United States Environmental Protection Agency Office of Air Quality Planning and Standards Research Triangle Park NC 27711 EPA-450/3-78-026 June 1978

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Comparison of Ambient NMHC/NOx Ratios with NMHC/NOx Ratios Calculated from Emission Inventories

Comparison of Ambient NMHC/NO_X Ratios with NMHC/NO_X Ratios Calculated from Emission Inventories

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Contract No 68-02-2583 Assignment No 4

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY Office of Air and Waste Management Office of Air Quality Planning and Standards Research Triangle Park, North Carolina 27711

June 1978

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Publication No. EPA-450/3-78-026

TABLE OF CONTENTS

Sect	<u>Pag</u>	<u>je</u>
1.0	INTRODUCTION AND SUMMARY	1
2.0	LOS ANGELES DATA ANALYSIS	.]
	2.1 Ambient Air Monitoring Data 2-	·]
	2.2 Emission Inventory Data 2-	3
	2.3 Ratio Comparison 2-	5
3.0	SAN FRANCISCO DATA ANALYSIS	1
	3.1 Ambient Air Monitoring Data	1
	3.2 Emission Inventory Data	3
	3.3 Ratio Comparison	7
4.0	ST. LOUIS DATA ANALYSIS	1
	4.1 Ambient Air Monitoring Data 4-	1
	4.2 Emission Inventory Data 4-	3
	4.3 Ratio Comparison 4-	5
5.0	DISCUSSION OF RESULTS	3
	5.1 Correlations Versus Numerical Values 5-	1
	5.2 Reasons for Ratio Differences 5-4	4
	5.2.1 Meteorological Factors 5-4	•
	5.2.2 Accuracy of Emission Inventory Data 5-5	
	5.2.4 Other Factors	
6.0	REFERENCES	1
4 D D C		
APPE		,
APPE	NDIX B. SAN FRANCISCO AMBIENT AIR MONITORING DATA B-	1
APPE	NDIX C. ST. LOUIS AMBIENT AIR MONITORING DATA C-	1

LIST OF TABLES

<u>Table</u>	Page
2-1 Los Angeles NMHC/NO $_{\rm X}$ Ratio Summary	2-2 2-4
Emission Data	2-6 3 - 2
3-2 San Francisco Gridded Emission Inventory Data	3-4
Classes	3 - 5 3 - 6
3-5 San Francisco NMHC/NO $_{\rm X}$ Ratio Comparison 4-1 St. Louis NMHC/NO $_{\rm X}$ Ratio Summary	3- 8
4-2 St. Louis Countywide Emission Inventory Data4-3 St. Louis NMHC/NO_X Ratio Comparison Using Countywide	4-4
Emission Data	4- 6 5-2
Emission Ratios in the Central Downtown Area	-
Figure	Page
2-1 Best-Fit Regression Lines for Five High-Oxidant 3/s in Los Angeles, Comparing Gridded Emission NMHC/NO _X Ratios with Ambient Ratios	2-7
3-1 Best Fit Regression Lines for Five High-Oxidant Days in San Francisco, Comparing Gridded Emission NMHC/NO _x Ratios with Ambient Ratios	3-9
3-2 Best-Fit Regression Lines for Five High-Oxidant Days in San Francisco, Comparing Countywide	
Emission NMHC/NO _X Ratios with Ambient Ratios 4-1 Best-Fit Regression Lines for Five High-Oxidant	3-10
Days in St. Louis, Comparing Countywide Emission NMHC/NO, Ratios with Ambient Ratios	4-7

1.0 INTRODUCTION AND SUMMARY

One method for revising State Implementation Plans to meet the ambient oxidant standards is the Empirical Kinetic Modeling Approach (EKMA). This method requires the determination of the ratio of non-methane hydrocarbons (NMHC) to oxides of nitrogen (NO $_{\rm X}$). It is recommended in the EKMA method (Environmental Protection Agency 1977, EPA-450/2-77-021a) that the ratio of NMHC/NO $_{\rm X}$ be calculated with ambient air monitoring data. However, due to the lack of adequate air monitoring data in some locations, local agencies have proposed using emission inventory data to calculate the appropriate NMHC/NO $_{\rm X}$ ratio. The purpose of this project was to determine what differences result from calculating NMHC/NO $_{\rm X}$ ratios from emission inventory data compared with the EKMA recommended technique of calculating NMHC/NO $_{\rm X}$ ratios from ambient monitoring data, and to rationally explain the differences between the two methods.

Three geographic locations were considered in analyzing the differences between NMHC/NO $_{\rm X}$ ratios calculated from emission inventory data and those from ambient monitoring data. The three locations were chosen due to the availability of detailed gridded emission inventories and the large number of air monitoring sites in each location. The following three locations were used:

- 1. Los Angeles, California
- 2. San Francisco, California
- 3. St. Louis, Missouri

Ambient monitoring data from five high oxidant days in each of the three locations were used to calculate 6-9 a.m. NMHC/NO $_{\rm X}$ ratios, as specified in the EKMA method.

The emission inventory data involved detailed hourly gridded emission data in Los Angeles and San Francisco in addition to county-wide emission data in each of the three locations. Because the EKMA

method requires volumetric NMHC/NO $_{\rm X}$ ratios in units of ppmC/ppm, it was necessary to adjust the emission NMHC/NO $_{\rm X}$ ratios from units of mass to units of volume. Since NO $_{\rm X}$ emission rates are normally expressed as NO $_{\rm Z}$ (molecular weight = 46) and hydrocarbon emission rates are normally expressed as CH $_{\rm Z}$ (molecular weight = 16), all emission NMHC/NO $_{\rm X}$ ratios were multiplied by 46/16 or 2.875 to convert to the volumetric units of ppmC/ppm.

The relationship between ambient monitoring NMHC/NO $_{\rm X}$ ratios and emission inventory NMHC/NO $_{\rm X}$ ratios was tested by applying a linear regression analysis to air quality and emission data from a number of monitoring stations in each region. The relationship was tested for each of five high-oxidant days in each of the three locations - Los Angeles, San Francisco, and St. Louis. The basic result found in all three locations was that there was little correlation between NMHC/NO $_{\rm X}$ ratios calculated from ambient monitoring data and the corresponding NMHC/NO $_{\rm X}$ ratios calculated from emission inventory data. There was so a improvement in correlation when gridded emission ratios were used instead of countywide emission ratios in the San Francisco area, but the correlations in general were not significant.

Since the EKMA method normally requires ambient monitoring data from the main downtown urban center in a region, a brief analysis was made comparing the numerical values of averaged ambient NMHC/NO $_{\rm X}$ ratios with emission NMHC/NO $_{\rm X}$ ratios in the central downtown areas of the three locations. Perhaps fortuitously, the countywide emission NMHC/NO $_{\rm X}$ ratio compared reasonably well with the averaged ambient NMHC/NO $_{\rm X}$ ratio in each of the three downtown locations. This relationship should be further studied for a larger number of cities to determine its usefulness.

Due to a lack of correlation between the two methods of ratio calculation, it was difficult to assess a definite reason for the discrepancy between the two methods. Probably the most important reason for the differences between ambient NMHC/NO $_{\rm X}$ ratios and emission ratios is the influence of meteorology on ambient pollutant concentrations. Emissions and ambient pollutants from different regions can be transported to the location of an air monitoring station. Another major reason for the discrepancy between the two methods of ratio calculation is probably the lack of detail and inaccuracy in most emission inventories, since day-to-day variations in emissions are normally not represented and some important sources may be omitted from inventories.

Because of the lack of correlation between $\mathrm{NMHC/NO_X}$ ratios calculated from ambient air monitoring data and $\mathrm{NMHC/NO_X}$ ratios calculated from emission inventory data, it is recommended that only ambient monitoring data be used in the EKMA technique to calculate the ratio of nonmethane hydrocarbons to oxides of nitrogen.

2.1 AMBIENT AIR MONITORING DATA

Ambient monitoring data for Los Angeles, California for nonmethane hydrocarbons (NMHC) and oxides of nitrogen (NO_x) were derived from the records of the Southern California Air Pollution Control District, Metropolitan Zone. A search was made of data from the year 1975 to determine the 5 days with the highest hourly oxidant readings in the region, as recommended in the Empirical Kinetic Modeling Approach (EKMA). When these five high oxidant days were determined, hourly data for NMHC and NO_x for the hours of 6-9 a.m. (local daylight time) were examined at eight air monitoring stations in the region. All of the eight air monitoring stations were in one large county, Los Angeles County. For each station, the hourly values from 6-9 a.m. were averaged for NMHC and NO_x concentrations, and these average values were used to calculate the $NMHC/NO_X$ ratio for each station. The ambient air monitoring data for each of the 5 days in Los Angeles are shown in the five tables in Appendix A.

