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A REVIEW OF NMOC, NO_x AND NMOC/NO_x RATIOS MEASURED IN 1984 AND 1985

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A REVIEW OF NMOC, NO_x AND NMOC/NO_x RATIOS MEASURED IN 1984 AND 1985

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1.0 Introduction

During the summers of 1984 and 1985, morning (6-9am) measurements of ambient nonmethane organic compounds (NMOC) were collected at 22 and 19 urban sites, respectively. The data were collected by State and local agencies which contributed grant funds and personnel. The EPA managed the analysis and provided NMOC sampling equipment. The method of determining NMOC levels was the cryogenic preconcentration direct flame-ionization detection (PDFID) described by McElroy et al.[1] Data were collected to provide input values for the Empirical Kinetic Modeling Approach (EKMA),[2-6] a computer program which estimates hydrocarbon control requirements necessary to attain the National Ambient Air Quality Standard (NAAQS) for ozone. One of the key inputs to EKMA is the Nonmethane Organic Compound/Nitrogen Oxides ($NMOC/NO_x$) ratio. Thus, a collocated NO_x instrument was operated at each NMOC site.

Generally, NMOC sites were located in an attempt to determine "city-wide" values. However, some sites, such as Houston, were located in industrial areas while others are located in small urban areas which have a large industrial component. The degree to which each site reflects city-wide conditions affects conclusions regarding all the variables considered in this report.

This report is broken into chapters which discuss various components of the data base. Each chapter will describe results for 1984 and 1985 and then compare statistics from the two years to indicate changes if any. Chapter 2 will discuss NMOC data. The NO_x results from continuous monitors collocated with the NMOC samplers are described in Chapter 3. Chapter 4 outlines results for the $NMOC/NO_x$ ratios. Carbon Bond splits used in the Carbon Bond-3 mechanism (CB-3) of EKMA are discussed in Chapter 5. Chapter 6 describes estimates of mobile source fractions, while findings regarding biogenic NMOC data are outlined in Chapter 7. In Chapter 8, a case study is presented which compares reductions in NMOC with changes in ozone levels. Overall conclusions are found in Chapter 9 and are briefly summarized below.

Summary of Conclusions

Because of known deficiencies in the quality of most historical ambient NMOC data, the high quality NMOC data collected during the summers of 1984 and 1985 provides a fairly unique opportunity to examine 6-9 a.m. summertime concentrations of NMOC, NO_x and NMOC/NO_x ratios in several urban areas. The analysis of these data indicates the following:

(1) In almost all cases, considerable day-to-day variability was found in the magnitude of ambient concentrations of NMOC and NO_x and in the NMOC/NO_x ratios measured at a given site within an urban area. A key implication of this finding is that the NMOC/NO_x ratio measured at a single site may not be adequate to determine the NMOC/NO_x ratio over an entire urban area. This is of concern for two reasons. First, most States measure NMOC/NO_x ratios at a single site. Secondly, and more importantly, the NMOC/NO_x ratio is a critical parameter in determining the level of VOC control needed to attain the ozone standard. For these reasons, it appears that the fewer the number of NMOC monitors, the greater the magnitude of uncertainty in estimated control estimates. At least two NMOC sites (and possibly more) should be operated to more adequately characterize the NMOC/NO_x ratio within an urban area. This finding also suggests that NMOC monitors should be operated more frequently (e.g., each summer) than the occasional sampling which is typically the case in many urban areas.

(2) The impact of mobile sources on measured ambient NMOC concentrations was estimated using NMOC species data for each of the cities. The estimates were based on an assumed relationship between the concentration of measured acetylene and total NMOC in an urban area. Using this approximation procedure, it is estimated that the mobile source contribution typically ranges from 45-70% (and, in some cases, 85-90%) of the total NMOC measured in most urban areas. Although the data may only be characteristic of conditions at the monitoring site (rather than of the entire urban area), they nevertheless suggest that mobile sources may have a larger impact on ambient NMOC concentrations than indicated by past VOC emission inventories. This is consistent with recent findings which indicate that the magnitude of mobile source emissions may have been underestimated in the past due to (a) larger than expected tampering rates and (b) increased volatility of gasoline which increases the magnitude of evaporative emissions. These findings suggest the need for updating VOC emission inventories, since they are used as the basis for control strategy decisions in SIPs.

(3) An analysis of the NMOC species data was performed to estimate the contribution of biogenic sources to ambient NMOC concentrations in urban areas. The estimation procedure assumes that reported concentrations of isoprene and α-pinene approximate the contribution of biogenic sources to NMOC concentrations. Using this procedure, it is estimated that biogenic emissions typically are less than 1% in most urban areas. Although the procedure may tend to understate the contribution of biogenic sources (since it does not include all species emitted by biogenic sources), the analysis lends support to the position that anthropogenic sources are the predominant source of ambient NMOC concentrations in urban areas.

(4) In many analyses, the Beaumont data appear to be anomalous. The data are valid. However, the reasons for this site exhibiting trends counter to all other sites are not known.

2.0 NMOC Data

2.1 1984 NMOC Data

NMOC was measured from 6-9 a.m. (local clock time) at each site, Monday through Friday. The sampling schedule varied slightly from site to site but, in general, covered the time period from mid-June until the end of September. The data consist of 3-hour integrated averages.

Table 2-1 lists key statistics for each city. Included are the number of samples, 10th & 90th percentiles, median, mean, and standard deviation. Figure 2-1 illustrates the median NMOC values measured at each of the 21 sites. A site was operated in Philadelphia, but the data have not been included due to ethylene contamination. In Figure 2-2, these values are displayed graphically in ascending order. The lowest median NMOC level (0.39 ppmC) was recorded in Charlotte, North Carolina, while the highest median NMOC level (1.27 ppmC) was measured in Memphis, Tennessee. No obvious geographical patterns are apparent. The overall median of all 21 cities is approximately 0.72 ppmC.

The range of NMOC values within a given city is large. Typical minimum NMOC levels for each city are on the order of 0.1-0.2 ppmC. Maximum NMOC values usually exceeded 2 ppmC. In fact, 19 of the 21 sites measured maximum NMOC levels greater than 2 ppmC, while 11 of the 21 sites measured maximum NMOC levels in excess of 3 ppmC.

2.2 1985 NMOC Data

In 1985, 19 sites were operated in 18 cities. Two sites were operated in Philadelphia. The sampling schedule varied slightly from site to site but, in general, covered the time period from the beginning of June until the end of September.

Table 2-2 lists key statistics for each city. Included are the number of samples, 10th & 90th percentiles, median, mean, and standard deviation. Figure 2-3 illustrates the median NMOC values measured at each of the 19 sites. On Figure 2-4, these values are displayed graphically in ascending order. The lowest median NMOC level (0.38 ppmC) was recorded in Boston, Massachusetts, while the highest median NMOC level (1.63 ppmC) was measured in Beaumont, Texas. No obvious geographical patterns are present. The overall median of all 19 sites is approximately 0.60 ppmC.

The range of NMOC values within a given city is large. Typical minimum NMOC levels for each city are on the magnitude of 0.1-0.3 ppmC. Maximum NMOC values usually exceeded 2 ppmC. In fact, 14 of the 19 sites measured NMOC levels greater than 2 ppmC, while 4 of the 19 sites measured NMOC levels in excess of 3 ppmC.

A comparison of the median NMOC levels for the two Philadelphia sites was made. The median NMOC level for Site 1 is 0.49, while the median NMOC level for Site 2 is 0.65. The Mann Whitney U-test of the median NMOC levels to determine if a significant difference exists, indicated that at the 95% confidence level, no significant difference in the medians existed. This is due to the large scatter in the NMOC levels. Figure 2-5 shows a frequency distribution plot of both sites. Site 1 is shown above the zero line, while Site 2 is shown below the zero line.

2.3 Comparison Of 1984 And 1985 NMOC Levels

It is inappropriate to compare overall medians from 1984 to 1985 and draw conclusions regarding NMOC levels since samples were not collected in the same cities in both years. However, 10 cities had NMOC measured at the same sites in both 1984 and 1985. Comparisons of levels for both years can be made and conclusions drawn for each city.

Table 2-3 lists these cities, along with the number of samples, 10th & 90th percentiles, median, mean, and standard deviation, for both years. A simple comparison of median NMOC levels would indicate that NMOC levels in 9 of the 10 cities decreased from 1984 to 1985. However, with the large spread in the data, such conclusions may not be correct. A statistical test of the medians (Mann Whitney U-test) was performed to determine whether changes from 1984 to 1985 were statistically significant at the 95% confidence level. Of the nine cities with decreases in NMOC concentrations, the decreases were statistically significant in five cities, but not in the other four cities. The NMOC increase in Beaumont was found to be statistically significant. Table 2-4 shows the results of the Mann Whitney test, along with the percent decrease (or increase) in NMOC. It should be noted that reductions > 20% occurred at three cities.

While this analysis indicates that 1985 NMOC levels at several cities were lower than 1984 NMOC levels, it does not explain the cause of these reductions. Lower NMOC levels may be due to varying meteorology, local economic conditions or Volatile Organic Compound (VOC) control programs.

2.4 Continuous Hydrocarbon Data Versus PDFID Data

Continuous hydrocarbon analyzers measure total hydrocarbons and methane and take the difference to determine nonmethane hydrocarbon concentrations. Typically total hydrocarbon and methane are large values of similar magnitude. The difference of these two large values is a smaller value than either total hydrocarbon or methane and is subject to errors. [The data from continuous hydrocarbon samplers are referred to as Nonmethane Hydrocarbons (NMHC) in this paper.] Comparisons of NMHC data with collocated NMOC data (from the

PDFID) indicate poor agreement between the two instruments. Table 2-5 shows comparisons for five cities where collocated NMOC/NMHC data were available for 1984. Also shown is a comparison between data from analysis of samples by both the PDFID and the Gas Chromatograph (GC). A GC determines the concentrations of individual species such as propane, butane, etc. Concentrations of these individual species are summed to arrive at a total NMOC level. This technique is considered to be the most accurate method of determining NMOC levels.

Figure 2-6 is a plot of NMHC versus NMOC for the Washington, D.C. case listed in Table 2-5. The good agreement between the NMOC and GC data and the poor agreement between the NMOC and NMHC data indicate that the NMHC data from continuous monitors are suspect. In fact, based upon this information, the Office of Air Quality Planning and Standards (OAQPS) has indicated that ambient hydrocarbon data measured with the continuous technique are no longer adequate for EKMA modeling analyses, unless the NMHC data are shown to be comparable with GC measurements.[7]

Table 2-1

1984 NMOC (ppmC)

6-9 AM
3-Hour Averages

City	n	10th Percentile	90th Percentile	Median	Mean	Standard Deviation
Akron, OH	65	0.35	1.41	0.60	0.75	0.51
Atlanta, GA	52	0.33	1.46	0.60	0.80	0.73
Beaumont, TX	64	0.26	1.54	0.75	0.89	0.68
Birmingham, AL	55	0.40	2.21	0.73	1.00	0.68
Charlotte, NC	56	0.22	0.83	0.39	0.55	0.45
Chattanooga, TN	44	0.72	2.61	1.16	1.36	0.72
Cincinnati, OH	64	0.37	1.83	0.74	0.93	0.71
Clute, TX	67	0.33	1.47	0.70	0.83	0.61
Dallas, TX	70	0.48	1.52	0.89	0.95	0.44
El Paso, TX	65	0.47	1.57	0.82	0.92	0.45
Fort Worth, TX	66	0.49	1.63	0.80	0.97	0.57
Indianapolis, IN	56	0.41	1.24	0.69	0.80	0.42
Kansas City, MO	66	0.38	1.56	0.62	0.79	0.54
Memphis, TN	51	0.74	2.42	1.27	1.44	0.85
Miami, FL	28	0.48	2.24	1.03	1.31	0.85
Richmond, VA	62	0.27	0.85	0.50	0.54	0.24
Texas City, TX	65	0.32	1.82	0.78	0.94	0.80
Washington, DC	60	0.46	1.33	0.71	0.82	0.42
West Orange, TX	67	0.26	1.27	0.65	0.69	0.47
West Palm Beach, FL	70	0.25	0.86	0.49	0.55	0.35
Wilkes, Barre, PA	61	0.15	0.75	0.43	0.45	0.23

Table 2-2

1985 NMOC (ppmC)

6-9 AM
3-Hour Averages

City	n	10th Percentile	90th Percentile	Median	Mean	Standard Deviation
Baton Rouge, LA	79	0.32	1.87	0.60	0.81	0.64
Beaumont, TX	83	0.95	2.60	1.63	1.76	0.78
Boston, MA	43	0.17	0.70	0.38	0.41	0.23
Cleveland, OH	73	0.44	1.55	0.78	0.87	0.44
Clute, TX	80	0.23	1.42	0.63	0.72	0.45
Dallas, TX	76	0.41	1.57	0.73	0.88	0.50
El Paso, TX	82	0.25	1.29	0.67	0.72	0.40
Fort Worth, TX	76	0.40	1.36	0.63	0.76	0.40
Houston, TX	72	0.35	1.55	0.74	0.92	0.61
Kansas City, MO	84	0.25	1.13	0.41	0.53	0.36
Lake Charles, LA	79	0.26	1.08	0.55	0.62	0.35
Philadelphia 1, PA	63	0.27	1.18	0.49	0.65	0.45
Philadelphia 2, PA	58	0.37	1.04	0.65	0.72	0.38
Portland, ME	54	0.13	0.82	0.43	0.49	0.37
Richmond, VA	60	0.28	0.86	0.45	0.52	0.28
St. Louis, MO	76	0.35	1.22	0.57	0.71	0.41
Texas City, TX	78	0.18	1.29	0.42	0.61	0.52
Washington, DC	56	0.38	1.06	0.60	0.68	0.28
West Orange, TX	84	0.26	0.97	0.52	0.58	0.29

Table 2-3

Comparison Of 1984 And 1985 NMOC (ppmC)

(Same Site)

City	Year	n	10th Percentile	90th Percentile	Median	Mean	Standard Deviation
Beaumont, TX	1984	64	0.26	1.54	0.75	0.89	0.68
	1985	83	0.95	2.60	1.63	1.76	0.78
Clute, TX	1984	67	0.33	1.47	0.70	0.83	0.61
	1985	80	0.23	1.42	0.63	0.72	0.45
Dallas, TX	1984	70	0.48	1.52	0.89	0.95	0.44
	1985	76	0.41	1.57	0.73	0.88	0.50
El Paso, TX	1984	65	0.47	1.57	0.82	0.92	0.45
	1985	82	0.25	1.29	0.67	0.72	0.40
Fort Worth, TX	1984	66	0.49	1.63	0.80	0.97	0.57
	1985	76	0.40	1.36	0.63	0.76	0.40
Kansas City, MO	1984	66	0.38	1.56	0.62	0.79	0.54
	1985	84	0.25	1.13	0.41	0.53	0.36
Richmond, VA	1984	62	0.27	0.85	0.50	0.54	0.24
	1985	60	0.28	0.86	0.45	0.52	0.28
Texas City, TX	1984	65	0.32	1.82	0.78	0.94	0.80
	1985	78	0.18	1.29	0.42	0.61	0.52
Washington, DC	1984	60	0.46	1.33	0.71	0.82	0.42
	1985	56	0.38	1.06	0.60	0.68	0.28
West Orange, TX	1984	67	0.26	1.27	0.65	0.69	0.47
	1985	84	0.26	0.97	0.52	0.58	0.29

Table 2-4

Median NMOC Increases Or Decreases

(Same Site)

City	Direction Of NMOC	% Change In NMOC (1984-85)
Beaumont, TX	↑	117%
Clute, TX	↓	-10%*
Dallas, TX	↓	-18%*
El Paso, TX	↓	-18%
Fort Worth, TX	↓	-21%
Kansas City, MO	↓	-34%
Richmond, VA	↓	-10%*
Texas City, TX	↓	-46%
Washington, DC	↓	-15%
West Orange, TX	↓	-20%*

* Not significant at the 95% confidence level.

