PB 278 196

EPA-600/3-78-019

February 1978

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VERIFICATION OF THE ISOPLETH METHOD FOR RELATING PHOTOCHEMICAL OXIDANT TO PRECURSORS

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ABSTRACT

Historical trend data for the Los Angeles region are used to check the ozone isopleth method that has been proposed as a replacement for the Appendix J model. Using the median 6-9 AM NMHC/NO_x ratio measured during the summer as an input to the isopleth model, significant discrepancies are found between the isopleth predictions and actual oxidant trends. Most of these discrepancies are statistically significant considering statistical errors in the actual oxidant trends and potential errors in our estimates of precursor trends. Using a range in the NMHC/NO_x ratio, in particular a low value for the ratio, much better agreement is found between the predicted and actual trends. Potential explanations for the discrepancies and possible improvements to the isopleth model are discussed.

CONTENTS

FIGURES

TABLES

CHAPTER 1

INTRODUCTION

In recent years Appendix J to Chapter IV, Part 51, Title 42 of the Code of Federal Regulations has been used to estimate the amount of hydrocarbon control needed to attain the National Ambient Air Quality Standard for photochemical oxidant. The Appendix J model is based on an upper-limit curve relating maximum afternoon oxidant concentrations to morning hydrocarbon concentrations observed at the same location. In spite of its widespread use in the past, however, Appendix J has come under increasing criticism for its limitations [1, 2]:

- The role of NO_x in oxidant formation is neglected.
- Relating oxidant and hydrocarbons at the same location neglects transport of the air mass.
- The observed relationship between oxidant and hydrocarbons may be distorted by unaccounted for meteorological variables.
- The upper-limit curve is not statistically well defined and no error bounds are provided.
- Background levels of oxidant and hydrocarbons are ignored.
- Emissions occurring after 9 AM are neglected.
- The effect of the spatial/temporal distribution of emissions is not accounted for.

Because of these shortcomings, various alternatives to Appendix J have been proposed. One of the most attractive alternatives involves oxidant isopleths derived by the Empirical Kinetic Modeling Approach (EKMA)[1]. The EKMA isopleth method offers several advantages over the Appendix J procedure. First, the EKMA isopleths are based on a chemical-kinetic model calibrated to smog chamber data and hence represent a cause-and-effect relationship between oxidant and precursors. Second, the effect of transport is implicitly included. Third, NO_x is explicitly considered as an oxidant precursor. Fourth, estimates of error bounds are possible. Fifth, the EKMA isopleth model can be modified, if necessary, to account for the effects of background oxidant, background precursors, and post 9 AM emissions.

Figure 1 presents a series of EKMA isopleths for the basinwide oxidant maximum during a 9-hour irradiation. Note that these isopleths are not

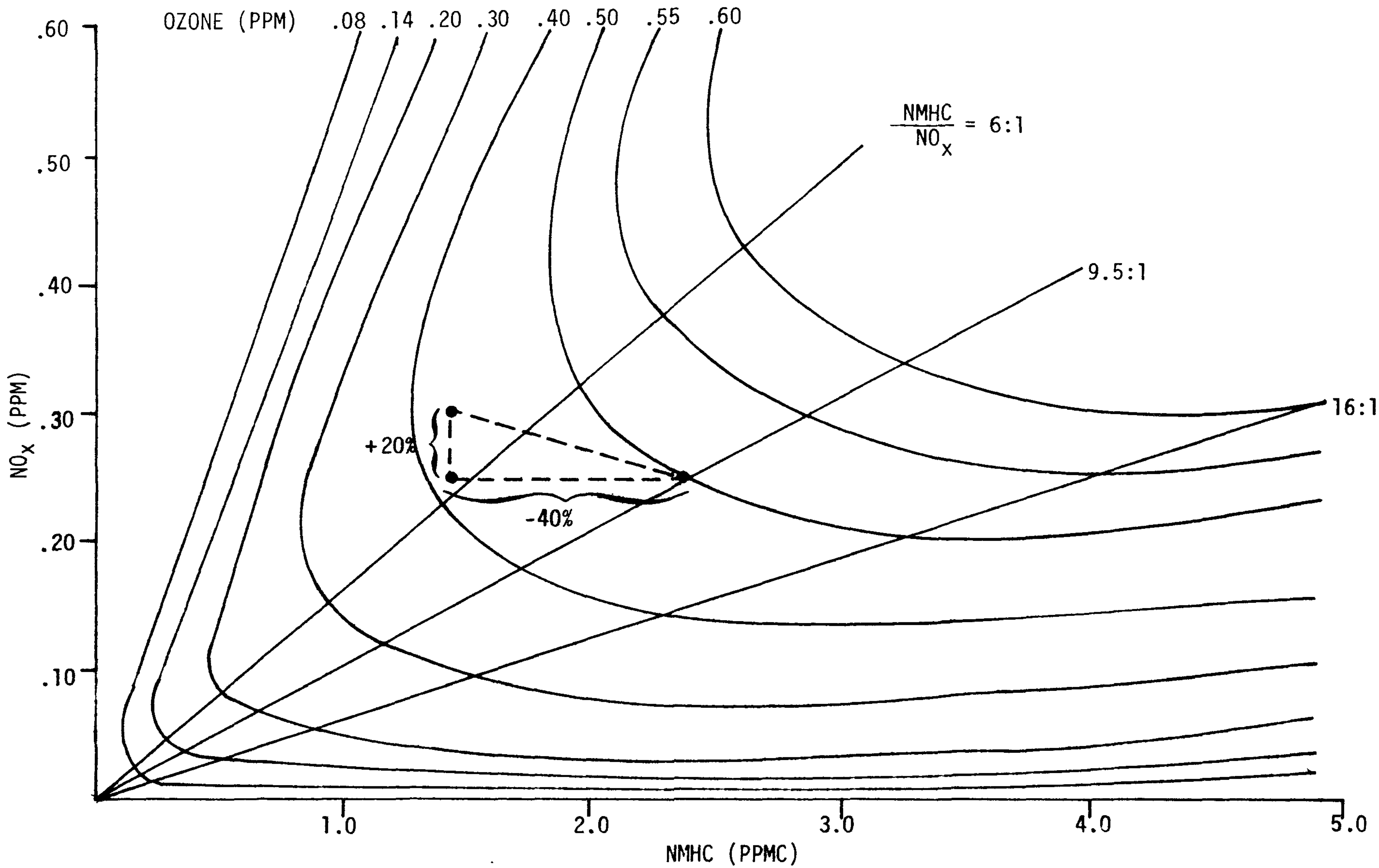

Figure 1. **Sensitivity of Maximum Afternoon Ozone Concentrations to Precursor Concentrations.**

intended to be used in an absolute sense; rather, they should be interpreted as representing the sensitivity of oxidant maxima to changes in presursor concentrations[1]. The isopleths can be used to predict future oxidant concentrations based on percent changes in presursor concentrations.

In order to predict future oxidant maxima, the isopleth approach requires three basic inputs: the present oxidant maximum (or second maximum), the present NMHC/NO_x ratio, and the future degree of hydrocarbon and NO_x control. For instance, as shown in Figure 1, for a present oxidant maximum of 0.50 ppm, NMHC/NO_x ratio of 9.5, hydrocarbon decrease of 40%, and NO_x increase of 20%, the predicted regionwide maximum would be 0.42 ppm.

VALIDATING THE ISOPLETH METHOD

The EKMA isopleth method should be subjected to validation studies before it is accepted as an accurate method for evaluating oxidant control strategies. Since the method is used in a relative sense to estimate the sensitivity of oxidant to changes in precursors, the most appropriate validation tests would involve historical changes in air quality, i.e. historical trend data. This report tests the EKMA model by "predicting" historical oxidant maxima based on past changes in precursors and comparing these predictions to actually observed oxidant maxima.

Testing the model against trends requires several years of historical data on oxidant and precursors. Also, since the location of the regionwide oxidant maximum may change with time, good spatial coverage is necessary in the historical air quality data. Based on these criteria, we chose the Los Angeles basin and the time period 1964-1975 for the analysis. Only for this region and time period can one find high-quality, long-term trend data with excellent spatial resolution.*

In this report, the regionwide isopleth model is tested against trends in the basinwide oxidant maximum for Los Angeles. To provide greater gener-

* It was originally planned that Denver and Chicago be included in the study. These sites were subsequently excluded because of the sparsity of trend data for emissions and air quality, and because of uncertainties in these data.

ality in validating the isopleth approach and to increase the number of test cases, four individual sites are also chosen for analysis: Downtown Los Angeles (DOLA), Anaheim, Azusa, and San Bernardino. The trends at the four individual locations are tested against isopleths that are specific to the time of occurrence of maximal oxidant at those locations.

All of the validation studies cover the time period 1965-1974, with tests made at every three-year interval. In order to provide robust data sets for the analysis, three-year averages (1964-1966, 1967-1969, 1970-1972, and 1973-1975) of air quality data are used.

SUMMARY OF CONCLUSIONS

Based on a variety of data sources, we are fairly confident that the (6-9 AM summertime) ambient NMHC/NO_x ratio was approximately 12:1 in 1965. The validation studies using this ratio indicate significant discrepancies between historical air quality trends and the predictions of the EKMA isopleth method. The basic disagreement is that the isopleth method underestimates the historical reductions that have occurred in maximal oxidant basinwide and in oxidant at DOLA, Anaheim, and Azusa. Considering the statistical errors in actual oxidant trends and the potential errors in our estimates of precursor trends, the discrepancies between actual and predicted trends (for a 12:1 ratio) are significant in four of the seven situations analyzed.

If we consider a range in the NMHC/NO_x ratio, in particular the possibility that the ratio may have been as low as 7:1 in 1965, most of the discrepancies become statistically insignificant. Using a 7:1 ratio, good agreement is found between actual and predicted trends in all cases except Anaheim.

We have investigated several factors which might contribute to the discrepancies between the isopleth predictions and actual oxidant trends. Some of these factors have been eliminated as plausible explanations for the disagreement. Factors that apparently do <u>not</u> account for the disagreement include the following: (1) the median NMHC/NO_x ratio is slightly greater on high oxidant days than on all summertime days; (2) our data for yearly average NO_x trends underestimate the historical increase in 6-9 AM summertime NO_x concentrations; and (3) historical trends may have been affected by changes in monitoring practices.

There are several factors that could account for the discrepancies between isopleth predictions and historical oxidant trends. The three most likely explanations are as follows:

- A 12:1 atmospheric NMHC/NO_x ratio may be equivalent to a lower ratio in the isopleth model. In particular, a given level of ambient NMHC may be equivalent to a lower level of NMHC in the isopleths. This would be the case if ambient NMHC were of lower reactivity (per ppmc) than the isopleth NMHC mix.
- The present versions of the EKMA isopleths neglect the effect of emissions after 9 AM. Adding post 9 AM emissions to the EKMA model might change the shape of the isopleths and produce better agreement in predicting historical trends. We would expect better agreement because the inclusion of post 9 AM emissions would give greater emphasis to the ozone inhibition role played by NO_x emissions increases.
- The isopleth method may underpredict the actual oxidant improvement from 1964-1966 to 1973-1975 because of meteorological bias in the actual oxidant trends. There is some evidence that pollution potential in Los Angeles appeared to be lower in 1973-1975 than in 1964-1966.

A fourth possible explanation is that our source areas have not been properly defined. The historical precursor changes of consequence to maximal oxidant may be the precursor changes in the sub-areas of greatest emissions density (which have low growth rates) rather than the precursor changes throughout the entire upwind source areas. Limited spatial coverage of oxidant monitoring sites is another factor that could account for some of the discrepancies in the tests involving the basinwide isopleths .

RECOMMENDATIONS FOR FUTURE WORK

There at least three analyses that should be performed to isolate the cause of the observed discrepancies and, possibly, the improve the isopleth method:

- The reactivity of ambient 6-9 AM NMHC in Los Angeles should be compared to the reactivity of the isopleth NMHC mix. This reactivity comparison should consider both the number of moles per ppmc and the oxidant producing potential per mole of hydrocarbons.
- EKMA isopleths should be prepared which include post 9 AM emissions. The verification studies should be repeated with these new isopleths.
- It would be useful to normalize the actual oxidant trends in Los Angeles for meteorological variance. This would eliminate meteorological bias in the trends and would also decrease the statistical error bounds on the actual oxidant trends, resulting in a more finely-tuned validation study.

Variance in Air Quality Indices

As an aid in selecting air quality indices for measuring oxidant trends, we conducted an analysis of the year-to-year statistical variance in alternative oxidant indices. Our goal was to identify an air quality index that is representative of high oxidant days but has low relative year-to-year variance.

The left hand column of Table 1 lists the oxidant air quality indices that we considered. For each index, and for each of the eleven monitoring sites, we computed the mean value of the index and a de-trended standard deviation* using data from 1965 to 1975. Table 1 lists the mean value of each index and the year-to-year deviation, both averaged over all eleven sites.

Table 1 indicates that the single yearly maximum value exhibits the highest relative deviation from year-to-year, $\pm$ 17.0%. An index that is representative of high oxidant days, but which has a relatively low variance, is the 95th percentile of daily maximum one-hour concentrations. Many of our analyses will be based on this latter index.

Basinwide Maximum

The EPA isopleth procedure [1] calls for the use of the second-highest yearly one-hour oxidant at the station(s) under consideration. This convention has been adopted because of the form of the oxidant standard which prohibits more than one violation each year. In order to test the EPA isopleth procedure in its conventional form, we will conduct the basinwide verification using the second-highest oxidant concentration each year.

Among the eleven monitoring sites, Azusa exhibited the greatest second-highest one-hour oxidant in nine of the twelve years (1964-1975). The string of Azusa worst-cases is broken only by Downtown Los Angeles (DOLA) in 1965, Pomona in 1968, and DOLA in 1973. In each of those three years, Azusa ranks as the second-worst station.

Basinwide trends in the second-highest one-hour oxidant can be studied in two ways. First, we could select, each year, the specific station which exhibited the greatest second-highest oxidant, i.e., Pomona in 1968, DOLA in 1965 and 1973, and Azusa in all other years. Second, recognizing that Azusa

---

*This is the standard error away from a least-squares trend line from 1965-1975, adjusted for degrees of freedom.

Table 1. **Average Yearly Values and Year-to-Year Deviations for Oxidant Air Quality Indices.**

OXIDANT AIR QUALITY INDEX	MEAN VALUE OF INDEX FOR 11 LOCATIONS DURING 1965-1975 (pphm)	DE-TRENDED YEAR-TO-YEAR DEVIATION AVERAGED OVER 11 LOCATIONS (as % of mean value for the index)
1. 99th Percentile of All Hours	17.4	± 11.5%
2. 95th Percentile of All Hours	10.9	± 12.1%
3. Annual Mean of All Hours	3.0	± 11.1%
4. Yearly Maximum 1-Hour	33.3	± 17.0%
5. Second Highest 1-Hour	30.8	± 16.5%
6. 99th Percentile of Daily Maximum 1-Hour	26.9	± 13.0%
7. 95th Percentile of Daily Maximum 1-Hour	20.3	± 11.5%
8. 90th Percentile of Daily Maximum 1-Hour	17.0	± 11.9
9. 3rd Quarter Mean of Daily Maximum 1-Hour	13.2	± 14.2%
10. Yearly Mean of Daily Maximum 1-Hour	8.6	± 10.6%

is typically the worst-case station, we could use data for Azusa only. Both methods will be tried in this report.

We will also test the basinwide isopleths against trends in the 95th percentile of daily maximum one-hour concentrations at Azusa. Using this air quality index should decrease the statistical error in the oxidant trends.

Individual Locations

The basinwide isopleths are based on maximal one-hour oxidant concentrations observed anytime in a nine-hour irradiation. Isopleths are also available for oxidant concentrations observed exactly at certain irradiation times:5 hours, 7 hours, or 9 hours (Personal communication with Gary Whitten, Science Applications, Inc., San Rafael, CA, August 1977). The 5-, 7-, and 9-hour isopleths will be checked against trend data at DOLA, Anaheim, Azusa, and San Bernardino. These locations typically experience maximal oxidant concentrations around 1:00 PM, 1:30 PM, 2:30 PM, and 4:00 PM respectively. Thus, they approximately correspond to 5, 5, 7, and 9 hour irradiations from a 7:30 AM start time.

In checking the isopleths for fixed irradiation times, only one oxidant trend index will be used: the 95th percentile of daily maximum one-hour concentrations. As indicated in Table 1, this index is representative of high oxidant days; yet it exhibits relatively low year-to-year variance. Another reason for selecting the 95th percentile of daily maxima (rather than, say, the second highest one-hour) is that we need to check the isopleths for fixed irradiation times against typical high oxidant days rather than worst-case high oxidant days. Worst-case days in downtown Los Angeles occur when the effective irradiation time is more than five hours; these days would not be appropriate for validating the 5-hour isopleths.

ERROR BOUNDS ON OXIDANT TRENDS

When comparing the actual oxidant trends to the oxidant trends predicted by the isopleth model, we would like to place error bounds on the actual trends to represent the variance due to meteorological fluctuations. Table 1 provides data relevant to this issue. However, two modifications must be made on the results in Table 1 to arrive at appropriate error bounds for our trend study.

Table 1 lists the year-to-year deviation (standard error) for various oxidant air quality indices. In our trend analysis, we will be working with 3-year averages of oxidant air quality, i.e., 1964-1966, 1967-1969, etc. The standard error of these three year averages will be lower than the single-year standard error by a factor of $\sqrt{3}$.

In validating the isopleths, we will take the base year (1964-1966) conditions as given and will examine changes relative to those conditions. The error of interest will be the error in the difference between base-year air quality (1964-1966) and air quality for subsequent periods (e.g., 1967-1969 or 1973-1975). To obtain the error in this difference we must multiply our (3-year) standard errors by $\sqrt{2}$.*

The two oxidant air quality indices that will be used in this study are the yearly second-highest one-hour concentration and the 95th percentile of daily maximal one-hour concentrations. Table 1 indicates that the year-to-year deviations for those two indices are $\pm$ 16.5% and $\pm$ 11.5%, respectively. From the line of reasoning presented in the preceding paragraphs, the error bounds that we will use in our verification study will be as follows:

$$\frac{\sqrt{2}}{\sqrt{3}} (\pm 16.5\%) = \pm 13.5\%$$ for the second-highest one hour concentrations

$$\frac{\sqrt{2}}{\sqrt{3}} (\pm 11.5\%) = \pm 9.4\%$$ for the 95th percentile of daily maximum concentrations

OXIDANT TREND DATA

Figures 3 to 7 present the oxidant trend data that will be used in the verification study[3]. Figure 3 presents trends in the basinwide second highest one-hour concentration. Figure 4 presents trends in the second highest one-hour and the 95th percentile of daily maxima at Azusa. Figures 5, 6, and 7 present data on the 95th percentile of daily maxima at DOLA, Anaheim, and San Bernadino, respectively. The data in Figures 3 to 7

*The standard error in the sum or difference of two variables, each with the same standard error (σ), is $\sqrt{2}\sigma$.

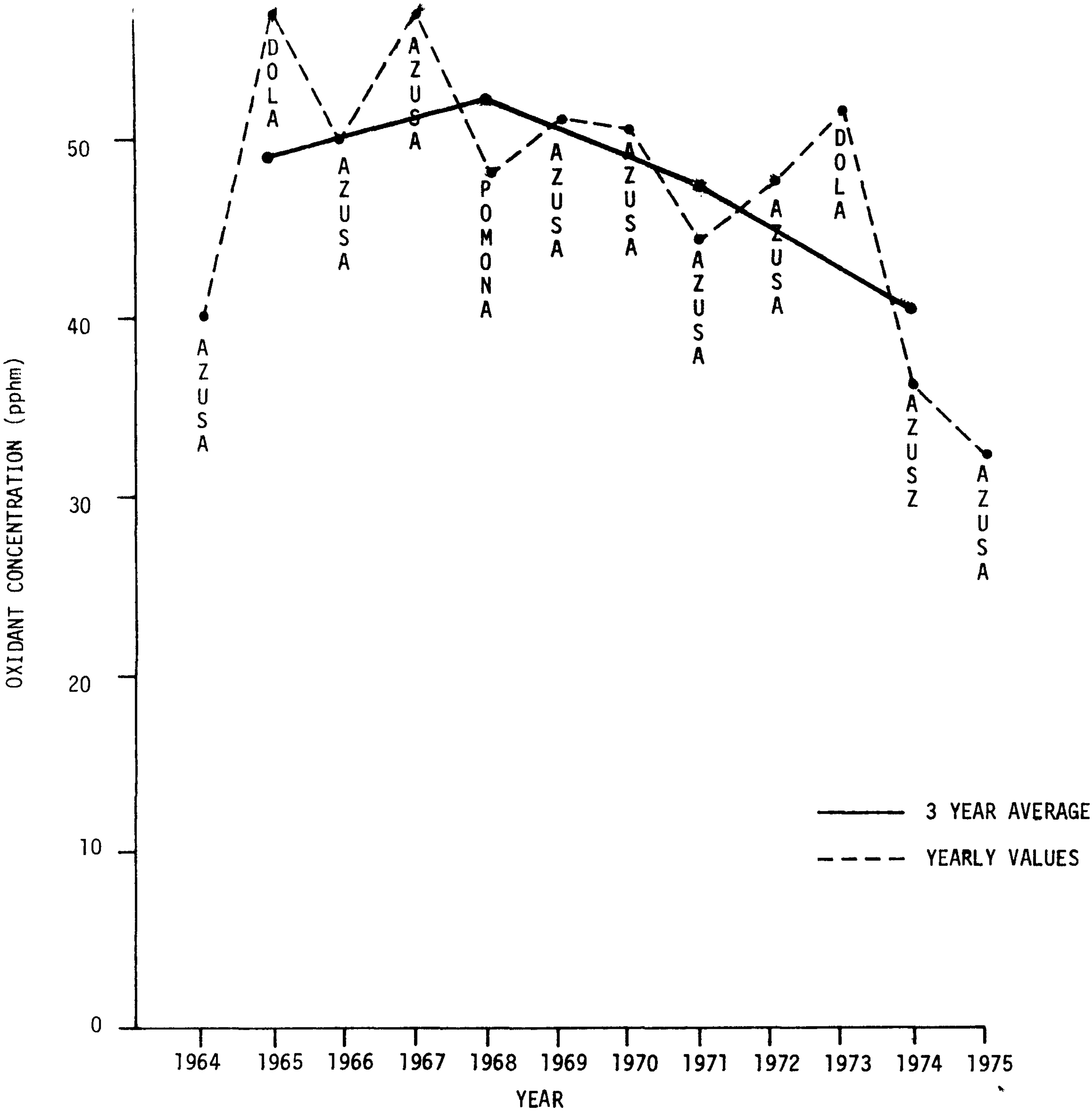

Figure 3. Trends in the Basinwide Second Maximum.

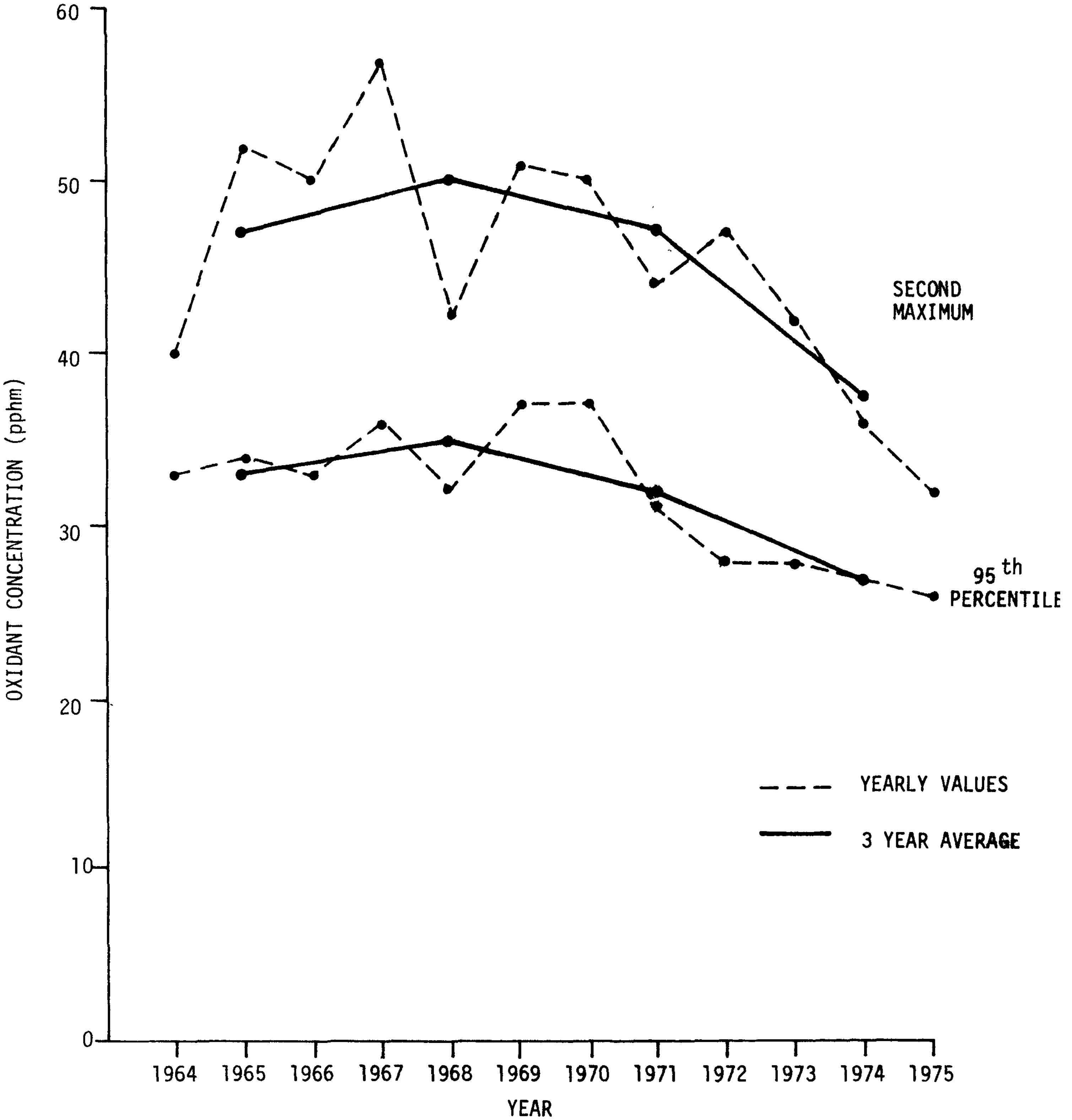

Figure 4. Trends in the Second-Highest One-Hour and the 95th Percentile of Daily Maxima at Azusa.

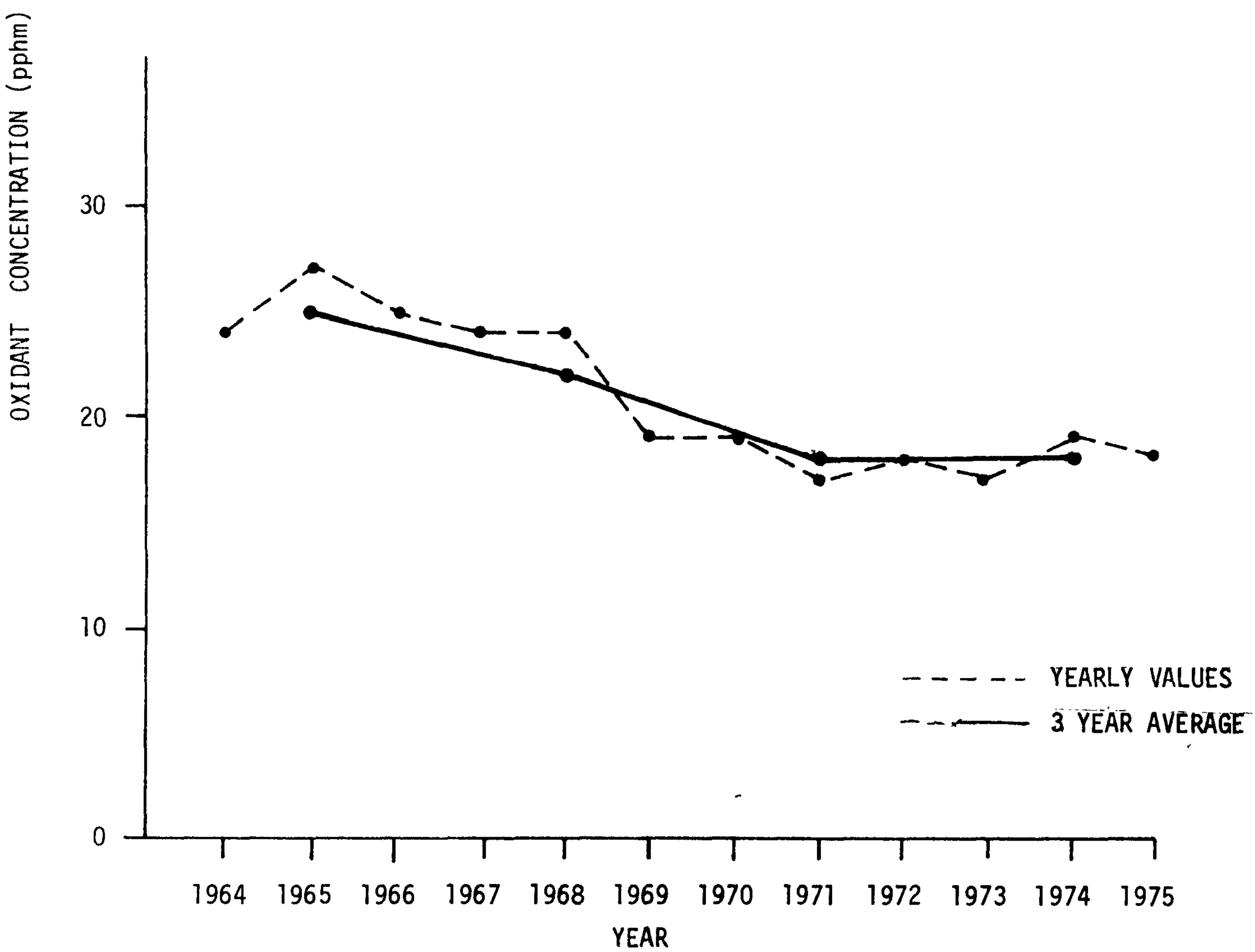

Figure 5. Trends in the 95th Percentile of the Daily Maxima at DOLA.

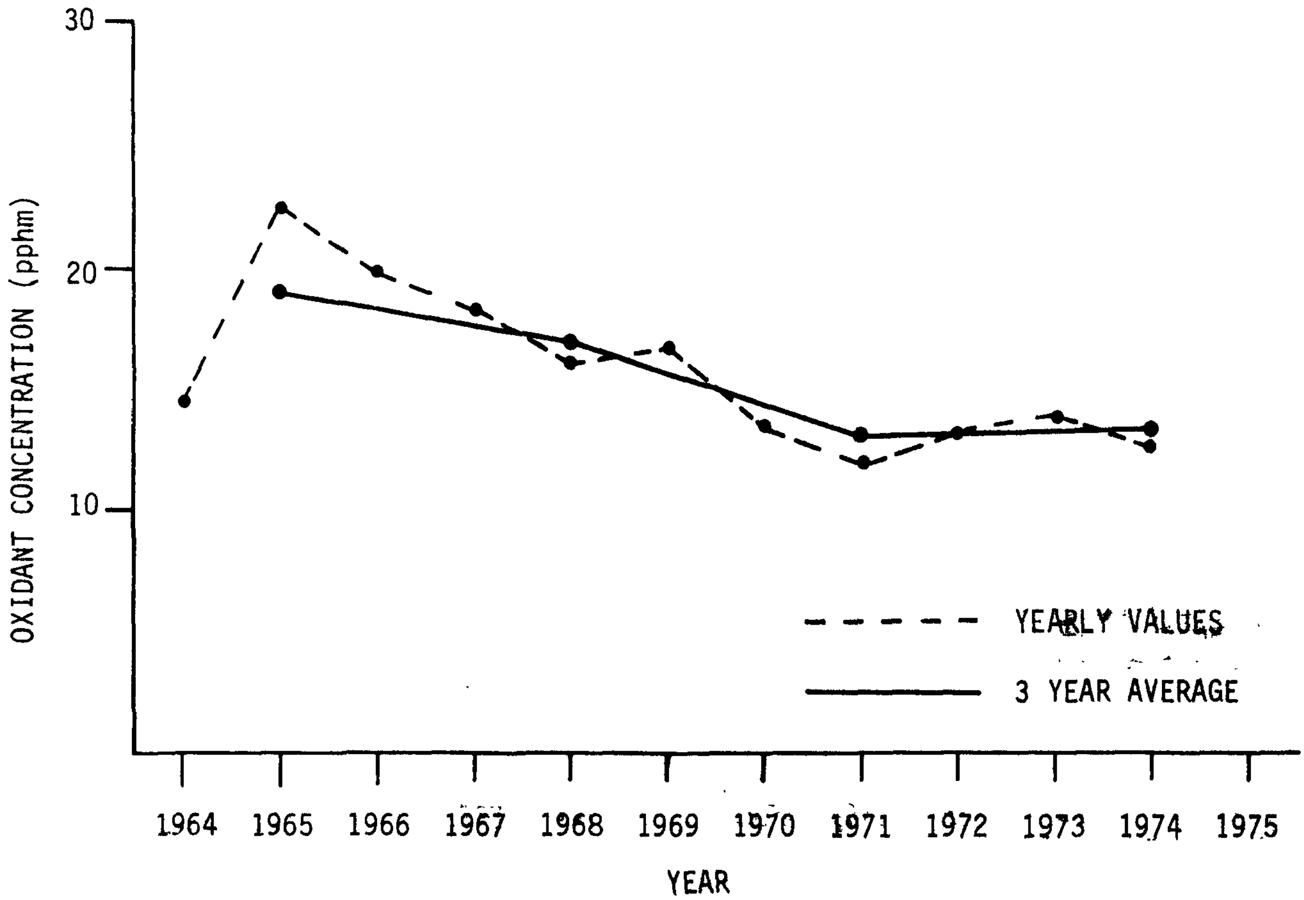

Figure 6. Trends in the 95th Percentile of the Daily Maxima at Anaheim.

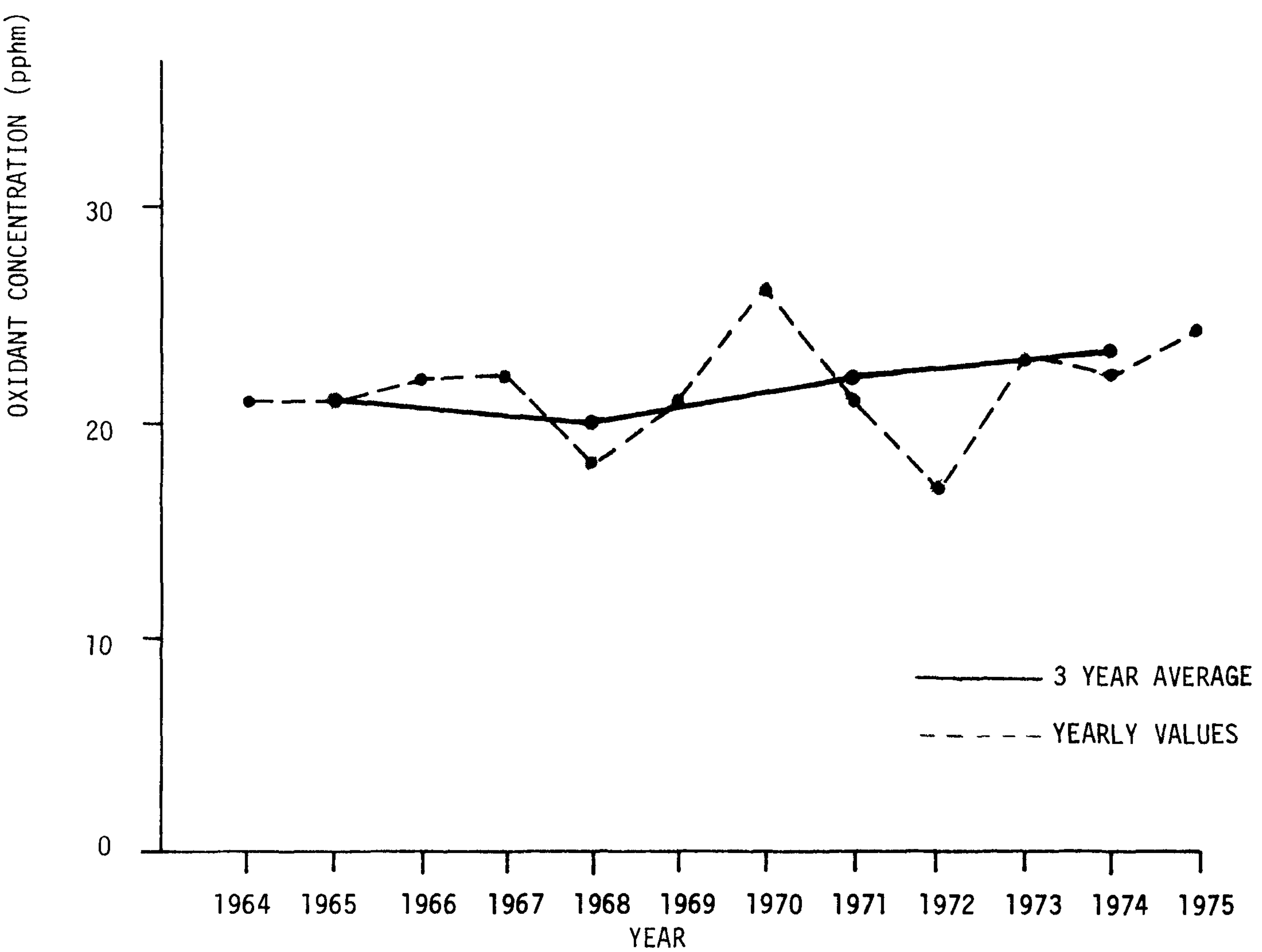

Figure 7. **Trends in the 95th Percentile of the Daily** Maxima at San Bernardino.

are listed in tabular form in Appendix A.

