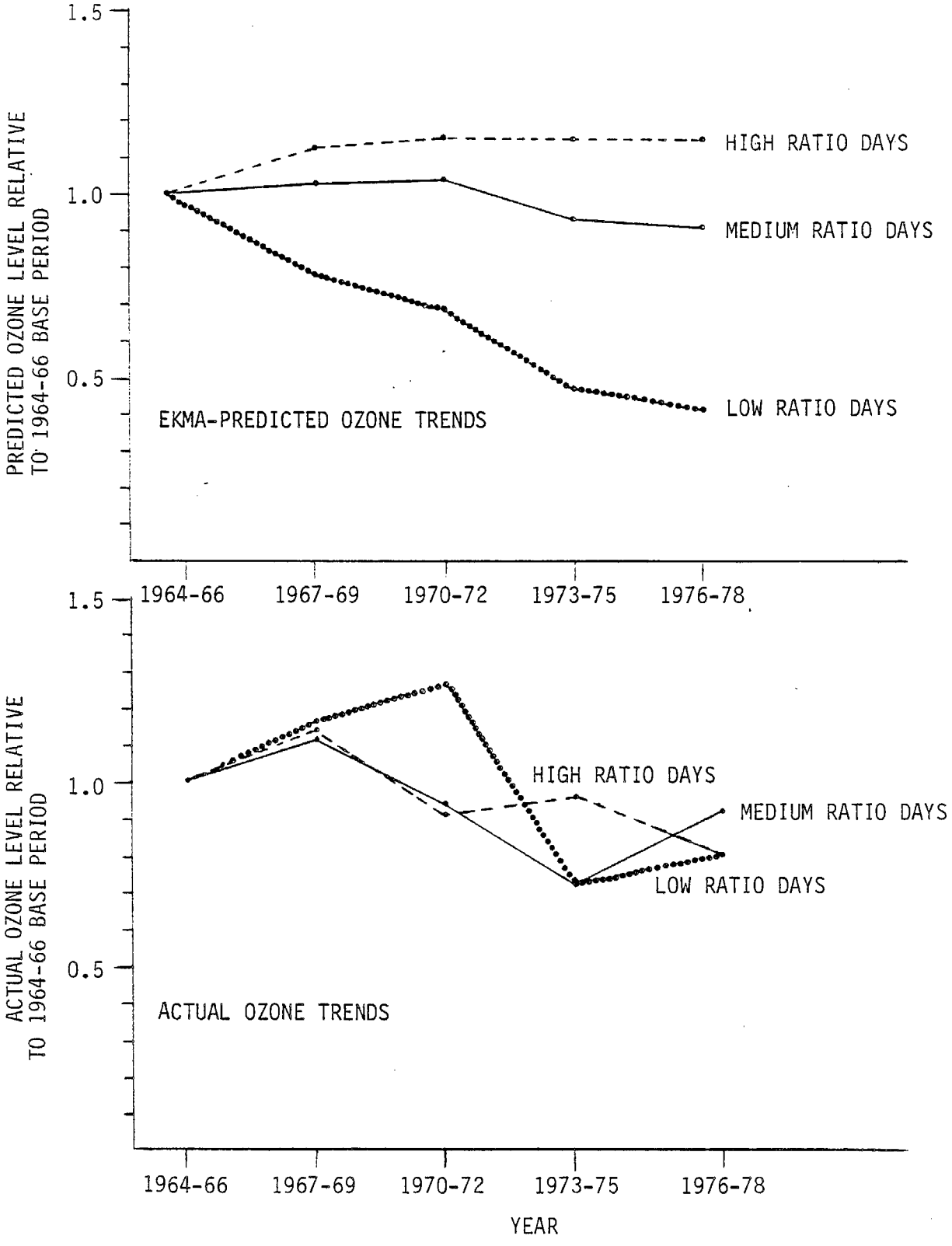


Figure 4.4 EKMA-predicted ozone trends for the three ratio groups and actual ozone trends for the three ratio groups at Azusa.