An examination of the individual hourly concentration data showed that the NO_x data were fairly uniform and did not exhibit extreme fluctuations from day to day; however, the NMHC values varied widely from one day to the next. NMHC concentrations are not measured directly, but are derived by subtracting measured methane concentration values from measured total hydrocarbon concentration values; thus, NMHC values are normally less accurate than measured NO_X concentration values. Because of possible inaccuracies in low NMHC values, it was decided to exclude data from a station where any of the three hourly NMHC values was 0.3 ppmC or less. The remaining 3-hour averaged ambient NMHC/NO $_{
m x}$ ratios are summarized in Table 2-1 for the eight stations in Los Angeles. Site descriptions of the Los Angeles monitoring stations are listed in Table 2-2. The 6-9 a.m. ambient air monitoring $NMHC/NO_{x}$ ratios ranged from a low of 1.39 to a high of 13.30, in units of ppmC/ppm.

Table 2-1. LOS ANGELES NMHC/NO $_{\rm X}$ RATIO SUMMARY

		m e 6-9		Ambient Air Ratio		6-9 a.m.	Countywide
Monitoring Station	7/11/75	8/2/75		9/21/75	10/3/75	Emission Ratio*	Emission Ratio*
Central Los Angeles	4.09	4.11	1	4.28	3.43	3.71	3.51
East San Gabriel Valley	ı	ı	3.24	1	ı	10.81	3.51
East San Fernando Valley	3.35	7.13	13.30	2.96	8.18	3.08	3.51
Northwest Coastal	1.39	1	1.31	5.53	3.63	6.04	3.51
West San Fernando Valley	2.63	1.96	1.92	2.38	3.13	6.27	3.51
Pomona- Walnut Valley	2.24	1.71	1.25	2.76	4.14	7.07	3.51
Southeast	9.81	7.00	6.85	6.88	6.30	7.39	3.51
West San Gabriel Valley	3.79	2.94	3.05	5.56	2.33	5.69	3.51

*Adjusted to represent ppmC/ppm

2.2 EMISSION INVENTORY DATA

A gridded emission inventory developed by Nordsieck (1974) was used to calculate the corresponding emission NMHC/NO $_{\rm X}$ ratios. The emission inventory was representative of a typical summer day in Los Angeles. Emissions were projected for the year 1975 from the base year of 1972. The emission inventory was based on a 2 mile x 2 mile square grid system, and emissions were adjusted to represent 6-9 a.m. (local daylight time) values by using appropriate diurnal patterns (CALTRANS 1975). The 6-9 a.m. emissions, due to the traffic rush hour, represented a higher fraction of mobile source emissions than the average daily emissions.

The position of each air monitoring station was located on the grid system, and a weighted emission average was calculated based on an inverse-square distance relationship among the four closest grid squares to the air monitoring station location. This technique was used so that the calculated emissions would represent 6-9 a.m. emissions in a 2 mile x 2 mile square centered on the air monitoring location. Thus, if an air monitoring station were located at the intersection point of four grid squares, emissions from the four grid squares would be averaged; conversely, if a monitoring station were located near the center of a grid square, the emissions from that square would be weighted most heavily. The calculated Los Angeles gridded emissions and the adjusted $NMHC/NO_x$ ratios (in units of ppmC/ppm) are shown in Table 2-2. The calculated emission NMHC/NO $_{_{\rm Y}}$ ratios ranged from a low of 3.08 to a high of 10.81. These emission ratios are representative of a typical summer day in Los Angeles.

The Los Angeles NMHC/NO $_{\rm X}$ ratios from ambient monitoring data and the corresponding ratios from the gridded emission inventory are summarized in Table 2-1. Also shown in Table 2-1 is the average countywide NMHC/NO $_{\rm X}$ emission ratio (adjusted to represent ppmC/ppm), which is calculated from annual emission estimates for Los Angeles County (Kinosian 1977). However, since all eight ambient monitoring stations were in the same large county, only the gridded emission NMHC/NO $_{\rm X}$ ratios were used in the following statistical analysis.

Table 2-2. LOS ANGELES GRIDDED EMISSION INVENTORY DATA

Monitoring Station	Site Description	County	6-9 a.m. NMHC(kg/hr)	6-9 a.m. NO _x (kg/hr)	NMHC/NOx*
Central Los Angeles	Center city, commercial	Los Angeles	172.0	133.1	3.71
East San Gabriel Valley	Center city, residential	Los Angeles	21.8	5.8	10.81
East San Fernando Valley	Center city, commercial	Los Angeles	23.7	22.2	3.08
Northwest Coastal	Center city, commercial	Los Angeles	9.66	47.4	6.04
West San Fernando Valley	Center city, residential	Los Angeles	176.7	81.1	6.27
Pomona-Walnut Valley	Center city, commercial	Los Angeles	66.8	27.2	7.07
Southeast	Center city, commercial	Los Angeles	211.8	82.3	7.39
West San Gabriel Valley	Center city, commercial-residential	Los Angeles	89.3	45.1	5.69

* Adjusted to represent ppmC/ppm

2.3 RATIO COMPARISON

A linear least-squares regression analysis (Bevington 1969) was carried out on the data in Table 2-1. Ambient $\mathrm{NMHC/NO}_{\mathrm{X}}$ ratios for each day in Los Angeles were compared with the corresponding gridded emission $\mathrm{NMHC/NO}_{\mathrm{X}}$ ratios. Only gridded emission data were analyzed since all eight monitoring stations were in the same county. The results are shown in Table 2-3.

There was no significant correlation for any of the 5 days in Los Angeles between NMHC/NO $_{\rm X}$ ratios calculated from ambient air monitoring data and NMHC/NO $_{\rm X}$ ratios calculated from the gridded emission inventory. The linear correlation coefficients ranged from -0.53 to 0.31, which are not significant for the number of data points analyzed. For seven data points to be significant at the 5 percent level, a correlation coefficient of 0.75 is necessary. The best fit linear regression lines through the data points are plotted for each day in Figure 2-1, with the emission ratio as the independent variable.

Although the correlations were not significant, it is interesting to examine the numerical values of the ratios for the downtown Los Angeles station, since this station might be used for an EKMA analysis over the entire Los Angeles area. For this station, the gridded emission NMHC/NO $_{\rm X}$ ratio was 3.71 and the countywide emission ratio was 3.51, as shown in Table 2-1. The averaged ambient monitoring NMHC/NO $_{\rm X}$ ratio for four high oxidant days at the Central Los Angeles station, as shown in Table 2-1, was 3.98, only 7 percent higher than the gridded emission ratio and 13 percent higher than the countywide emission ratio.

Table 2-3. LOS ANGELES NMHC/NO $_{\rm X}$ RATIO COMPARISON USING GRIDDED EMISSION DATA

Date	Number of Data Points	Correlation Coefficient	Slope, a	Intercept, b*
7/11/75	7	0.27	0.45	1.37
8/02/75	9	-0.35	-0.48	6.78
8/06/75	7	-0.53	-0.99	10.99
9/21/75	7	0.31	0.32	2.53
10/03/75	7	-0.30	-0.38	6.58

Linear regression equation, y=ax + b, where:

x = emission data ratio
y = ambient air ratio

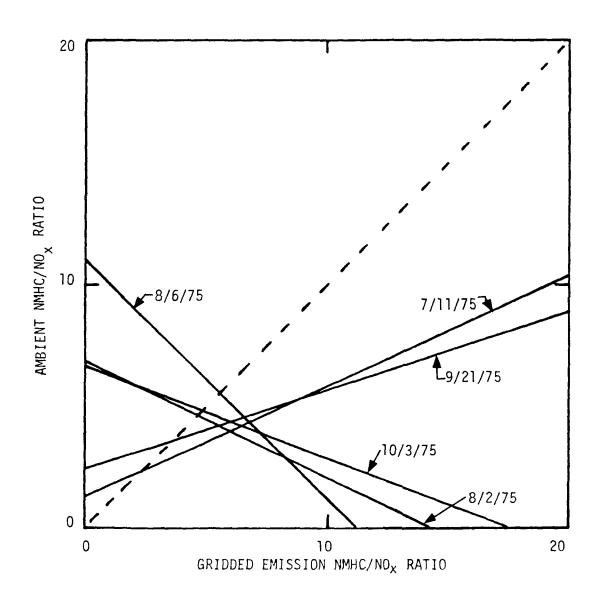


Figure 2-1. BEST-FIT REGRESSION LINES FOR FIVE HIGH-OXIDANT DAYS IN LOS ANGELES, COMPARING GRIDDED EMISSION NMHC/NO_X RATIOS WITH AMBIENT RATIOS. THE DASHED LINE REPRESENTS PERFECT THEORETICAL AGREEMENT.