As explained in the discussion of monitoring sites and air quality indices, the data in Figures 3 and 4 will be used to check the basinwide isopleths. The data in Figures 4, 5, 6 and 7 will be used to verify the isopleths for individual irradiation times.

CHAPTER 3

DATA ON HISTORICAL PRECURSOR TRENDS AND THE NMHC/NO_x RATIO

In order to validate the EKMA isopleth model, information is required concerning historical precursor trends and the ambient NMHC/NO_x ratio. This chapter provides that information for several source areas within the Los Angeles basin: the source area corresponding to the basinwide oxidant maximum and the source areas corresponding to oxidant maxima at Downtown Los Angeles, Anaheim, Azusa, and San Bernardino.

First, the source area for each location under study is defined. Next, historical trends in the photochemical precursors from 1965 to 1974 are estimated for each source area by considering both emission data and ambient data. The NMHC/NO_x ratio in 1965 (the base year for the validation study) is estimated from present ambient data on the ratio and from historical precursor trends. The chapter concludes with a sensitivity analysis of three critical assumptions inherent in our treatment of the precursor data.

BASINWIDE ANALYSIS FOR LOS ANGELES

The first test of the isopleth method will involve trends in the basinwide oxidant maximum for Los Angeles. This section defines the source area for the basinwide maximum and provides data on historical precursor trends and on the ambient NMHC/NO_x ratio for that area.

Definition of Source Area

From our discussion of historical oxidant data for the Los Angeles region in Chapter 2, we conclude that the source area for the basinwide maximum can be considered as the source area affecting the Azusa monitoring site. To define the boundaries of this source area, we rely on a study of source/receptor situations for the Los Angeles basin performed as part of a recent Technology Service Corporation project for the California Air Resources Board [4]. The TSC study reviewed various wind trajectory and streamline analyses [5-14] and concluded that the following wind patterns occur rather consistently during the summer smog season in Los Angeles:

- during the night and early morning hours--variable wind or near stagnation

- during the late morning--west or southerly sea breeze
- during the afternoon and evening--dominant westerly sea breeze

A small sample of the evidence supporting these conclusions is provided in Table 2 and Figures 8 through 10. Table 2 lists the frequency of occurrence (by time of day) of various air-flow patterns during the summer smog season [5]. The two most prevalent patterns (west and south) are illustrated in Figures 8 and 9. Figure 10 presents the most frequent streamline pattern during the month of July [7].

Table 2. Percent Occurrence of Air Flow Patterns During July to September in Los Angeles

TIME OF DAY	WEST	SOUTH	EAST	ALL OTHERS
4 AM	44%	19%	19%	19%
10 AM	43	38	3	18
4 PM	83	13	0	5
10 PM	62	28	5	5

From TSC's source/receptor analysis [4], we conclude that the source area typically affecting oxidant at Azusa is as shown in Figure 11. The source area covers most of the southwestern part of Los Angeles County.

Estimates of Historical Precursor Trends

Two types of data can be used to estimate historical trends in NO_x and reactive hydrocarbons: emissions data and ambient precursor data. Both are examined below in order to arrive at best estimates of precursor trends for the source area affecting the basinwide oxidant maximum in Los Angeles. The trend estimates are made at three-year intervals, 1965, 1968, 1971, and 1974.

Emission Trends

A recent report of the Caltech Environmental Quality Laboratory [15] provides emission trend data for the Los Angeles region. Figures 12 and 13 summarize the EQL estimates of basinwide emission trends for NO_x and RHC, respectively. Basinwide NO_x emissions increased by 35% from 1965 to 1974, while basinwide RHC emissions decreased by 18%. Nearly all of the NO_x

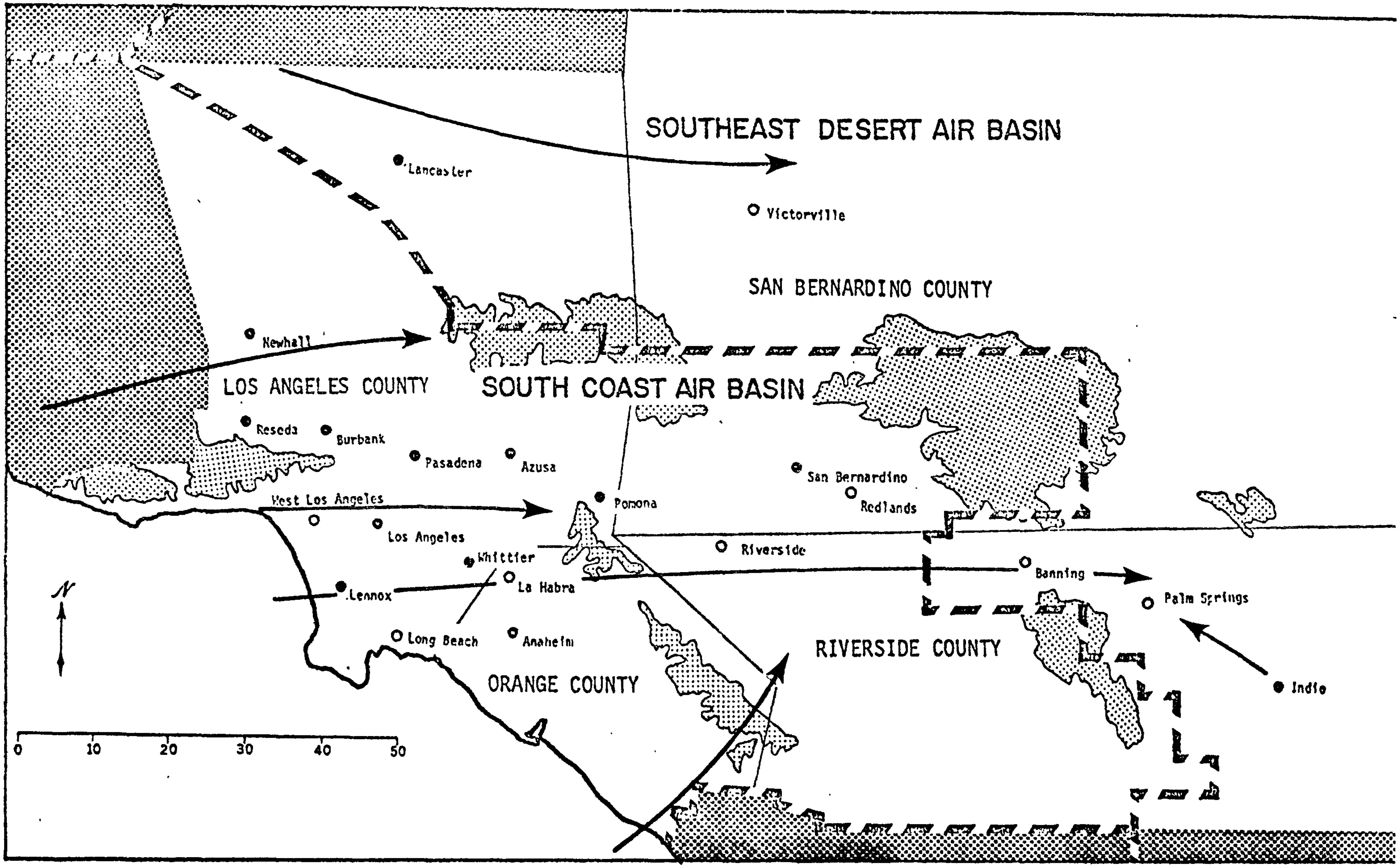

Figure 8. Streamlines for the Westerly Flow Pattern [5].

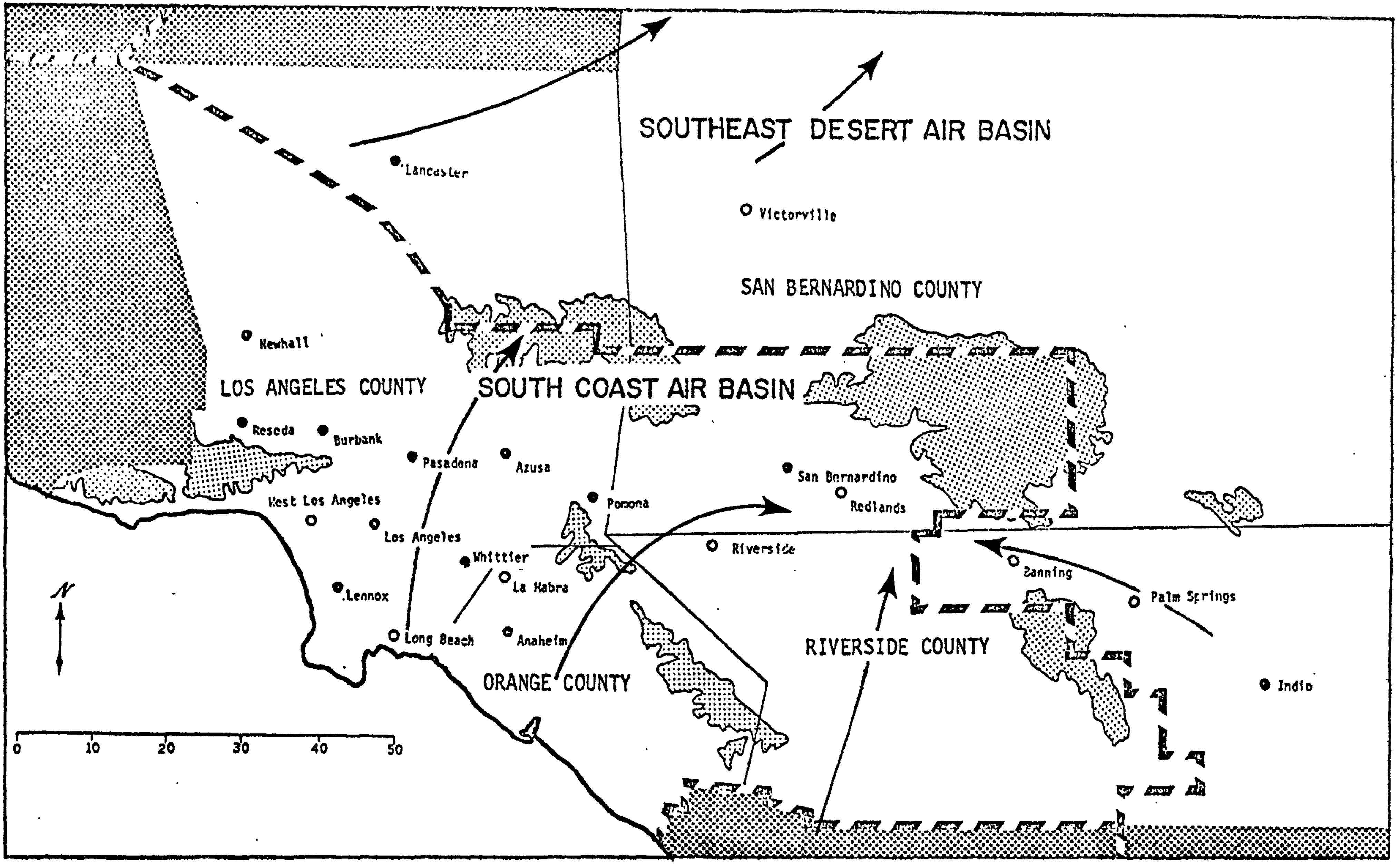

Figure 9. Streamlines for the Diurnal South Pattern [5].

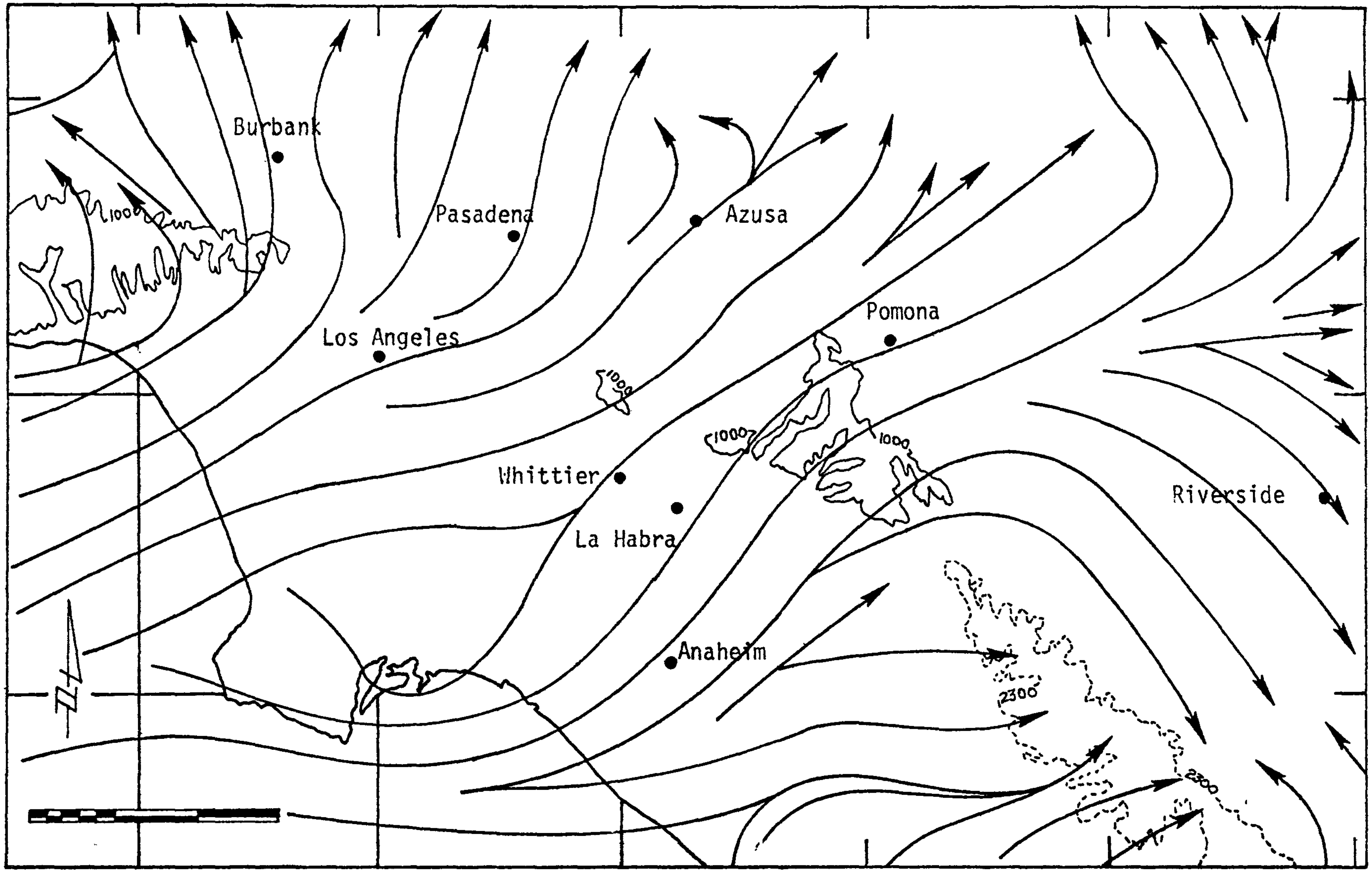

Figure 10. Streamlines of Most Frequent Surface Winds During July [7].

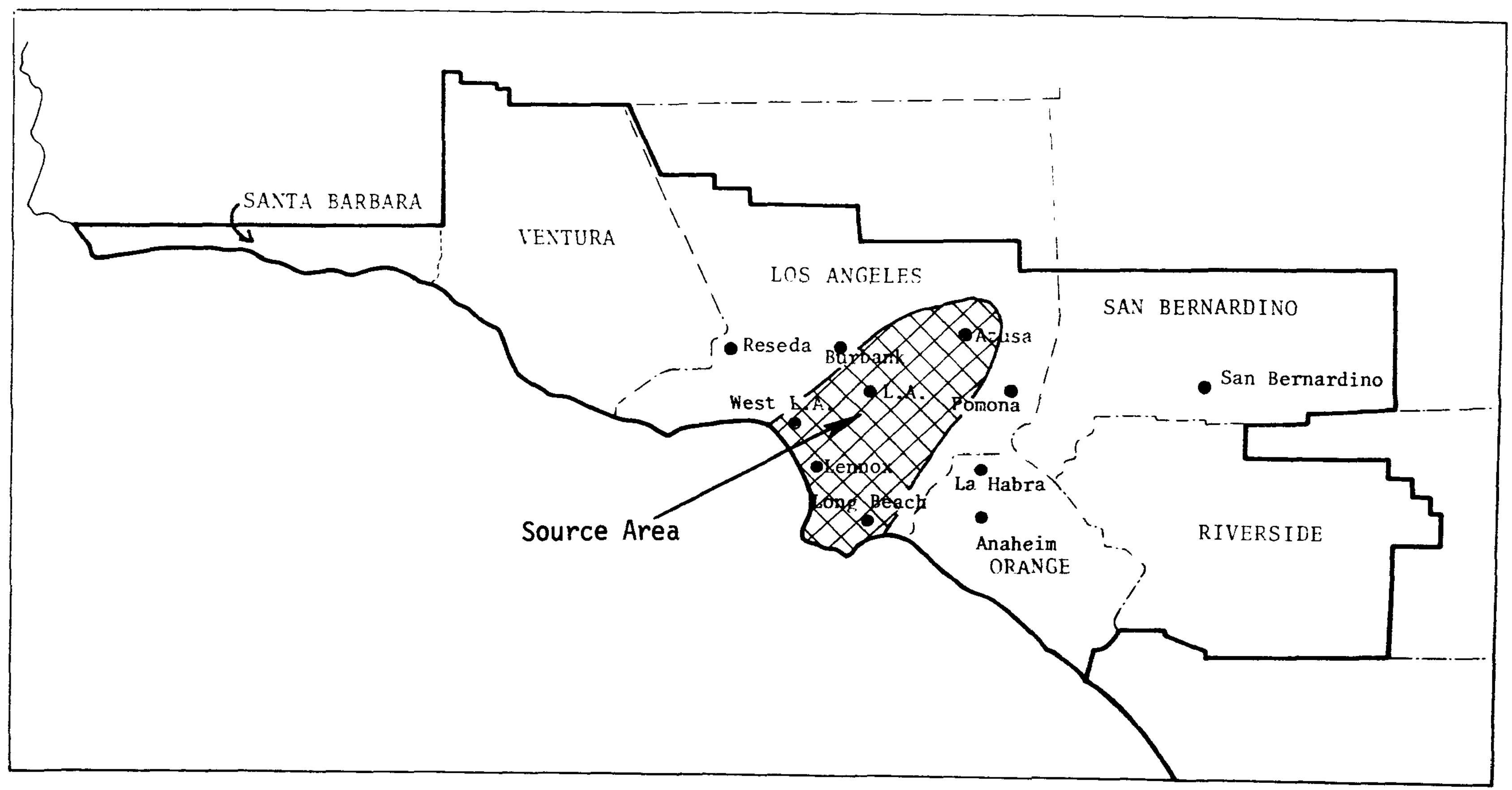

Figure 11. Approximate Source Area Affecting Basinwide Oxidant Maximum in the Los Angeles AQCR.

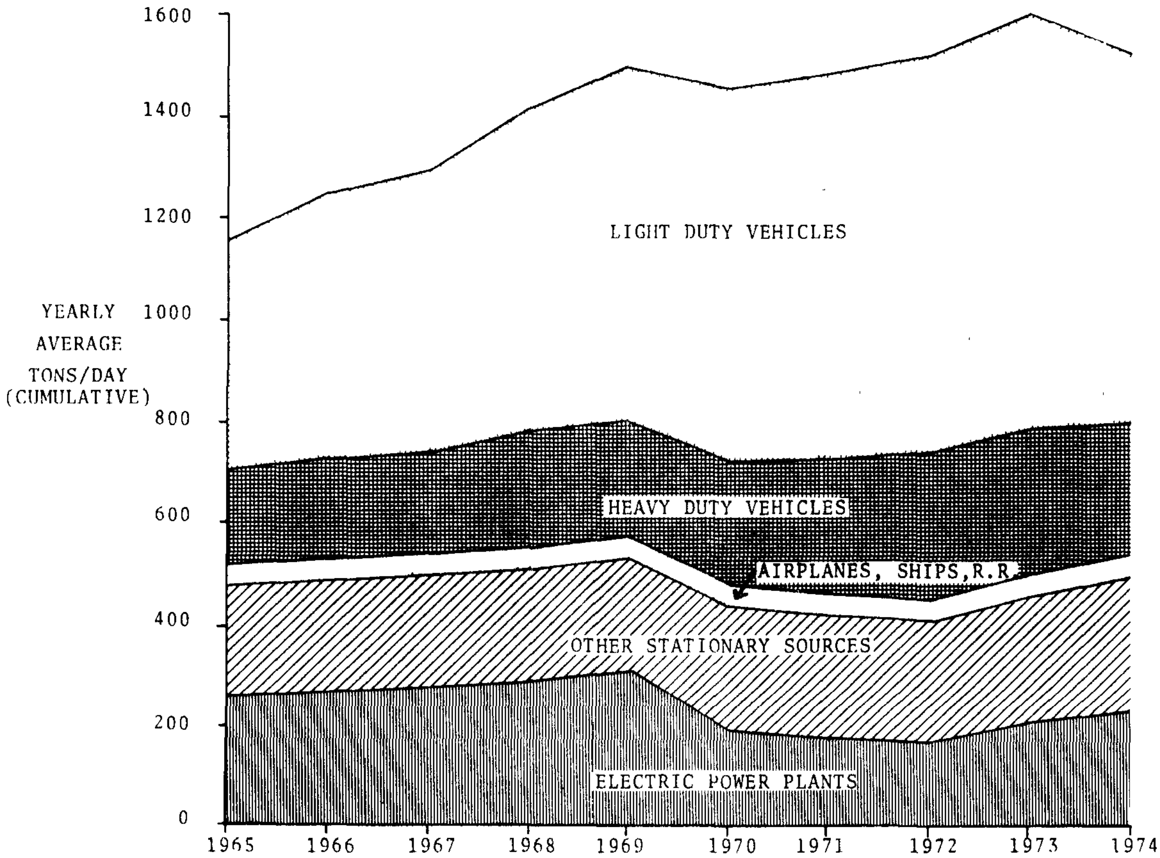

Figure 12. **Total NO_x Emission Trends in the Los Angeles Basin [15].**

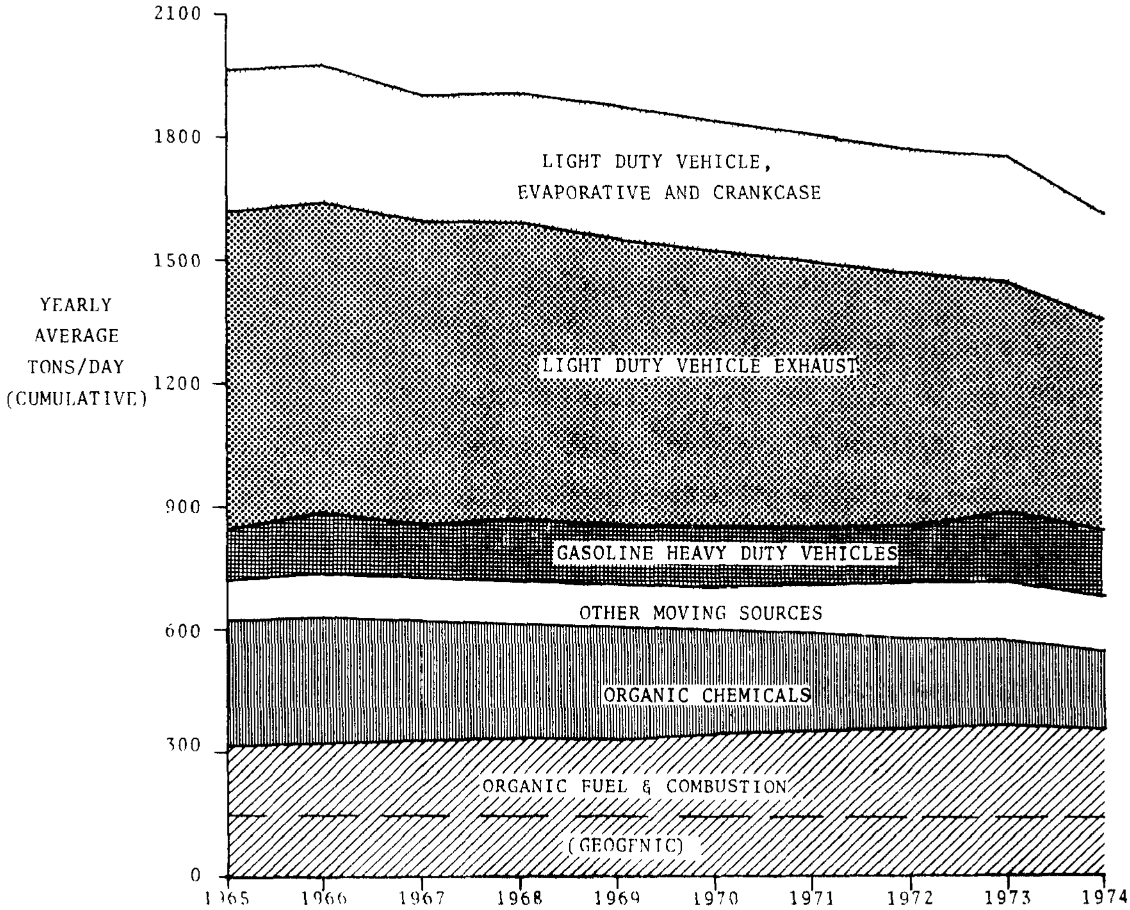

Figure 13. **Total RHC Emission Trends in the Los Angeles Basin [15].**

increase and most of the RHC decrease resulted from changes in emissions from gasoline-powered motor vehicles.

The EQL report also documents emission trends on a county by-county basis. Because of low growth rates in Los Angeles County (see Figure 14), Los Angeles County emissions decreased relative to basinwide total emissions. Los Angeles County emission changes were +25% for NO_x and -24% for RHC from 1965 to 1974 [15]. As was the case with basinwide RHC emissions, the decrease in RHC emissions for Los Angeles County was rather continuous over the nine-year period. Unlike basinwide NO_x emissions which peaked in 1973, Los Angeles County NO_x emissions reached a maximum around 1970-1971.

The emission trends for the source area of interest (Figure 11) should be similar to, but not exactly the same as the emission trends for Los Angeles County. A slight difference will arise because the source area is a lower growth area than the county as a whole (see Figures 11 and 14). Estimating emission trends specific to the source area involves educated guesswork based on relative growth rates (Figure 14) and the spatial distribution of various source types [16]. Judging from the results of the EQL trend study, we estimate that emissions in the source area changed as follows from 1965 to 1974:

Year	Estimated NO_x Emission Increase Relative to 1965	Estimated RHC Emission Decrease Relative to 1965
1965	0%	0%
1968	14-18%	3-11%
1971	19-26%	16-22%
1974	13-23%	24-33%

Note that the error range in our emission estimates increases with time because some of the uncertainties are compounded over time.

Ambient NO_x Trends

An alternative method of estimating precursor trends is to examine ambient data. To minimize statistical fluctuations in the trend estimates,

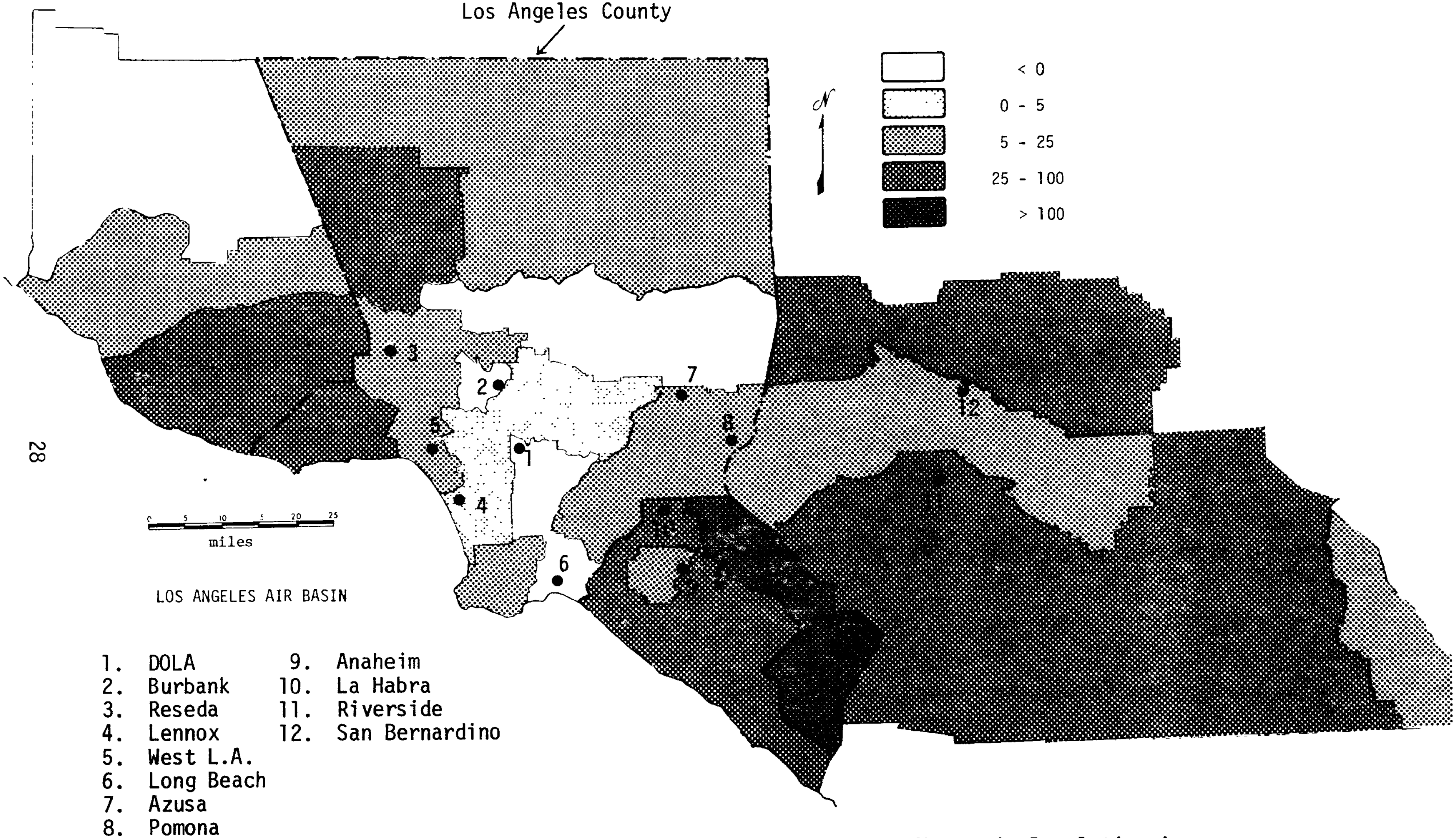

Figure 14. Geographical Distribution of Percent Change in Population in the Los Angeles Basin, 1965 to 1975.

a large sample of air quality data should be used. Table 3 summarizes trends in ambient NO_x for the source area; these trends are based on changes in annual mean NO_x and the yearly average of daily maximum NO_x for each three-year period from 1964-1966 to 1973-1975 [3]. All the listed changes are relative to the 1964-1966 ambient NO_x level.

The trends indicated by both the means and medians in Table 3 agree quite well with the NO_x emissions trend discussed previously. The trend of the medians in Table 3b most closely follows the emissions trend, which basically is a pattern of increasing values in the period 1964-1972 followed by decreasing values in the 1973-75 time period.

Ambient NMHC Trends

Long-term ambient trend data for total hydrocarbons (THC) are available at Downtown Los Angeles and Azusa. A partial history of THC trends is available at Burbank, Lennox, and Whittier. Estimating historical changes in NMHC concentrations with the THC data is a tenuous procedure. Ambient hydrocarbon measurements are considerably more error prone than other monitoring data [4]. Also, conceptual difficulties arise in translating THC trends into NMHC trends. Using a very simple procedure to calculate NMHC from THC levels*, approximate estimates of ambient NMHC trends can be derived; these trends are summarized in Table 4.

The trends in the median percent changes of ambient NMHC concentrations agree fairly well with the estimated trends in RHC emissions. The trends in the average percent changes of ambient NMHC concentrations don't agree as well with emissions, perhaps because the average of a given sample is inherently more susceptible to extreme values, such as the data from Burbank and Azusa. The discrepancies at Burbank and Azusa most likely arise from errors in the ambient trends. The basic trend for both emissions and ambient concentrations has been one of steadily decreasing values in the period 1965-1974.

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* NMHC trends are estimated from THC trends using the relation NMHC = (THC - 1 ppm)/2. The accuracy of this formula changes as relative THC and NMHC levels alter with time. This leads to a basic conceptual difficulty in estimating NMHC trends from THC trends.

Table 3. Trends in Ambient NO_x in the Source Area for the Los Angeles Basinwide Oxidant Maximum [3]

Table 3a. Percent Changes in Annual Mean NO_x Relative to 1964-1968

YEAR	STATION DOLA	LENNOX	WEST L.A.	BURBANK	LONG BEACH	AZUSA	AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
1964-66	0%	0%*	0%	0%	0%	0%	0%	0%
1967-69	+8	+21	+8	+39	+17	+16	+18	+16
1970-72	+22	+23	+19	+37	+10	+54	+28	+22
1973-75	+1	+5	+9	+7	-16	+46	+9	+6

Table 3b. Percent Changes in Yearly Average of Daily One-Hour Maximum NO_x Relative to 1964-1966

YEAR	STATION DOLA	LENNOX	WEST L.A.	BURBANK	LONG BEACH	AZUSA	AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
1964-66	0%	0%*	0%	0%	0%	0%	0%	0%
1967-69	+7	+22	+8	+34	+18	+17	+18	+18
1970-72	+22	+30	+17	+36	+20	+56	+30	+26
1973-75	0	+14	+10	+7	-8	+47	+12	+9

* based on two-year average

Table 4. Trends in Ambient NMHC in the Source Area for the Los Angeles Basinwide Oxidant Maximum [3]

Table 4a. Percent Changes in Annual Mean NMHC Relative to 1964-1966

YEAR	STATION					AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
	DOLA	LENNOX	WHITTIER	BURBANK	AZUSA		
1964-66	0%	0†%	0†%	0*%	0*%	0%	0%
1967-69	-15	-12†	-18†	+3Δ	+11	-6	-12
1970-72	-8	-24	-29	+7	+33	-4	-8
1973-75	-38	-35	-41	-7	+39	-16	-35

Table 4b. Percent Changes in Yearly Average of Daily One-Hour Maximum NMHC Relative to 1964-1966

YEAR	STATION					AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
	DOLA	LENNOX	WHITTIER	BURBANK	AZUSA		
1964-66	0%	0†%	0†%	0*%	0*%	0%	0%
1967-69	-15	-14†	-15†	+2Δ	+11	-6	-14
1970-72	-23	-31	-29	+5	+35	-9	-23
1973-75	-46	-48	-47	-13	+12	-28	-46

†based on extrapolation of 1970-1975 trend

*based on two-year average

Δlinear interpolation between 1970-72 and 1964-66

Best Estimates of Precursor Trends

By considering both emission trend data and ambient trend data, one can arrive at reasonable estimates of precursor trends in the source area. Both the emission estimates and the ambient precursor data are subject to potential errors from several factors. The principal factors affecting the ambient data are:

- characteristics of sampling site
- meteorological fluctuations
- uncertainties in analytical methodology (especially NMHC)

Emissions data are generally affected by the following:

- growth rate of source area
- changes in source emission rates

In spite of potential errors from all these factors, the general agreement between emissions estimates and ambient data for both precursors gives one confidence in ascertaining the historical trends of NMHC and NO_x. Table 5 which was constructed using both ambient and emissions data for NMHC and NO_x, summarizes our best estimates of precursor changes relative to 1964-1966. These data are shown graphically in Figure 15. Also included in the table and figure are error bounds based on a subjective analysis of the uncertainties, including the agreement or disagreement between emission trends and ambient trends.