Table 2-5

Results Of Linear Regression Analyses

NMHC Versus NMOC (1984)					
City	n	Slope	Intercept	r	r^2
Indianapolis, IN	37	1.34	-.07	.88	.77
Indianapolis, IN (excluding 1 outlier)	36	1.02	.11	.69	.47
Kansas City, MO	49	.26	.48	.50	.25
Richmond, VA	38	.91	.46	.56	.32
Washington, DC	59	1.28	.56	.41	.16
Wiles Barre, PA	33	.08	.39	.35	.12

GC Versus NMOC (1984)					
	n	Slope	Intercept	r	r^2
All Samples	336	1.08	.015	.97	.95

FIGURE 2-1

1984 Median NMOC Levels (ppmC)

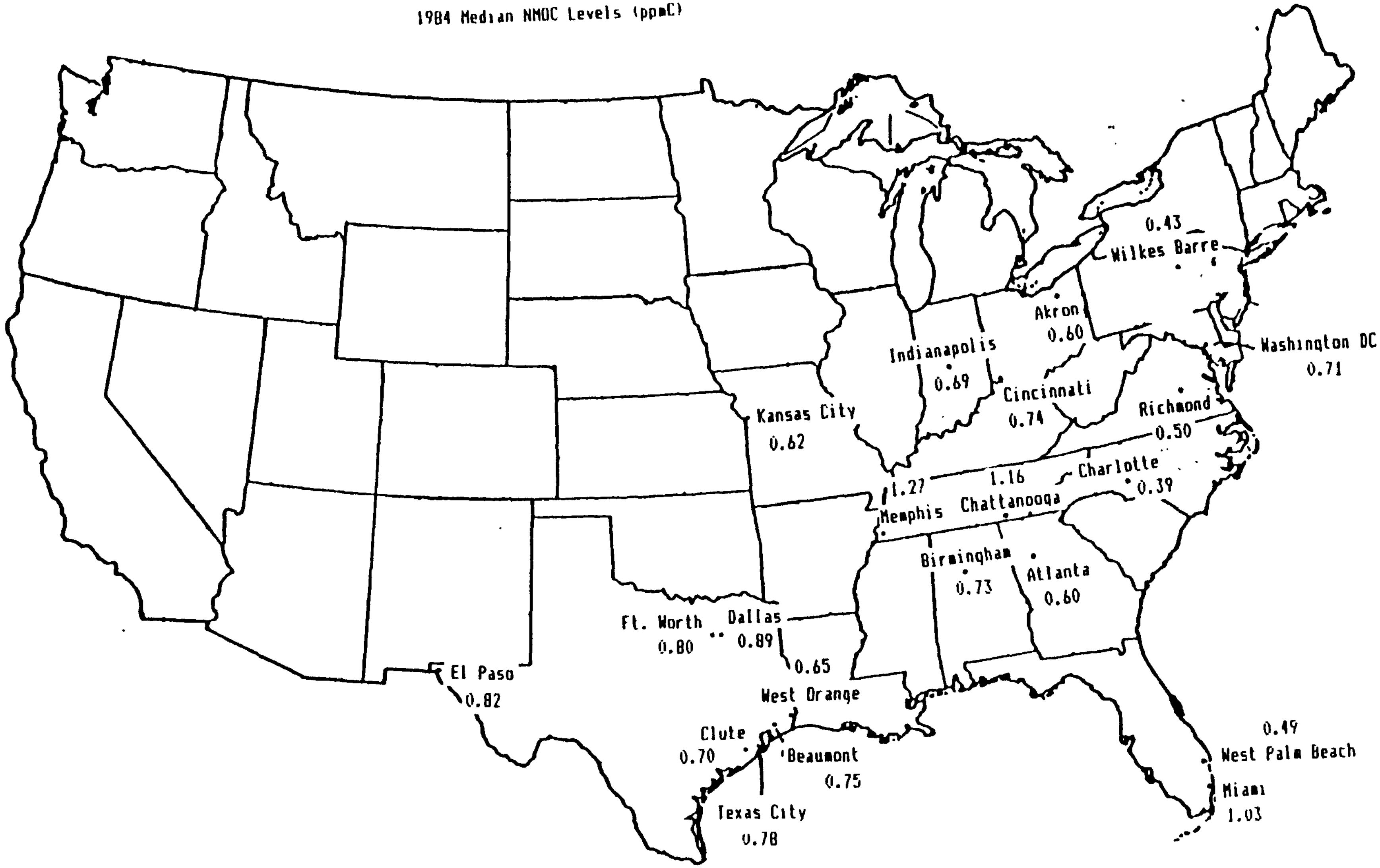


FIGURE 2-2

1984 MEDIAN NMOC LEVELS (ppmC)

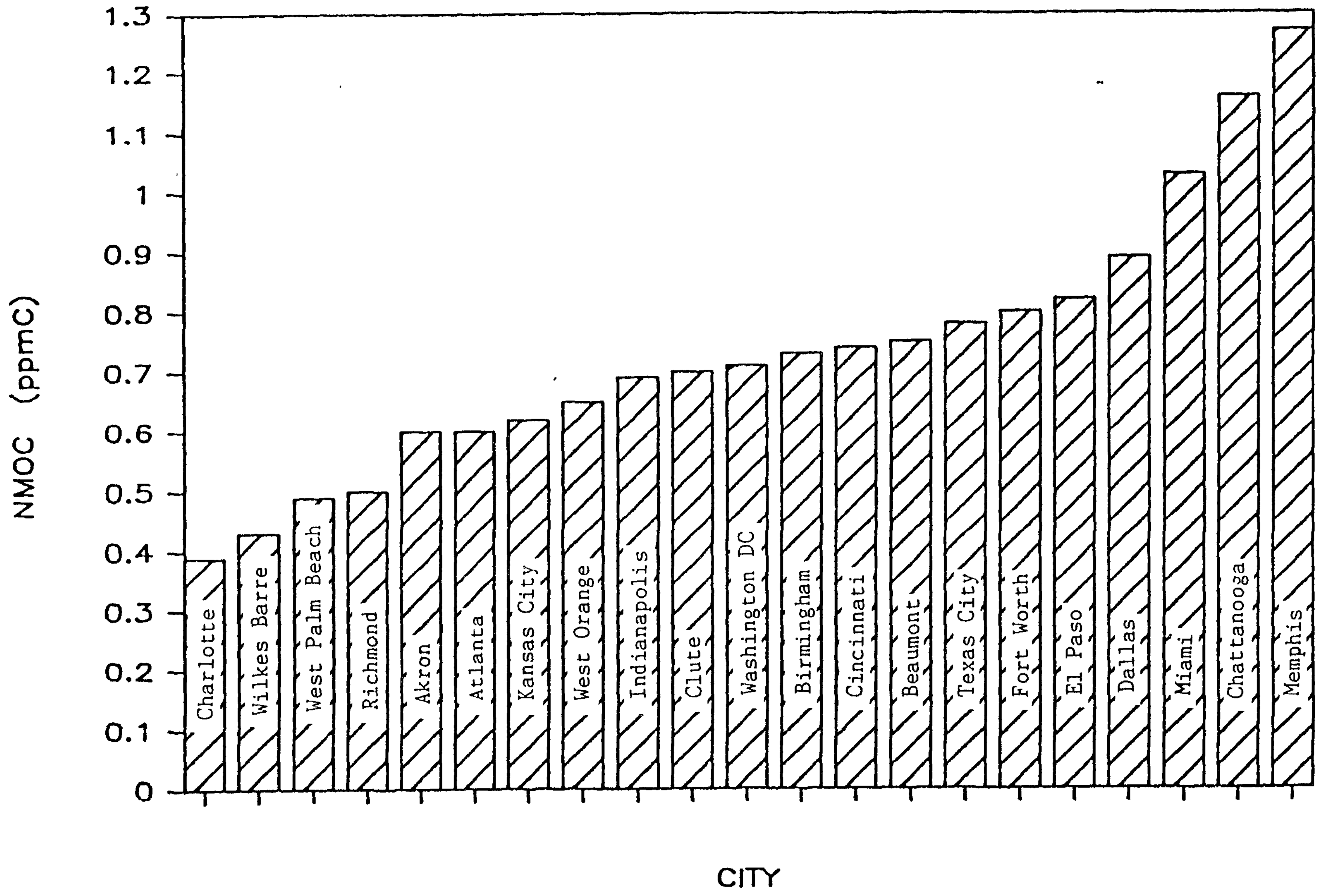


FIGURE 2-3

1985 Median NMOC Levels (ppmC)

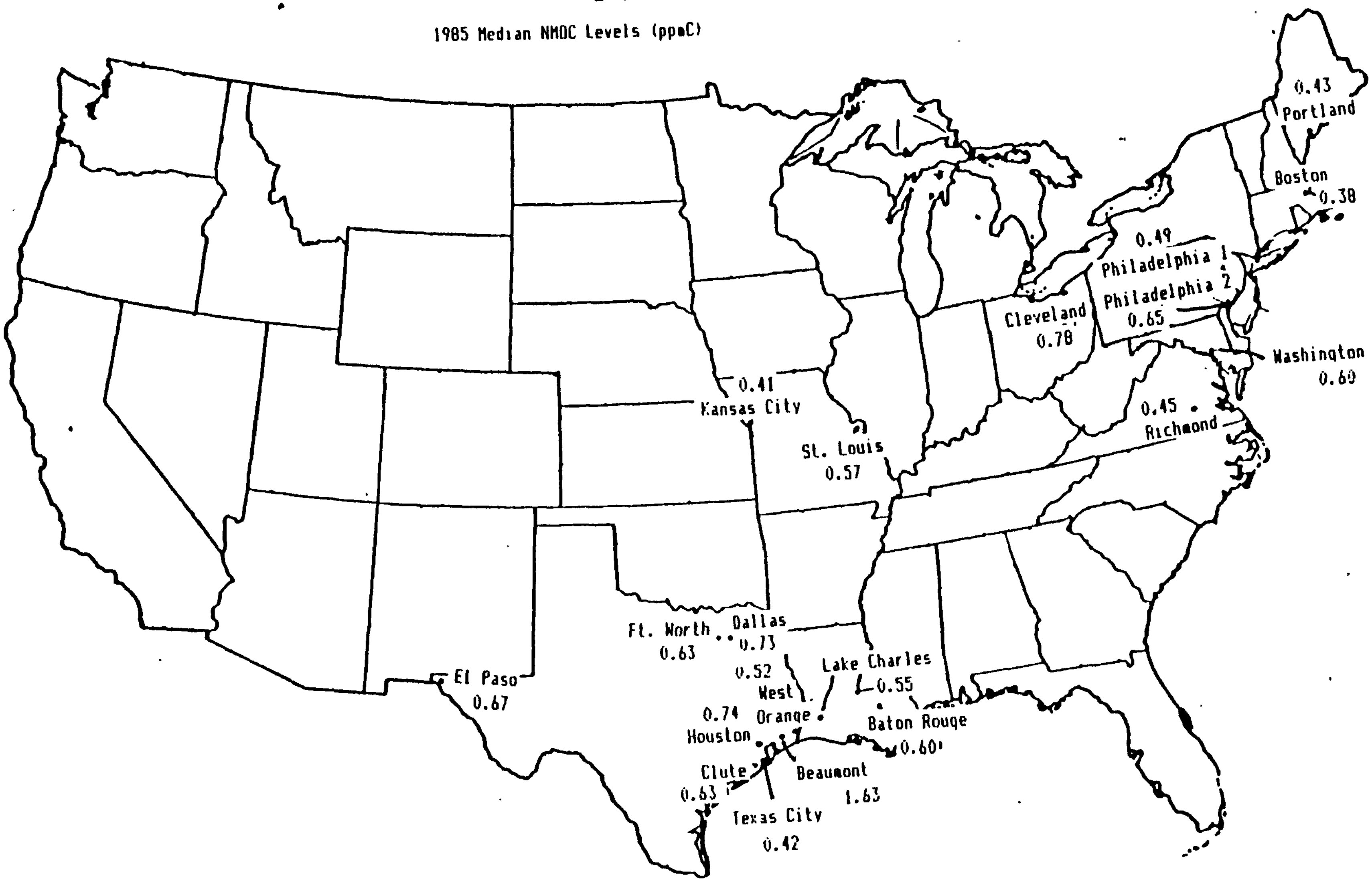


FIGURE 2—4

1985 MEDIAN NMOC LEVELS (ppmC)

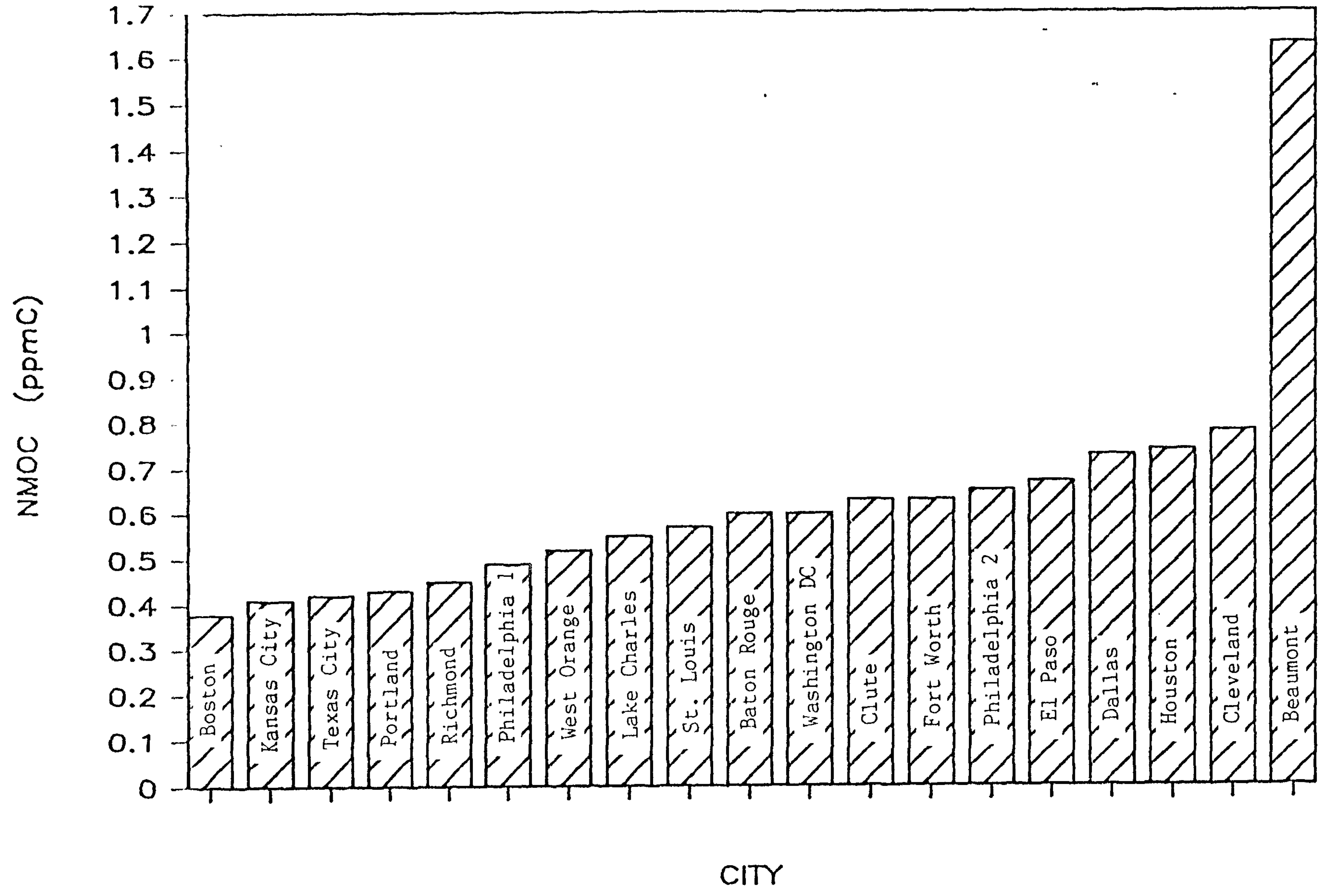
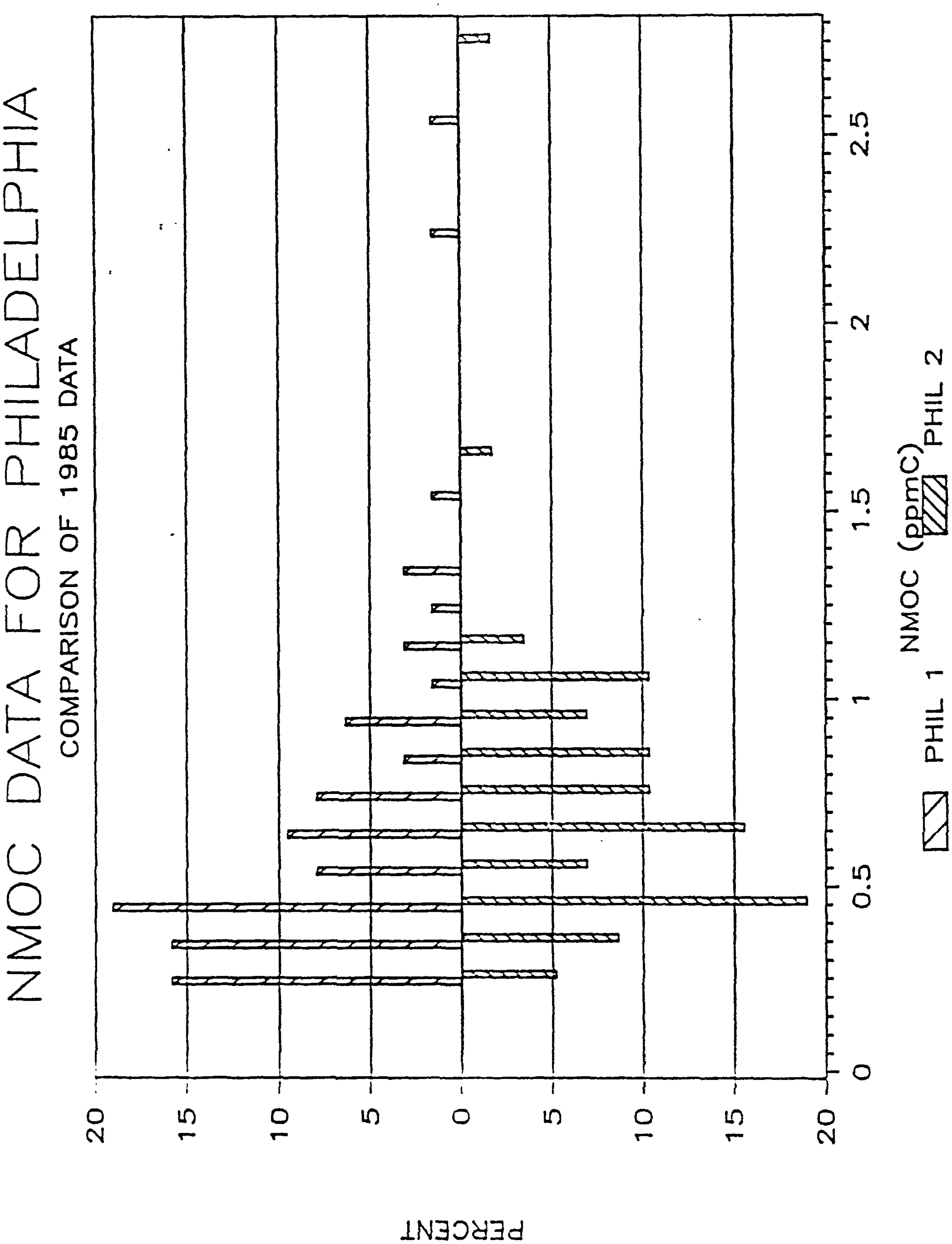
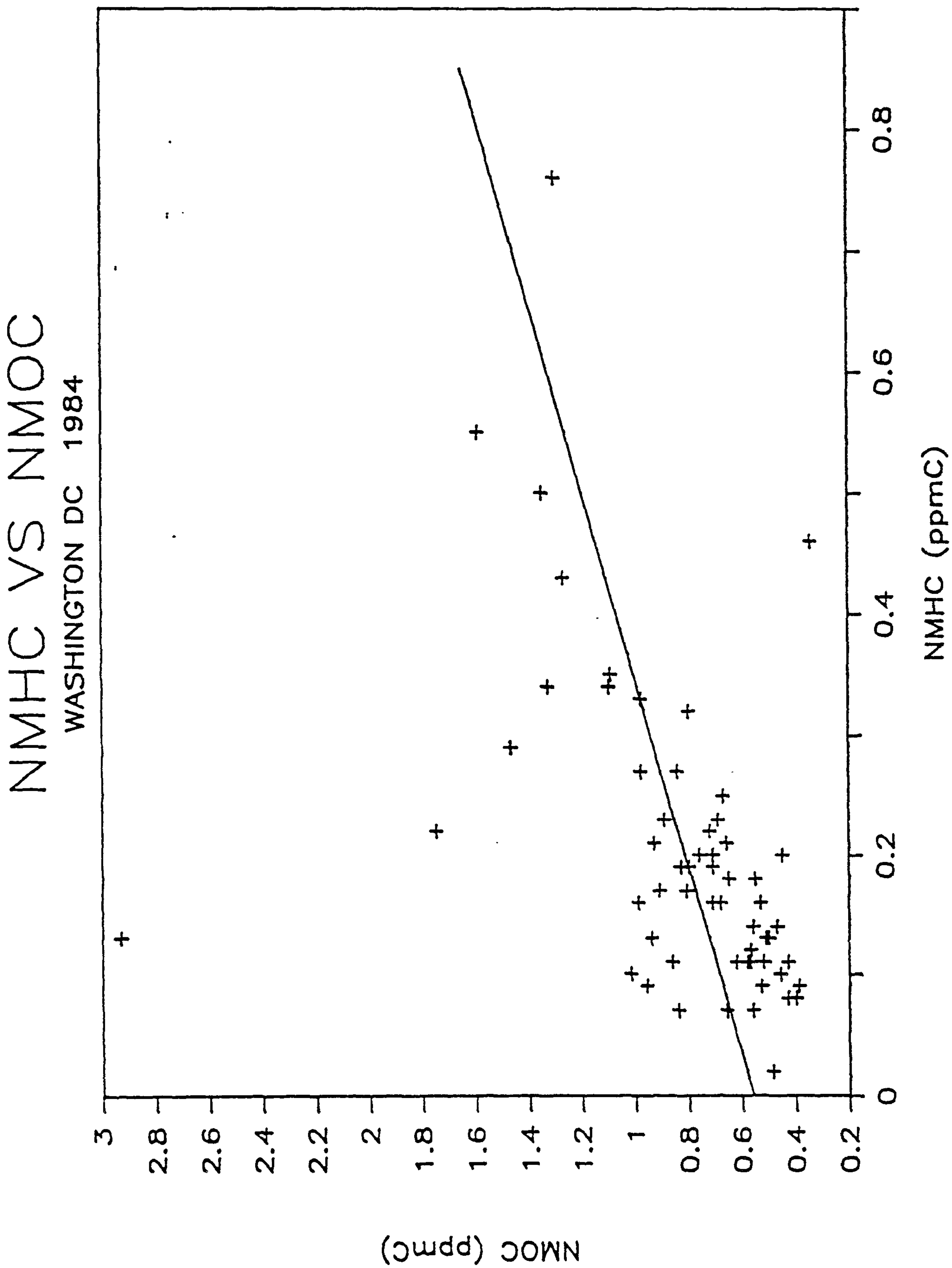