3.0 SAN FRANCISCO DATA ANALYSIS

3.1 AMBIENT AIR MONITORING DATA

Ambient air data for San Francisco, California were obtained from the records of the San Francisco Bay Area Pollution Control District. Although both total hydrocarbon concentrations and methane concentrations are measured in the Bay Area, only total hydrocarbon concentration data are reduced and reported on a regular basis. Fortunately, the Association of Bay Area Governments (ABAG) had reduced NMHC data for a number of stations for one month, October 1976. Thus, the ambient monitoring data used in the analysis were based on the five highest oxidant days for October 1976. Total hydrocarbon concentrations in October were similar to those measured during the summer months of 1976. For the five highest oxidant days in October, 6-9 a.m. (local standard time) averaged concentrations were calculated for NMHC and NO_X . These values were used to calculate the ambient ratios of $NMHC/NO_x$. The ambient air monitoring data for each day in the San Francisco area are shown in the five tables in Appendix B.

An examination of the hourly concentration data revealed that the NO $_{\rm X}$ data were much more uniform than the NMHC data, as was found in Los Angeles. Again, it was decided to eliminate data from a station in which any hourly value of NMHC was 0.3 ppmC or less. Also, it was decided to eliminate a very anomalous NMHC/NO $_{\rm X}$ ratio of 38.57 found at the Gilroy station on October 7, 1976. The remaining 3-hour averaged ambient air NMHC/NO $_{\rm X}$ ratios are summarized in Table 3-1. Site descriptions of the San Francisco monitoring stations are listed in Table 3-2. The 6-9 a.m. ambient air monitoring NMHC/NO $_{\rm X}$ ratios for nine stations in the San Francisco area ranged from a low of 1.31 to a high of 7.65, in units of ppmC/ppm.

Table 3-1. SAN FRANCISCO NMHC/NO_X RATIO SUMMARY

Air	6-9 a	.m. Ambien	ıt Air Moni	6-9 a.m. Ambient Air Monitoring Ratio	io	6-9 a.m. Gridded	Countywide
Station	10/5/76	10/6/76	10/7/76	92/8/01 92/2/01	10/9/76	Ratio*	Ratio*
Potrero	1.82	ı	ı	ı	ı	2.16	4.08
San Jose	3.72	4.41	3.33	2.26	5.10	98.6	4.23
Sunnyvale	1	2.78	4.75	ı	2.85	9.26	4.23
Vallejo	2.33	4.70	4.21	1	1	8.14	3,85
Livermore	7.22	7.65	ŧ	80.9	5.73	10.41	4.54
Pittsburg	4.00	ı	3.53	ı	ı	1.12	2.79
San Rafael	ı	1.31	1.88	1.24	1.50	5.49	4.77
Santa Rosa	2.00	2.27	ı	ı	ı	7.56	4.43
San Francisco	4.38	4.93	-	2.11	•	11.64	4.08

*Adjusted to represent ppmC/ppm

3.2 EMISSION INVENTORY DATA

A gridded emission inventory for the San Francisco area for the year 1973 was provided by the Bay Area Air Pollution Control District (Robinson 1977). Emissions were distributed on a 2 kilometer x 2 kilometer square grid system, and were representative of a typical summer day in San Francisco. It should be noted that emissions for the month of October may be different than for a typical summer day. As was done in Los Angeles, the air monitoring stations were located on the grid system, and a weighted emission average was calculated using an inverse-square distance relationship among the four closest grid squares to the air monitoring location. Thus, the resulting emissions represented values for a 2 kilometer x 2 kilometer square centered on the air monitoring station. Since hourly gridded emissions were available, averaged emissions of $\mathrm{NO}_{\mathbf{x}}$ and NMHC were calculated for 6-9 a.m. (local standard time). The resulting gridded emission data and the corresponding adjusted NMHC/NO, ratios (in units of ppmC/ppm) are shown in Table 3-2. The gridded emission ratios ranged from a low of 1.12 to a high of 12.05.

Average countywide emission inventory data were obtained from the California Air Resources Board (Kinosian 1977). These emissions data represented hydrocarbon emissions in three different reactivity categories, as shown in Table 3-3. It was assumed in the analysis that Classes II and III represented NMHC emissions; since some compounds other than methane are included in Class I, this assumption may result in a somewhat lower estimate of NMHC emissions. The average countywide emissions for the San Francisco area and the resulting adjusted NMHC/NO $_{\rm X}$ ratios (in units of ppmC/ppm) are shown in Table 3-4. The countywide emission ratios ranged from a low of 2.79 to a high of 4.74. The gridded emission NMHC/NO $_{\rm X}$ ratios and the countywide emission ratios, with the ambient air monitoring ratios, are summarized in Table 3-1 for the San Francisco area.

Table 3-2. SAN FRANCISCO GRIDDED EMISSION INVENTORY DATA

	Site Description	County	6-9 a.m. NMHC (kg/hr)	6-9 a.m. NO _x (kg/hr)	NMHC/NO _X *
Potrero (Center city, industrial	San Francisco	86.4	115.6	2.16
San Jose (Center city, residential	Santa Clara	135.7	39.6	9.86
	Center city, commercial	Santa Clara	63.7	19.8	9.26
Vallejo (Center city, commercial	Solano	35.6	12.6	8.14
Livermore (Center city, commercial	Alameda	100.4	27.7	10.41
	Center city, commercial	Contra Costa	61.2	23.4	7.53
Pittsburg (Center city, commercial- industrial	Contra Costa	43.2	110.2	1.12
San Rafael (Center city, commercial- residential	Marin	55.1	28.8	5.49
Napa	Center city, commercial	Napa	69.1	16.5	12.05
Gilroy	Center city, commercial	Santa Clara	47.5	17.6	7.76
Santa Rosa	Center city, commercial	Sonoma	61.6	23.4	7.56
San Fran- cisco	Center city, commercial- industrial	San Francisco	298.8	73.8	11.64

*Adjusted to represent ppmC/ppm

Table 3-3. CALIFORNIA AIR RESOURCES BOARD HYDROCARBON REACTIVITY CLASSES

Class I (Low Reactivity)	Class II (Moderate Reactivity)	Class III (High Reactivity)
C1-C2 paraffins	Mono-tert-alkyl-benzenes	All other aromatic hydrocarbons
Acetylene	Cyclic ketones	All olefinic hydrocarbons (inclu-
Benzene	Alkyl acetates	ding partially halogenated)
Benzaldehyde	2-Nitropropane	Aliphatic aldehydes
Acetone	C ₂ + paraffins	Branched alkyl ketones
Methanol	Cycloparaffins	Cellosolve acetate
Tert-alkyl alcohols	N-alkyl ketones	Unsaturated ketones
Phenyl acetate	N-methyl pyrrolidone	Primary and secondary C2 alcohols
Methyl benzoate	N,N-dimethyl acetamide	Ofacetone alcohol
Ethyl Amines	Alkyl phenols*	Fthere
Dimethyl formamide	Methyl phthalates**	Cellosolves
Perhalogenated hydrocarbons		G1vc01s*
Partially halogenated paraffins		Co+ alkvl ohthalates**
Phthalic anhydride**		Other esters**
Phthalic acids**		Alcohol amines**
Acetonitr11e*		C.+ organic acids + di acid**
Acetic acid		S _ cid anhydrides**
Aromatic amines		Formin**
Hydroxyl amines		(Hexa methylene-tetramine)
Naphthalene*		Terpenic hydrocarbon
Chlorobenzenes*		Olefin oxides**
Nitrobenzenes*		
Pheno1*		

Reactivity data are either nonexistent or inconclusive, but conclusive data from similar compounds are available; therefore, rating is uncertain but reasonable.
**
Reactivity data are uncertain.