Table 5. Best Estimates of Precursor Trends in the Source Area for the Basinwide Oxidant Maximum

Year	NO_x Change	NMHC Change
1964-66	0%	0%
1967-69	+17% ± 3%	-10% ± 3%
1970-72	+24% ± 5%	-16% ± 6%
1973-75	+15% ± 7%	-30% ± 6%

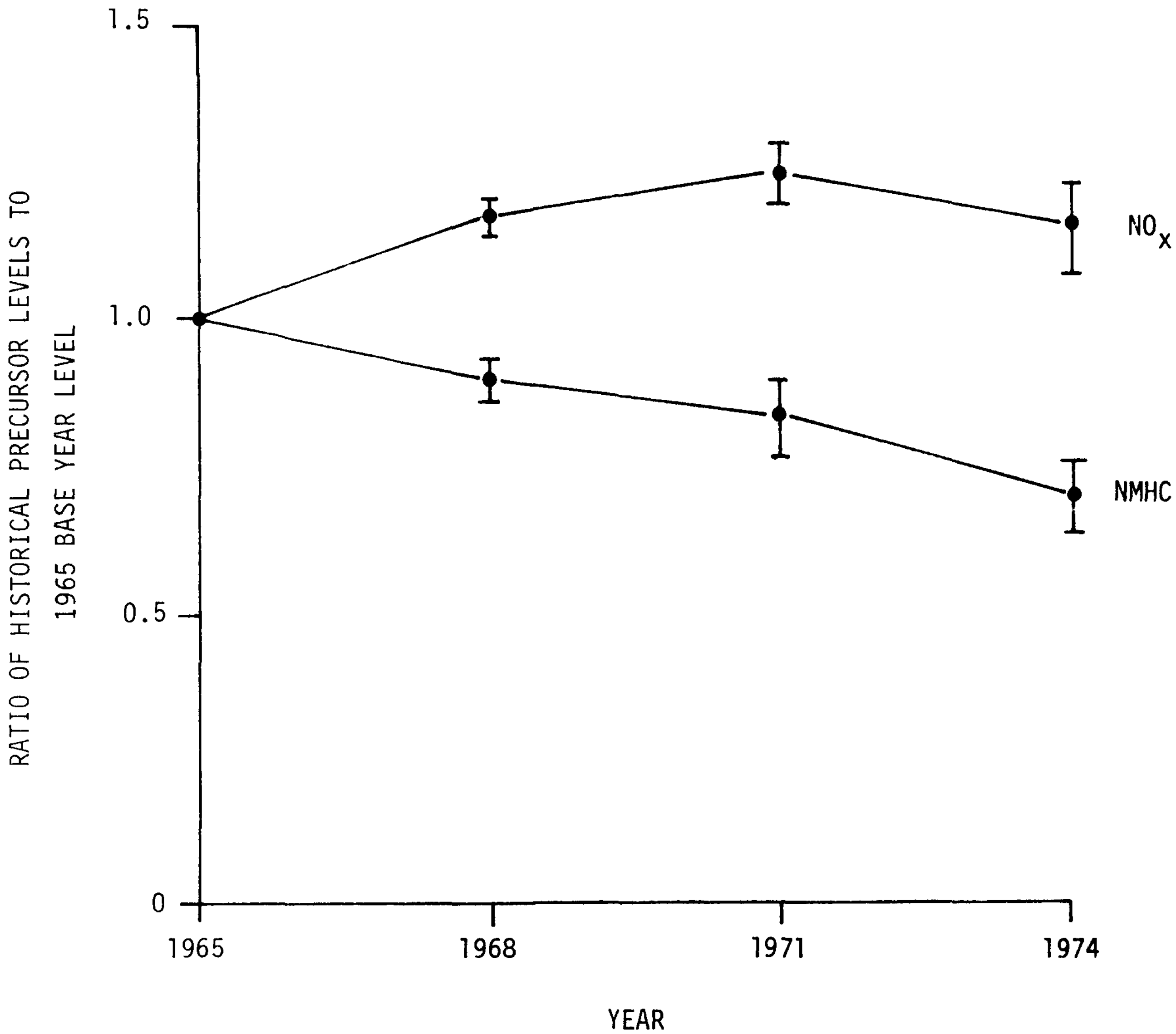

Figure 15. Best Estimates of Historical Precursor Trends in the Source Region for the Basinwide Oxidant Maximum.

Estimates of Ambient 6-9 AM $NMHC/NO_x$ Ratio

Considerable data on ambient NMHC and NO_x concentrations in Los Angeles are available for the early and mid-1970's. Based on these data, 6-9 AM $NMHC/NO_x$ ratios are calculated for various locations in the source region and for various times in the period 1969-1976. These results are summarized in Table 6.

With two exceptions, the $NMHC/NO_x$ ratio is very consistent in spite of the spatial and temporal variations in the monitoring of the precursors. The two data sources that aren't in agreement with the others are the APCD data, which tend to give low $NMHC/NO_x$ ratios, and the 1974 ARB data, which tend to give high ratios. The nature of this disagreement is thought to be due to the method of monitoring the NMHC. The flame ionization detection method used by both the ARB and APCD has been shown to give unaccountably poor readings [4]. Furthermore, the accuracy of the GC separation technique employed by the ARB is strongly dependent upon operator skill [4].

The ratios from the other data sources did not fluctuate much over the years 1970-76 because the ambient concentrations of both precursors were simultaneously decreasing. Based on the data in Table 6, our best estimate of the $NMHC/NO_x$ ratio in the 1970's is the following:

Median:	8
10th Percentile:	5
90th Percentile:	15

The $NMHC/NO_x$ ratio for the 1970's, together with the best estimate of the precursor trends from 1965-75 will now be used to estimate the $NMHC/NO_x$ ratio for 1965. Since NMHC have decreased about 20% and NO_x has increased about 20% from 1965 to the early 1970's, the 1965 $NMHC/NO_x$ ratio was therefore about 1.5 times the ratio in the 1970's. Consequently, the best estimate of the 1965 $NMHC/NO_x$ ratio is the following:

Median:	12
10th Percentile:	7
90th Percentile:	23

We are using a range of ratios for two basic reasons. First, the low quality of the ambient NMHC data introduces uncertainty concerning the real ambient ratio. Second, the $NMHC/NO_x$ ratio appears to fluctuate considerably

Table 6. Ambient 6-9 AM NHMC/NOx Ratios

DATA SOURCE	TIME PERIOD	LOCATION	MEASURED $NMHC/NO_x$ RATIO MEDIAN	10th%	90th%
NMHC [1] NO_x [1]	9 summer days 0600-0900 1976	Riverside	8	6	20
NMHC [2] NO_x [2]	19 summer days 0600-0900 1976	Temple City	8	4	10
NMHC [3] NO_x [3]	6 days per year in April-Sept. 0600-0900 1969-74	Azusa	5	0	14
		DOLA	3	0	7
		Lennox	4	0	8
		Pomona	3	0	6
NMHC [4] NO_x [3]	30 summer days 0600-0900 1974	Azusa	21	15	30
		DOLA	15	11	28
NMHC [4] NO_x [3]	30 summer days 0600-0900 1971	Azusa	8	7	13
		DOLA	8	4	11
NMHC [5] NO_x [5]	13 days 9/73-10/73 0800-1000	Central Los Angeles Area	7	4	14

1. Statewide Air Pollution Research Center, GC/FID Hydrocarbon Measurements.
2. Air Resources Board, GC/FID Hydrocarbon Measurements.
3. APCD Data Base 1969-1974, FI Hydrocarbon Measurements.
4. "Atmospheric Hydrocarbon Concentrations June-Sept. 1974," "Distribution of Hydrocarbons in the Los Angeles Atmosphere, Aug.-Oct. 1971," Air Resources Board, GC/FID Hydrocarbon Measurements.
5. LARPP, Semi-permeable CH_4 membrane + FID Hydrocarbon Measurements.

from day-to-day [2, 17], possibly due to specific wind trajectories and associated stationary source areas, or to variations in motor vehicle $NMHC/NO_x$ emission ratios because of temperature and relative humidity fluctuations.

ANALYSIS OF INDIVIDUAL LOCATIONS

Downtown Los Angeles, Anaheim, Azusa, and San Bernardino were selected for testing the model at specific sites and hence validating the isopleths for individual irradiation times.

Downtown Los Angeles

This section defines the source area for Downtown Los Angeles and presents the historical precursor trends and the ambient $NMHC/NO_x$ ratio for that location.

Source Area

Based on an analysis of wind flow patterns in the Los Angeles basin (see earlier discussion) we conclude that the source area affecting oxidant in Downtown Los Angeles is as shown in Figure 16. The source area essentially consists of the southwest quadrant from Downtown Los Angeles to the coastline.

Historical Precursor Trends

Emission trend estimates for the source area affecting Downtown Los Angeles are derived by modifying the results of the EQL emission trend study [15]. These modifications are based on relative growth rates (Figure 14) and the spatial distribution of various source types [16]. Our estimates indicate that emissions changed as follows in the source area from 1965 to 1974:

Year	Estimated NO_x Emission Increase	Estimated RHC Emission Decrease
1965	0%	0%
1968	10-15%	10-14%
1971	14-21%	20-28%
1974	7-16%	30-42%

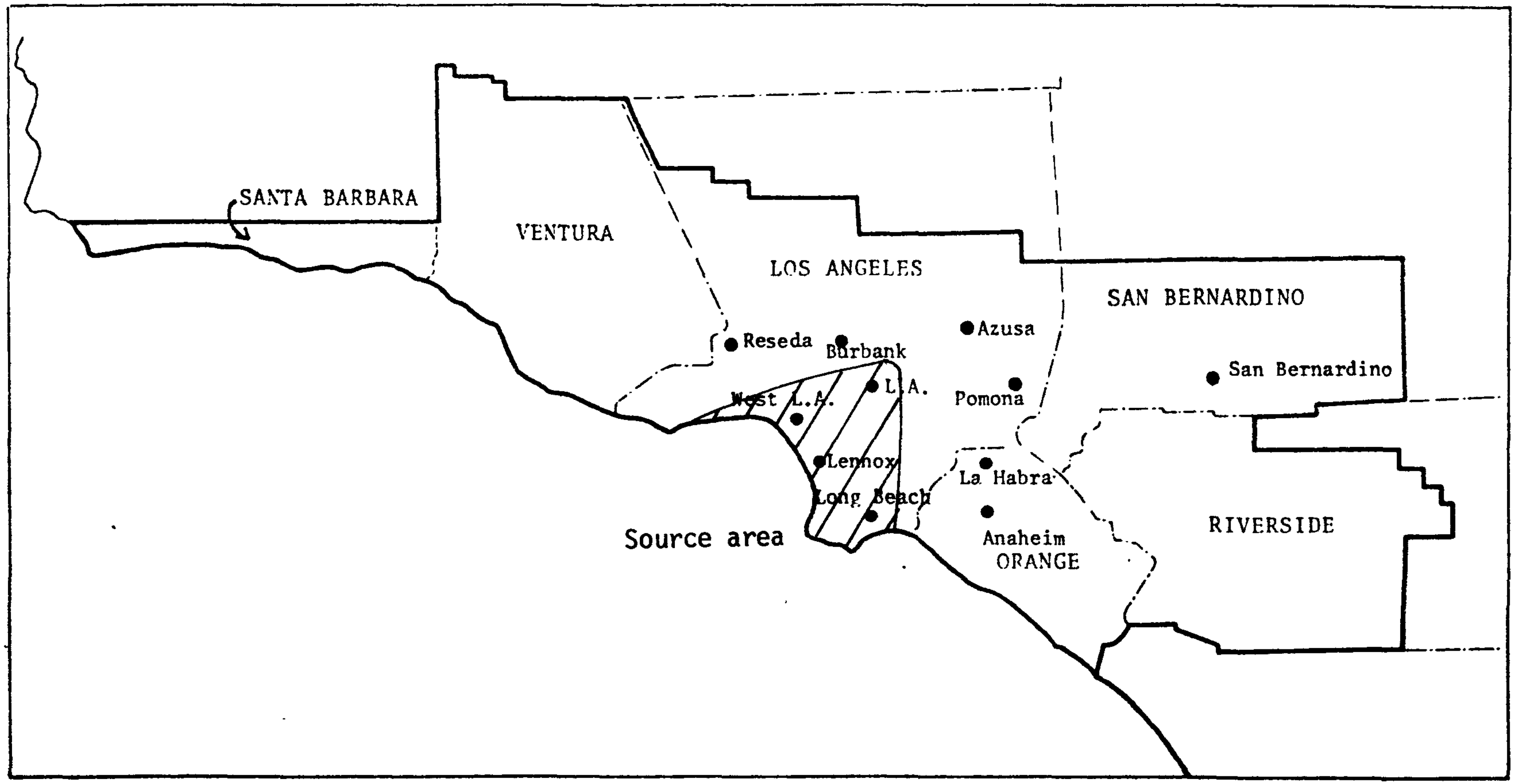

Figure 16. Approximate Source Area Affecting the Oxidant Maximum at Downtown Los Angeles.

Table 7. Trends in Ambient NO_x in the Source Area for Downtown Los Angeles [3]

Table 7a. Percent Changes in Annual Mean NO_x Relative to 1964-1966

YEAR	STATION				AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
	DOLA	LENNOX	WEST L.A.	LONG BEACH		
1964-66	0%	0%*	0%	0%	0%	0%
1967-1969	+8	+21	+8	+17	+14	+12
1970-1972	+22	+23	+19	+10	+18	+20
1973-1975	+1	+5	+9	-16	0	+3

Table 7b. Percent Changes in Yearly Average of Daily One-Hour Maximum NO_x Relative to 1964-1966

YEAR	STATION				AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
	DOLA	LENNOX	WEST L.A.	LONG BEACH		
1964-66	0%	0%*	0%	0%	0%	0%
1967-69	+7	+22	+8	+18	+14	+13
1970-72	+22	+30	+17	+20	+22	+21
1973-75	0	+14	+10	-8	+4	+5

*based on two-year average

Table 8. Trends in Ambient NMHC in the Source Area for Downtown Los Angeles [3]

Table 8a. Percent Changes in Annual Mean NMHC Relative to 1964-1966

YEAR	STATION DOLA	STATION LENNOX	STATION WHITTIER	AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
1964-66	0%	0%†	0%†	0%	0%
1967-69	-15	-12 †	-18 †	-15	-15
1970-72	-8	-24	-29	-20	-24
1973-75	-38	-35	-41	-38	-35

Table 8b. Percent Changes in Yearly Average of Daily One-Hour Maximum NMHC Relative to 1964-1966

YEAR	STATION DOLA	STATION LENNOX	STATION WHITTIER	AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
1964-66	0%	0%†	0%†	0%	0%
1967-69	-15	-14 †	-15 †	-15	-15
1970-72	-23	-31	-29	-28	-29
1973-75	-46	-48	-47	-47	-47

†based on extrapolation of 1970-1975 trend

The trends in ambient NO_x for the Downtown Los Angeles source area are presented in Table 7. Downtown Los Angeles, Lennox, West Los Angeles, and Long Beach were selected as being most representative of the source region's NO_x trends. The ambient NO_x trends agree fairly well with our estimates of NO_x emission changes for the DOLA source area.

Table 8 presents the trends in ambient NMHC for the Downtown Los Angeles source area. DOLA, Lennox, and Whittier were selected as being most representative of the ambient NMHC trends in the source area for DOLA. The basic hydrocarbon trend has been one of steadily decreasing concentrations over the years 1964-1975.

After considering both emission trend data and ambient trend data, our best estimates of historical precursor trends for the Downtown Los Angeles source region are as presented in Table 9. The results are expressed as percent changes in precursors relative to 1964-1966. We attach good confidence to these results because the ambient and emissions data agreed quite well for the Downtown Los Angeles source area. The data presented in Table 9 are shown graphically in Figure 17.

Table 9. Best Estimates of Precursor Trends for the DOLA Source Region

Year	NO_x Change	NMHC Change
1964-66	0%	0%
1967-69	+13% ± 2%	-13% ± 2%
1970-72	+18% ± 3%	-24% ± 3%
1973-75	+ 7% ± 5%	-38% ± 5%

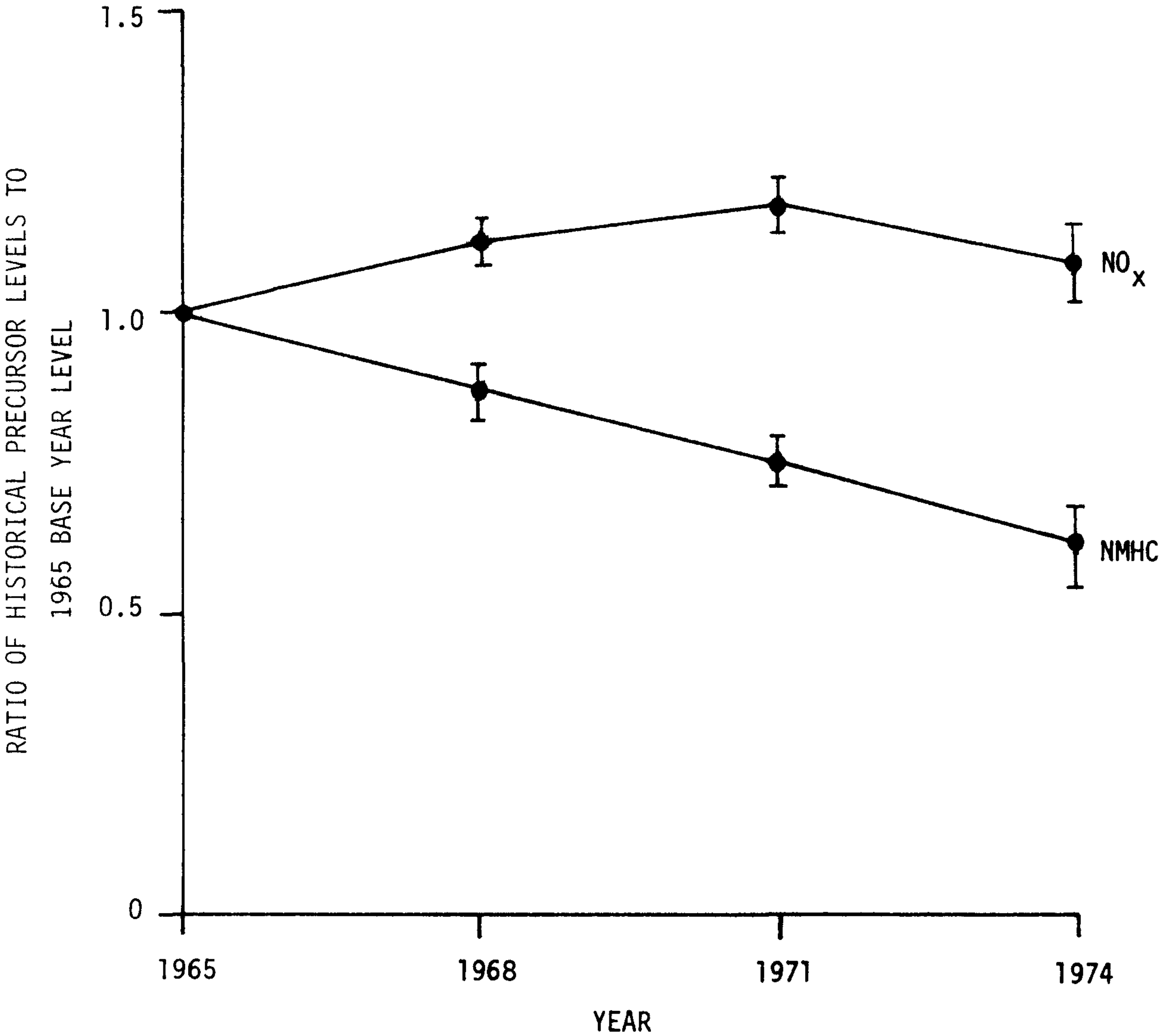

Figure 17. **Best Estimates of Historical Precursor Trends in the DOLA Source Region**

Ambient NMHC/NO_x Ratio

The 6-9 AM NMHC/NO_x ratio for the Downtown Los Angeles source area is assumed to be the same as that for the basinwide-maximum source area. In 1965 the ratio is estimated to be as follows:

Median:	12
10th Percentile:	7
90th Percentile:	23

Anaheim

This section discusses the source area, historical precursor trends, and ambient NMHC/NO_x ratio for the validation study at Anaheim.

Source Area

Our analyses of wind-flow patterns in the Los Angeles basin (see earlier discussion) indicates that the source area affecting oxidant in Anaheim is as shown in Figure 18. The area includes the northwest part of Orange County and the southern coast of Los Angeles County.

Historical Precursor Trends

Estimates of emission trends for the Anaheim source area are derived according to the procedures described earlier. Net changes in emissions relative to 1965 are approximately as follows:

Year	Estimated NO_x Emission Increase	Estimated RHC Emission Decrease
1965	0%	0%
1968	25-35%	2-8%
1971	35-50%	4-13%
1974	40-60%	6-18%

Trends in ambient NO_x for monitoring sites within or near the Anaheim source region are presented in Table 10. The average and median percent changes among the three monitoring sites are consistent with the estimated emission changes for the source area. There is of course an obvious difference between the low growth parts of the source area (e.g. Long Beach) and the high growth parts of the source area (e.g. Anaheim and La Habra).

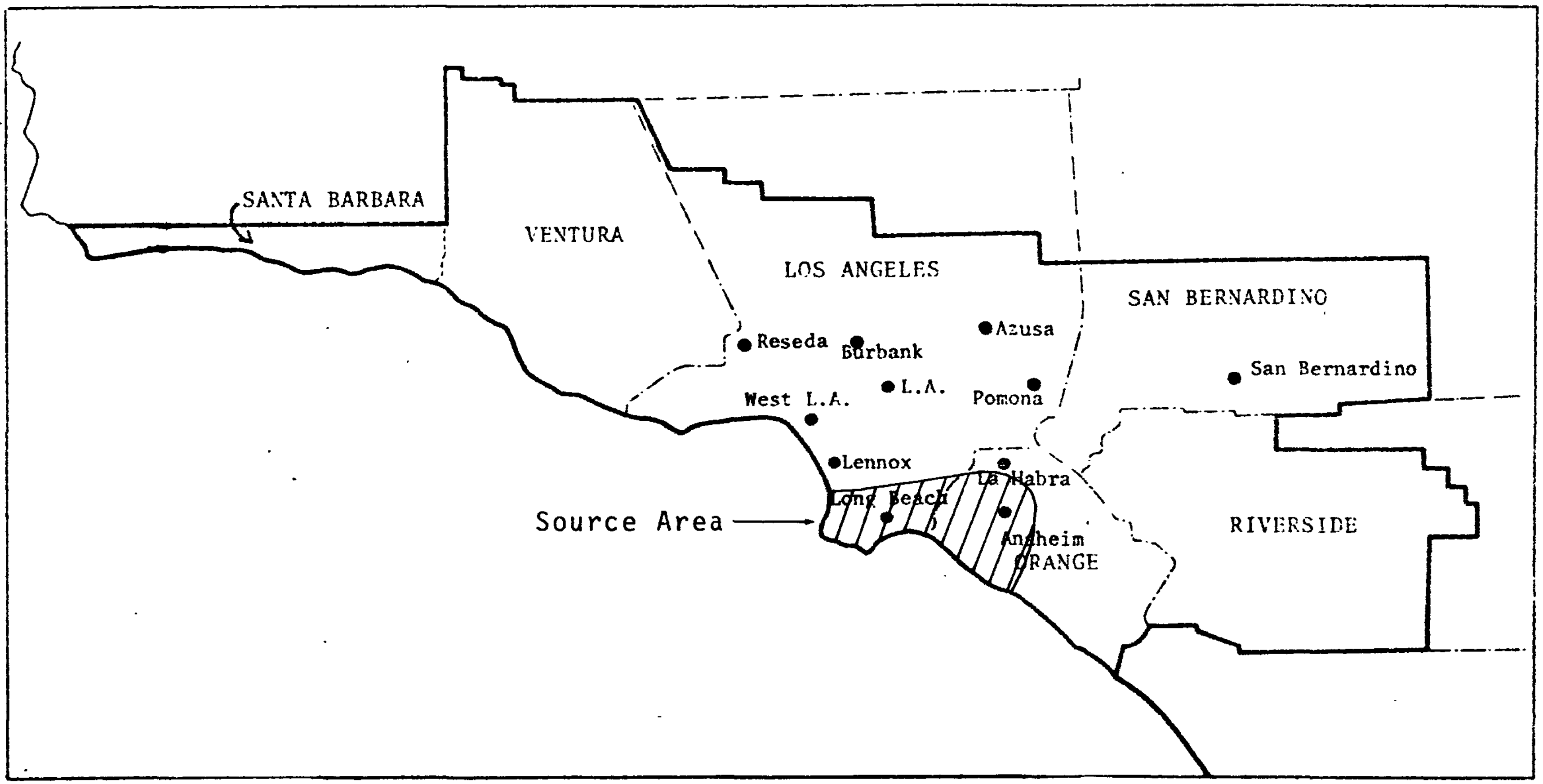

Figure 18. Approximate Source Area Affecting the Oxidant Maximum at Anaheim.

Table 10. Trends in Ambient NO_x in the Source Area for Anaheim [3]

Table 10a. Percent Changes in Annual Mean NO_x Relative to 1964-1966

YEAR	STATION			AVG. OF PERCENT CHANGES	MEDIAN PERCENT CHANGES
	LONG BEACH	LA HABRA	ANAHEIM		
1964-1966	0%	0%†	0%	0%	0%
1967-1969	+17	+19*	+75	+37	+19
1970-1972	+10	+26	+85	+40	+26
1973-1975	-16	+60	+78	+41	+60

Table 10b. Percent Changes in Yearly Average of Daily One-Hour Maximum NO_x Relative to 1964-1966

YEAR	STATION			AVG. OF PERCENT CHANGES	MEDIAN PERCENT CHANGES
	LONG BEACH	LA HABRA	ANAHEIM		
1964-1966	0%	0%*	0%	0%	0%
1967-1969	+18	+3	+92	+38	+18
1970-1972	+20	+14	+93	+42	+20
1973-1975	-8	+44	+86	+41	+44

* based on two-year average

† based on extrapolation

Table 11. Trends in Ambient NMHC in the Source Area for Anaheim [3]

Table 11a. Percent Changes in Annual Mean NMHC Relative to 1964-1966

YEAR	ANAHEIM
1964-66	0%*
1967-69	-12
1970-72	- 6
1973-75	-24

Table 11b. Percent Changes in Yearly Average of Daily One-Hour Maximum NMHC Relative to 1964-1966

YEAR	ANAHEIM
1964-66	0%*
1967-69	- 7
1970-72	- 3
1973-75	-20

* based on two-year average

There is only one monitoring site (Anaheim) providing data on ambient NMHC trends for the Anaheim source region. As shown in Table 11, the ambient NMHC decrease at Anaheim is slightly greater than the estimated RHC emission decrease. For the Anaheim source region, we place greater confidence in the RHC emission trend than in the ambient NMHC trend because only one monitoring site is available.

By considering both the emission trend data and the ambient trend data, we arrive at best estimates of historical precursor trends for the Anaheim source area. These best estimates are listed in Table 12 and illustrated in Figure 19.

Table 12. Best Estimates of Precursor Trends for the Anaheim Source Area

Year	NO_x Change	NMHC Change
1964-66	0%	0%
1967-69	+29%±8%	-6%±4%
1970-72	+37%±10%	-8%±5%
1973-75	+47%±12%	-15%±7%

Ambient NMHC/NO_x Ratio

The 6-9 AM NMHC/NO_x ratio for the Anaheim source area is assumed to be the same as that for the basinwide source area. For the base year 1965, our estimates for the ratio are as follows:

Median: 12
10th Percentile: 7
90th Percentile: 23

Azusa

The source area for oxidant at Azusa is assumed to be the same as the source area for the basinwide oxidant maximum. Thus, the historical precursor trends and ambient NMHC/NO_x ratio for the Azusa source area are as presented in the section on the basinwide maximum.

San Bernardino

This section defines the source area for San Bernardino and presents the historical precursor trends and the ambient NMHC/NO_x ratio for that source area.

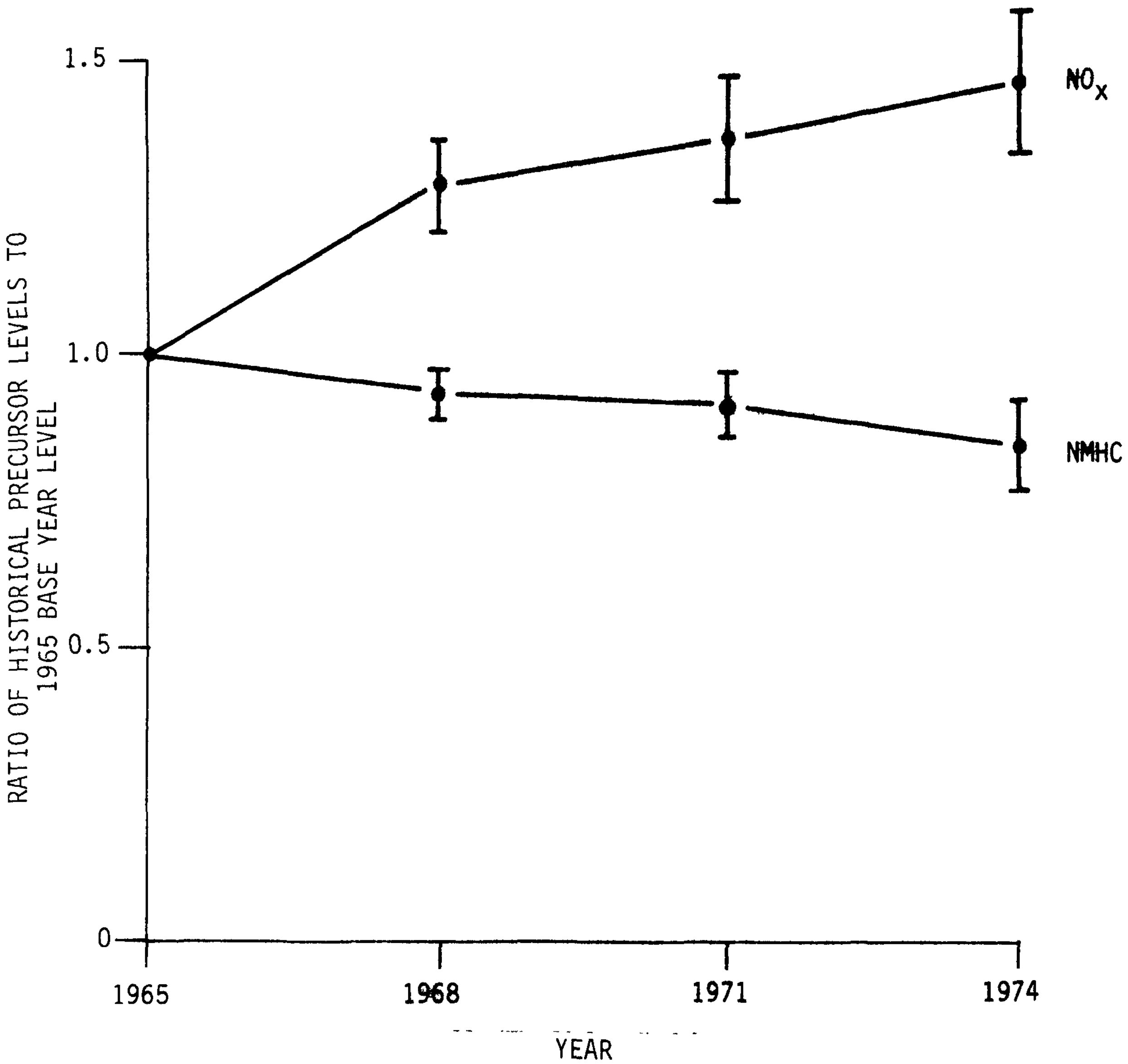

Figure 19. **Best Estimates of Historical Precursor Trends in the Anaheim Source Region.**

Source Area

After a study of the wind flow patterns in the Los Angeles Basin, (see section on basinwide analysis), we conclude that the source area governing oxidant concentrations in San Bernardino is as shown in Figure 20. The area extends from the coast to San Bernardino, encompassing parts of Los Angeles, Orange, San Bernardino, and Riverside Counties.

Historical Precursor Trends

The emission trend estimates for the source area affecting San Bernardino are derived following procedures discussed previously. We estimate that emissions changed as follows in the source area from 1965 to 1974:

Year	Estimated NO_x Emission Increase	Estimated RHC Emission Decrease
1965	0%	0%
1968	17-21%	6-9%
1971	23-30%	11-17%
1974	25-35%	15-24%

The trends in ambient NO_x for the San Bernardino source region are presented in Table 13. The 10 cities listed in the table were chosen because of data availability and geographical location. For both the daily maximum and hourly average NO_x concentrations, the ambient trends, averaged over the sites, are similar to the emission trends for the source area.

Table 14 presents the trends in ambient NMHC for the San Bernardino source area. The overall pattern of ambient NMHC has been one of steadily decreasing concentrations in agreement with emission trends; however, as one can see by examining Table 14 some stations deviated drastically from this overall pattern.

Table 15 presents our best estimates of historical precursor trends for the San Bernardino source area. These data are shown graphically in Figure 21.

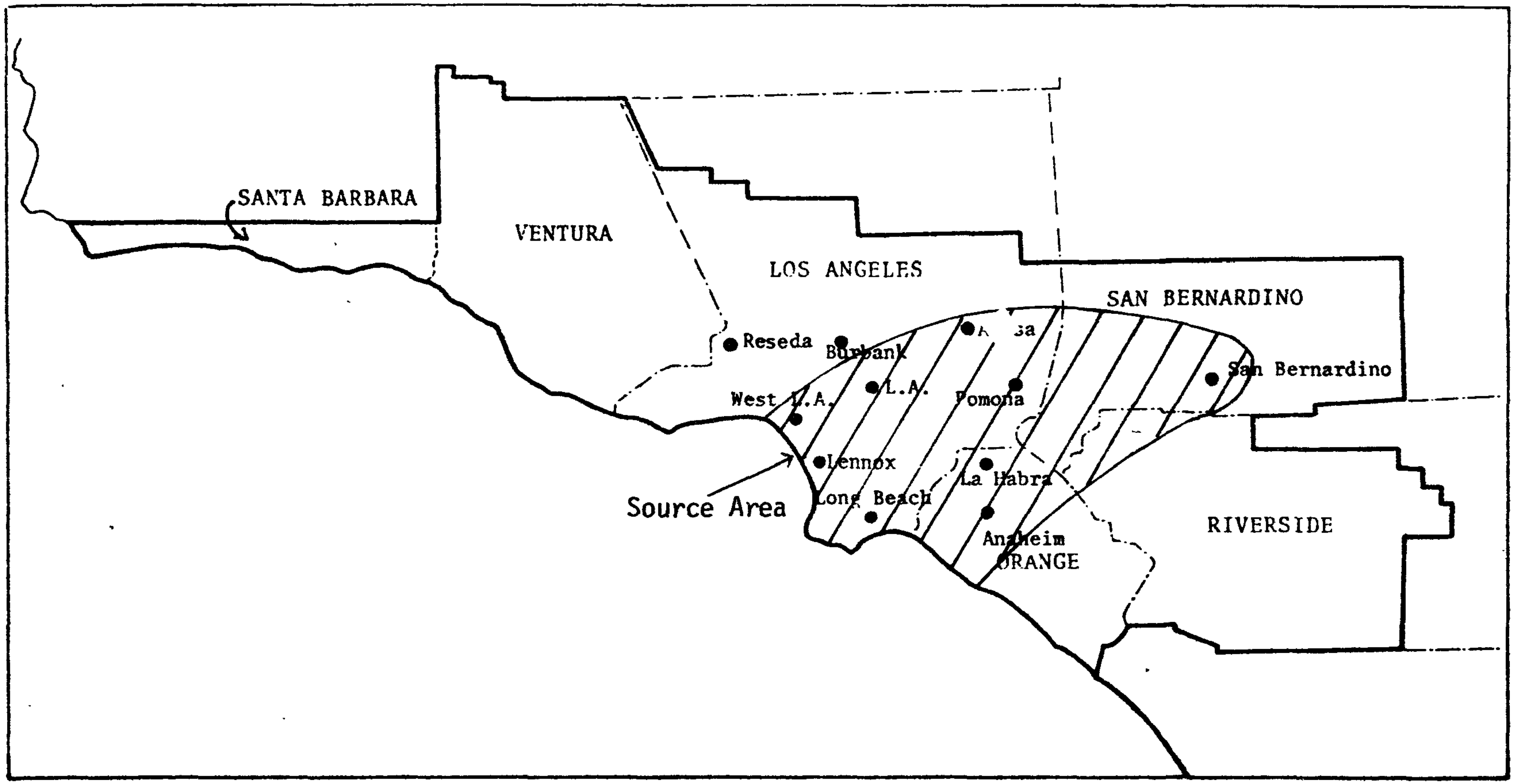

Figure 20. Approximate Source Area Affecting the Oxidant Maximum at San Bernardino.