Figure 2-5



NMOC DATA FOR PHILADELPHIA
COMPARISON OF 1985 DATA
NMOC (ppmC)
PHIL 1
PHIL 2
PERCENT
0
0.5
1
1.5
2
2.5
20
15
10
5
0
5
10
15
20

Figure 2-6


NMHC VS NMOC
WASHINGTON DC 1984
NMHC (ppmC)
0
0.2
0.4
0.6
0.8
NMOC (ppmC)
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3

3.0 NO_x Data

3.1 1984 NO_x Data

At each NMOC site, a continuous NO_x analyzer was operated. Values discussed and analyzed include only NO_x samples which were measured along with the 6-9 a.m. (local clock time) NMOC samples. If an NMOC sample was missed on a sample day and NO_x was available, the NO_x data were not included in the analysis.

Table 3-1 lists key statistics for each city. Included are the number of samples, 10th and 90th percentile, median, mean, and standard deviation. Figure 3-1 illustrates the median NO_x values measured at each of the 22 sites. On Figure 3-2, the medians are displayed graphically in ascending order. The lowest median NO_x level (0.010 ppm) was measured in West Orange, Texas, while the highest median NO_x level (0.088 ppm) was recorded in Memphis, Tennessee. No obvious geographical patterns are present. While several Texas cities show low NO_x levels, these cities are also the least populated cities analyzed. The levels at West Orange are considered so low as to be questionable, since the median value is within the noise level of the instrument.

The range of 6-9 AM average NO_x values within a given city is fairly large. Typical minimum NO_x levels for each city are in the range of 0.000-0.030 ppm. Maximum NO_x levels usually exceed 0.100 ppm. Seventeen of the 21 sites recorded maximum NO_x levels above 0.1 ppm, while 10 of the 21 sites recorded maximum NO_x levels above 0.2 ppm.

3.2 1985 NO_x Data

Table 3-2 lists key statistics for each city. Included are the number of samples, 10th and 90th percentiles, median, mean, and standard deviation. Figure 3-3 illustrates the median NO_x values measured at each of the 19 sites. On Figure 3-4, the medians are displayed graphically in ascending order. The lowest median NO_x level (0.005 ppm) was measured in West Orange, Texas, while the highest median NO_x level (0.100 ppm) was recorded in Cleveland, Ohio. No obvious geographical patterns are present. Once again, the NO_x levels at West Orange are considered so low as to be questionable. Since the values are less than the noise level of the instrument.

The range of NO_x values within a given city is fairly large. Typical minimum NO_x levels for each city are in the range of 0.000-0.030 ppm. Maximum NO_x levels usually exceed 0.1 ppm. Fifteen of the 19 sites recorded NO_x maximum levels above 0.1 ppm, while seven of the 19 sites recorded maximum NO_x levels above 0.2 ppm.

3.3 Comparison Of 1984 And 1985 NO_x Levels

Ten cities measured NO_x levels in both 1984 and 1985 at the same site. Table 3-3 lists these cities, along with the number of samples, 10th and 90th percentiles, median, mean, and standard deviation for both years. A quick review of mean NO_x levels would indicate that mean NO_x levels decreased in eight of the ten cities, went up in one, and remained constant in the tenth city. However, with the large spread in the data, such conclusions may not be correct. Since the median NO_x levels at West Orange are so low, no comparison was made for that city. A statistical test of the medians (Mann Whitney U-test) was performed to determine whether changes from 1984 to 1985 were statistically significant at the 95% confidence level. The results of the test are shown in Table 3-4, along with the percent decrease (or increase) in mean NO_x. Of the seven cities which showed decreases in median NO_x, the decreases were significant at only three of the cities. Of the two cities which showed increases in the median NO_x, the increase was significant at only one city.

Table 3-1

1984 NO_x (ppm)

6-9 AM Averages

City	n	10th Percentile	90th Percentile	Median	Mean	Standard Deviation
Akron, OH	49	0.028	0.128	0.049	0.065	0.054
Atlanta, GA	52	0.029	0.123	0.055	0.071	0.060
Beaumont, TX	45	0.010	0.050	0.030	0.028	0.013
Birmingham, AL	51	0.038	0.149	0.061	0.082	0.057
Charlotte, NC	55	0.020	0.086	0.037	0.054	0.049
Chattanooga, TN	35	0.036	0.117	0.069	0.073	0.035
Cincinnati, OH	51	0.040	0.170	0.070	0.091	0.059
Clute, TX	52	0.017	0.054	0.025	0.032	0.019
Dallas, TX	69	0.030	0.100	0.050	0.059	0.032
El Paso, TX	60	0.025	0.110	0.050	0.059	0.034
Fort Worth, TX	58	0.037	0.170	0.070	0.087	0.054
Indianapolis, IN	31	0.037	0.142	0.058	0.081	0.066
Kansas City, MO	61	0.035	0.116	0.063	0.070	0.039
Memphis, TN	35	0.032	0.168	0.083	0.088	0.054
Miami, FL	15	0.025	0.191	0.070	0.086	0.061
Richmond, VA	62	0.023	0.087	0.047	0.051	0.026
Texas City, TX	52	0.010	0.038	0.021	0.022	0.011
Washington, DC	54	0.047	0.150	0.076	0.094	0.062
West Orange, TX	41	0.005	0.037	0.010	0.016	0.012
West Palm Beach, FL	60	0.010	0.100	0.029	0.040	0.034
Wilkes Barre, PA	53	0.005	0.074	0.030	0.035	0.026

Table 3-2

1985 NO_x (ppm)

6-9 AM Averages

City	n	10th Percentile	90th Percentile	Median	Mean	Standard Deviation
Baton Rouge, LA	67	0.023	0.080	0.039	0.047	0.025
Beaumont, TX	62	0.020	0.040	0.027	0.028	0.009
Boston, MA	43	0.028	0.081	0.046	0.049	0.021
Cleveland, OH	72	0.054	0.202	0.100	0.114	0.059
Clute, TX	72	0.010	0.047	0.020	0.027	0.022
Dallas, TX	68	0.037	0.120	0.063	0.071	0.037
El Paso, TX	76	0.020	0.107	0.051	0.057	0.035
Fort Worth, TX	54	0.030	0.138	0.057	0.069	0.044
Houston, TX	69	0.027	0.117	0.050	0.065	0.035
Kansas City, MO	84	0.025	0.121	0.049	0.065	0.052
Lake Charles, LA	77	0.013	0.039	0.022	0.025	0.010
Philadelphia 1, PA	55	0.047	0.125	0.067	0.081	0.042
Philadelphia 2, PA	55	0.021	0.150	0.065	0.083	0.087
Portland, ME	52	0.013	0.087	0.031	0.044	0.032
Richmond, VA	58	0.022	0.085	0.038	0.046	0.026
St. Louis, MO	73	0.036	0.109	0.062	0.069	0.031
Texas City, TX	68	0.008	0.030	0.017	0.018	0.008
Washington, DC	48	0.039	0.123	0.067	0.078	0.037
West Orange, TX	78	0.005	0.010	0.005	0.006	0.003

Table 3-3

Comparison Of 1984 And 1985 NO_x (ppm)
6-9 AM Averages (Same Site)

City	Year	n	10th Percentile	90th Percentile	Median	Mean	Standard Deviation
Beaumont, TX	1984	45	0.010	0.050	0.030	0.028	0.013
	1985	62	0.020	0.040	0.027	0.028	0.009
Clute, TX	1984	52	0.017	0.054	0.025	0.032	0.019
	1985	72	0.010	0.047	0.020	0.027	0.022
Dallas, TX	1984	69	0.030	0.100	0.050	0.059	0.032
	1985	68	0.037	0.120	0.063	0.071	0.037
El Paso, TX	1984	60	0.025	0.110	0.050	0.059	0.034
	1985	76	0.020	0.107	0.051	0.057	0.035
Fort Worth, TX	1984	58	0.037	0.170	0.070	0.087	0.054
	1985	54	0.030	0.138	0.057	0.069	0.044
Kansas City, MO	1984	61	0.035	0.116	0.063	0.070	0.039
	1985	84	0.025	0.121	0.049	0.065	0.052
Richmond, VA	1984	62	0.023	0.087	0.047	0.051	0.026
	1985	58	0.022	0.085	0.038	0.046	0.026
Texas City, TX	1984	52	0.010	0.038	0.021	0.022	0.011
	1985	68	0.008	0.030	0.017	0.018	0.008
Washington, DC	1984	54	0.047	0.150	0.076	0.094	0.062
	1985	48	0.039	0.123	0.067	0.078	0.037

Table 3-4

Median NO_x Increases Or Decreases

6-9 AM Averages

City	Direction Of NO_x	% Change In NO_x (1984-85)
Beaumont, TX	↓	-10%*
Clute, TX	↓	-20%
Dallas, TX	↑	26%
El Paso, TX	↑	2%*
Fort Worth, TX	↓	-19%*
Kansas City, MO	↓	-22%
Richmond, VA	↓	-19%*
Texas City, TX	↓	-19%
Washington, DC	↓	-12%*

* Not significant at the 95% confidence level.