Table 3-4. SAN FRANCISCO COUNTYWIDE EMISSION INVENTORY DATA

County	NMHC (metric tons/day)	NO _x (metric tons/day)	NMHC/NO _X *
Alameda	163.3	103.4	4.54
Contra Costa	149.7	154.2	2.79
Marin	29.7	17.9	4.77
Napa	14.2	9.3	4.40
San Francisco	80.4	56.4	4.08
San Mateo	93.4	56.8	4.74
Santa Clara	179.6	122.5	4.23
Solano**	31.8	23.7	3.85
Sonoma**	34.3	22.2	4.43

* Adjusted to represent ppmC/ppm

**Emissions for portion of county in San Francisco Bay Area Air Basin

3.3 RATIO COMPARISON

A linear least-squares regression analysis (Bevington 1969) was conducted on the San Francisco data, comparing the ambient air monitoring NMHC/NO $_{\rm X}$ ratios with the gridded emission ratios in Table 3-1. A linear regression analysis was also conducted comparing the ambient air monitoring ratios with the countywide emission ratios; the ambient air ratios were averaged if two or more air monitoring stations were in the same county. The results are shown in Table 3-5.

Again, the correlations between NMHC/NO $_{\rm X}$ ratios calculated from ambient air monitoring data and NMHC/NO $_{\rm X}$ ratios calculated from emission inventory data were mostly not significant. However, the gridded emission inventory ratios provided somewhat better correlation than the countywide emission inventory ratios. The gridded emission correlation coefficients ranged from 0.35 to 0.89. As shown in Table 3-5, the ambient air NMHC/NO $_{\rm X}$ ratios on October 6, 1976 and the gridded emission ratios had a 0.74 correlation coefficient, which for seven data points is significant at the 5-percent level. Likewise, the ambient air ratios on October 9, 1976 and the gridded emission ratios had a correlation coefficient of 0.89, which for four data points is significant at the 10-percent level. The other 3 days did not have significant correlations with the gridded emission ratios. The regression lines for the gridded emission ratios are plotted for each day in Figure 3-1.

The comparison of the ambient air monitoring NMHC/NO $_{\rm X}$ ratios with the countywide emission ratios produced less significant correlations than with the gridded emission ratios. The countywide emission correlation coefficients ranged from -0.51 to 0.16, which are not significant for the number of data points analyzed. Regression lines for the countywide emission ratios are plotted in Figure 3-2.

Table 3-5. SAN FRANCISCO NMHC/NO $_{\rm X}$ RATIO COMPARISON

1. Using Gridded Emission Data

Date	Number of Data Points	Correlation Coefficient	Slope, a*	Intercept, b*
10/05/76	7	0.44	0.20	2.18
10/06/76	7	04	92.0	-2.80
10/01/76	2	0.35	0.11	2.82
10/08/76	4	0.44	0.36	-0.40
10/09/76	4	0.892	0.78	-3.07

2. Using Countywide Emission Data

Date	Number of Data Points	Correlation Coefficient	Slope, a	Intercept, b
10/05/76	9	0.16	0.48	1.81
10/06/76	9	-0.30	-2.02	12.81
10/07/76	4	-0.49	-0.62	5.83
10/08/76	4	0.10	0.17	-0.02
92/60/01	8	-0.51	-4.01	21.82

Linear regression equation, y = ax + b, where:
x = emission data ratio
y = ambient air ratio

'Significant at the 5% level

²Significant at the 10% level

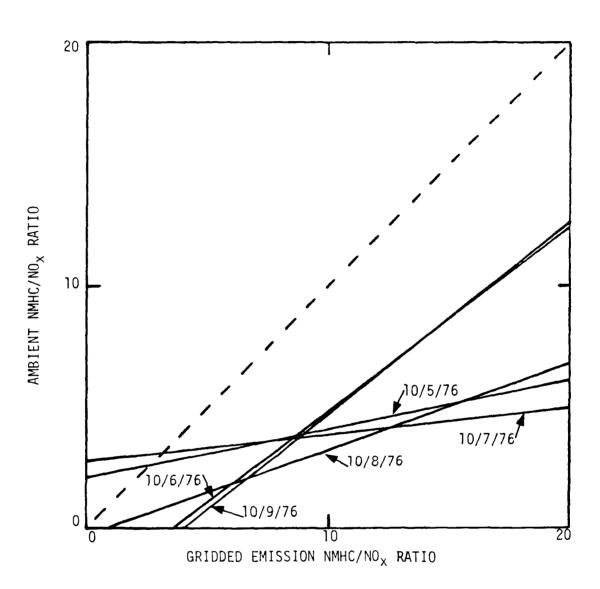
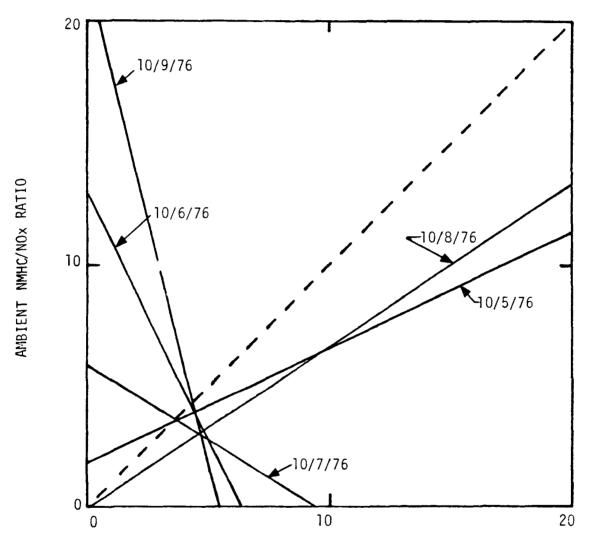


Figure 3-1. BEST-FIT REGRESSION LINES FOR FIVE HIGH-OXIDANT DAYS IN SAN FRANCISCO, COMPARING GRIDDED EMISSION NMHC/NO_X RATIOS WITH AMBIENT RATIOS. THE DASHED LINE REPRESENTS PERFECT THEORETICAL AGREEMENT.



COUNTYWIDE EMISSION NMHC /NO $_{\rm X}$ RATIO

Figure 3-2. BEST-FIT REGRESSION LINES FOR FIVE HIGH-OXIDANT DAYS IN SAN FRANCISCO, COMPARING COUNTYWIDE EMISSION NMHC/NO_X RATIOS WITH AMBIENT RATIOS. THE DASHED LINE REPRESENTS PERFECT THEORETICAL AGREEMENT

Although the correlations between ambient air and emission NMHC/NO $_{\rm X}$ ratios were not especially significant, it is interesting to examine the numerical values of the ratios for the downtown San Francisco station, since this station might be used for an EKMA analysis over the entire San Francisco area. For this station, the gridded emission NMHC/NO $_{\rm X}$ ratio was 11.64 and the countywide emission ratio was 4.08, as shown in Table 3-1. The averaged ambient air monitoring NMHC/NO $_{\rm X}$ ratio for three high-oxidant days at the downtown San Francisco station, as shown in Table 3-1, was 3.81, far lower than the gridded emission ratio but only 7 percent lower than the countywide emission ratio.

4.0 ST. LOUIS DATA ANALYSIS

4.1 AMBIENT AIR MONITORING DATA

Ambient air monitoring data for St. Louis, Missouri were obtained from the St. Louis Regional Air Pollution Study (Richter 1977). Ambient air data for 24 stations in the St. Louis area were examined to find the five highest oxidant days in 1976. For these five highest oxidant days, hourly concentration values of NMHC and NO $_{\rm X}$ were averaged over the time period 6-9 a.m. (local daylight time). The averaged NMHC and NO $_{\rm X}$ concentration values were used to calculate the NMHC/NO $_{\rm X}$ ratio for each station. The ambient air monitoring data results for each day in the St. Louis area are given in Appendix C.

An examination of the individual hourly averaged data points at each station revealed that the NO_{X} data were very uniform and the NMHC data were more uniform than the data from Los Angeles and San Francisco. Instead of rejecting NMHC values less than 0.3 ppmC, it was decided to eliminate all hourly averaged data which showed a change greater than 100 percent from hour to hour; 17 NMHC concentration values were eliminated by this procedure. Also, it was decided to eliminate a very anomalous NMHC/NO $_{\mathrm{X}}$ ratio of 48.5 reached at station 114 on September 24, 1976. The remaining NMHC/NO $_{\mathrm{X}}$ ratios were averaged if two or more stations were in the same county. The resulting ambient air averaged ratios for the St. Louis area are shown in Table 4-1. The 6-9 a.m. ambient air monitoring NMHC/NO $_{\mathrm{X}}$ ratios ranged from a low of 1.33 to a high of 15.17, in units of ppmC/ppm.