Table 13. Trends in Ambient NO_x in the Source Area for San Bernardino [3]

Table 13a. Percent Changes in Annual Mean NO_x Relative to 1964-1966

	STATION										
YEAR	DOLA	W.L.A.	AZUSA	POMONA	LENNOX	LONG BEACH	LA HABRA	ANAHEIM	SAN BERNARDINO	BURBANK	AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
1964-66	0%	0%	0%	0%*	0%*	0%	0%†	0%	0%*	0%	0%	0%
1967-69	+8	+8	+16	+29	+21	+17	+19*	+75	+22	+39	+25	+20
1970-72	+22	+19	+54	+44	+23	+10	+26	+85	+36	+37	+36	+31
1973-75	+1	+9	+46	+25	+5	-16	+60	+78	+27	+7	+24	+17

Table 13b. Percent Changes in Yearly Average of Daily One-Hour Maximum NO_x Relative to 1964-66

	STATION										
YEAR	DOLA	W.L.A.	AZUSA	POMONA	LENNOX	LONG BEACH	LA HABRA	ANAHEIM	SAN BERNARDINO	BURBANK	AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
1964-66	0%	0%	0%	0%*	0%*	0%	0%*	0%	0%*	0%	0%	0%
1967-69	+7	+8	+17	+34	+22	+18	+3	+92	+14	+34	+25	+18
1970-72	+22	+17	+56	+51	+30	+20	+14	+93	+30	+36	+37	+30
1973-75	0	+10	+47	+32	+14	-8	+44	+86	+27	+7	+26	+20

*based on two-year average

†based on extrapolation

Table 14. Trends in Ambient NMHC in the Source Area for San Bernardino [3]

Table 14a. Percent Changes in Annual Mean NMHC Relative to 1964-1966

YEAR	STATION								AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
	DOLA	LENNOX	WHITTIER	AZUSA	ANAHEIM	POMONA	BURBANK	SAN BERNARDINO		
1964-66	0%	0%†	0%*	0%*	0%*	0%†	0%*	0%*	0%	0%
1967-69	-15	-12†	-12†	+11	-12	+15†	+3Δ	- 5	-3	- 9
1970-72	- 8	-24	-29	+33	- 6	+34	+7	- 7	0	- 7
1973-75	-38	-35	-41	+39	-24	+55	-7	- 6	-7	- 16

Table 14b. Percent Changes in Yearly Average of Daily One Hour Maximum NMHC Relative to 1964-1966

YEAR	STATION								AVG. OF PERCENT CHANGES	MEDIAN OF PERCENT CHANGES
	DOLA	LENNOX	WHITTIER	AZUSA	ANAHEIM	POMONA	BURBANK	SAN BERNARDINO		
1964-66	0%	0%†	0%†	0%*	0%*	0%†	0%*	0%*	0%	0%
1967-69	-15	-14	-15†	+11	- 7	-6 †	+2Δ	-1	- 6	-7
1970-72	-23	-31	-29	+35	-3	-11	+5	-8	-8	-10
1973-75	-46	-48	-47	+12	-20	-17	-13	-8	-23	-19

† based on extrapolation of 1970-1975 trend
* based on two-year average
Δ linear interpolation between 1970-1972 and 1964-1966

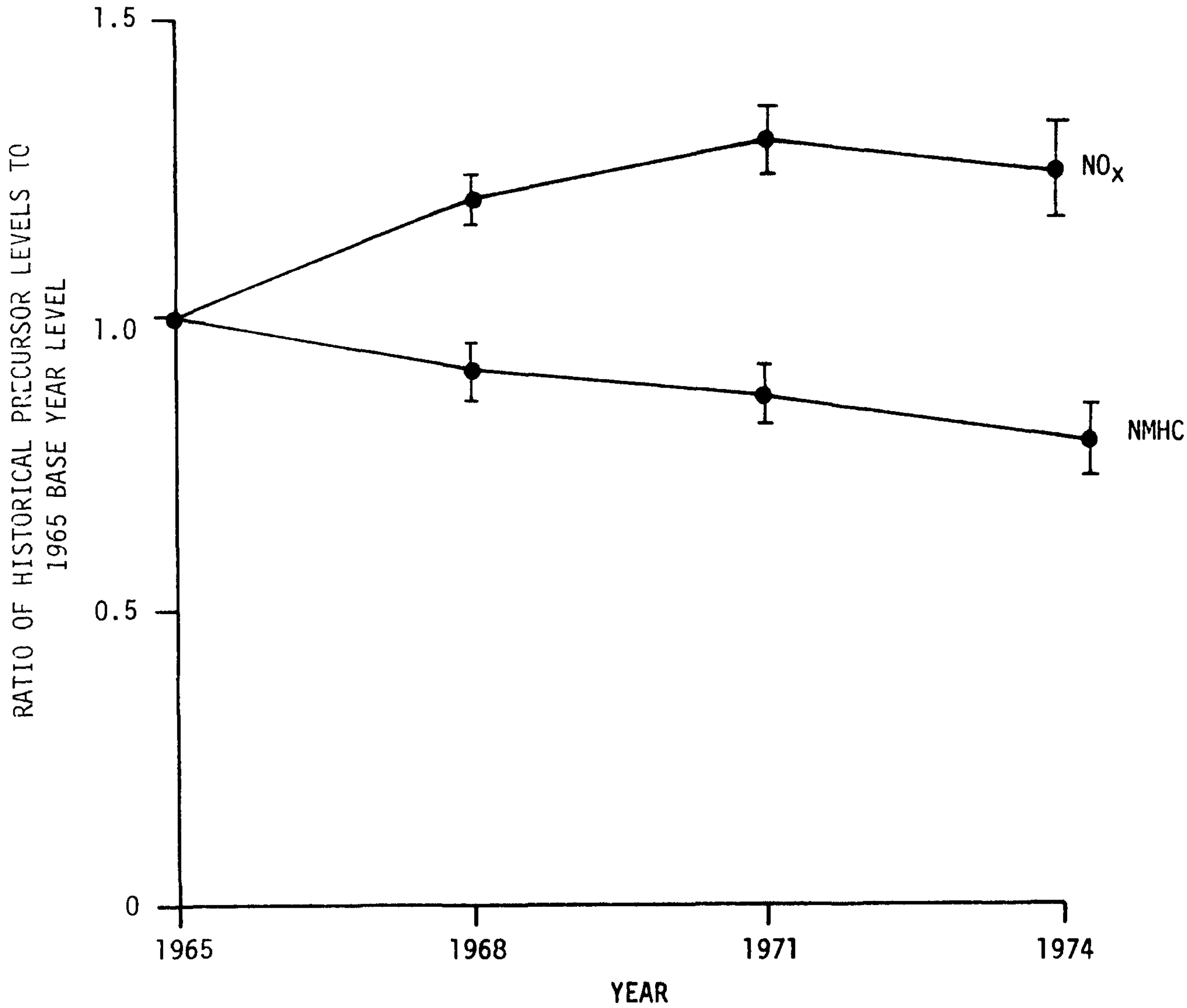

Figure 21. **Best Estimates of Historical Precursor Trends in the San Bernardino Source Region**

Table 15. Best Estimates of Precursor Trends for San Bernardino Source Area

Year	NO_x Change	NMHC Change
1964-66	0%	0%
1967-69	+20% ± 3%	-8% ± 3%
1970-72	+30% ± 5%	-13% ± 4%
1973-75	+25% ± 7%	-20% ± 5%

Ambient NMHC/NO_x Ratio

The 6-9 AM NMHC/NO_x ratio for the San Bernardino source area is assumed to be the same as that for the basinwide source area in 1965:

Median:	12
10th Percentile:	7
90th Percentile:	23

ANALYSIS OF CRITICAL ASSUMPTIONS

Several assumptions are implicit in our treatment of the precursor data for use in the EKMA isopleth model. This section assesses the validity of three assumptions that may be particularly critical to the isopleth verification study. The issues addressed are as follows:

1. The source areas have been selected based on the predominant wind flow pattern during the summer smog season in Los Angeles. Does this wind flow pattern also predominate on days with extreme oxidant (the days of interest in the isopleth validation study)?

2. Ambient precursor trends have been examined using two air quality indices: annual mean concentrations and yearly average of daily one-hour maximum concentrations. Are the trends in these indices representative of trends in 6-9 AM summertime concentrations (the precursor averaging time of interest in the isopleth validation study)?

3. The median NMHC/NO_x ratio has been estimated from ambient data for the entire summer smog season. Is the median ratio the same on days with extreme oxidant (the days of interest in the isopleth validation study)?

Wind Flow Patterns on High Oxidant Days

Our selection of source areas was based on the southwesterly (sea breeze) wind pattern that predominates in Los Angeles during daytime hours in the summer smog season. Since the isopleth validation studies involve days of extreme oxidant (either the second maximum or the 95th percentile of daily maxima), it is important to examine wind patterns on episode days. The source areas will be appropriate for the verification studies only if the southwesterly pattern also dominates on days of highest oxidant.

Figure 22 illustrates the frequency distribution of vector-average wind direction (7 AM to 2PM) at Downtown Los Angeles. The prevalence of the southwesterly pattern during the smog season is obvious in the upper graph, representing all days from May to October in the years 1971-1975. The lower graph, representing the 50 days of highest oxidant at Azusa during the May-October/1971-1975 period, indicates that the southwesterly pattern is even more consistent on days of extreme oxidant.

Figure 23 presents the frequency distribution of vector-averaged wind speed (7 AM to 2 PM) at Downtown Los Angeles. As was the case with wind direction, wind speeds are more concentrated around "normal" conditions on days of high oxidant. The median wind speed on high oxidant days (5.5 mph) is slightly greater than the median wind speed on all days (4.9 mph). Wind speeds of 4 to 7 miles per hour from the southwest are especially prevalent on days of high oxidant at Azusa because this wind pattern promotes transport from the source-intensive central-coastal parts of the basin toward Azusa.

The foregoing analysis demonstrates that the southwesterly wind pattern indeed predominates on days of excessive oxidant (at least at Azusa). Although possibly not as dominant as in the case of Azusa, we would expect that the general sea-breeze pattern also prevails for typical high oxidant days (95th percentiles) at the other locations under study. This is partially evidenced by high correlations between daily maximum oxidant at Azusa and daily maximum oxidant at the other locations (.78 with DOLA, .80 with Anaheim, and .86 with San Bernardino [4]), implying that high oxidant days at Azusa tend to be high oxidant days elsewhere.

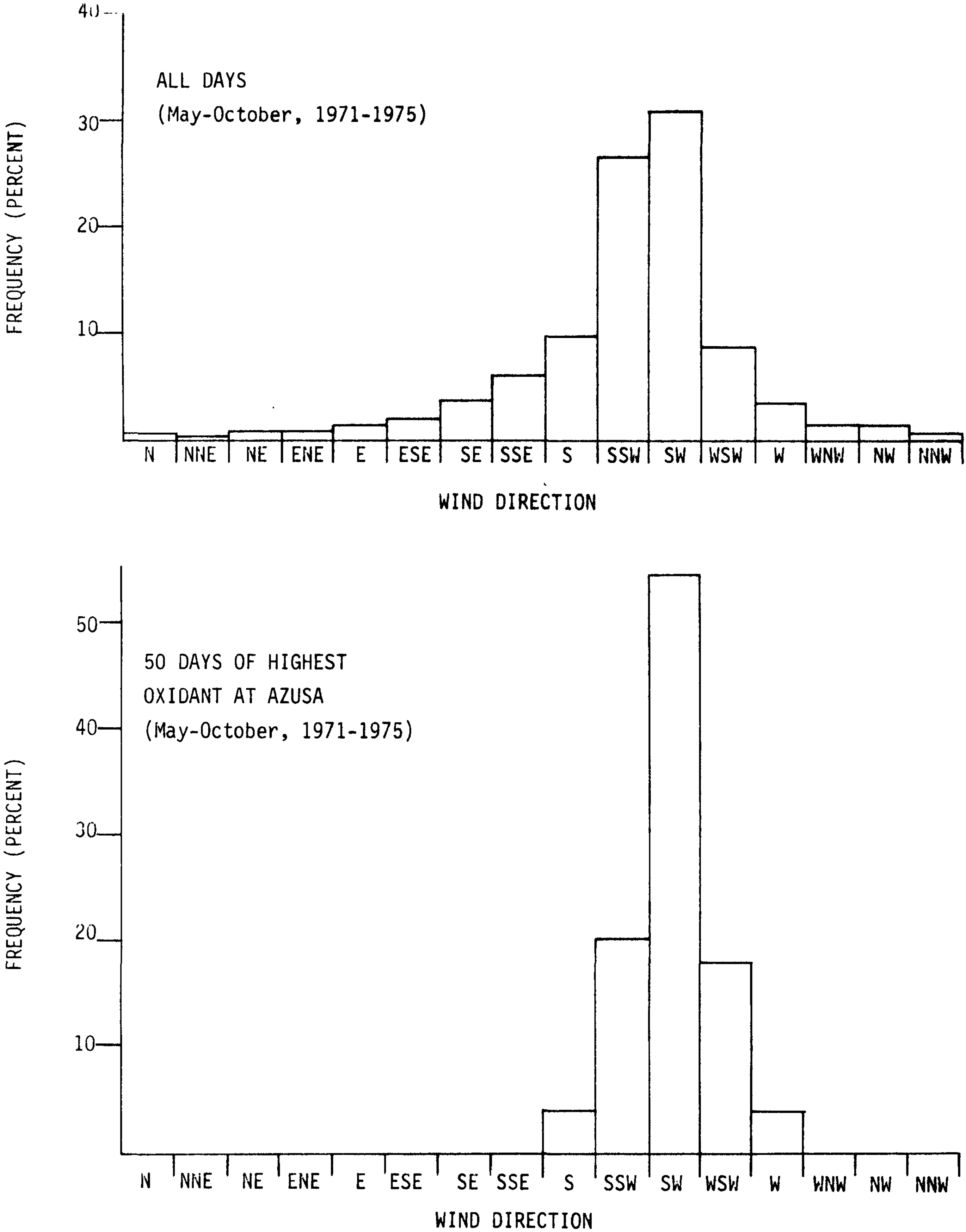

Figure 22. Frequency Distribution of Vector-Averaged Wind Direction (7 AM - 2 PM) at Downtown Los Angeles.

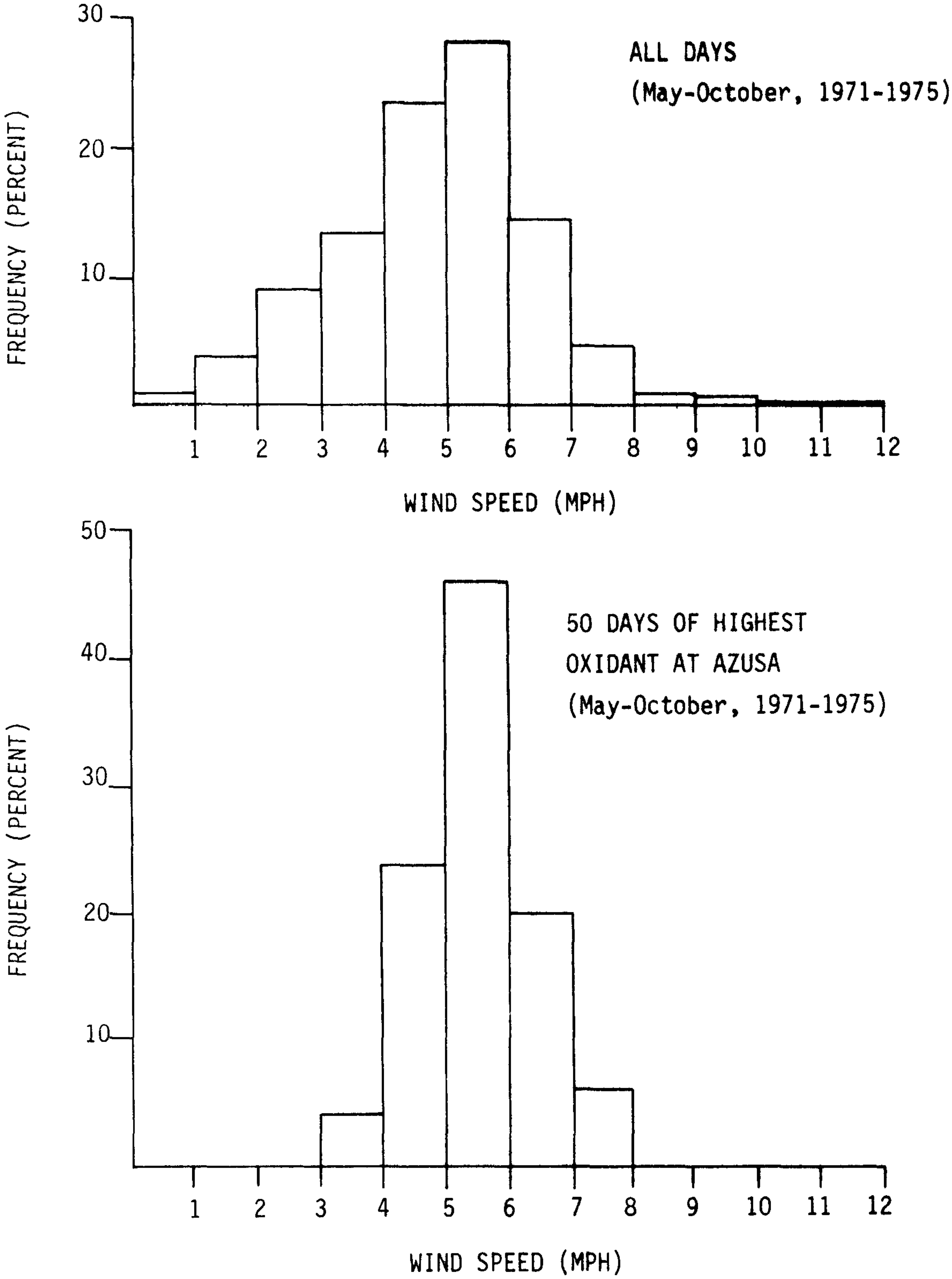

Figure 23. Frequency Distribution of Vector-Averaged Wind Speed (7 AM - 2 PM) at Downtown Los Angeles.

In future work it might be worthwhile to substantiate our conclusions further by repeating the analysis (i.e. Figures 22 and 23) for oxidant at other locations. However, the present evidence suggests that selecting source areas according to the prevalent sea-breeze wind pattern is appropriate for the isopleth validation studies.

6-9 AM Summertime Precursor Trends

We have estimated historical precursor trends by analyzing both emissions data and ambient precursor data. The ambient precursor trends were based on two air quality indices: annual mean concentrations and yearly average of daily maximal concentrations. In general, we found that the trends in these two air quality indices agreed fairly well with one another and with the emission trends. A question remains, however, as to whether these trends are consistent with trends in 6-9 AM summertime precursor concentrations which are most relevant in applying the isopleth model.

The California Air Resources Board has compiled data concerning trends in 6-9 AM summertime precursors for several locations over the period 1963 to 1972 [18]. Tables 16 and 17 compare the net changes in 6-9 AM summertime precursors during that period to corresponding changes in the precursor air quality indices we have used.

Table 16 indicates that trends in 6-9 AM summertime NMHC are basically very similar to trends in annual mean NMHC and yearly average of daily maximal NMHC. If we had used 6-9 AM summertime concentrations as the ambient NMHC trend indicator, our conclusions concerning historical NMHC trends in each source area probably would not have changed substantially.

Table 17 reveals a discrepancy between trends in 6-9 AM summertime NO_x versus trends in annual mean NO_x and yearly average of daily maximal NO_x. From 1965 to 1971, the 6-9 AM summertime concentrations appear to have increased 10 to 25% more than the other two air quality indices. The differences in the trends may be explained by the temporal distribution of NO_x emissions. Specifically, automotive emissions are relatively more important to 6-9 AM concentrations, and automotive emissions are relatively more important during the summer. Since large increases in NO_x emissions from

Table 16. Comparison of Alternative Ambient Trend Indices for NMHC†

LOCATION	TIME PERIOD*	NET PERCENT CHANGE IN NMHC CONCENTRATIONS		
		Annual Mean	Yearly Average of Daily Maxima	6-9 AM Concentrations July-September
Anaheim	1965-66 to 1970-72	-5%	-2%	+12%
Azusa	1963-64 to 1970-72	+47%	+43%	+35%
Burbank	1963-64 to 1971-72	+10%	+3%	+4%
DOLA	1964-66 to 1970-72	-8%	-23%	-16%
Riverside	1965-66 to 1970-71	-27%	-20%	-18%
San Bernardino	1965-66 to 1970-72	-7%	-8%	-11%
AVERAGE OF PERCENT CHANGES		+2%	-1%	+1%
MEDIAN OF PERCENT CHANGES		-6%	-5%	-4%

† Calculated from THC condentrations as explained previously

* Although often constrained by data availability, we have basically attempted to use changes in 3-year averages from 1964-66 to 1970-72

Table 17. Comparison of Alternative Ambient Trend Indices for NO_x

LOCATION	TIME PERIOD*	NET PERCENT CHANGE IN NO_x CONCENTRATIONS		
		Annual Mean	Yearly Average of Daily Maxima	6-9 AM Concentrations July-September
Anaheim	1964-66 to 1970-72	+89%	+93%	+69%
Azusa	1964-66 to 1970-72	+54%	+56%	+64%
Burbank	1964-66 to 1970-72	+37%	+37%	+61%
DOLA	1964-66 to 1970-72	+22%	+22%	+27%
Lennox	1965-66 to 1970-72	+23%	+30%	+19%
Long Beach	1964-66 to 1970-72	+10%	+20%	+54%
Pomona	1965-66 to 1970-75	+44%	+51%	+61%
Reseda	1965-66 to 1970-72	+47%	+48%	+56%
San Bernardino	1965-66 to 1970-72	+33%	+25%	+62%
West L.A.	1964-66 to 1970-72	+17%	+17%	+42%
AVERAGE OF PERCENT CHANGES		+38%	+40%	+52%
MEDIAN OF PERCENT CHANGES		+35%	+34%	+59%

*Although sometimes constrained by data availability, we have basically attempted to use changes in 3-year averages from 1964-1966 to 1970-1972 motor vehicles were the basic cause of the overall NO_x increase, it is not unreasonable that the rise in NO_x is more evident in 6-9 AM summertime concentrations.

The isopleth verification analyses will proceed using the "best estimate" of NO_x changes that were derived earlier in this chapter. That these "best estimates" may understate the increase in NO_x could have a significant effect on our results. The implications of this possible underestimate will be discussed in Chapter 5.

Ambient NMHC/NO_x Ratio on High Oxidant Days

Our estimate of the ambient NMHC/NO_x ratio was based on data for 6-9 AM precursor concentrations during the entire summer season. The latest procedural guidelines for the EKMA isopleth model [19] indicate that the NMHC/NO_x ratio on days of highest oxidant should be used. To test whether the ratio we are using is appropriate, we should compare it with ratios on extreme oxidant days.

Figure 24 presents frequency distributions of the 6-9 AM NMHC/NO_x ratio at Downtown Los Angeles based on APCD data. The NMHC concentrations have been computed from THC concentrations using an empirical formula derived by the California ARB [18].* As shown in the upper graph, the median ratio for the entire smog season during the early 1970's is approximately 8:1 (in exact agreement with our earlier conclusions **).

The lower graph in Figure 24 indicates that the median ratio on high oxidant days (8.9) is slightly greater than the median ratio on all summer days (8.1). It is also interesting to note that there is less spread in the frequency distribution on high oxidant days; the 10th and 90th percentiles of the ratio are 5.7 and 12.7 for high oxidant days and 4.5 and 13.6 for all summer days.

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* This formula is NMHC = .7 (THC - 1.3 ppm).

** In an earlier section we examined several sources of data and concluded that the median ratio during the smog season in the early 1970's was 8:1. We then used historical precursor trends to calculate a median ratio of 12:1 for the 1965 base year.

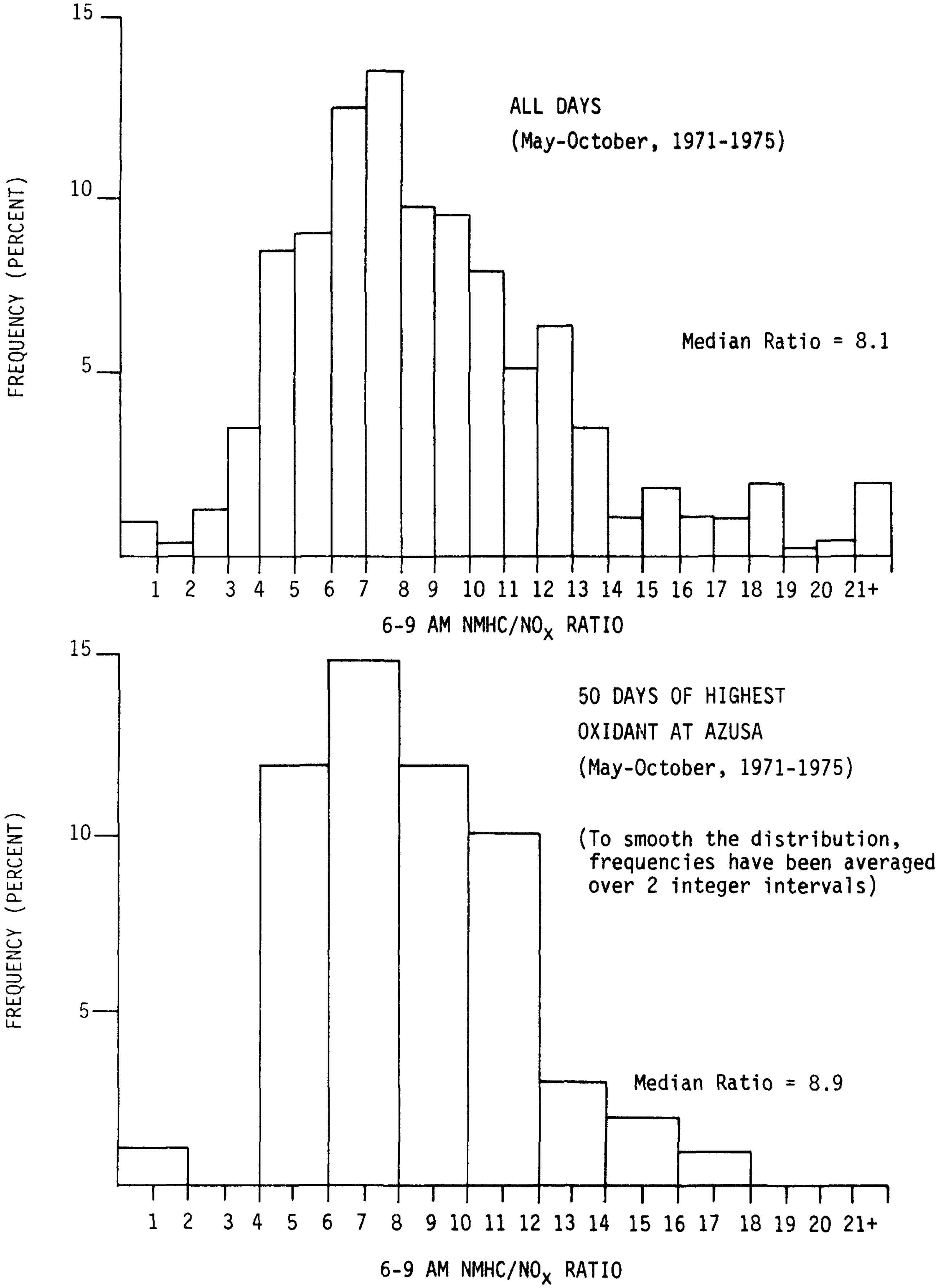

Figure 24. Frequency Distribution of 6-9 AM NMHC/NO$_X$ Ratio at Downtown Los Angeles.

To check the conclusion that the $NMHC/NO_x$ ratio tends to be slightly higher than normal on extreme oxidant days, we acquired recent data on 6-9 AM NMHC and NO_x concentrations from the ARB monitoring program at Temple City. For nineteen days selected at random during the 1976 smog season, the median ratio was 8. For the nine days of highest oxidant during the 1976 smog season, the median ratio was 10.

Our verification study will proceed using a median ratio of 12:1 for the 1965 base year (corresponding to a ratio of 8:1 in the early 1970's). The significance of slightly underestimating the ratio which is appropriate to high oxidant days will be discussed in Chapter 5.

CHAPTER 4

VALIDATION OF THE ISOPLETH METHOD AGAINST HISTORICAL TREND DATA

Chapters 2 and 3 described the two basic types of information needed to validate the EKMA isopleth method against historical trends. Chapter 2 presented the actually observed oxidant trends for the locations under study; Chapter 3 discussed the ambient precursor trends and the NMHC/NO_x ratio for the study areas. The present chapter uses the isopleth method to predict historical oxidant trends and compares the predicted trends with actual trends to assess the accuracy of the method.

The validation study is conducted for the basinwide oxidant maximum and for the oxidant maxima at four individual locations (DOLA, Anaheim, Azusa, and San Bernardino). In the following pages, four basic types of isopleths are referred to, and their descriptions are as follows:

(1) basinwide isopleths: corresponding to the maximum oxidant during 0 to 9 hours of irradiation.

(2) five-hour isopleths: corresponding to oxidant after five hours of irradiation; not neccessarily the maximum oxidant.

(3) seven-hour isopleths: as in (2) above, with seven hours of irradiation.

(4) nine-hour isopleths: as in (2) above, with nine hours of irradiation.

VALIDATION OF BASINWIDE ISOPLETHS

This section begins with a detailed description of the validation procedure using the basinwide isopleths and the 95th percentile of daily maxima at Azusa. The results of other validations with the basinwide isopleths, using the Azusa yearly second maximum and the basinwide yearly second maximum, are then summarized.

95th Percentile of Daily One-Hour Maxima at Azusa

Three types of input data are required to compute predicted oxidant trends: the oxidant value for the base year (1965, or actually 1964-1966), the 6-9 AM NMHC/NO_x ratio for the base year, and historical precursor trends for the source area. For Azusa, the 95th percentile of daily oxidant maxima in 1964-1966 was 0.33 ppm. The 1965 $NMHC/NO_x$ ratios chosen for all sites in this study are the following:

Median:	12
10th Percentile:	7
90th Percentile:	23

The historical precursor trends for the Azusa source area are summarized in Table 5 and Figure 15.

Figure 25 presents the basinwide isopleths and illustrates the prediction of oxidant values for the Azusa validation; for reasons of simplicity, only the 12:1 ratio is shown. The intersection of the isopleth corresponding to the 1965 oxidant level and the appropriate $NMHC/NO_x$ ratio line defines the reference point to which the changes in precursors are applied, thus arriving at the predicted oxidant values for the years 1968, 1971, and 1974.* The point labeled "1965" is the reference point; it was found by the intersection of the 0.33 ppm oxidant isopleth and the 12:1 ratio line. The NO_x and NMHC concentrations corresponding to the base year are read from the respective axes. In this particular diagram, the base-year values for Azusa are NMHC = 1.5 ppmC and NO_x = 0.125 ppm. The precursor trends presented in Table 5 are then applied to these levels to give the coordinates of points for each successive three year period. For example, in the period 1967-1969 for the Azusa source area, NO_x increased 17% ± 3%, and NMHC decreased 10% ± 3%. Thus, the point labeled "1968" is determined. The process is repeated to yield the points for 1971 and 1974.

The ellipses surrounding each point represent the uncertainties in precursor trends. These ellipses are drawn through four points: two from the uncertainty in NO_x (± 3% in 1968) and two from the uncertainty in NMHC (± 3% in 1968). The error bounds in the predicted oxidant for each year are obtained by taking the isopleth range that is covered by each ellipse.

The final step in the validation of the isopleths is to plot the predicted oxidant trends, with error bounds, on the same graph as the actually

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* Actually, these predictions are for the 3-year periods 1967-1969, 1970-1972, and 1973-1975.

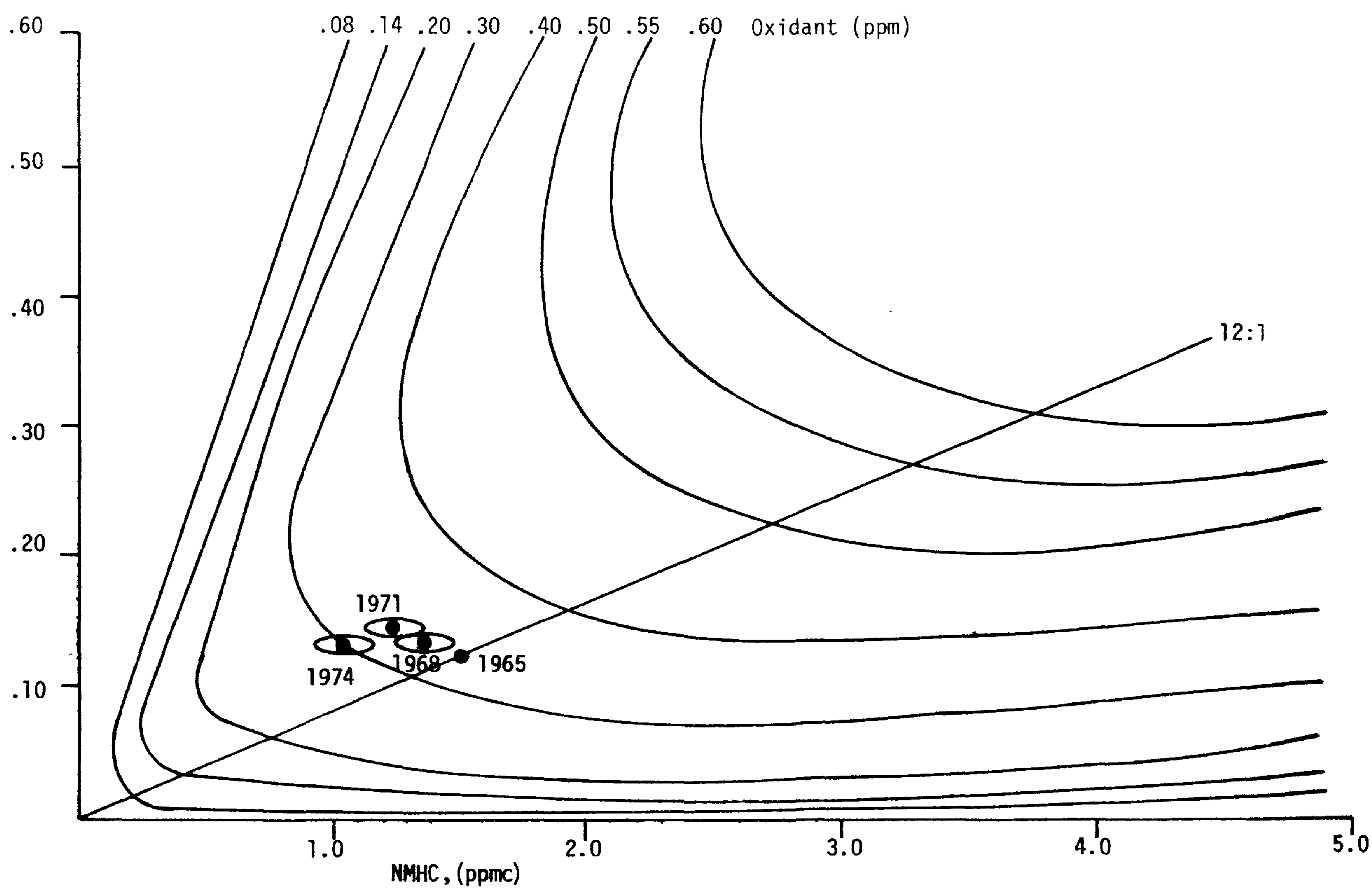

Figure 25. Prediction of Oxidant Trends for the 95th Percentile at Azusa Using Basinwide Isopleths.

observed oxidant trends, with error bounds. These graphs are shown in Figures 26 through 28, each corresponding to a single NMHC/NO_x ratio. The overall agreement between the predicted trend lines and the actual trend lines appears to be best for the 7:1 ratio and worst for the 23:1 ratio.