FIGURE 3-1

1984 Median NOx Levels (ppm)

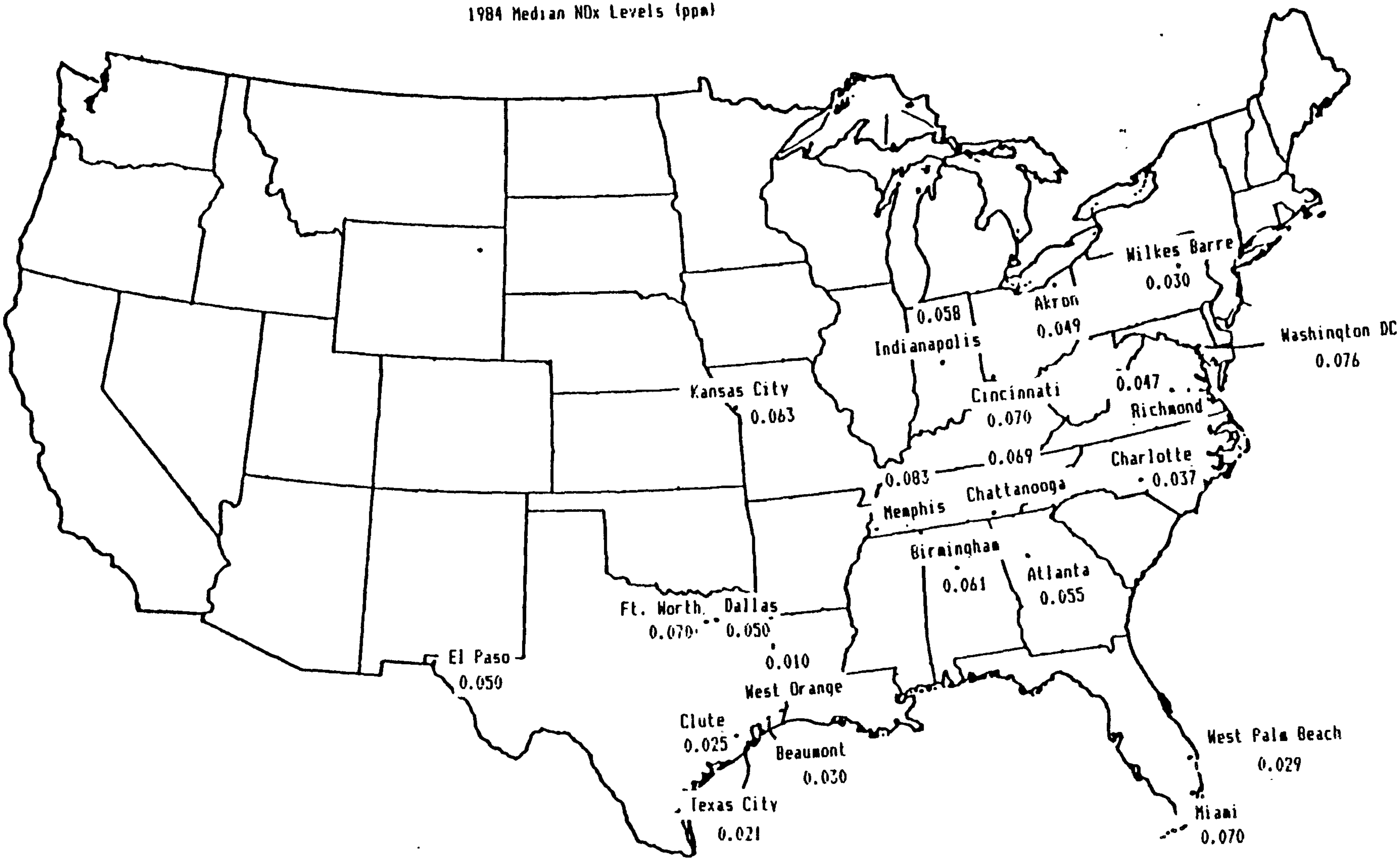


FIGURE 3-2

1984 MEDIAN NOx LEVELS (ppm)

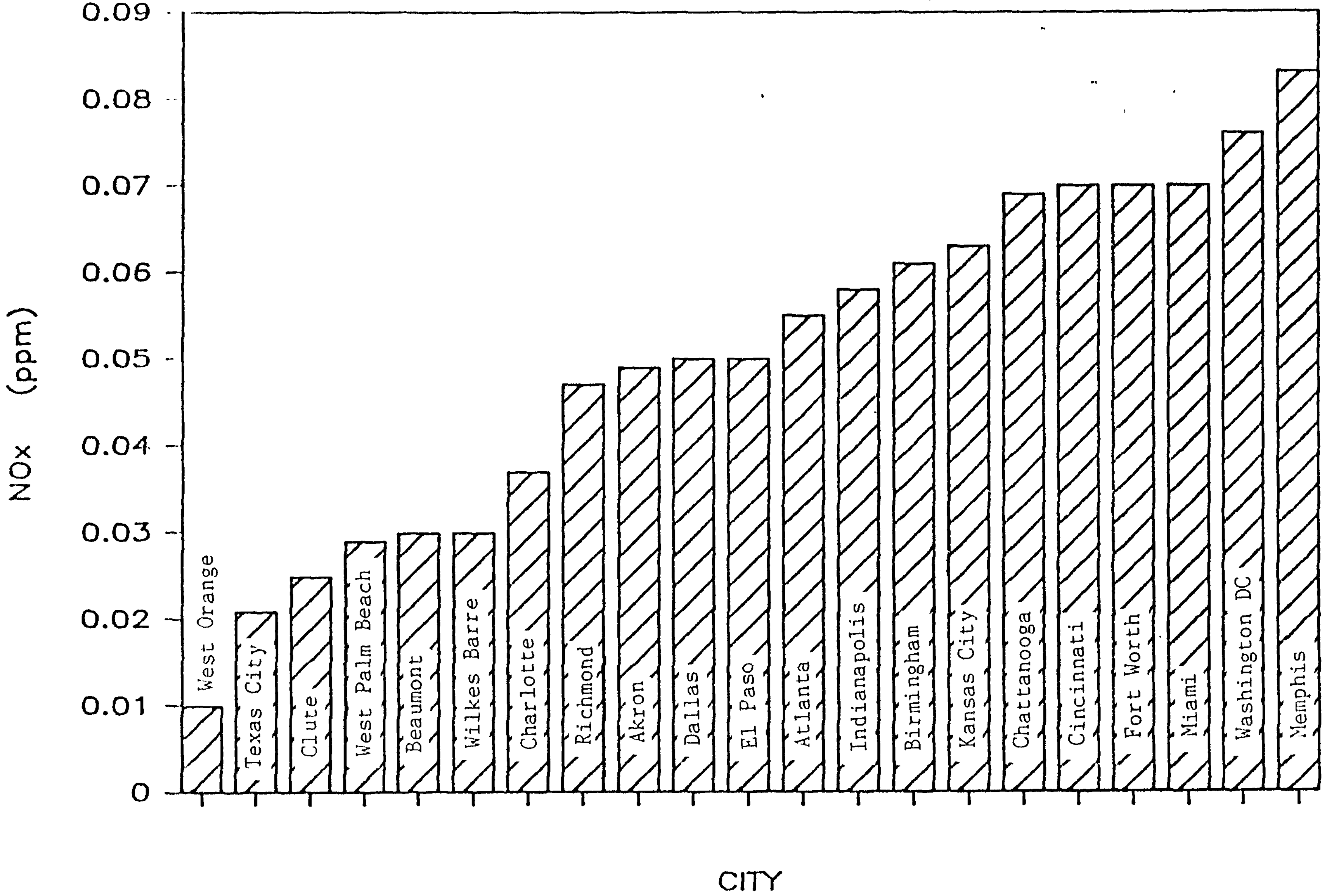


FIGURE 3-3

1985 Median NOx Levels (ppm)

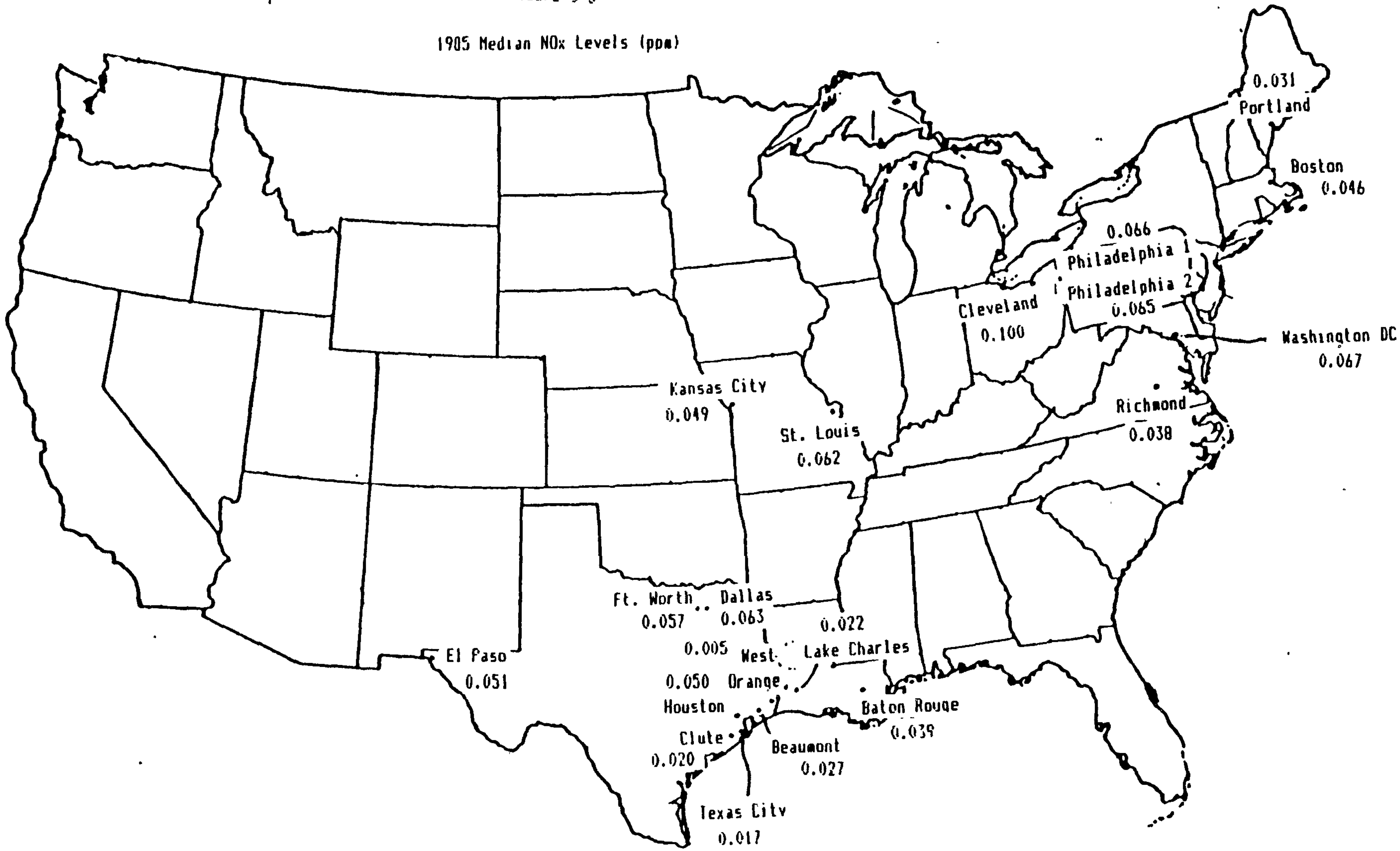
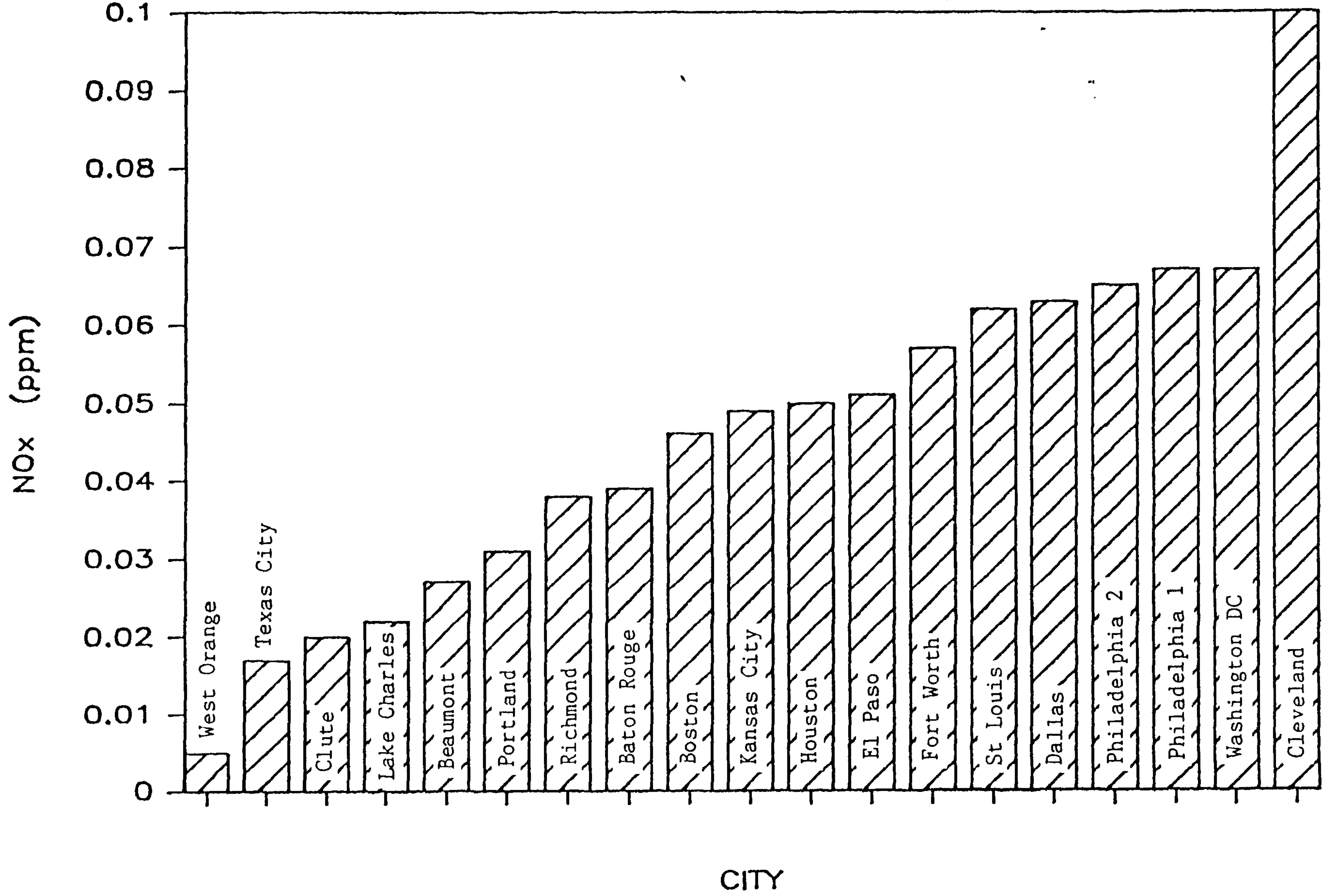


FIGURE 3—4

1985 MEDIAN NOx LEVELS (ppm)



4.0 $NMOC/NO_x$ Ratio

4.1 1984 $NMOC/NO_x$ Ratios

Perhaps the most important variable in an EKMA analysis is the $NMOC/NO_x$ ratio. All other factors being equal, the higher the $NMOC/NO_x$ ratio, the more control is necessary to reduce VOC to a level that will ensure attainment of the NAAQS for ozone. In most EKMA analyses for ozone SIPs, a median $NMOC/NO_x$ ratio is used for all days modeled (generally 5 days per site). The median $NMOC/NO_x$ ratio is determined by calculating a $NMOC/NO_x$ ratio for each day and then ranking those values and selecting the median. The median $NMOC/NO_x$ ratio is not the ratio of the median NMOC to the median NO_x level for all days.

Table 4-1 lists key statistics for each city. Included are the number of samples, 10th and 90th percentiles, median, mean, and standard deviation. Data for West Orange have been excluded due to the questionable NO_x values. Figure 4-1 illustrates the median $NMOC/NO_x$ ratios for each of the 20 cities. [Philadelphia is not shown, since the NO_x data are missing.] On Figure 4-2, those values are displayed graphically in ascending order. The lowest median $NMOC/NO_x$ ratio (9.1) was observed in Cincinnati, Ohio, while the highest median $NMOC/NO_x$ ratio (37.7) was observed in Texas City, Texas. No obvious geographical patterns are present. While the Gulf Coast of Texas has higher $NMOC/NO_x$ ratios than elsewhere, this difference is due to city size and therefore low NO_x levels, instead of location.

The range of daily $NMOC/NO_x$ ratios within a given city is large. Typical minimum day specific $NMOC/NO_x$ ratios for each city are in the range of 2-8. Maximum $NMOC/NO_x$ ratios usually exceed 40. Of the 20 sites, 15 had maximum $NMOC/NO_x$ ratios greater than 40. Eleven of the sites had maximum $NMOC/NO_x$ ratios greater than 60.

With the large spread in the range of the $NMOC/NO_x$ ratios within a given city, it is debatable whether the median ratio is a reliable representative value for these urban areas. Table 4-2 lists the percent of $NMOC/NO_x$ ratios within a given range (i.e., the median plus or minus a given percent). For example, 65% of the Akron $NMOC/NO_x$ ratios are contained in a range of the median ratio, plus or minus 30%. In order for the range to encompass 50% of the $NMOC/NO_x$ ratios, a range of the median $\pm$ 30% (or more) is usually necessary for nearly all cities. The typical median ratio is approximately 13. Thus, the range is 9.1-16.9 (13 $\pm$ 30%).

4.2 1985 $NMOC/NO_x$ Ratios

In 1985, 19 sites operated in 18 cities. Two sites were operated in Philadelphia. $NMOC/NO_x$ ratios will be discussed for only 18 of these sites since the West Orange NO_x data is questionable. Table 4-3 lists key statistics for each city. Figure 4-3 illustrates the median $NMOC/NO_x$ ratios for each of the 18 sites. On Figure 4-4, those values are displayed graphically in ascending order. The lowest median $NMOC/NO_x$ ratio (6.5) was observed in Philadelphia, Pennsylvania (Site 1), while the highest median $NMOC/NO_x$ ratio (53.2) was observed in Beaumont, Texas. No obvious geographical patterns are present.

The range of daily $NMOC/NO_x$ ratios within a given city is large. Typical minimum $NMOC/NO_x$ ratios for each city are in the range of 2-8. Maximum daily $NMOC/NO_x$ ratios usually exceed 40. Of the 18 sites, 16 observed maximum daily $NMOC/NO_x$ ratios equal to or greater than 40. Nine of the sites observed maximum daily $NMOC/NO_x$ ratios greater than or equal to 60.

Table 4-4 lists the percent of $NMOC/NO_x$ ratios within a given range for each city. Similarly to 1984, in order to encompass 50% of the $NMOC/NO_x$ ratios a range of the median $\pm$ 30% (or more) is necessary.

From the data presented it is doubtful that the median ratio at a single site would provide a representative ratio for an urban area. For this reason, EPA is recommending that a minimum of two NMOC sites be operated in a city to determine the appropriate NMOC/NO_x ratio. Additional sites are desirable. More specific guidance on the appropriate number of NMOC sites should be available in the Fall of 1987, at the completion of a special study designed to address this particular issue. This study will also examine the question of whether a median value or day-specific ratios are more suitable for characterizing a city's NMOC/NO_x ratios for EKMA modeling.

4.3 Comparison Of 1984 And 1985 NMOC/NO_x Ratios

Nine cities had NMOC/NO_x ratios in both 1984 and 1985 for the same site. Table 4-5 lists these cities, along with the number of ratios, 10th & 90th percentile range, median, mean, and standard deviation for both years. A quick review of the median NMOC/NO_x ratios would indicate that median NMOC/NO_x ratios increased in four cities and decreased in five other cities. However, with the large spread in the data, such conclusions may not be correct. A statistical test of the median NMOC/NO_x ratios (Mann-Whitney U Test) was performed to determine whether changes from 1984 to 1985 were statistically significant at the 95% confidence level. The results of the tests are shown in Table 4-6, along with the percent decrease (or increase) in median NMOC/NO_x ratio. Of the five cities with decreases in median NMOC/NO_x ratio, the decreases were statistically significant in four of the cities. Of the four cities with increases in median NMOC/NO_x ratio, the increases were statistically significant at only one site. In Beaumont, the median NMOC/NO_x ratio increased significantly from 1984 to 1985.

4.4 $NMOC/NO_x$ Ratio Versus Ozone Level

The Dallas NMOC site was chosen to compare maximum ozone concentrations to corresponding 6-9am $NMOC/NO_x$ ratios using 1984 data. All maximum daily ozone concentrations within a 50 mile radius of the NMOC sampling station were used for days when NMOC samples were taken. These ozone concentrations were compared with resultant wind directions from the 8 am - 3 pm period. to determine ozone readings that would correspond with NMOC parcels moving from the NMOC monitoring site to the ozone monitors. The maximum ozone level of all sites that met the above criteria was compared with the $NMOC/NO_x$ ratio for that day. Table 4-7 shows the results of this analysis. Median $NMOC/NO_x$ ratios associated with increasing ozone levels are shown. From the table it appears that the median $NMOC/NO_x$ ratios at the Dallas site do not significantly increase as the ozone level increases.

The failure of $NMOC/NO_x$ ratios to correlate with concurrent ozone levels is not surprising. Meteorological conditions play a critical part in the formation of ozone. Days with high 6-9 am $NMOC/NO_x$ ratios may be cloudy or have high winds which would result in low maximum ozone levels. Also, days with high maximum ozone levels may have large contributions from ozone aloft. These factors would tend to confuse a simple comparison of $NMOC/NO_x$ ratios with concurrent ozone maxima. Consideration of these variables in the comparison was beyond the scope of this analysis.

4.5 Comparison of $NMOC/NO_x$ Ratios - Historical vs. Recent

One area of special interest is how the recent $NMOC/NO_x$ ratios compare to $NMOC/NO_x$ ratios used in past analyses (State Implementation Plans). The $NMOC/NO_x$ ratios for the cities involved in the 1984 and 1985 studies were compared to data reported in earlier SIPs. These cities and ratios are listed in Table 4-8.

Of the seven cities shown in Table 4-8, higher median NMOC/NO_x ratios are observed in 1984 and 1985 than were used in previous SIP analyses in six cases. Boston is the lone exception. Since significant reductions in NMOC emissions should have occurred between approximately 1980 and 1984 or 1985 due to the Federal Motor Vehicle Control Program (FMVCP) and VOC control plans, NMOC/NO_x ratios should have decreased over this time period. Two caveats should be mentioned, however. First, the NMOC/NO_x ratios used in the SIP analyses were based upon continuous NMHC sampling and are therefore suspect. Secondly, expected emission reductions may have been offset by growth and higher than expected motor vehicle tampering rates.

Figure 4-5 shows a plot of 1984 NMOC/NO_x ratios versus population. While there appears to be a negative relationship between the NMOC/NO_x ratio and population (the ratio decreases as population increases) the correlation is poor.

Higher ratios may also be due to improved sampling and analysis procedures for NMOC and NO_x used in the 1984 and 1985 studies. Emission patterns for both NMOC and NO_x may have also changed.