Table 4-1. ST. LOUIS NMHC/NO_x RATIO SUMMARY

	5−9	om omb	ient Air N	6-9 a.m Ambient Air Monitoring Ratio	Ratio	Countywide
County	8/31/76	9/2/16	9/5/76 9/24/76	10/1/76	10/12/76	Ratio*
Madison, Ill.	96.9	15.17	1	4.20	3.45	3.05
Monroe, Ill.	1.33	10.00	2.00	14.25	2.50	3.28
St. Clair, Ill.	8.07	7.95	3.69	5.19	ı	3.97
St. Charles, Mo.	1	ı	4.50	ı	ı	1.64
St. Louis, Mo. (total)	6.65	10.19	99.9	7.39	5.29	5.12
1. St. Louis City	8.02	10.34	5.52	7.40	7.14	98.6
2. Remainder of St. Louis County	4.38	9.94	8.18	7.36	3.44	4.08

*Adjusted to represent ppmC/ppm

4. ENISSION INVENTORY DATA

Due to the unavailability of a detailed gridded emission inventory for the St. Louis area, only annual averaged countywide emissions were used in the data analysis. The countywide emissions were obtained from the National Emission Data System (NEDS). The emissions from one county, St. Louis County, were broken down into emissions from St. Louis City and emissions from the remainder of St. Louis County. The NEDS hydrocarbon emissions were given as total hydrocarbons; it was assumed that these emissions represented mainly NMHC emissions. The emissions for each county and the resulting adjusted NMHC/NO $_{\rm X}$ ratios (in units of ppmC/ppm) for the St. Louis area are given in Table 4-2. The countywide emission ratios ranged from a low of 1.64 to a high of 9.86. The countywide exist ion NMHC/NO $_{\rm X}$ ratios are compared with the ambient air monitoring ratios in Table 4-1.

Table 4-2. ST. LOUIS COUNTYWIDE EMISSION INVENTORY DATA

County	NMHC (metric tons/day)	NO _x (metric tons/day)	NMHC/NO _x *
Madison, Ill.	174.7	165.0	3.05
Mon: oe, Ill.	4.8	4.2	3.28
St. Clair, 111.	64.6	46.9	3.97
St. Charles, Mo.	29.2	51.1	1.64
St. Louis, Mo. (total)	489.3	274.3	5.12
1. St. Louis City	7.171	50.0	98.6
2. Remainder of St. Louis County	317.6	224.3	4.08

* Adjusted to represent ppmC/ppm

4.3 RATIO COMPARISON

A linear regression analysis (Bevington 1969) was conducted on the St. Louis data in Table 4-1, comparing the county-averaged ambient air monitoring NMHC/NO $_{\rm X}$ ratios with the countywide emission ratios. The ratios for St. Louis City and the remainder of St. Louis County were treated as separate data points. The results of the regression analysis for St. Louis are shown in Table 4-3.

Except for one day, there was no significant correlation between the NMHC/NO $_{\rm X}$ ratios calculated from ambient air monitoring data and the NMHC/NO $_{\rm X}$ ratios calculated from the countywide emission inventory data. However, on October 12, 1976, the correlation coefficient was 0.98, which is significant at the 2-percent level. It is likely that this corrrelation was fortuitous, since only four data points were involved in the analysis. The regression lines for the countywide emission ratios are plotted in Figure 4-1.

Although the correlations between ambient air and emission NMHC/NO $_{\rm X}$ ratios were not especially significant, it is interesting to examine the numerical values of the ratios for St. Louis City, since these ratios might be used for an EKMA analysis over the entire St. Louis area. For St. Louis city, the countywide NMHC/NO $_{\rm X}$ emission ratio was 9.86, as shown in Table 4-1. The averaged ambient air monitoring NMHC/NO $_{\rm X}$ ratio for five high oxidant days in the St. Louis city area, as shown in Table 4-1, was 7.68, or 22 percent lower than the countywide emission ratio.

Table 4-3. ST. LOUIS NMHC/NOX RATIO COMPARISON USING COUNTYWIDE EMISSION DATA

Date	Number of Data Points	Correlation Coefficient	Slope, a*	Intercept, b*
8/31/76	5	0.46	0.47	3.47
9/02/16	2	-0.19	-0.18	11.55
9/24/76	2	0.16	0.09	4.97
10/01/76	2	-0.07	-0.09	8.13
10/12/76	4	0.98	0.62	0.98

*Linear regression equation, y=ax + b, where: x = emission data ratio y = ambient data ratio

¹Significant at the 2% level

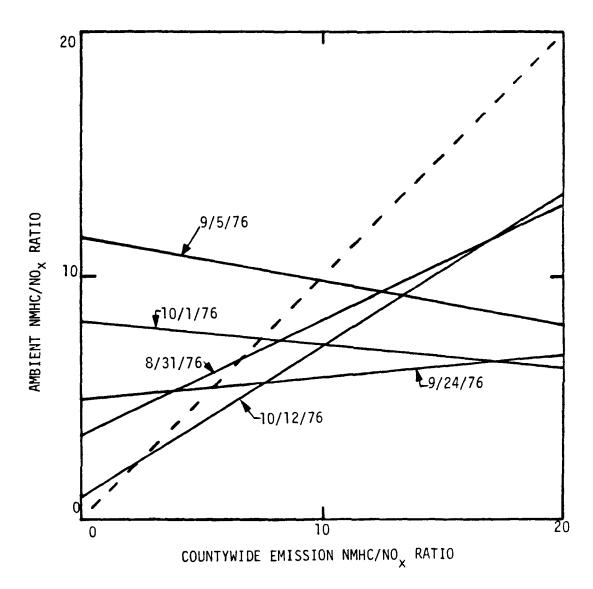


Figure 4-1. BEST-FIT REGRESSION LINES FOR FIVE HIGH-OXIDANT DAYS IN ST. LOUIS, COMPARING COUNTYWIDE EMISSION NMHC/NO_X RATIOS WITH AMBIENT RATIOS. THE DASHED LINE REPRESENTS PERFECT THEORETICAL AGREEMENT

5.0 DISCUSSION OF RESULTS

5.1 CORRELATIONS VERSUS NUMERICAL VALUES

The relationship between ambient air monitoring NMHC/NO $_{\rm X}$ ratios and emission inventory NMHC/NO $_{\rm X}$ ratios was tested by applying a linear regression analysis to ambient air and emission data from a number of air monitoring stations in a region. The relationship was tested for each of 5 high-oxidant days in each of 3 locations. The basic result found in all 3 locations - Los Angeles, San Francisco, and St. Louis - was that there was little correlation between NMHC/NO $_{\rm X}$ ratios calculated from ambient air monitoring data and the corresponding NMHC/NO $_{\rm X}$ ratios calculated from emission inventory data. There was some improvement in correlation when gridded emission ratios were used instead of countywide emission ratios in the San Francisco area, but the correlations in general were not significant.

However, since the EKMA method normally requires ambient air monitoring data from the main downtown urban center in a region, a brief analysis was made comparing the numerical values of averaged ambient NMHC/NO ratios with emission ratios from the central downtown areas of the 3 locations. The results are shown in Table 5-1. The gridded emission NMHC/NO ratio compared well with the ambient ratio in Los Angeles but poorly in San Francisco (a gridded emission inventory for St. Louis was unavailable). The countywide emission NMHC/NO ratio compared reasonably well with the ambient ratio in each of the 3 locations.

It is statistically possible to have poor correlation yet have numerical values be relatively close. However, it appears somewhat fortuitous that the three countywide emission NMHC/NO $_{\rm v}$

Table 5-1. AVERAGED AMBIENT AIR NMHC/NOX RATIOS COMPARED WITH EMISSION RATIOS IN THE CENTRAL DOWNTOWN AREA (units in ppmC/ppm)

Location	Averaged Ambient Air NMHC/NO _X	Gridded Emissions NMHC/NO x	Countywide Emission NMHC/NO
Los Angeles	3.98	3.71	3.51
San Francisco	3.81	11.64	4.08
St. Louis	7.68	(no data)	9.86*
	1		

^{*} St.Louis City only. Entire St.Louis County ratio is 5.12.

ratios matched up well with averaged ambient air ratios from the central downtown areas. For one reason, Los Angeles County has many sources over a very large area, 10,534 sq.km (4,069 sq.mi), and it seems unlikely that one air monitoring station could be representative of the entire county. Also, the gridded emission ratio for the San Francisco station, which should be more representative of the station during stagnant conditions than the countywide ratio, was 3 times greater than the ambient air ratio. Without additional work on this relationship for a larger number of cities, it cannot be recommended to use countywide emission NMHC/NO $_{\chi}$ ratios in lieu of ambient air ratios in the EKMA method.