Figures 26 to 28 indicate that, for all three ratios, the isopleth model tends to underpredict the net reduction in oxidant from 1965 to 1974. The underprediction is very small for the 7:1 ratio, moderate and not statistically significant for the 12:1 ratio, and fairly large and statistically significant for the 23:1 ratio.

Figure 29 presents predicted trends for the 12:1 ratio and the maximum possible error bounds based on both the errors in the precursor trends and the range in the NMHC/NO_x ratio. In other words, for any given year (1968, 1971, or 1974), the bottom error bound was found by taking the lowest error bound for any ratio; similarly, the upper error bound was found by taking the highest error bound for any ratio. Figure 29 indicates that the net oxidant and precursor changes are too small, and the potential errors in the analysis are too large, to arrive at a conclusive test of the isopleth method. Figures 27 and 29 do raise some doubt concerning the predictions of the method, especially if we accept 12:1 as the appropriate NMHC/NO_x ratio for 1965. However, considering the error bounds, we conclude that the isopleth predictions are not inconsistent with historical trends in the 95th percentile of daily maxima at Azusa.

Yearly Second Maximum One-Hour at Azusa

Figures 30 to 32 (corresponding to ratios of 7:1, 12:1, and 23:1) present the results of the validation study for the basinwide isopleths using the second highest yearly one-hour oxidant values at Azusa. Figure 33 summarizes the results, presenting the predicted trends for a 12:1 ratio and the maximum possible error bounds based on errors both in the precursor trends and in the range of the NMHC/NO_x ratio.

The overall agreement between the actual trend line and the predicted trend line is fair for the 7:1 ratio (Figure 30) and the 12:1 ratio (Figure 31), and very poor for the 23:1 ratio (Figure 32). Again, the predictions

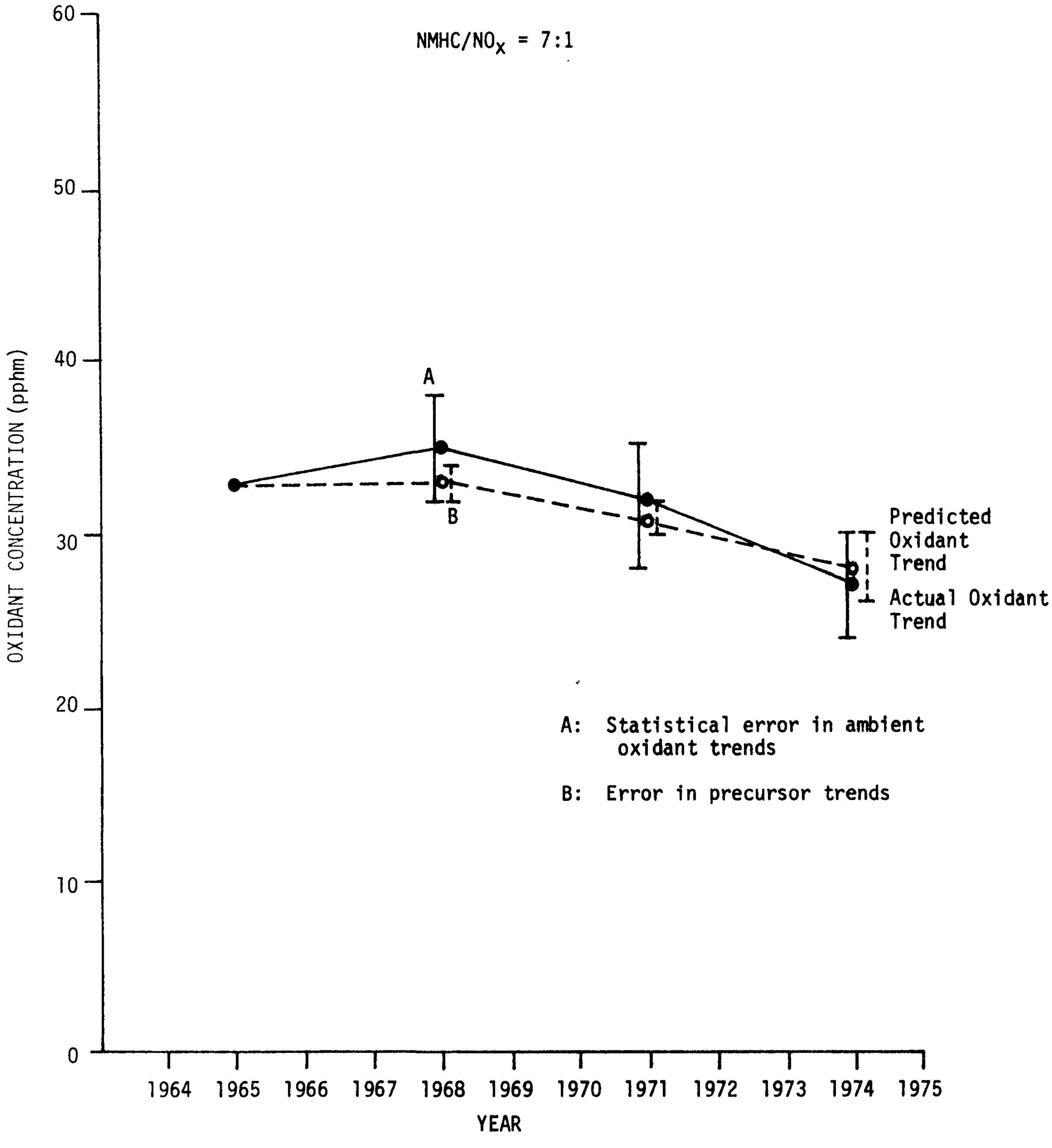

Figure 26. Oxidant Trends in the 95th Percentile of the Daily Maxima at Azusa, Predicted for 7:1 Ratio vs. Actual.

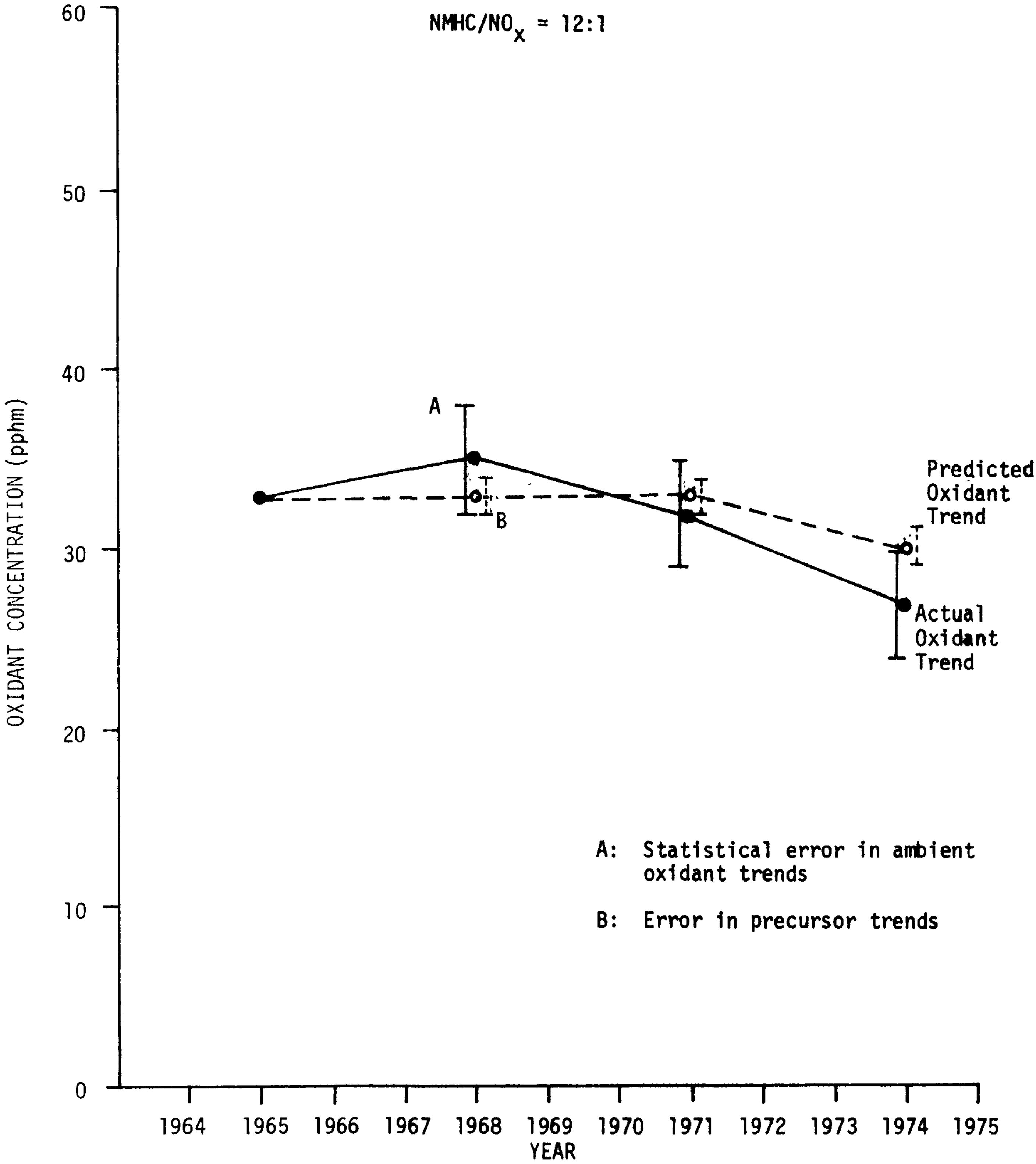

Figure 27. Oxidant Trends in the 95th Percentile of the Daily Maxima at Azusa, Predicted for 12:1 Ratio vs. Actual.

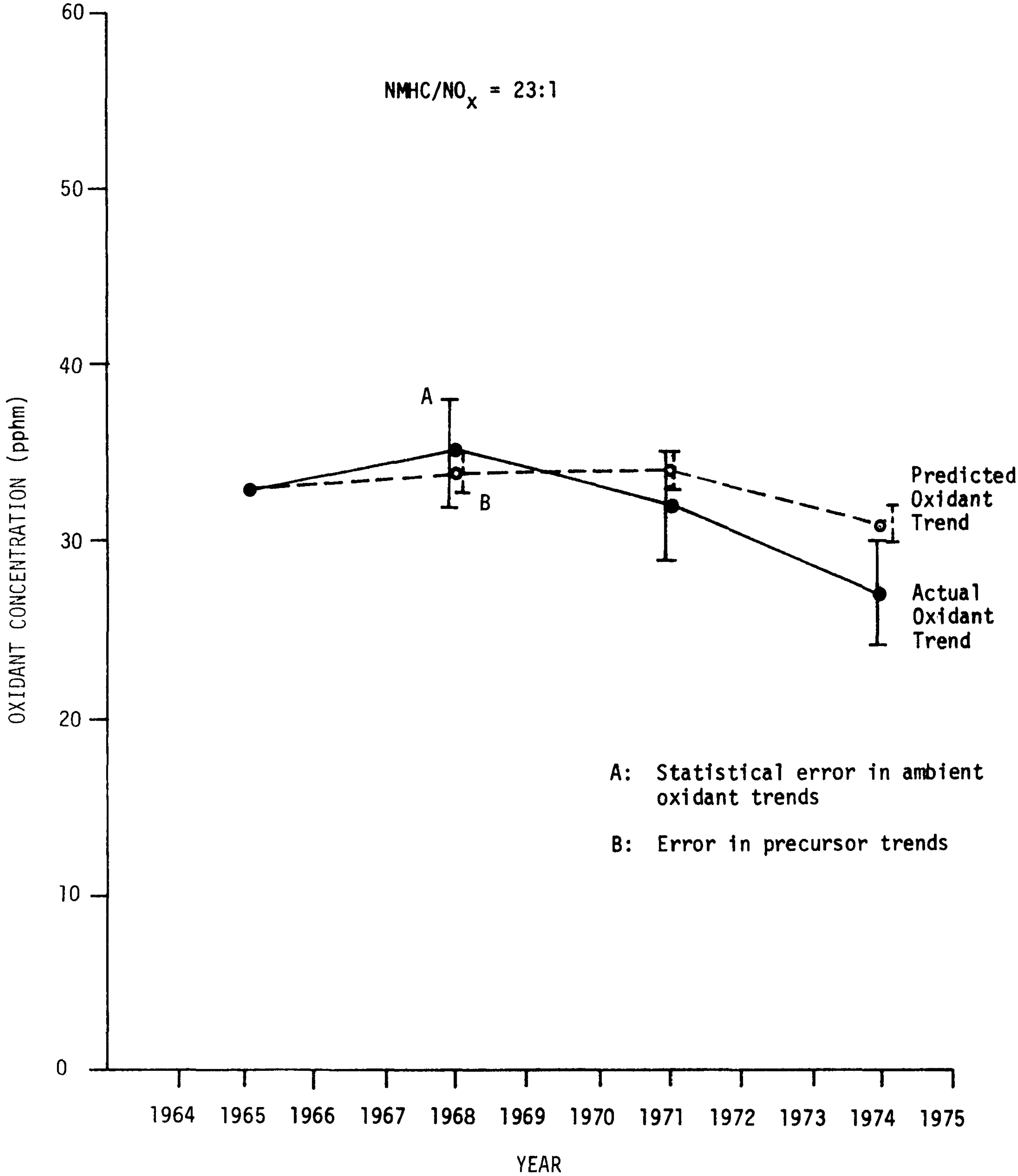

Figure 28. Oxidant Trends in the 95th Percentile of the Daily Maxima at Azusa, Predicted for 23:1 Ratio vs. Actual.

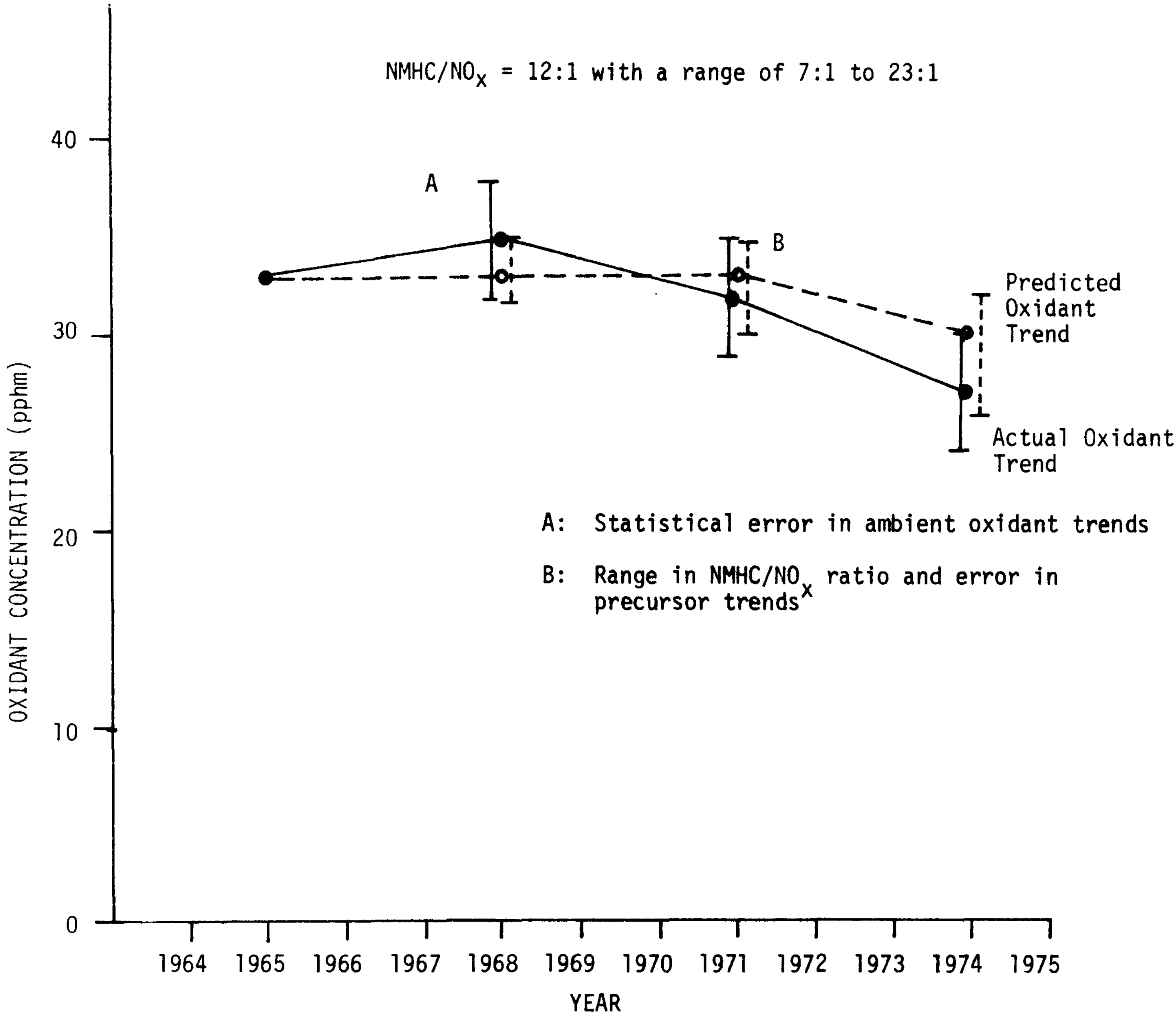

Figure 29. Summary of Oxidant Trends in the 95th Percentile at Azusa, Predicted vs. Actual.

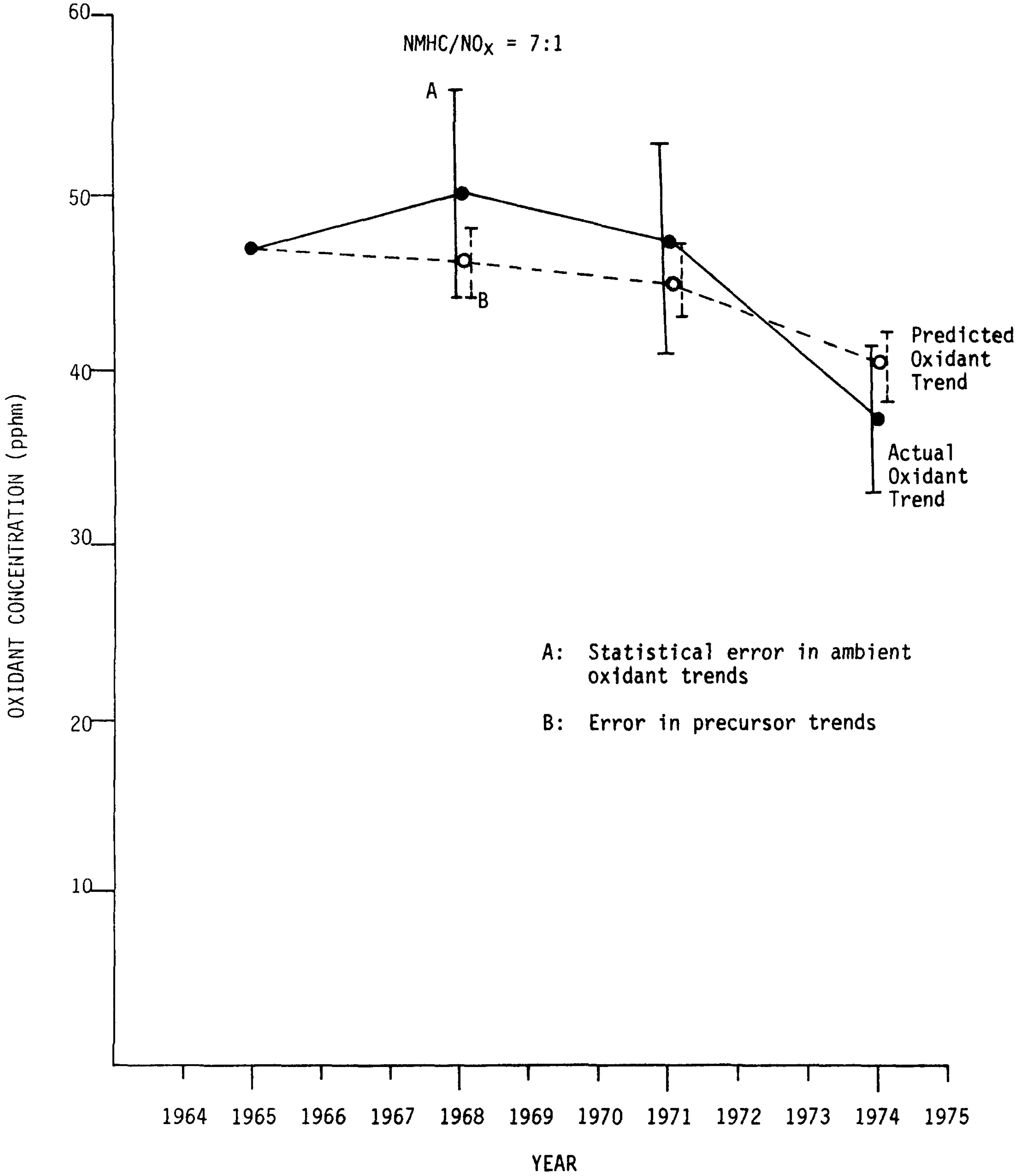

Figure 30. Oxidant Trends in the Second Maximum for Azusa, Predicted for 7:1 Ratio vs. Actual.

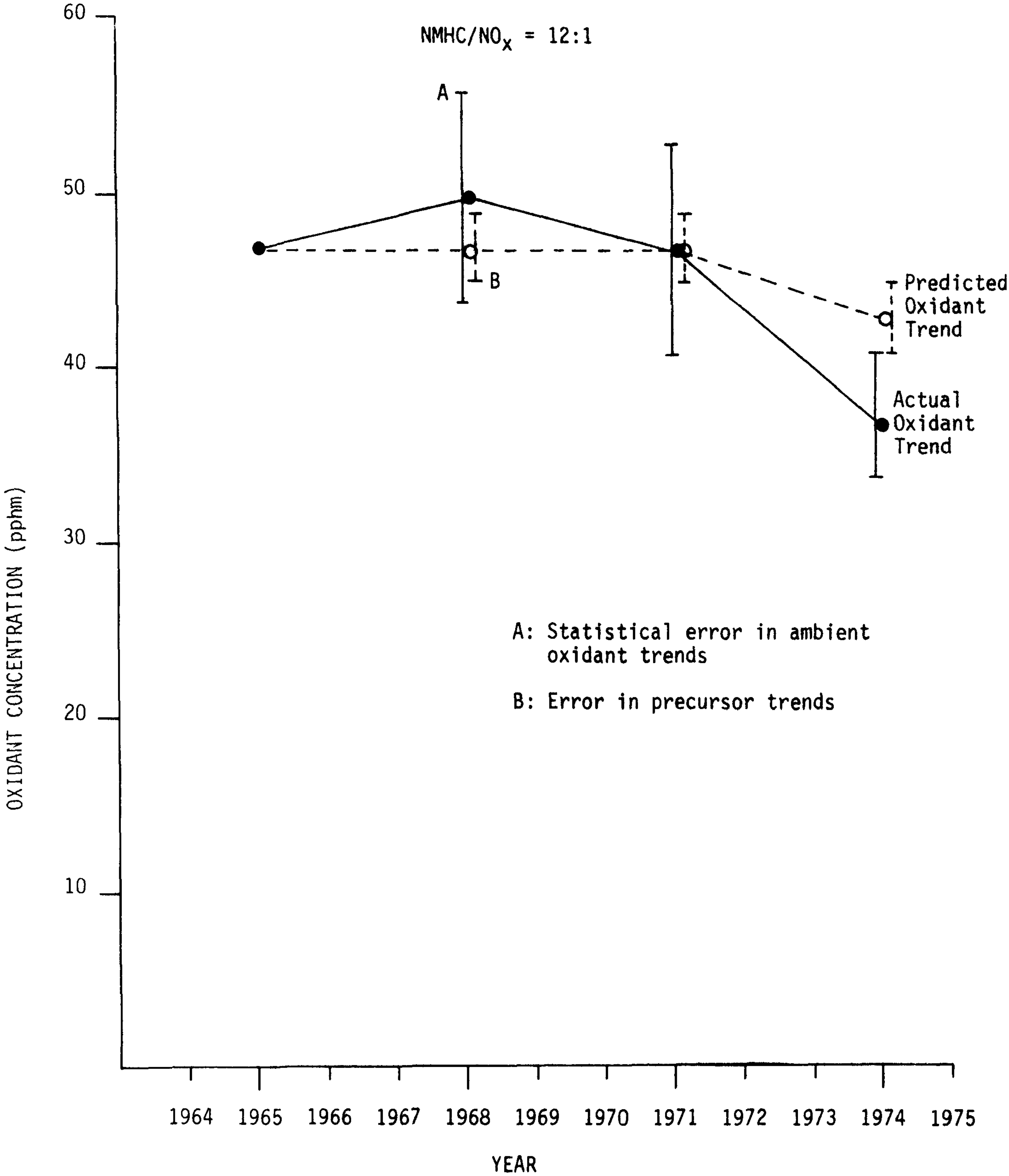

Figure 31. Oxidant Trends in the Second Maximum for Azusa, Predicted for 12:1 Ratio vs. Actual

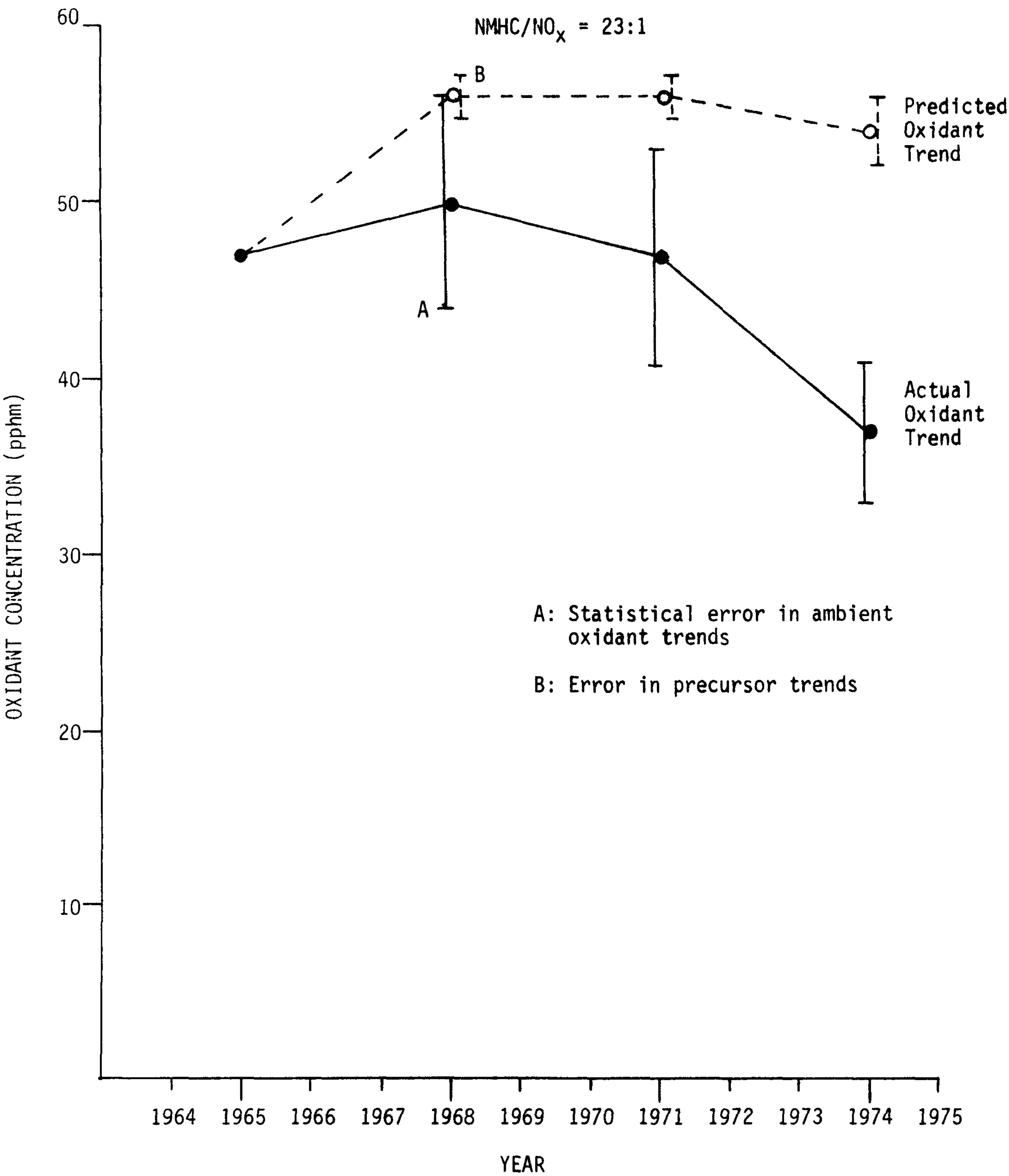

Figure 32. Oxidant Trends in the Second Maximum for Azusa, Predicted for 23:1 Ratio vs. Actual.

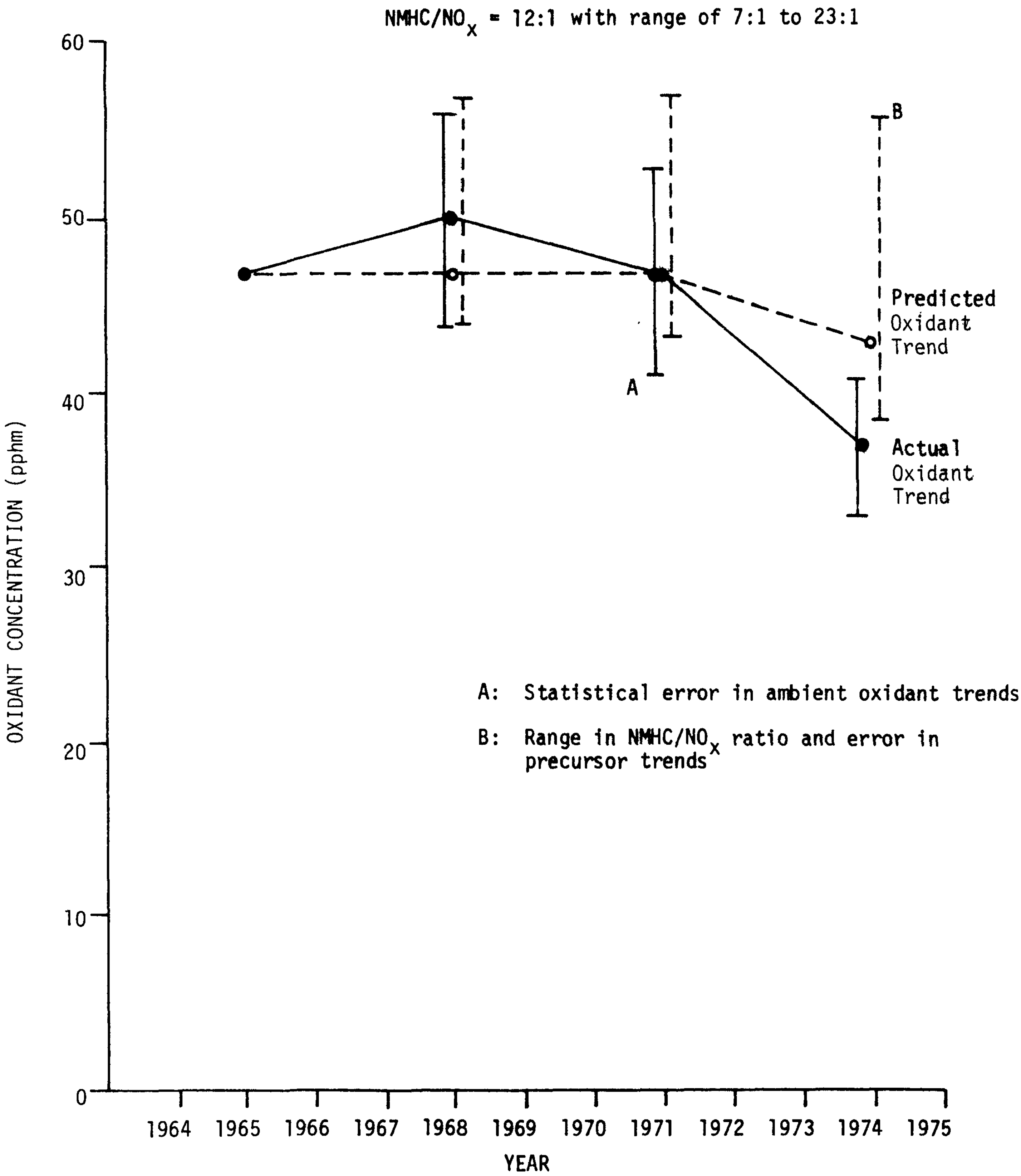

Figure 33. Summary of Oxidant Trends in the Second Maximum for Azusa, Predicted vs. Actual.

for all three ratios underestimate the net reduction in oxidant from 1965 to 1974. This underestimate is statistically insignificant for the 7:1 ratio, marginally statistically significant for the 12:1 ratio, and very significant for the 23:1 ratio.

Figures 30 to 33 do not provide a definitive test of the isopleth model. Considering the potential errors, including the possible range of the NMHC/NO_x ratio, we conclude that the isopleth predictions are not inconsistent with historical trends.

Yearly Second Maximum One-Hour, Basinwide

Figures 34 to 37 summarize the validation study for the basinwide isopleths using the basinwide second maximum one-hour oxidant. The agreement between predicted trends and actual trends is good for the 7:1 ratio (Figure 34), fair for the 12:1 ratio (Figure 35), and very poor for the 23:1 ratio (Figure 36). Overall, the patterns and conclusions are similar to those for Figures 30 to 33.

VALIDATION OF ISOPLETHS FOR FIXED IRRADIATION TIMES

This section tests isopleths for fixed irradiation times against trends at individual locations. Data for Downtown Los Angeles and Anaheim are used with 5-hour isopleths; data for Azusa and San Bernardino are used with 7-hour and 9-hour isopleths, respectively.

95th Percentile at Downtown Los Angeles (DOLA)

Figures 38 to 41 summarize the validation of 5-hour isopleths with trend data for Downtown Los Angeles. The agreement between the predicted trend line and the actual trend line is good for the 7:1 ratio (Figure 38) and poor for the 12:1 and 23:1 ratios (Figures 39 and 40). The tendency noted before, that the isopleth method underestimates historical oxidant reductions, is even more evident here for the 12:1 and 23:1 ratios.