Table 4-1

1984 NMOC/NO_x Ratio

City	n	10th Percentile	90th Percentile	Median	Mean	Standard Deviation
Akron, OH	49	8.0	18.4	12.8	13.1	4.7
Atlanta, GA	52	7.0	19.8	10.4	13.3	11.1
Beaumont, TX	45	13.8	46.5	25.3	30.8	22.2
Birmingham, AL	51	7.0	25.4	11.7	13.4	7.6
Charlotte, NC	55	6.6	22.2	10.4	11.8	5.6
Chattanooga, TN	35	11.9	30.5	16.7	22.3	21.3
Cincinnati, OH	51	6.0	15.4	9.1	14.2	19.2
Clute, TX	52	13.4	58.8	23.7	33.7	28.9
Dallas, TX	69	11.0	28.1	16.0	17.9	7.7
EL Paso, TX	60	10.5	31.5	15.1	19.8	16.3
Fort Worth, TX	58	6.9	20.2	11.5	13.4	9.6
Indianapolis, IN	31	6.7	16.6	10.9	11.6	4.5
Kansas City, MO	61	6.4	19.5	9.9	12.2	8.3
Memphis, TN	35	7.5	63.5	13.9	25.1	30.4
Miami, FL	15	9.5	20.5	13.3	13.7	3.8
Richmond, VA	62	6.1	16.9	10.5	12.1	7.2
Texas City, TX	52	20.2	79.8	37.7	54.3	66.5
Washington, DC	54	5.1	14.8	9.3	10.6	7.7
West Palm Beach, FL	60	7.0	38.0	14.2	19.2	15.1
Wilkes Barre, PA	53	6.1	56.7	14.3	23.5	22.4

Table 4-2

Percent Of NMOC/NO_x Ratios Within Specified Range

(1984 Data)

City	Median Ratio	Median ± 10%	Median ± 20%	Median ± 30%	Median ± 40%	Median ± 50%	Median ± 60%
Akron, OH	12.8	26	45	65	84	92	92
Atlanta, GA	10.4	25	40	63	77	79	83
Beaumont, TX	25.3	11	38	47	62	67	76
Birmingham, AL	11.7	20	35	53	71	75	78
Charlotte, NC	10.4	29	45	64	76	78	80
Chattanooga, TN	16.7	20	40	63	86	89	89
Cincinnati, OH	9.1	29	43	61	71	80	84
Clute, TX	23.7	19	29	35	54	63	71
Dallas, TX	16.0	23	49	70	80	86	88
El Paso, TX	15.1	15	40	60	67	75	83
Fort Worth, TX	11.5	22	40	57	69	79	83
Indianapolis, IN	10.9	19	39	61	74	87	97
Kansas City, MO	9.9	21	48	61	79	84	87
Memphis, TN	13.9	11	20	31	46	57	63
Miami, FL	13.3	27	47	67	87	87	100
Richmond, VA	10.5	26	39	61	68	84	89
Texas City, TX	37.7	19	37	56	62	71	79
Washington, DC	9.3	19	41	56	70	78	89
West Palm Beach, FL	14.2	12	17	30	45	57	73
Wilkes Barre, PA	14.3	6	21	30	43	55	64

Table 4-3

1985 NMOC/NO_x Ratio

City	n	10th Percentile	90th Percentile	Median	Mean	Standard Deviation
Baton Rouge, LA	67	8.9	27.6	14.9	17.7	11.1
Beaumont, TX	62	28.6	123.8	53.2	69.1	47.6
Boston, MA	43	4.5	14.7	7.6	8.9	5.0
Cleveland, OH	72	5.2	11.3	7.5	7.9	2.6
Clute, TX	72	11.7	77.8	24.6	37.6	34.7
Dallas, TX	68	6.8	29.2	11.8	15.2	13.2
El Paso, TX	76	9.1	21.2	11.9	14.3	7.2
Fort Worth, TX	54	6.6	20.6	11.8	13.1	8.1
Houston, TX	69	5.6	36.7	12.9	19.1	21.5
Kansas City, MO	84	4.6	15.3	8.5	11.2	13.8
Lake Charles, LA	77	14.8	35.8	23.7	26.2	13.2
Philadelphia 1, PA	55	4.2	14.8	6.5	8.6	6.1
Philadelphia 2, PA	55	5.5	27.5	9.5	12.3	9.5
Portland, ME	52	6.1	20.8	11.6	13.5	9.6
Richmond, VA	58	7.4	15.2	11.2	12.2	5.7
St. Louis, MO	73	6.4	18.2	9.6	11.2	5.9
Texas City, TX	68	12.9	91.2	28.7	41.7	32.9
Washington, DC	48	5.3	14.2	8.7	9.8	5.4

Table 4-4

Percent Of $NMOC/NO_x$ Ratios Within Specified Range

(1985 Data)

City	Median Ratio	Median ± 10%	Median ± 20%	Median ± 30%	Median ± 40%	Median ± 50%	Median ± 60%
Baton Rouge, LA	14.9	22	33	54	61	79	82
Beaumont, TX	53.2	11	29	40	52	61	73
Boston, MA	7.6	21	33	56	65	77	84
Cleveland, OH	7.5	32	54	74	81	89	94
Clute, TX	24.6	15	31	43	51	60	65
Dallas, TX	11.8	32	43	53	63	78	82
El Paso, TX	11.9	41	57	74	78	79	87
Fort Worth, TX	11.8	19	31	54	65	74	87
Houston, TX	12.9	16	28	38	43	57	68
Kansas City, MO	8.5	13	37	50	65	77	83
Lake Charles, LA	23.7	26	44	61	75	86	88
Philadelphia 1, PA	6.5	25	45	55	62	71	82
Philadelphia 2, PA	9.5	7	18	47	65	71	75
Portland, ME	11.6	19	35	42	63	73	81
Richmond, VA	11.2	29	53	76	84	90	93
St. Louis, MO	9.6	26	40	58	67	78	84
Texas City, TX	28.7	9	16	24	43	50	60
Washington, DC	8.7	25	46	67	73	79	85

Table 4-5

Comparison Of 1984 And 1985 NMOC/NO_x Ratios

Measured At The Same Site

City	Year	n	10th Percentile	90th Percentile	Median	Mean	Standard Deviation
Beaumont, TX	1984	45	13.8	46.5	25.3	30.8	22.2
	1985	62	28.6	123.8	53.2	69.1	47.6
Clute, TX	1984	52	13.4	58.8	23.7	33.7	28.9
	1985	72	11.7	77.8	24.6	37.6	34.7
Dallas, TX	1984	69	11.0	28.1	16.0	17.9	7.7
	1985	68	6.8	29.2	11.8	15.2	13.2
El Paso, TX	1984	60	10.5	31.5	15.2	19.8	16.3
	1985	76	9.1	21.2	11.9	14.3	7.2
Fort Worth, TX	1984	58	6.9	20.2	11.5	13.4	9.6
	1985	54	6.6	20.6	11.8	13.1	8.1
Kansas City, MO	1984	61	6.4	19.5	9.9	12.2	8.3
	1985	84	4.6	15.3	8.5	11.2	13.8
Richmond, VA	1984	62	6.1	16.9	10.5	12.1	7.2
	1985	58	7.4	15.2	11.2	12.2	5.7
Texas City, TX	1984	52	20.2	79.8	37.7	54.3	66.5
	1985	68	12.9	91.2	28.7	41.7	32.9
Washington, DC	1984	54	5.1	14.8	9.3	10.6	7.7
	1985	48	5.3	14.2	8.7	9.8	5.4

Table 4-6

Median NMOC/NO_x Ratio Increases Or Decreases

Measured At The Same Site

City	Direction Of Median NMOC/NO_x Ratio Change	% Change In Median NMOC/NO_x Ratio (1984-85)
Beaumont, TX	↑	110%
Clute, TX	↑	4%*
Dallas, TX	↓	-26%
El Paso, TX	↓	-22%
Fort Worth, TX	↑	3%*
Kansas City, MO	↓	-14%
Richmond, VA	↑	7%*
Texas City, TX	↓	-24%
Washington, DC	↓	- 6%*

* Not significant at the 95% confidence level.

Table 4-7

Median $NMOC/NO_x$ Ratio Vs. Ozone Level

Dallas 1984

Ozone Level	Number of $NMOC/NO_x$ Ratios	Median $NMOC/NO_x$ Ratio
All Data	69	16.0
≥ .1	32	15.0
≥ .11	26	15.0
≥ .12	18	16.1
≥ .13	13	17.0
≥ .14	9	17.0
≥ .15	9	17.0
≥ .16	6	14.9
≥ .17	1	17.0
≥ .18	1	17.0

Table 4-8

Comparison of Median NMOC/NO_x Ratios

(Historical vs Recent)

City	Past Analyses* NMOC/NO_x Ratio	1984 Data NMOC/NO_x Ratio	1985 Data NMOC/NO_x Ratio
Boston, MA	9.4	--	7.6
Cincinnati, OH	3.9	9.1	--
Cleveland, OH	5.8	--	7.5
Houston, TX	5.8	--	12.9
Philadelphia, PA	8.2	--	6.5/9.5
St. Louis, MO	6.0	--	9.6
Washington, DC	8.0	9.3	8.7

*From 1982 Ozone SIP Data Base Status and Summary Report, Air Management Technology Branch, February 1983.