5.2 REASONS FOR RATIO DIFFERENCES

If emissions from one area were completely responsible for the ambient pollutant concentrations in that area, then ambient air and emission NMHC/NO $_{\rm X}$ ratios should compare favorably. However, little correlation was found in 3 different locations between NMHC/NO $_{\rm X}$ ratios calculated from ambient air monitoring data and the corresponding NMHC/NO $_{\rm X}$ ratios calculated from emission inventory data. There are a number of possible reasons for this discrepancy, which are discussed below in order of importance.

5.2.1 METEOROLOGICAL FACTORS

Probably the most important reason for the discrepancy between ambient air $\mathrm{NMHC/NO_X}$ ratios and emission $\mathrm{NMHC/NO_X}$ ratios is the great influence of meteorology on ambient pollutant concentrations. The relationship between emission rates and antient air concentrations is quite complex, depending on many meteorological parameters such as wind speed and direction, atmospheric stability, temperature inversion heights, and horizontal and vertical diffusion rates.

The day-to-day variations in wind can advect pollutants from different regions to the location of an air monitoring station. As an example of possible variations, as shown in Table 4-1, ambient air monitoring ratios ranged from 1.3 to 14.3 during high oxidant days in one location. Even in locations which are dominated by automobile emissions, differing wind conditions on a given day could advect emissions from a major freeway to an air monitoring location, and these freeway emissions would have different NMHC/NO $_{\rm X}$ ratios than traffic emissions from surface streets. Since NMHC traffic emissions decrease

with car speed while ${\rm NO_X}$ emissions increase with speed, freeway emission NMHC/NO_X ratios may be lower than surface street ratios by a factor of two.

Also important is the transport of background pollutants from one location to another. Most air quality simulation models, which try to relate emissions to ambient air concentrations, are very sensitive to the effect of initial or background concentrations. Even the very simple linear rollback model (deNevers and Morris 1975), which assumes that pollutant concentrations are directly proportional to emission rates, considers the effect of background pollutants. Background concentrations above an inversion layer can also be entrained into a mixing layer if the inversion base rises.

5.2.2 ACCURACY OF EMISSION INVENTORY DATA

Another major reason for the discrepancy between ambient air $\mathsf{NMHC/NO}_X$ ratios and emission ratios is probably the lack of detail in emission inventories. Certainly annual averaged countywide emission estimates cannot be assumed to be representative of a specific day with high oxidant levels. Even detailed gridded emission inventories are normally representative only of a typical summer day and do not reflect the actual day-to-day variations which occur in a particular location.

Most emission inventories are also somewhat inaccurate or omit certain types of sources. For example, natural sources of hydrocarbons are normally emitted from most emission inventories. Also, fugitive sources of hydrocarbons, e.g., from pumps and valves in the oil and gas industries, may be omitted in inventories. The NO_{X} emission inventory, as well as the organic inventory, may be inaccurate; for example, the percentage of cold starts in a location greatly influences automobile NO_{X} emissions. However,

even if emission inventories were perfectly accurate, ambient and emission NMHC/NO $_{\rm X}$ ratios would probably still not correspond due to the influence of meteorological factors.

5.2.3 ELEVATED POINT SOURCES

Another minor reason why ambient air NMHC/NO $_{\rm X}$ ratios do not correspond to emission ratios is the fact that large elevated point sources near an air monitoring site may not impact that site significantly, since the site is at ground level while the elevated emissions may be above an inversion level. For example, in the San Francisco data analysis, the Pittsburg air monitoring station was located near a large power plant with considerable NO $_{\rm X}$ emissions. Thus, the NMHC/NO $_{\rm X}$ ratio calculated from the gridded emission inventory data was fairly low, 0.39. However, the ambient air monitoring NMHC/NO $_{\rm X}$ ratios for Pittsburg were 4.00 and 3.53, indicating that the elevated NO $_{\rm X}$ emissions were not impacting the air monitoring site significantly.

5.2.4 OTHER FACTORS

Another possible reason for the discrepancy between ambient ratios and emission ratios is the inaccuracy of the ambient air monitoring data. Nonmethane hydrocarbon concentrations are normally less reliable than NO_{X} concentrations, since NMHC concentrations are derived by subtracting measured methane concentrations from measured total hydrocarbon concentrations. Also, the flame ionization detector (FID) normally used for hydrocarbon measurement has different sensitivity to different types of hydrocarbons. Likewise, NO_{X} measurements may vary in accuracy depending on the measurement technique used. In the data analysis, all hourly NMHC concentrations were examined for uniformity, and any very low or obviously anomalous values were eliminated from the data set. However, in general, the NMHC concentration values were less consistent than the NO_{X} ambient monitoring values.

Another possible explanation for the lack of correlation between ambient $\mathrm{NMHC/NO_X}$ ratios and emission ratios is the role of photochemical reactions in changing the ambient concentrations. Both nonmethane hydrocarbons and oxides of nitrogen react significantly in photochemical smog formation. However, since the ambient air monitoring data are taken between the hours of 6 and 9 a.m., when solar radiation is low, the effect of photochemical reactions at this time on ambient concentrations should be negligible.

Since the significance of the correlation coefficient is dependent on the number of data points, the lack of correlation cannot be attributed to the small number of data points (limited by the number of monitoring stations) which were used in each analysis. However, a very restricted range of variables will normally lead to poor correlation. In most cases, this was not important, since the NMHC/NO $_{\rm X}$ ratios ranged over a factor of ten. However, the countywide emission NMHC/NO $_{\rm X}$ ratios in the San Francisco area ranged only from 2.8 to 4.5, and thus this comparison might be expected to have poor correlation.

6.0 REFERENCES

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APPENDIX A LOS ANGELES AMBIENT AIR MONITORING DATA

Table A-1. LOS ANGELES AMBIENT MONITORING DATA - 7/11/75

Table A-2. LOS ANGELES AMBIENT MONITORING DATA - 8/02/75

Monitoring Station	County	Maximum 0_3 (ppm)	6-9 a.m. NMHC(ppmC)	6-9 a.m. NO _X (ppm)	NMHC/NO _X
Central Los Angeles	Los Angeles	0.18	0.37	0.09	4.11
East San Gabriel Valley	Los Angeles	0.31	0.30	0.23	1.30
East San Fernando Valley	Los Angeles	0.21	0.57	0.08	7.13
Northwest Coastal	Los Angeles	0.09	0.10	0.02	5.00
West San Fernando Valley	Los Angeles	0.22	0.47	0.24	1.96
Pomona - Walnut Valley	Los Angeles	0.33	0.53	0.31	1.71
Southeast	Los Angeles	0.17	0.70	0.10	7.00
West San Gabriel Valley	Los Angeles	0.30	0.50	0.17	2.94

Table A-3. LOS ANGELES AMBIENT MONITORING DATA - 8/06/75

Monitoring Station	County	Maximum O ₃ (ppm)	6-9 a.m. NMHC(ppmC)	6-9 a.m. NO _X (ppm)	NMHC/NO _X
Central Los Angeles	Los Angeles	0.12	,	l	,
East San Gabriel Valley	Los Angeles	0.32	1.07	0.33	3.24
East San Fernando Valley	Los Angeles	0.16	1.33	0.10	13.30
Northwest Coastal	Los Angeles	0.08	0.47	0.36	1.31
West San Fernando Valley	Los Angeles	0.22	0.50	0.26	1.92
Pomona - Walnut Valley	Los Angeles	0.27	0.40	0.32	1.25
Southeast	Los Angeles	0.15	1.37	0.20	6.85
West San Gabriel Valley	Los Angeles	0.24	0.67	0.22	3.05

Table A-4. LOS ANGELES AMBIENT MONITORING DATA - 9/21/75

Monitoring Station	County	Maximum O ₃ (ppm)	6-9 a.m. NMHC(ppmC)	6-9 a.m. NO _X (ppm)	NMHC/NO _X
Central Los Angeles	Los Angeles	0.16	0.77	0.18	4.28
East San Gabriel Valley	Los Angeles	0.31	09.0	0.17	3.53
East San Fernando Valley	Los Angeles	ı	0.83	0.28	2.96
Northwest Coastal	Los Angeles	0.10	0.83	0.15	5.53
West San Fernando Valley	Los Angeles	0.22	0.57	0.24	2.38
Pomona - Walnut Valley	Los Angeles	0.29	0.47	0.17	2.76
Southeast	Los Angeles	0.15	1.10	0.16	6.88
West San Gabriel Valley	Los Angeles	0.26	0.50	0.09	5.56