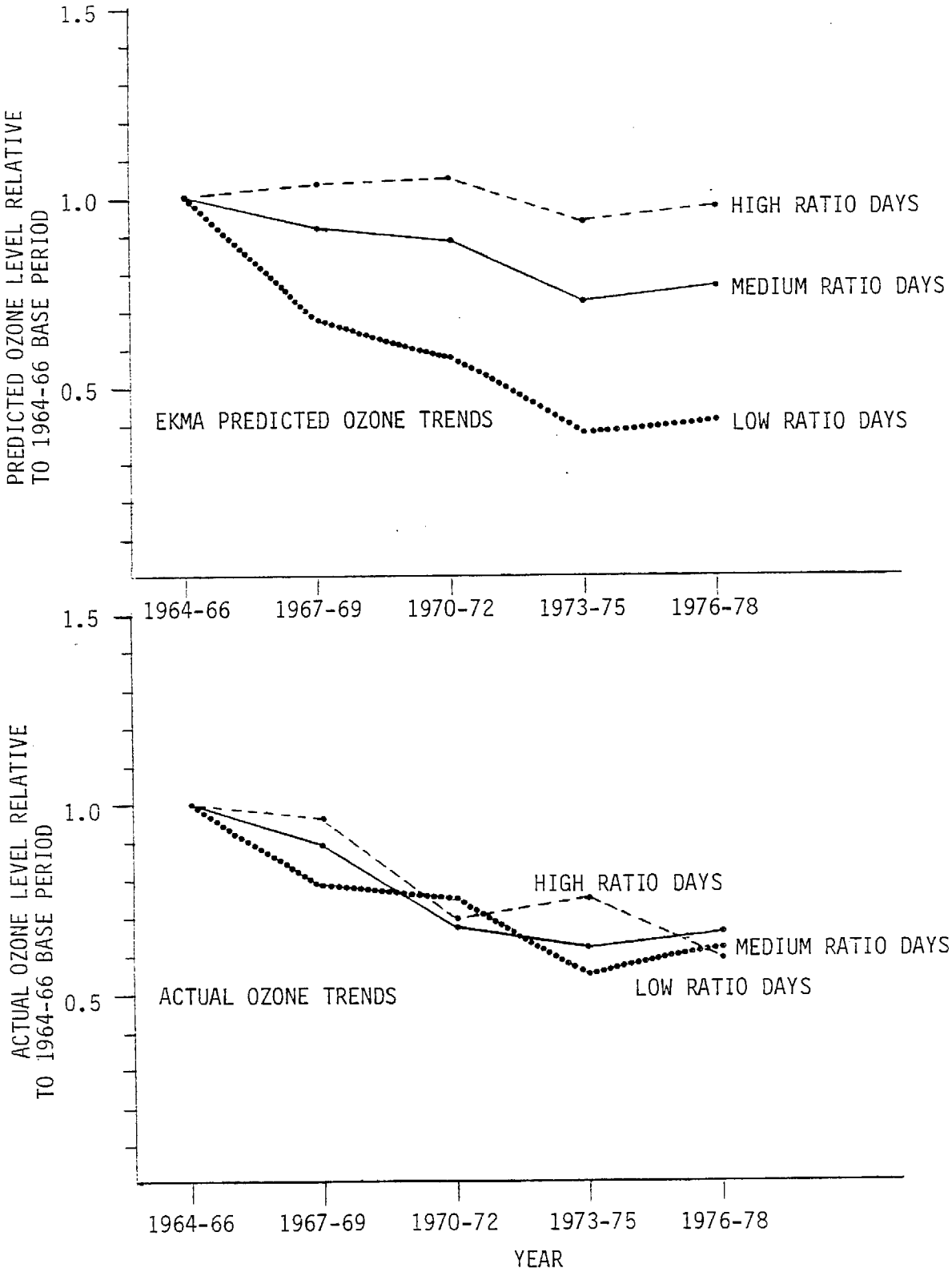


Figure 4.5 EKMA-predicted ozone trends for the three ratio groups and actual ozone trends for the three ratio groups at Downtown LA.

The top halves of Figures 4.4 and 4.5 show predicted ozone trends for the three ratio groups (based on averages of the two analyses using emissions data and ambient data for the precursors), while the bottom halves of the figures indicate actual ozone trends for the three ratio groups. The predicted ozone trends are widely divergent among the ratio groups, but the actual trends are about the same among the ratio groups (nearly identical in terms of the overall net change from 1964-66 to 1976-78). Most notably, actual ozone trends for the low ratio group do not exhibit especially large reductions historically.

## 4.3 CONCLUSIONS

If the actual ozone trend data had verified the EKMA predictions, the results would have been a definitive confirmation of our initial hypothesis. That is -- if ozone levels on low ratio days showed a unique and dramatic 50+% decrease historically while ozone levels on high ratio days remained unchanged, the only plausible explanation would be that the data for this study are indeed of good quality (with respect to the ambient NMHC/$NO_x$ ratio and with respect to wind transport stratification), and that the EKMA prediction of extreme ozone/hydrocarbon sensitivity at low NMHC/$NO_x$ ratios is correct. Furthermore, such a finding would have strongly suggested that Los Angeles photochemical smog could be nearly eliminated with just moderate future reductions in hydrocarbon emissions.

The actual ozone trend data, however, did not confirm the EKMA hypothesis. This finding is not only disappointing but also ambiguous. One potential explanation is that the EKMA model is in error, i.e., that ozone levels in Los Angeles are not currently in an extremely sensitive position with respect to the NMHC/$NO_x$ ratio. The second potential explanation concerns inadequacies in the data base. As discussed in Chapter 2, this study may have been seriously undermined by errors in the routine daily data for the NMHC/$NO_x$ ratio. Also, the wind transport specifications may not be precise enough to ensure that equivalent source/receptor air masses are preserved in the analysis.

If the first explanation -- that ozone is not sensitive to the NMHC/$NO_x$ ratio -- were true, the implication would seem to be that controlling both

NMHC and $NO_x$ is the safest and surest path to photochemical smog reductions in Los Angeles. If the second explanation -- that errors in the data base voided this study -- were true, there is little we can conclude from the results. Unfortunately, because of the ambiguities in our findings, we are left without a definitive conclusion.

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