FIGURE 4-1

1984 Median NMOC/NOx Ratios

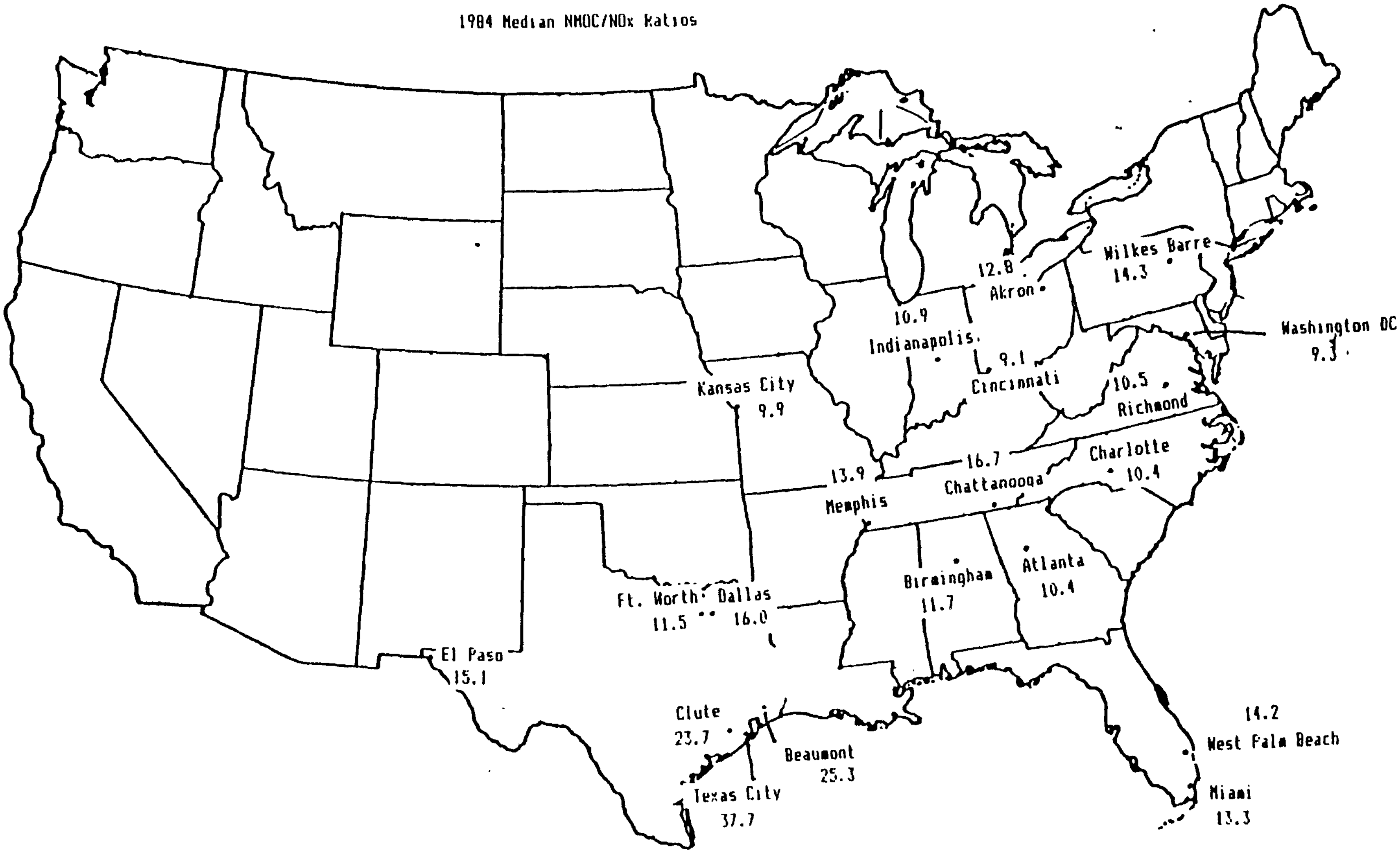


FIGURE 4–2

1984 MEDIAN NMOC/NOx RATIOS

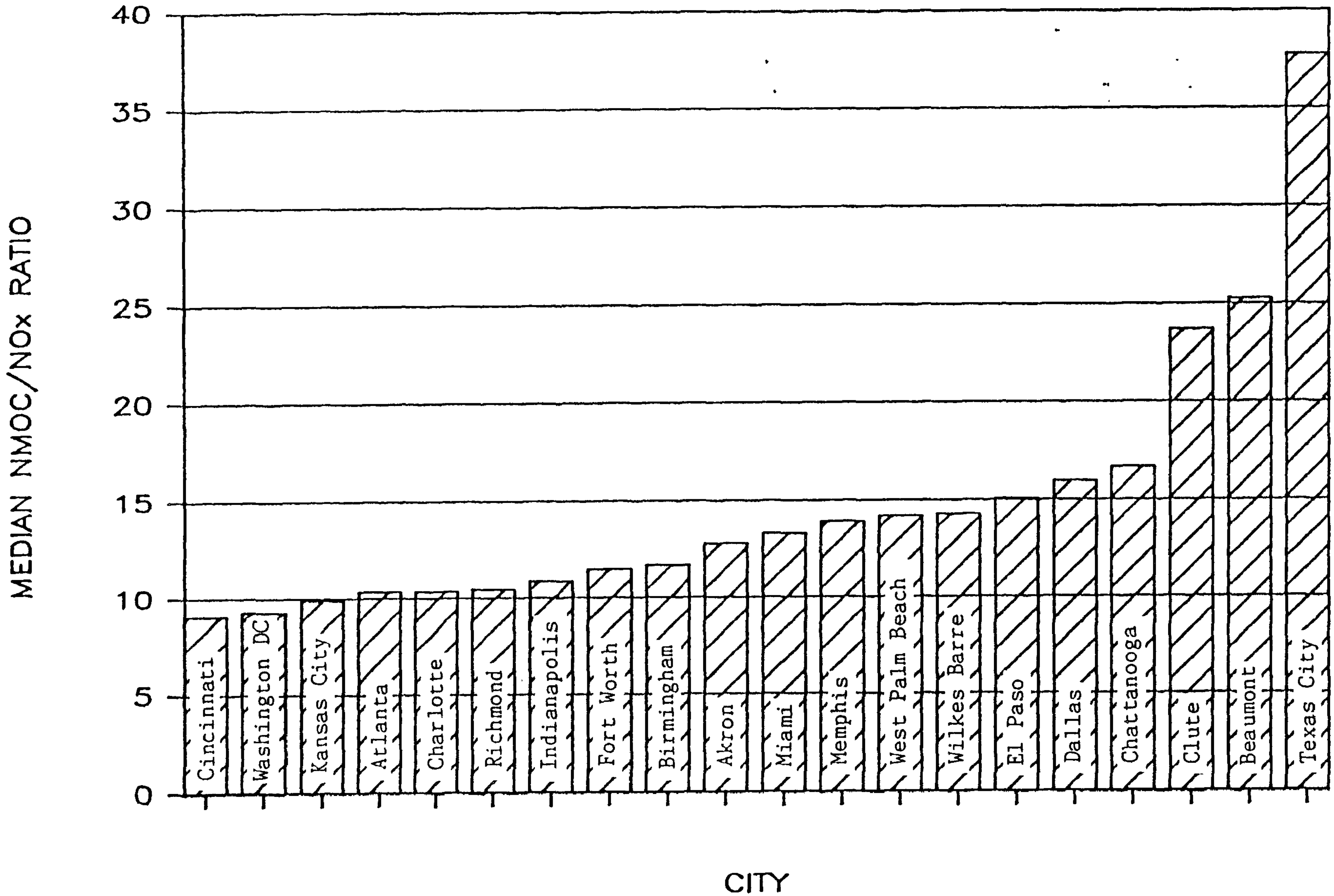


FIGURE 4-3

1985 Median NMOC/NOx Ratios

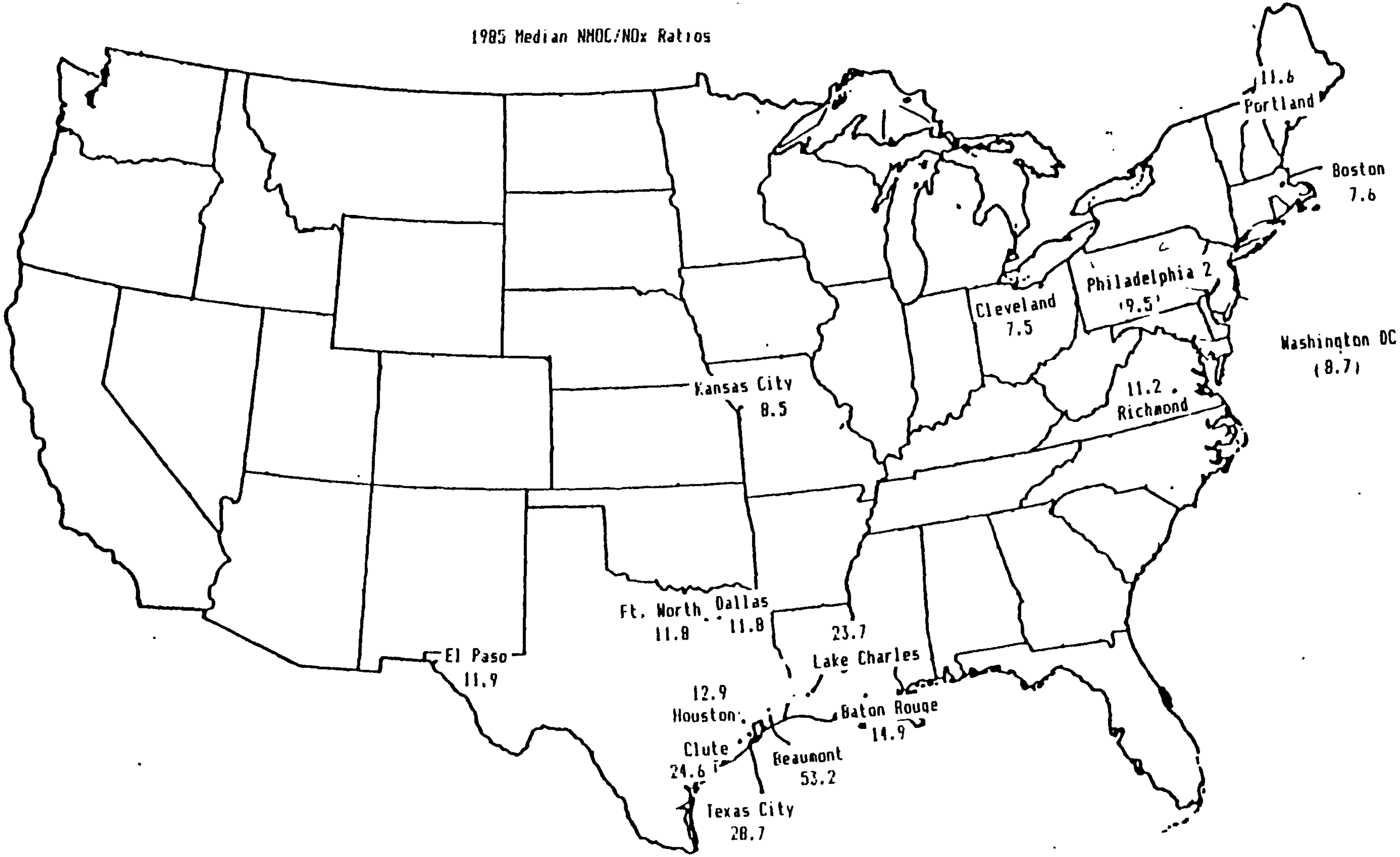


FIGURE 4—4

1985 MEDIAN NMOC/NOx RATIOS

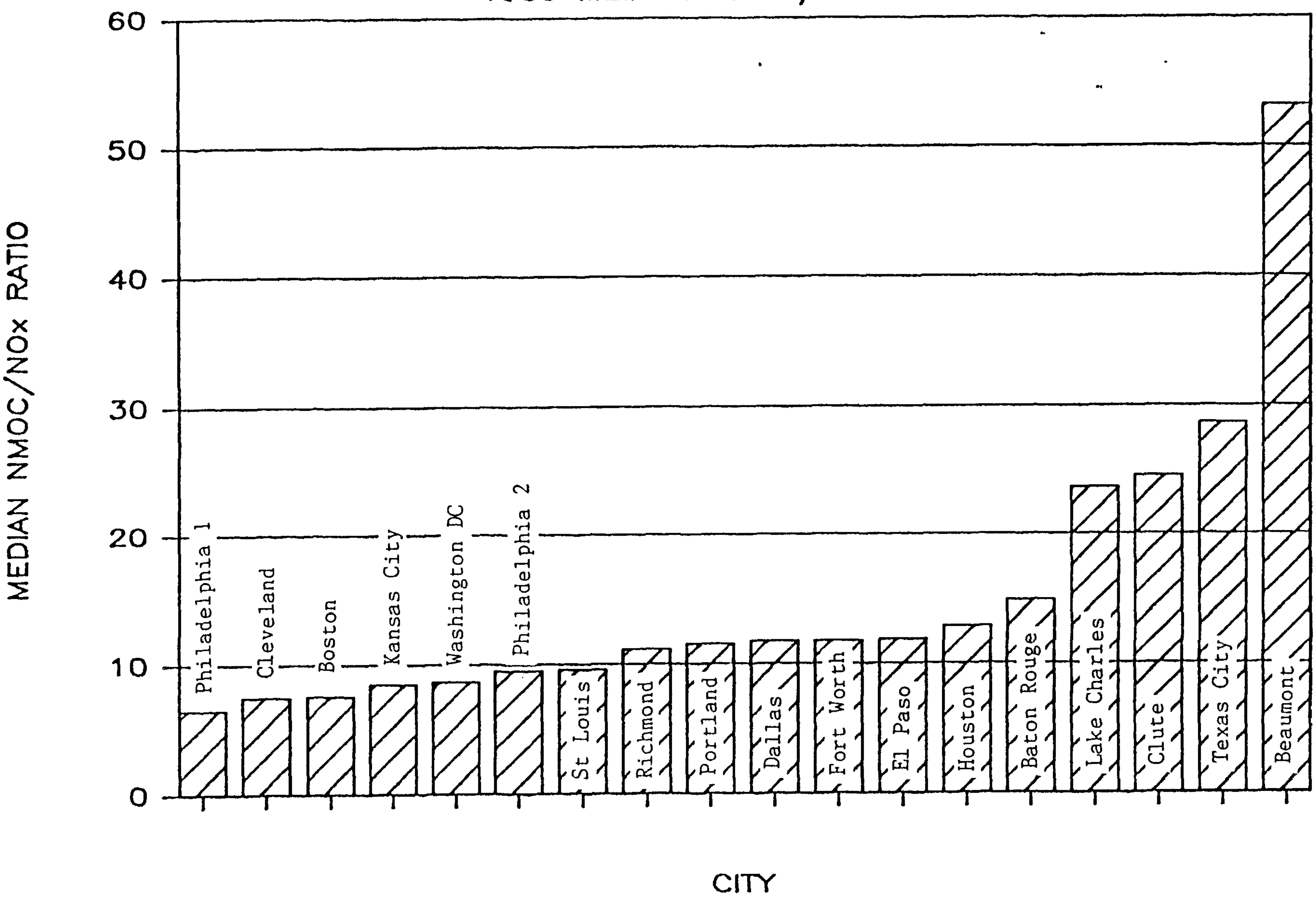
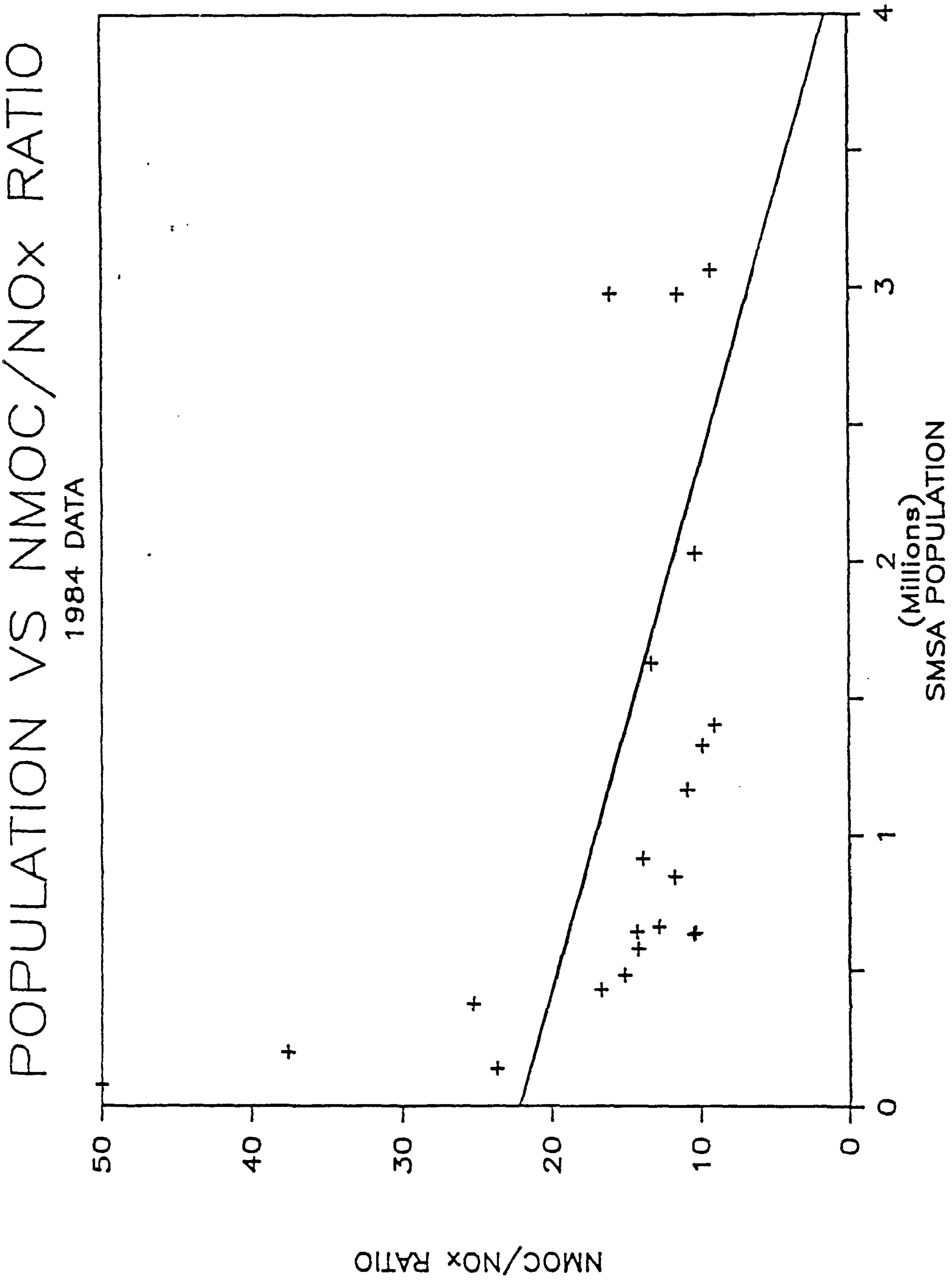


Figure 4-5


POPULATION VS NMOC/NOx RATIO
1984 DATA
NMOC/NOx RATIO
50
40
30
20
10
0
SMSA POPULATION
(Millions)
0
1
2
3
4

5.0 Carbon Bond Splits For The Carbon Bond-4 Mechanism

EKMA contains a procedure for considering the reactivity of ambient NMOC. This is done by subdividing measured NMOC into various groups. The exact groupings depend on the chemical mechanism employed by the model. One commonly employed mechanism is the CB-4 mechanism. This mechanism requires carbon fractions for eight carbon bond groups: paraffins, ethylene, olefins, toluene, xylene, formaldehyde, higher aldehydes (ALD2) and unreactive.[4]

5.1 1984 Carbon Fractions

Two hundred and three (203) samples were analyzed to determine the carbon fractions for 1984. Table 5-1 lists the median carbon fractions for each city, based upon GC analyses. At the bottom of the table, an overall median of the 1984 data and the currently recommended default values are listed.[5] Default values for the EKMA model are numbers derived from data for numerous cities and can be used for a city where these data are missing. These defaults are based upon GC analyses of NMOC samples.

In general, the overall median values agree with the default values, with the exception being that the 1984 samples show consistently higher carbon fractions of paraffins and consistently lower carbon fractions of unreactives. EPA plans followup modeling runs to determine the impact on estimated VOC control levels due to varying carbon fractions.

5.2 1985 Carbon Fractions

Three hundred and four (304) samples were analyzed to determine the carbon fractions for 1985. Table 5-2 lists the median carbon fractions for each city, based upon GC analyses. At the bottom of the table, an overall median of the 1985 data and the currently recommended default values are listed.

In general, the overall median values agree fairly well with the default values. The median of the 1985 samples show higher carbon fractions of paraffin and higher aldehydes and lower carbon fractions of unreactives than the current default values.

5.3 Comparison of 1984 and 1985 Carbon Fractions

Ten cities were involved in both the 1984 and 1985 NMOC studies. Carbon fractions for both years are compared for each city in Table 5-3. In general, the carbon fractions do not vary significantly from 1984 to 1985. Beaumont, Clute and Texas City appear to be exceptions. All are small cities which may be impacted by major industrial sources.

5.4 Selection of New Default Carbon Fractions for CB4

In Table 5-4 the median carbon fractions for 1984 and 1985 are listed along with the current default values. Data sets for 1984 and 1985 were combined to obtain an overall median set of carbon fractions. From this data set values for Beaumont, Clute, Texas City, West Orange and Lake Charles were deleted since it is likely that these small cities are heavily influenced by a particular industry and are not representative of values which would be seen by larger cities.

The default values selected (shown in Table 5-4) are based upon 1984 and 1985 with the cities excluded as explained above. In any event there is little difference between the overall data set and the "refined" data set. The new default carbon fractions for use in EKMA CB4 analyses are those shown at the bottom of Table 5-4.

Table 5-1

Median Carbon Fractions For EKMA CB-4 Analysis
(Based Upon 1984 Data)

City	n	Olefin	Paraffin	Toluene	Xylene	Formaldelyde	Higher Aldehydes	Ethylene	Unreactive
Akron, OH	10	.026	.582	.092	.133	.030	.040	.026	.122
Atlanta, GA	7	.031	.582	.133	.133	.030	.050	.041	.051
Beaumont, TX	9	.021	.646	.062	.062	.020	.051	.052	.135
Birmingham, AL	6	.041	.605	.108	.138	.030	.045	.036	.046
Charlotte, NC	16	.031	.572	.113	.149	.030	.051	.041	.062
Chattanooga, TN	12	.030	.589	.142	.127	.020	.050	.030	.061
Cincinnati, OH	7	.031	.629	.113	.124	.020	.051	.031	.052
Clute, TX	10	.031	.599	.094	.099	.020	.040	.062	.104
Dallas, TX	13	.030	.600	.110	.120	.020	.060	.030	.080
El Paso, TX	8	.030	.596	.111	.121	.025	.050	.040	.076
Fort Worth, TX	13	.031	.602	.104	.112	.020	.050	.041	.092
Indianapolis, IN	10	.029	.581	.118	.133	.030	.050	.039	.069
Kansas City, MO	11	.030	.626	.101	.111	.020	.050	.030	.081
Memphis, TN	8	.035	.583	.121	.121	.020	.065	.040	.065
Miami, FL	3	.020	.610	.120	.140	.020	.050	.030	.060
Richmond, VA	10	.030	.569	.117	.162	.030	.050	.030	.061
Texas City, TX	13	.031	.629	.072	.072	.020	.040	.021	.165
Washington, DC	10	.030	.586	.121	.131	.025	.060	.045	.051
West Orange, TX	10	.021	.617	.067	.104	.030	.040	.036	.135
West Palm Beach, FL	8	.030	.589	.116	.157	.030	.050	.030	.051
Wiles Barre, PA	9	.030	.604	.109	.119	.030	.050	.030	.079
Overall	203	.031	.605	.113	.123	.020	.051	.036	.072
Current Recommended Value		.03	.51	.12	.10	.02	.03	.04	.15

*The formaldehyde and higher aldehydes fractions represent a "surrogate" fraction plus a recommended additional fraction. This is due to the fact that neither the PDFID nor the GC method measure aldehydes.

Table 5-2

Median Carbon Fractions For EKMA CB4 Analyses

(Based Upon 1985 Data)

City	n	Olefin	Paraffin	Toluene	Xylene	Formaldelyde	Higher Aldehydes	Ethylene	Unreactive
Baton Rouge, LA	16	.025	.624	.087	.093	.023	.048	.028	.122
Beaumont, TX	19	.080	.691	.071	.060	.022	.036	.024	.068
Boston, MA	8	.027	.568	.119	.148	.023	.057	.039	.069
Cleveland, OH	17	.022	.586	.118	.115	.022	.047	.039	.101
Clute, TX	18	.050	.524	.079	.058	.022	.040	.170	.106
Dallas, TX	23	.027	.608	.112	.106	.022	.058	.032	.085
El Paso, TX	17	.026	.595	.109	.110	.023	.049	.039	.099
Fort Worth, TX	19	.033	.582	.113	.123	.024	.055	.038	.080
Houston, TX	22	.038	.618	.087	.083	.022	.051	.033	.119
Kansas City, MO	18	.024	.594	.114	.109	.022	.046	.041	.099
Lake Charles, LA	16	.018	.618	.074	.077	.022	.042	.019	.180
Philadelphia[1], PA	13	.027	.586	.138	.118	.022	.052	.030	.076
Philadelphia[2], PA	11	.032	602	.124	.108	.022	.054	.034	073
Portland, ME	14	.028	.647	.104	.093	.022	.065	.025	.067
Richmond, VA	13	.029	.600	.120	.113	.023	.054	.039	073
St. Louis, MO	18	.025	.598	.130	.122	.022	.049	.029	.077
Texas City, TX	15	.041	.651	.079	.080	.023	.048	.029	.098
Washington, DC	11	.032	.549	.139	.140	.023	.052	.041	.073
West Orange, TX	16	.040	.637	.066	.077	.025	.042	.026	.137
<u>Overall</u>	304	.029	.613	.107	.105	.022	.050	.034	.089
Current Recommended Value		.03	.51	.12	.10	.02	.03	.04	.15

*The formaldehyde and higher aldehydes fractions represent a "surrogate" fraction plus a recommended additional fraction. This is due to the fact that neither the PDFID nor the GC method measure aldehydes.

Table 5-3

Comparison of Median Carbon Fractions For EKMA CB4 Analyses

(1984 and 1985 Data)

City		n	Olefin	Paraffin	Toluene	Xylene	Formaldelyde	Higher Aldehydes	Ethylene	Unreactive
Beaumont, TX	(84)	9	.021	.646	.062	.062	.020	.051	.052	.135
Beaumont, TX	(85)	19	.080	.691	.071	.060	.022	.036	.024	.068
Clute, TX	(84)	10	.031	.599	.094	.099	.020	.040	.062	.104
Clute, TX	(85)	18	.050	.524	.079	.058	.022	.040	.170	.106
Dallas, TX	(84)	13	.030	.600	.110	.120	.020	.060	.030	.080
Dallas, TX	(85)	23	.027	.608	.112	.106	.022	.058	.032	.085
El Paso, TX	(84)	8	.030	.596	.111	.121	.025	.050	.040	.076
El Paso, TX	(85)	17	.026	.595	.109	.110	.023	.049	.039	.099
Fort Worth, TX	(84)	13	.031	.602	.104	.112	.020	.050	.041	.092
Fort Worth, TX	(85)	19	.033	.582	.113	.123	.024	.055	.038	.080
Kansas City, MO	(84)	11	.030	.626	.101	.111	.020	.050	.030	.081
Kansas City, MO	(85)	18	.024	.594	.114	.109	.022	.046	.041	.099
Richmond, VA	(84)	10	.030	.569	.117	.162	.030	.050	.030	.061
Richmond, VA	(85)	13	.029	.600	.120	.113	.023	.054	.039	.073
Texas City, TX	(84)	13	.031	.629	.072	.072	.020	.040	.021	.165
Texas City, TX	(85)	15	.041	.651	.079	.080	.023	.048	.029	.098
Washington, DC	(84)	10	.030	.586	.121	.131	.025	.060	.045	.051
Washington, DC	(85)	11	.032	.549	.139	.140	.023	.052	.041	.073
West Orange, TX	(84)	10	.021	.617	.067	.104	.030	.040	.036	.135
West Orange, TX	(85)	16	.040	.637	.066	.077	.025	.042	.026	.137

Table 5-4

Overall Carbon Fractions (1984 and 1985)

	n	OLE	PAR	TOL	XYL	FORM	ALD2	ETH	UNREACT
1984 Overall	203	.031	.605	.113	.123	.020	.051	.036	.072
1985 Overall	304	.029	.613	.107	.105	.022	.050	.034	.089
Current Default	-	.03	.51	.12	.10	.02	.03	.04	.15
1984 and 1985 Overall	507	.031	.606	.111	.113	.022	.051	.034	.082
1984 and 1985 Overall (minus exclusions)	374	.031	.598	.114	.123	.022	.050	.035	.078
NEW DEFAULT	-	.031	.598	.114	.123	.022	.050	.035	.078

6.0 Mobile Source Contribution

Studies of ambient NMOC levels due solely to mobile sources have been made in tunnels.[8] By comparing NMOC-acetylene ratios measured in tunnels to NMOC-acetylene ratios in the ambient air, it is possible to estimate the mobile source contribution to measured ambient NMOC levels. Acetylene is believed to be a good tracer of mobile source emissions since only a few stationary sources emit acetylene (e.g., welding, carbon black plants). Since carbon black plants and acetylene welding are not typically found in significant amounts in urban areas, acetylene data for urban areas is probably a good indicator of mobile source emissions. This technique of estimating mobile source contributions is considered a fairly reliable procedure although its accuracy has not be quantified. The equation is:

$$\text{\% Mobile Source Contribution} = \frac{NMOC}{Acet_{Tun}} \times \frac{Acet}{NMOC_{AMB}} \times 100\%$$

An NMOC-acetylene ratio of 27.0 was used for the tunnel ratio.[8]

6.1 1984 Mobile Source Contributions

In Table 6-1, the estimated median mobile source contributions (MMSCs) are listed for the 22 sites. The lowest MMSC (18%) was observed in Texas City, Texas. The highest MMSC (88%) was observed in Miami, Florida. The median overall MMSC is approximately 57%. Fifteen of the 22 sites had MMSCs greater than or equal to 50%. Ten sites had MMSCs greater than or equal to 60%. As expected mobile sources make a significant contribution to 6-9 a.m. NMOC levels.