Table A-5. LOS ANGELES AMBLENT MONITORING DATA - 10/03/75

Monitoring Station	County	0 ³ (ppm)	6-9 a.m. NMHC(ppmC)	6-9 a.m. NO _x (ppm)	NMHC/NO _x
Central Los Angeles	Los Angeles	0.18	1.27	0.37	3.43
East San Gabriel Valley	Los Angeles	0.31	ı	ı	l
East San Fernando Valley	Los Angeles	0.15	2.70	0.33	8.18
Northwest Coastal	Los Angeles	0.13	0.87	0.24	3.63
West San Fernando Valley	Los Angeles	0.11	1.00	0.32	3.13
Pomona - Walnut Valley	Los Angeles	0.19	0.87	0.21	4.14
Southeast	Los Angeles	0.24	2.77	0.44	6.30
West San Gabriel Valley	Los Angeles	0.22	0.77	0.33	2.33

APPENDIX B SAN FRANCISCO AMBIENT AIR MONITORING DATA

Table B-1. SAN FRANCISCO AMBIENT MONITORING DATA - 10/05/76

Monitoring Station	County	Maximum O ₃ (ppm)	6-9 a.m. NMHC(ppmC)	6-9 a.m. NO _x (ppm)	NMHC/NO _X
Potrero	San Francisco	ı	0.40	0.22	1.82
San Jose	Santa Clara	0.10	0.93	0.25	3.72
Sunnyvale	Santa Clara	0.11	0.13	0.26	0.50
Vallejo	Solano	0.10	1.33	0.57	2.33
Livermore	Alameda	0.07	1.30	0.18	7.22
Richmond	Contra Costa	0.05	00.0	0.12	00.0
Pittsburg	Contra Costa	0.09	09.0	0.15	4.00
San Rafael	Marin	0.07	0.30	0.40	0.75
Napa	Napa	0.05	0.10	0.08	1.25
Gilroy	Santa Clara	0.14	0.20	0.08	2.50
Santa Rosa	Sonoma	0.04	0.40	0.20	2.00
San Francisco	San Francisco	0.04	0.70	0.16	4.38

Table B-2. SAN FRANCISCO AMBIENT MONITORING DATA - 10/06/76

Monitoring Station	County	Maximum O ₃ (ppm)	6-9 a.m. NMHC(ppmC)	6-9 a.m. NO _X (ppm)	NMHC/NO _X
Potrero	San Francisco	•	ŧ	•	•
San Jose	Santa Clara	0.10	0.97	0.22	4.41
Sunnyvale	Santa Clara	0.09	1.00	0.36	2.78
Vallejo	Solano	0.08	2.07	0.44	4.70
Livermore	Alameda	0.09	1.30	0.17	7.65
Richmond	Contra Costa	0.11	00.0	0.13	00.00
Pittsburg	Contra Costa	0.10	0.10	0.10	1.00
San Rafael	Marin	90.0	0.67	0.51	1.31
Napa	Napa	90.0	0.07	0.09	0.78
Gilroy	Santa Clara	0.10	0.30	0.08	3.75
Santa Rosa	Sonoma	0.07	0.50	0.22	2.27
San Francisco	San Francisco	0.13	1.43	0.29	4.93

Table B-3. SAN FRANCISCO AMBIENT MONITORING DATA - 10/07/76

County (ppm) Maximum $6-9$ a.m. $6-9$ a.m. 0_3 (ppm) NMHC(ppmC) NO_x	Francisco	ta Clara 0.15 0.70 0.21 3.33	ta Clara 0.11 0.95 0.20 4.75	ano 0.13 0.80 0.19 4.21	neda 0.12	tra Costa 0.10 0.00 0.08 0.00	tra Costa 0.14 0.53 0.15 3.53	in 0.10 0.47 0.25 1.88	0.10 0.27 0.09 3.00	ta Clara 0.21 2.70 0.07 38.57	oma 0.07 0.30 0.20 1.50	Examples 0.10 0.17 0.10 1.70
County	San Francisco	Santa Clara	Santa Clara	Solano	Alameda	Contra Costa	Contra Costa	Marin	Napa	Santa Clara	Sonoma	Can Evancieco
												Confined Res

Table B-4. SAN FRANCISCO AMBIENT MONITORING DATA - 10/08/76

Monitoring Station	County	Maximum O ₃ (ppm)	6-9 a.m. NMHC(ppmC)	6-9 a.m. NO _X (ppm)	NMHC/NO _X
Potrero	San Francisco	1	1	ı	ı
San Jose	Santa Clara	0.10	0.43	0.19	2.26
Sunnyvale	Santa Clara	0.11	0.30	0.13	2.31
Vallejo	Solano	0.08	0.17	0.08	2.13
Livermore	Alameda	0.10	0.73	0.12	6.08
Richmond	Contra Costa	90.0	0.00	0.16	0.00
Pittsburg	Contra Costa	0.10	0.27	0.12	2.25
San Rafael	Marin	0.07	0.47	0.38	1.24
Napa	Napa	90.0	0.27	0.08	3.38
Gilroy	Santa Clara	0.13	0.20	90.0	3.33
Santa Rosa	Sonoma	0.05	0.17	0.10	1.70
San Francisco	San Francisco	0.02	0.57	0.27	2.11

Table B-5. SAN FRANCISCO AMBIENT MONITORING DATA - 10/09/76

Monitoring Station	County	Maximum O ₃ (ppm)	6-9 a.m. NMHC(ppmC)	6-9 a.m. NO _x (ppm)	NMHC/NO _X
Potrero	San Francisco	1	•	•	1
San Jose	Santa Clara	0.15	1.07	0.21	5.10
Sunnyvale	Santa Clara	0.11	0.37	0.13	2.85
Vallejo	Solano	0.18	١	ı	ı
Livermore	Alameda	0.10	0.63	0.11	5.73
Richmond	Contra Costa	90.0	0.00	0.03	0.00
Pittsburg	Contra Costa	0.15	0.73	0.15	4.87
San Rafael	Marin	0.07	0.33	0.22	1.50
Napa	Napa	0.11	0.17	0.08	2.13
Gilroy	Santa Clara	0.18	0.10	0.07	1.43
Santa Rosa	Sonoma	0.04	1	,	į
San Francisco	San Francisco	0.02	00.0	0.04	00.00

APPENDIX C

ST. LOUIS AMBIENT AIR MONITORING DATA

Table C-1. ST. LOUIS AMBIENT MONITORING DATA - 8/31/76

Monitoring Station	County	Maximum O ₃ (ppm)	6-9 a.m. NMHC(ppmC)	6-9 a.m. NO _X (ppm)	NMHC/NO _x
101	St. Louis (city), Mo.	0.08	0.80	0.12	6.67
102	St. Louis (city), Mo.	0.0	1.55	0.18	8.61
103	Madison, Ill.	0.09	0.54	0.14	3.86
104	St. Clair, Ill.	90.0	1.08	0.11	9.85
105	St. Louis (city), Mo.	0.08	0.93	0.11	8.45
106	St. Louis (city), Mo.	0.28	1.32	0.09	14.67
107	St. Louis (city), Mo.	0.02	1.07	0.13	8.23
108	Madison, Ill.	0.09	0.87	0.14	6.21
109	St. Clair, Ill.	0.10	0.34	0.07	4.86
110	St. Clair, 111.	0.09	0.37	0.05	7.40
ווו	St. Louis (city), Mo.	0.08	1.14	0.14	8.14
112	St. Louis (county), Mo.	0.08	1.14	0.13	8.77
113	St. Louis (county), Mo.	0.10	0.74	0.16	4.63
114	St. Louis (county), Mo.	0.03	0.54	0.12	4.50
115	Madison, Ill.	0.11	•	ı	1
116	Madison, Ill.	0.08	0.33	0.04	8.25
117	St. Clair, 111.	0.08	0.21	0.03	7.00
118	Monroe, Ill.	0.00	0.04	0.03	1.33
119	St. Louis (county), Mo.	0.08	0.32	0.08	4.00
120	St. Louis (county), Mo.	0.10	0.87	0.15	5.80
121	St. Louis (county), Mo.	0.0	1	ı	ı
122	Madison, III.	0.13	0.38	0.04	9.50
124	Monroe, 111.	ı	•	1	ı
125	St. Charles, Mo.	0.09	ı	•	1