In the summary graph for the 12:1 ratio (Figure 41), we see that the discrepancies between predicted and actual are within the overall error bounds. The overall error bounds include statistical errors in ambient oxidant trends, errors in estimated precursor trends, and the potential range

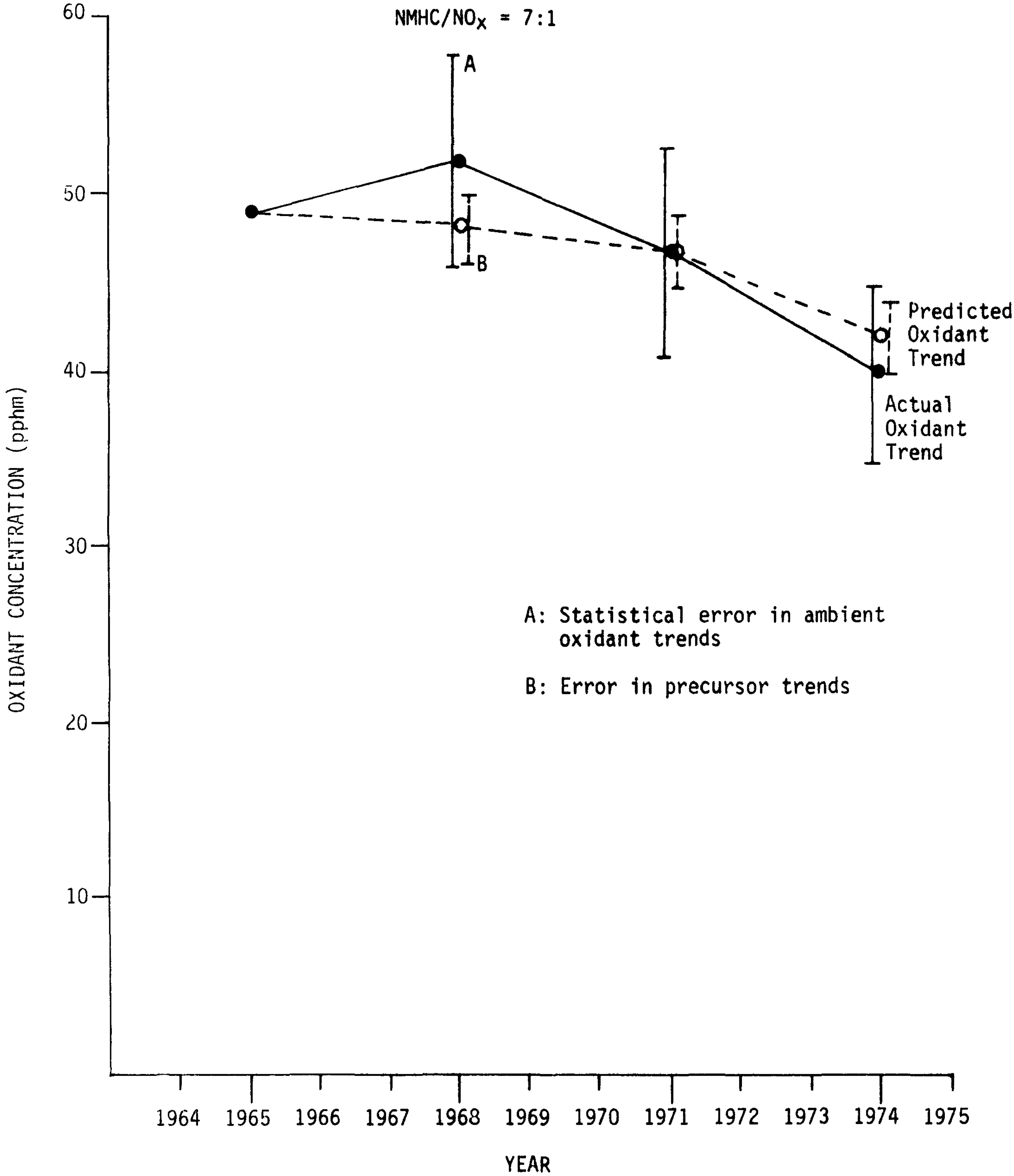

Figure 34. Oxidant Trends in the Basinwide Second Maximum, Predicted for 7:1 Ratio vs. Actual.

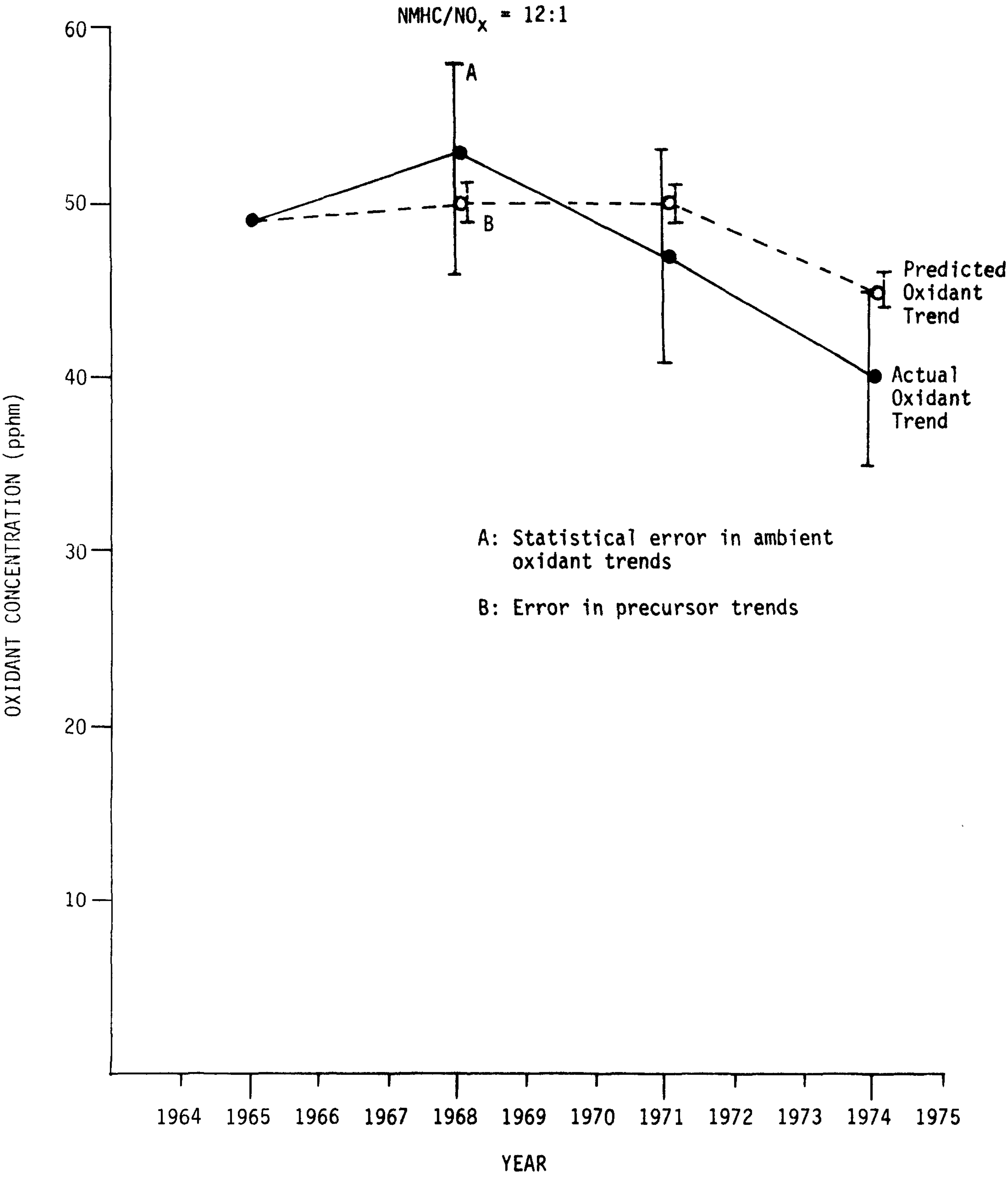

Figure 35. Oxidant Trends in the Basinwide Second Maximum, Predicted for 12:1 Ratio vs. Actual.

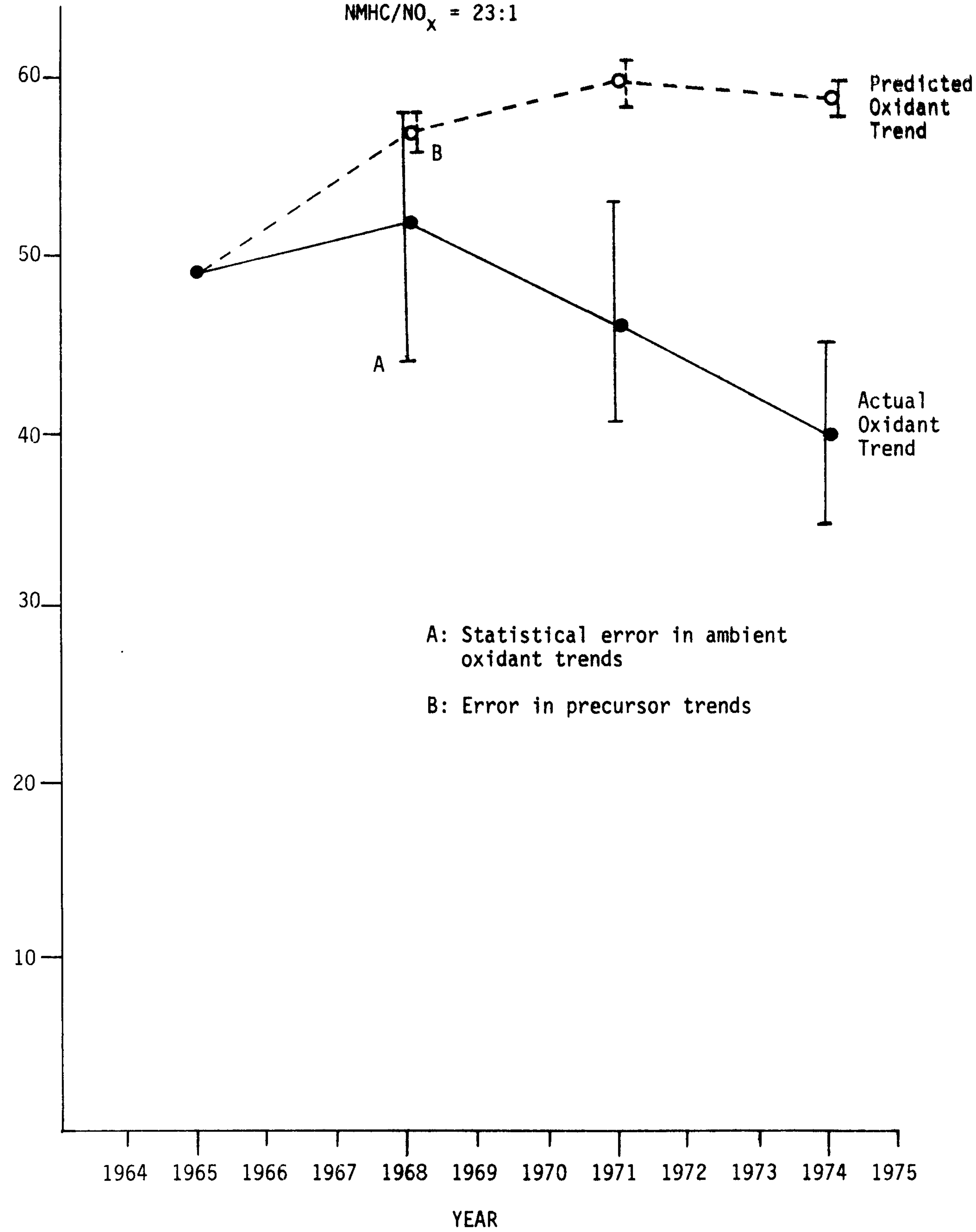

Figure 36. Oxidant Trends in the Basinwide Second Maximum, Predicted for 23:1 Ratio vs. Actual.

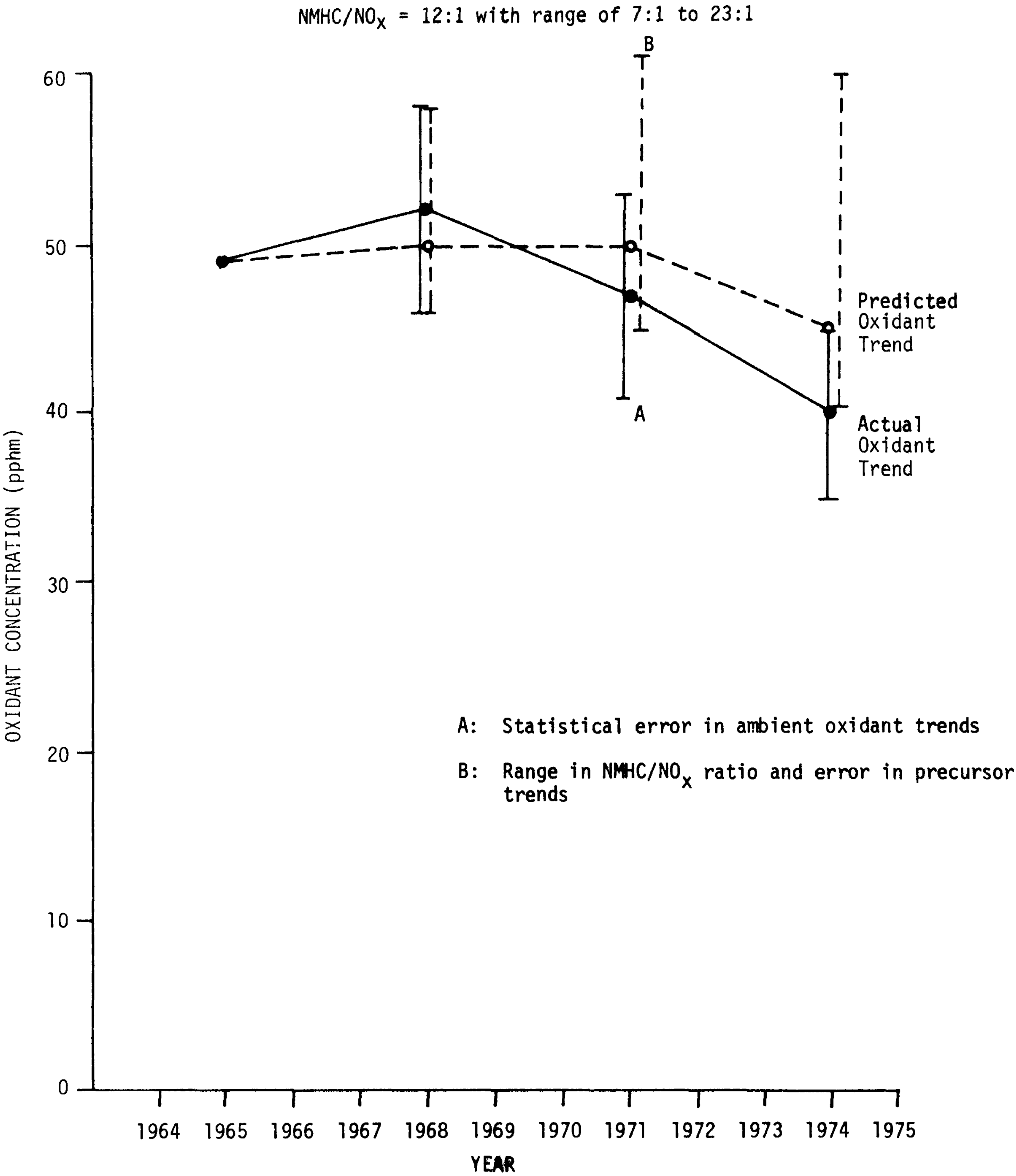

Figure 37. Summary of Oxidant Trends in the Basinwide Second Maximum, Predicted vs. Actual.

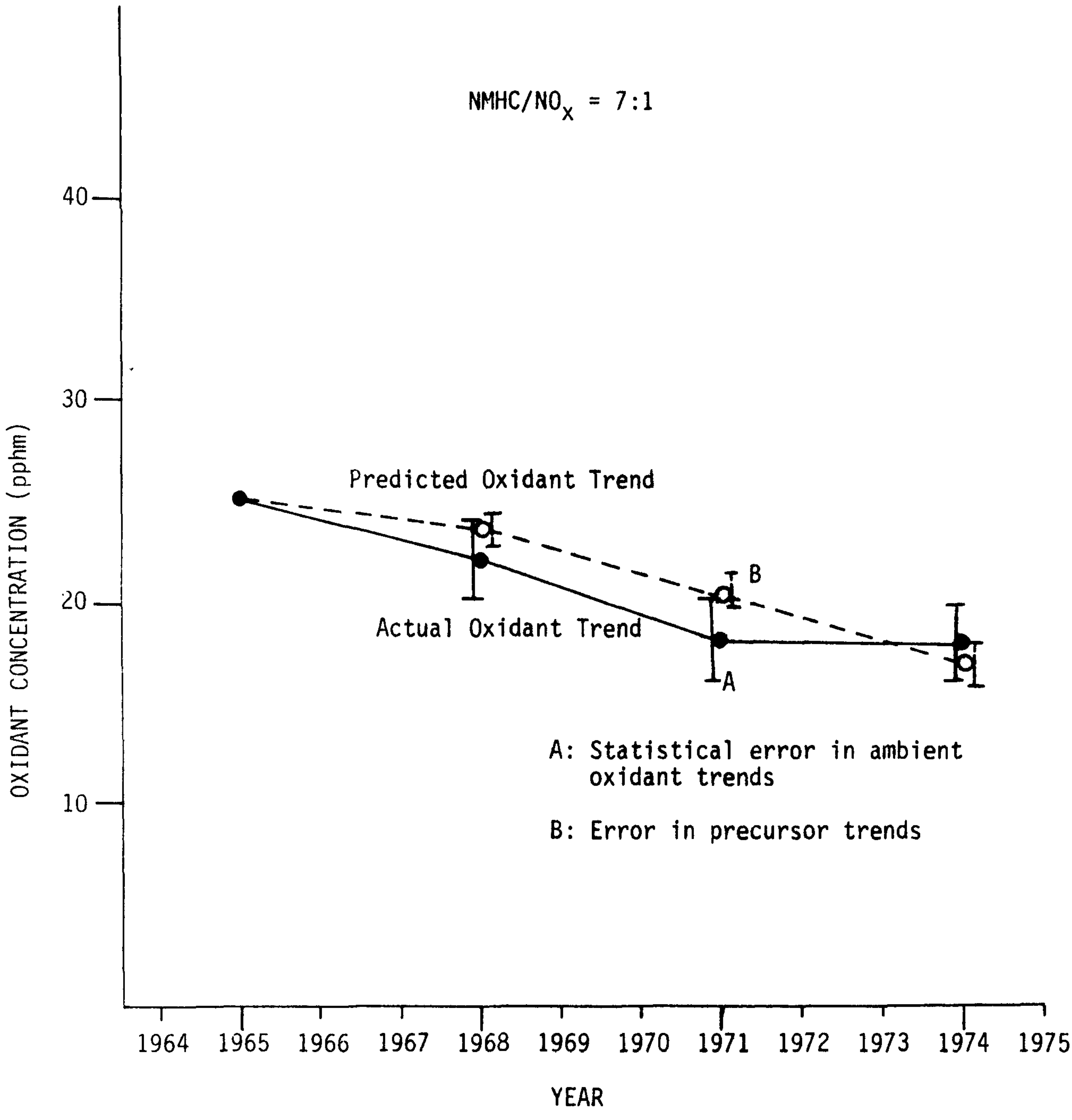

Figure 38. Oxidant Trends in the 95th Percentile of the Daily Maxima at DOLA, Predicted for 7:1 Ratio vs. Actual.

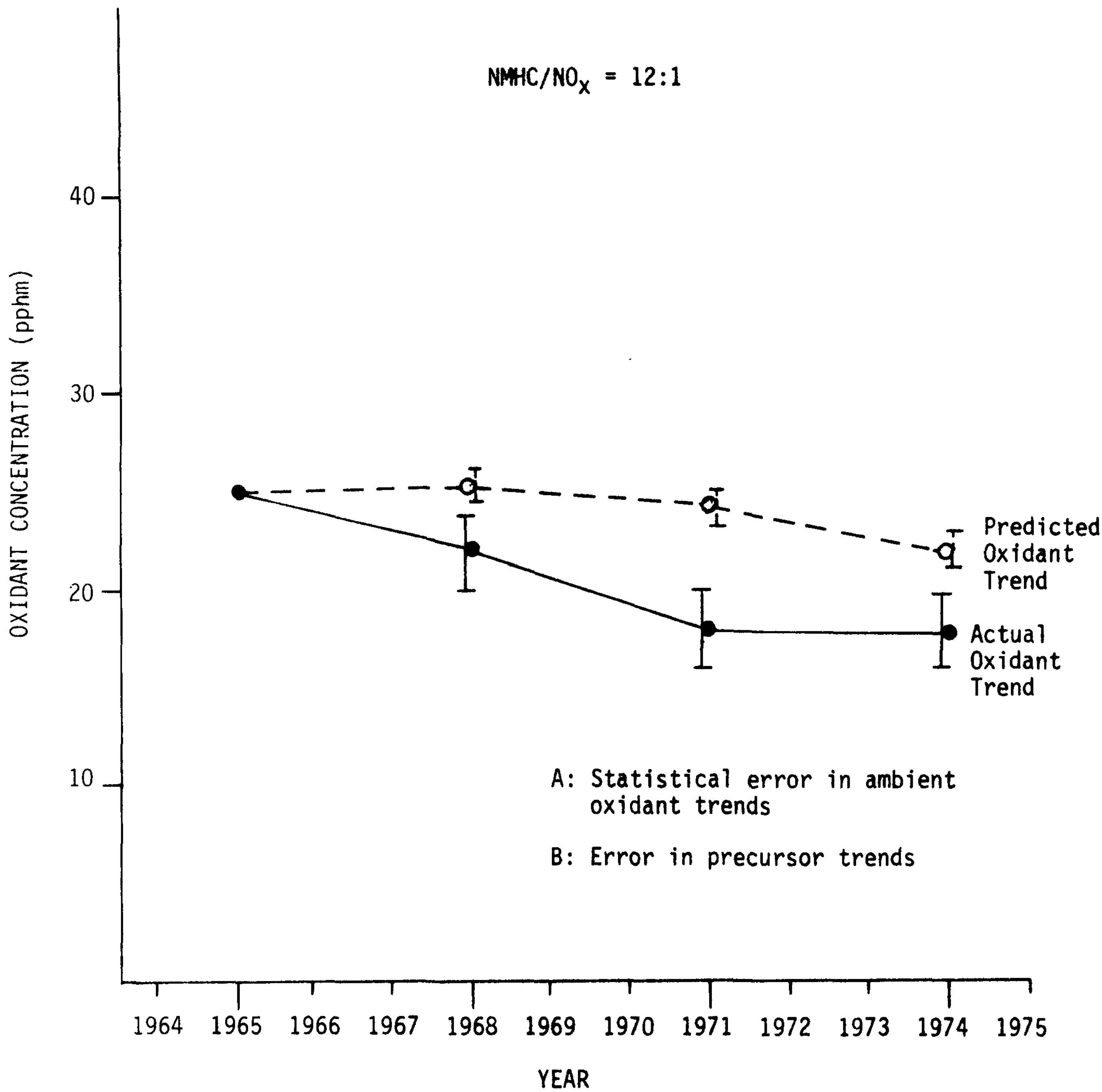

Figure 39. Oxidant Trends in the 95th Percentile of the Daily Maxima at DOLA, Predicted for 12:1 Ratio vs. Actual.

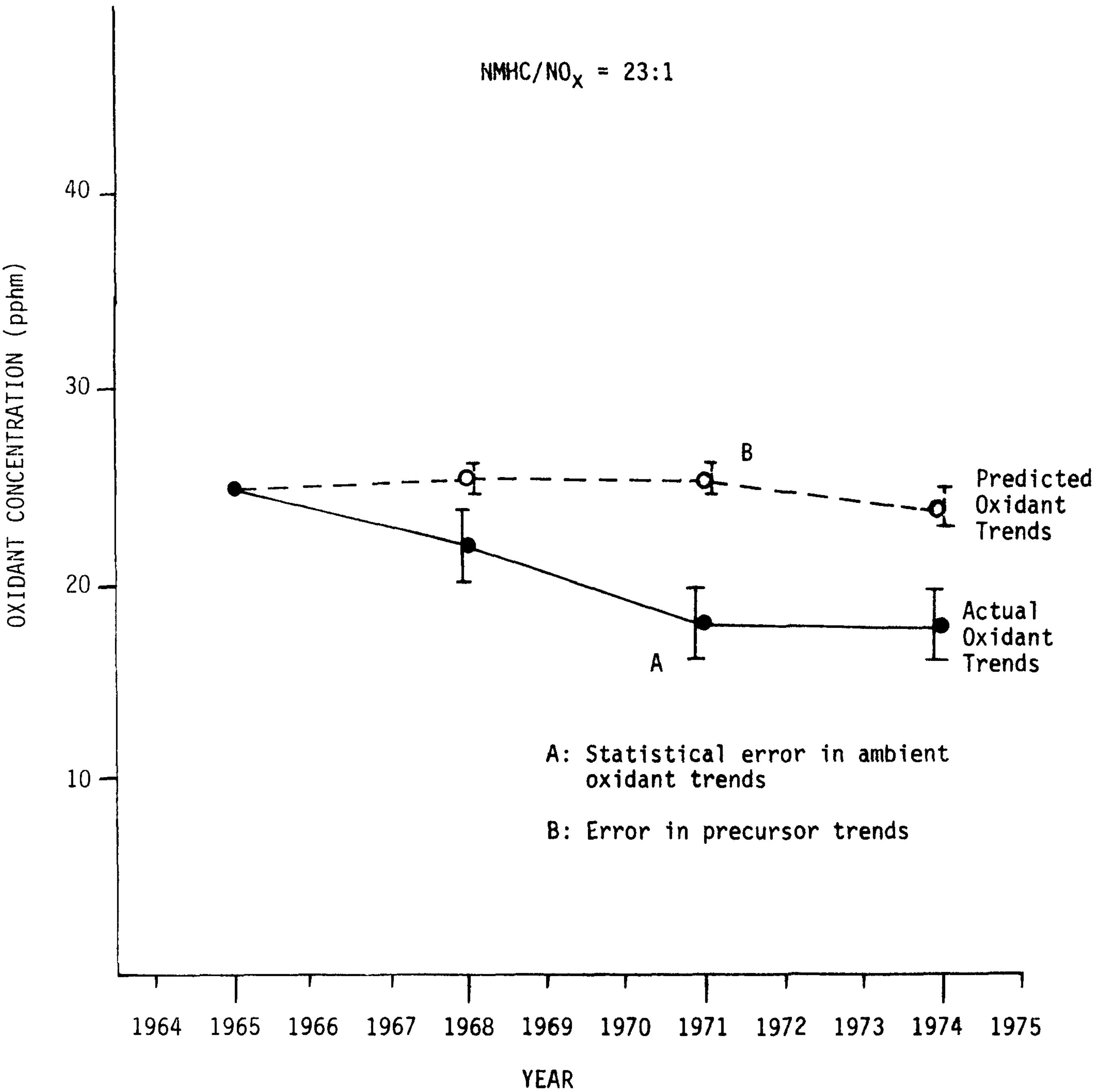

Figure 40. Oxidant Trends in the 95th Percentile of the Daily Maxima at DOLA, Predicted for 23:1 Ratio vs. Actual.

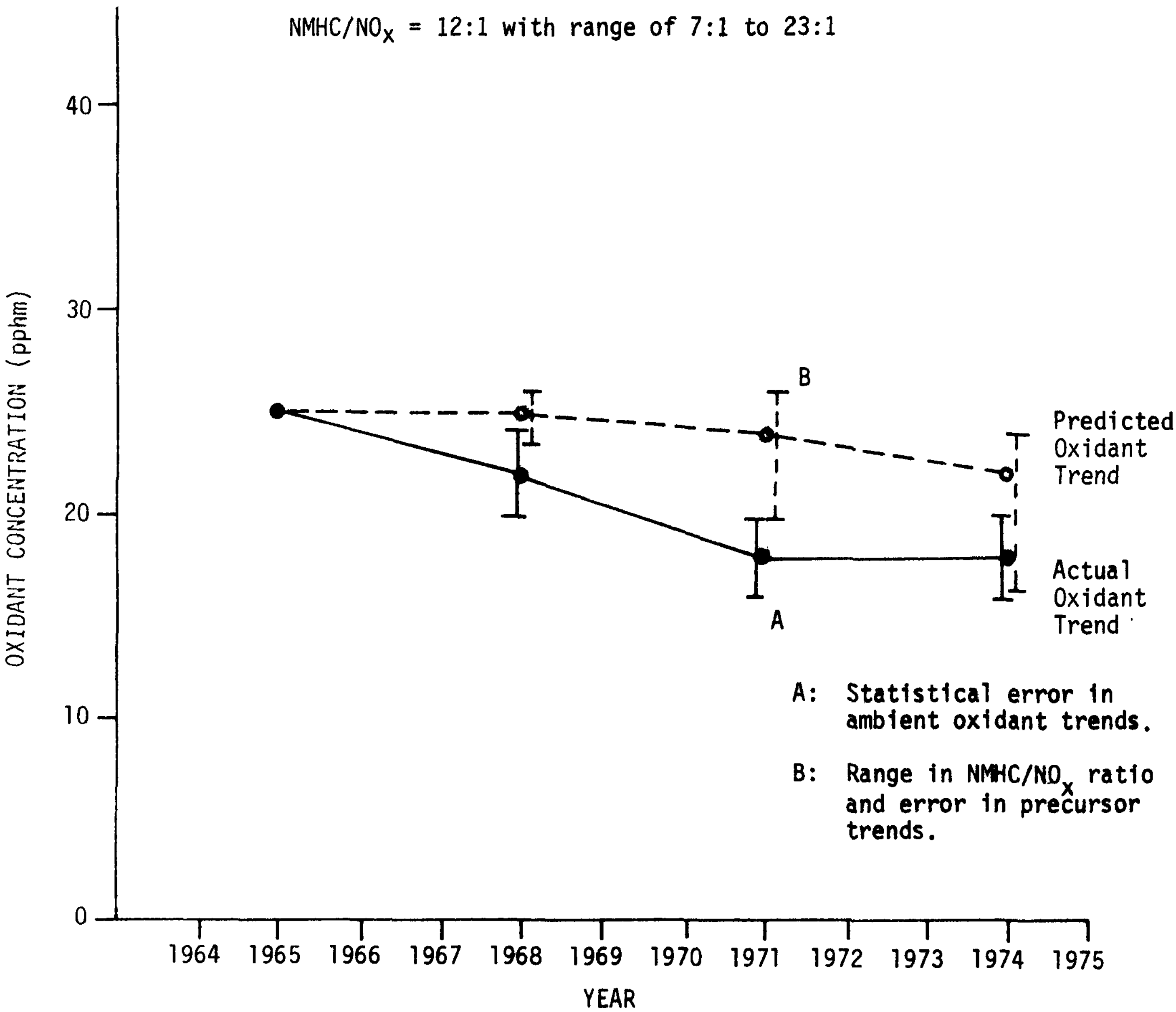

Figure 41. Summary of Oxidant Trends in the 95th Percentile at DOLA, Predicted with 5-Hour Isopleths vs. Actual.

in the NMHC/NO_x ratio. If we do not consider the potential range in the ratio (i.e. as in Figure 39), the discrepancies between actual and predicted, for the 12:1 ratio, become very significant statistically. This raises substantial doubts concerning the consistency between historical oxidant trends and the isopleth predictions (for the median ratio of 12:1).

We questioned whether the disagreement might be due to the specific air quality index used. The validation procedure was repeated using the 90th percentile of daily maximum one-hour concentrations. No significant improvement was obtained in the agreement between actual and predicted trends for the 12:1 ratio.

95th Percentile at Anaheim

Figures 42 to 45 present the results of the validation study using the 5-hour isopleths with trend data for Anaheim. The tendency for the isopleth method to underestimate the historical oxidant reductions in Los Angeles is very evident here. The agreement between predicted and actual trends is fair to poor for the 7:1 ratio (Figure 42), very poor for the 12:1 ratio (Figure 43), and very poor for the 23:1 ratio (Figure 44).

As shown in the summary graph (Figure 45), the differences between predicted and actual trends are significant even if we consider all three potential sources of error: statistical error in ambient oxidant trends, error in precursor trends, and possible range in the NMHC/NO_x ratio. In the case of Anaheim, the isopleth method distinctly fails to pass the verification test against historical oxidant trends.

95th Percentile at Azusa

Figures 46 to 49 summarizes the validation study using the 7-hour isopleths with the 95th percentile of daily maximum oxidant at Azusa. The overall agreement is excellent for the 7:1 ratio (Figure 46), poor for the 12:1 ratio (Figure 47), and very poor for the 23:1 ratio (Figure 48). For all three ratios the isopleth model underpredicts the net reduction in oxidant from 1965 to 1974. This underprediction is very significant statistically for the 12:1 and 23:1 ratios.

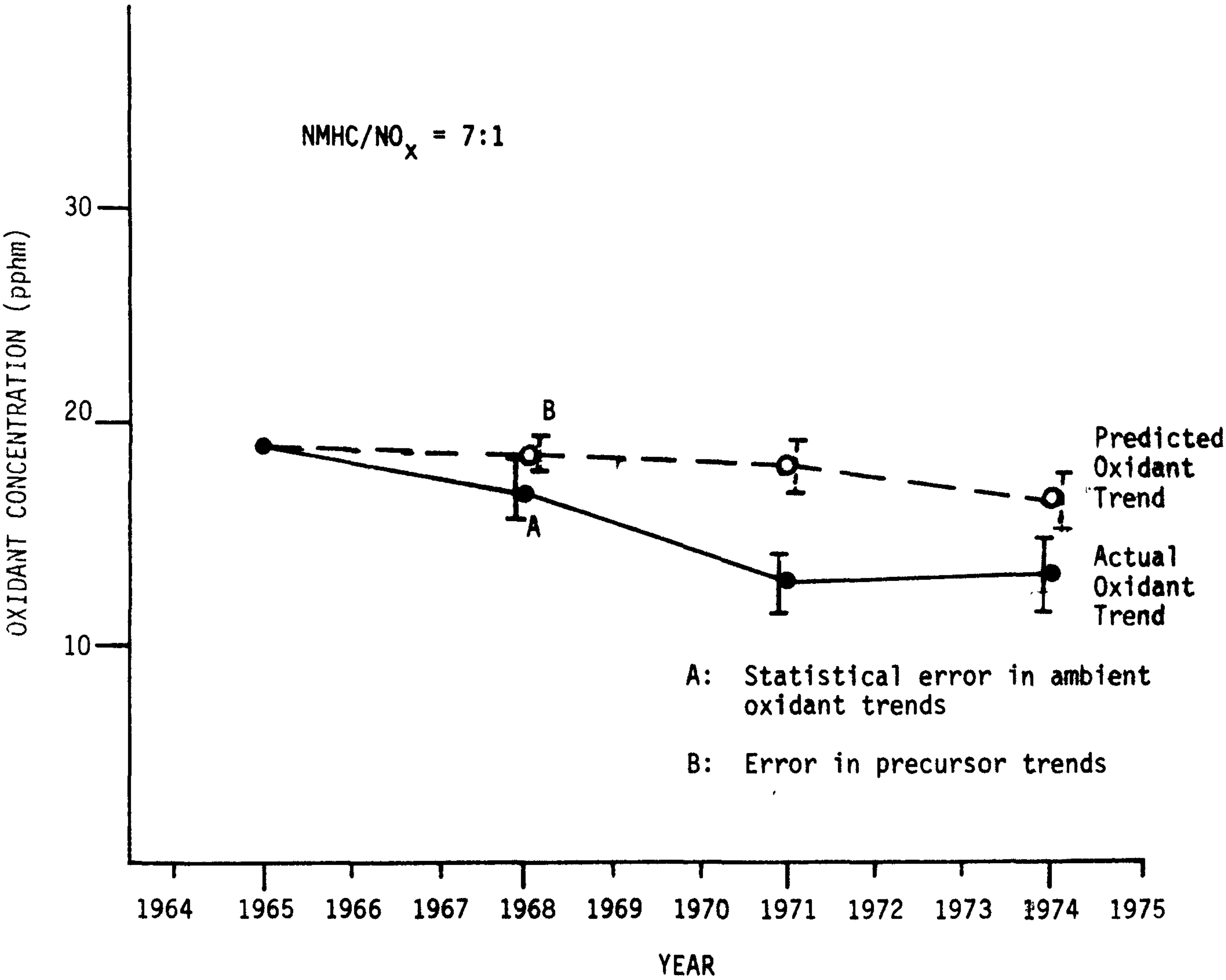

Figure 42. Oxidant Trends in the 95th Percentile of the Daily Maxima at Anaheim, Predicted for 7:1 Ratio vs. Actual.