6.2 1985 Mobile Source Contributions

The estimated median mobile source contributions (MMSCs) for the 19 sites are listed in Table 6-1. The lowest MMSC (7%) was observed in Beaumont, Texas. The highest MMSC (96%) was observed in Washington, DC. The median overall MMSC is approximately 66%. Twelve of the 19 sites had MMSCs greater than 50%. Eleven sites had MMSCs greater than 60%.

One fact that must be kept in mind is that the mobile source contribution is dependent upon where the NMOC sites are located. For example, the 39% median mobile source contribution for Houston would appear low. However, the NMOC site was not a center city site, but was located in an industrial area near the ship channel. The MMSC in Table 6-1 for Houston (39%) is probably not representative of center city conditions.

The MMSCs should only be considered a rough estimate for two reasons: (1) the NMOC-acetylene ratio for the tunnel was based upon 28 samples with some scatter, and (2) the vehicle fleet mix and therefore the relationship of NMOC to acetylene will vary from city to city.

6.3 Comparison Of 1984 And 1985 Mobile Source Contributions

MMSCs are available for 11 sites which operated in both 1984 and 1985. Of these 11 sites, estimates of MMSCs increased at eight sites and decreased at the other three. In most cases, the differences between 1984 and 1985 are not large. There are two exceptions, however. The MMSC for Beaumont was 25% in 1984 and 7% in 1985. This significant decrease in percentage may indicate that the activity at major industrial sources have increased from 1984 to 1985. NMOC and $NMOC/NO_x$ ratios from 1984 to 1985 in Beaumont support this observation.

The MMSC for Kansas City was 57% in 1984 and 83% in 1985. This may be an indication that industrial emissions decreased from 1984 to 1985. NMOC and $NMOC/NO_x$ ratios also decreased from 1984 to 1985 to support this observation Changes in MMSCs from 1984 to 1985 may also be due to varying meteorology, local economic conditions or VOC control programs.

6.4 Mobile Source Contributions From Emission Inventories

In Table 6-2 median highway vehicle contributions for seven cities is compared with the percent of the VOC emission inventory used in the State Implementation Plan that was reported from highway sources. In all cases the MMSC from ambient data is higher than the percentage obtained from the emission inventory. This suggests that mobile source emissions may have been under-estimated in the past. This hypothesis is supported by the recent findings that tampering and evaporative emissions are considerably higher than believed at the time 1982 ozone SIPs were developed. On the other hand, implementation of industrial controls since 1980 may have resulted in higher mobile source contributions in 1984-85. Both of these situations would lead to higher MMSC's from the emission inventory. It should also be noted that the MMSCs from ambient NMOC data represent 6-9 AM averages for summer conditions, a time of peak traffic. MMSCs from emission inventories are based upon daily averages and do not represent 6-9 AM conditions.

Table 6-1

Percent Mobile Source Contributions In 1984 And 1985 (Median Values)

City	1984 Mobile Source Contribution	1985 Mobile Source Contribution
Akron, OH	48	----
Atlanta, GA	68	----
Baton Rouge, LA	----	53
Birmingham, AL	46	----
Boston, MA	----	82
Charlotte, NC	77	----
Chattanooga, TN	67	----
Cincinnati, OH	50	----
Cleveland, OH	----	70
Houston, TX	----	39
Indianapolis, IN	67	----
Lake Charles, LA	----	31
Memphis, TN	79	----
Miami, FL	88	----
Philadelphia 2, PA	----	69
Portland, ME	----	49
St. Louis, MO	----	63
West Palm Beach, FL	47	----
Wilkes Barre, PA	60	----
Beaumont, TX	25	7
Clute, TX	37	33
Dallas, TX	58	71
El Paso, TX	78	81
Fort Worth, TX	67	74
Kansas City, MO	57	83
Philadelphia 1, PA	50	66
Richmond, VA	53	66
Texas City, TX	18	24
Washington, DC	87	96
West Orange, TX	32	29

Table 6-2

Comparison Of Mobile Source Contributions From Ambient Data Vs. Emission Inventory Data

City	Percent of 1980 VOC Emission Inventory: Point	Area	Highway	Mobile Source Contribution (From Ambient NMOC Data)	Year
Boston	19	35	46	82	1985
Philadelphia	38	30	32	50	1984
				66	
				69	1985
Washington, D.C.	3	31	66	87	1984
				96	1985
Cincinnati	31	28	41	50	1984
Cleveland	15	40	45	70	1985
Houston	60	14	26	39	1985
St. Louis	35	38	27	63	1985

7.0 Biogenic NMOC Data

Natural sources contribute to ambient NMOC levels. These emissions are usually from vegetative sources. The amount of ambient biogenic NMOC can be estimated by adding two components from the GC analysis. These are isoprene and α-pinene. It should be noted that the isoprene and α-pinene peaks have been identified by retention time only and have not been confirmed by other techniques such as GC/Mass Spec. This procedure provides a rough estimate of biogenic NMOC values. While few industrial activities emit isoprene or α-pinene, it is possible to misidentify other species as isoprene or α-pinene. (As discussed later, this misidentification is believed to have occurred with the 1985 Beaumont data). Biogenics emissions do include species other than isoprene and α-pinene, such as β-pinene, Δ^3-carene and myrcene. However, the procedure of identifying species by retention time only is not accurate enough to reliably estimate these compounds. As such, the estimates provided below should be considered as fairly rough estimates.

7.1 1984 Biogenic NMOC Data

Table 7-1 lists the estimated contribution of biogenic sources for each of the 22 sites. Included are the number of samples, range, mean, and median of the biogenic concentrations, and range, mean and median of the percent of biogenics compared to total NMOC. The median biogenic concentration is displayed graphically in Figure 7-1. The lowest median biogenic concentration (0.70 ppbC) was measured in Miami, Florida, while the highest median biogenic concentration (9.87 ppbC) was measured in Richmond, Virginia. No obvious geographical patterns are present.

Estimated biogenic NMOC concentrations expressed as a percent of total NMOC range from a low of 0.11 (median) in Miami, Florida, to a high of 2.02 in Charlotte, North Carolina.

7.2 1985 Biogenic NMOC Data

Table 7-2 lists the estimated contribution of biogenic sources for each of the 19 sites. The median biogenic concentration is displayed graphically in Figure 7-2. The lowest median biogenic concentration (2.93 ppbC) was measured in Texas City, Texas, while the highest median biogenic concentration (142.68 ppbC) was measured in Beaumont, Texas. No obvious geographical patterns are present.

Biogenic NMOC concentrations expressed as a percent of total NMOC range from a low of 0.35% (median) in Cleveland, Ohio, to a high of 10.17 in Beaumont, Texas.

It is obvious that the values for Beaumont do not reflect solely biogenic emission levels. If the values are truly biogenic levels, such large changes should not occur from one year to the next. The Beaumont biogenic level is an order of magnitude greater than any other city. Some industrial component must be included in either of the peaks identified as isoprene or α-pinene.

7.3 Comparison Of 1984 And 1985 Biogenic NMOC Data

Table 7-3 lists the estimated median biogenic NMOC concentrations for 1984 and 1985 for the 11 cities which were analyzed for both years. Also shown is the percent change in biogenic NMOC from 1984 to 1985 and the percent change in total (mean) NMOC from 1984 to 1985.

The most obvious change is in Beaumont, Texas, where the median biogenic concentrations went up by a factor of 31 from 1984 to 1985. The total NMOC in Beaumont nearly doubled from 1984 to 1985. No reason for such a large increase in biogenic NMOC concentrations has been determined and therefore the levels identified as biogenic are questionable.

At eight other sites, the median biogenic NMOC concentration increased from 1984 to 1985 and decreased at the other two sites.

At 8 of the 11 sites percent biogenic increased from 1984 to 1985, while total NMOC decreased at 7 of these 8 sites.

Table 7-4 lists the biogenic NMOC concentrations as a percent of total NMOC for 1984 and 1985. Once again, Beaumont shows a large increase from 1984 to 1985.

With the exception of questionable estimates for Beaumont, most of the estimates of biogenic contributions to ambient NMOC concentrations are less than 1%. These data support the position that anthropogenic sources are the predominant cause of ambient NMOC concentrations in urban areas.

Table 7-1

Biogenic NMOC Data (1984)

Estimated

City	n	Concentration (ppbC) Range	Mean	Median	% Of Total NMOC Range	Mean	Median
Akron, OH	10	0.68- 2.03	1.31	1.30	0.15-0.52	0.29	0.27
Atlanta, GA	7	2.17-12.13	5.80	4.41	0.44-1.29	0.82	0.78
Beaumont, TX	9	2.96- 8.04	5.18	4.51	0.17-1.08	0.70	0.71
Birmingham, AL	6	3.44- 8.94	5.89	5.55	0.38-1.34	0.70	0.55
Charlotte, NC	16	0.81-27.07	9.95	6.79	0.53-3.63	1.91	2.02
Chattanooga, TN	12	3.76-34.14	11.04	8.85	0.16-1.59	0.62	0.53
Cincinnati, OH	7	1.80-26.62	8.97	3.53	0.27-1.20	0.54	0.44
Clute, TX	10	0.36- 4.87	2.64	2.75	0.03-0.90	0.53	0.56
Dallas, TX	13	0.56-11.19	4.06	3.85	0.21-1.19	0.59	0.57
El Paso, TX	8	0.48- 3.52	2.08	1.95	0.09-0.56	0.25	0.24
Fort Worth, TX	13	2.03- 7.50	4.88	5.03	0.30-1.16	0.56	0.43
Indianapolis, IN	10	0.56- 6.03	2.25	1.76	0.14-0.31	0.23	0.25
Kansas City, MO	11	0.50- 7.62	2.86	1.87	0.15-0.50	0.29	0.31
Memphis, TN	8	3.93-12.82	6.38	5.55	0.15-0.77	0.42	0.39
Miami, FL	3	0.51- 2.00	1.07	0.70	0.11-0.23	0.15	0.11
Philadelphia 1, PA	7	1.40- 5.08	3.28	2.88	0.19-0.96	0.44	0.38
Richmond, VA	10	1.71-13.07	8.06	9.87	0.49-3.26	1.88	1.72
Texas City, TX	13	0.27-23.99	4.89	3.02	0.04-2.06	0.55	0.44
Washington, DC	10	2.50-11.66	5.40	3.84	0.42-0.87	0.57	0.51
West Orange, TX	10	0.83-11.00	4.77	3.66	0.27-1.63	0.85	0.82
West Palm Beach, FL	8	1.93- 4.31	2.95	2.91	0.18-1.46	0.82	0.97
Wilkes Barre, PA	9	2.35- 9.55	4.67	4.56	0.55-2.30	1.02	0.74

Table 7-2

Biogenic NMOC Data (1985)

Estimated

City	n	Concentration (ppbC) Range	Mean	Median	% Of Total NMOC Range	Mean	Median
Baton Rouge, LA	16	0.65-22.76	4.89	2.98	0.17-2.09	0.72	0.60
Beaumont, TX	19	51.40-313.42	154.75	142.68	1.21-16.65	9.92	10.17
Boston, MA	8	1.50- 5.43	3.35	3.43	0.19-2.14	1.25	1.35
Cleveland, OH	17	0.61- 9.32	3.55	3.04	0.14-0.88	0.39	0.35
Clute, TX	18	0.23-17.70	4.15	3.29	0.16-2.26	0.62	0.40
Dallas, TX	23	1.04-24.84	6.42	4.20	0.17-1.93	0.80	0.75
El Paso, TX	17	1.37-10.45	4.29	3.20	0.17-1.26	0.56	0.53
Fort Worth, TX	19	1.10-16.45	6.09	6.54	0.18-2.24	0.89	0.87
Houston, TX	22	0.73-30.23	9.64	6.36	0.11-3.41	1.06	0.73
Kansas City, MO	17	0.28- 8.84	4.18	3.73	0.10-1.66	0.67	0.66
Lake Charles, LA	16	0.68-17.15	6.88	6.13	0.32-1.89	0.87	0.72
Philadelphia 1, PA	13	1.31-18.75	4.86	4.13	0.31-0.84	0.51	0.44
Philadelphia 2, PA	11	1.82-12.91	5.07	4.06	0.38-0.83	0.55	0.54
Portland, ME	14	0.29-43.17	9.61	4.45	0.06-4.00	1.29	0.89
Richmond, VA	14	2.17-13.35	6.88	6.64	0.19-2.49	1.27	1.29
St. Louis, MO	18	0.52-18.80	5.15	4.01	0.22-2.22	0.78	0.68
Texas City, TX	15	0.22-38.39	4.86	2.93	0.03-1.43	0.63	0.43
Washington, DC	11	2.96-24.00	6.98	4.97	0.54-2.09	1.00	0.90
West Orange, TX	16	3.69-13.97	7.96	7.45	0.33-7.45	1.94	1.47

Table 7-3

Comparison Of Biogenic NMOC Data (1984 And 1985)

Estimated

City	Median 1984 Biogenic NMOC (ppbC)	Median 1985 Biogenic NMOC (ppbC)	% Change Biogenic NMOC	% Change Total Median NMOC
Beaumont, TX	4.51	142.68	3064% ↑	↑ 117%
Clute, TX	2.75	3.29	20% ↑	↓ 10%
Dallas, TX	3.85	4.20	13% ↑	↓ 18%
El Paso, TX	1.95	3.20	64% ↑	↓ 18%
Fort Worth, TX	5.03	6.54	30% ↑	↓ 21%
Kansas City, MO	1.87	3.73	99% ↑	↓ 34%
Philadelphia 1, PA	2.88	4.13	43% ↑	↓ 47%
Richmond, VA	9.87	6.64	33% ↓	↓ 10%
Texas City, TX	3.02	2.93	3% ↓	↓ 46%
Washington, DC	3.84	4.97	29% ↑	↓ 15%
West Orange, TX	3.66	7.45	104% ↑	↓ 20%

Table 7-4

1984 And 1985 Biogenic NMOC Data

(Expressed As A Percent Of Total NMOC)

City	Median 1984 Biogenic %	Median 1985 Biogenic %
Beaumont, TX	0.71	10.17
Clute, TX	0.56	0.40
Dallas, TX	0.57	0.75
El Paso, TX	0.24	0.53
Fort Worth, TX	0.43	0.87
Kansas City, MO	0.31	0.66
Philadelphia 1, PA	0.38	0.44
Richmond, VA	1.72	1.29
Texas City, TX	0.44	0.43
Washington, DC	0.51	0.90
West Orange, TX	0.82	1.47

FIGURE 7-1

Median Biogenic NMOC Concentrations (ppbC)

1984 Data

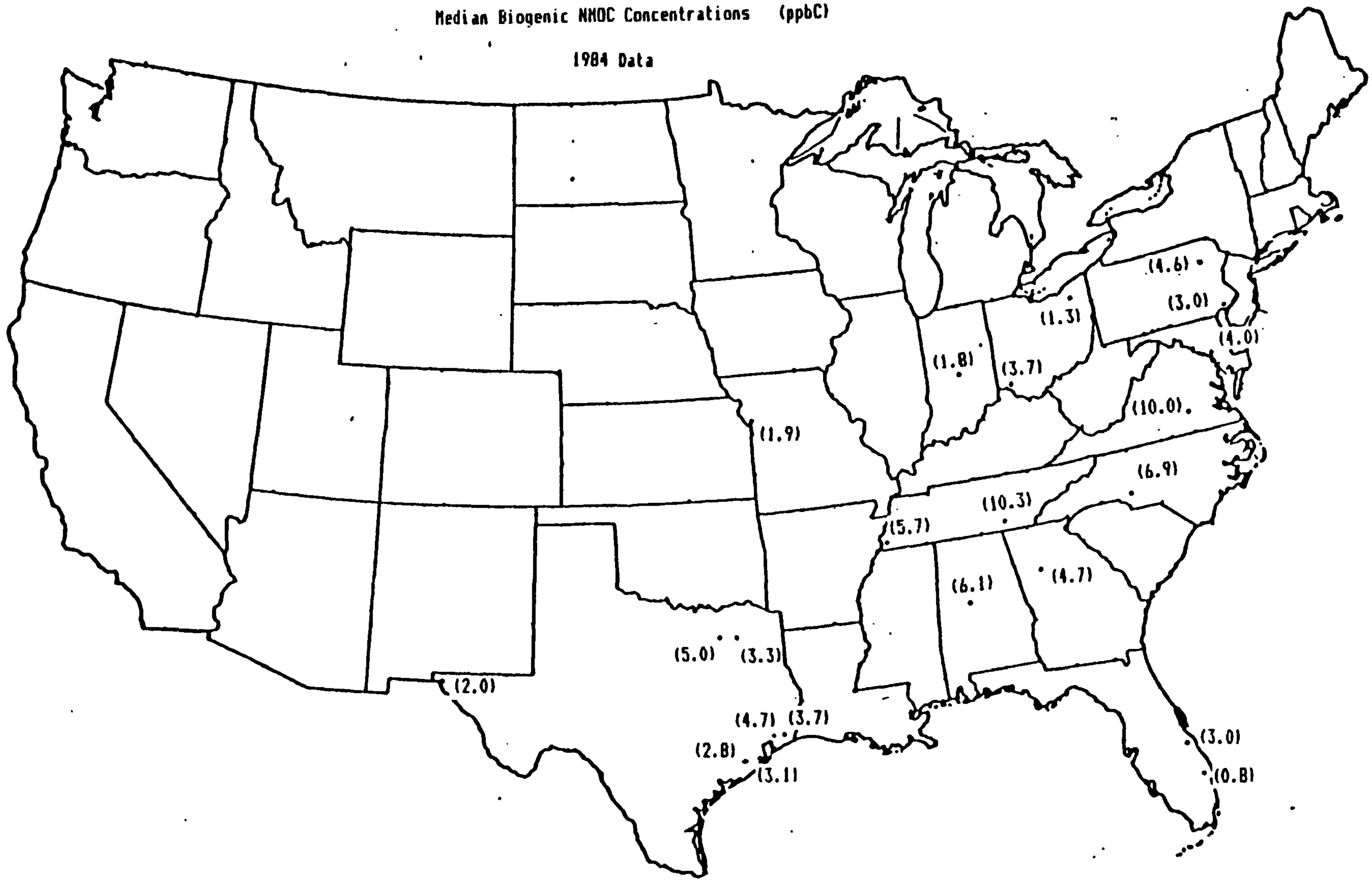
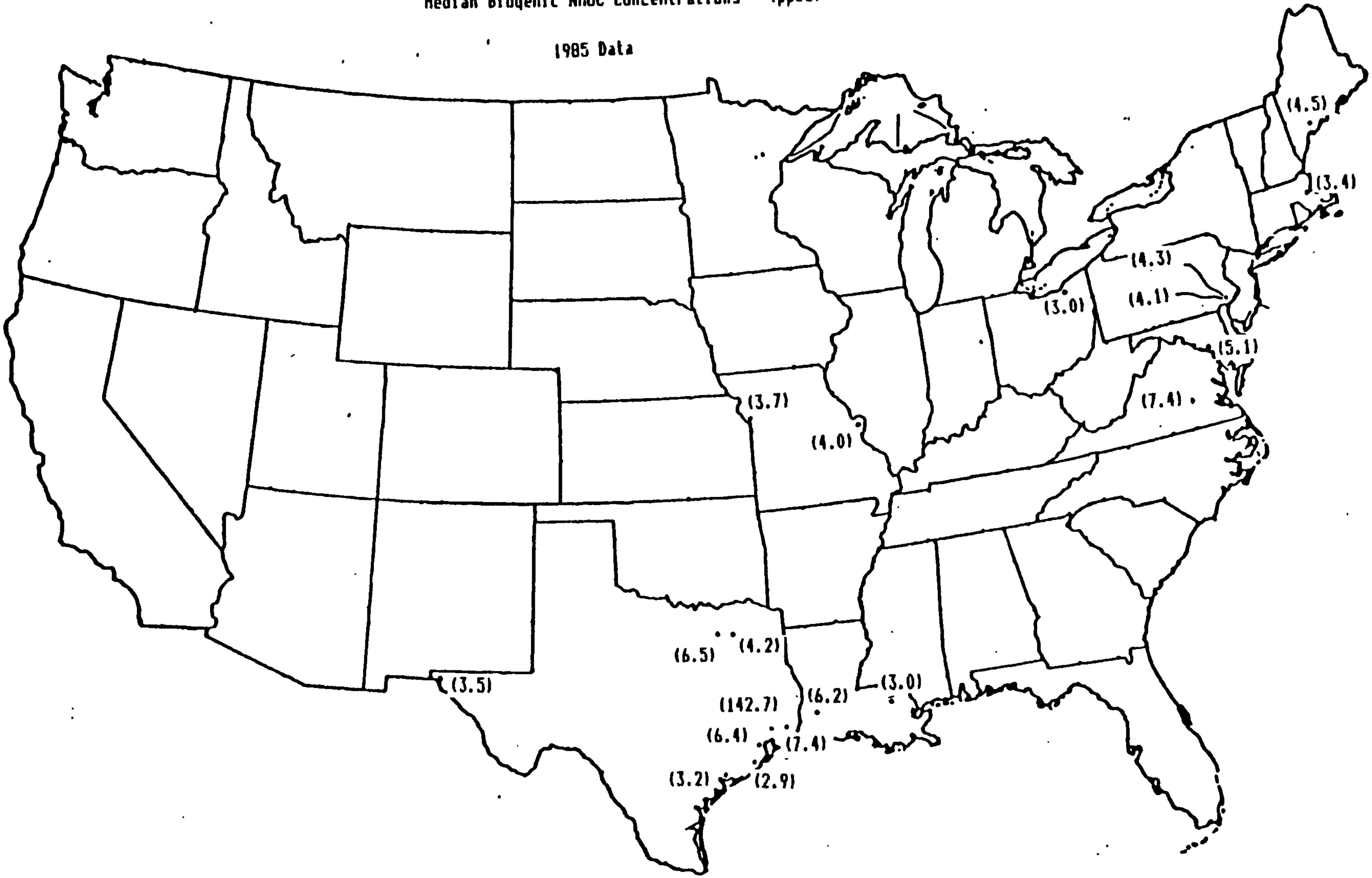