Table C-2. ST. LOUIS AMBIENT MONITORING DATA - 9/05/76

Monitoring Station	County	Maximum O ₃ (ppm)	6-9 a.m. NMHC(ppmC)	6-9 a.m. NO _X (ppm)	NMHC/NO _x
101	St. Louis (city), Mo.	0.08	ı	ı	,
102	St. Louis (city), Mo.	0.08	0.47	90.0	7.83
103	Madison, Ill.	0.26	0.37	0.03	12.33
104	St. Clair, 111.	90.0	0.43	0.05	8.60
105	St. Louis (city), Mo.	0.08	0.31	0.05	6.20
106	St. Louis (city), Mo.	0.08	06.0	0.07	12.86
107	St. Louis (city), Mo.	0.07	0.71	0.05	14.20
108	Madison, Ill.	0.08	0.54	0.03	18.00
109	St. Clair, III.	0.08	0.46	0.07	6.57
110	St. Clair, Ill.	0.08	0.52	90.0	8.67
111	St. Louis (city), Mo.	0.08	0.53	0.05	10.60
112	St. Louis (county), Mo.	0.08	0.37	0.04	9.25
113	St. Louis (county), Mo.	0.10	ı	1	ı
114	St. Louis (county), Mo.	0.10	1.49	0.02	74.50
115	Madison, Ill.	ı	1	ı	1
911	Madison, Ill.	0.02	ı	ı	1
117	St. Clair, Ill.	0.08	ı	1	1
118	Monroe, Ill.	0.11	0.40	0.04	10.00
119	St. Louis (county), Mo.	0.08	0.35	0.04	8.75
120	St. Louis (county), Mo.	60.0	0.71	90.0	11.83
121	St. Louis (county), Mo.	0.08	ı	,	ı
122	Madison, 111.	0.08	ŀ	,	1
124	Monroe, Ill.	0.08	0.07	0.01	7.90
125	St. Charles, Mo.	0.10	1	1	,

Table C-3. ST. LOUIS AMBIENT MONITORING DATA - 9/24/76

Monitoring Station	County	Maximum 0 ₃ (กก.ศ.)	6-9 a.m. NMHC(ppnC)	6-9 a.m. NO _x (ppm)	NMHC/NO _x
101	St. Louis (city), Mo.	0.05	0.61	90.0	10.17
102	St. Louis (city), Mo.	90.0	0.10	0.04	2.50
103	Madison, Ill.	0.25	ı	ı	ı
104	St. Clair, Ill.	0.05	0.47	0.10	4.70
105	St. Louis (city), Mo.	0.07	0.20	0.05	4.00
106	St. Louis (city), Mo.	90.0	1.04	0.09	11.56
107	St. Louis (city), Mo.	0.04	1	ı	1
108	Madison, Ill.	90.0	1.13	0.03	37.67
109	St. Clair, 111.	0.07	0.04	0.02	2.00
110	St. Clair, Ill.	0.08	0.08	0.03	2.67
111	St. Louis (city), Mo.	0.07	0.27	0.05	5.40
112	St. Louis (county), Mo.	0.05	0.49	0.05	9.80
113	St. Louis (county), Mo.	0.05	1	ı	1
114	St. Louis (county), Mo.	,	0.97	0.02	48.50
115	Madison, Ill.	90.0	1	ı	1
116	Madison, Ill.	90.0	1	ı	ı
117	St. Clair, Ill.	0.07	1	ı	ı
118	Monroe, 111.	0.09	1	ı	ı
119	St. Louis (county), Mo.	0.07	0.20	0.04	5.00
120	St. Louis (county), Mo.	ı	0.39	0.04	9.75
121	St. Louis (county), Mo.	0.08	1	ı	ı
122	Madison, Ill.	90.0	0.03	0.003	10.00
124	Monroe, Ill.	0.07	0.05	0.01	5.00
125	St. Charles, Mo.	0.11	0.09	0.02	4.50

Table C-4. ST. LOUIS AMBIENT MONITORING DATA - 10/01/76

NMHC/NO _x	5	5.68	5.39	ı	10.78	8.53	7.53	5.56	00.00	6.88	4.48	5.42	ı	6.67	3.50	2.33	3.50	22.00	10.00	1	1	1	14.25	1
6-9 a.m. NO _x (ppm)	ı	0.34	0.18	ı	0.18	0.17	0.30	0.27	0.15	0.08	0.23	0.12	ı	0.21	0.10	90.0	0.04	0.03	0.09	ı	•	1	0.04	1
6-9 a.m. NMHC(ppmC)	1	1.93	0.97	ı	1.94	1.45	2.26	1.50	00.00	0.55	1.03	0.65	ı	1.40	0.35	0.14	0.14	99.0	06.0	ı	ı	ı	0.57	ı
Maximum O ₃ (ppm)	0.24	0.24	0.20	0.20	10.0	0.22	0.21	0.15	0.18	0.22	0.20	0.14	0.20	0.16	0.16	0.14	0.14	0.24	0.12	ı	0.10	ı	0.08	0.08
County	St. Louis (city), Mo.	St. Louis (city), Mo.	Madison, 111.	St. Clair, 111.	St. Louis (city), Mo.	St. Louis (city), Mo.	St. Louis (city), Mo.	Madison, 111.	St. Clair, 111.	St. Clair, Ill.	St. Louis (city), Mo.	St. Louis (county), Mo.	St. Louis (county), Mo.	St. Louis (county), Mo.	Madison, 111.	Madison, 111.	St. Clair, Ill.	Monroe, Ill.	St. Louis (county), Mo.	St. Louis (county), Mo.	St. Louis (county), Mo.	Madison, Ill.	Monroe, Ill.	St. Charles, Mo.
Monitoring Station	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	124	125

Table C-5. ST. LOUIS AMBIENT MONITORING DATA - 10/12/76

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·	completing)				
1. REPORT NO. EPA-450/3-78-026	2.	3. RECIPIENT'S ACCESSION NO.			
4. TITLE AND SUBTITLE COMPARISON OF AMBIENT NMHC RATIOS CALCULATED FROM EMI	C/NO RATIOS WITH NMHC/NO	5 REPORT DATE June 1978			
RATIOS CALCULATED FROM EMI	SSION INVENTORIES ^	6. PERFORMING ORGANIZATION CODE			
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.			
Peter J. Drivas					
9. PERFORMING ORGANIZATION NAME A Pacific Environmental Serv		10 PROGRAM ELEMENT NO.			
1930 14th Street	00404	11. CONTRACT/GRANT NO			
Santa Monica, California 9	U4U4	68-02-2583 Assignment No. 4			
12. SPONSORING AGENCY NAME AND ACU.S. Environmental Protect	ion Agency	13 TYPE OF REPORT AND PERIOD COVERED Final			
Office of Air and Waste Ma Office of Air Quality Plan Research Triangle Park, No	14. SPONSORING AGENCY CODE				

15. SUPPLEMENTARY NOTES

16 ABSTRACT

The Empirical Kinetic Modeling Approach (EKMA) requires the determination of the ratio of nonmethane hydrocarbons (NMHC) to oxides of nitrogen (NO $_{\rm X}$). Three geographic locations were used in analyzing the differences between NMHC/NO $_{\rm X}$ ratios calculated from emission inventory data and those from ambient monitoring data. The three locations were: Los Angeles, California; San Francisco, California; and St. Louis, Missouri.

The relationship between ambient monitoring NMHC/NO $_{\rm X}$ ratios and emission inventory NMHC/NO $_{\rm X}$ ratios was tested by applying a linear regression analysis to air quality and emission data from a number of monitoring stations in each region. The relationship was tested for each of five high-oxidant days in each of the three locations. The basic result found in all three locations was that there was little correlation between NMHC/NO $_{\rm X}$ ratios calculated from ambient monitoring data and the corresponding NMHC/NO $_{\rm X}$ ratios calculated from emission inventory data

17.	KEY WO	ORDS AND DOCUMENT ANALYSIS	
a	DESCRIPTORS	b IDENTIFIERS/OPEN ENDED TERMS	COSATI Field/Group
Air Polluti Hydrocarbor Nitrogen Ox Ozone	ıs		4B 7A 13B
18. DISTRIBUTIO	SE TO PUBLIC	19 SECURITY CLASS (This Report) UNCLASSIFIED 20 SECURITY CLASS (This page) UNCLASSIFIED	21 NO. OF PAGES 58 22 PRICE