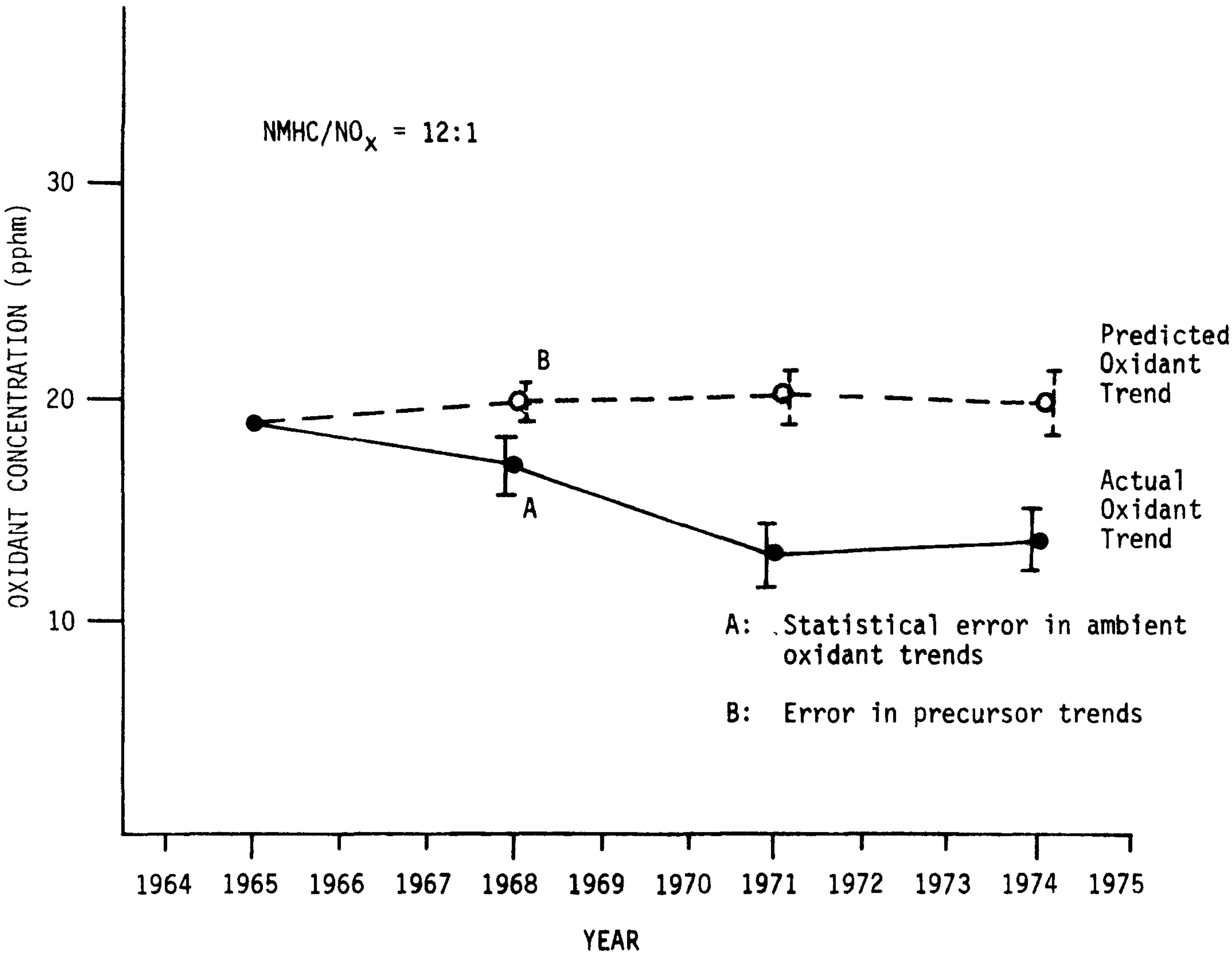

Figure 43. Oxidant Trends in the 95th Percentile of the Daily Maxima at Anaheim, Predicted for 12:1 Ratio vs. Actual

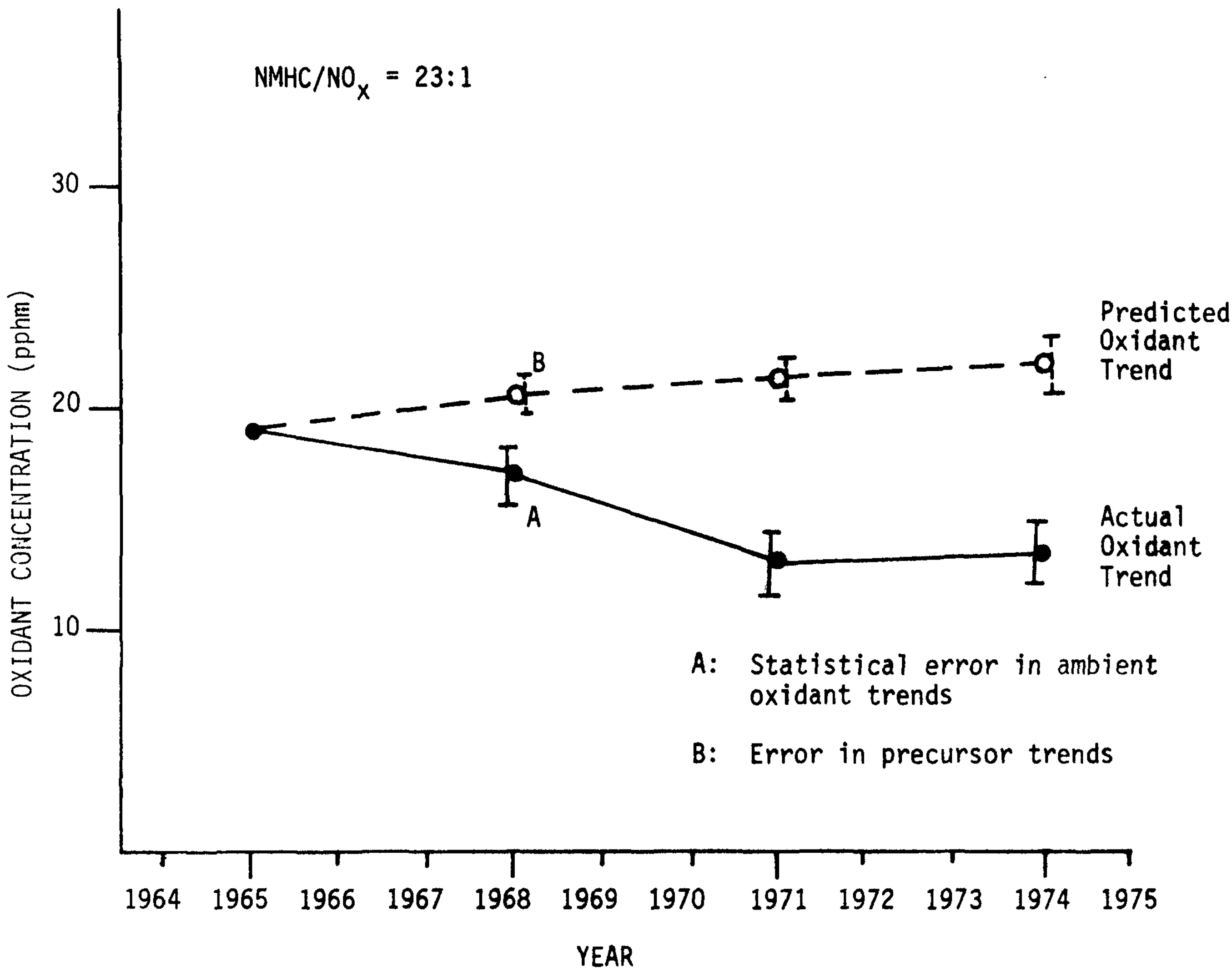

Figure 44. Oxidant Trends in the 95th Percentile of the Daily Maxima at Anaheim, Predicted for 23:1 Ratio vs. Actual

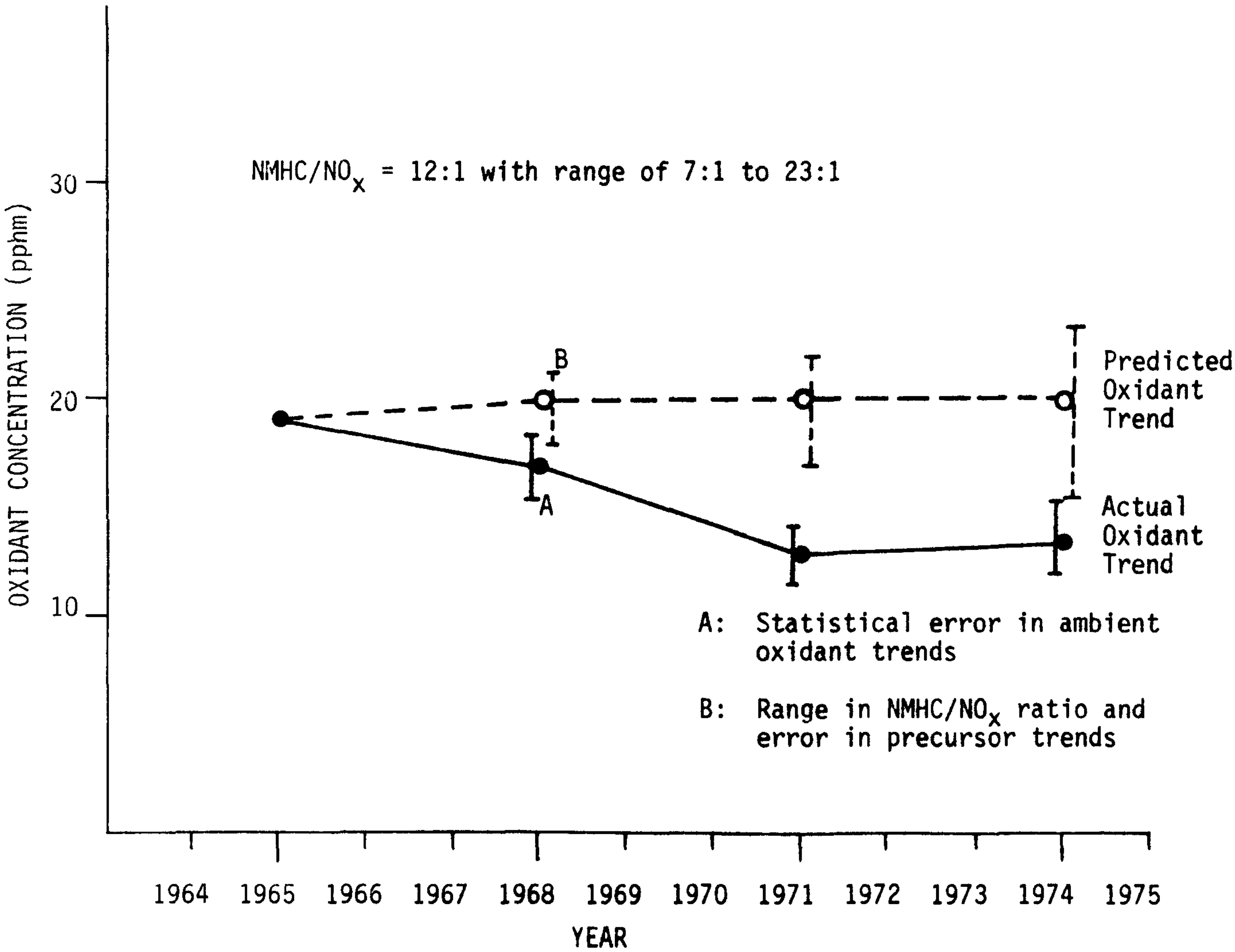

Figure 45. Summary of Oxidant Trends in the 95th Percentile at Anaheim, Predicted with 5-Hour Isopleths vs. Actual.

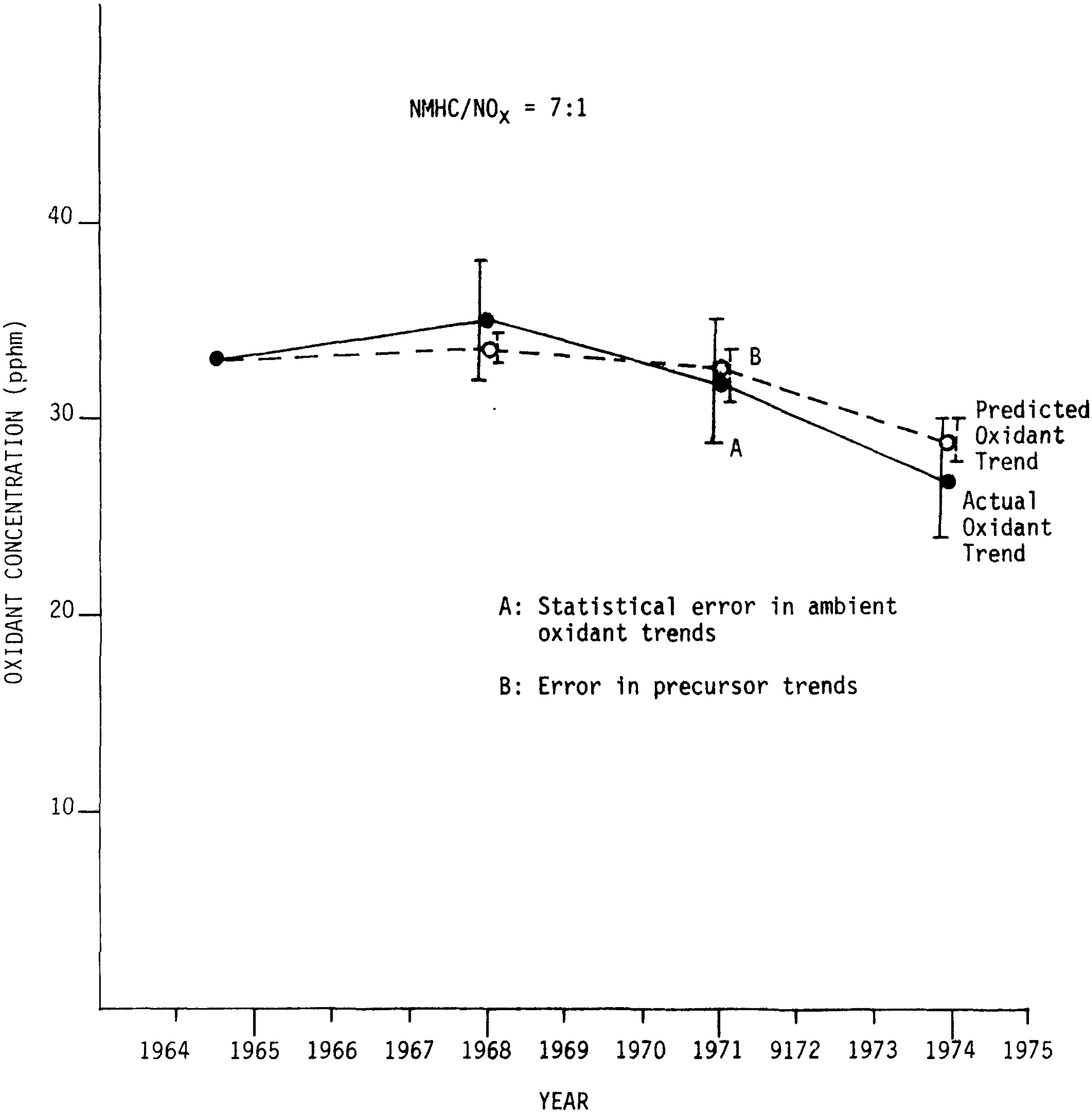

Figure 46. Oxidant Trends in the 95th Percentile of Daily Maxima at Azusa, Predicted for 7:1 Ratio vs. Actual.

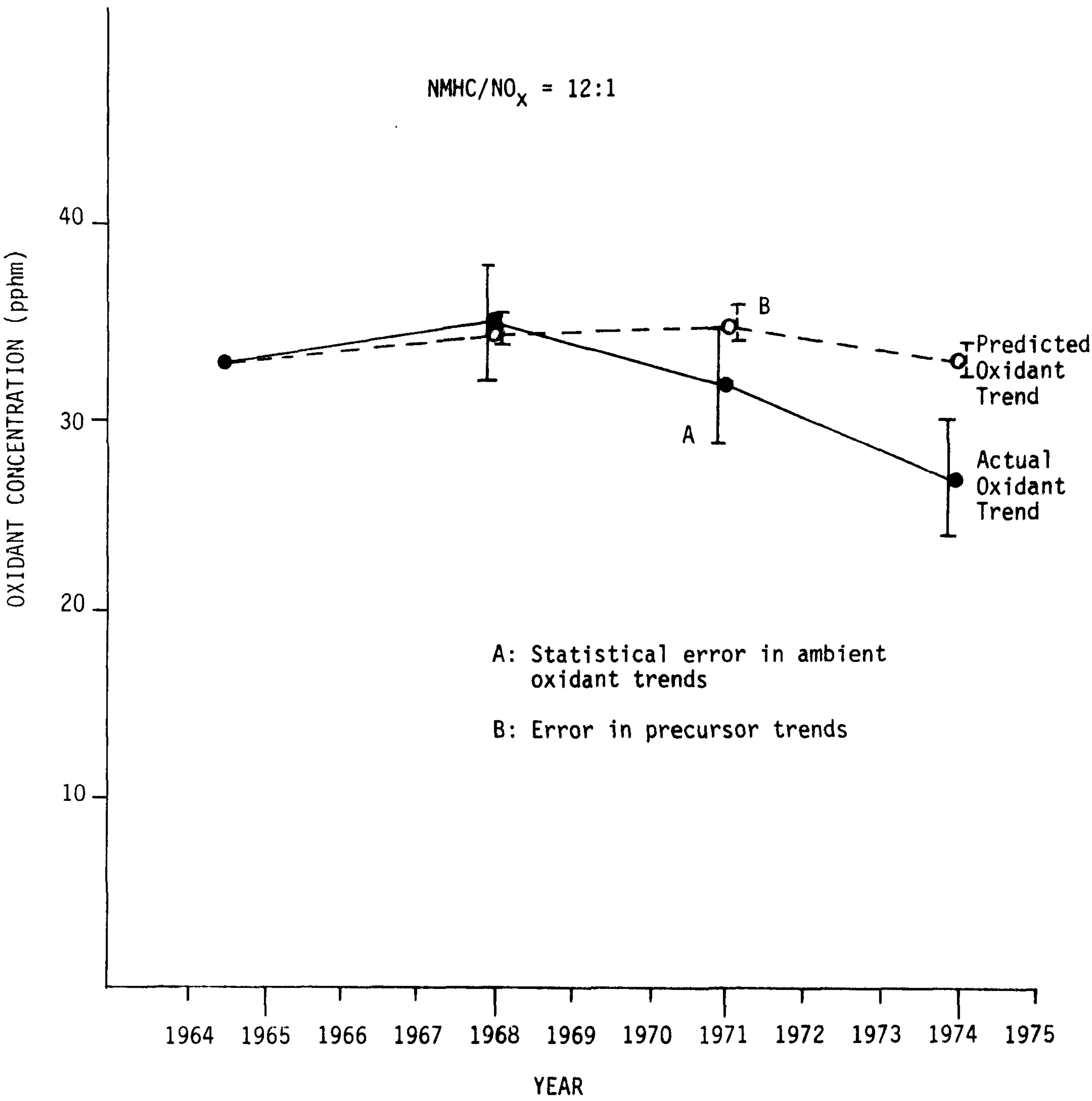

Figure 47. Oxidant Trends in the 95th Percentile of Daily Maxima at Azusa, Predicted for 12:1 Ratio vs. Actual.

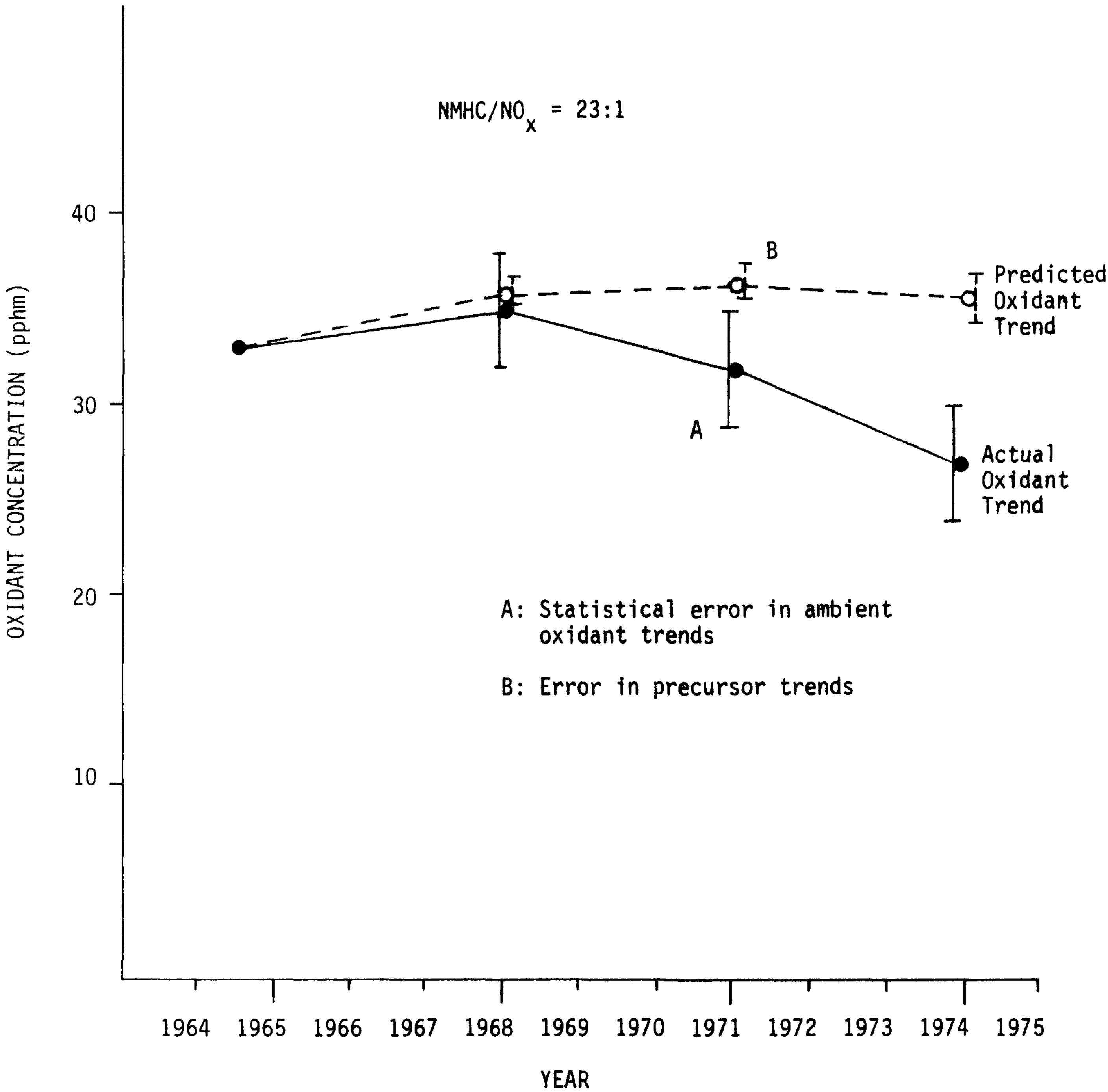

Figure 48. Oxidant Trends in the 95th Percentile of Daily Maxima at Azusa, Predicted for 23:1 Ratio vs. Actual.

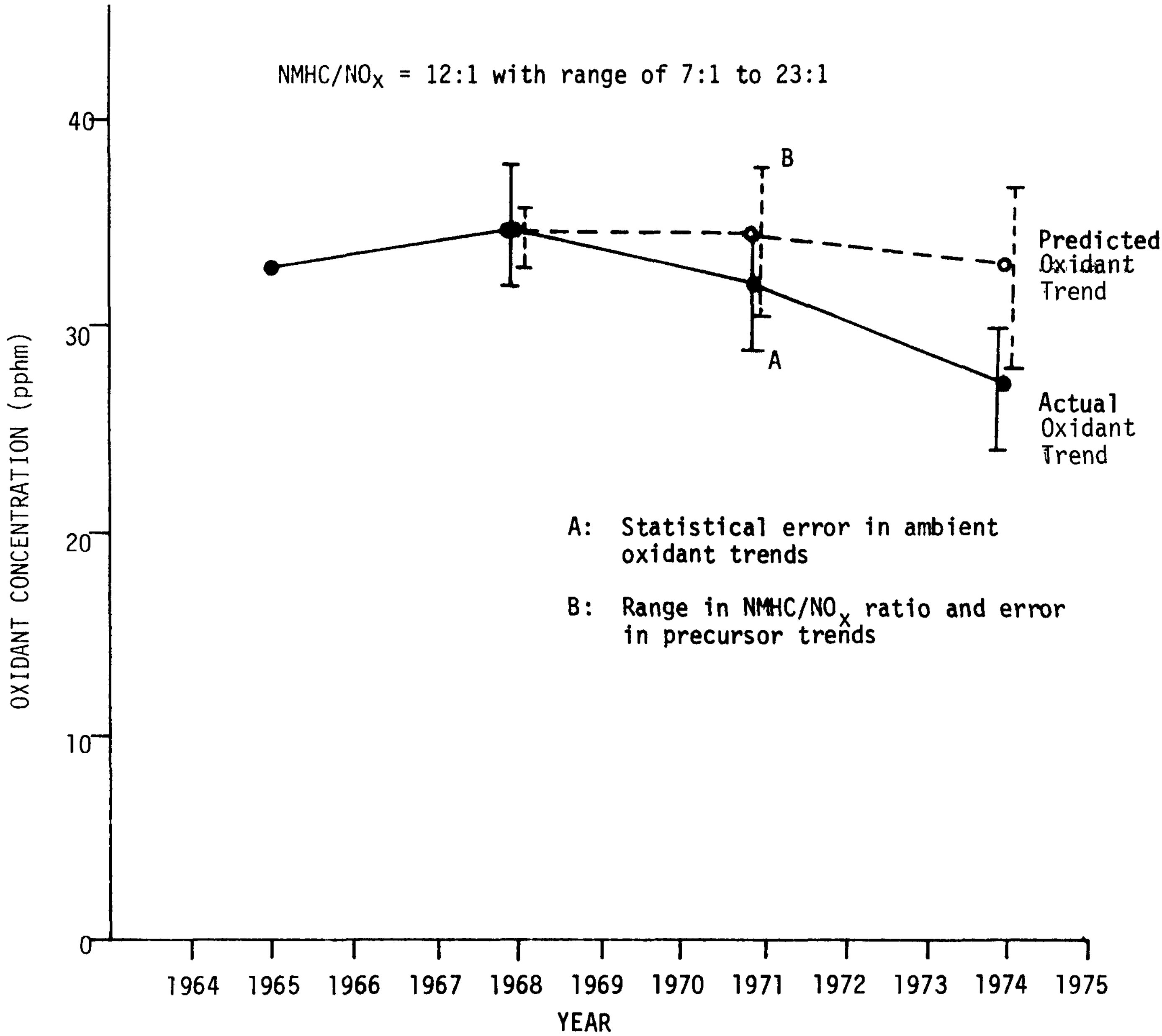

Figure 49. Summary of Oxidant Trends in the 95th Percentile at Azusa, Predicted with 7-Hour Isopleths vs. Actual.

As shown in Figure 49, the differences between predicted and actual trends are within the overall error bounds. However, the major factor in the overall error bounds is the range in the NMHC/NO_x ratio, from 7:1 to 23:1. If we did not consider the possibility that 7:1 is the appropriate ratio, statistically significant discrepancies would appear (as in Figure 47).

95th Percentile at San Bernardino

The results of the validation study using the 9-hour isopleths with the 95th percentile of daily maximum oxidant at San Bernardino are presented in Figures 50 to 53. The agreement between the predicted and actual trend lines is fair for all three ratios. The actual and predicted changes in oxidant at San Bernardino are too small for a conclusive test of the isopleth model.

Zeldin [20] has reported anomalies in the San Bernardino oxidant that cannot be explained by meteorology. He attributes these anomalies to instrumentation problems that were not noticeable enough at the time to warrant exclusion of the measurements from the San Bernardino APCD data base. Applying Zeldin's correction factors for the anomalous data affects only the 1970-1972 point; the actual oxidant point for those years is moved up slightly to be in better agreement with the predicted points.

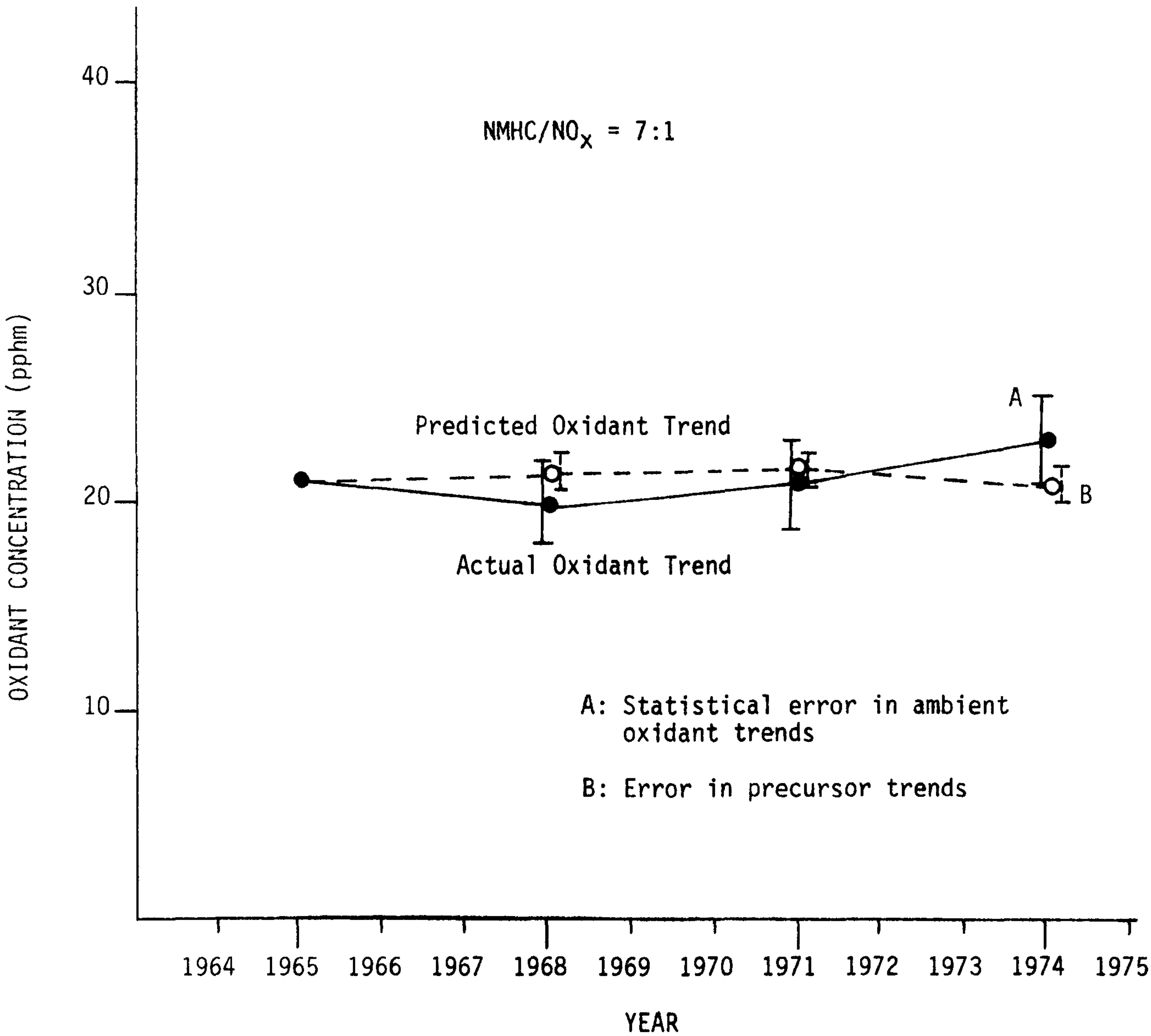

Figure 50. Oxidant Trends in the 95th Percentile of Daily Maxima at San Bernardino, Predicted for 7:1 Ratio vs. Actual.

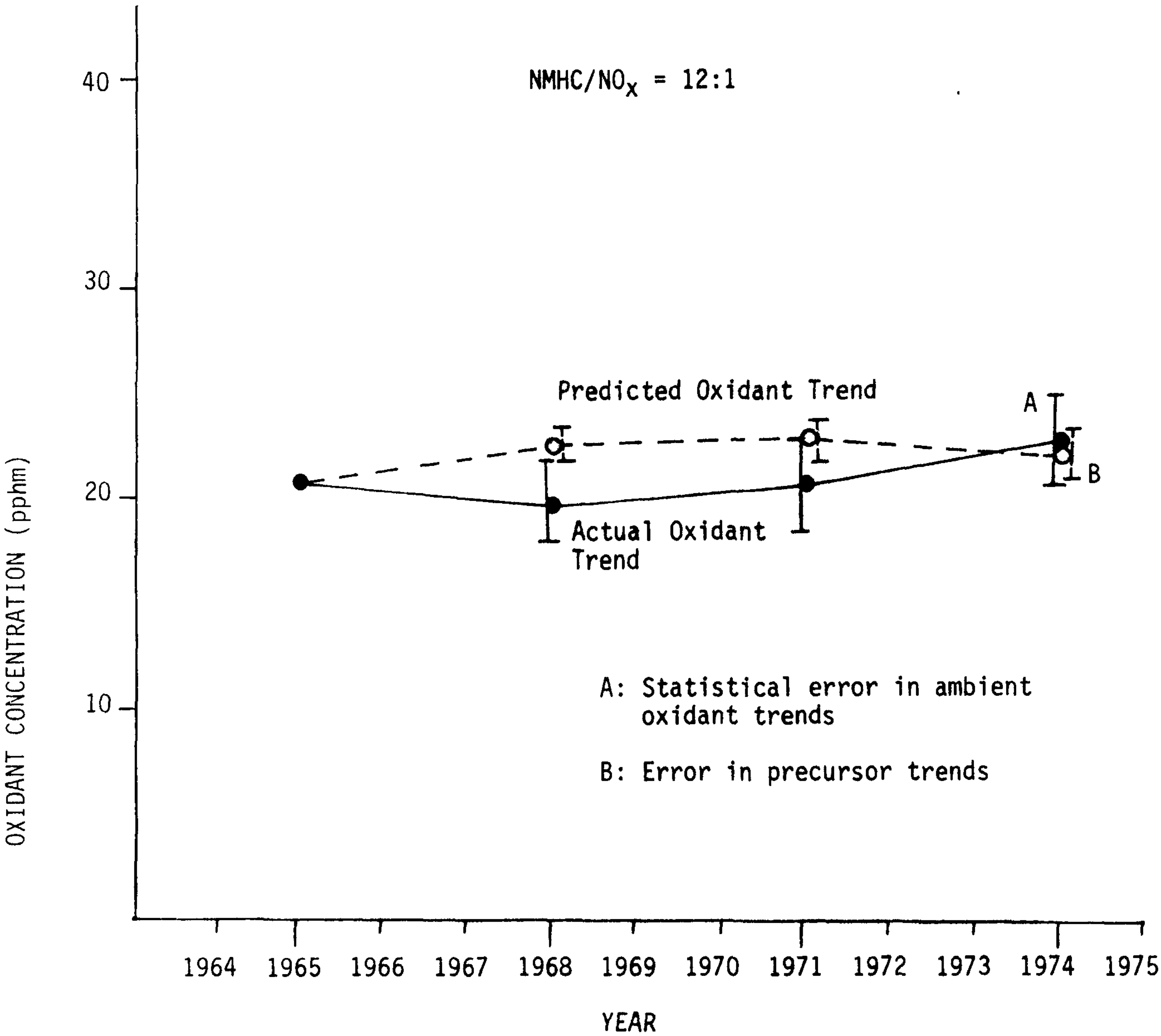

Figure 51. Oxidant Trends in the 95th Percentile of Daily Maxima at San Bernardino, Predicted for 12:1 Ratio vs. Actual.