FIGURE 7-2

Median Biogenic NMOC Concentrations (ppbC)

1985 Data



8.0 NMOC Versus Ozone

This chapter describes a case study which compares reductions in ambient NMOC levels with ozone data. The city selected for analysis is Kansas City, Missouri. As discussed in Chapter 2, median NMOC levels dropped 34% from 1984 to 1985. Did ozone levels also decrease and, if so, how much? Five ozone sites were analyzed. These were 260840002F01, 261020003F01, 261020005F01, 262380023H01, and 262380025H01. These sites are referred to as 2F01, 3F01, 5F01, 23H01, and 25H01 throughout the remainder of this chapter. One other site was considered but not included in the analysis (171800001F01) since this site located in Kansas City, Kansas, missed considerable ozone data in June and August 1985.

Figure 8-1 shows the distribution of NMOC data in Kansas City for 1984 and 1985. The data for 1984 are displayed above the zero line, while 1985 is plotted below the zero line. The distribution of 1985 NMOC has shifted substantially to the left, indicating lower NMOC levels in 1985 than in 1984. The hypothesis that mean NMOC levels were lower in 1985 than 1984 was tested (see Chapter 2) and found to be true at the 95% confidence level. The mean NMOC level dropped 33% from 1984 to 1985.

In Figure 8-2 the distribution of ozone at the 2F01 site is shown. The data analyzed included June through September for 1984 and 1985. Once again, 1984 values are shown above the zero line and 1985 values below the zero line. The 1985 distribution has shifted to the left, indicating that ozone levels have decreased from 1984 to 1985. The other four sites showed similar results. This was further confirmed by performing t-tests, using mean ozone levels. In each case, a reduction in ozone from 1984 to 1985 was indicated at the 95% confidence level.

Table 8-1 compares 1984 and 1985 ozone statistics for each site. The mean ozone levels decreased from 7 to 23%. Maximum ozone levels increased 1% at one site, but decreased at the other four sites between 9 and 22%. The number of hours with ozone levels above .125 ppm is also reduced at each site.

It would appear that ozone levels decreased in Kansas City as NMOC levels decreased. No attempt has been made to determine the cause of the NMOC reductions.

Table 8-1

Comparison Of 1984 And 1985 Ozone Data

(June-September --- Kansas City Sites)

	2F01	3F01	5F01	23H01	25H01
Percent Decrease In Mean Ozone (1984-1985)	7%	23%	18%	10%	15%
Maximum Ozone (ppm)					
1984	.149	.160	.167	.133	.115
1985	.116	.145	.132	.114	.116
Percent Decrease In Maximum Ozone (1984-1985)	22%	9%	21%	14%	↑ 1%
Number Of Hours With Ozone ≥ .125 ppm					
1984	1	4	5	3	0
1985	0	1	1	0	0

Figure 8-1

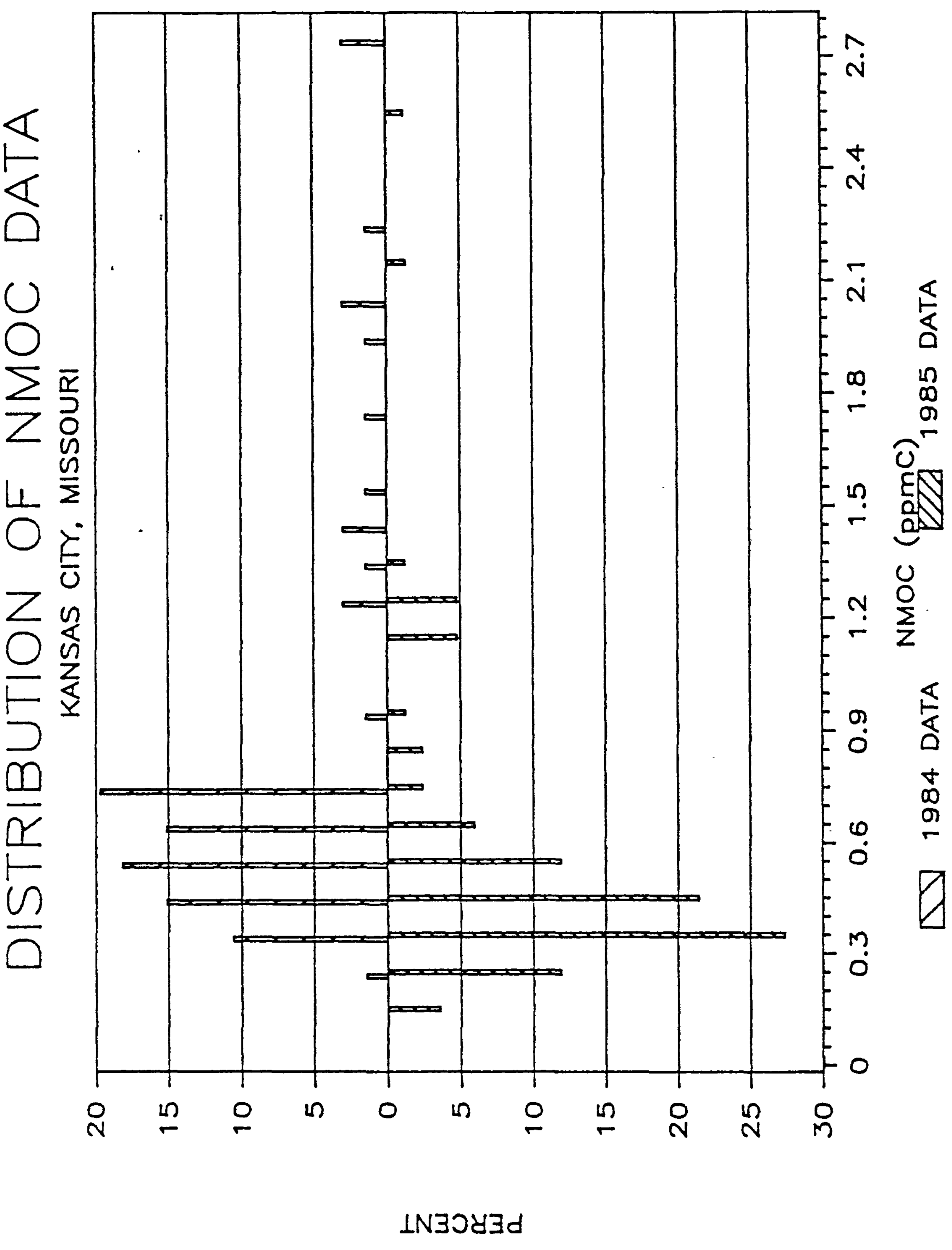
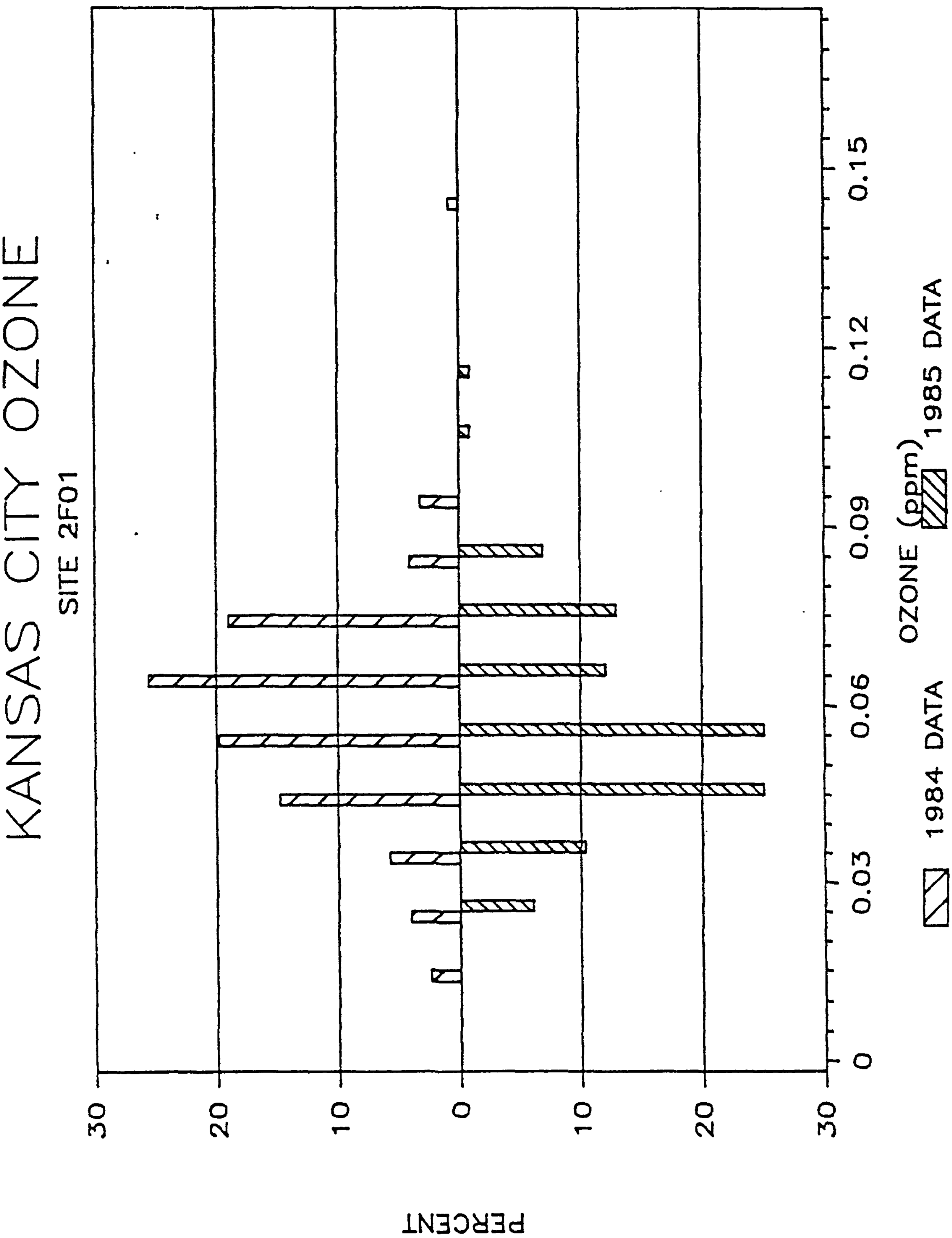

DISTRIBUTION OF NMOC DATA
KANSAS CITY, MISSOURI
NMOC (ppmC)
1984 DATA
1985 DATA
PERCENT
0
0.3
0.6
0.9
1.2
1.5
1.8
2.1
2.4
2.7
20
15
10
5
0
5
10
15
20
25
30

Figure 8-2


KANSAS CITY OZONE
SITE 2F01
OZONE (ppm)
1984 DATA
1985 DATA
PERCENT
0
0.03
0.06
0.09
0.12
0.15
30
20
10
0
10
20
30

9.0 Conclusions

9.1 NMOC

1. 6-9 AM NMOC levels vary from day to day at a given site.

2. Median NMOC levels decreased from 1984 to 1985 in many cities. Decreases were statistically significant at five of the nine cities which showed a decrease.

3. Continuous NMHC measurements and those made with the PDFID do not agree. Continuous data are suspect.

9.2 NO_x

1. 6-9 AM NO_x levels vary widely from day to day at a given site.

2. Median NO_x levels decreased in most cities from 1984 to 1985. Decreases were statistically significant at three of the seven cities which showed a decrease. Only one city showed a statistically significant increase in median NO_x.

9.3 NMOC/NO_x Ratios

1. 6-9 AM NMOC/NO_x ratios vary widely from day to day at a given site.

2. Further investigation is underway to determine whether use of robust statistics (e.g., medians) or day specific data is most suitable for characterizing a city's NMOC/NO_x ratios.

3. Median NMOC/NO_x ratios decreased at five of the nine sites from 1984 to 1985 and increased at four. The reductions are statistically significant at four of the sites, while the increases are statistically significant only in Beaumont.

4. A comparison of NMOC/NO_x ratios with ozone level indicates a poor correlation. The relationship is probably overwhelmed by the importance of variable meteorological parameters.

9.4 Carbon Fractions

1. 1984 and 1985 carbon fractions match fairly well with current default conditions, except that 1984 and 1985 fractions of paraffins are slightly higher and unreactives lower. New default values are listed (in Table 5-4).

9.5 Mobile Source Contributions

1. Estimated Mobile source contributions to ambient NMOC levels varied from 7 to 96%. Contributions on the order of 45-75% appear most common at the sites in the 1984-85 network.

2. The mobile source contributions based upon 1984 and 1985 ambient NMOC data are significantly different from values determined from emission inventories. Because these ratios were determined in different ways and for different time periods, there may be logical reasons for the differences.

9.6 Estimated Biogenic NMOC data

1. Excluding Beaumont, median Biogenic (natural) NMOC levels make up between .1 and 1.5% of total NMOC. Most sites are on the order of 0.3 - 0.7 % biogenic of total NMOC.

9.7 NMOC Versus Ozone

1. A 34% reduction in ambient median NMOC levels from 1984 to 1985 was seen in Kansas City.

2. Hourly mean ozone levels from June-September 1984 decreased from 7 to 23% at the five Kansas City ozone sites.

3. Maximum hourly ozone levels decreased at four of five sites.

9.8 Additional Data Needs

1. Many cities showed substantial reductions in mean NMOC levels from 1984 to 1985, but two points do not define a long term trend. It would be interesting and useful to observe mean NMOC levels over many years to see

if a trend exists. Unfortunately, NMOC ambient data are not routinely collected from year to year. There will be few sites where long term trends can be determined. In some cases, these will be small Texas cities that may not represent "typical" size cities. States are encouraged to establish fixed networks of NMOC monitors in large cities and operate them for several years.

2. Median NMOC/NO_x ratios decreased significantly from 1984 to 1985 at nearly half of the sites. It does not appear reasonable for States to use an NMOC/NO_x ratio for a State Implementation Plan (SIP), unless it were current (no more than one to two years old). It is recommended that States sample NMOC concentrations for more than one summer to provide reliable estimates.

3. Since 6-9 AM NMOC levels are significantly impacted by mobile sources, States are encouraged to focus increased attention on mobile source VOC emissions. Analysis of hourly traffic counts may also be necessary to properly define mobile source contributions during the early morning rush hour.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

During the summers of 1984 and 1985, morning (6-9am) measurements of ambient nonmethane organic compounds (NMOC) were collected at 22 and 19 urban sites, respectively. The data were collected by State and local agencies which contributed grant funds and personnel. The EPA managed the analysis and provided NMOC sampling equipment. The method of determining NMOC levels was the cryogenic preconcentration direct flame-ionization detection (PDFID) described by McElroy et al. Data were collected to provide input values for the Empirical Kinetic Modeling Approach (EKMA), a computer program which estimates hydrocarbon control requirements necessary to attain the National Ambient Air Quality Standard (NAAQS) for ozone. One of the key inputs to EKMA is the Nonmethane Organic Compound/Nitrogen Oxides (NMOC/NO_x) ratio. Thus, a collocated NO_x instrument was operated at each NMOC site.

17. KEY WORDS AND DOCUMENT ANALYSIS

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