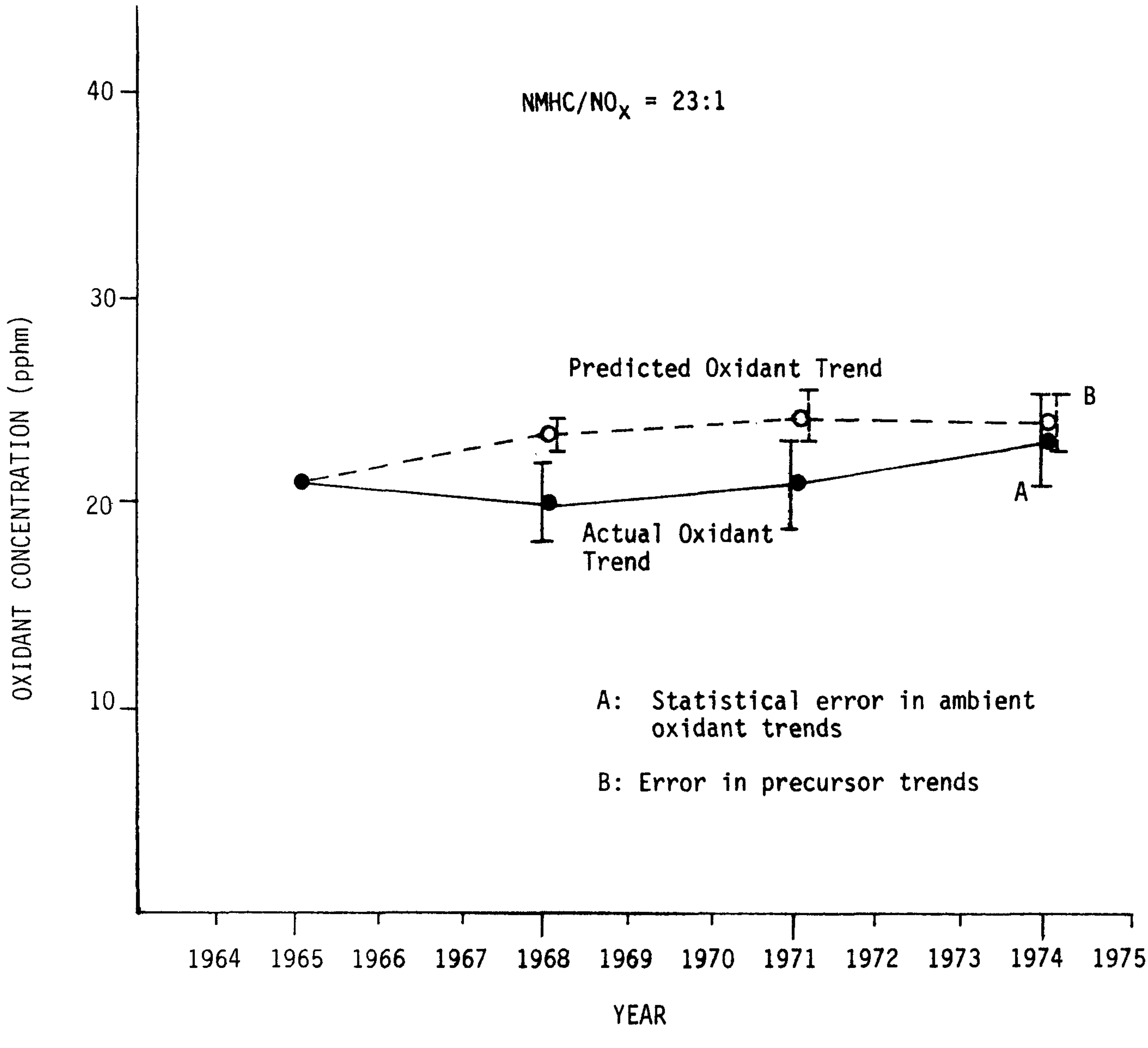

Figure 52. Oxidant Trends in the 95th Percentile of Daily Maxima at San Bernardino, Predicted for 23:1 Ratio vs. Actual.

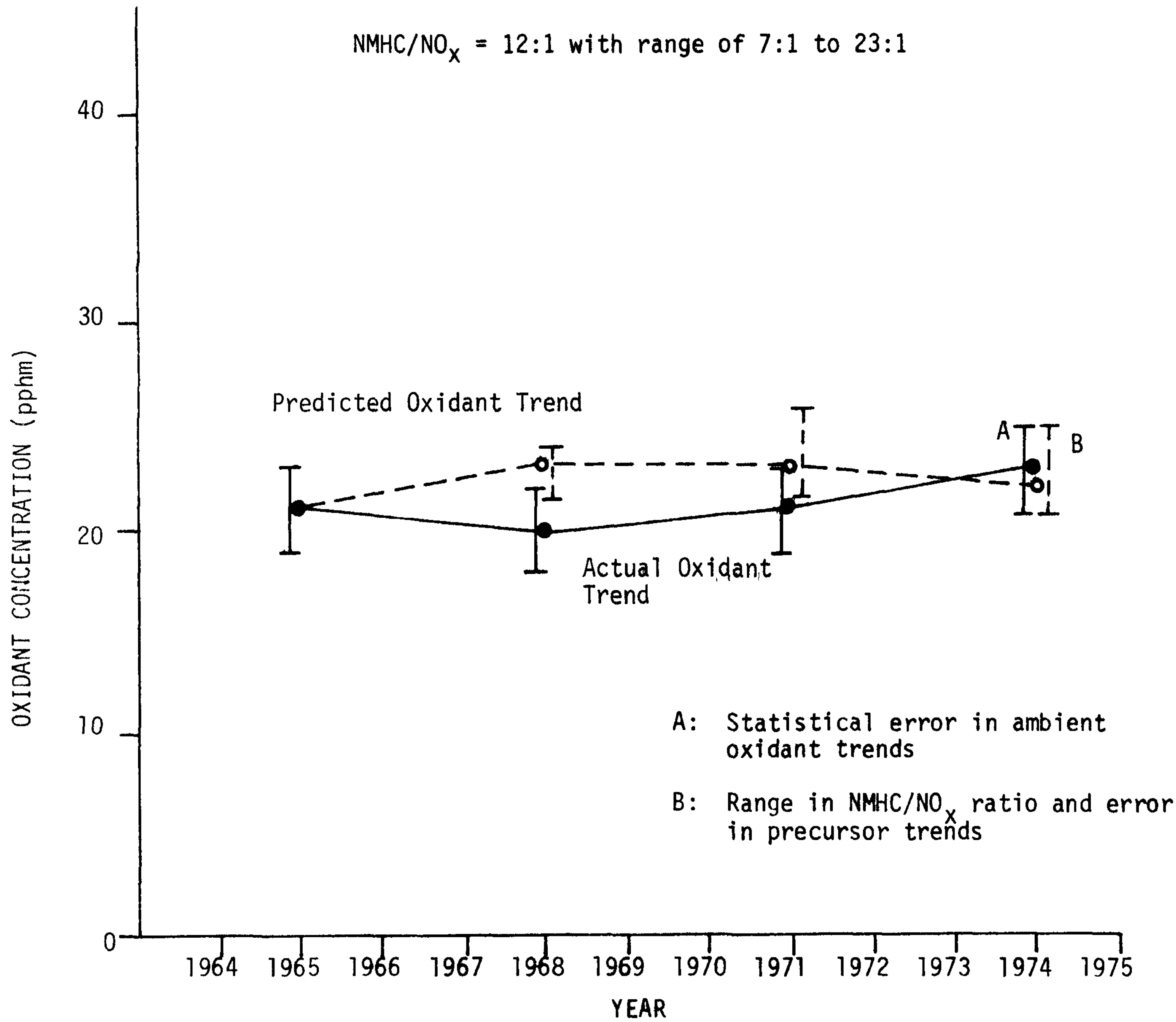

Figure 53. Summary of Oxidant Trends in the 95th Percentile at San Bernardino, Predicted with 9-Hour Isopleths vs. Actual.

CHAPTER 5

DISCUSSION OF RESULTS

If one accepts 12:1 as the appropriate NMHC/NO_x ratio in 1965 (equivalent to an 8:1 ratio in the early 1970's), the validation studies indicate significant discrepancies between historical air quality trends in Los Angeles and the predictions of the EKMA isopleth method. Considering the statistical errors in actual oxidant trends and the potential errors in our estimates of precursor trends, we found significant differences between the isopleth predictions (for a 12:1 ratio) and actual oxidant trends in four of the seven situations that were analyzed. Only if we consider a range in the NMHC/NO_x ratio, in particular the possibility that the ratio may have been as low as 7:1, do most of these discrepancies become statistically insignificant.

The disagreement for a 12:1 NMHC/NO_x ratio is highlighted in Table 18 which lists the actual and predicted changes in oxidant from 1964-1966 to 1973-1975. Although the isopleth method usually predicts the right direction of the change, it always underpredicts the magnitude of the change. In the central parts of the Los Angeles basin (all stations but San Bernardino), the isopleth method substantially underpredicts the reductions in oxidant that have actually occurred; this underprediction is especially large in the tests involving isopleths for fixed irradiation times.

This chapter discusses possible reasons for the disagreement and potential improvements in the isopleth method. First we eliminate those factors which would not account for the observed discrepancies; then we list the factors which may be the cause of the discrepancies and describe possible modifications to the isopleth method.

FACTORS NOT ACCOUNTING FOR THE DISAGREEMENT

We have investigated several factors which might contribute to the discrepancies between the isopleth predictions and actual oxidant trends. Before describing the factors that are the most likely explanations for the disagreement, it is useful to discuss the factors that we have been able to eliminate as plausible reasons for the disagreement.

Ambient NMHC/NO_x Ratio on High Oxidant Days

Our estimate of the ambient NMHC/NO_x ratio is based on 6-9 AM data for the entire summer smog season. It would be more appropriate to use the

Table 18. Summary of Actual and Predicted Oxidant Changes 1965 to 1974 ($NMHC/NO_x$ Ratio of 12:1)

VALIDATION STUDY	ACTUAL % OXIDANT CHANGE, 1965-1974	PREDICTED % OXIDANT CHANGE, 1965-1974
Basinwide Isopleths, Azusa 95th Percentile	-18%	- 9%
Basinwide Isopleths, Azusa 2nd Maximum	-21%	- 8%*
Basinwide Isopleths, Basinwide 2nd Maximum	-18%	- 8%
5-Hour Isopleths, DOLA 95th Percentile	-28%	-14%*
5-Hour Isopleths, Anaheim 95th Percentile	-29%	+ 5%*
7-Hour Isopleths, Azusa 95th Percentile	-18%	- 1%*
9-Hour Isopleths, San Bernardino, 95th Percentile	+ 9%	+ 6%

*significant difference based on potential errors in actual oxidant trends and in estimates of precursor trends.

6-9 AM ratio on days of highest oxidant. A sensitivity analysis (see Chapter 3) reveals that the median ratio on high oxidant days is 10 to 20% higher than the median ratio on all summer days.

The foregoing consideration indicates that a median ratio of approximately 14:1 in 1965 might be more appropriate than a median ratio of 12:1. This, however, would not explain the discrepancies in the validation studies. In fact, using a 14:1 ratio would slightly increase the disagreement between the isopleth predictions and actual oxidant trends.

6-9 AM Summertime Precursor Trends

The "best estimates" of precursor trends that we have used in the validation studies are essentially based on yearly average changes in precursor emissions and ambient precursor concentrations. A more appropriate precursor trend index for testing the isopleth method would be changes in ambient 6-9 AM summertime concentrations. A sensitivity analysis (Chapter 3) indicates that our "best estimates" are representative of ambient trends in 6-9 AM summertime NMHC but may underestimate the increase in 6-9 AM summertime NO_x by 10 to 25%.

Using a greater historical NO_x increase would affect our verification study in two ways. First, in extrapolating the present NMHC/NO_x ratio (8:1) backwards to 1965, we would arrive at a higher median ratio (say 14:1 or 15:1 instead of 12:1). As noted earlier, this would worsen the discrepancies in the validation study. Second, the NO_x level of the predicted points on the isopleth model would be increased. In the cases involving the median NMHC/NO_x ratio, this would increase the predicted oxidant levels, again making the discrepancies greater. Thus, if we increased our estimate of the historical rise in NO_x to be representative of 6-9 AM summertime trends, we would only worsen the discrepancies in the validation studies.

Monitoring Changes

An obvious factor that could lead to disagreement between the isopleth predictions and actual oxidant trends would be errors produced by monitoring changes. Such errors could be introduced either in the ambient precursor trends or the actual oxidant trends. We expect, however, that such errors will be minimal for the following reasons:

- None of the monitoring stations changed location during the period.
- The same analytical methods were used throughout the period (flame ionization for hydrocarbons, colorimetric for NO_x, and colorimetric for oxidant).
- The trends were continual over the period and were usually consistent among stations located in the same part of the basin.
- The trends at DOLA and Anaheim provide an independent check on changes in monitoring practices since the data are collected by two separate monitoring agencies.

POSSIBLE EXPLANATIONS FOR THE DISAGREEMENT

There are several factors that could account for the discrepancies between the isopleth predictions and historical oxidant trends. These factors are discussed in the paragraphs that follow. To determine which of these factors is most critical would require additional research effort (see recommendations for future work in Chapter 1).

Atmospheric NMHC Versus Isopleth NMHC

One possible reason for the observed discrepancies could be that the median ratio of 12:1 is inappropriate. In Chapter 4 (Figures 26 to 53), we found better agreement between predicted trend lines and actual trend lines for the 7:1 ratio than for the 12:1 ratio. As evidenced by Table 19, the 7:1 ratio leads to a much better prediction of the net oxidant changes from 1965 to 1974.

Table 19. Summary of Actual and Predicted Oxidant Changes, 1965 to 1974 ($NMHC/NO_x$ Ratio of 7:1 and 12:1)

VALIDATION STUDY	ACTUAL % OXIDANT CHANGE, 1965 to 1974	PREDICTED % OXIDANT CHANGE, 1965 to 1974	
		7:1 RATIO	12:1 RATIO
Basinwide Isopleths, Azusa 95th Percentile	-18%	-15%	- 9%
Basinwide Isopleths, Azusa 2nd Maximum	-21%	-15%	- 8%*
Basinwide Isopleths, Basinwide 2nd Maximum	-18%	-14%	- 8%
5-Hour Isopleths, DOLA 95th Percentile	-28%	-32%	-14%*
5-Hour Isopleths, Anaheim 95th Percentile	-29%	-12%*	+ 5%*
7-Hour Isopleths, Azusa 95th Percentile	-18%	-12%	+ 1%*
9-Hour Isopleths, San Bernardino 95th Percentile	+ 9%	0%	+ 6%

*significant difference based on potential errors in actual oxidant trends and in estimates of precursor trends

The ambient data for NMHC and NO_x (Chapter 3) gave us fairly good confidence that the median atmospheric 6-9 AM ratio was 12:1 (or slightly higher) in 1965. However, a 12:1 atmospheric ratio may not be equivalent to a

12:1 ratio in the isopleth model (which is a mathematical model using propylene and n-butane, calibrated with smog-chamber results using auto exhaust). It is possible that a given level of ambient NMHC in Los Angeles is equivalent to a lower level of NMHC in the isopleth model. This would be the case if the atmospheric NMHC were of lower reactivity (per ppmc) than the isopleth NMHC. Thus, an ambient ratio of 12:1 may possibly be equivalent to a ratio of 7:1 in the isopleth model.

To investigate this factor further, the reactivity of atmospheric NMHC in Los Angeles should be compared to the reactivity of the isopleth NMHC mix. Such a reactivity analysis should consider both the number of moles per ppmc and the oxidant producing potential per mole of the hydrocarbons.

Post 9 AM Emissions

The existing versions of the EKMA isopleths relate ozone to initial NO_x and NMHC (assumed equivalent to 6-9 AM NO_x and NMHC), neglecting emissions after 9 AM. It is expected that NO_x emitted after 9 AM would act more as an ozone inhibitor than initial (6-9 AM) NO_x. If post 9 AM emissions were added to the model, the isopleths in the upper left-hand corner of Figure 1 (or Figure 25) should bend more to the right because of greater ozone inhibition from NO_x. The critical ratio in the isopleth model (the top of the ozone "hill" or the ratio at which hydrocarbon control becomes effective) might also become larger. These effects would tend to reduce the discrepancies between the isopleth predictions and historical oxidant trends in Los Angeles.

The addition of post 9 AM emissions should be most important for short irradiation times; the most significant changes should occur in the 5-hour isopleths. This is encouraging because the greatest discrepancies between actual and predicted values have been found in the cases involving short irradiation times, i.e. DOLA and Anaheim.

EPA is presently investigating the possibility of adding post 9 AM emissions to the isopleth model (Personal communication with Edwin Meyer, EPA Office of Air Quality Planning and Standards, Durham, N.C., November 1977). When these new isopleths become available, the verification studies should be repeated. We would expect the results of the verification tests to improve.

Meteorology

Another reason for the disagreement could be meteorological bias in the actual oxidant trends. The greatest discrepancies occur in 1973-1975, when actual oxidant is, in most cases, substantially lower than predicted oxidant. This may, in part, be due to meteorology; it has been previously noted [21, 22] that pollution potential in Los Angeles appeared to be lower in 1973-1975 than in 1964-1966.

It would be useful in future work to normalize the actual oxidant trends for meteorological variance. This would provide a more appropriate test of the isopleth method. Normalization for meteorology should also decrease the error bounds on the actual oxidant trends, resulting in a more finely-tuned validation study. Zeldin and Meisel [23] have recently completed a guideline document for EPA on meteorological normalization of air quality trends; in the future they may be applying their method to the Los Angeles oxidant data.

Source Area Definition

Another potential explanation for the disagreement is that the source areas have not been properly defined. Perhaps the precursor changes of consequence are the precursor changes in the sub-areas of greatest emission density (which have low growth rates) rather than the precursor changes throughout the entire upwind area.

To assess the effect of redefining source areas, we repeated the analysis for the Azusa second maximum using the precursor trends for the DOLA source region (a high-density/low-growth sub-area of the Azusa source region). The results of this analysis are presented in Figures 54 to 57. There is some improvement in the verification study for the 12:1 ratio (compare Figure 55 to Figure 31), but predicted oxidant still exceeds actual oxidant in 1974. Overall, the predicted values for a 12:1 ratio using the DOLA source area (Figure 55) resemble the predicted values for a 7:1 ratio using the Azusa source area (Figure 30).

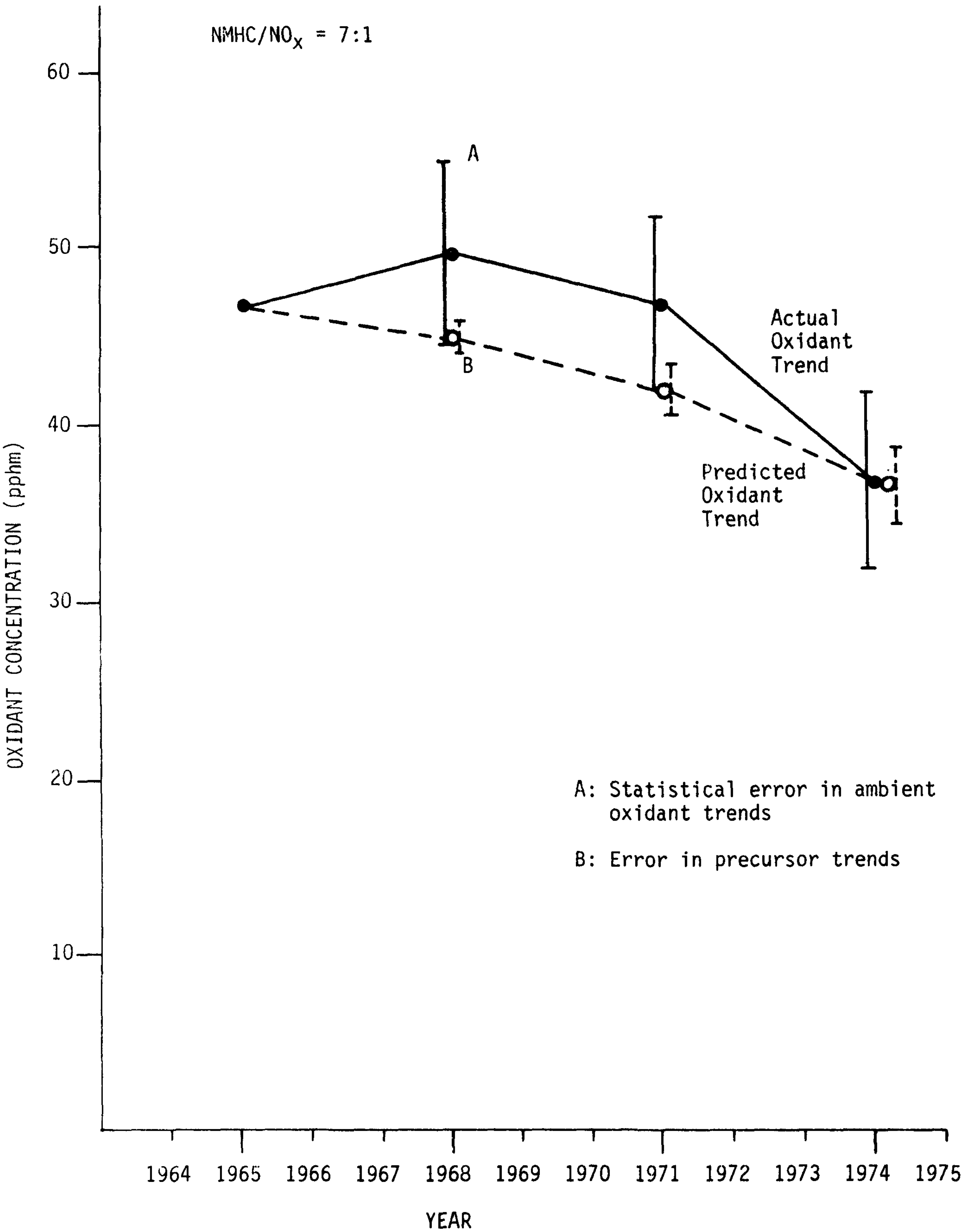

Figure 54. Oxidant Trends in the Second Maximum for Azusa, Predicted for 7:1 Ratio vs. Actual, Predicted Values Based on DOLA Source Region

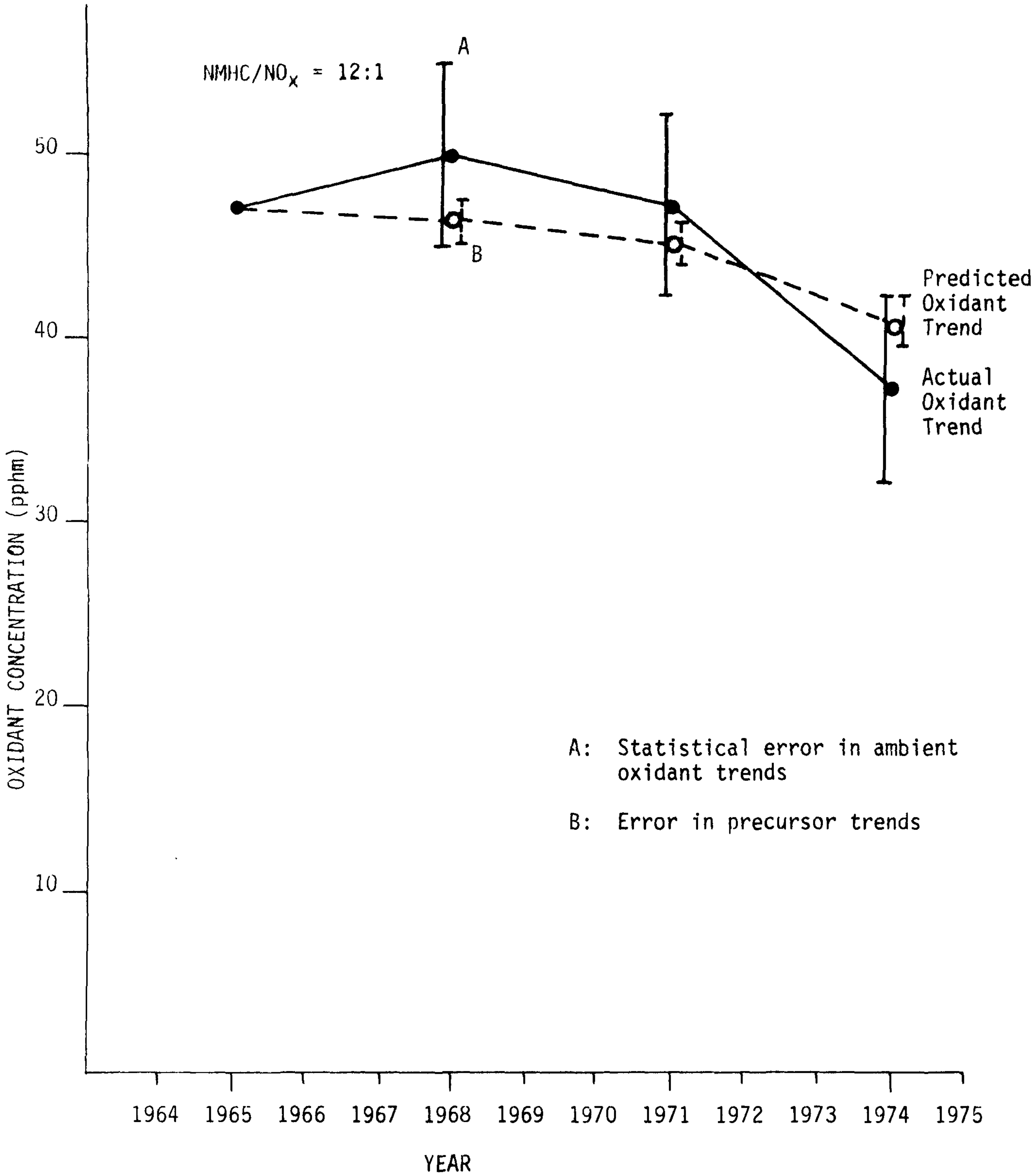

Figure 55. Oxidant Trends in the Second Maximum for Azusa, Predicted for 12:1 Ratio vs. Actual, Predicted Values Based on DOLA Source Region

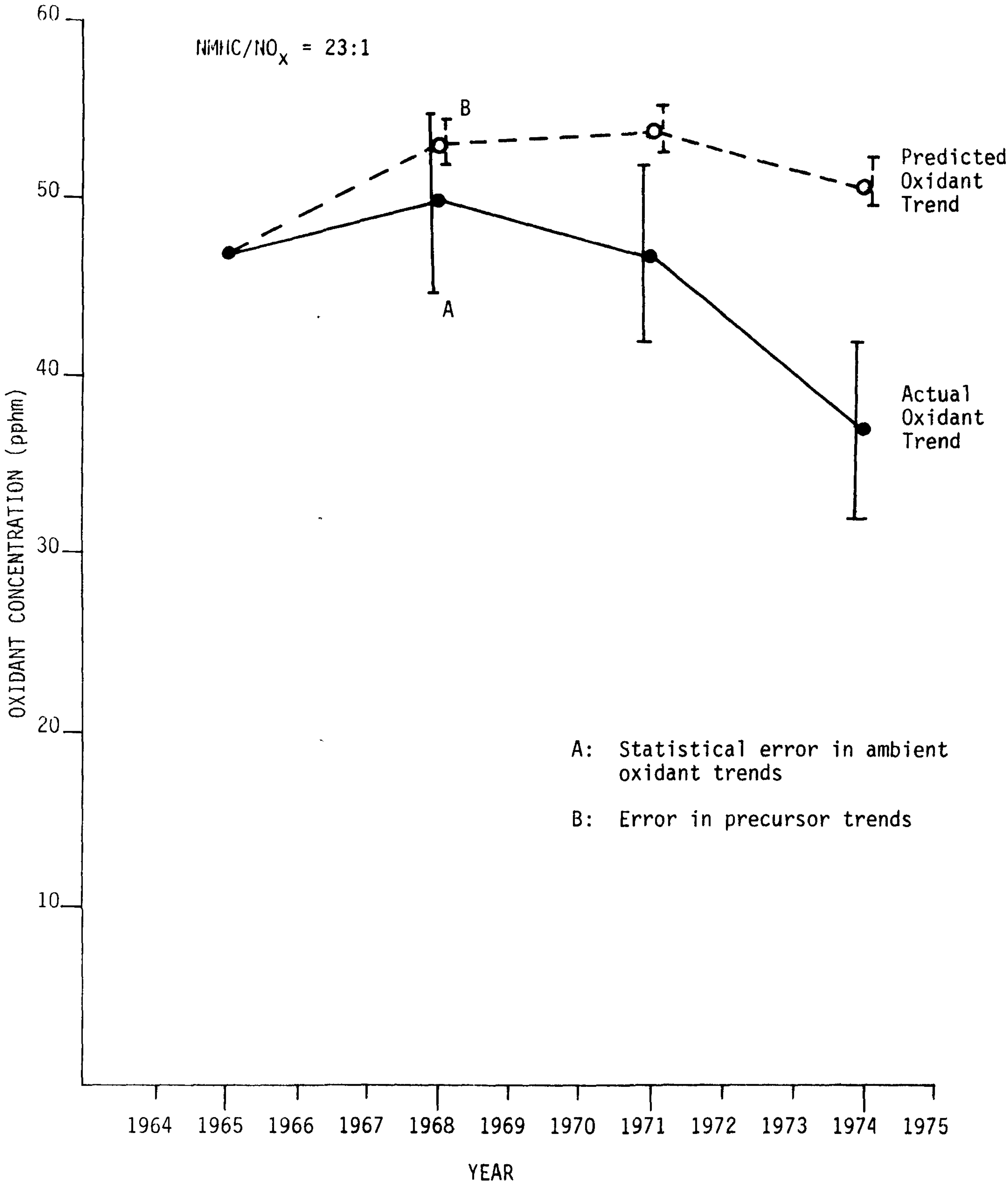

Figure 56. Oxidant Trends in the Second Maximum for Azusa, Predicted for 23:1 Ratio vs. Actual, Predicted Values Based on DOLA Source Region

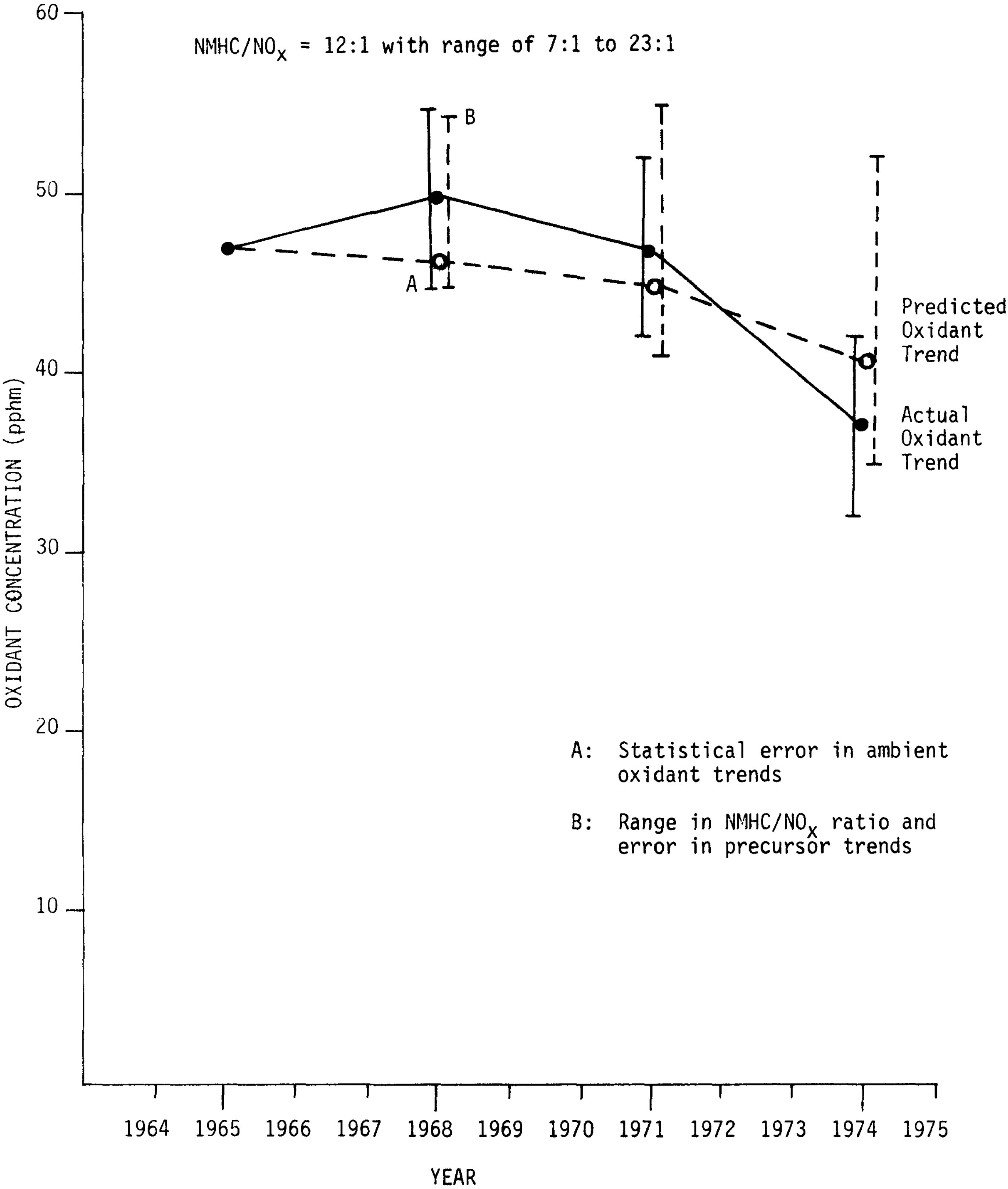

Figure 57. Summary of Oxidant Trends in the Second Maximum for Azusa, Predicted vs. Actual, Predicted Values Based on DOLA Source Region

Spatial Coverage of Oxidant Monitoring Stations

Our analyses with the basinwide EKMA isopleths rely essentially on oxidant trend data for the Azusa monitoring site. Oxidant trends at Azusa may not be representative of the trends in the basinwide oxidant maximum; in particular, the historical oxidant decrease at Azusa may have been greater than the decrease in the basinwide oxidant maximum. This is plausible because the location of the basinwide oxidant maximum has been shifting eastward, downwind of Azusa, as reductions in the NMHC/NO_x ratio have retarded the photochemical reaction rates.* The oxidant maximum at Azusa may have decreased relative to the basinwide maximum because of this spatial shift.

That we may have overestimated the historical decrease in the basinwide oxidant maximum because of the limited spatial coverage of the monitoring stations could explain some of the discrepancies in the verification tests using the basinwide isopleths. This, however, would not explain the even greater discrepancies found in the tests using isopleths for fixed irradiation times.

Inappropriate definition of source areas and limited spatial coverage of oxidant monitoring stations are possible factors contributing to the observed discrepancies. However, it is our opinion that the three most likely explanations for the disagreements are (1) non-equivalency between atmospheric NMHC and chamber NMHC, (2) omission of post 9 AM emissions in the isopleth model, and (3) meteorological bias in the actual oxidant trends.

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*Maximal oxidant in the Los Angeles basin presently tends to occur near Upland, approximately 20 miles downwind of Azusa. As explained in Chapter 2, we did not include Upland in our trend analysis because only three years of data were avaliable for that location.

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APPENDIX A

TABLE OF OXIDANT TREND DATA

STATION	OXIDANT AIR QUALITY INDEX	TRENDS IN 3-YEAR AVERAGES (pphm) 1964-66	1967-69	1970-72	1973-75
BASINWIDE	ANNUAL SECOND HIGHEST ONE HOUR CONCENTRATION	49.0	52.0	47.0	39.7
AZUSA	ANNUAL SECOND HIGHEST ONE HOUR CONCENTRATION	47.3	50.0	47.0	36.7
	95TH PERCENTILE OF DAILY MAXIMAL ONE HOUR CONCENTRATIONS	33.3	35.0	32.0	27.0
DOWNTOWN LA	95TH PERCENTILE OF DAILY MAXIMAL ONE HOUR CONCENTRATIONS	25.3	22.3	18.0	18.0
ANAHEIM†	"	18.9	17.0	13.0	13.5*
SAN BERNARDINO†	"	21.1	20.3	21.1	23.0

†Oxidant measurements taken at locations outside Los Angeles County have been multiplied by 0.80 to account for differences in calibration procedures.

*Two-year average (1973-74).

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-78-019		

4. TITLE AND SUBTITLE	5. REPORT DATE / 6. PERFORMING ORGANIZATION CODE
VERIFICATION OF THE ISOPLETH METHOD FOR RELATING PHOTOCHEMICAL OXIDANT TO PRECURSORS	5. February 1978 6.
7. AUTHOR(S) J. Trijonis D. Hunsaker	**8. PERFORMING ORGANIZATION REPORT NO.**
9. PERFORMING ORGANIZATION NAME AND ADDRESS Technology Service Corporation 2811 Wilshire Boulevard Santa Monica, CA 90403	**10. PROGRAM ELEMENT NO.** 1AA603 AC-29 (FY-78) **11. CONTRACT/GRANT NO.** 68-02-2299
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	**13. TYPE OF REPORT AND PERIOD COVERED** Final **14. SPONSORING AGENCY CODE** EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Historical trend data for oxidant concentrations in the Los Angeles region were used to check the isopleth method that has been proposed as a replacement for the Appendix J method for relating oxidant to non-methane hydrocarbon (NMHC) and nitrogen oxide (NO_x) precursors. Using the median 6-9 AM NMHC/NO_x ratio measured during the summer as input to the isopleth model, significant discrepancies were found between the isopleth predictions and actual oxidant trends. Using a range in the NMHC/NO_x ratio, in particular a low value for the ratio, much better agreement was found between the predicted and actual trends. Potential explanations for the discrepancies are discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution *Ozone *Mathematical Models *Verifying	Los Angeles	13B 07B 12A 14B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	123
	20. SECURITY CLASS (This page) UNCLASSIFIED	**22. PRICE**

EPA Form 2220-1 (9-73)